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COLORIMETER
PROCEDURES MANUAL

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AccuGrow®
AccuVac®
AccuVer™
AccuVial™
Add-A-Test™
AgriTrak™
AluVer®
AmVer™
APA 6000™
AquaChek™
AquaTrend®
BariVer®
BODTrak™
BoroTrace™
BoroVer®
C. Moore Green™
CA 610™
CalVer®
ChromaVer®
ColorQuik®
CoolTrak®
CuVer®
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TitraStir®
TitraVer®
ToxTrak™
UniVer®
VIScreen™
Voluette®
WasteAway™
ZincoVer®

TABLE OF CONTENTS

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

TABLE OF CONTENTS, continued

INTRODUCTION

This manual is divided into five sections:

Section 1 Chemical Analysis Information

This section applies to all the procedures. It provides background information and reference/review material for the technician or chemist. Commonly used techniques are explained in detail.

Section 2 Sample Pretreatment

This section provides a brief overview of sample pretreatment and two USEPA digestions. A brief discussion of the Hach Digesdahl Digestion Apparatus and the Hach Distillation Apparatus is included.

Section 3 Waste Management and Safety

Section 3 includes information on waste management, regulations, waste disposal and resources on waste management. The Safety portion covers reading an MSDS and general safety guidelines.

Section 4 Procedures

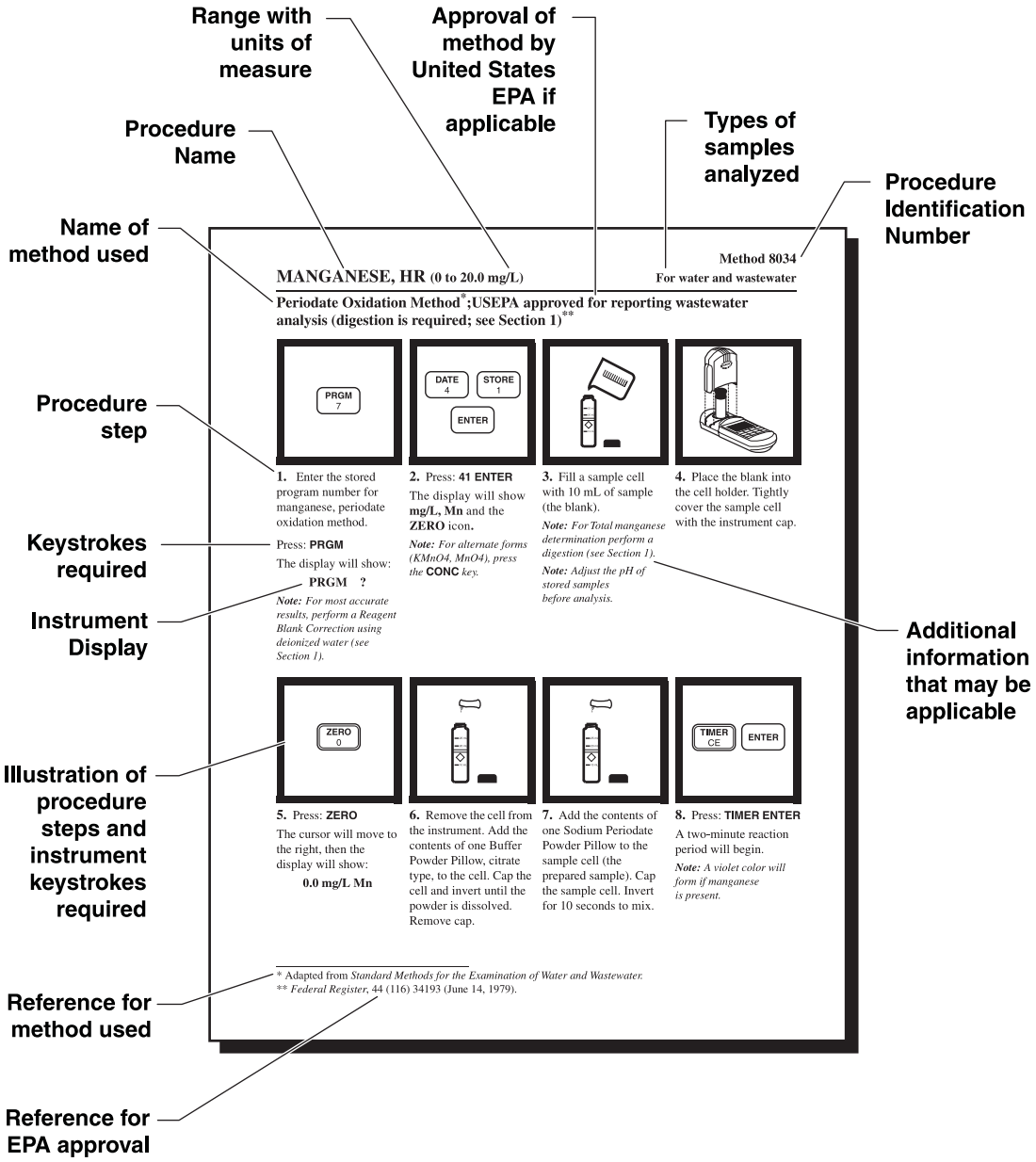
Section 4 contains step-by-step illustrated instructions for measuring parameters. The steps also include helpful notes. Each procedure contains information on sample collection, storage and preservation, accuracy checks, possible interferences, summary of method and a list of the reagents and apparatus necessary to run the test.

Section 5 Ordering Information

This section provides information needed for ordering, shipping, return of items and Hach trademarks.

Before attempting the analysis procedures the analyst should read the instrument manual to learn about the colorimeter's features and operation.

Sample Procedure Explained



Sample Procedure Explained, continued

Specific sampling and storage information for this test

Confirm accuracy with these steps (in addition, may also be used to troubleshoot a test, improve technique, check reagents and to assure cleanliness of glassware)

MANGANESE, HR, continued

9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

10. Press: **READ**

The cursor will move to the right, then the result in mg/L manganese will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Manganese may be lost by adsorption to glass container walls. Adjust the pH to less than 2 with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as manganese may be lost as a precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1* for more information. If only dissolved Mn is to be determined, filter before acid addition.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Manganese Voluette Ampule Standard Solution, 250 mg/L Mn.

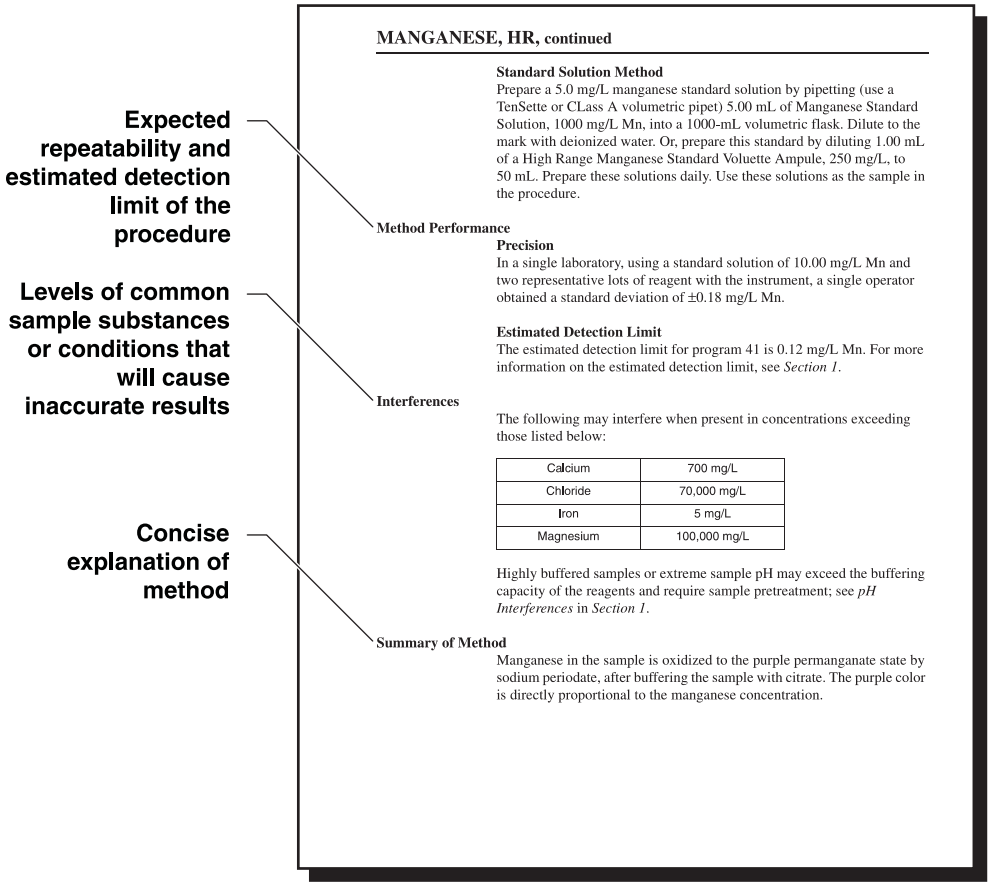
b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three 25-mL water samples. Swirl to mix.

c) Transfer only 10 mL of each solution to the 10-mL sample cells.

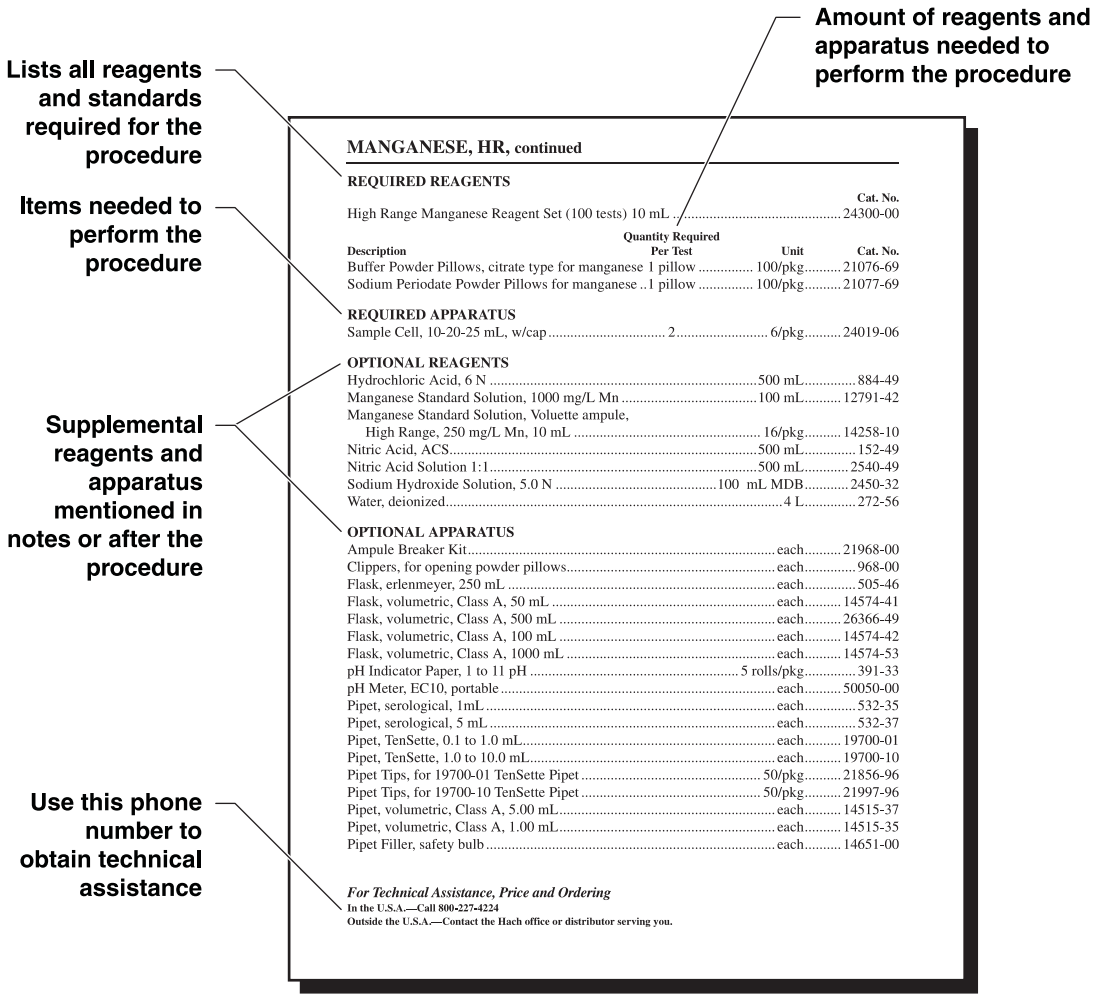
d) Analyze each standard addition sample as described in the procedure. The manganese concentration should increase 1.0 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Sample Procedure Explained, continued



Sample Procedure Explained, continued



MANGANESE, HR, continued

REQUIRED REAGENTS

	Cat. No.
High Range Manganese Reagent Set (100 tests) 10 mL	24300-00

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Powder Pillows, citrate type for manganese	1 pillow	100/pkg	21076-69
Sodium Periodate Powder Pillows for manganese	1 pillow	100/pkg	21077-69

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Hydrochloric Acid, 6 N	500 mL	884-49
Manganese Standard Solution, 1000 mg/L Mn	100 mL	12791-42
Manganese Standard Solution, Voluette ampule, High Range, 250 mg/L Mn, 10 mL	16/pkg	14258-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution 1:1	500 mL	2540-49
Sodium Hydroxide Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Clippers, for opening powder pillows	each	968-00
Flask, erlenmeyer, 250 mL	each	505-46
Flask, volumetric, Class A, 50 mL	each	14574-41
Flask, volumetric, Class A, 500 mL	each	26366-49
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, EC10, portable	each	50050-00
Pipet, serological, 1mL	each	532-35
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg	21997-96
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

SECTION 1 CHEMICAL ANALYSIS INFORMATION

Abbreviations

The following abbreviations are used throughout the text of the procedure section:

Abbrev-iation	Definition	Abbrev-iation	Definition
°C	degree(s) Celsius (Centigrade)	MDL	Method detection limit
°F	degree(s) Fahrenheit	MDB	marked dropping bottle
ACS	American Chemical Society reagent grade purity	mg/L	milligrams per liter (ppm)
APHA Standard Methods	*Standard Methods for the Examination of Water and Wastewater.*[1]	µg/L	micrograms per liter (ppb)
AV	AccuVac	mL	(milliliter)-approximately the same as a cubic centimeter (cc) or 1/1000 of a liter. Also known as a “cc”.
conc	concentrated	MR	medium range
CFR	Code of Federal Regulations	NIPDWR	National Interim Primary Drinking Water Regulations
DB	dropping bottle	NPDES	National Pollutant Discharge Elimination System
EDL	Estimated detection limit	PCB	Poly chlorinated biphenyl
FAU	Formazin Attenuation Units. Turbidity unit of measure based on a Formazin stock suspension.	SCDB	self-contained dropping bottle
g	grams	TNT	Test ‘N Tube™
gr/gal	grains per gallon (1 gr/gal = 17.12 mg/L)	TPH	Total petroleum hydrocarbons
HR	high range	TPTZ	(2,4,6-Tri-(2-Pyridyl)-1,3,5-Triazine)
L	Liter. Volume equal to one cubic decimeter (dm^3)	ULR	Ultra low range
LR	low range	USEPA	United States Environmental Protection Agency

[1]Published jointly by the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF). Order from Hach requesting Cat. No. 22708-00 or from the Publication Office of the American Public Health Association. This book is the standard reference work for water analysis. Many procedures contained in this manual are based on *Standard Methods.*

Converting Chemical Species

Species conversion factors for many commonly used substances are pre-programmed into the instrument (see *Table 1*). Conversions are method specific and are viewable after taking the reading by pressing **CONC**.

Table 1 Conversion Factors

To Convert From...	To...	Multiply By...
mg/L Al	mg/L Al_2O_3	1.8895
mg/L B	mg/L H_3BO_3	5.7
mg/L Ca-$CaCO_3$	mg/L Ca	0.4004
mg/L $CaCO_3$	mg/L Ca	0.4004
mg/L $CaCO_3$	mg/L Mg	0.2428
µg/L Carbohydrazide	µg/L Hydroquinone	1.92
µg/L Carbohydrazide	µg/L ISA	2.69
µg/L Carbohydrazide	µg/L MEKO	3.15
mg/L Cr^{6+}	mg/L CrO_4^{2-}	2.231
mg/L Cr^{6+}	mg/L Na_2CrO_4	3.115
mg/L Mg-$CaCO_3$	mg/L Mg	0.2428
mg/L Mn	mg/L $KMnO_4$	2.876
mg/L Mn	mg/L MnO_4^-	2.165
mg/L Mo^{6+}	mg/L MoO_4^{2-}	1.667
mg/L Mo^{6+}	mg/L Na_2MoO_4	2.146
mg/L N	mg/L NH_3	1.216
mg/L N	mg/L NO_3^-	4.427
mg/L Na_2CrO_4	mg/L Cr^{6+}	0.321
mg/L Na_2CrO_4	mg/L CrO_4^{2-}	0.72
mg/L NH_2Cl-N	mg/L Cl_2	5.0623
mg/L NH_2Cl-N	mg/L NH_2Cl	3.6750
mg/L NH_3-N	mg/L NH_3	1.216
mg/L NH_3-N	mg/L NH_4^+	1.288
mg/L NO_2^-	mg/L $NaNO_2$	1.5
mg/L NO_2^-	mg/L NO_2^--N	0.3045
mg/L NO_2^--N	mg/L $NaNO_2$	4.926
µg/L NO_2^--N	µg/L $NaNO_2$	4.926
mg/L NO_2^--N	mg/L NO_2^-	3.284
µg/L NO_2^--N	µg/L NO_2^-	3.284
mg/L NO_3^--N	mg/L NO_3^-	4.427
mg/L PO_4^{3-}	mg/L P	0.3261
µg/L PO_4^{3-}	µg/L P	0.3261
mg/L PO_4^{3-}	mg/L P_2O_5	0.7473
µg/L PO_4^{3-}	µg/L P_2O_5	0.7473
mg/L SiO_2	mg/L Si	0.4674
µg/L SiO_2	µg/L Si	0.4674

Hardness Conversion

Table 2 lists the factors for converting one unit of measure for hardness to another unit of measure. For example, to convert mg/L $CaCO_3$ to German parts/100,000 CaO, multiply the value in mg/L x 0.056.

Table 2 Hardness Conversion Factors

Units of Measure	mg/L $CaCO_3$	British gr/gal (Imperial) $CaCO_3$	American gr/gal (US) $CaCO_3$	French parts/ 100,000 $CaCO_3$	German Parts/ 100,000 CaO	meq/L[1]	g/L CaO	lbs./cu ft $CaCO_3$
mg/L $CaCO_3$	1.0	0.07	0.058	0.1	0.056	0.02	$5.6x10^{-4}$	$6.23x10^{-5}$
English gr/gal $CaCO_3$	14.3	1.0	0.83	1.43	0.83	0.286	$8.0x10^{-3}$	$8.9x10^{-4}$
US gr/gal $CaCO_3$	17.1	1.2	1.0	1.72	0.96	0.343	$9.66x10^{-3}$	$1.07x10^{-3}$
Fr. p/ 100,000 $CaCO_3$	10.0	0.7	0.58	1.0	0.56	0.2	$5.6x10^{-3}$	$6.23x10^{-4}$
Ger. p/ 100,000 CaO	17.9	1.25	1.04	1.79	1.0	0.358	$1x10^{-2}$	$1.12x10^{-3}$
meq/L	50.0	3.5	2.9	5.0	2.8	1.0	$2.8x10^{-2}$	$3.11x10^{-2}$
g/L CaO	1790.0	125.0	104.2	179.0	100.0	35.8	1.0	0.112
lbs./cu ft $CaCO_3$	16,100.0	1,123.0	935.0	1,610.0	900.0	321.0	9.0	1.0

[1]'epm/L, or 'mval/L'
Note: 1 meq/L = 1N/1000

Dissolved Oxygen

Table 3 lists the mg/L dissolved oxygen in water at saturation for various temperatures and atmospheric pressures. The table was formulated in a laboratory using pure water. The values given are only approximations for estimating the oxygen content of a particular body of surface water.

Table 3 Dissolved Oxygen Saturation In Water

		Pressure in Millimeters and Inches Hg							
		mm							
		775	760	750	725	700	675	650	625
Temp		inches							
°F	°C	30.51	29.92	29.53	28.45	27.56	26.57	25.59	24.61
32.0	0	14.9	14.6	14.4	13.9	13.5	12.9	12.5	12.0
33.8	1	14.5	14.2	14.1	13.6	13.1	12.6	12.2	11.7
35.6	2	14.1	13.9	13.7	13.2	12.9	12.3	11.8	11.4
37.4	3	13.8	13.5	13.3	12.9	12.4	12.0	11.5	11.1
39.2	4	13.4	13.2	13.0	12.5	12.1	11.7	11.2	10.8
41.0	5	13.1	12.8	12.6	12.2	11.8	11.4	10.9	10.5
42.8	6	12.7	12.5	12.3	11.9	11.5	11.1	10.7	10.3
44.6	7	12.4	12.2	12.0	11.6	11.2	10.8	10.4	10.0
46.4	8	12.1	11.9	11.7	11.3	10.9	10.5	10.1	9.8
48.2	9	11.8	11.6	11.5	11.1	10.7	10.3	9.9	9.5
50.0	10	11.6	11.3	11.2	10.8	10.4	10.1	9.7	9.3
51.8	11	11.3	11.1	10.9	10.6	10.2	9.8	9.5	9.1
53.6	12	11.1	10.8	10.7	10.3	10.0	9.6	9.2	8.9
55.4	13	10.8	10.6	10.5	10.1	9.8	9.4	9.1	8.7
57.2	14	10.6	10.4	10.2	9.9	9.5	9.2	8.9	8.5
59.0	15	10.4	10.2	10.0	9.7	9.3	9.0	8.7	8.3
60.8	16	10.1	9.9	9.8	9.5	9.1	8.8	8.5	8.1
62.6	17	9.9	9.7	9.6	9.3	9.0	8.6	8.3	8.0
64.4	18	9.7	9.5	9.4	9.1	8.8	8.4	8.1	7.8
66.2	19	9.5	9.3	9.2	8.9	8.6	8.3	8.0	7.6
68.0	20	9.3	9.2	9.1	8.7	8.4	8.1	7.8	7.5
69.8	21	9.2	9.0	8.9	8.6	8.3	8.0	7.7	7.4
71.6	22	9.0	8.8	8.7	8.4	8.1	7.8	7.5	7.2
73.4	23	8.8	8.7	8.5	8.2	8.0	7.7	7.4	7.1

Table 3 Dissolved Oxygen Saturation In Water (continued)

		Pressure in Millimeters and Inches Hg							
		mm							
		775	760	750	725	700	675	650	625
Temp		inches							
°F	°C	30.51	29.92	29.53	28.45	27.56	26.57	25.59	24.61
75.2	24	8.7	8.5	8.4	8.1	7.8	7.5	7.2	7.0
77.0	25	8.5	8.4	8.3	8.0	7.7	7.4	7.1	6.8
78.8	26	8.4	8.2	8.1	7.8	7.6	7.3	7.0	6.7
80.6	27	8.2	8.1	8.0	7.7	7.4	7.1	6.9	6.6
82.4	28	8.1	7.9	7.8	7.6	7.3	7.0	6.7	6.5
84.2	29	7.9	7.8	7.7	7.4	7.2	6.9	6.6	6.4
86.0	30	7.8	7.7	7.6	7.3	7.0	6.8	6.5	6.2
87.8	31	7.7	7.5	7.4	7.2	6.9	6.7	6.4	6.1
89.6	32	7.6	7.4	7.3	7.0	6.8	6.6	6.3	6.0
91.4	33	7.4	7.3	7.2	6.9	6.7	6.4	6.2	5.9
93.2	34	7.3	7.2	7.1	6.8	6.6	6.3	6.1	5.8
95.0	35	7.2	7.1	7.0	6.7	6.5	6.2	6.0	5.7
96.8	36	7.1	7.0	6.9	6.6	6.4	6.1	5.9	5.6
98.6	37	7.0	6.8	6.7	6.5	6.3	6.0	5.8	5.6
100.4	38	6.9	6.7	6.6	6.4	6.2	5.9	5.7	5.5
102.2	39	6.8	6.6	6.5	6.3	6.1	5.8	5.6	5.4
104.0	40	6.7	6.5	6.4	6.2	6.0	5.7	5.5	5.3
105.8	41	6.6	6.4	6.3	6.1	5.9	5.6	5.4	5.2
107.6	42	6.5	6.3	6.2	6.0	5.8	5.6	5.3	5.1
109.4	43	6.4	6.2	6.1	5.9	5.7	5.5	5.2	5.0
111.2	44	6.3	6.1	6.0	5.8	5.6	5.4	5.2	4.9
113.0	45	6.2	6.0	5.9	5.7	5.5	5.3	5.1	4.8
114.8	46	6.1	5.9	5.9	5.6	5.4	5.2	5.4	4.8
116.6	47	6.0	5.9	5.8	5.6	5.3	5.1	4.8	4.7
118.4	48	5.9	5.8	5.7	5.5	5.3	5.0	4.8	4.6
120.2	49	5.8	5.7	5.6	5.4	5.2	5.0	4.7	4.5
122.0	50	5.7	5.6	5.5	5.3	5.1	4.9	4.7	4.4

Sample Collection, Preservation and Storage

Correct sampling and storage are critical for accurate testing. For greatest accuracy, thoroughly clean sampling devices and containers to prevent carryover from previous samples. Preserve the sample properly; each procedure has information about sample preservation.

- The least expensive containers are polypropylene or polyethylene.
- The best and most expensive containers are quartz or PTFE (polytetrafluoroethylene, Teflon).
- Avoid soft glass containers for metals in the microgram-per-liter range.
- Store samples for silver determination in light-absorbing containers, such as amber bottles.

Avoid contaminating the sample with metals from containers, deionized water or membrane filters. Thoroughly clean sample containers as described under Acid Washing Bottles.

Preservation slows the chemical and biological changes that continue after collection. These processes may change the amount of a chemical species available for analysis. Normally, analyze the samples as soon as possible after collection, especially when the analyte concentration is expected to be low. This also reduces the chance for error and minimizes labor.

Preservation methods include pH control, chemical addition, refrigeration and freezing. *Table 4* gives the recommended preservation for various substances. It also includes suggested types of containers and the maximum recommended holding times for properly preserved samples.

Preserve aluminum, cadmium, chromium, cobalt, copper, iron, lead, nickel, potassium, silver and zinc samples for at least 24 hours by adding one Nitric Acid Solution Pillow 1:1 (Cat. No. 2540-98) per liter of sample. Check the pH with pH indicator paper or a pH meter to assure the pH is 2 or less. Add additional pillows if necessary. Adjust the sample pH prior to analysis by adding an equal number of Sodium Carbonate Anhydrous Powder Pillows (Cat. No. 179-98). Or raise the pH to 4.5 with Sodium Hydroxide Standard Solution, 1 N or 5 N. Correct for the added volume of the preservatives; see *Correcting For Volume Additions*.

Table 4 Required Containers, Preservation Techniques and Holding Times[1]

Parameter No./Name	Container[2]	Preservation[3,4]	Maximum Holding Time[5]
Table 1A - Bacterial Tests:			
1-4. Coliform, fecal and total	P,G	Cool, 4°C, 0.008%, $Na_2S_2O_3$[6]	6 hours
5. Fecal streptococci	P,G	Cool, 4°C, 0.008%, $Na_2S_2O_3$	6 hours
Table 1B - Inorganic Tests:			
1. Acidity	P, G	Cool, 4°C	14 days
2. Alkalinity	P, G	Cool, 4°C	14 days
4. Ammonia	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
9. Biochemical oxygen demand (BOD)	P, G	Cool, 4°C	48 hours
10. Boron	P, PFTE or quartz	HNO_3 to pH<2	6 months
11. Bromide	P, G	None required	28 days
14. Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours
15. Chemical oxygen demand	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
16. Chloride	P, G	None required	28 days
17. Chlorine, total residual	P, G	None required	Analyze immediately
21. Color	P, G	Cool, 4°C	48 hours
23-24. Cyanide, total and amenable to chlorination	P, G	Cool, 4°C, NaOH to pH>12, 0.6 g ascorbic acid[6]	14 days[7]
25. Fluoride	P	None required	28 days
27. Hardness	P, G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately
31, 43. Kjeldahl and organic nitrogen	P, G	Cool 4°C, H_2SO_4 to pH<2	28 days
Metals:[8]			
18. Chromium VI	P, G	Cool, 4°C	24 hours
35. Mercury	P, G	HNO_3 to pH<2	6 months
3, 5-8, 12, 13, 19, 20, 22, 26, 29, 30, 32-34, 36, 37, 45, 47, 51, 52, 58-60, 62, 63, 70-72, 74, 75.[9] Metals, except boron, chromium VI and mercury	P, G	do	6 months
38. Nitrate	P, G	Cool, 4°C	48 hours
39. Nitrate-nitrite	P, G	Cool 4°C, H_2SO_4 to pH<2	28 days
40. Nitrite	P, G	Cool, 4°C	48 hours
41. Oil and grease	G	Cool, 4°C, HCl or H_2SO_4 to pH<2	28 days
42. Organic Carbon	P, G	Cool, 4°C, HCl or H_2SO4 or H_3PO_4 to pH<2	28 days
44. Orthophosphate	P, G	Filter immediately; Cool, 4°C	48 hours

Table 4 Required Containers, Preservation Techniques and Holding Times[1] (continued)

Parameter No./Name	Container[2]	Preservation[3,4]	Maximum Holding Time[5]
46. Oxygen, dissolved probe	G Bottle and top	None required	Analyze immediately
47. Winkler	G Bottle and top	Fix on site and store in dark	8 hours
48. Phenols	G only	Cool 4°C, H_2SO_4 to pH<2	28 days
49. Phosphorus, elemental	G	Cool, 4°C	48 hours
50. Phosphorus, total	P, G	Cool, 4°C, H_2SO_4 to pH<2	28 days
53. Residue, total	P, G	Cool, 4°C	7 days
54. Residue, filterable	P, G	Cool, 4°C	7 days
55. Residue, Nonfilterable (TSS)	P, G	Cool, 4°C	7 days
56. Residue, Settleable	P, G	Cool, 4°C	48 hours
57. Residue, volatile	P, G	Cool, 4°C	7 days
61. Silica	P, PFTE or quartz	Cool, 4°C	28 days
64. Specific conductance	P, G	Cool, 4°C	28 days
65. Sulfate	P, G	Cool, 4°C	28 days
66. Sulfide	P, G	Cool 4°C, add zinc acetate plus sodium hydroxide to pH>9	7 days
67. Sulfite	P, G	none required	Analyze immediately
68. Surfactants	P, G	Cool, 4°C	48 hours
69. Temperature	P, G	None required	Analyze immediately
73. Turbidity	P, G	Cool, 4°C	48 hours

[1]This table was taken from Table II published in the Federal Register, July 1, 1995, 40 CFR, Part 136.3, pages 643-645. Organic tests are not included.

[2]Polyethylene (P) or glass (G).

[3]Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

[4]When any sample is to be shipped by common carrier or sent through United States Mails, it must comply with the Department of Transportation Hazardous Material Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[5]Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permitee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administer under §136.3(e). Some samples may not be stable for the maximum time period given in the table. A permitee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See §136.3(e) for details. The term “analyze immediately” usually means within 15 minutes or less after sample collection.

[6]Should only be used in the presence of residual chlorine.

[7]Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

[8]Samples should be filtered immediately on-site before adding preservative for dissolved metals.

[9]Numbers refer to parameter numbers in 40 CFR Part 136.3, Table 1B.

Collecting Water Samples

Obtain the best sample by careful collection. In general, collect samples near the center of the vessel or duct and below the surface. Use only clean containers (bottles, beakers). Rinse the container several times first with the water to be sampled.

Take samples as close as possible to the source of the supply. This lessens the influences of the distribution system on the sample. Let the water run long enough to flush the system. Fill sample containers slowly with a gentle stream to avoid turbulence and air bubbles. Collect water samples from wells after the pump has run long enough to deliver water representative of the ground water feeding the well.

It is hard to obtain a truly representative sample when collecting surface water samples. Obtain best results by testing several samples. Use samples taken at different times from several locations and depths. The results can be used to establish patterns for that particular body of water.

Generally, as little time as possible should elapse between collecting the sample and analyzing it.

Depending on the test, special precautions in handling the sample may be necessary. This prevents natural interferences such as organic growth or loss or gain of dissolved gases. Each procedure describes sample preservatives and storage techniques for samples that are held for testing.

Acid Washing Bottles

If a procedure suggests acid-washing, use the following instructions:

a) Clean the glassware or plasticware with laboratory detergent (phosphate-free detergent is recommended).

b) Rinse well with tap water.

c) Rinse with a 1:1 Hydrochloric Acid Solution or 1:1 Nitric Acid Solution.

d) Rinse well with deionized water at least four times. Up to 12-15 rinses may be necessary if chromium is being determined.

e) Air dry.

Use chromic acid or chromium-free substitutes to remove organic deposits from glass containers. Rinse containers thoroughly with water to remove traces of chromium.

Wash glassware for phosphate determinations with phosphate-free detergents and acid-wash with 1:1 HCl. Thoroughly rinse the glassware with deionized water. For ammonia and Kjeldahl nitrogen, rinse with ammonia-free water.

Correcting for Volume Additions

If you use a large volume of preservative, correct for the volume of preservative added. This accounts for dilution due to the acid added to preserve the sample and the base used to adjust the pH to the range of the procedure. This correction is made as follows:

1. Determine the volume of initial sample, the volume of acid and base added, and the total or final volume of the sample.

2. Divide the total volume by the initial volume of sample.

3. Multiply the test result by this factor.

Example:
A one-liter sample was preserved with 2 mL of nitric acid. It was neutralized with 5 mL of 5 N sodium hydroxide. The result of the analysis procedure was 10.00 mg/L. What is the volume correction factor and correct result?

1. Total Volume = 1000 mL + 2 mL + 5 mL = 1007 mL

2. $\frac{1007}{1000}$ = 1.007 = volume correction factor

3. 10.0 mg/L $\times$ 1.007 = 10.07 mg/L = correct result

Hach 1:1 Nitric Acid Pillows contain 2.5 mL of acid; correct for this volume. The addition of a Sodium Carbonate Power Pillow (neutralizes the 1:1 Nitric Acid Solution Pillow) does not need to be corrected for.

Boiling Aids

Boiling is necessary in some procedures. Using a boiling aid such as boiling chips (Cat. No. 14835-31) helps reduce bumping. Bumping is caused by the sudden, almost explosive conversion of water to steam as it is heated. Avoid bumping; it may cause injury or sample loss.

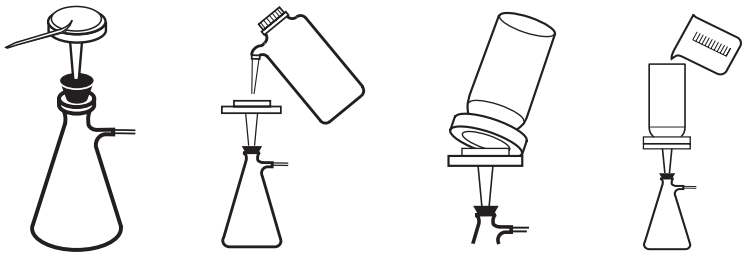
Make sure the boiling aids will not contaminate the sample. Do not use boiling aids (except glass beads) more than once. Loosely covering the sample during boiling will prevent splashing, reduce the chances of contamination and minimize sample loss.

Sample Filtration

Filtering separates particles from the aqueous sample. Filtration uses a medium, usually filter paper, to retain particles but pass solution. This is especially helpful when sample turbidity interferes with analysis. Two general methods of filtration are gravity and vacuum. Gravity filtration uses gravity to pull the sample though the filter paper. Vacuum filtration uses suction and gravity to move the sample through the filter. An aspirator or vacuum pump creates the suction. Vacuum filtration is faster than gravity filtration. Vacuum filter (see *Figure 1*) as follows:

1. Using tweezers, place a filter paper into the filter holder.
2. Place the filter holder assembly in the filtering flask. Wet the filter with deionized water to ensure adhesion to the holder. Empty the flask before filtering the sample.
3. Position the funnel housing on the filter holder assembly.
4. While applying a vacuum to the filtering flask, transfer the sample to the filtering apparatus.
5. Slowly release the vacuum from the filtering flask and transfer the solution from the filter flask to another container.

Figure 1 Vacuum Filtration



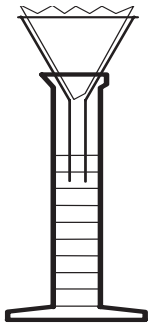
REQUIRED APPARATUS FOR VACUUM FILTRATION

Description	Unit	Cat. No.
Filter Discs, glass 47 mm, 1.5 µm	100/pkg	2530-00
Filter Holder, membrane	each	13529-00
Flask, filter, 500 mL	each	546-49
Pump, vacuum, hand operated	each	14283-00
OR		
Pump, vacuum, portable, 115 V	each	14697-00
Pump, vacuum, portable, 230 V	each	14697-02

Several procedures in this manual use gravity filtration. The only labware required is filter paper, a conical funnel and a receiving vessel. This labware is included under Optional Apparatus at the end of a procedure. Gravity filtration is better for retaining fine particles. For faster filtering, add solution until the filter paper cone is three-fourths filled. Never fill the cone completely. Gravity filter (see *Figure 2*) as follows:

1. Place a filter paper into the funnel.
2. Wet the filter with deionized water to ensure adhesion to the funnel. Allow all the deionized water to drain.
3. Place the funnel into an erlenmeyer flask or graduated cylinder.
4. Pour the sample into the funnel.

Figure 2 Gravity Filtration



REQUIRED APPARATUS FOR GRAVITY FILTRATION

Description	Unit	Cat No.
Cylinder, graduated, 100 mL	each	508-42
Funnel, poly, 65 mm	each	1083-67
Filter Paper, 12.5 cm	each	1894-57
Flask, erlenmeyer, 125 mL	each	505-43

Testing for metals requires acid and heat to pretreat the sample. Since these conditions destroy filter paper, vacuum filtration with glass fiber filter discs is recommended. Also, glass filter discs, unlike paper, do not retain colored species.

Temperature Considerations

For best results, perform most tests in this manual with sample temperatures between 20 °C (68 °F) and 25 °C (77 °F). If a test requires closer temperature control, notes in the procedure will indicate this.

Sample Dilution Techniques

Ten and 25 mL are the volumes used for most colorimetric tests. However, in some tests, the color developed in the sample may be too intense to be measured. Unexpected colors may develop in other tests. In both cases, dilute the sample to determine if interfering substances are present.

To dilute the sample easily, pipet the chosen sample portion into a clean graduated cylinder (or volumetric flask for more accurate work). Fill the cylinder (or flask) to the desired volume with deionized water. Mix well. Use the diluted sample when running the test.

To help with dilutions, *Table 5* shows the amount of sample used, the amount of deionized water used to bring the volume up to 25 mL and the multiplication factor.

The concentration of the sample is equal to the diluted sample reading multiplied by the multiplication factor.

More accurate dilutions can be done with a pipet and a 100-mL volumetric flask (see *Table 6* for more information). Pipet the sample and dilute to volume with deionized water. Swirl to mix.

Table 5 Sample Dilution Volumes

Sample Volume (mL)	mL Deionized Water Used to Bring the Volume to 25 mL	Multiplication Factor
25.0	0.0	1
12.5	12.5	2
10.0[1]	15.0	2.5
5.0[1]	20.0	5
2.5[1]	22.5	10
1.0[1]	24.0	25
0.250[1]	24.75	100

[1]For sample sizes of 10 mL or less, use a pipet to measure the sample into the graduated cylinder or volumetric flask.

Table 6 Multiplication Factors for Diluting to 100 mL

Sample Volume (mL)	Multiplication Factor
1	100
2	50
5	20
10	10
25	4
50	2

Sample Dilution and Interfering Substances

Sample dilution may influence the level at which a substance may interfere. The effect of the interferences decreases as the dilution increases. In other words, higher levels of an interfering substance can be present in the original sample if it is diluted before analysis.

An Example:

Copper does not interfere at or below 100 mg/L for a 25.00 mL sample in a procedure. If the sample volume is diluted with an equal volume of water, what is the level at which copper will not interfere?

$$\frac{\text{Total volume}}{\text{Sample volume}} = \text{Dilution factor}$$

$$\frac{25}{12.5} = 2$$

$$\text{Interference Level} \times \text{Dilution Factor} = \text{Interference level in sample}$$

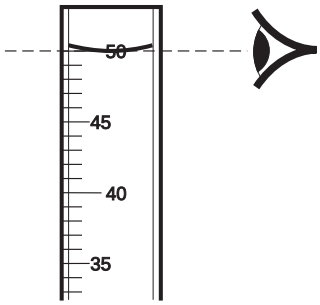
$$100 \times 2 = 200$$

The level at which copper will not interfere in the undiluted sample is at or below 200 mg/L.

Using Pipets and Graduated Cylinders

When small sample quantities are used, the accuracy of measurements is important. *Figure 3* illustrates the proper way of reading the sample level or the meniscus formed when the liquid wets the cylinder or pipet walls.

Figure 3 Reading the Meniscus



Rinse the pipet or cylinder two or three times with the sample to be tested before filling. Use a pipet filler or pipet bulb to draw the sample into the pipet. Never pipet chemical reagent solutions or samples by mouth. When filling a pipet, keep the tip of the pipet below the surface of the sample as the sample is drawn into the pipet.

Serological pipets have marks that indicate the volume of liquid delivered by the pipet. The marks may extend to the tip of the pipet or may be only on the straight portion of the tube. If the marks are only on the straight part of the tube, fill serological pipets to the zero mark and discharge the sample by draining the sample until the meniscus is level with the desired mark. If the serological pipet has marks extended to the tip of the pipet, fill the pipet to the desired volume and drain all the sample from the pipet. Then blow the sample out of the pipet tip for accurate measurements.

Volumetric (transfer) pipets have a bulb in the middle and a single ring above the bulb to indicate the volume of liquid when it is filled to the mark. To discharge a volumetric pipet, hold the pipet vertical until only a small amount of liquid remains (about ¾ inch), then hold the pipet at a slight angle against the container wall to drain. Do not attempt to discharge the solution remaining in the tip of the pipet after draining. Volumetric pipets are designed to retain a small amount of sample in the pipet tip.

If sample drops stay on the walls of the pipet, the pipet is dirty and is not delivering the correct amount of sample. Wash the pipet thoroughly with a laboratory detergent or cleaning solution and rinse several times with deionized water.

Using the TenSette Pipet

For best results use a new tip each time you pipet. After several uses, the pipet tip may retain some liquid, causing inaccurate delivery. Each pipet is supplied with 50 tips; order Hach replacement tips for best results.

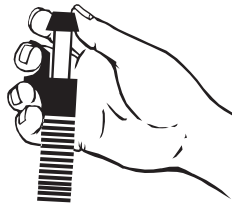
Always use careful, even hand movements for best reproducibility. If the pipet does not operate smoothly, disassemble and coat the piston and retainer with high-quality stopcock grease. Also coat the metering turret lightly with grease. Refer to the TenSette Pipet manual.

For best pipetting accuracy, the solution and the room temperature should be between 20-25 °C.

Never lay the pipet down with the liquid in the tip. Solution could leak into the pipet and cause corrosion.

Operating the TenSette Pipet

1. Attach a clean tip by holding the pipet body in one hand and gently pressing the large end of the pipet tip onto the tapered end of the pipet. Be sure a good seal is obtained.

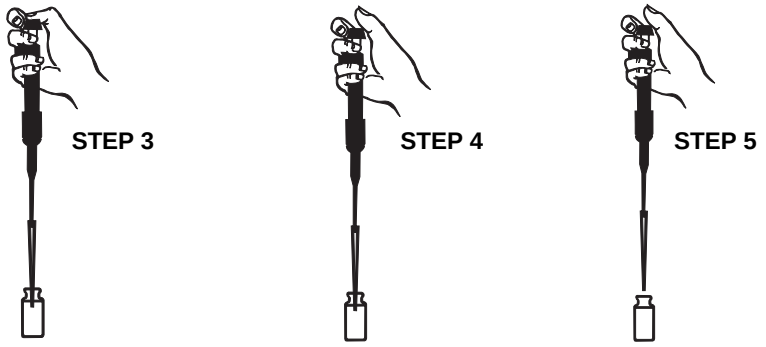


2. Turn the turret cap to align the desired volume with the mark on the pipet body.

3. Using a smooth motion, press down on the turret cap until it reaches the stop. Immerse the tip about 5 mm (¼ inch) below the solution surface to avoid drawing air into the pipet. Do not insert the tip any deeper or the delivery volume may be affected.

4. While maintaining a constant pressure, allow the turret to return slowly to the extended position. A rapid return may affect the delivery volume.

5. With the turret up, take the tip out of the solution and move it to the receiving vessel. Do not press on the turret cap while moving the pipet.



6. Use the thumb and forefinger to twist the turret cap to the next higher volume position to ensure quantitative transfer of the sample. The “F” position provides full blowout.

7. With the tip in contact with the side of the receiving vessel, slowly and smoothly press down on the turret cap until it reaches the stop and the solution is completely discharged.

Mixing Water Samples

The following two methods may be helpful in tests that require mixing sample with chemicals (usually indicated by "invert to mix" instructions).

1. When mixing sample in a round sample cell or mixing cylinder, invert the cell or cylinder; see *Figure 4*. Hold the cell in a vertical position with the cap on top. Invert the cell so the cap is on the bottom. Return the cell to the original position. Do the same with the mixing cylinder.

2. Swirling is recommended when mixing samples in a graduated cylinder or a titration flask. Grip the cylinder (or flask) firmly with the tips of three fingers; see *Figure 5*. Hold the cylinder at a 45-degree angle and twist the wrist. This should move the cylinder in an approximately 12-inch circle, creating enough rotation to complete the mixing in a few turns.

These mixing procedures are the most gentle. Both methods are simple but take a bit of practice to obtain the best results.

Figure 4 Inverting a Sample Cell

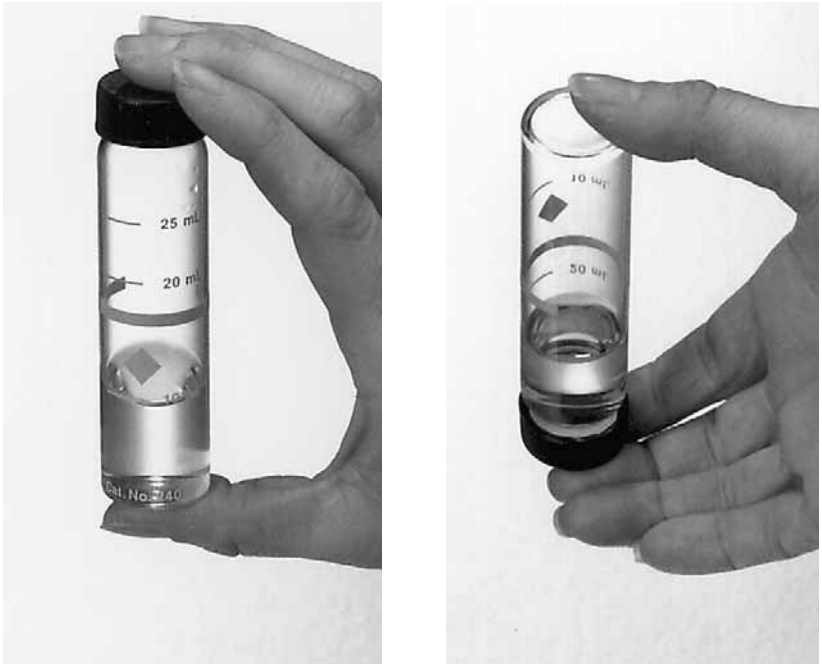
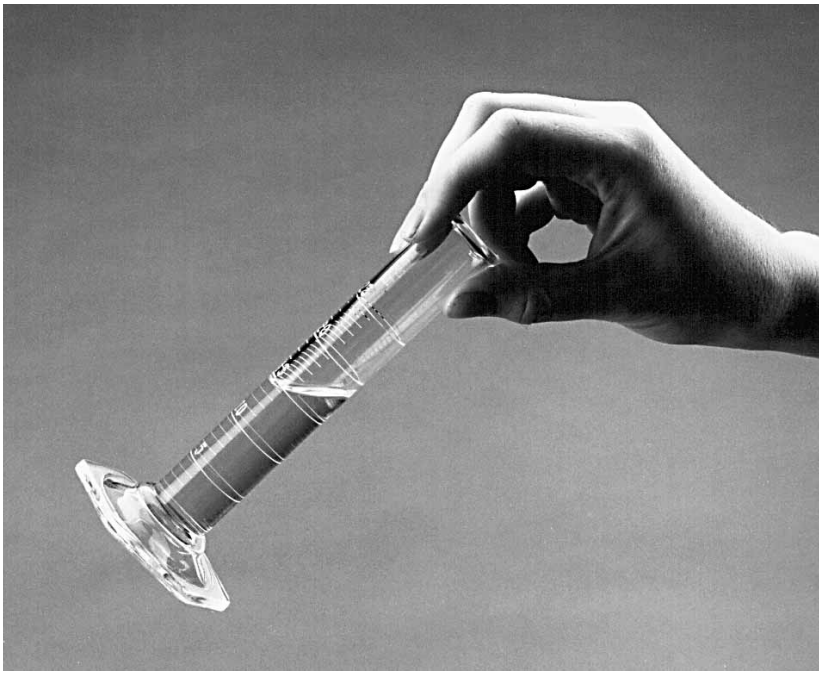


Figure 5 Swirling a Graduated Cylinder



Using Sample Cells

Orientation of Sample Cells

Two round sample cells are shipped with the DR/820, DR/850 and DR/890. They are marked with 10-, 20- and 25-mL fill lines which may be used to measure the sample volume unless the procedure instructs you to use other glassware to measure the sample volume.

To minimize variability of measurements using a particular cell, always place the cell into the cell holder with the same orientation. The cells are placed in the instrument with the fill marks facing the user.

In addition to proper orientation, the sides of the cells should be free of smudges, fingerprints, etc. to ensure accurate readings. Wipe the sides of the cells with a moist cloth followed by a dry soft cloth to clean the surface before taking measurements.

Care of Hach Sample Cells

Store sample cells in their boxes when not in use to protect them from scratching and breaking. It is good laboratory practice to empty and clean sample cells after analyses are complete--avoid leaving colored solutions in the cells for extended periods of time. Finish the cleaning procedure with a few rinses of deionized water and allow to dry. Individual procedures often recommend specific cleaning methods.

Cleaning Sample Cells

Most laboratory detergents can be used at recommended concentrations. Neutral detergents such as Neutracon are safer if regular cleaning is required, as in the case of protein residues.

If using a detergent, you can speed cleaning by increasing the temperature or using an ultrasonic bath.

Rinsing is more efficient when using deionized water.

Using the COD/TNT Adapter

Use care when seating a vial into the COD/ TNT adapter (for COD vials and Test ‘N Tubes). Place the vial into the adapter and press straight down on the top of the vial until it seats solidly. Do not move the vial from side to side; this can cause errors.

Volume Measurement Accuracy

The sample cells supplied with the instrument have fill marks to indicate 10, 20 or 25 mL. The fill marks are intended to measure the volume to be analyzed. Do not use these fill marks to perform sample dilutions.

If a sample must be diluted, use a pipet, graduated mixing cylinder and/or a volumetric flask for accurate measurement. When diluting, accuracy is important because a slight mistake in measuring a small sample will cause

a substantial error in the result. For instance, a 0.1-mL mistake in the dilution of a 1.0-mL final volume produces a 10% error in the test result.

Volumes for standard additions can be measured using the 25-mL mark, but it is not recommended for the 10-mL mark due to a potentially excessive relative error. An error of 0.5 mL in 25 mL is only 2%, while 0.5 mL error in 10 mL is 5%.

For 10 mL standard additions, follow this procedure:

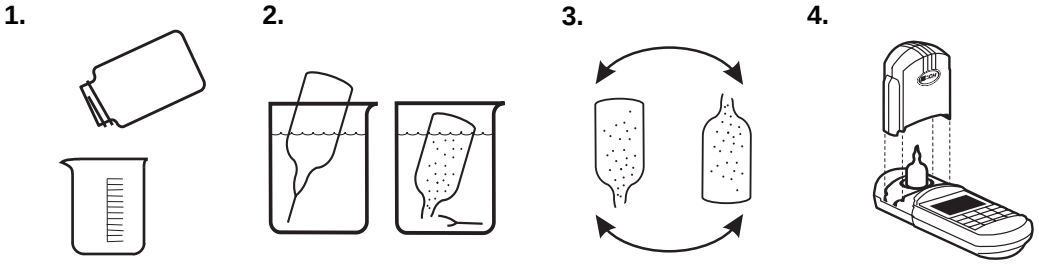
1. Transfer 10.0 mL of sample into a clean, dry sample cell (the unspiked sample).
2. Add the standard (spike) to a 25 mL portion of sample in a 25-mL mixing cylinder. Stopper and mix thoroughly.
3. Transfer 10 mL to another sample cell (use fill mark) for analysis.

Using AccuVac Ampuls

AccuVac ampuls contain pre-measured powder or liquid in optical-quality glass ampuls.

1. Collect the sample in a beaker or other open container.
2. Place the ampul tip well below the sample surface and break the tip off (see *Figure 6*) against the beaker wall. The break must be far enough below the surface to prevent air from being drawn in as the level of the sample lowers (the AccuVac Breaker may be used instead of breaking the ampul against the beaker side).
3. Invert the ampul several times to dissolve the reagent. Do not place your finger over the broken end; the liquid will stay in the ampul when inverted. Wipe the ampul with a towel to remove fingerprints, etc.
4. Insert the ampul into the instrument and read the results directly.

Figure 6 Using AccuVac Ampuls



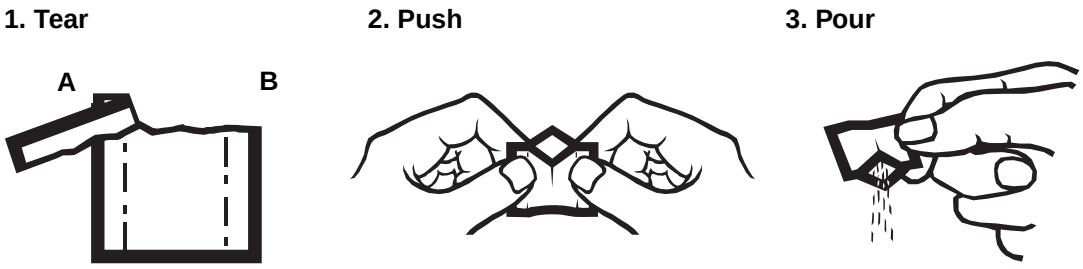
Using Reagent Powder Pillows

Hach uses dry powdered reagents when possible. This minimizes leakage and deterioration problems. Some powders are packaged in individual, pre-measured, polyethylene "powder pillows" or foil pillows called PermaChem® pillows. Each pillow contains enough reagent for one test. Open the poly powder pillows with nail clippers or scissors; see *Figure 7*.

Figure 7 Opening Powder Pillows

Using PermaChem Pillows

1. Tap the pillow on a hard surface to collect the powdered reagent in the bottom.
2. Tear (or cut) across the top of the pillow, from B to A, holding the pillow away from your face.
3. Using two hands, push both sides toward each other to form a spout.
4. Pour the pillow contents into the sample cell and continue the procedure according to the instructions. Tap the pillow to remove any powder from the corners.



Reagent and Standard Stability

Hach always strives to make stable formulations and package them to provide maximum protection. Most chemicals and prepared reagents do not deteriorate after manufacture. However, the way they are stored and the packaging can affect how long the reagents are stable. Light, bacterial action, and absorption of moisture and gases from the atmosphere can affect shelf life. Some chemicals may react with the storage container or they may react with other chemicals.

Chemicals supplied with the colorimeter have an indefinite shelf life when stored under average room conditions, unless the packaging says something different. Product labels state any special storage conditions required. Otherwise, store reagents in a cool, dry, dark place for maximum life. It is always good practice to date chemicals when you receive them. Use older supplies first. If in doubt about the reagent shelf life, run a standard to check its effectiveness.

Interferences

Substances in the sample may interfere with a measurement. Hach mentions common interferences in the test procedures. The reagent formulations eliminate many interferences. You can remove others with sample pretreatments described in the procedure.

If you get an unusual answer, a color that you don't expect, or you notice an unusual odor or turbidity, the result may be wrong. Repeat the test on a sample diluted with deionized water; see *Sample Dilution Techniques.* Compare the result (corrected for the dilution) with the result of the original test. If these two are not close, the original result may be wrong and you should make an additional dilution to check the second test (first dilution). Repeat this process until you get the same corrected result twice in a row.

More information about interferences and methods to overcome them is contained in *Standard Additions* of this manual and the *General Introduction* section of APHA Standard Methods. Hach urges the analyst to obtain this book and refer to it when problems are encountered.

One of the greatest aids is knowing what is in the sample. You don't need to know exactly what is in each sample, but be aware of substances that are likely to interfere in the analysis method you use. When using a method, it may be helpful to determine if those interferences are present.

pH Interference

Many of the procedures in this manual only work within a certain pH range. Hach reagents contain buffers to adjust the pH of the typical sample to the correct pH range. However, the reagent buffer may not be strong enough for some samples. This occurs most often with highly buffered samples or samples with extreme sample pH.

The *Sampling and Storage* section of each procedure usually gives the proper pH range for the sample.

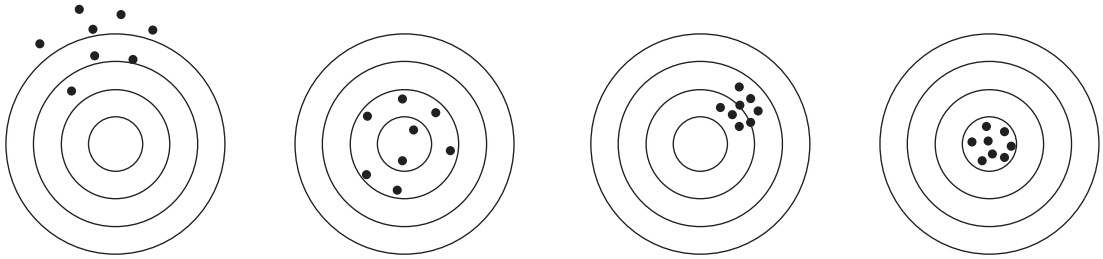
Adjust the sample to the proper pH range before testing. If this information is not given, follow these steps:

1. Measure the pH of your analyzed sample with a pH meter. For measuring Ag^+, K^+ or Cl^- , use pH paper.
2. Prepare a sample using deionized water. Add all reagents called for in the procedure. Timer sequences, etc., may be ignored. Mix well.
3. Measure the pH of the reagent blank with a pH meter.
4. Compare the pH values of your analyzed sample with the reagent blank.
5. If there is little difference in the values of your analyzed sample and the reagent blank, then pH interference is not the problem. Follow the *Accuracy Check* given in the procedure to help identify the problem.
6. If there is a large difference between the value of your analyzed sample and the reagent blank, adjust the sample pH to the value of the reagent blank. Adjust the sample pH to this same pH for all future samples from the same source before analysis. Use the appropriate acid, usually nitric acid, to lower the pH (do not use nitric acid for nitrate or nitrogen testing). Use the appropriate base, usually sodium hydroxide, to raise the pH. Adjust the final result for any dilution caused by adding acid or base; see *Correcting for Volume Additions*.
7. Analyze the sample as before.
8. Some purchased standards may be very acidic and will not work directly with Hach procedures. Adjust the pH of these standards as described above. Adjust the final concentration of the standard for the dilution. The Hach standard solutions suggested in the procedures are formulated so that no pH adjustment is necessary.

Accuracy and Precision

Accuracy is the nearness of a test result to the true value. Precision is how closely repeated measurements agree with each other. Although good precision suggests good accuracy, precise results can be inaccurate (see *Figure 8*). The following paragraphs describe how to improve accuracy and precision of analyses by using Standard Additions.

Figure 8 Precision and Accuracy Illustrated



Standard Additions

Standard Additions is a common technique for checking test results. Other names are “spiking” and “known additions.” The standard additions technique can test for interferences, bad reagents, faulty instruments, and incorrect procedures.

Perform Standard Additions by following the Standard Additions Method section in the procedure under *Accuracy Check*. Follow the detailed instructions given.

If you get about 100% recovery for each addition, everything is working right and your results are correct.

If you don’t get about 100% recovery for each addition, a problem exists. You can tell if you have an interference. Repeat the Standard Additions using deionized water as your sample. If you get about 100% recovery for each addition, you have an interference. If you didn’t get good recoveries with the deionized water, the following checklist may help to find the problem quickly:

1. Check to see that you are following the procedure exactly:

a) Are you using the proper reagents in the proper order? Are you using 10-mL reagents with a 10-mL sample or 25-mL reagents with a 25-mL sample?

b) Are you waiting the necessary time for color to develop?

c) Are you using the correct glassware?

d) Is the glassware clean?

e) Does the test need a specific sample temperature?

f) Is the sample's pH in the correct range?

Hach's written procedure should help you to answer these questions.

2. Check your reagents. Repeat the Standard Additions using new, fresh reagents. If your results are good, the original reagents were bad.

3. If nothing else is wrong, the standard is almost certainly bad. Repeat the Standard Additions with a new standard.

If the check list does not determine the problem, use the decision tree (*Figure 9*) and explanation of each branch, below, to identify the problem.

Branch A

Suppose a single standard addition to the sample did not give the correct concentration increase. A possible cause could be interferences. Other causes include defective reagents, incorrect technique, a defective instrument/apparatus or defective standard used for the standard addition.

If interferences are known or assumed to be absent, proceed to Branch B. If interferences are known to be present, proceed to Branch C.

Branch B

Perform multiple standard additions on a sample of deionized water as in the following example using iron as the analyte of interest:

1. Pour 25 mL of deionized water into a 25-mL sample cell.

2. Add 0.1 mL of a 50-mg/L iron standard solution to a second 25 mL sample of deionized water.

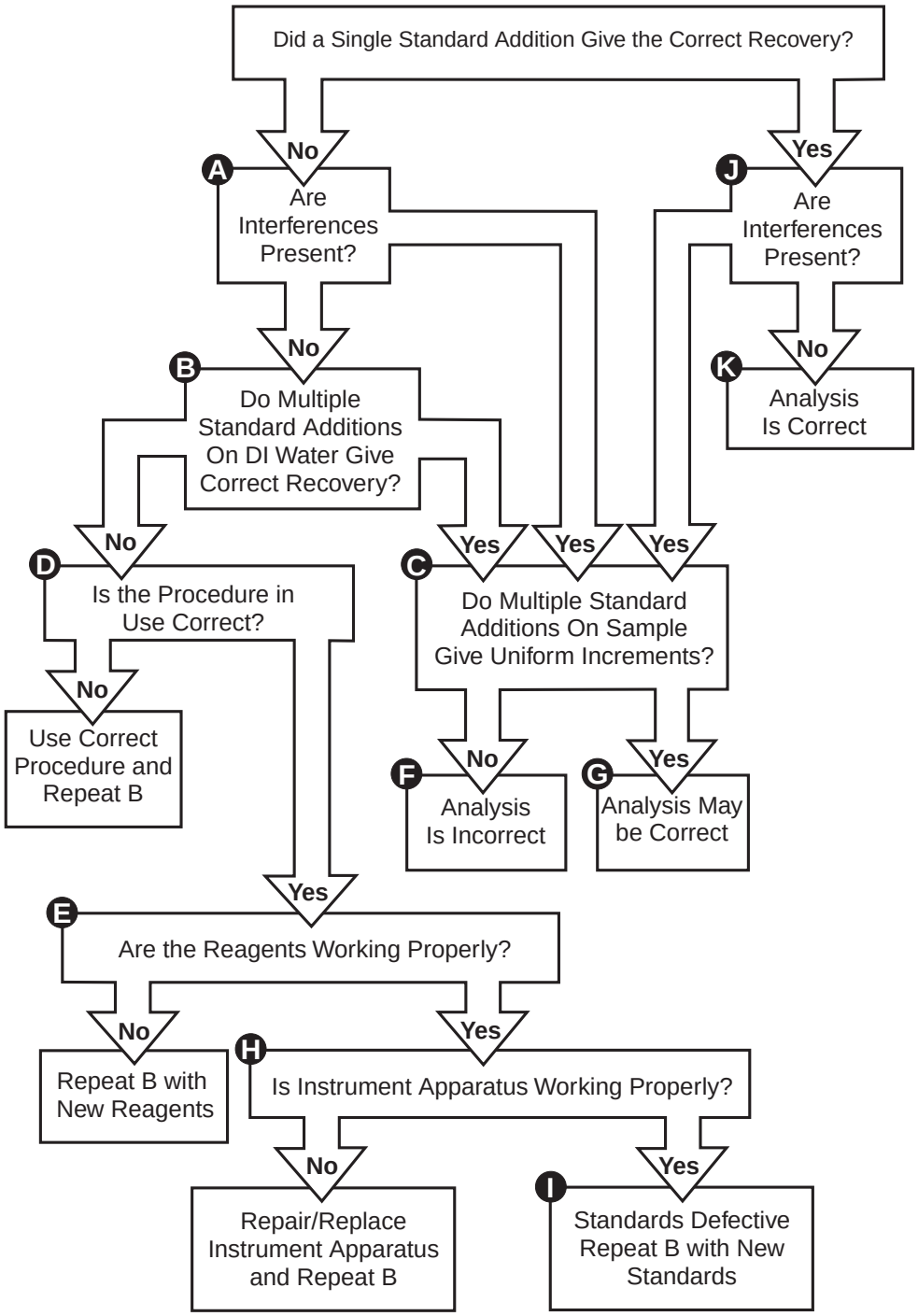
3. Add 0.2 mL of the same standard to a third 25 mL sample of deionized water.

4. Add 0.3 mL of the same standard to a fourth 25 mL sample of deionized water. Analyze all these samples for iron.

5. Tabulate the data as shown below:

mL of Standard Added	mg/L of Standard Added	mg/L of Iron Found
0	0	0
0.1	0.2	0.2
0.2	0.4	0.4
0.3	0.6	0.6

Figure 9 Standard Additions Decision Tree



The data show several points:

- The chemicals, instrument, procedure/technique and standards are working correctly because the iron added to the water sample was completely recovered in the same uniform steps that match the standard addition increments.
- Because iron added to the deionized water was recovered, but iron added to an actual sample was not recovered (Branch A), the sample contains an interference which prevents the test reagents from working properly.
- An iron analysis previously done on the actual sample using this method gave an inaccurate result.

If the results of multiple standard additions give the correct increment for each addition, proceed to Branch C.

If the results of multiple standard additions do not give the correct increment for each addition, go to Branch D.

Branch C

If interfering substances are present, the analysis may be incorrect. However, with multiple standard additions, it may be possible to arrive at an approximate result if the increases are uniform.

Suppose the sample result for iron was 1.0 mg/L. Because interferences may be present, a standard addition of 0.1 mL of a 50 mg/L iron standard to a 25 mL sample is made. The expected increase in the iron concentration is 0.2 mg/L, but the actual increase is 0.1 mg/L. Then 0.2 and 0.3 mL of the same standard are added to two more 25 mL samples and analyzed for iron.

If there is a uniform increase in concentration between each addition (i.e., 0.1 mg/L difference between each addition), use Branch G. If the increase in concentration is not uniform (i.e., 0.1, 0.08, 0.05), go to Branch F.

Branch D

Carefully check the instructions for the test. Make sure to use the correct reagents in the correct order. Be sure the glassware in use is what is required. Be sure time for color development and the sample temperature are as specified. If the procedure technique was incorrect, repeat Branch B. If the procedure was correctly followed, proceed to Branch E.

Branch E

Check the reagent performance. This may be done by obtaining a fresh lot of reagent or by using a known standard solution to run the test. Make sure the color development time given in the procedure is equal to the

time required for the reagent in question. If the reagent(s) is defective, repeat Branch B with new reagents. If the reagents are good, proceed with Branch H.

Branch F

Examples of non-uniform increments between standard additions are shown below.

Example A

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	1.0
0.1	0.2	1.10
0.2	0.4	1.18
0.3	0.6	1.23

Example B

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0
0.1	0.2	0
0.2	0.4	0.2
0.3	0.6	0.4

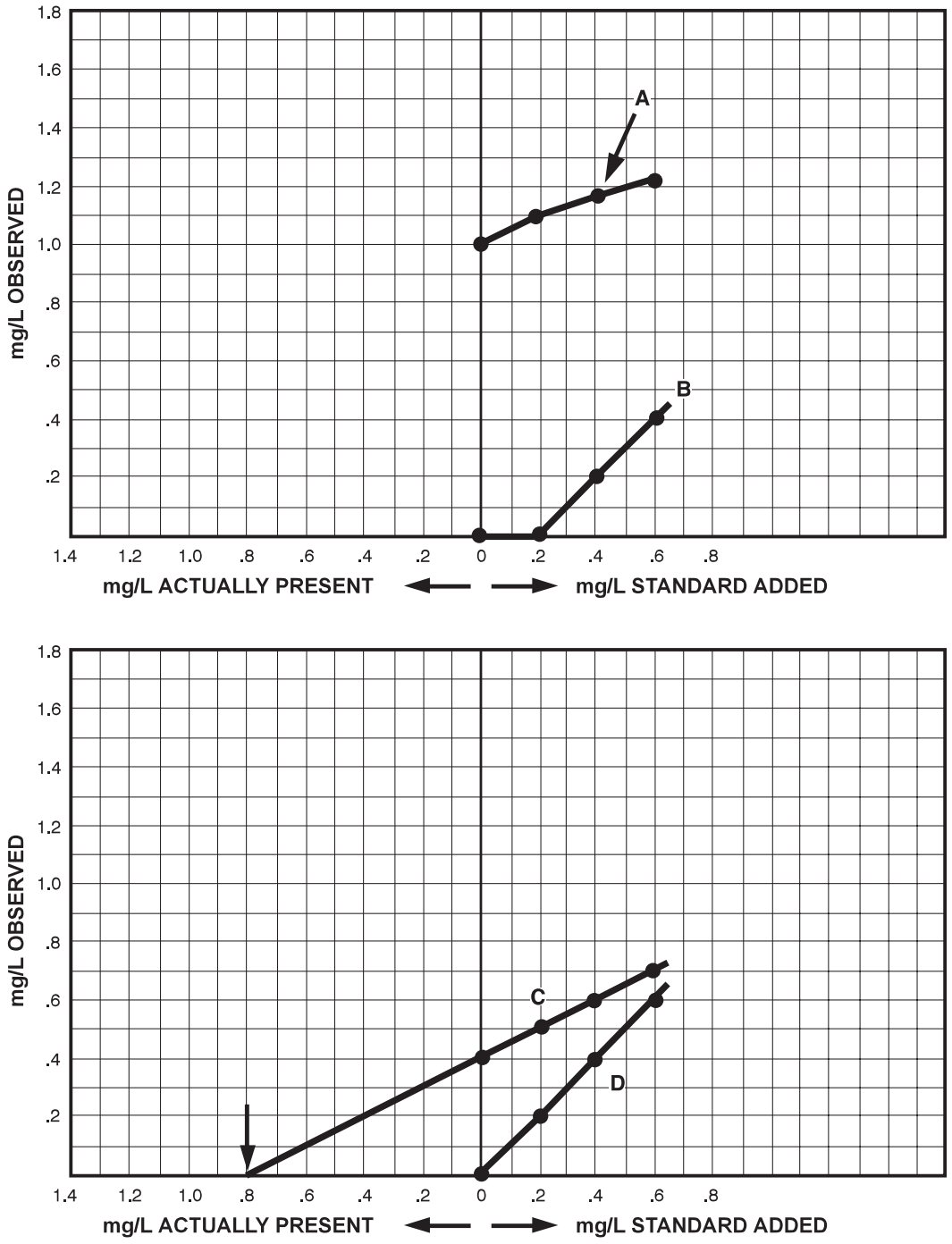
These examples show the effect of interferences on the standard addition. Data plotted on the graph in *Figure 10* for samples A and B show that the four data points do not lie on a straight line.

The plot for sample A illustrates an interference that becomes progressively worse as the concentration of the standard increases. This type of interference is uncommon and may be caused by an error or malfunction of the procedure, reagents or instrument. It is recommended Branch B be performed to verify the supposed interference.

The plot for sample B shows a common chemical interference which becomes less or even zero as the concentration of standard increases. The graph shows the first addition was consumed by the interference and the remaining additions gave the correct increment of 0.2 mg/L.

The apparent interference in Example B could be the result of an error made in the standard addition. Repeat the analysis to see if an error was made during standard addition. If not, the method is not appropriate for the sample matrix. When these two types of interferences occur, try to analyze the sample with a method which uses a different type of chemistry.

Figure 10 Multiple Standard Additions Graph



Branch G

Examples of uniform increments between standard additions are given below.

Example C

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0.4
0.1	0.2	0.5
0.2	0.4	0.6
0.3	0.6	0.7

The plot for sample C illustrates a common interference with a uniform effect on the standard and the substances in the sample. The four data points form a straight line which may be extended back through the horizontal axis. The point where the line meets the axis can be used to determine the concentration of the substance you are measuring.

In this example, the first analysis gave 0.4 mg/L. After extrapolating the line to the horizontal axis, the graph shows the result should be much closer to the correct result: 0.8 mg/L.

Apparent interferences may also be caused by a defect in the instrument or standards. Before assuming the interference is chemical, check Branch B.

Example D

mL of Standard Added	mg/L Standard Added	mg/L Found
0	0	0
0.1	0.2	0.2
0.2	0.4	0.4
0.3	0.6	0.6

The plot for sample D illustrates a problem for the analyst. The increments are uniform and the recovery of the standard was complete. The result of the first analysis was 0 mg/L and the line extrapolates back through 0 mg/L. If interferences are known to be present, the interferences may be present in an amount equal to the substance in question, preventing the analyst from finding the substance. This would be an uncommon situation.

Branch H

Check operation of the instrument and/or apparatus used to perform the test. Check glassware used in the procedure and make sure it is extremely clean. Dirty pipets and graduated cylinders can cause contamination and will not deliver the correct volume. Check delivery of pipets by using deionized water and a balance; 0.2 mL = 0.2 grams.

If a defect is found in the instrument and/or apparatus, repeat Branch B after repair or replacement. If the instrument and apparatus are working, proceed with Branch I.

Branch I

After determining the procedure, reagents, instrument and/or apparatus are correct and working properly, you may conclude the only possible cause for standard additions not functioning correctly in deionized water is the standard used for performing standard additions. Obtain a new standard and repeat Branch B.

Branch J

If the standard additions gives the correct result, the analyst must then determine if an interfering substance(s) is present. If interfering substances are present, proceed to Branch C. If they are not present, the analysis is correct.

If you still cannot identify the problem, extra help is available. Please call our Technical Support Group at 800-227-4224 (U.S.A.) or 970-669-3050. A representative will be happy to help you.

Method Performance

Estimated Detection Limit

Ranges for chemical measurements have limits. The lower limit is important because it determines whether a measurement is different from zero. Many experts disagree about the definition of this detection limit, and determining it can be difficult. The Code of Federal Regulations (40 CFR, Part 136, Appendix B) provides a procedure to determine the “Method Detection Limit” or MDL. The MDL is the lowest concentration that is different from zero with a 99% level of confidence. A measurement below this MDL may be useful, but there is a greater chance that it is actually zero.

The MDL is not fixed; it varies for each reagent lot, instrument, analyst, sample type, etc. Therefore, a published MDL may be a useful guide, but is only accurate for a specific set of circumstances. Each analyst should determine a more accurate MDL for each specific sample matrix using the same equipment, reagents and standards that will routinely be used for measurements.

Hach provides a value called the Estimated Detection Limit (EDL) for all programs. It is the calculated lowest average concentration in a deionized water matrix that is different from zero with a 99% level of confidence. Specifically, it is the upper 99% confidence limit for zero concentration based on the calibration data used to prepare the pre-programmed calibration curve. **Do not use the EDL as the MDL**. The conditions for MDL determination must be exactly the same as the conditions used for analysis. The EDL may be useful to the analyst as a starting point in determining a MDL or as a way to compare methods. Measurements below the EDL may also be valuable because they can show a trend, indicate the presence of analyte and/or provide statistical data. However, these values have a large uncertainty.

Method Detection Limit (MDL)

This method is in accordance with the USEPA definition in 40 CFR, Part 136, Appendix B (see most current edition).

The USEPA defines the method detection limit (MDL) as the minimum concentration that can be determined with 99% confidence that the true concentration is greater than zero. Since the MDL will vary from analyst to analyst, it is important that analysts determine the MDL based on their unique operating conditions.

The procedure for determining MDL is based on replicate analyses at a concentration 1 to 5 times the estimated detection limit. The MDL value is calculated from the standard deviation of the replicate study results multiplied by the appropriate Student's *t* value for a 99% confidence interval. For this definition, the MDL does not account for variation in sample composition and can only be achieved under ideal conditions.

1. Estimate the detection limit. Use the Hach estimated detection limit (EDL) value stated in the *Method Performance* section of the analysis procedure.
2. Prepare a laboratory standard of the analyte in deionized water which is free of the analyte that is 1 to 5 times the estimated detection limit.
3. Analyze at least seven portions of the laboratory standard and record each result.
4. Calculate the average and standard deviation *(s)* of the results.

5. Compute the MDL using the appropriate Student's *t* value (see table below) and the standard deviation value:

MDL = Student's *t* x *s*

Number of Test Portions	Student's *t* Value
7	3.143
8	2.998
9	2.896
10	2.821

For example:
The EDL for measuring iron using the FerroZine method is 0.003 mg/L. An analyst accurately prepared 1 liter of a 0.010 mg/L (about 3x the EDL) laboratory standard by diluting a 10-mg/L iron standard in iron-free deionized water.

Eight portions of the standard were tested according to the FerroZine method with the following results:

Sample #	Result (mg/L)
1	0.009
2	0.010
3	0.009
4	0.010
5	0.008
6	0.011
7	0.010
8	0.009

Using a calculator program, the average concentration = 0.010 mg/L and the standard deviation (*s*) = 0.0009 mg/L

Based on the USEPA's definition, calculate the MDL as follows:

MDL for FerroZine method = 2.998 (Student's *t*) x 0.0009 (*s*)

MDL = 0.003 mg/L (agrees with initial estimate)

Note: *Occasionally, the calculated MDL may be very different than Hach's estimate of the detection limit. To test how reasonable the calculated MDL is, repeat the procedure using a standard near the calculated MDL. The average result calculated for the second MDL derivation should agree with the initial calculated MDL. Refer to 40 CFR, Part 136, Appendix B (7-1-94), pages 635-637 for detailed procedures to verify the MDL determination.*

Note: *Run a laboratory blank, containing deionized water without analyte, through the test procedure to confirm that the blank measurement is less than the calculated MDL. If the blank measurement is near the calculated MDL, repeat the MDL procedure using a separate blank for analysis for each standard solution portion analyzed. Subtract the average blank measurement from each standard and use the corrected standard values to calculate the average and standard deviation used in the MDL.*

Precision

Every measurement has some degree of uncertainty. Just as a ruler with markings of 0.1 mm leaves some doubt as to the exact length of a measurement, chemical measurements also have some degree of uncertainty. The quality of the entire chemical method determines the precision.

Uncertainty in chemical measurements may be due to systematic errors and/or random errors. A systematic error is a mistake that is always the same for every measurement made. For example, a blank can add to each measurement for a specific compound, giving consistently high results (a positive bias). Random errors are different for every test and add either positive or negative bias. Random errors may be caused by variation in analytical technique and cause response variation. Hach chemists work hard to eliminate systematic errors in Hach procedures using Hach reagents, but response variation occurs in all chemical measurements.

Estimating Precision

The method performance section in each procedure provides an estimate of the procedure's precision. The procedures use a "replicate analysis" estimate, based on real data.

In replicate analysis, a Hach chemist prepares a specific concentration of the analyte in a deionized water matrix. The standard is then analyzed seven individual times with the two reagent lots used in the calibration (14 total samples). A standard deviation of the two sets of seven values is calculated. The larger value is reported in the method. The reported value provides an estimate of the "scatter" of results at a particular point in the calibration curve.

It is important to stress that the estimates are based on a deionized water matrix. Precision on real samples with varying matrices can be quite different than these estimates.

Reagent Blank Correction

The Reagent Blank Correction subtracts the color absorbed when running the test with deionized water instead of sample. The blank value is subtracted from every result to correct for any background color due to reagents.

When using the Reagent Blank Correction feature, the blank correction should be entered before the Standard Adjust feature is used.

To enter a programmed correction for the reagent blank:

1. Run the test using deionized water with each new lot of reagents.
2. Press **READ** to obtain the blank value.
3. Press **SETUP**, scroll to **BLANK** and press **ENTER**. The display will show **BLANK?**.
4. Enter the blank value just read from the instrument.
5. Press **ENTER** to accept the value as the blank to be subtracted from each reading.
6. The display will show 0.00 mg/L (resolution and units vary) and the sample cell icon will be displayed, indicating that the reagent blank feature is enabled and the blank value will be subtracted from each reading. Repeat the reagent blank adjust for each new lot of reagents.

Note: *After entering a reagent blank adjust, the display may flash "limit" when zeroing if the sample used for zeroing has a lower absorbance value than the reagent blank.*

To disable the Reagent Blank adjust feature, press **SETUP**, scroll to **BLANK** and press **ENTER** twice. The concentration readings will be displayed without subtracting the blank. The sample cell icon will no longer appear in the display.

Do not use the Reagent Blank Adjust feature if the procedure uses a reagent blank for zeroing.

Standard Adjust (Adjusting the Standard Curve)

The colorimeter has Hach Programs permanently installed in memory. A program usually includes a pre-programmed calibration curve. Each curve is the result of an extensive calibration performed under ideal conditions and is normally adequate for most testing. Deviations from the curve can occur from using compromised testing reagents, defective sample cells, incorrect test procedure, incorrect technique, or other correctable causes. Interfering substances or other causes may be beyond the analyst's control.

In some situations, using the pre-programmed curve may not be convenient:

a) Running tests where frequent calibration curve checks are required.

b) Testing samples which give a consistent test interference.

Consider the following before adjusting the calibration curve:

1. Will future test results be improved by adjusting the curve?

2. Are interfering substances consistent in all the samples that you will test?

Any precision and test range information provided with the procedure may not apply to an adjusted curve calibration.

You can adjust many of the calibration curves by following the steps found in the test procedures. Working carefully is important. After the adjustment, it is wise to run standard solutions of several concentrations to make sure the adjusted curve is satisfactory. Perform standard additions on typical samples to help determine if the adjusted curve is acceptable.

Think of the standard adjust measurement as a two-step process. First, the instrument measures the sample using the pre-programmed calibration. Second, it multiplies this measurement by an adjustment factor. The factor is the same for all concentrations. The instrument will remember the factor indefinitely and will display the standard adjustment icon when it is used.

Adjust the calibration curve using the reading obtained with a Hach Standard Solution or carefully prepared standard made from a concentrated Hach Standard Solution. It is important to adjust the curve in the correct concentration range. For most purposes, Hach recommends adjusting the curve using a standard concentration that is 70 to 85% of the maximum concentration range of the test.

For example, the Hach pre-programmed method for fluoride has a range of 0-2.0 mg/L F. To adjust the calibration curve, use a standard with a concentration between 1.4-1.6 mg/L. Hach provides a 1.60 mg/L Fluoride Standard Solution (80% of the full range). This is a convenient standard to use for adjusting the calibration curve.

If the range of all your samples is known to be below a concentration that is less than 50% of the full range (50% of 2.0 is 1.0 mg/L), then adjust the standard curve with a standard that is within that range. For example, if all the samples contain 0.6-0.9 mg/L F, you may use a 1.00 mg/L fluoride standard to adjust the curve. You may use the 1.00 mg/L standard because it is closer to the sample range you are working with.

If you are using a Reagent Blank Correction, the blank correction should be entered before the standard curve is adjusted.

To adjust the standard curve:

1. Prepare the standard.
2. Use the standard as the sample in the procedure.
3. When the reading for the standard is obtained, press **SETUP**.
4. Use the arrow keys to scroll to the "**STD**" setup option.
5. Press **ENTER** to activate the standard adjust option.
6. Edit the standard concentration to match that of the standard used.
7. Press **ENTER**. A small plot of a line through a point will be displayed, indicating that the curve has been adjusted with the standard.

Note: *If the attempted correction is outside the allowable adjustment limit, the instrument will beep and flash Ø and the operation will not be allowed.*

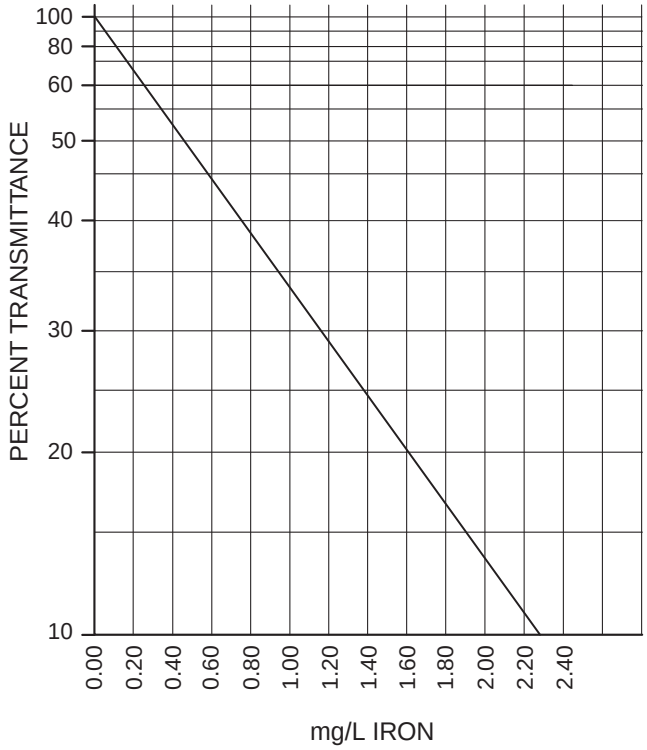
Preparing a User-Entered Calibration Curve

1. Prepare five or more standards of known concentration that cover the expected range of the test. Run tests as described in the procedure on each prepared standard. Pour the customary volume of each known solution into a separate clean sample cell of the type specified for your instrument.
2. Standardize (zero) the instrument using an untreated water sample or a reagent blank, whichever the procedure instructs you to use.
3. Measure and record the absorbance or %T of the known solutions. To use %T vs. concentration see *%T Versus Concentration Calibration*. To use absorbance vs. concentration, see *Absorbance Versus Concentration Calibration*. Or create a user-entered program by storing a custom calibration in the non-volatile memory of the instrument. Refer to the section on entering user-entered programs in the instrument manual.

%T Versus Concentration Calibration

If measuring %T, use semilogarithmic graph paper and plot %T (vertical scale) versus concentration (horizontal scale). In *Figure 11*, iron standard solutions of 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, and 2.0 mg/L were measured on a spectrophotometer at 500 nm using half-inch test tubes. Results were plotted and the calibration table values were extrapolated from the curve (*Table 7*).

Figure 11 Logarithmic Calibration Curve



To convert %T readings to concentration, prepare a table such as *Table 7* and select the appropriate line from the "%T Tens" column and the appropriate column from the %T Units columns. The %T Ten value is the first number of the %T reading and the %T Units value is the second number of the %T reading. For example, if the instrument reading was 46%, the 40 line in the %T Tens column and the 6 column in the %T Units would be selected. The cell where these two intersect (0.78 mg/L) is the iron concentration of the sample.

Table 7 Calibration Table

%T Tens	%T Units									
	0	1	2	3	4	5	6	7	8	9
0										
10	2.30	2.21	2.12	2.04	1.97	1.90	1.83	1.77	1.72	1.66
20	1.61	1.56	1.51	1.47	1.43	1.39	1.35	1.31	1.27	1.24
30	1.20	1.17	1.14	1.11	1.08	1.04	1.02	.99	.97	.94
40	.92	.89	.87	.84	.82.	.80	.78	.76	.73	.71
50	.69	.67	.65	.64	.62	.60	.58	.56	.55	.53
60	.51	.49	.48	.46	.45	.43	.42	.40	.39	.37
70	.36	.34	.33	.32	.30	.29	.28	.26	.25	.24
80	.22	.21	.20	.19	.17	.16	.15	.14	.13	.12
90	.11	.09	.08	.07	.06	.05	.04	.03	.02	.01

Absorbance Versus Concentration Calibration

To read concentration values directly from the instrument, create a user-entered program. See the instrument manual for more information.

If absorbance values are measured, plot the results on linear graph paper. Plot the absorbance value on the vertical axis and the concentration on the horizontal axis.

Plot increasing absorbance values from bottom to top. Plot increasing concentration values from left to right. Values of 0.000 absorbance units and 0 concentration will begin at the bottom left corner of the graph. A calibration table can be extrapolated from the curve or the concentration values can be read directly from the graph for determining an equation for the line using the slope and the y-intercept.

USEPA Approved and Accepted Definitions

The United States Environmental Protection Agency (USEPA) establishes limits for maximum contamination levels of certain constituents in water. It also requires that specific methodology be used to analyze for these constituents. These methods originate from several sources. The USEPA has developed some of these methods. In other cases, the USEPA has evaluated and approved methods developed by manufacturers, professional groups and public agencies such as:

- American Public Health Association

- American Water Works Association
- Water Environmental Federation
- American Society for Testing and Materials
- United States Geological Survey
- Associates of Official Analytical Chemists

All USEPA approved methods are cited in the *Federal Register* and compiled in the Code of Federal Regulations. USEPA approved methods may be used for reporting results to the USEPA and other regulatory agencies.

USEPA Accepted

Hach has developed several procedures that are equivalent to USEPA approved methods. Even though minor modifications exist, the USEPA has reviewed and accepted certain procedures for reporting purposes. These methods are not published in the *Federal Register,* but are referenced to the equivalent USEPA method in the procedure.

SECTION 2 SAMPLE PRETREATMENT

Digestion

Several procedures require sample digestion. Digestion uses chemicals and heat to break down a substance into components that can be analyzed. This section has three different digestion procedures.

The Hach Digesdahl® system is a process that yields a digest suitable for the determination of metals, total phosphorus and total kjeldahl nitrogen (TKN). It is rapid, convenient and the method of choice for digesting most samples analyzed by Hach methods.

For USEPA reporting purposes, USEPA-approved digestions are required. USEPA presents two digestions (mild and vigorous) for metals analysis. These are much more inconvenient and time consuming compared to the Hach Digesdahl system. Other digestion procedures are required for phosphorus and TKN.

EPA Mild Digestion with Hot Plate for Metals Analysis Only

1. Acidify the entire sample at the time of collection with concentrated nitric acid by adding 5 mL of acid per liter (or quart) of sample.

2. Transfer 100 mL of well-mixed sample to a beaker or flask. Add 5 mL of distilled 1:1 hydrochloric acid (HCl).

3. Heat using a steam bath or hot plate until the volume has been reduced to 15-20 mL. Make certain the sample does not boil.

4. After this treatment, the sample may be filtered to remove any insoluble material.

5. Adjust the digested sample to pH 4 by drop-wise addition of 5.0 N Sodium Hydroxide Standard Solution. Mix thoroughly and check the pH after each addition.

6. Quantitatively transfer the sample with deionized water to a 100-mL volumetric flask and dilute to volume with deionized water. Continue with the procedure. This mild digestion may not suffice for all sample types. A reagent blank also should be carried through the digestion and measurement procedures.

EPA Vigorous Digestion with Hot Plate for Metals Analysis Only

A vigorous digestion can be followed to ensure all organo-metallic bonds are broken.

1. Acidify the entire sample with redistilled 1:1 Nitric Acid Solution to a pH of less than two. Do not filter the sample before digestion.

2. Transfer an appropriate sample volume (see *Table 8*) into a beaker and add 3 mL of concentrated redistilled nitric acid.

3. Place the beaker on a hot plate and evaporate to near dryness, making certain the sample does not boil.

4. Cool the beaker and add another 3 mL of the concentrated redistilled nitric acid.

5. Cover the beaker with a watch glass and return it to the hot plate. Increase the temperature of the hot plate so that a gentle reflux occurs. Add additional acid, if necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change color or appearance with continued refluxing).

6. Again, evaporate to near dryness (do not bake) and cool the beaker. If any residue or precipitate results from the evaporation, add redistilled 1:1 hydrochloric acid (5 mL per 100 mL of final volume). See *Table 8*.

7. Warm the beaker. Add 5 mL of 5.0 N sodium hydroxide and quantitatively transfer the sample with deionized water to a volumetric flask. See *Table 8* below for the suggested final volume.

8. Adjust the sample to pH 4 by drop-wise addition of 5.0 N Sodium Hydroxide Standard Solution; mix thoroughly and check the pH after each addition. Dilute to volume with deionized water. Multiply the result by the correction factor in *Table 8*. A reagent blank also should be carried through the digestion and measurement procedures.

Table 8 Vigorous Digestion Volumes

Expected Metal Concentration	Suggested Sample Vol. for Digestion	Suggested Volume of 1:1 HCl	Suggested Final Volume After Digestion	Correction Factor
1 mg/L	50 mL	10 mL	200 mL	4
10 mg/L	5 mL	10 mL	200 mL	40
100 mg/L	1 mL	25 mL	500 mL	500

General Digesdahl Digestion (Not USEPA accepted)

Many samples may be digested using the Digesdahl Digestion Apparatus (Cat. No. 23130). It is designed to digest many types of samples such as oils, wastewater, sludges, feeds, grains, plating baths, food, and soils. In this procedure the sample is oxidized by a mixture of sulfuric acid and hydrogen peroxide. Digestion of a dry sample requires less than ten minutes, while liquid samples require about 1 minute/mL. The digestion is done in a special flat-bottomed 100-mL volumetric flask. Aliquots (sample portions) are taken for analysis using colorimetric methods.

Procedures for digestion and using the Digesdahl Digestion Apparatus are based on the type and form of the sample, and are found in the Digesdahl Digestion Apparatus Instruction Manual, which is included with each Digesdahl Digestion Apparatus.

Distillation

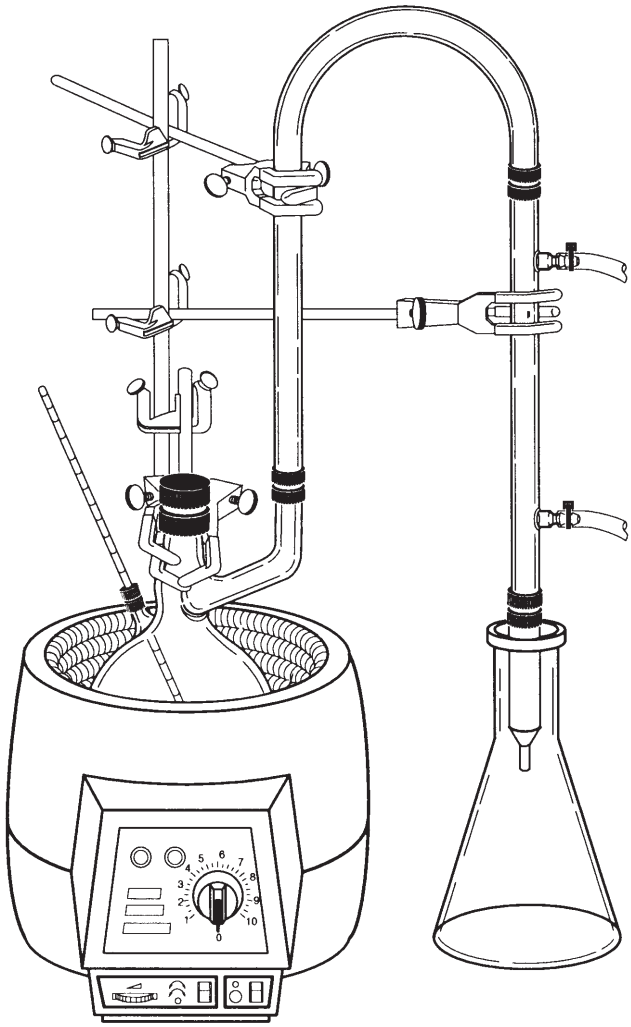
Distillation is an effective way of separating chemical components for analysis. The Hach Distillation Apparatus (see *Figure 12*) is adapted easily for many test needs and is suitable for water and wastewater samples. Sample distillations are easy and safe to perform.

Applications for the General Purpose Distillation Apparatus include:

- fluoride
- albuminoid nitrogen
- ammonia nitrogen
- phenols
- selenium
- volatile acids

Arsenic and cyanide require special glassware sets in addition to the General Purpose Set (the Arsenic Distillation Apparatus and the Cyanide Distillation Apparatus). All connecting glassware is manufactured with threaded connectors for ease and safety. The General Purpose Heater provides efficient heating and the Support Apparatus anchors the glassware.

Figure 12 General Purpose Distillation Apparatus with Heater and Support Apparatus



SECTION 3 WASTE MANAGEMENT AND SAFETY

Waste Management

This section provides guidelines for laboratory waste management. It should assist you in complying with USEPA regulations governing waste management. It summarizes basic requirements, but does not contain all USEPA regulations. It does not relieve people from complying with all regulations contained in the Code of Federal Regulations. Regulations change regularly and additional state and local laws may apply to your waste. Each waste generator is responsible for knowing and obeying the laws that apply to them.

Waste Minimization

Waste minimization is the foundation of good waste management. Minimizing waste greatly reduces the disposal problems and expense. If possible, try to generate less waste rather than recycle or re-use it. For laboratories, ways to reduce waste include:

- Use the smallest sample size possible.
- Choose methods that use non-hazardous or “less” hazardous reagents when possible.
- Buy chemicals in small quantities which will be used before they expire. This eliminates disposal of outdated materials.
- Clean glassware and laboratory apparatus with non-hazardous soaps when possible, rather than solvents or acids which may be hazardous.

Regulatory Overview

Federal waste disposal regulations were issued in accordance with the Resource Conservation and Recovery Act (RCRA). They are given in Title 40 Code of Federal Regulations (CFR) part 260. The Act controls all forms of solid waste disposal and encourages recycling and alternative energy sources. The major emphasis is controlling hazardous waste disposal. The regulations create a system to identify wastes and track waste generation, transport, and ultimate disposal. Each facility involved in managing hazardous waste must be registered with the USEPA. This includes the generator, transporters, and treatment, storage, and disposal facilities (TSDF).

Under federal regulations, there are three categories of generators with increasingly more strict regulation for larger quantity generators. The categories are based on the amount of hazardous waste generated in any given month.

The categories are as follows:

- Conditionally Exempt Small Quantity Generator - less than 100 kg (220 lb.) per month
- Small Quantity Generator - between 100 kg (220 lb.) and 1,000 kg (2,200 lb.) per month
- Large Quantity Generator - greater than 1,000 kg (2,200 lb.) per month

Note: *If a laboratory generates acutely hazardous waste (as defined on 40 CFR 261) or accumulates more than a certain amount of waste, the facility may be moved into a larger generator status. Check with your environmental compliance manager or state and local officials to determine which category your facility is in.*

Hazardous Waste Definition

For regulatory purposes, a "hazardous waste" is a material which is subject to special laws by the USEPA under 40 CFR 261. In addition, many states or local authorities regulate additional materials as hazardous waste. Be aware that many very toxic compounds are not regulated by this definition of hazardous waste. However, improper management or disposal of these compounds may lead to legal problems under other laws such as CERCLA (Superfund) or common law torts.

The 40 CFR 261 defines a hazardous waste as a solid waste which is not excluded from regulation and meets any of the following criteria:

- It is a discarded commercial chemical product, off-specification species, container residue, or spill residue of materials specifically listed in 40 CFR 261.33;
- It is a waste from a specific source listed in 40 CFR 261.32;
- It is a waste from a non-specific source listed in 40 CFR 261.31; or
- It displays any of the following characteristics of hazardous waste defined in 40 CFR 261.20-24:
    - ignitability
    - corrosivity
    - reactivity
    - toxicity

There are many exceptions to these regulations, and each generator should review the regulations and determine if they are excluded from the regulations.

Characteristic Hazardous Waste Codes

Hazardous wastes are categorized by specific codes assigned in 40 CFR 261.20-261.33. These codes will help you identify hazardous waste. The generator is responsible for making the actual waste code determination.

Selected characteristic waste codes for chemicals which may be generated using Hach methods for water analysis are given in the following table. A complete list of waste codes is found in 40 CFR 261.24.

USEPA Code	Characteristic	CAS No.	Regulatory Level (mg/L)
D001	Ignitability	na	na
D002	Corrosivity	na	na
D003	Reactivity	na	na
D004	Arsenic	6440-38-2	5.0
D005	Barium	6440-39-3	100.0
D018	Benzene	71-43-2	0.5
D006	Cadmium	7440-43-9	1.0
D022	Chloroform	67-66-3	6.0
D007	Chromium	7440-47-3	5.0
D008	Lead	7439-92-1	5.0
D009	Mercury	7439-97-6	0.2
D010	Selenium	7782-49-2	1.0
D011	Silver	7440-22-4	5.0

How to Determine if Waste is Hazardous

Federal laws do not require you to test a material to decide if it is a hazardous waste. You may apply product knowledge to decide if a material is hazardous. Often, information on a material safety data sheet (MSDS) is enough to decide. If the product is specifically listed in the regulation, it is a hazardous waste.

You also need to decide if it has any characteristics of a hazardous waste. Physical information on the MSDS may help you decide. If the flash point is below 60 °F (15 °C) or is classified by DOT as an oxidizer, the material may be ignitable. If the pH of the material is ≤2 or ≥12.5, the material may be corrosive. If the material is unstable, reacts violently with water, or may generate toxic gases, vapors, or fumes when mixed with water, it may be reactive.

Use the chemical composition data to decide if a material is toxic. This decision is based on the concentration of certain contaminants (heavy metals and a number of organic compounds). If the waste is a liquid, compare the concentration of the contaminants in the liquid to the concentrations listed in 40 CFR 261.24. If the waste is a solid, analyze the sample by the Toxicity Characteristic Leachability Procedure (TCLP) and compare the results to the concentration listed in the 40 CFR 261.24. Levels above the threshold amount listed in the table are hazardous.

See “Sections of the MSDS” on page 65. describing the MSDS for help in finding information for making hazardous waste determinations.

Examples of Hazardous Waste

A number of chemicals used in and final solutions created from Hach procedures are hazardous wastes when they are disposed. In addition, substances in the sample matrix may be a hazardous waste. Sometimes, reagents which would be hazardous are neutralized or changed during the analytical procedure. In that case, the final solutions are not regulated. Finally, many reagents and final solutions may be non-regulated. The generator must either use their knowledge of the materials used or conduct analytical tests to determine if the final material is a hazardous waste.

Examples of tests using Hach reagents that generate hazardous waste include those containing mercury or mercury compounds such as COD tests or Nessler’s reagent. Conversely, a test using Hach reagents such as ManVer 2 Hardness Indicator Powder Pillows and EDTA Titration Cartridges do not produce a hazardous waste unless the sample contains a hazardous substance.

Hazardous Waste Disposal

Hazardous waste must be managed and disposed of according to federal, state, and local regulations. The waste generator is responsible for making hazardous waste determinations. Analysts should check with the facility’s environmental compliance people for specific instructions.

Hazardous wastes should be handled by treatment, storage, and disposal facilities (TSDF) that have USEPA permits. In some cases, the generator may treat the hazardous waste. In most cases, a permit from the USEPA is required to treat hazardous waste. Laboratories are not exempt from these regulations. If your facility is a “Conditionally Exempt Small Quantity Generator,” special rules may apply. Check 40 CFR 261 to determine if have to comply with all the laws.

The most common allowed treatment is elementary neutralization. This refers to neutralizing wastes that are hazardous only because they are corrosive or are listed only for that reason. Neutralize acidic solutions by adding a base such as sodium hydroxide; neutralize basic solutions by

adding an acid such as hydrochloric acid. Slowly add the neutralizing agent while stirring. Monitor the pH. When it is at or near 7, the material is neutralized and may be flushed down the drain. Many wastes generated from Hach procedures may be treated in this manner.

Other chemical or physical treatments such as cyanide destruction or evaporation may require a permit. Check with your environmental department or local regulators to determine which rules apply to your work facility.

Laboratory chemicals may be mixed and disposed of with other hazardous wastes generated at your facility. They may also be accumulated in accordance with 40 CFR 262.34 satellite accumulation rules. After collection they may be disposed of in a "labpack." A number of environmental and hazardous waste companies offer labpacking services. They will inventory, sort, pack, and arrange proper disposal for hazardous waste. Find companies offering these services in the Yellow Pages under "Waste Disposal - Hazardous" or contact state and local regulators for assistance.

Management of Specific Wastes

Hach has several documents to assist customers in managing waste generated from our products. You can obtain the following documents by calling 1-800-227-4224 or 970-669-3050 and requesting the literature codes given:

Literature Code	Title
1321	Waste Reduction: A Primer
9323	Mercury Waste Disposal Firms
9325	COD Waste Management
9326	COD Heavy Metal Total Concentrations

Special Considerations for Cyanide-Containing Materials

Several procedures in this manual use reagents that contain cyanide compounds. These materials are regulated as reactive (D003) waste by the Federal RCRA. Waste disposal instructions provided with each procedure tell you how to collect these materials for proper disposal. It is imperative that these materials be handled safely to prevent the release of hydrogen cyanide gas (an extremely toxic material with the smell of bitter almonds). Most cyanide compounds are stable and can be safely stored for disposal in highly alkaline solutions (pH >11) such as 2 N sodium hydroxide. Never mix these wastes with other laboratory wastes that may contain lower pH materials such as acids or even water.

If a cyanide-containing compound is spilled, you must be careful not to be exposed to hydrogen cyanide gas. Take the following steps to destroy the cyanide compounds in an emergency:

a) Use a fume hood, supplied air or self-contained breathing apparatus.

b) While stirring, add the waste to a beaker containing a strong solution of sodium hydroxide and either calcium hypochlorite or sodium hypochlorite (household bleach).

c) Add an excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.

d) Neutralize the solution and flush it down the drain with a large amount of water. If the solution contains other regulated materials such as chloroform or heavy metals, it may still need to be collected for hazardous waste disposal. Never flush hazardous wastes down the drain.

Resources

Many sources of information on proper waste management are available. The USEPA has a hotline number for questions about the Resource Conservation and Recovery Act (RCRA). The RCRA Hotline number is 1-800-424-9346. You may also get a copy of the appropriate regulations. Federal hazardous waste regulations are found in 40 CFR 260- 99. Obtain this book from the U.S. Government Printing Office or a number of other vendors. Other documents which may be helpful to the laboratory hazardous waste manager include:

1. Task Force on Laboratory Waste Management. *Laboratory Waste Management, A Guidebook*; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1994.

2. Task Force on Laboratory Waste Management. *Waste Management Manual for Laboratory Personnel*; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1990.

3. Task Force on Laboratory Waste Management. *Less is Better*; 2nd ed.; American Chemical Society, Department of Government Relations and Science Policy: Washington, DC 1993.

4. Committee on Chemical Safety. *Safety in Academic Chemistry Laboratories*, 5th ed.; American Chemical Society: Washington, DC, 1990.

5. Armour, Margaret-Ann. *Hazardous Laboratory Chemicals Disposal Guide*; CRC Press: Boca Raton, FL, 1991.

6. *Environmental Health and Safety Manager's Handbook*; Government Institutes, Inc.: Rockville, MD, 1988.

7. Lunn, G.; Sansone, E.B. *Destruction of Hazardous Chemicals in the Laboratory*; John Wiley and Sons: New York, 1990.

8. National Research Council. *Prudent Practices for Disposal of Chemicals from Laboratories*; National Academy Press: Washington, DC, 1983.

9. National Research Council. *Prudent Practices for Handling Hazardous Chemicals in Laboratories*; National Academy Press: Washington, DC, 1981.

10. Environmental Protection Agency, Office of Solid Waste and Emergency Response. *The RCRA Orientation Manual*; U.S. Government Printing Office: Washington, DC, 1991.

11. Environmental Protection Agency, Office of Solid Waste and Emergency Response. *Understanding the Small Quantity Generator Hazardous Waste Rules: A Handbook for Small Business*; U.S. Government Printing Office: Washington, DC, 1986.

Material Safety Data Sheets

Material safety data sheets (MSDS) describe the hazards of chemical products. This section describes the information provided on a Hach MSDS and how to locate important information for safety and waste disposal. The information provided on the MSDS applies to the product as sold by Hach. The properties of any mixtures obtained by using this product will be different.

How to Obtain an MSDS

Hach ships an MSDS to each customer with the first order of any chemical product. A new MSDS may be sent when the information on the data sheet is updated. Please review all new MSDS's for new information. If you need another copy of an MSDS, simply call 1-800-227-4227.

Sections of the MSDS

Each MSDS has ten sections. The sections and the information found in them are described below.

Header Information

The Hach catalog number, MSDS date, change number, company address and telephone number, and emergency telephone numbers are listed at the top of the MSDS.

WASTE MANAGEMENT AND SAFETY, continued

1 Product Identification

This section contains:

- Hach product name
- Chemical Abstract Services (CAS) number
- Chemical name
- Chemical formula, if appropriate
- Chemical family to which the material belongs

2 Ingredients

This section lists each component in the product. It contains the following information for each component:

- PCT: Percent by weight of this component
- CAS NO.: Chemical Abstract Services (CAS) registry number for this component
- SARA: Superfund Amendments and Reauthorization Act, better known as the “Community Right to Know Law” tells you if the component is listed in SARA 313. If the component is listed and you use more than the amount listed, you must report this to the USEPA every year.
- TLV: Threshold Limit Value. The maximum airborne concentration for an 8 hour exposure that is recommended by the American Conference of Governmental Industrial Hygienists (ACGIH).
- PEL: Permissible Exposure Limit. The maximum airborne concentration for an 8 hour exposure that is regulated by the Occupational Safety and Health Administration (OSHA).
- HAZARD: Physical and health hazards of the component are explained.

3 Physical Data

The physical properties of the product are given in this section. They include the physical state, color, odor, solubility, boiling point, melting point, specific gravity, pH, vapor density, evaporation rate, corrosivity, stability, and storage precautions.

4 Fire, Explosion Hazard And Reactivity Data

This section contains the flash point and flammable limits of the material. It also includes how to fight fires if the material catches on fire. Key terms in this section include:

- Flashpoint: The temperature at which a liquid will give off enough flammable vapor to ignite.
- Flammability and ignitability are usually defined by the flash point.
- Lower Flammable Limit (LFL or LEL): The lowest concentration that will produce a fire or flash when an ignition source is present.
- Upper Flammable Limit (UFL or UEL): The vapor concentration in air above which the concentration is too rich to burn.
- NFPA Codes: The National Fire Protection Association (NFPA) has a system to rate the degree of hazards presented by a chemical. These codes are usually placed in a colored diamond. The codes range from 0 for minimal hazard to 4 for extreme hazard. They are grouped into the following hazards: health (blue), flammability (red), reactivity (yellow), and special hazards (white).

5 Health Hazard Data

This section describes different ways the chemical can enter your body (ingestion, inhalation, skin contact). It also gives acute (immediate) and chronic (long-term) health effects. If the material causes cancer or genetic damage, it is identified in this section.

6 Precautionary Measures

This section contains special precautions for the material. These may include special storage instructions, handling instructions, conditions to avoid, and protective equipment required to use this material safely.

7 First Aid

First aid instructions for exposures to the chemical are given in this section. Be sure to read this section before inducing vomiting in a victim. Some chemicals are better treated by not inducing vomiting. Seek prompt medical attention for all chemical exposures.

8 Spill And Disposal Procedures

This section tells about safe work practices for cleaning up and disposing of spilled material. Please refer to the Waste Management section of this manual. Final determination of proper and legal disposal options is the responsibility of the waste generator. Be sure you know the federal, state, and local laws that apply to your facility.

9 Transportation Data

Domestic and International shipping information is provided in this section. It gives shipping name, hazard class, and ID number of the product.

10 References

This section lists the reference materials used to write the MSDS.

Following the Reference section, the product is listed as having SARA 313 chemicals or California Proposition 65 List Chemicals, if applicable. Also found here is any special information about the product.

Safety

Safety is the responsibility of each person performing analytical procedures. Because many of the procedures in this methods manual use potentially hazardous chemicals and equipment, it is important to prevent accidents by practicing good laboratory techniques. The following guidelines apply to water analysis. These guidelines do not cover every aspect of safety, but they are important for preventing injuries.

Material Safety Data Sheet

A material safety data sheet (MSDS) comes with the first shipment of all products. The MSDS provides environmental and safety information about the products. Always read the MSDS before using a new product.

Reading Labels Carefully

Read each reagent label carefully. Pay particular attention to the precautions given. Never remove or block the label on a reagent container while it contains reagent. Do not put a different reagent into a labeled container without changing the label. When preparing a reagent or standard solution, label the container clearly. If a label is hard to read, re-label promptly according to your facility's hazard communication program.

Warning labels also appear on some of the apparatus used with the test procedures. The protective shields with the COD Reactor and the Digesdahl Digestion Apparatus point out potential hazards. Be sure these shields are in place during use and observe the precautions on the label.

Protective Equipment

Use the right protective equipment for the chemicals and procedures. The MSDS contains this information. Protective equipment may include:

- Eye protection such as safety glasses or goggles to protect from flying objects or chemical splashes.
- Gloves to protect skin from toxic or corrosive materials, sharp objects, very hot or very cold materials, or broken glass. Use tongs or finger cots when transferring hot apparatus.

- Laboratory coats or splash aprons to protect skin and clothing from splashes.
- Footwear to protect feet from spills. Open toed shoes should not be worn in chemistry settings.
- Respirators may be needed to protect you from breathing toxic vapors if adequate ventilation, such as fume hoods, are not available.
- Use fume hoods as directed by the procedure or as recommended in the MSDS.
- For many procedures, adequate ventilation is enough. Be sure there is enough fresh air and air exhaust to protect against unnecessary exposure to chemicals.

First Aid Equipment and Supplies

Most first aid instructions for chemical splashes in eyes or on skin call for thorough flushing with water. Laboratories should have eyewash and shower stations. For field work, carry a portable eyewash unit. Laboratories should also have appropriate fire extinguishers and fume hoods.

General Safety Rules

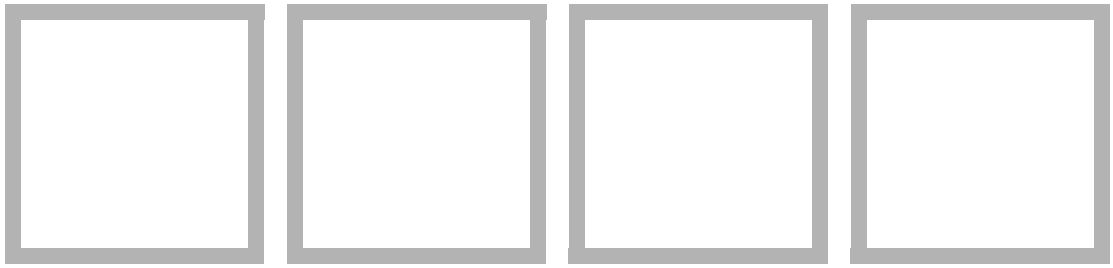
Follow these rules to make work with toxic and hazardous chemicals safer:

1. **Never** pipet by mouth. Always use a mechanical pipet or pipet bulb to avoid ingesting chemicals.
2. Follow test procedures carefully and observe all precautionary measures. Read the entire procedure carefully before beginning.
3. Wipe up all spills promptly. Get proper training and have the right response equipment to clean up spills. See your safety director for more information.
4. **Do not** smoke, eat, or drink in an area where toxic or irritating chemicals are used.
5. Use reagents and equipment only as directed in the test procedure.
6. **Do not** use damaged labware and broken equipment.
7. Minimize all chemical exposures. **Do not** breathe vapors or let chemicals touch your skin. Wash your hands after using chemicals.
8. Keep work areas **neat** and **clean**.
9. **Do not** block exits or emergency equipment.

OSHA Chemical Hygiene Plan

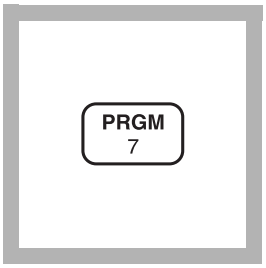
The Occupational Safety and Health Administration (OSHA) enforces laws about the control exposure to hazardous chemicals in laboratories. These regulations are in Title 29 CFR 1910.1450. They apply to all employers who use hazardous chemicals. They require employers to develop and use a written Chemical Hygiene Plan and appoint a qualified person as the Chemical Hygiene Officer.

SECTION 4 PROCEDURES



ALUMINUM (0 to 0.80 mg/L)

Aluminon Method*



1. Enter the stored program number for aluminum (Al).

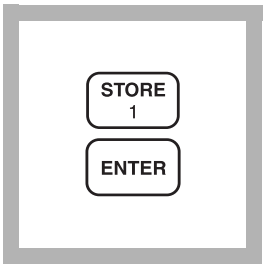
Press: **PRGM**

The display will show:

PRGM ?

Note: *Adjust the pH of stored samples before analysis.*

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **1 ENTER**

The display will show **mg/L, Al** and the **ZERO** icon**.**

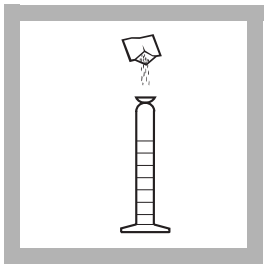
Note: *Total aluminum determination requires a digestion prior to analysis (see Section 2).*

Note: *For alternate form (Al_2O_3), press* **CONC**.

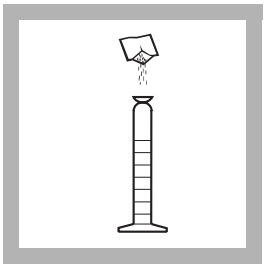
3. Fill a 50-mL graduated mixing cylinder to the 50-mL mark with sample.

Note: *Rinse cylinder with 1:1 Hydrochloric Acid and deionized water before use to avoid errors due to contaminants absorbed on the glass.*

Note: *Sample temperature must be 20-25 °C (68-77 °F) for accurate results.*



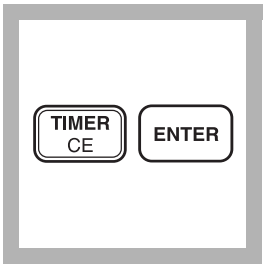
4. Add the contents of one Ascorbic Acid Powder Pillow. Stopper. Invert several times to dissolve powder.



5. Add the contents of one AluVer® 3 Aluminum Reagent Powder Pillow. Stopper.

Note: *A red-orange color develops if aluminum is present.*

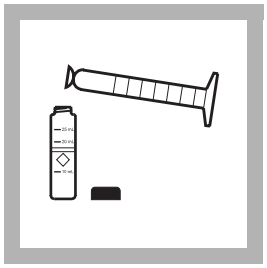
Note: *Inconsistent results will occur if any powder is undissolved.*



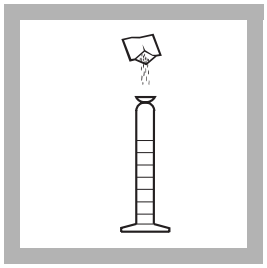
6. Press:

TIMER ENTER

A three-minute reaction period will begin. Invert the cylinder repeatedly for the three minutes.

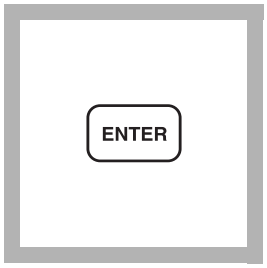


7. Pour 25 mL of mixture into a 25-mL sample cell (the prepared sample).



8. Add the contents of one Bleaching 3 Reagent Powder Pillow to the remaining 25 mL in the mixing graduated cylinder (the blank). Stopper the cylinder.

* Adapted from *Standard Methods for the Examination of Water and Wastewater*

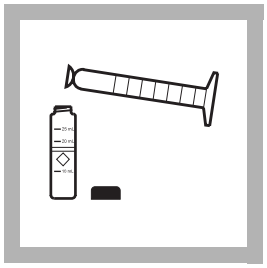


9. The display will show: **00:30 Timer 2**

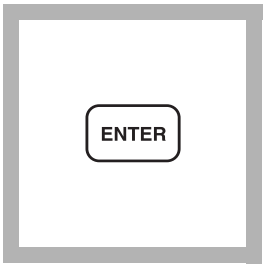
Press: **ENTER**

A thirty-second reaction period will begin. Vigorously shake the cylinder for the 30-second period.

Note: *This solution should turn a light to medium orange upon bleaching. It will not become colorless.*



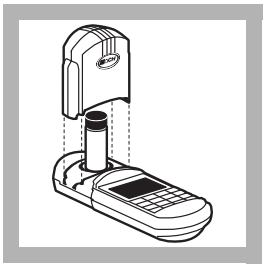
10. Pour the 25 mL of mixture in the cylinder into a second 25-mL sample cell (the blank).



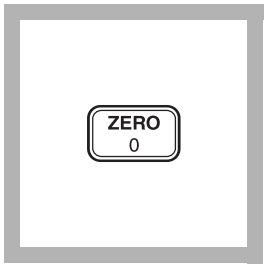
11. The display will show: **15:00 TIMER 3**

Press: **ENTER**

A 15-minute reaction period will begin.



12. Within three minutes after the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

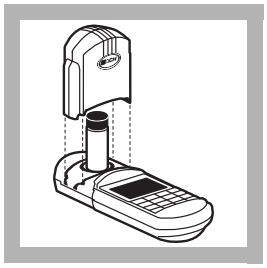


13. Press: **ZERO**

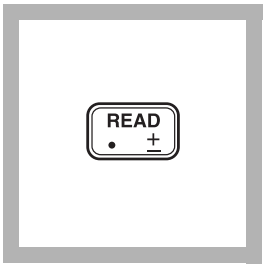
The cursor will move to the right, then the display will show:

0.000 mg/L Al

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



14. Immediately place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



15. Press: **READ**

The cursor will move to the right, then the result in mg/L aluminum will be displayed.

Note: *Clean the graduated cylinder and sample cells with soap and brush immediately following the test.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in a clean glass or plastic container. Preserve the sample by adjusting the pH to 2 or less with nitric acid (about 1.5 mL per liter). Preserved samples can be stored up to six months at room temperature. Before analysis, adjust the pH to 3.5–4.5 with 5.0 N Sodium Hydroxide. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1* for more information.

Accuracy Check

Standard Additions Method

a) Snap the neck off an Aluminum Voluette Ampule Standard Solution, 50 mg/L as Al.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to three 50-mL samples. Swirl gently to mix. Also prepare a sample without any standard added (the unspiked sample).

c) Analyze each sample as described above. The aluminum concentration should increase 0.1 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions (Section 1)* for more information.

Standard Solution Method

Prepare a 0.40-mg/L aluminum standard solution by pipetting 1.00 mL of Aluminum Standard Solution, 100 mg/L as Al^{3+}, into a 250-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution immediately before use. Perform the aluminum procedure as described above. The mg/L Al reading should be 0.40 mg/L Al.

Or, using the TenSette Pipet, add 0.8 mL of solution from an Aluminum Voluette Ampule Standard Solution (50 mg/L as Al) into a 100-mL volumetric flask. Dilute to volume with deionized water. Prepare this standard immediately before testing and use as the sample.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.40 mg/L Al and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.013 mg/L Al.

Estimated Detection Limit

The estimated detection limit for program #1 is 0.013 mg/L Al. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Acidity interferes at greater than 300 mg/L as $CaCO_3$. Treat samples with greater than 300 mg/L acidity as $CaCO_3$ as follows: **1.** Add one drop of m-Nitrophenol Indicator Solution to the sample taken in Step 3. **2.** Add one drop of 5.0 N Sodium Hydroxide Standard Solution. Stopper the cylinder. Invert to mix. Repeat as often as necessary until the color changes from colorless to yellow. **3.** Add one drop of 5.25 N Sulfuric Acid Standard Solution to change the solution from yellow back to colorless. Continue with the test.
Alkalinity	1000 mg/L as $CaCO_3$. Eliminate interferences from higher alkalinity concentrations using the following pretreatment: **1.** Add one drop of m-Nitrophenol Indicator Solution to the sample taken in Step 3. A yellow color indicates excessive alkalinity. **2.** Add one drop of 5.25 N Sulfuric Acid Standard Solution. Stopper the cylinder. Invert to mix. If the yellow color persists, repeat until the sample becomes colorless. Continue with the test.
Calcium	Does not interfere.
Fluoride	Interferes at all levels. See graph below.
Iron	Greater than 20 mg/L.
Phosphate	Greater than 50 mg/L.
Polyphosphate	Polyphosphate interferes at all levels by causing negative errors and must not be present. Before running the test, polyphosphate must be converted to orthophosphate by acid hydrolysis as described under the phosphorus procedures.

Fluoride interferes at all levels by complexing with aluminum. The actual aluminum concentration can be determined using the Fluoride Interference Graph when the fluoride concentration is known. To use the fluoride interference graph:

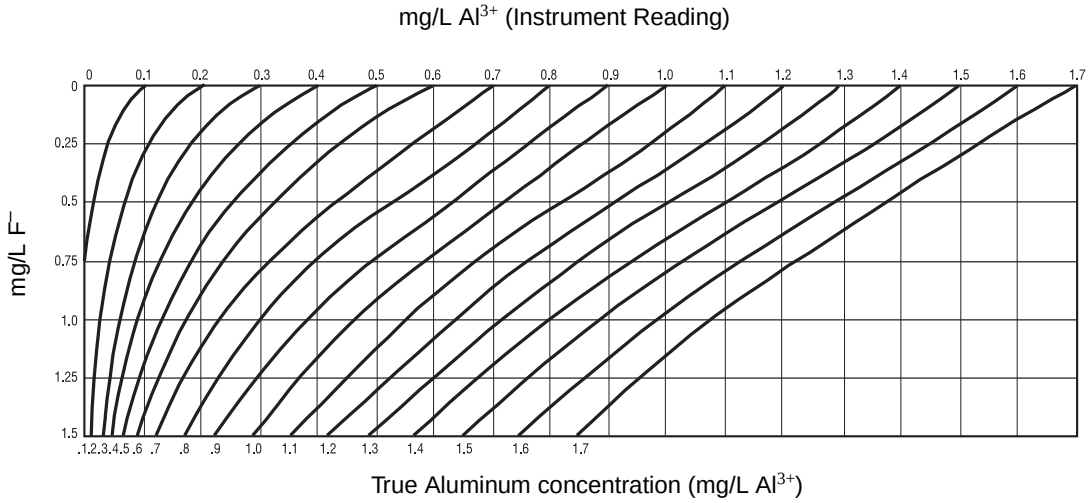
1. Select the vertical grid line along the top of the graph that represents the aluminum reading obtained in Step 15.

2. Locate the point of the vertical line (instrument reading) where it intersects with the horizontal grid line that indicates how much fluoride is present in the sample.

3. Extrapolate the true aluminum concentration by following the curved lines on either side of the intersect point down to the true aluminum concentration.

For example, if the aluminum test result was 0.7 mg/L Al^{3+} and the fluoride present in the sample was 1.0 mg/L F^{-}, the point where the 0.7 grid line intersects with the 1.0 mg/L F^{-} grid line falls between the 1.2 and 1.3 mg/L Al curves. In this case, the true aluminum content would be 1.27 mg/L.

Fluoride Interference Graph



Summary of Method

Aluminon indicator combines with aluminum in the sample to form a red-orange color. The intensity of color is proportional to the aluminum concentration. Ascorbic acid is added to remove iron interference. The AluVer 3 Aluminum Reagent, packaged in powder form shows exceptional stability and is applicable for fresh water samples.

ALUMINUM, continued

REQUIRED REAGENTS

	Cat. No.
Aluminum Reagent Set (100 Tests)	22420-00
Includes: (1) 14290-99, (1) 14577-99, (1) 14294-49	

Description	Quantity Required Per Test	Unit	Cat. No.
AluVer 3 Aluminum Reagent Powder Pillow	1 pillow	100/pkg	14290-99
Ascorbic Acid Powder Pillow	1 pillow	100/pkg	14577-99
Bleaching 3 Reagent Powder Pillow	1 pillow	100/pkg	14294-49

REQUIRED APPARATUS

Cylinders, graduated mixing, 50 mL	1	each	1896-41
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Aluminum Standard Solution, 100 mg/L	100 mL	14174-42
Aluminum Standard Solution, Voluette ampule, 50 mg/L as Al, 10 mL	16/pkg	14792-10
Hydrochloric Acid Solution, 6N (1:1)	500 mL	884-49
m-Nitrophenol Indicator Solution, 10 g/L	100 mL	2476-32
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Brush	each	690-00
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 250 mL	each	14574-46
Fluoride Combination Electrode	each	51928-00
Fluoride ISA Powder Pillows	25/pkg	2589-99
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH/ISE Meter, *sens**ion***™***2**, portable	each	51725-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, Volumetric, Class A, 1.00 mL	each	14515-35
Thermometer, –20 to 110 °C, non-mercury	each	26357-02

For Technical Assistance, Price and Ordering

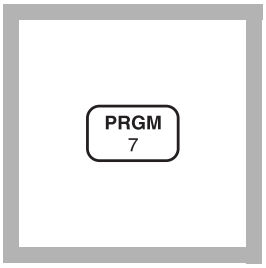
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

BENZOTRIAZOLE (0 to16.0 mg/L) or TOLYLTRIAZOLE (0 to 16.0 mg/L)

UV Photolysis Method*

For cooling or boiler water



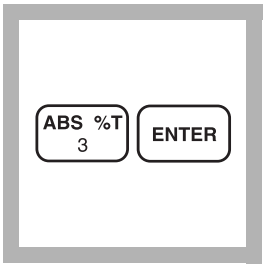
1. Enter the stored program number for benzotriazole (Benzo) or tolyltriazole (Toly).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **3 ENTER** for either triazole test.

The display will show **mg/L, BENZO,** and the **ZERO** icon

or

the display will show **mg/L, TOLY,** and the **ZERO** icon.

Press the **CONC** key to choose the desired triazole.

3. Fill a sample cell with 25 mL of sample.

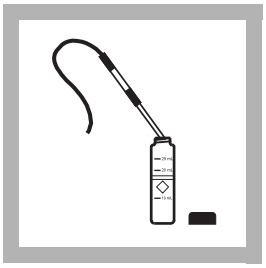
Note: *Sample temperature should be between 20-25 °C (68-77 °F).*

Note: *If sample contains nitrite or borax (sodium borate), adjust the pH to between 4 and 6 with 1 N sulfuric acid.*

4. Add the contents of one Triazole Reagent Powder Pillow. Swirl to dissolve completely.

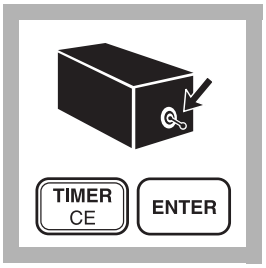
Note: *If the sample contains more than 500 mg/L hardness (as $CaCO_3$), add 10 drops of Rochelle Salt Solution.*

* Adapted from Harp, D., Proceedings 45th International Water Conference, 299 (October 22-24, 1984)



5. Insert the ultraviolet lamp into the sample cell.

Note: *UV safety goggles should be worn while the lamp is on.*

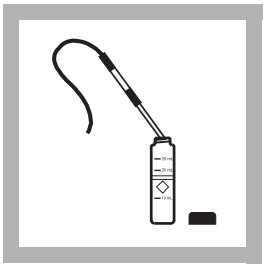


6. Turn the UV lamp ON and press:

TIMER ENTER

A five-minute reaction period will begin.

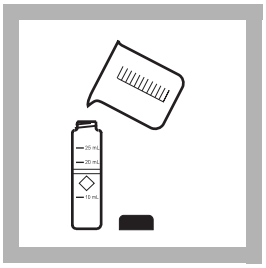
Note: *A yellow color will form if triazole is present.*



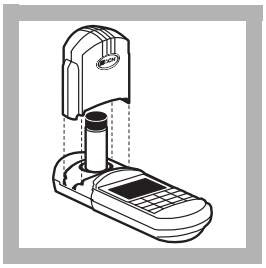
7. When the timer beeps, turn the lamp off and remove it from the cell (the prepared sample). Swirl the cell to mix thoroughly.

Note: *Low results will occur if photolysis (lamp ON) takes place for more or less than five minutes.*

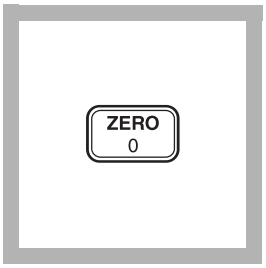
Note: *Avoid handling the quartz surface of the lamp. Rinse the lamp and wipe with a soft, clean tissue between tests.*



8. Fill another sample cell with 25 mL of sample (the blank).



9. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **ZERO**

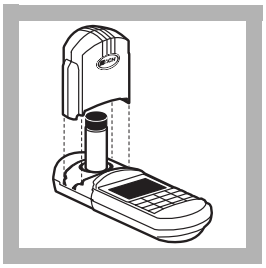
The cursor will move to the right, then the display will show:

0.0 mg/L Benzo

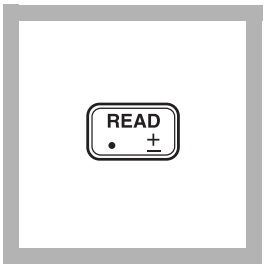
or

0.0 mg/L Toly

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L benzotriazole or tolyltriazole will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

BENZOTRIAZOLE OR TOLYLTRIAZOLE, continued

Sampling And Storage

The most reliable results are obtained when samples are analyzed as soon as possible after collection.

Accuracy Check

Standard Additions Method

a) Use the TenSette pipet to add 0.1, 0.2 and 0.3 mL of 500-mg/L Benzotriazole Standard Solution to three 25-mL samples. Perform the test according to the above procedure.

Note: *The test will not distinguish between benzotriazole and tolyltriazole.*

b) Each addition of 0.1 mL of standard solution should increase the benzotriazole reading by 2 mg/L over the reading of an unspiked sample.

c) If these increases are not obtained see *Standard Additions* in *Section 1* for more information.

UV Lamp Check

To verify the ultraviolet lamp (normal life equals 5000 hours) is working properly, perform the following test:

a) Prepare a 5.0 mg/L benzotriazole standard solution by pipetting 10.0 mL of Benzotriazole Standard Solution, 500 mg/L benzotriazole, into a 1000-mL volumetric flask. Dilute to volume.

b) Analyze according to the above procedure. If the result is significantly below 5.0 mg/L, replace the lamp.

Method Performance

Precision

In a single laboratory using a standard solution of 9.0 mg/L triazole and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.21 mg/L benzotriazole and ±0.20 mg/L tolyltriazole.

Estimated Detection Limit

The estimated detection limit for program 3 is 0.7 mg/L benzotriazole or tolyltriazole. For more information on the estimated detection limit, see *Section 1*.

BENZOTRIAZOLE OR TOLYLTRIAZOLE, continued

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Acrylates (as methyl acrylate)	50 mg/L
Alum	400 mg/L
Borate (as sodium tetraborate)	4000 mg/L
Chlorine (as Cl_2)	20 mg/L
Chromium (as chromate)	12 mg/L
Copper	10 mg/L
Hardness	500 mg/L as $CaCO_3$
Iron	20 mg/L
Lignosulfonates	40 mg/L
Magnesium	300 mg/L as $CaCO_3$
Molybdenum (as molybdate)	200 mg/L
Nitrite	4000 mg/L
Phosphonates (AMP or HEDP)	100 mg/L
Sulfate	200 mg/L
Zinc	80 mg/L

Strong oxidizing or reducing agents present in the sample will interfere directly with the test.

Summary of Method

Benzotriazole or tolyltriazole, used in many applications as corrosion inhibitors for copper and copper alloys, are determined by a proprietary catalytic ultraviolet (UV) photolysis procedure requiring less than 10 minutes to perform.

BENZOTRIAZOLE OR TOLYLTRIAZOLE continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Triazole Reagent Powder Pillows	1 pillow	100/pkg	21412-99

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06
Select one based on available voltage:			
Lamp, UV, with power supply, 115 V, 60 Hz, with goggles	1	each	20828-00
Lamp, UV, with power supply, 230 V, 50 Hz, with goggles	1	each	20828-02

OPTIONAL REAGENTS

Benzotriazole Standard Solution, 500 mg/L	100 mL		21413-42
Rochelle Salt Solution	29 mL*	DB	1725-33
Sulfuric Acid Standard Solution, 1.00 N	100 mL	MDB	1270-32
Water, deionized	4 L		272-56

OPTIONAL APPARATUS

Flask, volumetric, Class A, 1000 mL		each	14574-53
Lamp, UV (lamp only)		each	26710-00
pH Paper, 1 to 11 pH		5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable with electrode		each	51700-10
Pipet Filler, safety bulb		each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Pipet, volumetric, 10.0 mL, Class A		each	14515-38
Safety Goggles, UV		each	21134-00
Stopwatch		each	14645-00
Thermometer, –20 to 110 °C, non-mercury		each	26357-02
Timer, interval, 1 second to 99 hours		each	23480-00

For Technical Assistance, Price and Ordering

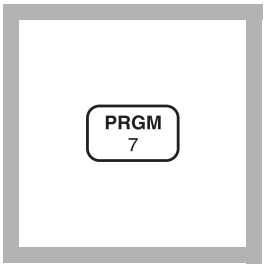
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes.

BORON, Low Range (0 to 1.60 mg/L as B)

Azomethine-H Method*

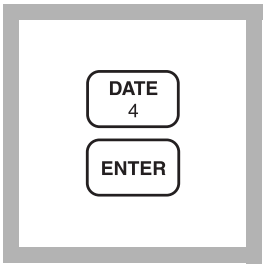


1. Enter the stored program number for low range boron (B).

Press: **PRGM**

The display will show:

PRGM ?



2. Press: **4 ENTER**

The display will show **mg/L, B** and the **ZERO** icon**.**

Note: *For alternate form (H_3BO_3), press the* **CONC** *key.*

3. Fill a clean plastic erlenmeyer flask with 25 mL of Ultra-Pure water (the blank).

Note: *For most accurate work, perform a blank analysis with each sample analysis.*

4. Fill a second clean plastic erlenmeyer flask with 25 mL of sample.

Note: *If the sample is highly colored, turbid, or contains interferences, see* Interferences *section for sample pretreatment.*

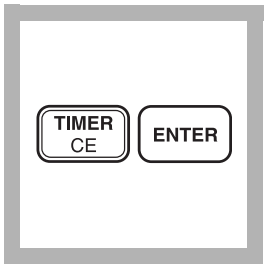
Note: *Sample temperature should be between 22-24 °C (72-75 °F). If outside this range, measure and record the sample temperature; see* Sample Temperature Compensation, *below.*

5. Add 10 drops of 1 M EDTA Solution to each flask. Swirl each flask to mix.

6. Add the contents of one BoroTrace 2 Reagent pillow to the flask containing the sample.

7. Immediately cap the flask and swirl vigorously to dissolve the powder.

Note: *Proceed with Steps 8 and 9 immediately.*



8. Press:

TIMER ENTER

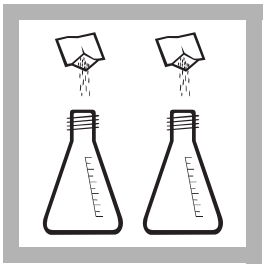
A 10-minute reaction period will begin.

* Adapted from ISO Method 9390; Adapted from Harp, D. L., *Analytica Chimica Acta,* 346 (1997), 373–379

9. Continue vigorous swirling for 30 seconds. Let the flask sit capped for the duration of the reaction period.

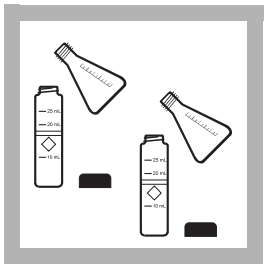
10. During the reaction period, add the contents of a second BoroTrace 2 Reagent pillow to the flask containing the blank.

11. Cap the flask containing the blank and swirl vigorously until the powder is dissolved.



12. After the timer beeps, add the contents of one BoroTrace 3 Reagent pillow to each flask. Cap and swirl both flasks to dissolve the powder.

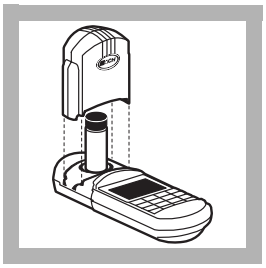
Note: *The addition of BoroTrace 3 Reagent "stops" the reaction.*



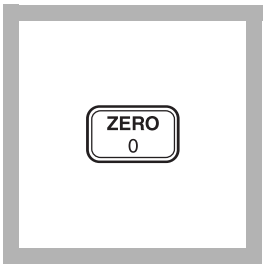
13. Transfer the contents of the blank flask to a clean sample cell. Fill another clean sample cell with the prepared sample. Label both cells appropriately.

14. Wipe the sample cells to remove any liquid or fingerprints.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



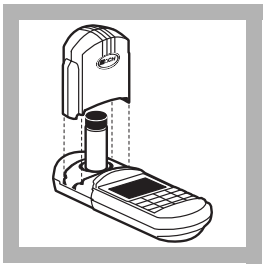
15. Place the blank cell into the cell holder. Tightly cover the sample cell with the instrument cap.



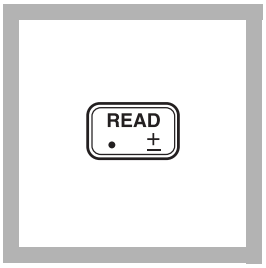
16. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L B



17. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



18. Press: **READ**

The cursor will move to the right, then the result in mg/L boron will be displayed.

Note: *Correct the result for sample temperature. If outside 22-24 °C (72-75 °F) see Sample Temperature Compensation section.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sample Collection, Preservation and Storage

Collect samples in clean polyethylene bottles. Do not use borate-based detergents or soaps to clean sample containers or labware used for this method. After use, rinse all plastic containers with large amounts of deionized water, allow to air dry, and keep covered.

Accuracy Check

Standard Additions Method

1. Prepare a 50.0 mg/L boron standard by pipeting 5.0 mL of a 1000 mg/L Boron Standard Solution into a 100-mL plastic volumetric flask. Dilute with deionized water, stopper and mix thoroughly.

2. Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 50.0 mg/L boron standard to three 25-mL water samples, respectively.

3. Analyze each sample as described above.

4. The boron concentration should increase 0.20 mg/L for each 0.1 mL of standard added.

Standard Solution Method

Using a plastic pipet, transfer 4.0 mL of Boron Standard Solution, 250 mg/L as B, into a 1000 mL plastic volumetric flask. Dilute to volume with deionized water, stopper and mix thoroughly. Use this 1.0-mg/L standard as the sample in Step 4 and analyze according to the procedure.

Sample Temperature Compensation

The reaction chemistry is very dependent on the sample temperature. Hach calibrations are performed at 23 °C (73 °F). If the sample temperature is outside the range of 22-24 °C (72-75 °F), multiply the results, in mg/L (Step 18), by the appropriate multiplier.

Sample Temperature		
°C	°F	Multiplier
5	41	0.70
7	44	0.73
10	50	0.78
12	53	0.81
14	57	0.84
16	61	0.87
18	64	0.91
20	68	0.94
25	77	1.04
26	79	1.06
27	81	1.08
28	82	1.10
29	84	1.12
30	86	1.15

Method Performance

Precision

In a single laboratory, using a standard solution of 1.0 mg/L B and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.04 mg/L B. For more information on Hach's precision statements, see *Section*

1.

Estimated Detection Limit
The estimated detection limit for program 4 is 0.03 mg/L B. For more information on the estimated detection limit, see *Section 1*.

Interferences

The following have been tested for interference and found *not* to interfere up to the indicated levels (in mg/L):

Non-interfering Substances/Maximum Level Tested

Substance	Maximum Level Tested (mg/L)
Aluminum (3^+)	10
Benzotriazole	20
Biocides:	
Carbamate-type	120
Isothiazolin-type	120
Quat-type	90
Thiocyanate-type	60
Bromide	120
Calcium	1000 (as $CaCO_3$)
Chloride	2500
Copper (2^+)	20
Fluoride	25
Magnesium	1000 (as $CaCO_3$)
Manganese (7^+)	5
Molybdate (Mo^{6+})	60
Nitrate	1000
Phosphonates, AMP	20
Phosphonates, HEDP	20
Polyacrylates	20 (as Acumer 1000, 1100)
Polymaleic Acid	40 (as Belcene 200)
Silica	120
Sulfate	1800
Sulfite	40
Tolyltriazole	20
Zinc (2^+)	10

Interfering Substances and Suggested Treatments

Interfering Substance, Interference Level, (positive or negative interference)	Recommended Treatment
Alkalinity >500 mg/L (+ or -)	**1.** Adjust the sample pH to between 5 and 7 using 1.0 N Sulfuric Acid Solution. **2.** Continue with Step 4 of the test procedure.
Color (+)	**1.** Zero the instrument (0.00 mg/L B) using Ultra-Pure water. **2.** Adjust the sample pH to between 3 andf 4, using 1.0 N Sulfuric Acid Solution. **3.** Measure the apparent concentration, in mg/L B, of the acidified sample. **4.** Subtract the apparent concentration of the acidified sample from the result obtained in Step 18 of the test procedure.
Halogens (Bromine or Chlorine) all levels (+)	Halogen disinfectants in the sample can produce a red color after the addition of BoroTrace #2 Reagent. To eliminate this interference: **1.** Add 1 pillow Dechlorinating Reagent to 25 mL each of Ultra-Pure Water and sample. **2.** Cap and shake to dissolve. **3.** Continue with Step 4 of the test procedure.
Iron (Fe^{3+} or Fe^{2+}), above 8 mg/L (+)	High levels of iron in the sample can produce a red-color after the addition of BoroTrace #2 Reagent. To compensate, increase the amount of EDTA that is added to each cell (Step 5) from 10 drops to 15 drops. Alternatively, dilute the sample with Ultra-Pure water and continue with Step 4. Correct the results in Step 18 using the appropriate dilution factor.
Nitrites, all levels (+)	**1.** Add a 0.1-gram scoop Sulfamic Acid to 25 mL each Ultra-Pure water and sample in plastic cells. **2.** Cap and shake to dissolve. **3.** Uncap and wait 5 minutes. **4.** Add 5 N Sodium Hydroxide Reagent solution to each cell to adjust pH to between 5 and 8 (using pH paper). **5.** Continue with Step 4 of the test procedure.
Turbidity (+)	Filter the sample through a 3-µm membrane prior to testing. Do not use a glass fiber filter.

Summary of Method

Azomethine-H, a Schiff base, is formed by the condensation of an aminonaphthol with an aldehyde by the catalytic action of boron. The boron concentration in the sample is proportional to the developed color.

BORON, Low Range, continued

REQUIRED REAGENTS

Description	Cat. No.
BoroTrace Reagent Set	26669-00
Includes: (1) 26666-69, (1) 26667-99, (1) 22419-26, (1) 25946-49	

Description	Quantity Required Per Test	Unit	Cat. No.
BoroTrace 2 Reagent Pillows	2	100/pkg	26666-69
BoroTrace 3 Reagent Pillows	2	100/pkg	26667-99
EDTA Solution, 1 M	20 drops	50 mL SCDB	22419-26
Water, Ultra-Pure Aldehyde-Free	25 mL	500 mL	25946-49

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Flask, eErlenmeyer, poly, 125-mL, w/cap	2	each	20898-43
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Boron Standard Solution, 250 mg/L as B, 10-mL Voluette Ampule	16/pkg	14249-10
Boron Standard Solution, 1000 mg/L as B	100 mL	1914-42
Dechlorinating Reagent Powder Pillows	100/pkg	14363-69
Eluant Solution	1 L	22256-53
Phosphate Buffer Solution, pH 7.2	1 L	431-53
Sodium Hydroxide Standard Solution, 5.0 N	50 mL DB	2450-26
Sulfamic Acid	113 g	2344-14
Sulfuric Acid Standard Solution, 1.000 N	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit (for 10-mL ampules)	eacu	21968-00
Filter Holder Assembly	each	2468-00
Flask, volumetric, polypropylene, 100 mL, w/cap	each	14060-42
Flask, volumetric, polypropylene, 1000 mL, w/cap	each	14060-53
Membrane Filters, 3-micron	25/pkg	25940-25
pH Paper, pH 1-11	each	391-33
Pipet, Mohr-type, polypropylene, 5 mL	each	2106-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Spoon, measuring, 0.1 g	each	511-00
Syringe, 30-cc	each	22258-00
Thermometer, –20 to 110 °C, non-mercury	each	26357-02

For Technical Assistance, Price and Ordering

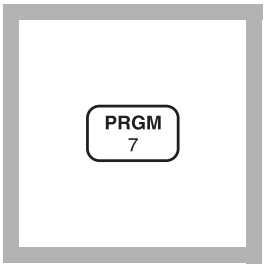
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

BROMINE (0 to 4.50 mg/L)

DPD Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



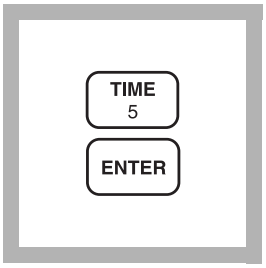
1. Enter the stored program number for bromine (Br_2)-powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

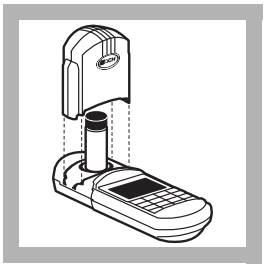


2. Press: **5 ENTER**

The display will show **mg/L, Br2** and the **ZERO** icon**.**

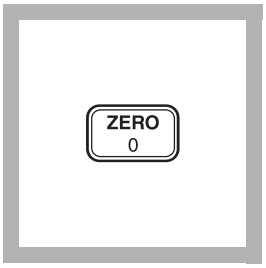
3. Fill a sample cell with 10 mL of sample (the blank).

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

* Adapted from *Standard Methods for the Examination of Water and Wastewater*

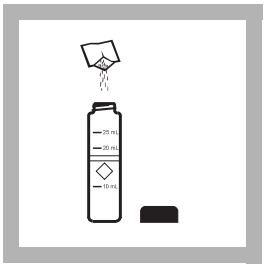


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

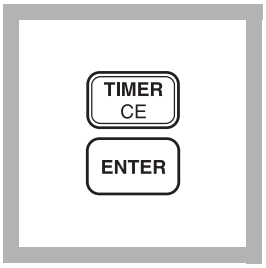
0.00 mg/L Br2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



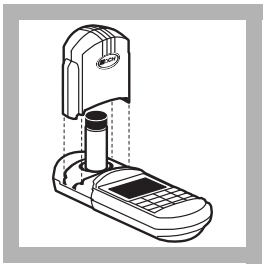
6. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl vigorously to dissolve the powder.

Note: *It is not necessary that all the powder dissolves. A pink color will develop if bromine is present.*

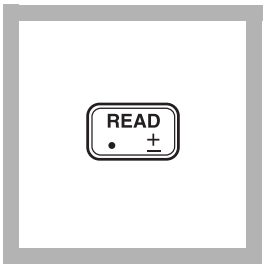


7. Press:**TIMER ENTER**

A three-minute reaction period will begin.



8. When the timer beeps, place the sample into the cell holder. Tightly cover the sample cell with the instrument cap.



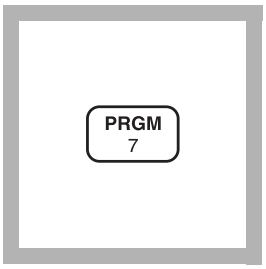
9. Press: **READ**

The cursor will move to the right, then the result in mg/L bromine will be displayed.

Note: *If samples temporarily turn yellow after reagent addition, or the display flashes "limit", it is due to high bromine levels. Dilute fresh samples and repeat the test. A slight loss of bromine may occur during dilution. Multiply results by the dilution factor; see Section 1.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls



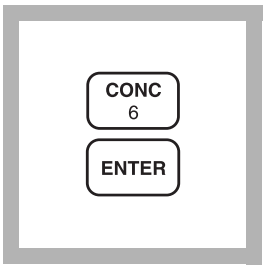
1. Enter the stored program number for bromine (Br_2) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

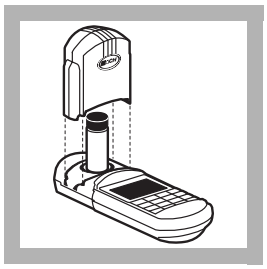


2. Press: **6 ENTER**

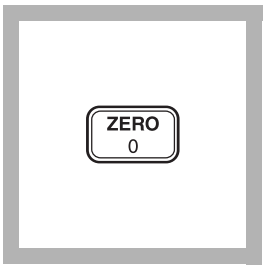
The display will show **mg/L, Br2** and the **ZERO** icon**.**

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



4. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

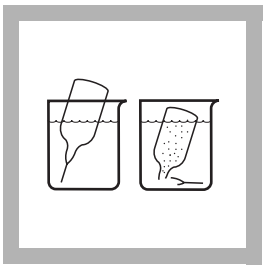


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

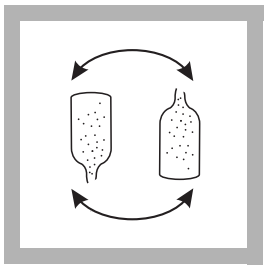
0.00 mg/L Br2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



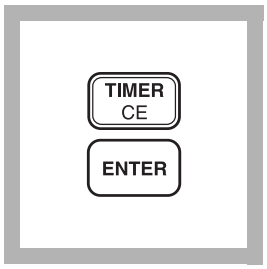
6. Fill one DPD Total Chlorine Reagent AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



7. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

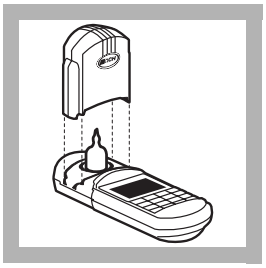
Note: *A pink color will form if bromine is present.*



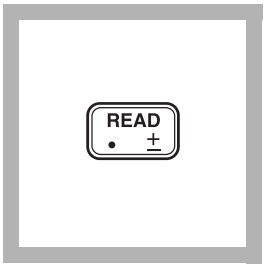
8. Press: **TIMER ENTER**

A three-minute reaction period will begin.

BROMINE, continued



9. After the timer beeps, place the AccuVac ampul into the cell holder. Tightly cover the ampule with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L bromine will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high bromine levels. Dilute a fresh sample and repeat the test. A slight loss of bromine may occur during dilution. Multiply the result by the dilution factor; see Section 1.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Analyze samples for bromine **immediately** after collection.

Avoid plastic containers since these may have a large bromine demand. **Pretreat glass** sample containers to remove any bromine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for bromine is introduced when a representative sample is not obtained. If sampling from a tap, let the sample flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the bromine analysis immediately after collection.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Snap the top off a LR Chlorine PourRite® Ampule Standard Solution.

b) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Re-zero the instrument using the original sample (the blank).

d) Place the spiked sample in the cell holder and press **READ**. Record the result.

e) Calculate the equivalent concentration of mg/L bromine added to the sample:

$$\text{mg/L Bromine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)} \times 2.25}{10.1\ (\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result + the calculated mg/L Br_2 added (step e).

g) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Total Chlorine AccuVac completely from each beaker.

e) Analyze the spiked and unspiked sample as described in the procedure.

f) Calculate the equivalent concentration of mg/L bromine added to the sample:

$$\text{mg/L Bromine added} = \frac{0.2\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)} \times 2.25}{25.2\ (\text{sample + standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the calculated mg/L Br_2 added (step f).

h) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 2.34 mg/L bromine and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.02 mg/L bromine.

In a single laboratory using a standard solution of 2.31 mg/L bromine and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation ± 0.02 mg/L bromine.

Estimated Detection Limit

The estimated detection limit for program 5 is 0.04 mg/L Br_2 and 0.03 mg/L Br_2 for program 6. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1*, *Correcting for Volume Additions*).
Chlorine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium , Oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct bromine concentration.
Monochloramine	Interferes at all levels
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences, Section 1*.

Summary of Method

Bromine reacts with DPD (N,N-diethyl-p-phenylenediamine) to form a magenta color which is proportional to the total bromine concentration.

BROMINE, continued

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interference will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	21056-69

REQUIRED REAGENTS (USING ACCUVAC AMPULS)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampule	25/pkg	25030-25

REQUIRED APPARATUS (USING POWDER PILLOWS)

Sample Cells, 10-20-25-mL, w/ cap		6/pkg	24019-06

REQUIRED APPARATUS (USING ACCUVAC AMPULS)

Beaker, 50 mL	1	each	500-41

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 25-30 mg/L, 2 mL		20/pkg	26300-20
DPD Total Chlorine Reagent, SwifTest		250 Tests	28024-00
Potassium Iodide Solution, 30 g/L		100 mL* MDB	343-32
Sodium Arsenite, 5 g/L		100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N		100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1 N		100 mL* MDB	1270-32
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

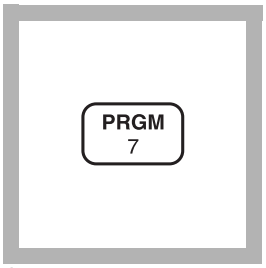
AccuVac Snapper Kit		each	24052-00
PourRite Ampule Breaker		each	24846-00
Cylinder, graduated, 25 mL		each	508-40
pH Meter, *sens**ion***™*1*, portable		each	51700-00
pH Indicator Paper, 1 to 11 pH units		5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

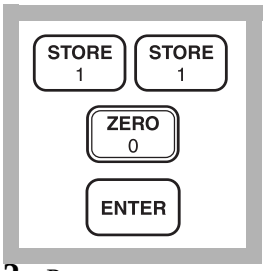
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes



1. Enter the user program number for monochloramine.

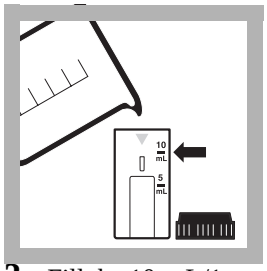
Press: **PRGM**
The display will show:
PRGM?



2. Press:
110 ENTER

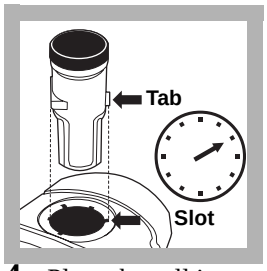
The display will show
mg/L Cl_2
then: **ZERO**

Note: *For alternate forms, press the* **CONC** *key.*



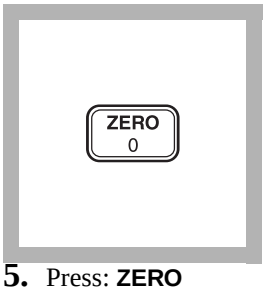
3. Fill the 10-mL/1-cm cell to the 10-mL line with sample.

Note: *For the most accurate results, determine a reagent blank for each new lot of reagent by running the test using deionized water instead of sample.*



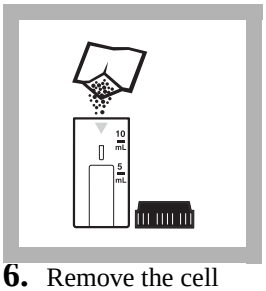
4. Place the cell into the instrument. Tightly cover the sample cell with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The cell's tab should be at the 2 o'clock position. Make sure the sample cell tab is completely seated in the cell holder slot.*

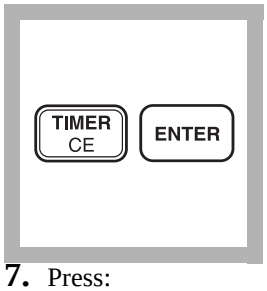


5. Press: **ZERO**

The cursor will move to the right, then the display will show:
0.00 mg/L Cl_2



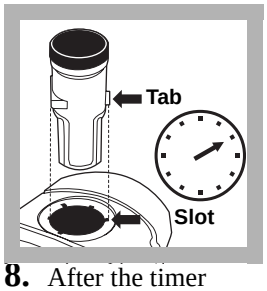
6. Remove the cell from the cell holder and add the contents of one pillow of Monochlor–F to the sample. Cap and shake the cell about 20 seconds to dissolve.



7. Press:
TIMER ENTER

A 5-minute reaction period will begin.

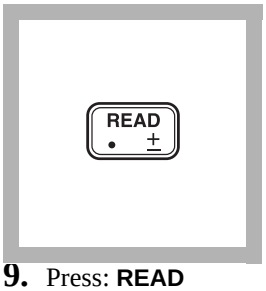
Note: *The color development time depends on the sample temperature. Refer to Table 3 for the actual time required.*



8. After the timer beeps, place the cell into the instrument. Tightly cover the sample cell with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The cell's tab should be at the 2-o'clock position. Make sure the sample cell tab is completely seated in the cell holder slot.*

* Patent pending



9. Press: **READ**

The cursor will move to the right, then the result in mg/L monochloramine (as Cl_2 or chosen units) will be displayed.

Sampling and Storage

Analyze samples for monochloramine immediately after collection. If sampling with the sample cell, rinse the sample cell several times with the sample, then carefully fill to the 10-mL mark. If sampling from a tap, let the water flow for at least 5 minutes. Let the container overflow with the sample several times, then cap the container so there is no headspace (air) above the sample.

Accuracy Check

1. Prepare the following monochloramine standard fresh before use.

2. Add the contents of one Buffer Powder Pillow, pH 8.3 to about 50-mL of organic-free water in a clean 100-mL Class A volumetric flask. Swirl to dissolve the powder.

3. Using a Class A volumetric pipet, transfer 2.00 mL of Nitrogen, Ammonia Standard Solution, 100 mg/L as NH_3–N into the flask.

4. Dilute to volume with organic-free water, cap and mix thoroughly. This is a 2.00 mg/L buffered ammonia standard.

5. Pipet 50.00 mL of the buffered ammonia standard into a clean 100-mL beaker. Add a stir bar.

6. Obtain a recent lot of Chlorine Solution Ampules, 50–70 mg/L, and note the actual free chlorine concentration for this lot.

7. Calculate the amount of Chlorine Solution to be added to the ammonia standard using the following equation:

$$\text{mL chlorine solution required} = \frac{455}{\text{free chlorine concentration}}$$

8. Open an ampule and, using a glass Mohr pipet, add the calculated amount of Chlorine Solution slowly to the ammonia standard, while mixing at medium speed on a stir-plate.

9. Allow the monochloramine solution to mix for 1 minute after all Chlorine Solution is added.

10. Quantitatively transfer the monochloramine solution to a clean 100-mL Class A volumetric flask. Dilute to the mark with organic-free water, cap, and mix thoroughly. This is a nominal 4.5 mg/L (as Cl_2) monochloramine standard.

Use this standard within 1 hour of preparation.

Method Performance

Precision

In a single laboratory, using a monochloramine standard solution of 2.10 mg/L Cl_2 and representative lots of reagent, a single operator obtained a standard deviation of ±0.12 mg/L Cl_2.

Estimated Detection Limit

The estimated detection limit for Method 10171 is 0.05 mg/L Cl_2. For more information on the estimated detection limit, see *Section 1* of the *Procedure Manual*.

Interferences

The following have been tested for interference and found *not* to interfere up to the indicated levels:

Table 9 Non-interfering Substances

Substance	Maximum Level Tested
Alanine	1 mg/L N

Table 9 Non-interfering Substances (Continued)

Substance	Maximum Level Tested
Aluminum	10 mg/L
Bromide	100 mg/L Br^-
Bromine	15 mg/L Br_2
Calcium	1000 mg/L $CaCO_3$
Chloride	18,000 mg/L
Chlorine Dioxide	5 mg/L ClO_2
Chromium (III)	5 mg/L
Copper	10 mg/L
Cyanide	10 mg/L CN^-
Free chlorine	10 mg/L Cl_2
Glycine	1 mg/L N
Iron (II)	10 mg/L
Iron (III)	10 mg/L
Lead	10 mg/L
Nitrate	100 mg/L as N
Nitrite	50 mg/L N
Phosphate	100 mg/L PO_4^{3-}
Silica	100 mg/L SiO_2
Silver	10 mg/L
Sulfate	2600 mg/L
Sulfite	50 mg/L SO_3^{2-}
Tyrosine	1 mg/L N
Urea	10 mg/L N
Zinc	5 mg/L

Table 10 Interfering Substances

Interfering Substance and its effect		Interference Level	Recommended Treatment
Magnesium	+	Above 400 mg/L $CaCO_3$	Add 5 drops Rochelle Salt Solution prior to testing.
Manganese (+7)	–	Above 3 mg/L	
Ozone	–	Above 1 mg/L	Usually doesn't coexist with monochloramine.

Table 10 Interfering Substances

Sulfide	+	Turns a “rust” color if present.	Usually doesn’t coexist with monochloramine.
Thiocyanate	–	Above 0.5 mg/L	

Summary of Method

In the presence of a cyanoferrate catalyst, monochloramine in the sample reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green-colored indophenol, which is proportional to the amount of monochloramine present in the sample.

Sample Temperature		Minutes
° C	° F	
5	40	10
7	42	9
9	48	8
10	50	8
12	54	7
14	58	7
16	61	6
18	68	4
20	73	3
23	75	2.5
25	77	2
>25	>77	2

Instrument Setup

This procedure will add the current method as a new Hach program to your DR/850 or DR/890.

1. Turn on the instrument by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the down arrow key until the prompt line shows **USER**.
4. Press the **ENTER** key.
5. Enter **8138**, followed by **ENTER**.

6. Enter each of the numbers in the right column, each followed by **ENTER**. The line numbers in the left column relate to the line number on the display. At any time, you may use the arrow keys to scroll back to review or change a number already entered.

Line Number	Entry	Line Number	Entry
1	110	29	108
2	42	30	78
3	74	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	63
8	0	36	57
9	0	37	199
10	0	38	104
11	0	39	62
12	64	40	74
13	176	41	61
14	120	42	45
15	106	43	1
16	0	44	204
17	0	45	0
18	0	46	5
19	0	47	10
20	67	48	1
21	108	49	44
22	50	50	0
23	0	51	0
24	0	52	0
25	78	53	0
26	72	54	3
27	50	55	0
28	67	56	255

CHLORAMINE, MONO, Low Range, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Monochlor F Reagent Pillows	1	50/pkg	28022-46

REQUIRED APPARATUS

Sample Cell, 10-mL/1-cm	1	2/pkg	48643-02
Clippers, shears	1	each	23694-00

OPTIONAL REAGENTS

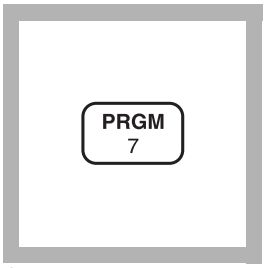
Rochelle Salt Solution		29-mL DB	1725-33
Organic-Free Water		500-mL	26415-49
Buffer Powder Pillows, pH 8.3		25/pkg	898-68
Nitrogen, Ammonia Standard Solution, 100 mg/L as NH_3-N		500-mL	24065-49
Chlorine Solution Voluette Ampule, 50–75 mg/L		16/pkg	14268-10

OPTIONAL APPARATUS

Beaker, 100-mL		each	500-42H
Flask, Volumetric, Class A, 100-mL		each	14574-42
Pipet, Mohr, Glass, 10-mL		each	20934-38
Pipet, Volumetric, Class A, 2.00 mL		each	14515-36
Pipet, Volumetric, Class A, 50.00 mL		each	14515-41
Stir Bar, Octagonal		each	20953-52
Stirrer, Magnetic, 110 V, 4” x 4”		each	28812-00

CHLORAMINE, MONO, High Range (0–10.0 mg/L Cl_2) Method 10172

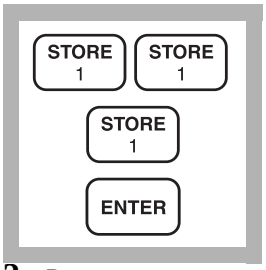
Indophenol Method* For chlorinated drinking water and chlorinated wastewater



1. Enter the user program number for Chloramine, HR.

Press: **PRGM**
The display will show:
PRGM?

Note: *For most accurate results, perform a Reagent Blank Correction (Section 1 of the DR/800 Instrument Manual).*



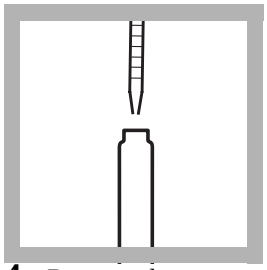
2. Press:
111 ENTER

The display will show:
mg/L Cl_2
and then
Zero

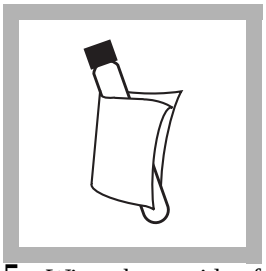
Note: *For alternate forms, press the* **CONC** *key.*

3. Insert the COD/TNT Vial Adapter into the cell holder by rotating the adapter until it drops in place. Push down to fully insert it.

Note: *For better performance, adiffuser band covers the light path holes on the adapter. Do not remove the band.*

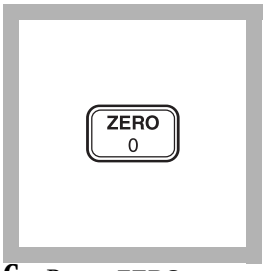


4. Remove the cap from one HR Monochloramine Diluent vial. Use a glass pipet to add 2.0 mL of sample to the vial. Re-cap and invert several times to mix.



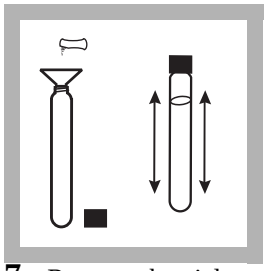
5. Wipe the outside of the vial clean.

Place the vial into the adapter. Cover the sample vial tightly with the instrument cap.



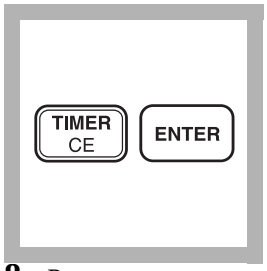
6. Press: **ZERO**

The cursor will move to the right and the display will show:
0.0 mg/L Cl_2



7. Remove the vial from the cell holder, uncap, and add the contents of one Monochlor–F pillow to the sample. Cap and shake the vial about 20 seconds to dissolve.

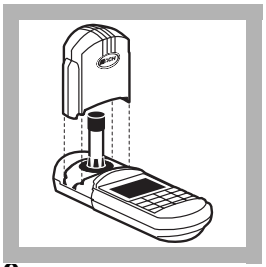
Note: *Use the microfunnel as an aid in adding reagent powder to the vial.*



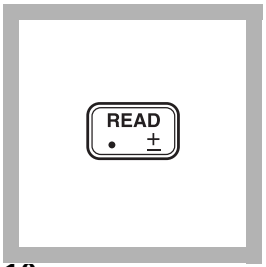
8. Press:
TIMER ENTER

A five-minute reaction period will begin.

* U.S. Patent 6,315,950



9. After the timer beeps, wipe the prepared vial and place it into the instrument. Cover the sample vial tightly with the instrument cap.



10. Press: **READ.**

The cursor will move to the right , then the results in mg/L monochloramine (as Cl_2) will be displayed.

Sampling and Storage

Analyze samples for monochloramine immediately after collection. Rinse the sample container several times with the sample water allowing it to overflow each time. If sampling from a tap, let the water flow for at least 5 minutes. Cap the container so that there is no head space (air) above the sample.

Accuracy Check

Prepare the following monochloramine standard fresh before use:

1. Using a clean 100-mL Class A volumetric flask, add the contents of one Buffer Powder Pillow, pH 8.3, to approximately 50 mL of organic-free water. Swirl to dissolve the powder.

2. Use a Class A volumetric pipet to transfer 2.00 mL of Nitrogen Ammonia Standard Solution, 100-mg/L as NH_3–N, into a flask.

3. Dilute to volume with organic-free water. Cap and mix thoroughly. This is the 2.00-mg/L buffered ammonia standard.

4. Pipet 50.00 mL of the buffered ammonia standard into a clean 100-mL beaker. Add a magnetic stir bar and place the beaker on a stir plate.

5. Note the free chlorine concentration for the Chlorine Solution Ampules, 50–70 mg/L. Use ampules from a recent lot.

6. Calculate the amount of Chlorine Solution to be added to the ammonia standard using the following equation:

$$\text{mL chlorine solution required} = \frac{455}{\text{free chlorine concentration}}$$

7. Turn the stir plate on to medium speed.

8. Open an ampule. Use a glass Mohr pipet to add the calculated amount of Chlorine Solution slowly to the ammonia standard while it is mixing.

9. Allow the monochloramine solution to mix for 1 minute after all the Chlorine Solution is added.

10. Quantitatively transfer the monochloramine solution to a clean 100-mL Class A volumetric flask. Dilute to the mark with organic-free water. Cap and mix thoroughly. This is a nominal 4.5-mg/L (as Cl_2) monochloramine standard.

Use this solution within 1 hour of preparation.

Method Performance

Precision

In a single laboratory, using a standard solution of 3.5 mg/L monochloramine as chlorine and two representative lots of reagent, a single operator obtained a standard deviation of ± 0.2 mg/L Cl_2.

Estimated Detection Limit

The estimated detection limit (EDL) for Method 10172 is 0.2 mg/L Cl_2. For more information on the EDL, see *Section 1* of the DR/800 Procedure Manual.

Interferences

The following have been tested for interference and found not to interfere up to the indicated levels:

Table 11 Non-interfering Substances

Substance	Maximum Level Tested
Alanine	1 mg/L N
Aluminum	10 mg/L
Bromide	100 mg/L Br^-
Bromine	15 mg/L Br_2
Calcium	1000 mg/L as $CaCO_3$

Table 11 Non-interfering Substances (Continued)

Substance	Maximum Level Tested
Chloride	18,000 mg/L
Chlorine Dioxide	5 mg/L ClO_2
Chromium (III)	5 mg/L
Copper	10 mg/L
Cyanide	10 mg/L CN^-
Free Chlorine	10 mg/L Cl_2
Glycine	1 mg/L N
Iron (II)	10 mg/L
Iron (III)	10 mg/L
Magnesium	1000 mg/L as $CaCO_3$
Manganese (VII)	10 mg/L
Lead	10 mg/L
Nitrate	100 mg/L N
Nitrite	50 mg/L N
Phosphate	100 mg/L PO_4
Silica	100 mg/L SiO_2
Silver	10 mg/L
Sulfate	2600 mg/L
Sulfite	50 mg/L SO_3^{2-}
Tyrosine	1 mg/L as N
Urea	10 mg/L as N
Zinc	5 mg/L

Table 12 Interfering Substances

Interfering Substance and its effect		Interference Level	Recommended Treatment
Ozone	–	Above 1 mg/L	Usually doesn't coexist with monochloramine
Sulfide	+	Turns a "rust" color if present.	Usually doesn't coexist with monochloramine
Thiocyanate	–	Above 0.5 mg/L	

CHLORAMINE, MONO, High Range, continued

Summary of Method

The sample is first diluted in a Test 'N Tube™. In the presence of a cyanoferrate catalyst, monochloramine (NH_2Cl) in the sample reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate compound couples with excess substituted phenol to form a green indophenol. Color intensity is proportional to the amount of monochloramine present in the sample.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for information specific to the reagent used.

Instrument Setup

This procedure will add the current method as a new Hach program to your DR/850 or DR/890 instrument.

1. Turn the instrument on by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the down arrow key until the prompt line shows **USER**.
4. Press the **ENTER** key.
5. Key in "8138", then press **ENTER**.
6. Key the number in the "Enter" column corresponding to line number 1 on the display. Press **ENTER**. Repeat for lines 2–56 on the display.

Table 13

Line number on display	Enter	Line number on display	Enter
1	111	29	108
2	42	30	78
3	73	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	63
8	0	36	58
9	0	37	61
10	0	38	112

Table 13

11	0	39	62
12	65	40	74
13	116	41	61
14	49	42	112
15	248	43	0
16	0	44	110
17	0	45	0
18	0	46	0
19	0	47	10
20	67	48	1
21	108	49	44
22	50	50	0
23	0	51	0
24	0	52	0
25	78	53	0
26	72	54	153
27	50	55	0
28	67	56	255

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
HR Monochloramine Test 'N Tubes, 50 tests			28051-45
Includes:			
HR Monochloramine Diluent Vials	50		*
Funnel, micro	1	each	25843-35
Monochlor F Reagent Pillows	1	50/pkg	28022-46

REQUIRED APPARATUS

COD/TNT Vial Adapter, DR/800	1	each	48464-00
Pipet, Mohr, glass, 2.00-mL	1	each	20936-36
Test Tube Rack	1	each	18641-00

OPTIONAL REAGENTS

Organic-free Water		500-mL	26415-49
Buffer Powder Pillows, pH 8.3		25/pkg	898-68

* Not sold separately.

CHLORAMINE, MONO, High Range, continued

Nitrogen, Ammonia Standard Solution, 100-mg/L as NH_3–N 500-mL 24065-49
Chlorine Solution Voluette® Ampule, 50–75 mg/L, 10-mL 16/pkg 14268-10

OPTIONAL APPARATUS

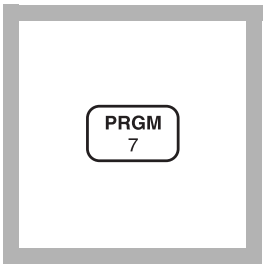
Beaker, 100-mL .....each 500-42H
Clippers (medium powder pillows) .....each 968-00
Clippers (shears) .....each 23694-00
Flask, Volumetric, Class A, 100-mL .....each 14574-42
Pipet, Mohr, Glass, 10-mL .....each 20934-38
Pipet, Volumetric, Class A, 2.00-mL .....each 14515-36
Pipet, Volumetric, Class A, 50.00-mL .....each 14515-41
Stir Bar, Octagonal .....each 20953-52
Stirrer, Magnetic, 110 V, 4” x 4” .....each 23436-00

CHLORINE DIOXIDE (0 to 5.00 mg/L) Method 10126

DPD Method* **For water**

USEPA accepted for reporting for drinking water analysis

Using Powder Pillows

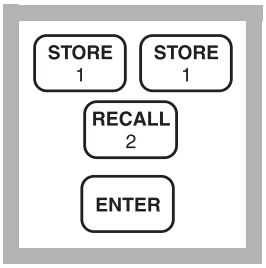


1. Enter the stored program number for chlorine dioxide (ClO_2) powder pillows.

Press: **PRGM**

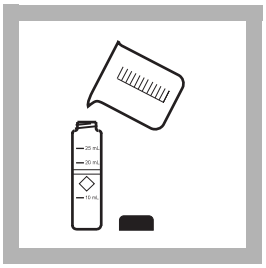
The display will show:

PRGM ?



2. Press: **112 ENTER**

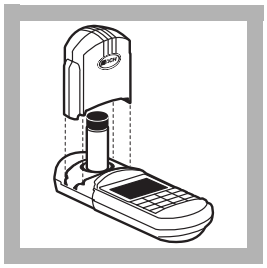
The display will show **mg/L, ClO2**, and the **ZERO** icon.



3. Fill a sample cell with 10 mL of sample (the blank).

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*

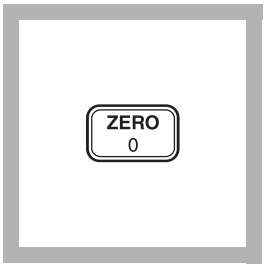


4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result. See* Reagent Blank Correction *in Section 1 of the DR/800 Procedure Manual.*

* Procedure is equivalent to *Standard Method 4500, $Cl0_2P$*

CHLORINE DIOXIDE, continued

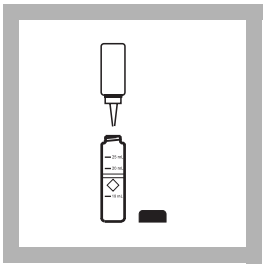


5. Press: **ZERO**

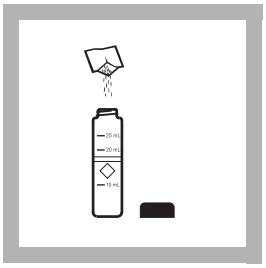
The cursor will move to the right, then the display will show:

0.00 mg/L ClO2

Note: *If Reagent Blank Correction is on, the display may flash* **"limit"***. See Section 1 of the DR/800 Procedures Manual.*



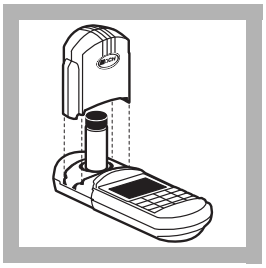
6. Add four drops of Glycine Reagent to the sample cell. Swirl to mix.



7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl to mix.

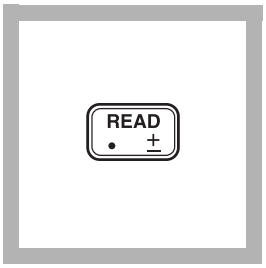
Note: *A pink color will develop if free chlorine dioxide is present.*

Note: *Perform step 9 within one minute of reagent addition.*



8. Allow 30 seconds for undissolved powder to settle. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*

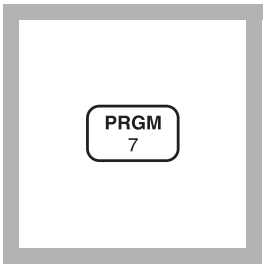


9. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine dioxide will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes* **"limit"***, it is due to high chlorine dioxide levels. Dilute a fresh sample with chlorine dioxide-free water and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the dilution factor.*

Using AccuVac® Ampuls

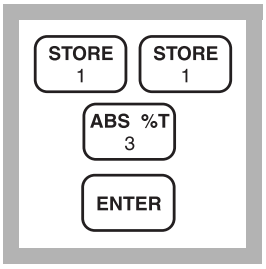


1. Enter the stored program number for chlorine dioxide (ClO_2) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?



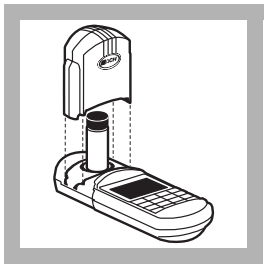
2. Press: **113 ENTER**

The display will show **mg/L, ClO2** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Fill a 50-mL beaker with 40 mL of sample. Using the correct sample volume is important.

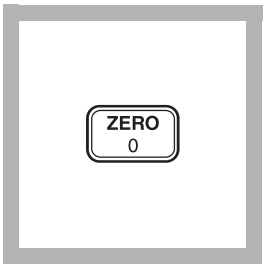
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result. See* Reagent Blank Correction *in Section 1 of the DR/800 Procedure Manual.*

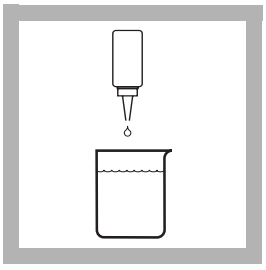


5. Press: **ZERO**

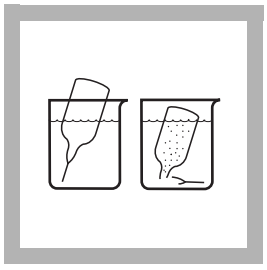
The cursor will move to the right, then the display will show:

0.00 mg/L ClO2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1 of the DR/800 Procedures Manual.*



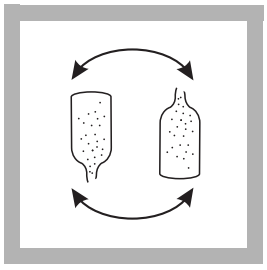
6. Add 16 drops of Glycine Reagent to the sample in the beaker. Swirl to mix.



7. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

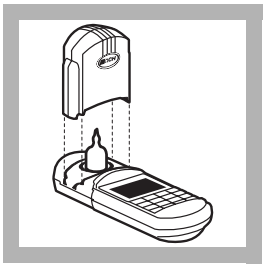
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *Perform step 10 within one minute of reagent addition.*

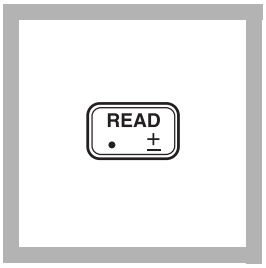


8. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A pink color will form if chlorine dioxide is present.*



9. Allow 30 seconds for undissolved powder to settle. Place the AccuVac Ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine dioxide will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine dioxide levels. Dilute a fresh sample with chlorine dioxide-free water and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the dilution factor.*

Sampling and Storage

Analyze samples for chlorine dioxide **immediately** after collection. Chlorine dioxide is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of chlorine dioxide in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine dioxide demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for chlorine dioxide is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the analysis immediately.

Accuracy Check

Because chlorine dioxide is difficult and hazardous to produce, check the DPD and glycine reagents by using chlorine standards. Proceed as follows:

1. Prepare a 1-mg/L free chlorine standard.

Method 1

a. Obtain Free Chlorine Standards, (Cat. No. 14268-10).

b. Determine the concentration of the standard from the certificate of analysis shipped with the standard (50-75 mg/L). Calculate the volume of standard needed as follows:

mL standard needed = 100 ÷ standard concentration

c. Pipet the volume of standard needed into a 100-mL volumetric flask. Dilute to the line with chlorine demand-free deionized water. Invert to mix.

Method 2

a. Dilute 1 drop of commercial 5% chlorine bleach in 1 liter of chlorine demand-free deionized water. Use this as the standard.

2. Verify the standard's concentration using the Hach Free Chlorine Method, #8021.

3. Perform the chlorine dioxide test on the standard without adding glycine (*step 6*).

4. The chlorine dioxide reading should be about 2.45 times greater than the chlorine result. If so, this verifies the DPD and the instrument are functioning properly.

5. Repeat the chlorine dioxide test on the chlorine standard, including the glycine addition (*step 6*). The reading should be less than 0.10 mg/L. This verifies that the glycine is eliminating free chlorine interference.

Method Performance

Precision

Program	Standard	95% Confidence Limits
112	0.24 mg/L	0.22–0.26 mg/L ClO_2
112	4.79 mg/L	4.67–4.91 mg/L ClO_2
113	0.26 mg/L	0.21–0.27 mg/L ClO_2
113	4.83 mg/L	4.71–4.97 mg/L ClO_2

For more information on determining precision data and method detection limits, see *Section 1* of the *DR/800 Procedures Manual*.

Estimated Detection Limit (EDL)

Program	EDL
112	0.04 mg/L ClO_2
113	0.04 mg/L ClO_2

For more information on derivation and use of Hach's estimated detection limit, see *Section 1* of the *DR/800 Procedures Manual*.

Interferences

A substance interferes if it changes the final reading by 0.1 mg/L ClO_2 or more.

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Section 1, Correction For Volume Additions, in the DR/800 Procedures Manual).*
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Section 1*, *Correction For Volume Additions, in the DR/800 Procedures Manual).*
Bromine, Br_2	Interferes at all levels.
Chlorine, Cl_2	May interfere at levels greater than 6 mg/L. Additional glycine may be able to compensate for this interference.
Chloramines, organic	May interfere.
Flocculating agents	High levels of most flocculating agents can be tolerated. This tolerance is decreased if chlorine is present. See the information about metals in this table. In the presence of 0.6 mg/L Cl_2, $Al(SO_4)_3$ (< 500 mg/L) and $FeCl_2$ (<200 mg/L) may be tolerated.
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$.

Interfering Substance	Interference Levels and Treatments
Iodine, I_2	Interferes at all levels.
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	Oxidized manganese interferes at all levels. Oxidized chromium interferes at levels greater than 2 mg/L. To remove the interferences: **1.** Adjust sample pH to 6–7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result of this test from the original analysis to obtain the correct chlorine dioxide concentration.
Metals	Various metals may interfere by combining with the glycine needed to remove the chlorine interference. Metal interference is limited except when chlorine is present. In the presence of 0.6 mg/L Cl_2, both copper (>10 mg/L) and nickel (>50 mg/L) interfere. Other metals may also interfere, depending on their ability to prevent glycine from reacting with any Cl_2 in the sample. It may be necessary to add more glycine to overcome this interference.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L ClO_2 increase in the reading.
Ozone	Interferes at levels greater than 1.5 mg/L.
Peroxides	May interfere.
Extreme sample pH	Adjust to pH 6–7. See *Section 1, pH Interferences, in the DR/800 Procedures Manual.*
Highly buffered samples	Adjust to pH 6–7. *See Section 1, pH Interferences, in the DR/800 Procedures Manual.*

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004).

Summary of Method

Chlorine dioxide reacts with DPD (N,N-diethyl-p-phenylenediamine) Indicator Reagent (to the extent of one-fifth of its total available chlorine content corresponding to reduction of chlorine dioxide to chlorite) to form a pink color. The color intensity is proportional to the ClO_2 in the sample. Chlorine interference is eliminated by adding glycine, which converts free chlorine to chloroaminoacetic acid, but has no effect on chlorine dioxide at the test pH.

CHLORINE DIOXIDE, continued

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required per test	Unit	Cat. No.
Chlorine Dioxide DPD/Glycine Reagent Set (100 tests)			27709-00
Includes one of each:			
DPD Free Chlorine Reagent Powder Pillows, 10 mL . 1 pillow		100/pkg	21055-69
Glycine Reagent	4 drops	29 mL	27621-33

REQUIRED REAGENTS (Using AccuVac® Ampuls)

Chlorine Dioxide DPD/Glycine AccuVac® Ampul Reagent Set (25 tests)			27710-00
Includes one of each:			
DPD Free Chlorine Reagent AccuVac® Ampuls	1	25/pkg	25020-25
Glycine Reagent	16 drops	29 mL	27621-33

OPTIONAL REAGENTS

Chlorine Standard Solution, Voluette™ ampule, 50-75 mg/L, 10 mL	16/pkg	14268-10
DPD Free Chlorine Reagent, SwifTest™	250 tests	28023-00
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270-32
Water, deionized	4 L	272-56
Water, sterile, chlorine dioxide-free	500 mL	26415-49

OPTIONAL APPARATUS

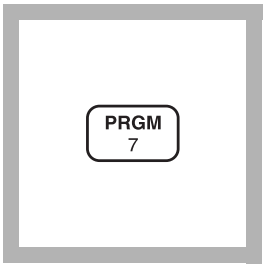
AccuVac® Snapper Kit	each	24052-00
Cylinder, graduated, 25 mL	each	508-40
pH Meter, *sens**ion**™1*, portable, with electrode	each	51700-10
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette® Pipet	1000/pkg	21856-28
PourRite™ Ampule Breaker	each	24846-00

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Marked Dropper Bottle - contact Hach for larger sizes.

CHLORINE DIOXIDE, Mid Range (0 to 50.0 mg/L) For water and wastewater

Direct Reading Method

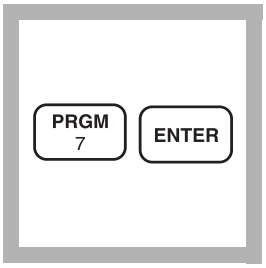


1. Enter the stored program number for mid-range chlorine dioxide (ClO_2).

Press: **PRGM**

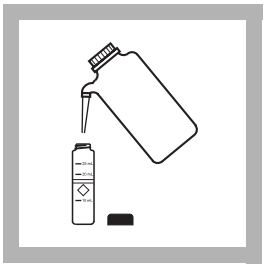
The display will show:

PRGM ?



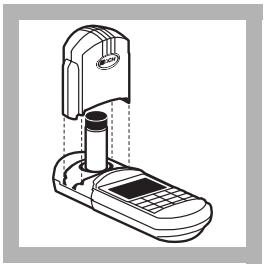
2. Press: **7 ENTER**

The display will show **mg/L, ClO2** and the **ZERO** icon**.**

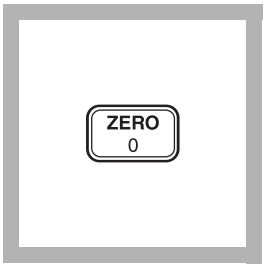


3. Fill a sample cell (the blank) with 10 mL of deionized water.

Note: *Analyze samples immediately after collection.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

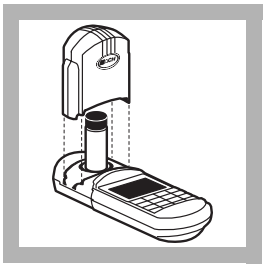


5. Press: **ZERO**

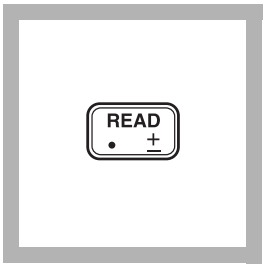
The cursor will move to the right, then the display will show:

0.0 mg/L ClO2

6. Fill another sample cell with 10 mL of sample (the prepared sample).



7. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



8. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine dioxide will be displayed.

Note: *If the display flashes "limit" it is due to high ClO_2 levels. A slight loss of chlorine dioxide may occur during dilution. Dilute a fresh sample and repeat the test. Multiply the result by the dilution factor; see Section 1.*

CHLORINE DIOXIDE, MR, continued

Sampling and Storage

Collect samples in clean plastic or glass bottles. Chlorine dioxide is very volatile and unstable; analyze samples immediately upon collection.

Accuracy Check

Standard Solution Method

Preparing chlorine dioxide standards is difficult and dangerous. In addition, **these standards are both explosive and volatile!** Only a trained chemist should prepare the standards using appropriate safety equipment and precautions. Hach does not recommend independent standard preparation of chlorine dioxide standards. If independent standard preparation is required, please refer to the instructions in *Standard Methods for the Examination of Water and Wastewater*, 19th ed., under the headings "Stock chlorine dioxide solution" and "Standard chlorine dioxide solution" (pg. 4-54).

Method Performance

Precision

In a single laboratory, using a standard solution of 25.0 mg/L ClO_2, a single operator obtained a standard deviation of ±0.3 mg/L ClO_2. For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit

The estimated detection limit for program 7 is 7.3 mg/L ClO_2. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

Chlorine dioxide, a yellow gas, can be measured directly in a water solution. This method uses a wavelength of 420 nm to increase the range of the test.

REQUIRED REAGENTS AND APPARATUS

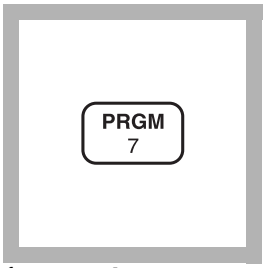
Description	Quantity Required Per Test	Unit	Cat. No.
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06
Water, deionized	10 mL	4 L	272-56

Outside the U.S.A.—Contact the Hach office or distributor serving you.

CHLORINE, FREE, Ultra-high Range (0.0–10.0 mg/L Cl_2) Method 10069

DPD Method

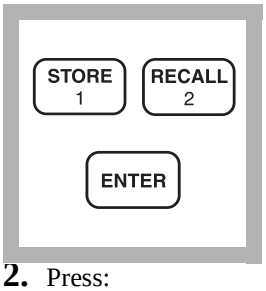
USEPA accepted for reporting drinking water analyses*
For testing higher levels of free chlorine (hypochlorous acid and hypochlorite) in drinking water, cooling water, and industrial process waters



1. Enter the user program number for Chlorine, UHR.

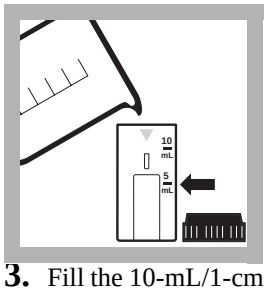
Press: **PRGM**
The display will show:
PRGM?

Note: *If the chlorine is typically less than 2.0 mg/L, use method 8021, program number 9.*

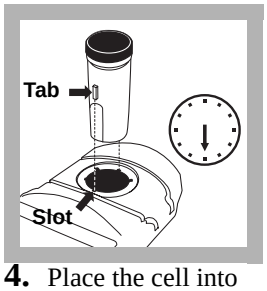


2. Press:
12 ENTER

The display will show
mg/L Cl_2
then: **ZERO**



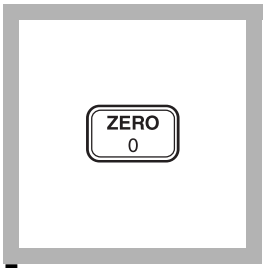
3. Fill the 10-mL/1-cm cell to the 5-mL line with sample.



4. Place the cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The sample cell tab should be at the 6 o'clock position and completely seated in the cell holder slot.*

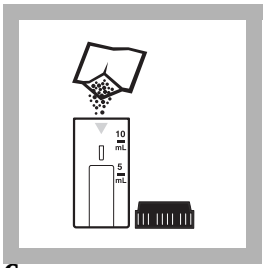
* Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-C1-G for drinking water.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

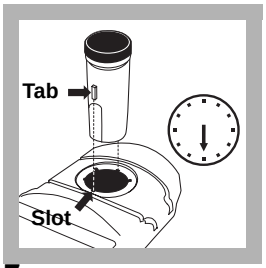
0.0 mg/L Cl_2



6. Remove the sample cell from the cell holder and add the contents of one 25-mL DPD Free Chlorine Reagent pillow to the sample. Cap and shake the sample cell about 20 seconds to dissolve.

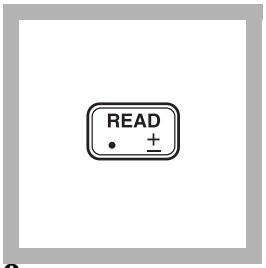
Proceed **immediately** to *step 7*.

Note: *A pink color will develop if chlorine is present.*



7. Place the sample cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the sample cell into the cell holder as illustrated. The sample cell tab should be at the 6-o'clock position and completely seated in the cell holder slot.*



8. Within one minute after reagent addition, press: **READ**.

The cursor will move to the right. The result in mg/L chlorine (as Cl_2) will be displayed.

Note: *See "Interferences" on page 130 for samples with high monochloramine concentrations.*

Sampling and Storage

Analyze samples for chlorine immediately after collection. Free chlorine is a strong oxidizing agent and reacts rapidly with various compounds. Many factors such as sunlight, pH, temperature, and sample composition will influence decomposition of free chlorine in water.

- Avoid plastic containers which may have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand by soaking in a dilute bleach solution (1 mL of commercial bleach to 1 liter of deionized water) for at least one hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.
- Use separate, dedicated sample cells for free and total chlorine determinations. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere.

- A common error in testing for chlorine is failure to obtain a representative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the sample container overflow with sample several times. Cap the container so there is no air above the sample.
- If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 5-mL mark. Proceed with the chlorine test immediately.

Accuracy Check

1. Fill three mixing cylinders (Cat. No. 20886-38) with 5-mL of sample.
2. Snap the neck of a HR Chlorine Ampule Standard, 50–75 mg/L Cl_2. Using the TenSette® Pipet, add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each cylinder and mix thoroughly.
3. Analyze each standard addition sample as described in the procedure. Record each result.
4. Calculate the concentration of mg/L chlorine added to each sample.

$$\text{mg/L chlorine added} = \frac{\text{volume of standard added} \times \text{label value of } Cl_2 \text{ standard ampule}}{\text{sample volume} + \text{volume of standard added}}$$

The spiked sample results should reflect the analyzed sample result plus the calculated mg/L Cl_2 added to each sample. If these increases do not occur, see Standard Additions in Section 1 of a DR/800 Procedure Manual for more information.

Method Performance

Precision

In a single laboratory, using a chlorine standard solution of 5.05 mg/L Cl_2 and representative lots of reagent, a single operator obtained a standard deviation of ± 0.05 mg/L Cl_2.

Estimated Detection Limit

The estimated detection limit for Method 10069 is 0.1 mg/L Cl_2. For more information on the estimated detection limit, see Section 1 of the DR/800 Procedure Manual.

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sodium Hydroxide. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sulfuric Acid. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Iodine, I_2	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	**1.** Adjust sample pH to 6–7. **2.** Add 2 drops Potassium Iodide (30 g/L) to a 5-mL sample. **3.** Mix and wait 1 minute. **4.** Add 2 drops of Sodium Arsenite (5 g/L) and mix. **5.** Analyze the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.

<table>
<tr><th>Interfering Substance</th><th>Interference Levels and Treatments</th></tr>
<tr><td>Monochloramine</td><td>For conventional free chlorine disinfection (beyond the breakpoint), monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test varies with the sample temperature, the relative amount of monochloramine to free chlorine, and the time required to do the analysis. Approximate interference levels of monochloramine in the free chlorine test are listed below (as mg/L Cl_2).
<table>
<tr><th>NH_2Cl</th><th colspan="4">Sample Temperature °C (°F)</th></tr>
<tr><th>(as Cl_2)</th><th>5 (40)</th><th>10 (50)</th><th>20 (68)</th><th>30(83)</th></tr>
<tr><td>1.2</td><td>0.2</td><td>0.2</td><td>0.3</td><td>0.3</td></tr>
<tr><td>2.5</td><td>0.4</td><td>0.5</td><td>0.6</td><td>0.6</td></tr>
<tr><td>3.5</td><td>0.5</td><td>0.6</td><td>0.7</td><td>0.8</td></tr>
</table></td></tr>
<tr><td>Ozone</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH or highly buffered samples</td><td>Adjust the sample pH to 6–7 with Sulfuric Acid or Sodium Hydroxide</td></tr>
</table>

Summary of Method

The range of analysis using the DPD method for free chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Free Chlorine Reagent is added to a 5-mL sample portion.

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) reacts immediately with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color which is proportional in intensity to the chlorine concentration.

Instrument Setup

The following procedure will add this method as a new Hach program to a DR/800 instrument.

1. Turn on the instrument by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the **DOWN** arrow key until the prompt line shows USER.
4. Press the **ENTER** key.
5. Enter “8138”, followed by **ENTER**.

6. Key the number in the "Enter" column corresponding to line number 1 on the display. Press **ENTER**. Repeat for lines 2–56 on the display.

Line Number	Enter	Line Number	Enter
1	12	29	0
2	24	30	0
3	73	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	0
8	62	36	0
9	55	37	0
10	23	38	0
11	88	39	0
12	64	40	0
13	113	41	0
14	242	42	0
15	18	43	0
16	0	44	110
17	0	45	0
18	0	46	0
19	0	47	10
20	67	48	0
21	108	49	180
22	50	50	0
23	0	51	0
24	0	52	0
25	0	53	0
26	0	54	236
27	0	55	0
28	0	56	255

CHLORINE, FREE, Ultra-high Range, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Free Chlorine Reagent Powder Pillows, 25-mL	1	100/pkg	14070-99

REQUIRED APPARATUS

Sample Cell, 10-mL/1-cm	1	2/pkg	48643-02

OPTIONAL REAGENTS

Chlorine Standard Solution, 2-mL Voluette® Ampule, 50–75 mg/L		20/pkg	14268-20
Potassium Iodide Solution, 30-g/L		100 mL MDB	343-32
Sodium Arsenite Solution, 5-g/L		100 mL MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N		100 mL MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL MDB	1270-32
Water, deionized		4 L	272-56

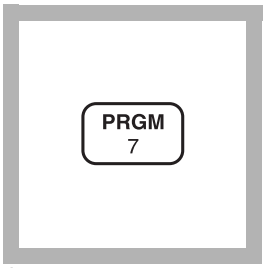
OPTIONAL APPARATUS

Ampule Breaker Kit		each	24846-00
Cylinder, graduated, 10-mL, mixing		each	20886-38
pH Meter, sens***ion***™1, portable, with electrode		each	51700-10
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

CHLORINE, TOTAL, Ultra-High Range (0.0–10.0 mg/L Cl_2) Method 10070

DPD Method

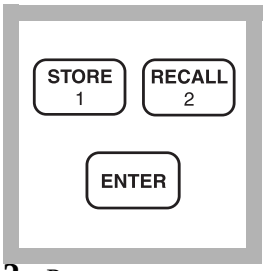
USEPA accepted for reporting water and wastewater analyses*
For testing higher levels of total chlorine (free and combined) in drinking water, cooling water, industrial process waters, or treated wastewater



1. Enter the user program number for Chlorine, UHR.

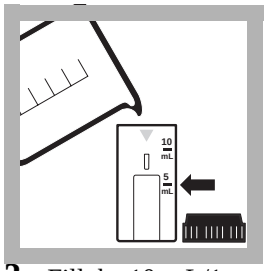
Press: **PRGM**
The display will show:
PRGM?

Note: *If the chlorine is typically less than 2.0 mg/L, use method 8167, program number 9.*

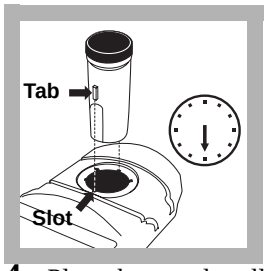


2. Press:
12 ENTER

The display will show
mg/L Cl_2
then: **ZERO**



3. Fill the 10-mL/1-cm cell to the 5-mL line with sample.

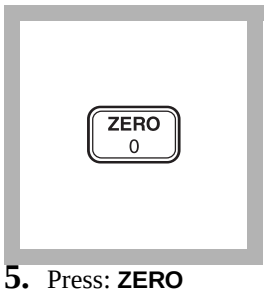


4. Place the sample cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The sample cell tab should be at the 6 o'clock position and completely seated in the cell holder slot.*

* Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-C1-G for drinking water.

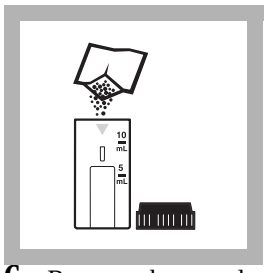
CHLORINE, TOTAL, Ultra-High Range, continued



5. Press: **ZERO**

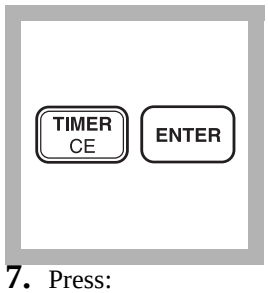
The cursor will move to the right, then the display will show:

0.0 mg/L Cl_2



6. Remove the sample cell from the cell holder and add the contents of one 25- mL DPD Total Chlorine Reagent pillow to the sample. Cap and shake the sample cell about 20 seconds to dissolve.

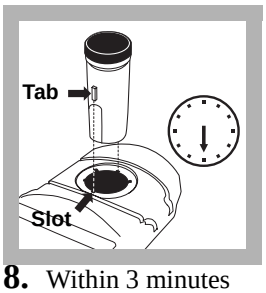
Note: *A pink color will develop if chlorine is present.*



7. Press:

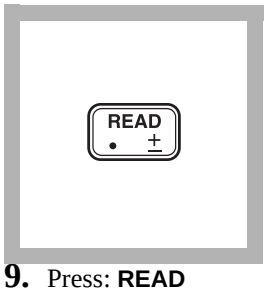
TIMER ENTER

A 3-minute reaction period will begin.



8. Within 3 minutes after the timer beeps, place the sample cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: *Place the cell into the cell holder as illustrated. The sample cell tab should be at the 6-o'clock position and completely seated in the cell holder slot.*



9. Press: **READ**

The cursor will move to the right. The result in mg/L chlorine (as Cl_2) will be displayed.

Sampling and Storage

Analyze samples for chlorine immediately after collection. Free and combined chlorine are strong oxidizing agents and react rapidly with various compounds. Many factors such as sunlight, pH, temperature, and sample composition will influence decomposition of chlorine in water.

- Avoid plastic containers which may have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand by soaking in a dilute bleach solution (1 mL of commercial bleach to 1 liter of deionized water) for at least one hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.
- Use separate, dedicated sample cells for free and total chlorine determinations. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere.
- A common error in testing for chlorine is failure to obtain a representative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the sample container overflow with sample several times. Cap the container so there is no air above the sample.
- If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 5-mL mark. Proceed with the chlorine test immediately.

Accuracy Check

1. Fill three mixing cylinders (Cat. No. 20886-38) with 5-mL of sample.
2. Snap the neck of a HR Chlorine Ampule Standard, 50–75 mg/L Cl_2. Using the TenSette® Pipet, add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each cylinder and mix thoroughly.
3. Analyze each standard addition sample as described in the procedure. Record each result.

4. Calculate the concentration of mg/L chlorine added to each sample.

$$\text{mg/L chlorine added} = \frac{\text{volume of standard added} \times \text{label value of } Cl_2 \text{ standard ampule}}{\text{sample volume} + \text{volume of standard added}}$$

The spiked sample results should reflect the analyzed sample result plus the calculated mg/L Cl_2 added to each sample. If these increases do not occur, see Standard Additions in Section 1 of a DR/800 Procedure Manual for more information.

Method Performance

Precision

In a single laboratory, using a chlorine standard solution of 5.05 mg/L Cl_2 and representative lots of reagent, a single operator obtained a standard deviation of ± 0.05 mg/L Cl_2.

Estimated Detection Limit

The estimated detection limit for Method 10070 is 0.05 mg/L Cl_2. For more information on the estimated detection limit, see Section 1 of a DR/800 Procedure Manual.

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sodium Hydroxide. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. **1.** Neutralize to pH 6–7 with 1 N Sulfuric Acid. **2.** Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. **3.** Correct for volume addition.
Bromine, Br_2	Interferes at all levels
Chlorine Dioxide, ClO_2	Interferes at all levels
Chloramines, organic	May interfere
Iodine, I_2	Interferes at all levels

Interfering Substance	Interference Levels and Treatments
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	**1.** Adjust sample pH to 6–7. **2.** Add 2 drops Potassium Iodide (30 g/L) to a 5-mL sample. **3.** Mix and wait 1 minute. **4.** Add 2 drops of Sodium Arsenite (5 g/L) and mix. **5.** Analyze the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH or highly buffered samples	Adjust the sample pH to 6–7 with Sulfuric Acid or Sodium Hydroxide

Summary of Method

The range of analysis using the DPD method for total chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Total Chlorine Reagent is added to a 5-mL sample portion.

The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N,N-diethyl-p-phenylenediamine) along with free chlorine present in the sample to form a pink color which is proportional in intensity to the total chlorine concentration.

Instrument Setup

The following procedure will add this method as a new Hach program to a DR/800 instrument.

1. Turn on the instrument by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the **DOWN** arrow key until the prompt line shows USER.
4. Press the **ENTER** key.
5. Enter “8138”, followed by **ENTER**.
6. Key the number in the “Enter” column corresponding to line number 1 on the display. Press **ENTER**. Repeat for lines 2–56 on the display.

CHLORINE, TOTAL, Ultra-High Range, continued

Line Number	Enter	Line Number	Enter
1	12	29	0
2	24	30	0
3	73	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	0
8	62	36	0
9	55	37	0
10	23	38	0
11	88	39	0
12	64	40	0
13	113	41	0
14	242	42	0
15	18	43	0
16	0	44	110
17	0	45	0
18	0	46	0
19	0	47	10
20	67	48	0
21	108	49	180
22	50	50	0
23	0	51	0
24	0	52	0
25	0	53	0
26	0	54	236
27	0	55	0
28	0	56	255

CHLORINE, TOTAL, Ultra-High Range, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows, 25-mL	1	100/pkg	14064-99

REQUIRED APPARATUS

Sample Cell, 10-mL/1-cm	1	2/pkg	48643-02

OPTIONAL REAGENTS

Chlorine Standard Solution, 2-mL Voluette® Ampule, 50–75 mg/L		20/pkg	14268-20
Potassium Iodide Solution, 30-g/L		100 mL MDB	343-32
Sodium Arsenite Solution, 5-g/L		100 mL MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N		100 mL MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL MDB	1270-32
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit		each	24846-00
Cylinder, graduated, 10-mL, mixing		each	20886-38
pH Meter, sens***ion***™1, portable, with electrode		each	51700-10
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

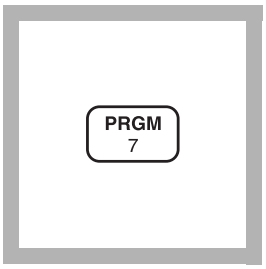
CHLORINE, FREE (0 to 2.00 mg/L)

For water, wastewater, and seawater

DPD Method (Powder Pillows or AccuVac Ampuls)

USEPA accepted for reporting wastewater and drinking water analyses*

Using Powder Pillows



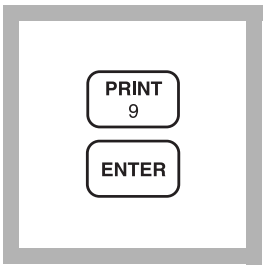
1. Enter the stored program number for free and total chlorine (Cl_2) powder pillows.

Press: **PRGM**

The display will show:

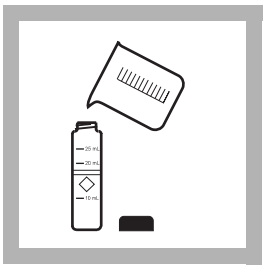
PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **9 ENTER**

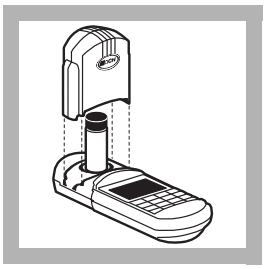
The display will show **mg/L, Cl2** and the **ZERO** icon.



3. Fill a sample cell with 10 mL of sample (the blank).

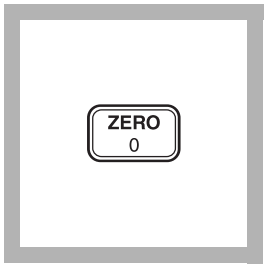
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

Note: *The SwifTest Dispenser for Free Chlorine can be used in place of the powder pillows in step 7.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

* Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-Cl G for drinking water.



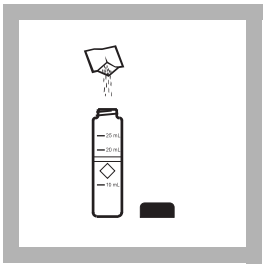
5. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cl2

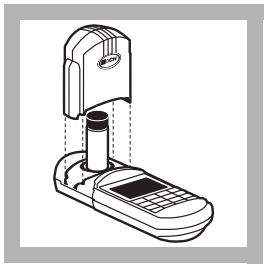
Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*

6. Fill another cell with 10 mL of sample.



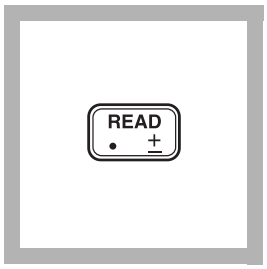
7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl vigorously to dissolve the powder.

Note: *A pink color will develop if free chlorine is present.*



8. Immediately place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Perform Step 9 within one minute of reagent addition.*



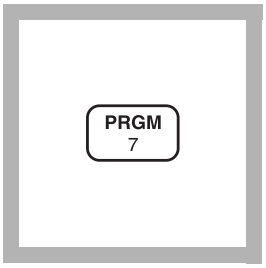
9. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1. Or, use the High Range Free Chlorine test, program #8.*

Using AccuVac Ampuls



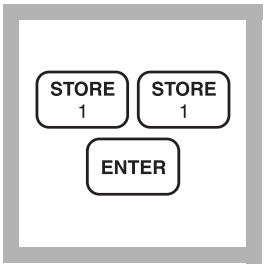
1. Enter the stored program number for free and total chlorine (Cl_2)-AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

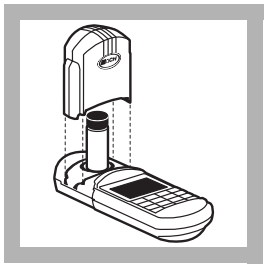


2. Press: **11 ENTER**

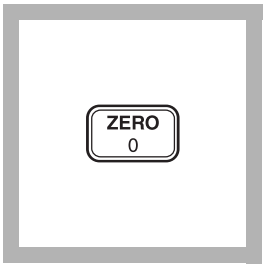
The display will show **mg/L, Cl2** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

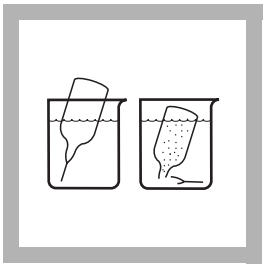


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

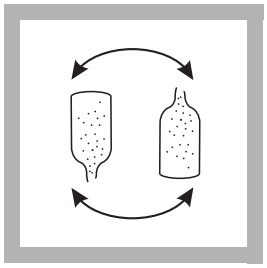
0.00 mg/L Cl2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



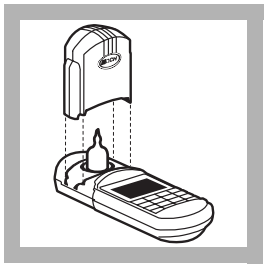
6. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampule fills completely.*



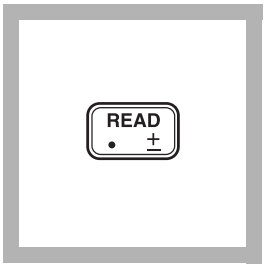
7. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

Note: *A pink color will form if chlorine is present.*



8. Immediately place the AccuVac Ampul into the cell holder. Tightly cover the ampule with the instrument cap.

Note: *Perform step 9 within one minute of reagent addition.*



9. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1.*

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let

the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample container so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the analysis immediately.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Re-zero the instrument using the original sample (the blank).

d) Place the spiked sample in the cell holder and press **READ**. Record the results.

e) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine added} = \frac{0.1(\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step e).

g) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Free Chlorine AccuVac completely from each beaker.

e) Analyze the spiked and unspiked sample as described in the procedure.

f) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine added} = \frac{0.2(\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{25.2(\text{sample + standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step f).

h) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for programs 9 and 11 is 0.02 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1*, *Correcting for Volume Additions*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium , Oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L increase in the reading.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences, Section 1*.

Summary of Method

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a magenta color which is proportional to the chlorine concentration.

CHLORINE, FREE continued

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Free Chlorine Powder Pillows, 10 mL	1 pillow	100/pkg	21055-69
Sample Cell, 10, 20, 25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (Using AccuVac Ampuls)

DPD Free Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25020-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, PourRite ampule, 25-30 mg/L, 2 mL	20/pkg	26300-20
DPD Free Chlorine Reagent, SwifTest	250 tests	28023-00
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Cylinder, graduated, 25 mL	each	508-40
pH Meter, *sens**ion***™*1*, portable, with electrode	each	51700-10
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96Pipet
Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
PourRite Ampule Breaker	each	24846-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Marked Dropper Bottle - contact Hach for larger sizes.

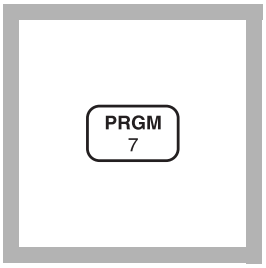
CHLORINE, TOTAL (0 to 2.00 mg/L)

For water, wastewater and seawater

DPD Method (Powder Pillows or AccuVac Ampuls)

USEPA accepted for reporting water and wastewater analyses*

Using Powder Pillows



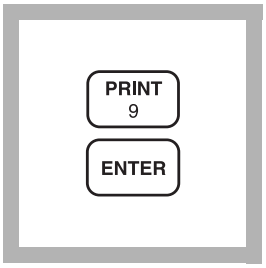
1. Enter the stored program number for total chlorine (Cl_2) powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

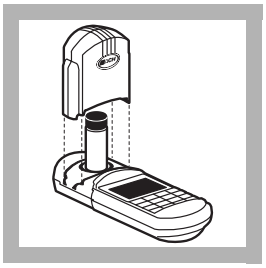


2. Press: **9 ENTER**

The display will show **mg/L, Cl2** and the **ZERO** icon**.**

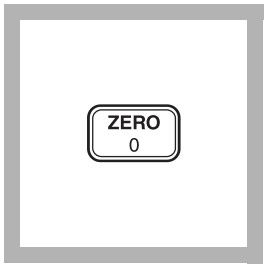
3. Fill a sample cell with 10 mL of sample (the blank).

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

* Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-Cl G for drinking water.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

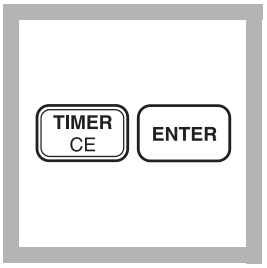
0.00 mg/L Cl2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*

6. Fill a second cell to the 10-mL mark with sample.

7. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Cap and swirl the sample cell vigorously to dissolve the powder.

Note: *It is not necessary that all the powder dissolves.*

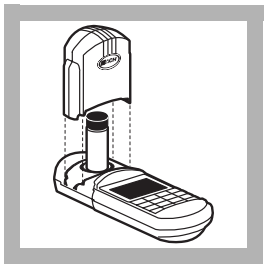


8. Press:

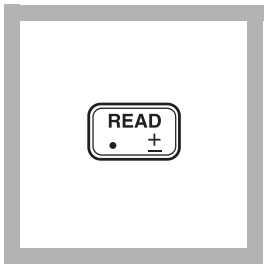
TIMER ENTER

A three-minute reaction period will begin. A pink color will develop if chlorine is present.

Note: *The SwifTest Dispenser for Total Chlorine can be used in place of the powder pillows in step 7.*



9. After the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



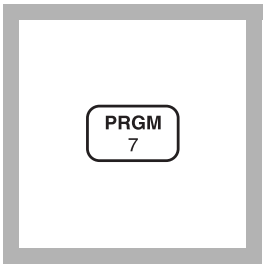
10. Press: **READ**

The cursor will move to the right, then the result in mg/L total chlorine will be displayed.

Note: *It the sample temporarily turns yellow after sample addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1. Or use the High Range Total Chlorine test, program #8.*

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Using AccuVac Ampuls



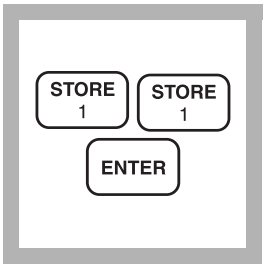
1. Enter the stored program number for total chlorine (Cl_2) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

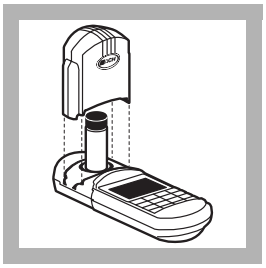


2. Press: **11 ENTER**

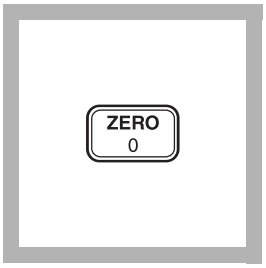
The display will show **mg/L, Cl2** and the **ZERO** icon**.**

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

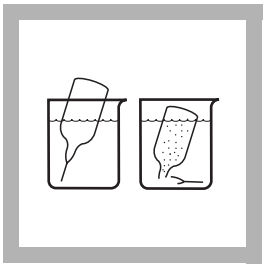


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

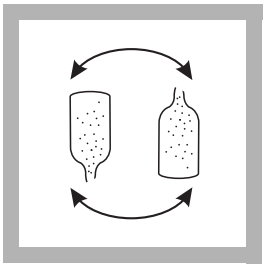
0.00 mg/L Cl2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



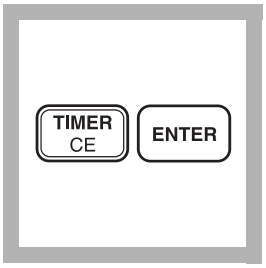
6. Fill a DPD Total Chlorine Reagent AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampule fills completely.*



7. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

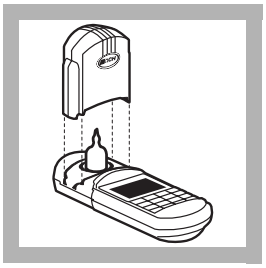
Note: *A pink color will form if chlorine is present.*



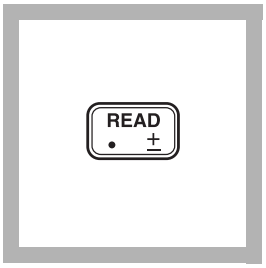
8. Press:

TIMER ENTER

A three-minute reaction period will begin.



9. When the timer beeps, place the AccuVac Ampul into the cell holder. Tightly cover the ampule with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L total chlorine will be displayed.

Note: *If the sample temporarily turns yellow after sample addition, or the display shows "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the appropriate dilution factor; see Section 1.*

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

Do not use the same sample cells for free and total chlorine. If

trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

A common error in testing for chlorine is introduced when a representative sample is not obtained. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the chlorine analysis immediately.

Accuracy Check

Standard Additions Method (using powder pillows)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Re-zero the instrument using the original sample (the blank).

d) Place the spiked sample into the cell holder and press **READ**. Record the results.

e) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

f) The spiked sample result (step d) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step e).

g) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (using AccuVac Ampuls)

a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.

b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.

c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.

d) Fill a DPD Total Chlorine AccuVac completely from each beaker.

e) Analyze the spiked and unspiked sample as described in
the procedure.

f) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.2\ (\text{vol. standard added}) \times \text{Label value (mg/L Chlorine)}}{25.2\ (\text{sample + standard volume})}$$

g) The spiked sample result should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step f).

h) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 1.00 mg/L chlorine and two lots of reagents with the instrument, a single operator obtained standard deviations of ±0.01 mg/L chlorine.

In a single laboratory, using a standard solution of 1.00 mg/L chlorine and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for programs 9 and 11 is 0.02 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1*, *Correcting for Volume Additions*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium , Oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences, Section 1*.

Summary of Method

Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms can exist in the same water and be determined together as the total available chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives.

The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N, N-diethyl-p-phenylenediamine)

along with free chlorine present in the sample to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run free chlorine and total chlorine tests. Subtract the results of the free chlorine test from the results of the total chlorine test to obtain combined chlorine.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS & APPARATUS (USING POWDER PILLOWS)

Description	Qty/Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	21056-69
Sample Cell, 10-20-25 mL, w/caps	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (USING ACCUVAC AMPULS)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25030-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Chlorine Standard Solution, PourRite ampule, 25-30 mg/L Cl_2	20/pkg	26300-20
DPD Total Chlorine Reagent, SwifTest	250 tests	28024-00
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343-32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1 N	100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1 N	100 mL* MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
PourRite Ampule Breaker	each	24846-00
Cylinder, graduated, 25 mL	each	508-40
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable	each	51700-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28

For Technical Assistance, Price and Ordering

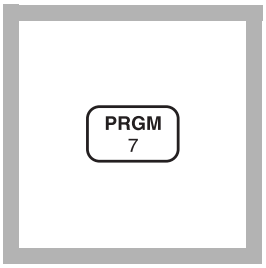
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Marked Dropper Bottle - contact Hach for larger sizes.

CHLORINE, FREE (0 to 5.00 mg/L)

DPD Test 'N Tube™ Method*



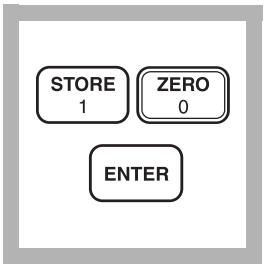
1. Enter the stored program number for Test 'N Tube free chlorine (Cl_2).

Press: **PRGM**

The display will show:

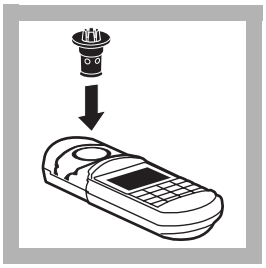
PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



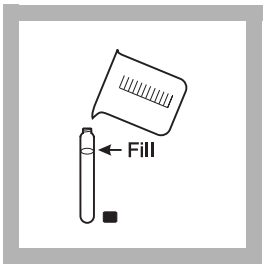
2. Press: **10 ENTER**

The display will show **mg/L, Cl2** and the **ZERO** icon**.**



3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down fully to insert it.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



4. Fill an empty Test 'N Tube vial with sample (the blank).

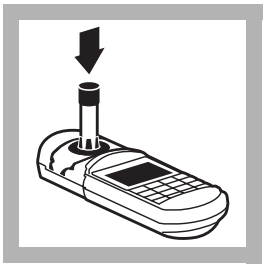
Note: *Fill to the top of the Hach logo "oval" mark.*

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater*

5. Wipe the outside of the blank vial with a towel.

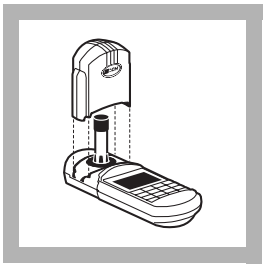
Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



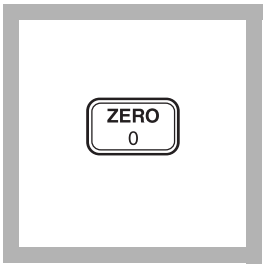
6. Place the blank in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



7. Cover the vial tightly with the instrument cap.

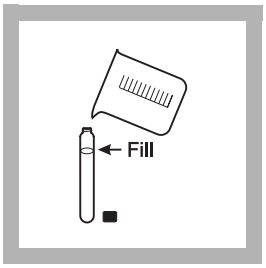


8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cl2

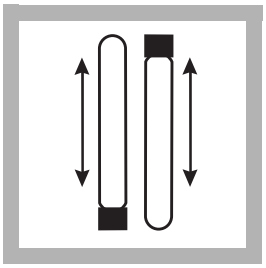
Note: *If Reagent Blank Correction is on, the display may show "limit". See Section 1.*



9. Remove the cap from a Free Chlorine DPD-TNT tube. Add 10 mL of sample.

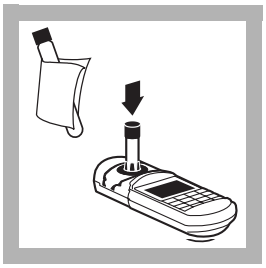
Note: *Fill to the top of the Hach logo "oval" mark.*

Note: *A pink color will develop if chlorine is present.*



10. Cap and invert at least 10 times to dissolve the powder. This is the prepared sample.

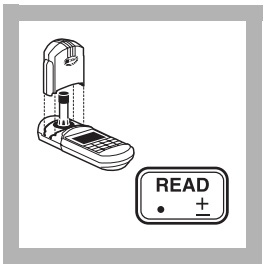
Note: *Use slow, deliberate inversion for complete recovery. Ten inversions should take at least 30 seconds. One inversion equals turning the vial upside down, then returning it to an upright position.*



11. Within 30 seconds after mixing, wipe the prepared sample vial with a towel, then place it in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Cover the vial tightly with the instrument cap.

Press: **READ**

The cursor will move to the right, then the result in mg/L free chlorine will be displayed.

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent and is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for chlorine is obtaining an unrepresentative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. Perform the analysis immediately.

Accuracy Check

Standard Additions Method

a) Snap the top off a HR Chlorine PourRite™ Ampule Standard Solution.

b) Use a TenSette® Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.

c) Analyze the spiked sample, beginning at Step 8 of the procedure.

d) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1(\text{vol. standard added}) \times \text{Label value}(\text{mg/L } Cl_2)}{10.1(\text{sample} + \text{standard volume})}$$

e) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step d).

f) If this increase does not occur, see *Standard Additions, Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 2.53 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of ±0.14 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for program 10 is 0.03 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1, Correcting for Volume Additions* in the *DR/800 Series Procedures Manual*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Section 1 Correcting for Volume Additions*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium , oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.

<table>
<tr><th>Interfering Substance</th><th>Interference Level and Treatment</th></tr>
<tr><td>Monochloramine</td><td>For conventional free chlorine disinfection (beyond the breakpoint), typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on the sample temperature, relative amount of monochloramine to free chlorine, and the time required to do the analysis. Typical interference level of monochloramine in the free chlorine test are listed below (as mg/L Cl_2).
<table>
<tr><th>NH_2Cl as Cl_2</th><th colspan="4">Sample Temp. °C (°F)</th></tr>
<tr><td></td><td>5 (40)</td><td>10 (50)</td><td>20 (68)</td><td>30 (83)</td></tr>
<tr><td>1.2 mg/L</td><td>+0.15</td><td>+0.19</td><td>+0.30</td><td>+0.29</td></tr>
<tr><td>2.5 mg/L</td><td>0.35</td><td>0.38</td><td>0.55</td><td>0.61</td></tr>
<tr><td>3.5 mg/L</td><td>0.38</td><td>0.56</td><td>0.69</td><td>0.73</td></tr>
</table></td></tr>
<tr><td>Ozone</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH and highly buffered samples</td><td>Adjust to pH 6-7. See Interferences, Section 1.</td></tr>
</table>

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004). See *Section 3* for more information on proper disposal of these materials.

Summary of Method

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD
(N,N-diethyl-p-phenylenediamine) indicator to form a magenta color which is proportional to the chlorine concentration.

CHLORINE, FREE continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Test 'N Tube DPD Free Chlorine Reagent	1 vial	50/pkg	21055-45
Test 'N Tube Vials	1 vial	6/pkg	22758-06

REQUIRED APPARATUS

Caps, white	1 cap	6/pkg	22411-06
COD/TNT Adapter	1	each	48464-00

OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 50-75 mg/L, 2 mL		20/pkg	14268-20
Potassium Iodide Solution, 30 g/L		100 mL* MDB	343-32
Sodium Arsenite, 5 g/L		100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N		100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL* MDB	1270-32

OPTIONAL APPARATUS

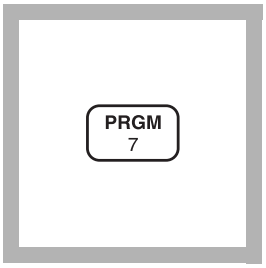
Beaker, 50 mL		each	500-41H
pH Meter, *sens**ion**™1*, portable, with electrode		each	51700-10
pH Paper, pH 1 to 11 pH		5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
PourRite Ampule Breaker		each	24846-00
Test Tube Rack		each	18641-00

* Marked Dropper Bottle - contact Hach for larger sizes.

CHLORINE, TOTAL (0 to 5.00 mg/L)

For water, wastewater and seawater

DPD Test 'N Tube™ Method*



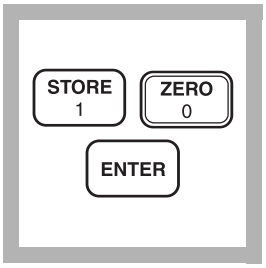
1. Enter the stored program number for Test 'N Tube total chlorine (Cl_2).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

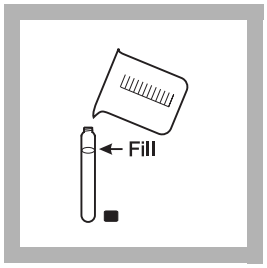


2. Press: **10 ENTER**

The display will show **mg/L, Cl2** and the **ZERO** icon**.**

3. Insert the COD/TNT Vial Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



4. Fill an empty Test 'N Tube vial with sample (the blank).

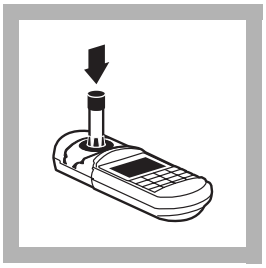
Note: *Fill to the top of the Hach logo "oval" mark.*

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater*.

5. Wipe the outside of the blank vial with a towel.

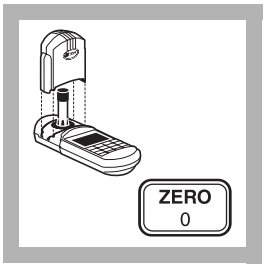
Note: *Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



6. Place the blank in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



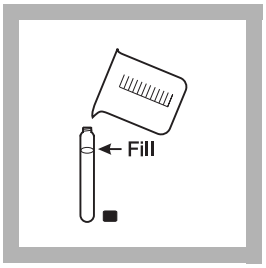
7. Cover the vial tightly with the instrument cap.

Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cl2

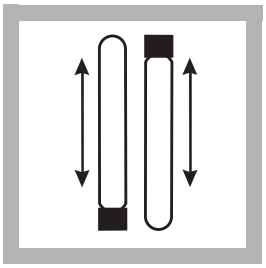
Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



8. Remove the cap from a Total Chlorine DPD-TNT tube. Add 10 mL of sample.

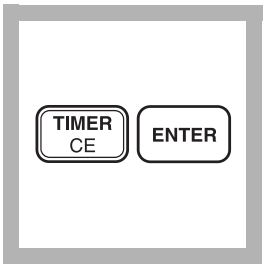
Note: *Fill to the top of the Hach logo "oval" mark.*

Note: *A pink color will develop if chlorine is present.*



9. Cap and invert at least 10 times to dissolve the powder. This is the prepared sample.

Note: *Use slow, deliberate inversion for complete recovery. Ten inversions should take at least 30 seconds. One inversion equals turning the vial upside down, then returning it to an upright position.*

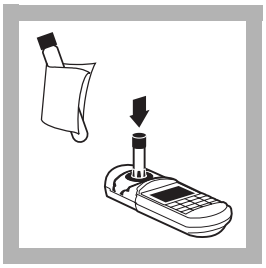


10. Press:

TIMER ENTER

A three-minute reaction period will begin.

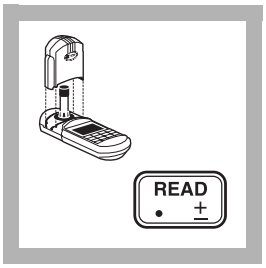
Note: *A pink color will develop if chlorine is present.*



11. When the timer beeps, wipe the prepared sample vial with a towel, then place it in the vial adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Cover the vial tightly with the instrument cap.

Press: **READ**

The cursor will move to the right, then the result in mg/L total chlorine will be displayed.

Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free and combined chlorine are strong oxidizing agents and are unstable in natural waters. They react rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. **Pretreat glass** sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

A common error in testing for chlorine is obtaining an unrepresentative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. Perform the analysis immediately.

Accuracy Check

Standard Additions Method

a) Snap the top off a High Range Chlorine PourRite™ Ampule Standard Solution.

b) Use a TenSette® Pipet to add 0.1 mL of the standard to 10 mL of sample (this is the spiked sample). Swirl to mix.

c) Analyze the spiked sample, beginning at Step 8 of the procedure.

d) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{Label value (mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

e) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl_2 added (step d).

f) If this increase does not occur, see *Standard Additions, Section 1* for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 2.53 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained standard deviations of ±0.14 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for programs 10 is 0.03 mg/L Cl_2. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sodium hydroxide. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Correcting for Volume Additions* in *Section 1*).
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (See *Correcting for Volume Additions* in *Section 1*).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as $CaCO_3$
Iodine	Interferes at all levels
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium , oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7. **2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Ozone	Interferes at all levels
Peroxides	May interfere

Interfering Substance	Interference Level and Treatment
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See *Interferences* in *Section 1*.

Summary of Method

Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms can exist in the same water and be determined together as the total available chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives.

The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N, N-diethyl-p-phenylenediamine) along with free chlorine present in the sample to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run free chlorine and total chlorine tests. Subtract the results of the free chlorine test from the results of the total chlorine test to obtain combined chlorine.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004).

CHLORINE, TOTAL, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Test 'N Tube DPD Total Chlorine Reagent	1 vial	25/pkg	21056-25
Test 'N Tube Vials	1 vial	6/pkg	22758-06

REQUIRED APPARATUS

COD/TNT Adapter, DR/800	1	each	48464-00

OPTIONAL REAGENTS

Chlorine Standard Solution, 2-mL PourRite ampule, 50-75 mg/L		20/pkg	14268-20
Potassium Iodide Solution, 30 g/L		100 mL* MDB	343-32
Sodium Arsenite Solution, 5 g/L		100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N		100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL* MDB	1270-32

OPTIONAL APPARATUS

Beaker, 50 mL		each	500-41H
PourRite Ampule Breaker		each	24846-00
pH Indicator Paper, pH 1 to 11		5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable, with electrode		each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Test Tube Rack		each	18641-00

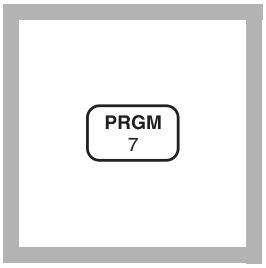
* Marked Dropper Bottle - contact Hach for larger sizes.

CHROMIUM, HEXAVALENT (0 to 0.60 mg/L Cr^{6+}) For water and wastewater

1,5-Diphenylcarbohydrazide Method* (Powder Pillows or AccuVac Ampuls)

USEPA accepted for wastewater analyses**

Using Powder Pillows

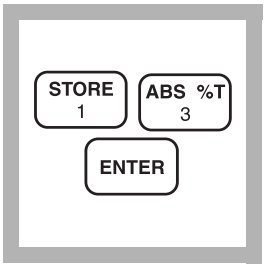


1. Enter the stored program number for hexavalent chromium (Cr^{6+})- powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

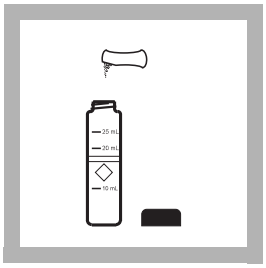


2. Press: **13 ENTER**

The display will show **mg/L, Cr6** and the **ZERO** icon**.**

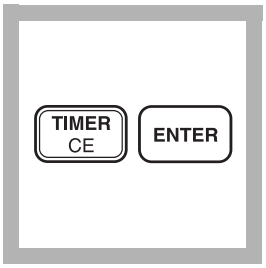
Note: *For alternate forms (CrO_4, Cr_2O_7), press the* **CONC** *key.*

3. Fill a sample cell with 10 mL of sample.



4. Add the contents of one ChromaVer 3 Reagent Powder Pillow to the cell (the prepared sample). Cap the cell and invert several times to mix.

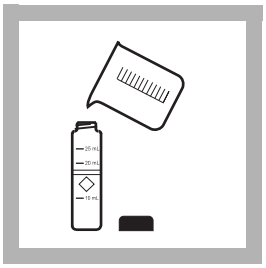
Note: *A purple color will form if Cr^{6+} is present.*



5. Press:

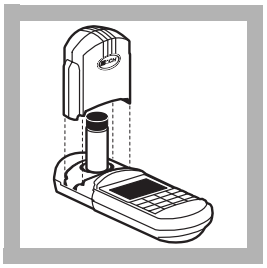
TIMER ENTER

A five-minute reaction period will begin.

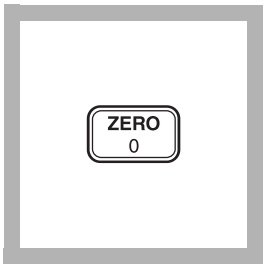


6. Fill another sample cell with 10 mL of sample (the blank).

Note: *For turbid samples, add the contents of one Acid Reagent Powder Pillow. This ensures turbidity dissolved by the acid in the ChromaVer 3 Chromium Reagent is also dissolved in the blank.*



7. When the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cr6

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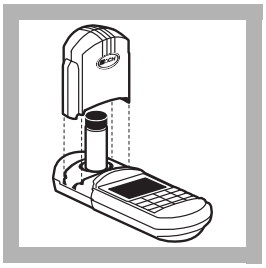
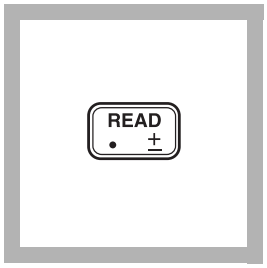
* Adapted from *Standard Methods for the Examination of Water and Wastewater*

** Procedure is equivalent to USGS method I-1230-85 for wastewater.



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

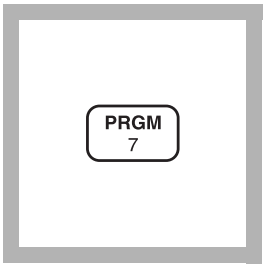


10. Press: **READ**

The cursor will move to the right, then the result in mg/L hexavalent chromium will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Using Accuvac Ampuls



1. Enter the stored program number for hexavalent chromium (Cr^{6+})- AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

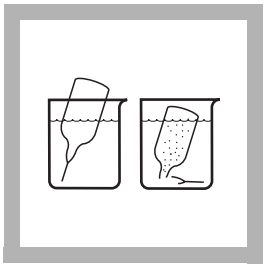
2. Press: **14 ENTER**

The display will show **mg/L, Cr6** and the **ZERO** icon**.**

Note: *For alternate forms (CrO_4, Cr_2O_7), press the* **CONC** *key.*

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

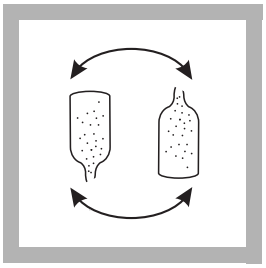
Note: *For turbid samples, add the contents of one Acid Reagent Powder Pillow to 10 mL of the blank. This ensures turbidity dissolved by the acid in the ChromaVer 3 Chromium Reagent is also dissolved in the blank.*



4. Fill a ChromaVer 3 Reagent AccuVac Ampul (the prepared sample) with sample.

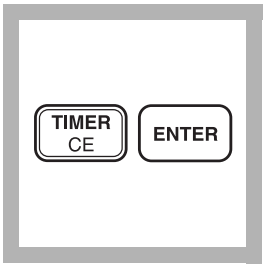
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *ChromaVer 3 should be white to tan in color. Replace if it is brown or green.*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

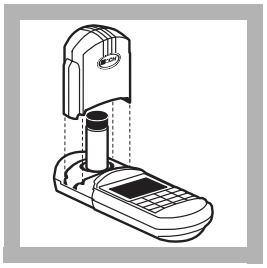
Note: *A purple color will form if hexavalent chromium is present.*



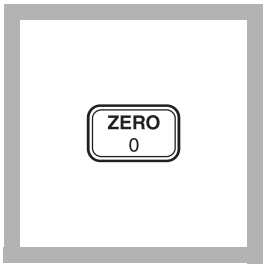
6. Press:

TIMER ENTER

A five-minute reaction period will begin.



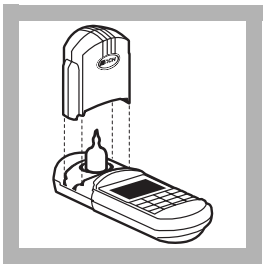
7. When the timer beeps place the blank into the cell holder.



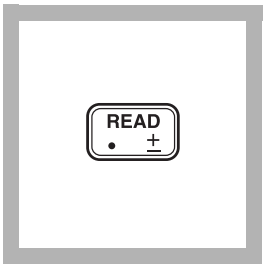
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L Cr6



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L hexavalent chromium will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in a cleaned glass or plastic container. Store at 4 °C (39 °F) up to 24 hours. Samples must be analyzed within 24 hours.

Accuracy Check

Standard Additions Method (powder pillows)

a) Snap the neck off a Hexavalent Chromium PourRite Standard Ampule, 5 mg/L Cr^{6+}.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard to three 10-mL samples, respectively. Swirl to mix.

c) Analyze each sample as described above. The chromium concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (AccuVac Ampuls)

a) Snap the neck off a Hexavalent Chromium Voluette Standard Ampule, 12.5 mg/L Cr^{6+}.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard to three 25-mL samples in beakers. Swirl gently to mix.

c) Analyze each sample as described above. The chromium concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Prepare a 0.50-mg/L Cr^{6+} solution by pipetting 10.00 mL of Hexavalent Chromium Standard Solution, 50.0 mg/L Cr^{6+}, into a 1000-mL volumetric flask and diluting to the mark with deionized water. Invert repeatedly to mix. Prepare this solution daily. Perform the chromium procedure as described above, using this solution in place of the sample.

Method Performance

Precision

In a single laboratory using a standard solution of 0.6 mg/L Cr^{6+} and two representative lots of powder pillow reagent with the instrument, a single operator obtained a standard deviation of ±0.008 mg/L Cr^{6+}.

In a single laboratory using a standard solution of 0.6 mg/L Cr^{6+} and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.005 mg/L Cr^{6+}.

Estimated Detection Limit (EDL)

The EDL for program 13 (powder pillows) and program 14 (AccuVac Ampuls) is 0.01 mg/L Cr^{6+}. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

The following substances do not interfere in the test, up to the following concentration:

Substance	Concentration
Mercurous & Mercuric Ions	Interferes slightly
Iron	1 mg/L
Vanadium	1 mg/L. At higher levels vanadium interference can be overcome by waiting ten minutes before reading.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interference* in *Section 1*.

Summary of Method

Hexavalent chromium is determined by the 1,5-diphenylcarbohydrazide method using a single dry powder formulation called ChromaVer 3 Chromium Reagent. This reagent contains an acidic buffer combined with 1,5-diphenylcarbohydrazide, which reacts to give a purple color which is proportional to the amount of hexavalent chromium present.

REQUIRED REAGENTS AND APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
ChromaVer 3 Chromium Reagent Powder Pillows	1 pillow	100/pkg	12710-99
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS AND APPARATUS (Using AccuVac Ampuls)

ChromaVer 3 AccuVac Ampuls	1 ampul	25/pkg	25050-25

Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Description	Unit	Cat. No
Acid Reagent Powder Pillows	100/pkg	2126-99
Chromium, Hexavalent, Standard Solution, 50 mg/L Cr^{6+}	100 mL	810-42
Chromium, Hexavalent, Standard Solution, Voluette Ampule, 12.5 mg/L Cr^{6+}, 10 mL	16/pkg	14256-10
Chromium, Hexavalent, Standard Solution, PourRite Ampule, 5 mg/L Cr^{6+}, 2 mL	20/pkg	26056-20
Water, deionized	4 L	272-56

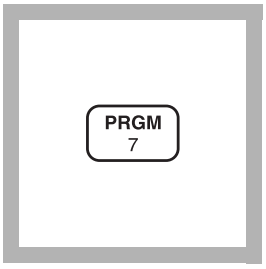
OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Flask, volumetric, Class A, 1000 mL	each	14574-53
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, EC10, portable	each	50050-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, 5.00 mL, Class A	each	14515-37
Pipet Filler, safety bulb	each	14651-00
PourRite Ampule Breaker, 2 mL	each	24846-00

In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

CHROMIUM, TOTAL (0 to 0.60 mg/L)

Alkaline Hypobromite Oxidation Method* **



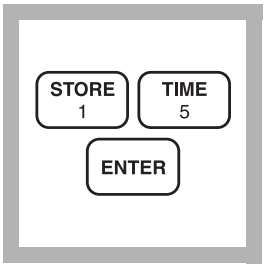
1. Enter the stored program number for total chromium (Cr).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



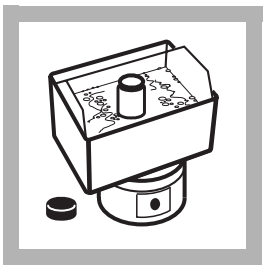
2. Press: **15 ENTER**

The display will show **mg/L, Cr** and the **ZERO** icon**.**

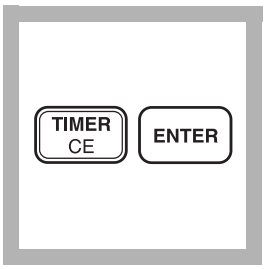
3. Fill a clean sample cell with 25 mL of sample.

Note: *Adjust the pH of stored samples before analysis.*

4. Add the contents of one Chromium 1 Reagent Powder Pillow (the prepared sample). Cap the cell and invert repeatedly to mix. Remove the cap.



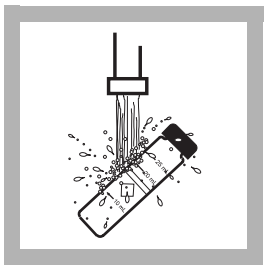
5. Place the prepared sample into a boiling water bath.



6. Press:

TIMER ENTER

A five-minute reaction period will begin.



7. After the beeper beeps, remove the prepared sample. Cap the cell. Use running tap water to cool the cell to 25 °C.

Note: *Use finger cots to handle the hot sample cell.*

8. Add the contents of one Chromium 2 Reagent Powder Pillow. Cap the cell and invert repeatedly to mix. Remove the cap.

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater*

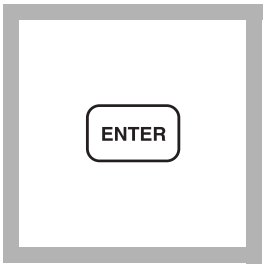
** Procedure is equivalent to Standard Method 3500-Cr D for wastewater.

9. Add the contents of one Acid Reagent Powder Pillow. Cap the cell and invert repeatedly to mix. Remove the cap.

10. Add the contents of one ChromaVer 3 Chromium Reagent Powder Pillow. Cap the cell and invert repeatedly to mix.

Note: *A purple color will form if chromium is present.*

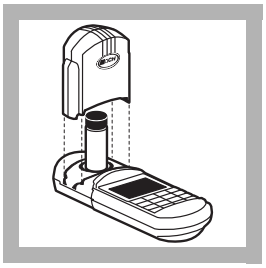
Note: *ChromaVer 3 is white to tan in color. Replace brown or green powder. Undissolved powder does not affect accuracy.*



11. The display will show: **05:00 TIMER 2**

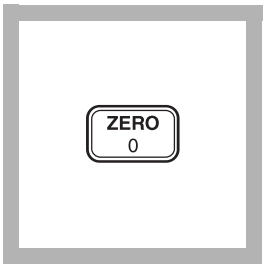
Press: **ENTER**

A five-minute reaction period will begin.



12. After the timer beeps, fill another sample cell with 25 mL of sample (the blank). Place it into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For turbid samples, treat the blank as a sample, adding all reagents except the ChromaVer 3.*

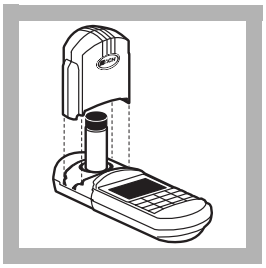


13. Press: **ZERO**

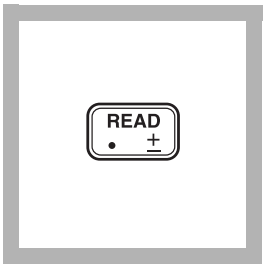
The cursor will move to the right, then the display will show:

0.00 mg/L Cr

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



14. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



15. Press: **READ**

The cursor will move to the right, then the result in mg/L total chromium (Cr) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-washed glass or plastic containers. To preserve samples, adjust the pH to 2 or lower with nitric acid (about 2 mL per liter). Store preserved samples at room temperature up to six months. Adjust the pH to about 4 with 5.0 N Sodium Hydroxide before analysis. Correct the test results for volume additions (see *Section 1*).

Accuracy Check

Standard Additions Method

a) Fill three sample cells with 25 mL of sample.

b) Snap the top off a Trivalent Chromium Standard Ampule, 12.5 mg/L as Cr^{3+}.

c) Use the TenSette pipet to add 0.1, 0.2, and 0.3 mL of standard to the three sample cells. Cap and invert repeatedly to mix .

d) Analyze each sample as described above. The chromium concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur see *Standard Additions* (*Section 1*).

Standard Solution Method

Prepare a 0.5 mg/L trivalent chromium standard by diluting 1.00 mL of Trivalent Chromium Standard Solution, 50 mg/L as Cr^{3+}, to 100 mL with deionized water. Mix thoroughly. Prepare this solution daily. Perform the chromium procedure as described above. The mg/L Cr reading should be 0.5 mg/L.

Method Performance

Precision

In a single laboratory using a standard solution of 0.4 mg/L trivalent chromium and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.004 mg/L chromium.

Estimated Detection Limit

The estimated detection limit for program 15 is 0.01 mg/L Cr. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Suggested Treatment
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section 1*.
Large amounts of organic material	May inhibit complete oxidation of trivalent chromium. If high levels of organic material are present, see *Digestion* in *Section 2* for instruction on sample digestion. Perform the analysis as described on the digested sample.

Summary of Method

Trivalent chromium in the sample is oxidized to the hexavalent form by hypobromite ion under alkaline conditions. The sample is acidified. The total chromium content is determined by the 1,5-diphenylcarbohydrazide method. Determine trivalent chromium by subtracting the results of a separate hexavalent chromium test from the results of the total chromium test.

CHROMIUM, TOTAL, continued

REQUIRED REAGENTS

	Cat. No.
Total Chromium Reagent Set (100 Tests)	22425-00
Includes: (1) 2126-99, (1) 12066-99, (1) 2043-99, (1) 2044-99	

Description	Quantity Required Per Test	Unit	Cat. No.
Acid Reagent Powder Pillows	1 pillow	100/pkg	2126-99
ChromaVer 3 Chromium Reagent Powder Pillows	1 pillow	100/pkg	12066-99
Chromium 1 Reagent Powder Pillows	1 pillow	100/pkg	2043-99
Chromium 2 Reagent Powder Pillows	1 pillow	100/pkg	2044-99

REQUIRED APPARATUS

Hot plate, 4" diameter, 120 V	1	each	12067-01
OR			
Hot plate, 4" diameter, 240 V	1	each	12067-02
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06
Water bath and rack	1	each	1955-55

OPTIONAL REAGENTS

Chromium, trivalent, Standard Solution, 50 mg/L Cr^{3+}		100 mL	14151-42
Chromium, trivalent, Standard Solution, PourRite ampule, 12.5 mg/L Cr^{3+}, 10 mL		16/pkg	14257-10
Nitric Acid, ACS		500 mL	152-49
Nitric Acid Solution 1:1		500 mL	2540-49
Sodium Hydroxide Standard Solution 5.0 N		50 mL* DB	2450-26
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Cylinder, graduated, polypropylene, 25 mL		each	1081-40
Finger Cots		2/pkg	14647-02
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
pH Meter, sens*ion 1*, with electrode		each	51700-10
Pipet, serological, 2 mL		each	532-36
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Pipet Filler, safety bulb		each	14651-00
Ampule Breaker, 10-mL		each	21968-00

For Technical Assistance, Price and Ordering

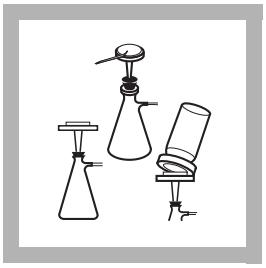
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes.

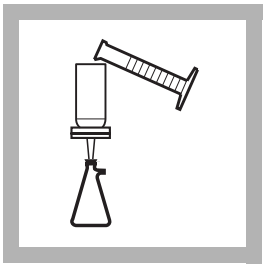
COLOR, TRUE AND APPARENT (0 to 500 units)

APHA Platinum-Cobalt Standard Method* For water, wastewater and seawater

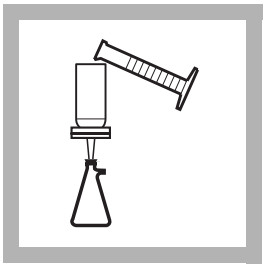


1. Assemble the filtering apparatus (membrane filter, filter holder, filter flask, and aspirator).

Note: *To test for apparent color, do not filter; begin at Step 4 and skip Step 7.*



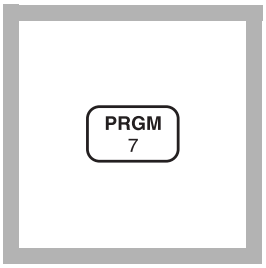
2. Rinse the filter by pouring about 50 mL of deionized water through the filter. Discard the rinse water.



3. Pour another 50 mL of deionized water through the filter. Keep this for Step 4.

4. Fill a sample cell (the blank) with 25 mL of filtered deionized water. Discard the excess.

Note: *For apparent color use unfiltered deionized water.*

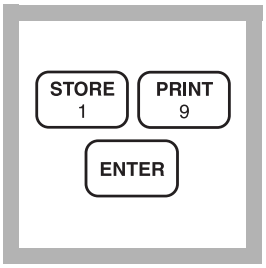


5. Enter the stored program number for APHA color.

Press: **PRGM**

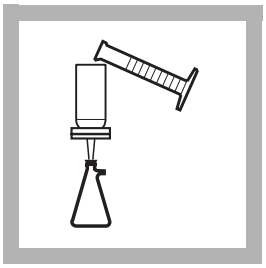
The display will show:

PRGM ?

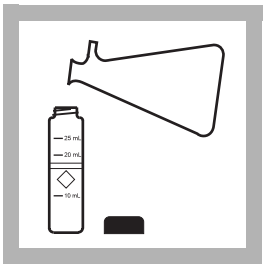


6. Press: **19 ENTER**

The display will show **PtCo** and the **ZERO** icon**.**



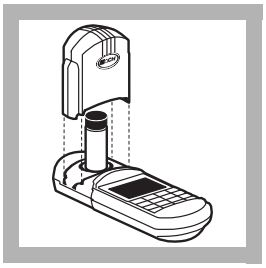
7. Pour about 50 mL of sample through the filter.



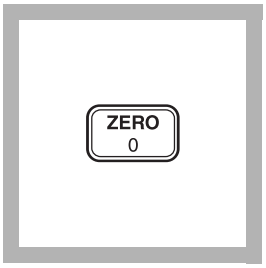
8. Fill a second sample cell (the prepared sample) with 25 mL of the filtered sample.

* Adapted from *Standard Methods for the Examination of Water and Wastewater*

COLOR, TRUE AND APPARENT, continued



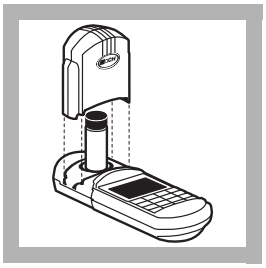
9. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



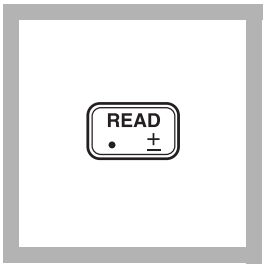
10. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L Pt Co



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in Platinum-Cobalt color units (Pt-Co) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze the sample as soon as possible after collection for best results. If prompt analysis is impossible, fill bottles completely and cap tightly. Avoid excessive agitation or prolonged contact with air. Samples can be stored for 48 hours by cooling to 4 °C (39 °F). Warm to room temperature before running the test.

Accuracy Check

Standard Solution Method

A 500 Platinum-Cobalt Units Color Standard solution is available for checking test accuracy. A 250 Platinum-Cobalt Units Standard can be made by pipetting 50.0 mL of the 500 Platinum-Cobalt Units Standard into a 100-mL volumetric flask and diluting to volume with deionized water.

Method Performance

Precision

In a single laboratory, using a standard solution of 250 Pt-Co color units and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±10 Pt-Co color units. For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit

The estimated detection limit for program 19 is 25 Pt-Co color units. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

Color may be expressed as “apparent” or “true” color. The apparent color includes color from dissolved materials plus that from suspended matter. By filtering or centrifuging out the suspended materials, the true color can be determined. The procedure describes true color analysis. If apparent color is desired, it can be determined by measuring an unfiltered water sample. The stored program is used for both forms of color.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Units	Cat. No.
Water, deionized	50 mL	4 L	272-56

REQUIRED APPARATUS

Aspirator, vacuum	1	each	2131-00
Filter Holder, 47 mm, 300 mL graduated	1	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	1	100/pkg	13530-00
Flask, filtering, 500 mL	1	each	546-49
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06
Stopper, No. 7, one hole	1	6/pkg	2119-07

OPTIONAL REAGENTS

Color Standard Solution, 500 platinum-cobalt units		1 L	1414-53

OPTIONAL APPARATUS

Cylinder, graduated, 50-mL, glass		each	508-41
Flask, volumetric, Class A, 100 mL		each	14574-42
Pipet, volumetric, Class A, 50 mL		each	14515-41
Thermometer, –20 to 110 °C, non-mercury		each	26357-02

For Technical Assistance, Price and Ordering

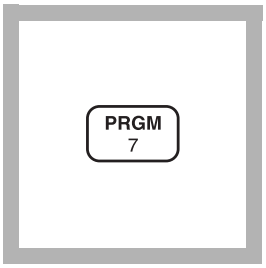
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

COPPER (0 to 5.00 mg/L)

For water, wastewater and seawater*

Bicinchoninate Method** (Powder Pillows or AccuVac Ampuls); USEPA approved for reporting wastewater analysis (digestion needed; See Section 2)*** Using Powder Pillows



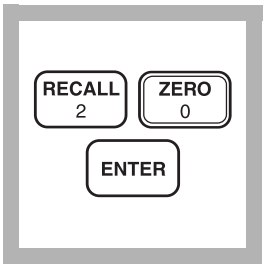
1. Enter the stored program number for bicinchoninate copper (Cu)- powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



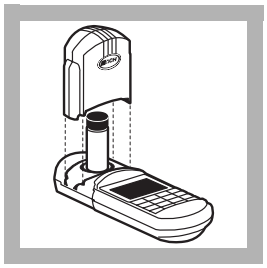
2. Press: **20 ENTER**

The display will show **mg/L, Cu** and the **ZERO** icon**.**

Note: *Determination of total copper needs a prior digestion (see Digestion in Section 2).*

3. Fill a sample cell with 10 mL of sample (the blank).

Note: *Adjust the pH of acid-preserved samples to 4-6 with 8 N KOH before analysis. Do not exceed pH 6 or copper may precipitate.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

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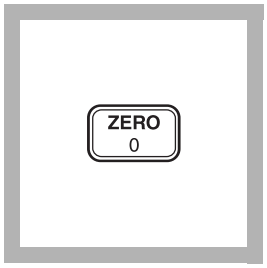
* Pretreatment required; see *Interferences (Using Powder Pillows)*

** Adapted from Nakano, S., *Yakugaku Zasshi*, 82 486-491 (1962) [*Chemical Abstracts*, 58 3390e (1963)]

*** Powder Pillows only: *Federal Register*, 45 (105) 36166 (May 29, 1980)



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

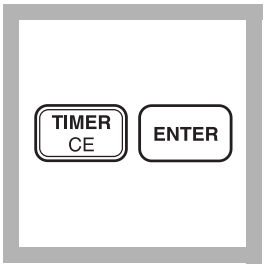
0.00 mg/L Cu

Note: *If Reagent Blank Correction is on, the display may flash "limit".*

6. Fill another sample cell with 10 mL of the sample.

7. Add the contents of one CuVer 1 Copper Reagent Powder Pillow to the sample cell (the prepared sample). Swirl the cell to mix.

Note: *If copper is present, A purple color will develop.*

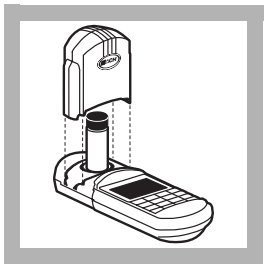


8. Press:

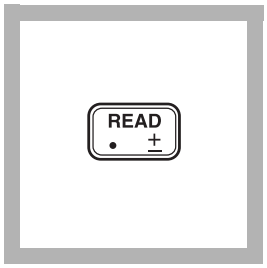
TIMER ENTER

A two-minute reaction period will begin.

Note: *Accuracy is not affected by undissolved powder.*



9. Within 30 minutes after the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

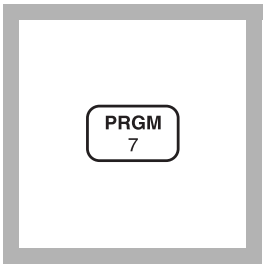


10. Press: **READ**

The cursor will move to the right, then the result in mg/L copper will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls **Method 8026**



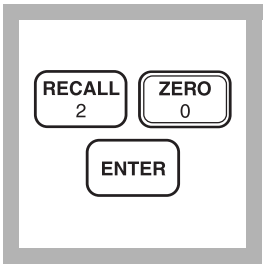
1. Enter the stored program number for bicinchoninate copper (Cu)- AccuVac ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



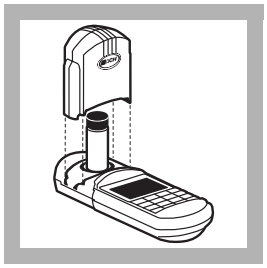
2. Press: **20 ENTER**

The display will show **mg/L, Cu** and the **ZERO** icon**.**

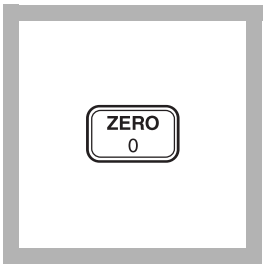
Note: *Determination of total copper needs a prior digestion (see Digestion in Section 2).*

Note: *Adjust the pH of stored samples before analysis.*

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

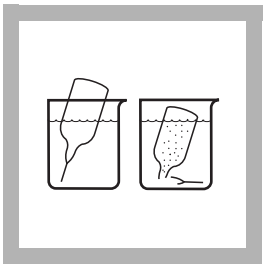


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

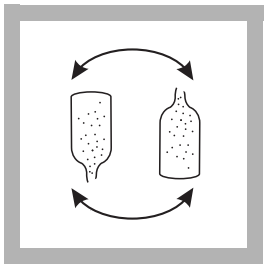
0.00 mg/L Cu

Note: *If Reagent Blank Correction is on, the display may flash "limit".*



6. Fill a CuVer 2 Copper Reagent AccuVac Ampul with sample.

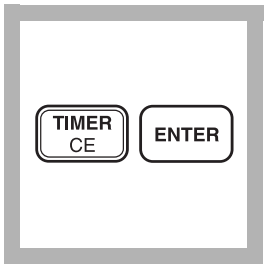
Note: *Keep the tip immersed while the ampul fills completely.*



7. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A purple color will form if copper is present.*

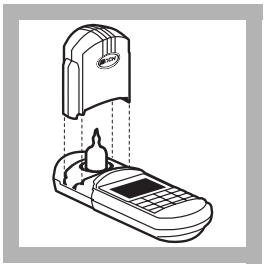
Note: *Accuracy is not affected by undissolved powder*



8. Press:

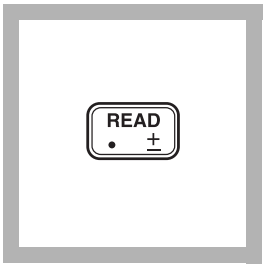
TIMER ENTER

A two-minute reaction period will begin.



9. After the timer beeps, place the AccuVac ampul in the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Step 10 must be completed within 30 minutes after the timer beeps.*



10. Press: **READ**

The cursor will move to the right, then the result in mg/L copper (Cu) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see in Section 1).*

Sampling and Storage

Collect samples in acid-cleaned glass or plastic containers. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Store preserved samples up to six months at room temperature. Before analysis, adjust the pH to 4 to 6 with 8 N potassium hydroxide. Do not exceed pH 6, as copper may precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1* for more information. If only dissolved copper is to be determined, filter the sample before acid addition using the labware listed under *Optional Apparatus*.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Copper Voluette Ampule Standard, 75 mg/L
as Cu.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to the mixing cylinders. Stopper and mix thoroughly.

d) For analysis with AccuVac Ampuls, transfer the solutions to dry, clean 50-mL beakers to fill the ampules. For analysis with powder pillows, transfer only 10 mL of the solution to 10-mL sample cells.

e) Analyze each sample as described in the procedure. The copper concentration should increase about 0.3 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Prepare a 1.00 mg/L copper standard by pipetting 1.00 mL of Copper Standard Solution, 100 mg/L as Cu, into 100-mL volumetric flask. Dilute to volume with deionized water and mix well. Prepare this solution daily. Using this solution as the sample, perform the copper procedure as described above.

Method Performance

Precision

In a single laboratory, using a standard solution of 2.25 mg/L Cu

and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.02 mg/L Cu.

In a single laboratory, using a standard solution of 2.25 mg/L Cu and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.02 mg/L Cu.

Estimated Detection Limit (EDL)
The EDL for program 20 (Powder Pillows and AccuVac Ampuls) is 0.02 mg/L Cu. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substances and Suggested Treatments for Powder Pillows

Interfering Substance	Interference Level and Treatment
Acidity	If the sample is extremely acidic (pH 2 or less) a precipitate may form. Add 8 N Potassium Hydroxide Standard Solution drop-wise while swirling to dissolve the turbidity. Continue with Step 3.
Aluminum, Al^{3+}	Follow the powder pillow procedure above, but substitute a CuVer 2 Copper Reagent Powder Pillow for the CuVer 1 Pillow used in Step 4. Results obtained will include total dissolved copper (free and complexed).
Cyanide, CN^-	Prevents full color development. Add 0.2 mL of formaldehyde to the 10-mL sample. Wait 4 minutes before taking the reading. Multiply the test results by 1.02 to correct for sample dilution by the formaldehyde.
Hardness	Follow the powder pillow procedure above, but substitute a CuVer 2 Copper Reagent Powder Pillow for the CuVer 1 Pillow used in Step 4. Results obtained will include total dissolved copper (free and complexed).
Iron, Fe^{3+}	Follow the powder pillow procedure above, but substitute a CuVer 2 Copper Reagent Powder Pillow for the CuVer 1 Pillow used in Step 4. Results obtained will include total dissolved copper (free and complexed).
Silver, Ag^+	If a turbidity remains and the precipitate turns black, silver interference is likely. Add 10 drops of saturated Potassium Chloride Solution to 75 mL of sample, followed by filtering through a fine or highly retentive filter. Use the filtered sample in the procedure.

To differentiate free copper from that complexed to EDTA or

other complexing agents, use a Free Copper Reagent Powder Pillow in place of the CuVer 1 pillow in Step 4. Results in Step 10 will be free copper only. Add a Hydrosulfite Reagent Powder Pillow to the same sample and
re-read the result. This result will include the total dissolved copper (free and complexed).

Interfering Substances and Suggested Treatments for AccuVac Ampuls

Interfering Substance	Interference Level and Treatment
Acidity	If the sample is extremely acidic (pH 2 or less) a precipitate may form. Add 8 N Potassium Hydroxide Standard Solution drop-wise until sample pH is above 4. Continue with Step 3.
Aluminum, Al^{3+}	Reagents accommodate high levels.
Cyanide, CN^-	Prevents full color development. Add 1.0 mL of formaldehyde to a 50-mL sample. Wait 4 minutes before taking the reading. Multiply the test results by 1.02 to correct for sample dilution by the formaldehyde.
Hardness	Reagents accommodate high levels
Iron, Fe^{3+}	Reagents accommodate high levels
Silver, Ag^+	If a turbidity remains and the precipitate turns black, silver interference is likely. Add 10 drops of saturated Potassium Chloride Solution to 75 mL of sample, followed by filtering through a fine or highly retentive filter. Use the filtered sample in the procedure.

Unlike CuVer 1 Reagent, CuVer 2 Reagent reacts directly with copper which is complexed by chelants such as EDTA. If free copper is to be determined separately from complexed copper, see the Powder Pillow Interference section above.

Summary of Method

Copper in the sample reacts with a salt of bicinchoninic acid contained in CuVer 1 or 2 Copper Reagent to form a purple colored complex in proportion to the copper concentration. This method includes procedures for both powder pillow and AccuVac reagents.

COPPER, continued

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
CuVer 1 Copper Reagent Powder Pillows	1 pillow	100/pkg	21058-69
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (Using AccuVac Ampuls)

CuVer 2 Copper Reagent AccuVac Ampuls	1 ampul	25/pkg	25040-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Copper Standard Solution, 100 mg/L	100 mL	128-42
Copper Standard Solution, Voluette Ampule, 75 mg/L Cu, 10 mL	16/pkg	14247-10
CuVer 2 Reagent Powder Pillows	100/pkg	21882-99
Formaldehyde, 37%, ACS	100 mL* MDB	2059-32
Free Copper Reagent Powder Pillows	100/pkg	21186-69
Hydrochloric Acid Solution, 6.0 N	500 mL	884-49
Hydrosulfite Reagent Powder Pillows	100/pkg	21188-69
Metals Drinking Water Standard, LR for Cu, Fe, Mn	500 mL	28337-49
Metals Drinking Water Standard, HR for Cu, Fe, Mn	500 mL	28336-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Potassium Chloride Solution, saturated	100 mL	765-42
Potassium Hydroxide Standard Solution, 8.0 N	100 mL* MDB	282-32H
Sodium Hydroxide Standard Solution, 5.0 N	100 mL* MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Cylinder, graduated, polypropylene, 25 mL	each	1081-40
Cylinder, graduated, 100 mL	each	508-42
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Filter Pump	each	2131-00
Flask, volumetric, 100 mL, Class A	each	14547-42
Funnel, polypropylene, 65 mm	each	1083-67
Hot Plate, 4" diameter, 120 V	each	12067-01
Hot Plate, 4" diameter, 240 V	each	12067-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, sens***ion 1***, with electrode	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01

* Contact Hach for larger sizes.

COPPER, continued

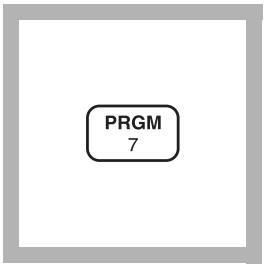
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

Porphyrin Method*

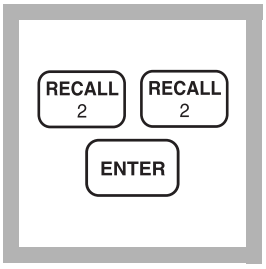


1. Enter the stored program number for copper (Cu), porphyrin method.

Press: **PRGM**

The display will show:

PRGM ?



2. Press: **22 ENTER**

The display will show **µg/L, Cu** and the **ZERO** icon**.**

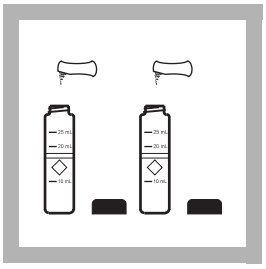
Note: *Total copper determination needs a prior digestion; use either the Digesdahl or vigorous digestion (Section 2).*

3. Fill two sample cells with 10 mL of sample.

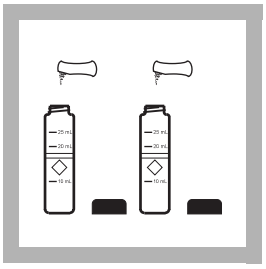
Note: *Wash all glassware with detergent. Rinse with tap water. Rinse again with Nitric Acid Solution, 1:1. Rinse a third time with copper-free, deionized water.*

4. Add the contents of one Copper Masking Reagent Powder Pillow to one of the sample cells (the blank). Swirl to dissolve.

Note: *The other sample cell is the prepared sample.*

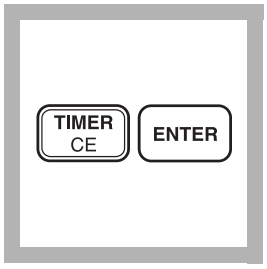


5. Add the contents of one Porphyrin 1 Reagent Powder Pillow to each sample cell. Swirl to dissolve the powder.



6. Add the contents of one Porphyrin 2 Reagent Powder Pillow to each sample cell. Swirl to dissolve the powder.

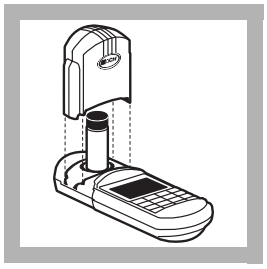
Note: *The yellow color will turn blue momentarily. If any copper is present, the yellow color will return.*



7. Press:

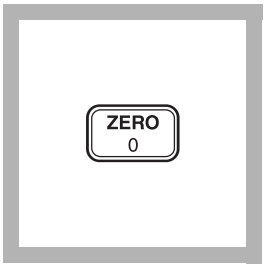
TIMER ENTER

A three-minute reaction period will begin.



8. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

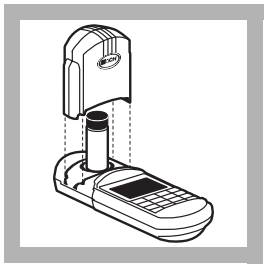
* Adapted from Ishii and Koh, *Bunseki Kagaku,* 28 473 (1979)



9. Press: **ZERO**

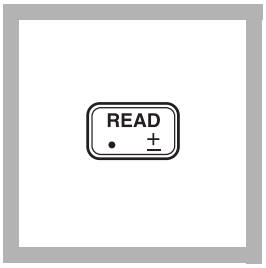
The cursor will move to the right, then the display will show:

0.0 µg/L Cu



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *If samples with high levels of metal are analyzed, a slight metallic deposit or yellow buildup may appear on the sample cell wall. Remove by rinsing with nitric acid. Dilute a fresh sample and repeat the test. Multiply the result by the dilution factor; see Section 1.*



11. Press: **READ** .

The cursor will move to the right, then the result in µg/L copper (Cu) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in acid-washed plastic bottles. To preserve, adjust the pH to 2 or less with nitric acid (about 5 mL per liter). Store preserved samples up to six months at room temperature.

Before testing, adjust the pH of the sample to between 2 and 6. If the sample is too acidic, adjust the pH with 5.0 N Sodium Hydroxide Standard Solution. Correct test results for volume additions; see *Correction for Volume Additions* in *Section 1* for more information.

Accuracy Check

Standard Additions Method

a) Fill six (3 pairs) 25-mL graduated mixing cylinders with 25 mL of sample. Properly mark each pair of cylinders as

"sample"
and "blank".

b) Using a TenSette Pipet, add 0.1 mL of Copper Standard Solution, 10.0 mg/L Cu, to two of the cylinders. Add 0.2 mL of standard to two more of the cylinders. Add 0.3 mL of standard to the other two cylinders, making a total of six samples (2 for each volume of standard).

c) Analyze the samples as described above. The copper concentration reading should increase by 40 µg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

To assure the accuracy of the test, prepare a 100 µg/L copper standard:

a) Pipet 1.00 mL of Copper Standard Solution, 10.0 mg/L Cu, into a 100-mL volumetric flask.

b) Dilute to volume with copper-free, reagent-grade water.

c) Use this standard in place of the sample in the procedure. The reading should be 100 µg/L Cu.

d) Prepare this solution daily.

Method Performance

Precision

In a single laboratory, using a standard solution of 100 µg/L copper and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±3.4 µg/L copper.

Estimated Detection Limit

The estimated detection limit for program 22 is 5.4 µg/L Cu. For more information on the estimated detection limit, see *Section 1*.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Substance	Concentration	Substance	Concentration
Aluminum	60 mg/L	Magnesium	10,000 mg/L
Cadmium	10 mg/L	Manganese	140 mg/L
Calcium	15,000 mg/L	Mercury	3 mg/L
Chloride	90,000 mg/L	Molybdenum	11 mg/L
Chromium (Cr^{6+})	110 mg/L	Nickel	60 mg/L
Cobalt	100 mg/L	Potassium	60,000 mg/L
Fluoride	30,000 mg/L	Sodium	90,000 mg/L
Iron (Fe^{2+})	6 mg/L	Zinc	9 mg/L
Lead	3 mg/L		

Chelating agents, such as EDTA, interfere at all levels unless either the Digesdahl or vigorous digestion (*Section 2*) is performed.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment: see pH Interferences in *Section 1*.

Summary of Method

The porphyrin method is very sensitive to trace amounts of free copper. Due to the sensitivity of the method, a masking agent is used to prepare a “blank” for each sample. The method is free from most interferences and does not require any sample extraction or preconcentration. Interferences from other metals are eliminated by the copper masking reagent. The porphyrin indicator forms an intense, yellow-colored complex proportional to any free copper present in the sample. Total copper may be determined if a digestion is performed prior to analysis.

COPPER, continued

REQUIRED REAGENTS

	Cat. No.
Copper Reagent Set, 10-mL samples (100 tests) Includes: (1) 26034-49, (2) 26035-49, (2) 26036-49	26033-00

Description	Quantity Required Per Test	Unit	Cat. No.
Copper Masking Reagent Powder Pillows	1 pillow	100/pkg	26034-49
Porphyrin 1 Reagent Powder Pillows	2 pillows	100/pkg	26035-49
Porphyrin 2 Reagent Powder Pillows	2 pillows	100/pkg	26036-49

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/ caps	2	6/pkg	24019-06

OPTIONAL REAGENTS

Copper Standard Solution, 10 mg/L Cu		100 mL	128-42
Hydrochloric Acid Solution, 1:1 (6 N)		500 mL	884-49
Nitric Acid, ACS		500 mL	152-49
Nitric Acid Solution, 1:1		500 mL	2540-49
Sodium Hydroxide Standard Solution, 5 N		1 L	2450-53
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Beaker, 100 mL		each	500-42H
Cylinder, mixing, graduated, 25 mL		each	20886-40
Flask, volumetric, Class A, 100 mL		each	14574-42
Hot Plate, 7 x 7 inches, 120 V		each	23441-00
Hot Plate, 7 x 7 inches, 240 V		each	23441-02
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable, with electrode		each	51700-10
Pipet, Mohr, 5 mL		each	20934-37
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01		50/pkg	21856-96
Pipet Tips, for 19700-01		1000/pkg	21856-28
Pipet, volumetric, 1.0 mL, Class A		each	14515-35
Pipet Filler, safety bulb		each	14651-00
Watch Glass, Pyrex®, 100 mL		each	578-70

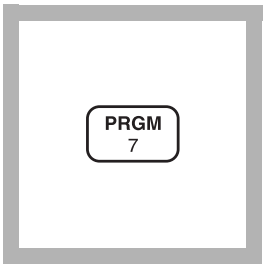
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

CYANIDE (0 to 0.240 mg/L)

Pyridine-Pyrazalone Method*



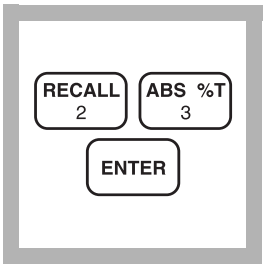
1. Enter the stored program number for cyanide (CN).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



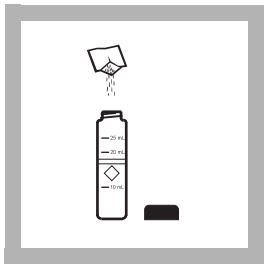
2. Press: **23 ENTER**

The display will show **mg/L, CN** and the **ZERO** icon**.**

Note: *Adjust the pH of stored samples before analysis.*

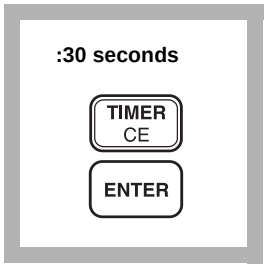
3. Fill a sample cell with 10-mL of sample.

Note: *Samples at less than 23 °C require a longer reaction time and samples at greater than 25 °C give low test results. Sample temperature must be 23-25 °C.*



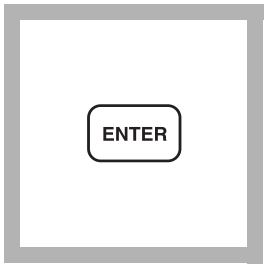
4. Add the contents of one CyaniVer 3 Cyanide Reagent Powder Pillow. Cap the sample cell.

* Adapted from Epstein, Joseph, *Anal. Chem*. 19 (4), 272 (1947)



5. Press: **TIMER ENTER**

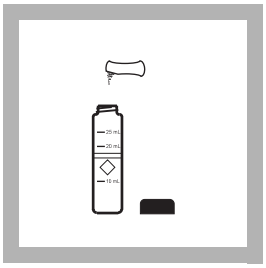
A 30-second reaction period will begin. Shake the sample cell for the 30 seconds.



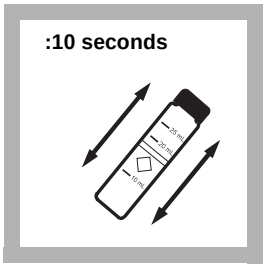
6. After the first timer beeps, the display will show: **0:30 TIMER 2**

Press **ENTER.**

A 30-second reaction period will begin. Let the sample cell sit undisturbed for this 30-second period.



7. After the timer beeps, add the contents of one CyaniVer 4 Cyanide Reagent Powder Pillow. Cap the sample cell.

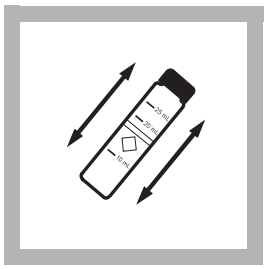


8. Shake the sample cell for ten seconds. Immediately proceed with Step 9.

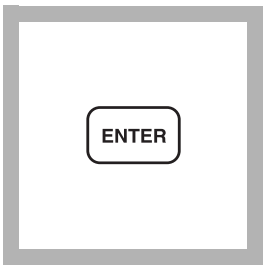
Note: *Delaying the addition of the CyaniVer 5 Cyanide Reagent Powder for more than 30 seconds after the addition of the CyaniVer 4 Cyanide Reagent Powder will give lower test results.*

Note: *Accuracy is not affected by undissolved CyaniVer 4 Cyanide Reagent Powder.*

9. Add the contents of one CyaniVer 5 Cyanide Reagent Powder Pillow. Cap the cell.



10. Shake vigorously to completely dissolve the CyaniVer 5 Cyanide Reagent Powder (the prepared sample).

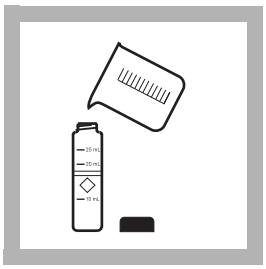


11. The display will show: **30:00 Timer 3**

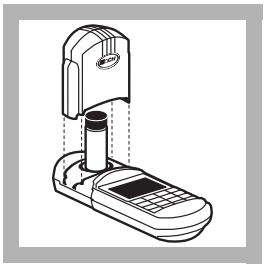
Press: **ENTER**

A 30-minute reaction period will begin.

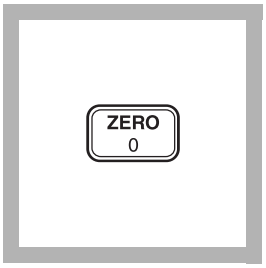
Note: *If cyanide is present, a pink color will develop which then turns blue after a few minutes.*



12. Fill another 10-mL sample cell (the blank) with 10 mL of sample.



13. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

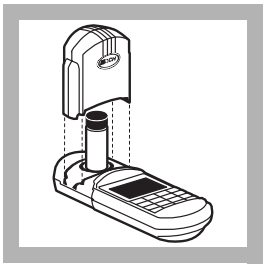


14. Press: **ZERO**

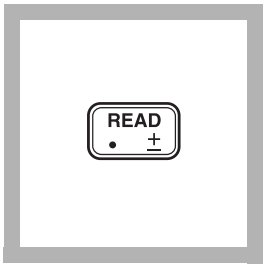
The cursor will move to the right, then the display will show:

0.000 mg/L CN

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



15. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



16. Press: **READ**

The cursor will move to the right, then the result in mg/L cyanide (CN) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in glass or plastic bottles and analyze as soon as possible.

The presence of oxidizing agents, sulfides and fatty acids can cause cyanide loss during sample storage. Samples containing these substances must be pretreated as described in the following procedures before preservation with sodium hydroxide. If the sample contains sulfide and is not pretreated, it must be analyzed within 24 hours.

Preserve the sample by adding 4.0 mL of 5.0 N Sodium Hydroxide Standard Solution to each liter (or quart) of sample, using a glass serological pipet and pipet filler. Check the sample pH. Four mL of sodium hydroxide are usually enough to raise the pH of most water and wastewater samples to 12. Add more 5.0 N sodium hydroxide if necessary. Store the samples at 4 °C (39 °F) or less. Samples preserved in this manner can be stored for 14 days.

Before testing, samples preserved with 5.0 N sodium hydroxide or samples that are highly alkaline due to chlorination treatment processes or distillation procedures should be adjusted to

approximately pH 7 with
2.5 N Hydrochloric Acid Standard Solution. If significant amounts of preservative are used, correct for the volume added; see *Correction for Volume Additions* in *Section 1* for more information.

Oxidizing Agents
Oxidizing agents such as chlorine decompose cyanides during storage. To test for their presence and eliminate their effect, pretreat the sample
as follows:

a) Take a 25-mL portion of the sample and add one drop of m-Nitrophenol Indicator Solution, 10 g/L. Swirl to mix.

b) Add 2.5 N Hydrochloric Acid Standard Solution drop-wise until the color changes from yellow to colorless. Swirl the sample thoroughly after the addition of each drop.

c) Add two drops of Potassium Iodide Solution, 30 g/L, and two drops of Starch Indicator Solution, to the sample. Swirl to mix. The solution will turn blue if oxidizing agents are present.

d) If Step c suggests the presence of oxidizing agents, add two level 1-g measuring spoonfuls of ascorbic acid per liter of sample.

e) Withdraw a 25-mL portion of sample treated with ascorbic acid and repeat Steps a to c. If the sample turns blue, repeat Steps d and e.

f) If the 25-mL sample remains colorless, adjust the remaining sample to pH 12 for storage with 5 N Sodium Hydroxide Standard Solution (usually 4 mL/L).

g) Perform the procedure given under Interferences, Reducing Agents, to eliminate the effect of excess ascorbic acid, before following the cyanide procedure.

Sulfides
Sulfides quickly convert cyanide to thiocyanate (SCN). To test for the presence of sulfide and eliminate its effect, pretreat the sample as follows:

a) Place a drop of sample on a disc of hydrogen sulfide test paper that has been wetted with pH 4 Buffer Solution.

b) If the test paper darkens, add a 1-g measuring spoon of lead acetate to the sample. Repeat Step a. (Purchase lead acetate from a local supplier.)

c) If the test paper continues to turn dark, keep adding lead acetate until the sample tests negative for sulfide.

d) Filter the black lead sulfide precipitate using the apparatus listed under Optional Apparatus. Preserve the sample for storage with 5 N Sodium Hydroxide Standard Solution or neutralize to a pH of 7 for analysis.

Fatty Acids

Caution—perform this operation in a hood as quickly as possible.

When distilled, fatty acids will pass over with cyanide and form soaps under the alkaline conditions of the absorber. If the presence of fatty acid is suspected, do not preserve samples with sodium hydroxide until the following pretreatment is performed. The effect of fatty acids can be minimized as follows:

a) Acidify 500 mL of sample to pH 6 or 7 with Acetic Acid Solution. (Prepare a 1:10 dilution of Acetate Acid concentration in water.)

b) Pour the sample into a 1000-mL separatory funnel and add 50 mL of hexane.

c) Stopper the funnel and shake for one minute. Allow the layers to separate.

d) Drain off the sample (lower) layer into a 600-mL beaker. If the sample is to be stored, add 5 N Sodium Hydroxide Standard Solution to raise the pH to above 12.

Accuracy Check

Standard Solution Method

Caution—Cyanides and their solutions, and the hydrogen cyanide liberated by acids, are very poisonous. Both the solutions and the gas can be absorbed through the skin.

Prepare a 100 mg/L cyanide stock solution weekly by dissolving

0.2503 grams of potassium cyanide in deionized water and diluting to 1000 mL.

Immediately before use, prepare a 0.10 mg/L cyanide working solution by diluting 1.00 mL of the 100 mg/L stock solution to 1000 mL using deionized water. Use this prepared standard in place of sample in Step 3. Results should be 0.10 mg/L CN^-.

Method Performance

Precision
In a single laboratory, using a standard solution of 0.19 mg/L CN^- and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.017 mg/L CN^-.

Estimated Detection Limit (EDL)
The estimated detection limit for program 23 is 0.008 mg/L CN. For more information on the estimated detection limit, see *Section 1*.

Interferences

Turbidity
Large amounts of turbidity will interfere and cause high readings. If the water sample is highly turbid, it should first be filtered before use in Steps 3 and 12. Filter using the labware listed under Optional Apparatus. The test results should then be recorded as soluble cyanide.

Oxidizing and Reducing Agents
Large amounts of chlorine in the sample will cause a milky white precipitate after the addition of the CyaniVer 5 Reagent. If chlorine or other oxidizing agents are known to be present, or if reducing agents (such as sulfide or sulfur dioxide) are known to be present, use adequate ventilation and pretreat the sample before testing as follows:

Oxidizing Agents

a) Adjust a 25-mL portion of the alkaline sample to between pH 7 and 9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops of acid added.

b) Add two drops of Potassium Iodide Solution and two drops of Starch Indicator Solution to the sample. Swirl to mix. The sample will turn blue if oxidizing agents are present.

c) Add Sodium Arsenite Solution drop-wise until the sample turns colorless. Swirl the sample thoroughly after each drop. Count the number of drops.

d) Take another 25-mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a.

e) Subtract one drop from the amount of Sodium Arsenite Solution added in Step c. Add this amount to the sample and mix thoroughly.

f) Using 10 mL of this sample, continue with Step 3 of the cyanide procedure.

Reducing Agents

a) Adjust a 25-mL portion of the alkaline sample to between pH 7 and 9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops added.

b) Add four drops of Potassium Iodide Solution and four drops of Starch Indicator Solution to the sample. Swirl to mix. The sample should be colorless.

c) Add Bromine Water drop-wise until a blue color appears. Count the number of drops, and swirl the sample after the addition of each drop.

d) Take another 25 mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a.

e) Add the total number of drops of Bromine Water counted in Step c to the sample and mix thoroughly.

f) Using 10 mL of this sample, continue with Step 3 of the cyanide procedure.

Metals

Nickel or cobalt in concentrations up to 1 mg/L do not interfere. Eliminate the interference from up to 20 mg/L copper and 5 mg/L

iron by adding the contents of one HexaVer Chelating Reagent Powder Pillow to the sample and then mixing before adding the CyaniVer 3 Cyanide Reagent Powder Pillow in Step 4. Prepare a reagent blank of deionized water and reagents to zero the instrument in Step 13.

Acid Distillation

For USEPA reporting purposes, samples must be distilled.

All samples should be treated by acid distillation except when experience has shown that there is no difference in results obtained with or without distillation. With most compounds, a one-hour reflux is adequate.

If thiocyanate is present in the original sample, a distillation step is absolutely necessary as thiocyanate causes a positive interference. High concentrations of thiocyanate can yield a substantial quantity of sulfide in the distillate. The “rotten egg” smell of hydrogen sulfide will accompany the distillate when sulfide is present. The sulfide must be removed from the distillate prior to testing.

If cyanide is not present, the amount of thiocyanate can be determined. The sample is not distilled and the final reading is multiplied by 2.2. The result is mg/L thiocyanate.

The distillate can be tested and treated for sulfide after the last step of the distillation procedure by using the following lead acetate
treatment procedure.

a) Place a drop of the distillate (already diluted to 250 mL) on a disc of hydrogen sulfide test paper that has been wetted with pH 4.0 Buffer Solution.

b) If the test paper darkens, add 2.5 N Hydrochloric Acid Standard Solution drop-wise to the distillate until a neutral pH is obtained.

c) Add a 1-g measuring spoon of lead acetate to the distillate and mix. Repeat Step a.

d) If the test paper continues to turn dark, keep adding lead acetate until the distillate tests negative for sulfide.

e) Filter the black lead sulfide precipitate through filter paper

and funnel. This sample should now be neutralized to pH 7 and analyzed for cyanide without delay.

Distillation Procedures

A detailed procedure for the distillation of cyanide samples is included with the Hach Distillation Apparatus. Three detailed procedures, Free Cyanides, Cyanides Amenable to Chlorination, and Total Cyanides, are included with the four- and ten-position Midi-Dist Distillation System. See the Optional Apparatus listing.

Summary of Method

The pyridine-pyrazolone method gives an intense blue color with free cyanide. A sample distillation is required to determine cyanide from transition and heavy metal cyanide complexes.

REQUIRED REAGENTS

	Cat. No.
Cyanide Reagent Set (100 Tests), 10 mL samples	24302-00
Includes: (1) 21068-69, (1) 21069-69, (1) 21070-69	

Description	Quantity Required Per Test	Unit	Cat. No.
CyaniVer 3 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	21068-69
CyaniVer 4 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	21069-69
CyaniVer 5 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	21070-69

REQUIRED APPARATUS

Sample Cell, 10-20-25, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Acetic Acid, Glacial	500 mL	100-49
Ascorbic Acid	100 g	6138-26
Bromine Water	25 mL	2211-20
Buffer Solution, pH 4.0	500 mL	12223-49
Hexanes, ACS	500 mL	14478-49
HexaVer Chelating Reagent Powder Pillows	100/pkg	243-99
Hydrochloric Acid Standard Solution, 2.5 N	100 mL MDB	1418-32
Magnesium Chloride Solution	1 L	14762-53
m-Nitrophenol Indicator	100 mL MDB	2476-32
Potassium Iodide Solution, 30 g/L	100 mL MDB	343-32
Sodium Arsenite Solution, APHA	100 mL MDB	1047-32

CYANIDE, continued

Potassium Cyanide, ACS	28 g	767-14
Sodium Hydroxide Standard Solution, 0.25 N	1 L	14763-53
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Starch Indicator Solution	10 mL MDB	349-32
Sulfuric Acid Standard Solution, 19.2 N	500 mL	2038-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Beaker, glass, 600 mL	each	500-52
Bottle, wash, 500 mL	each	620-11
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, 250 mL	each	508-46
Distillation Apparatus, cyanide accessories	each	22658-00
Distillation Apparatus, general purpose accessories	each	22653-00
Distillation Apparatus Heater and Support Apparatus, 115 Vac, 60 Hz	each	22744-00
Distillation Apparatus Heater and Support Apparatus, 230 Vac, 50 Hz	each	22744-02
Dropper, plastic	each	6080-00
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, Class A, 1000 mL	each	14574-53
Flask, volumetric, Class A, 250 mL	each	14574-46
Funnel, poly, 65 mm	each	1083-67
Funnel, separatory, 500 mL	each	520-49
Hydrogen Sulfide Test Papers	100/pkg	25377-33
pH Meter, *sens**ion**™1*, portable	each	51700-10
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00
Scoop, double ended	each	12257-00
Spoon, measuring, 1.0 g	each	510-00
Support Ring, 4 inch	each	580-01
Support Stand	each	563-00
Thermometer, –20 to 110 °C, non-mercury	each	26357-02

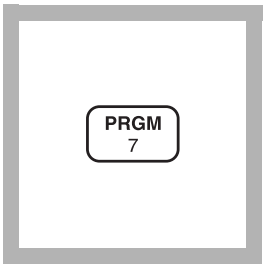
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

CYANURIC ACID (7 to 55 mg/L)

Turbidimetric Method



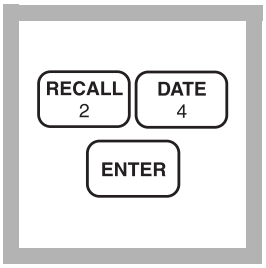
1. Enter the stored program number for cyanuric acid.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

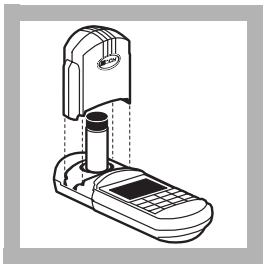


2. Press: **24 ENTER**

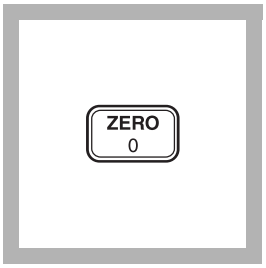
The display will show **mg/L, CYACD** and the **ZERO** icon.

3. Fill a sample cell with 25 mL of sample (the blank).

Note: *Filtering is required for highly turbid samples.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

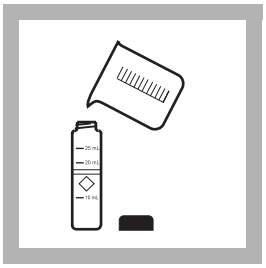


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

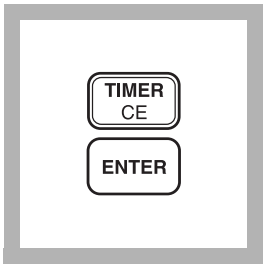
0 mg/L CYACD

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



6. Fill another cell with 25 mL of sample.

7. Add the contents of one Cyanuric Acid 2 Reagent Powder Pillow (the prepared sample). Swirl to mix.

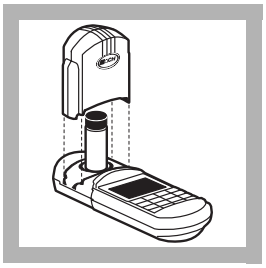


8. Press **TIMER ENTER**

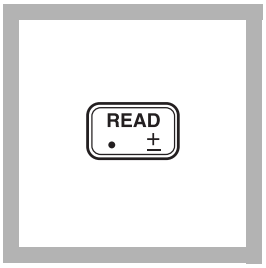
A three-minute reaction period will begin.

Note: *A white turbidity will form if cyanuric acid is present.*

Note: *Accuracy is not affected by undissolved powder.*



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L cyanuric acid will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *Clean sample cells with soap, water and a brush soon after each test to prevent a white film from forming.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Samples must be analyzed within 24 hours.

Accuracy Check

Standard Solution Method

a) Dissolve 1.000 gram of cyanuric acid in 1000 mL of deionized water to make a 1000 mg/L solution. It takes several hours for the cyanuric acid to dissolve. This solution is stable for several weeks.

b) Dilute 2.00 mL of the 1000 mg/L solution to 100 mL with deionized water to make a 20 mg/L solution. Prepare fresh daily.

c) Testing the 20 mg/L solution should give test results of about 20 mg/L cyanuric acid.

Method Performance

Precision

In a single laboratory, using a standard solution of 25.0 mg/L cyanuric acid and two lots of reagent with the instrument, a single

operator obtained a standard deviation of ±1.2 mg/L cyanuric acid.

Estimated Detection Limit
The estimated detection limit for program 24 is 7.0 mg/L cyanuric acid. For more information on the estimated detection limit, see *Section 1*.

Interferences

Turbidity will interfere. Filter turbid samples before running the test.

Summary of Method

The test for cyanuric acid uses the turbidimetric method. Cyanuric Acid 2 Reagent precipitates any cyanuric acid present and holds it in suspension. The amount of turbidity caused by the suspended particles is directly proportional to the amount of cyanuric acid present. Due to the nature of the precipitation reaction, low levels of cyanuric acid (less than 7 mg/L) are not detected by this method.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Cyanuric Acid 2 Reagent Powder Pillow	1 pillow	50/pkg	2460-66
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Cyanuric Acid		25 g	7129-24
Water, deionized		4 L	272-56

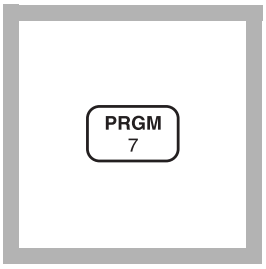
OPTIONAL APPARATUS

Balance, Acculab UI Series		each	26947-00
Filter Paper, folded 12.5 cm		100/pkg	1894-57
Flask, volumetric, Class A, 100 mL		each	14574-42
Flask, volumetric, Class A, 1000 mL		each	14574-53
Funnel, poly, 65 mm		each	1083-67
Pipet, Bulb		each	14651-00
Pipet, volumetric, Class A, 2.00 mL		each	14515-36

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

DEHA (0 to 500 µg/L)

Iron Reduction Method for Oxygen Scavengers*



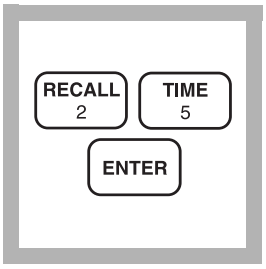
1. Enter the stored program number for diethylhydroxylamine (DEHA).

Press: **PRGM**

The display will show:

PRGM ?

Note: *To determine other oxygen scavengers, multiply the result by the appropriate factor. See* Other Oxygen Scavengers *following these steps.*



2. Press: **25 ENTER**

The display will show **µg/L, DEHA** and the **ZERO** icon**.**

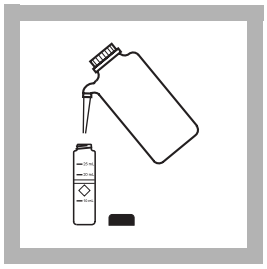
Note: *To prevent contamination from iron deposits, rinse sampling containers and sample cells with 1:1 Hydrochloric Acid Solution. Follow with several rinsings of deionized water.*

Note: *Samples must be analyzed immediately.*

3. Fill a sample cell with 25 mL of sample (the prepared sample).

Note: *The sample temperature should be 25 ±3°C (77 ±5 °F).*

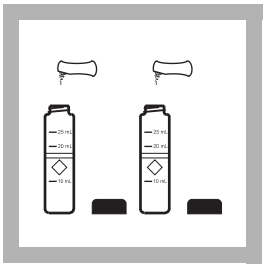
Note: *When testing for compounds that react quickly with oxygen at room temperature, stopper the cell containing the sample in Steps 5–11.*



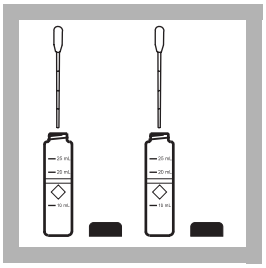
4. Fill a second sample cell with 25 mL of deionized water (the blank).

* Adapted from Ishii and Koh, *Buneseki Kagaku,* 28 473 (1979)

DEHA (N,N-DIETHYLHYDROXYLAMINE), continued

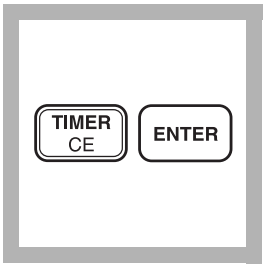


5. Add the contents of one DEHA Reagent 1 Powder Pillow to each sample cell. Cap. Swirl to mix.



6. Add exactly 0.5 mL of DEHA Reagent 2 Solution to each sample cell. Cap and swirl to mix. Place both sample cells in the dark.

Note: *A purple color will slowly develop if DEHA is present.*



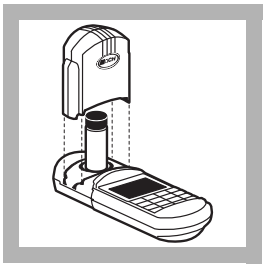
7. Immediately, press:

TIMER ENTER

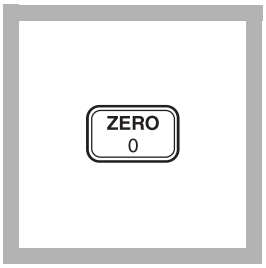
A 10-minute reaction period will begin. For hydroquinone, allow only a two-minute reaction period.

Note: *Both sample cells must remain in the dark for the entire reaction period.*

Note: *Temperature and reaction time affect results.*



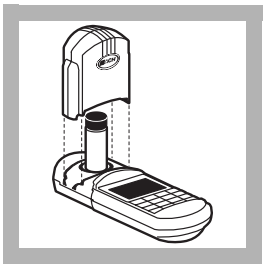
8. Immediately after the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



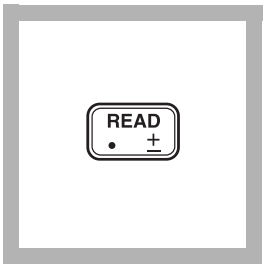
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 µg/L DEHA



10. Immediately place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in µg/L DEHA will be displayed.

Note: *If the display flashes "limit" it is due to high DEHA levels. Dilute a fresh sample with deoxygenated deionized water and repeat the test. Multiply the result by the dilution factor; see Section 1.*

Ferrous Iron Adjustment

Note: *Repeat the above procedure, but do not add DEHA Reagent 2 (Step 6) to determine the ferrous iron content in the sample. Then press SETUP, scroll to "BLANK" and press* **ENTER**. *The display will show; "BLANK?" Enter the blank value just read. Press* **ENTER** *to accept the value as the blank to be subtracted from each reading.*

DEHA (N,N-DIETHYLHYDROXYLAMINE), continued

Sampling and Storage

Most oxygen scavengers will react quickly with atmospheric oxygen. Collect samples in acid-rinsed plastic or glass containers, allowing the sample to overflow. Cap the container so there is no head space above the sample. Rinse each sample cell several times with sample, then carefully fill to the fill mark. Analyze the sample immediately.

Other Oxygen Scavengers

To determine other oxygen scavengers, perform the test as directed above, then multiply the DEHA result by the appropriate factor below:

Oxygen Scavenger	Factor
Erythorbic Acid (Iso-ascorbic acid)	3.5
Hydroquinone	2.5
Methylethylketoxime (MEKO)	4.1
Carbohydrazide	1.3

Method Performance

Precision

In a single laboratory, using a standard solution of 242 µg/L DEHA and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±6.2 µg/L DEHA.

Estimated Detection Limit

The estimated detection limit for program 25 is 9 µg/L DEHA. For more information on the estimated detection limit, see *Section 1*.

Interferences

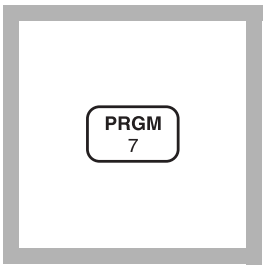
Substances which reduce ferric iron will interfere. Substances which complex iron strongly may also interfere. Light interferes with the color development. The following may also interfere when present in concentrations exceeding those listed below:

Borate (as $Na_2B_4O_7$)	500 mg/L	Molybdenum	80 mg/L
Cobalt	0.025 mg/L	Nickel	0.8 mg/L
Copper	8.0 mg/L	Phosphate	10 mg/L
Hardness (as $CaCO_3$)	1000 mg/L	Phosphonates	10 mg/L
Lignosulfonates	0.05 mg/L	Sulfate	1000 mg/L
Manganese	0.8 mg/L	Zinc	50 mg/L

FLUORIDE (0 to 2.00 mg/L F^-)

SPADNS Method* (Reagent Solution or AccuVac Ampuls)

Using SPADNS Reagent Solution

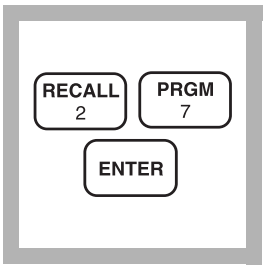


1. Enter the stored program number for fluoride (F) powder pillows.

Press: **PRGM**

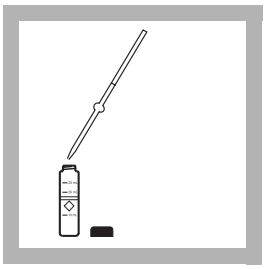
The display will show:

PRGM ?

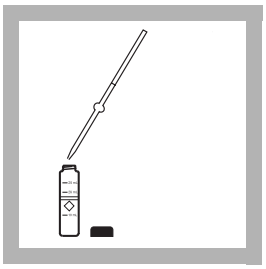


2. Press: **27 ENTER**

The display will show **mg/L, F** and the **ZERO** icon.

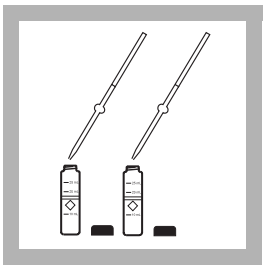


3. Pipet 10.0 mL of sample into a dry 10-mL sample cell (the prepared sample).



4. Measure 10.0 mL of deionized water into a second dry sample cell (the blank).

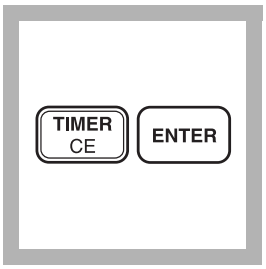
Note: *The sample and blank should be at the same temperature (±1 °C). Temperature adjustments may be made before or after reagent addition.*



5. Pipet 2.00 mL of SPADNS Reagent into each cell. Swirl to mix.

Note: *SPADNS Reagent is toxic and corrosive; use care while measuring. Use a pipet filler.*

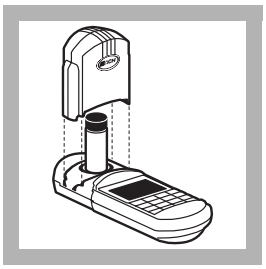
Note: *The SPADNS Reagent must be measured accurately.*



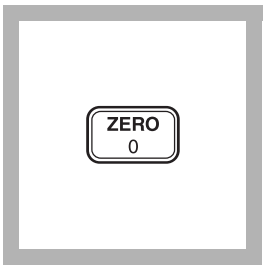
6. Press:

TIMER ENTER

A one minute reaction period will begin.



7. When the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



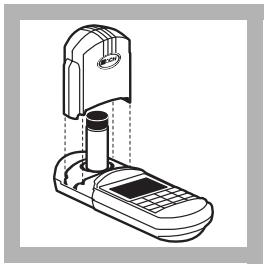
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

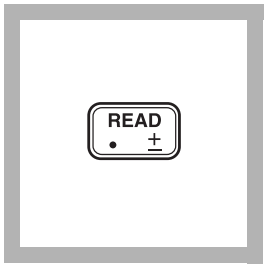
0.00 mg/L F

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater. The procedure for this instrument uses an alternate wavelength outside the accepted 550-580 nm range. The reagents used are the same as those in the USEPA accepted method.*



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L fluoride will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check following these steps.*

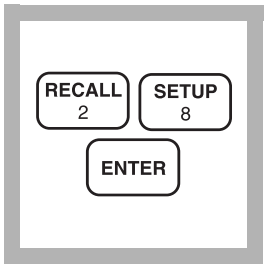
Using AccuVac Ampuls

1. Enter the stored program number for fluoride (F^-)- AccuVac Ampuls.

Press: **PRGM**

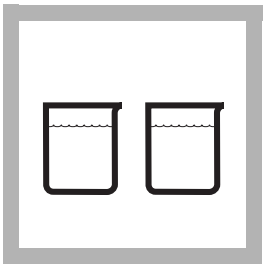
The display will show:

PRGM ?

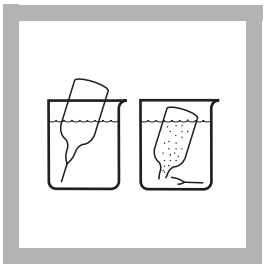


2. Press: **28 ENTER**

The display will show **mg/L, F** and the **ZERO** icon**.**

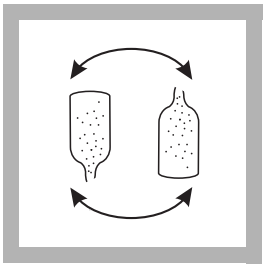


3. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second beaker.



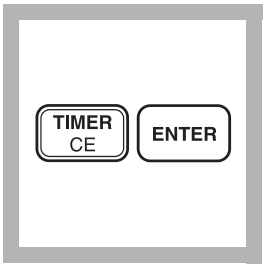
4. Fill a SPADNS Fluoride Reagent AccuVac Ampul with sample by breaking the tip on the bottom of the beaker. Fill a second AccuVac Ampul with deionized water (the blank).

Note: *Keep the tip immersed while the ampule fills completely.*



5. Quickly invert the ampules several times to mix. Wipe off any liquid or fingerprints.

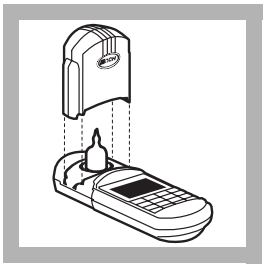
Note: *Do not place finger over the broken tip- the liquid will remain in the ampul.*



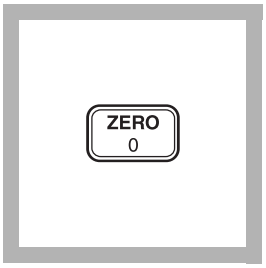
6. Press:

TIMER ENTER

A one-minute reaction period will begin.



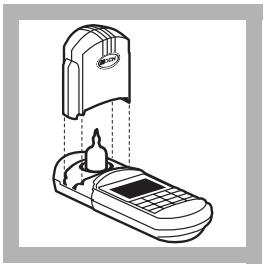
7. After the timer beeps place the blank into the cell holder. Tightly cover the ampule with the instrument cap.



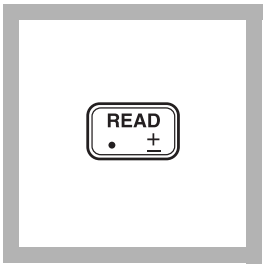
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.0 mg/L F



9. Place the AccuVac Ampul containing the sample into the instrument. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L fluoride will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check following these steps.*

Sampling and Storage

Collect samples in plastic bottles. Samples may be stored up to 28 days.

Accuracy Check

Standard Solution Method

A variety of standard solutions covering the entire range of the test are available from Hach. Use these in place of sample to verify technique. Minor variations between lots of reagent become measurable above
1.5 mg/L. While results in this region are usable for most purposes, better accuracy may be obtained by diluting a fresh sample 1:1 with deionized water and retesting. Multiply the result by 2.

Standard Adjust

To adjust the calibration curve using the reading obtained with a 1.80-mg/L Standard Solution, press **SETUP** and use the arrow keys to scroll to the "STD" setup option. Press **ENTER** to activate the option. Then enter **1.80** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Standard Curve Adjustment* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory, using standard solutions of 1.00 mg/L fluoride and two lots of SPADNS Reagent with the instrument, a single operator obtained standard deviations of ±0.035 mg/L fluoride.

In a single laboratory, using standard solutions of 1.00 mg/L fluoride and two lots of SPADNS AccuVac Reagent with the instrument, a single operator obtained standard deviations of ±0.040 mg/L fluoride.

Estimated Detection Limit (EDL)

The EDL for programs 27 and 28 is 0.05 mg/L F^-. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

This test is sensitive to small amounts of interference. Glassware

must be very clean. Repeating the test with the same glassware is recommended to ensure that results are accurate.

The following substances interfere to the extent shown:

Substance	Concentration	Error
Alkalinity (as $CaCO_3$)	5000 mg/L	-0.1 mg/L F^-
Aluminum	0.1 mg/L	-0.1 mg/L F^-
Chloride	7000 mg/L	+0.1 mg/L F^-
Iron, ferric	10 mg/L	-0.1 mg/L F^-
Phosphate, ortho	16 mg/L	+0.1 mg/L F^-
Sodium Hexametaphosphate	1.0 mg/L	+0.1 mg/L F^-
Sulfate	200 mg/L	+0.1 mg/L F^-

SPADNS Reagent contains enough arsenite to eliminate interference up to 5 mg/L chlorine. For higher chlorine levels, add one drop of Sodium Arsenite Solution to 25 mL of sample for each 2 mg/L of chlorine.

To check for interferences from aluminum, read the concentration one minute after reagent addition, then again after 15 minutes. An appreciable increase in concentration suggests aluminum interference. Waiting two hours before making the final reading will eliminate the effect of up to 3.0 mg/L aluminum.

Most interferences can be eliminated by distilling the sample from an acid solution as described below:

a) Set up the distillation apparatus for the general purpose distillation. See the Hach Distillation Apparatus Manual. Turn on the water and make certain it is flowing through the condenser.

b) Measure 100 mL of sample into the distillation flask. Add a magnetic stirring bar and turn on the heater power switch.
Turn the stir control to 5.

c) Cautiously measure 150 mL of StillVer Distillation Solution (2:1 Sulfuric Acid) into the flask. If high levels of chloride are present, add 5 mg silver sulfate for each mg/L chloride present.

d) Turn the heat control to setting 10, with the thermometer in place. The yellow pilot lamp shows when the heater is on.

e) When the temperature reaches 180 °C (about one hour), turn the still off.

f) Dilute the collected distillate to 100 mL, if necessary. Analyze the distillate by the above method.

Summary of Method

The SPADNS Method for fluoride determination involves the reaction of fluoride with a red zirconium-dye solution. The fluoride combines with part of the zirconium to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration. Seawater and wastewater samples require distillation. See Optional Apparatus for Distillation Apparatus listing.

Pollution Prevention and Waste Management

SPADNS Reagent contains sodium arsenite. Final solutions will contain sodium arsenite (D004) in sufficient concentration to be regulated as hazardous waste for Federal RCRA. See *Section 3* for more information on disposal of these materials.

FLUORIDE, continued

REQUIRED REAGENTS (Using Solution)

Description	Quantity Required Per Test	Unit	Cat. No.
SPADNS Reagent for Fluoride	4 mL	500 mL	444-49
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS (Using Solution)

Pipet Filler safety bulb	1	each	14651-00
Pipet, volumetric, Class A, 10.00 mL	1	each	14515-38
Pipet, volumetric, Class A, 2.00 mL	1	each	14515-36
Sample Cell, 10-20-25 mL w/ cap	2	6/pkg	24019-06
Thermometer, –20 to 110°C, non-mercury	1	each	26357-02

REQUIRED REAGENTS (Using AccuVac Ampuls)

SPADNS Fluoride Reagent AccuVac Ampuls	2 ampuls	25/pkg	25060-25
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS (Using AccuVac Ampuls)

Beaker, 50 mL	2	each	500-41H

OPTIONAL REAGENTS

Drinking Water Inorganics Standard for F^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}	500 mL	28330-49
Fluoride Standard Solution, 0.2 mg/L F^-	500 mL	405-02
Fluoride Standard Solution, 0.5 mg/L F^-	500 mL	405-05
Fluoride Standard Solution, 0.8 mg/L F^-	500 mL	405-08
Fluoride Standard Solution, 1.0 mg/L F^-	1000 mL	291-53
Fluoride Standard Solution, 1.0 mg/L F^-	500 mL	291-49
Fluoride Standard Solution, 1.2 mg/L F^-	500 mL	405-12
Fluoride Standard Solution, 1.5 mg/L F^-	500 mL	405-15
Fluoride Standard Solution, 2.0 mg/L F^-	500 mL	405-20
Silver Sulfate, ACS	113 g	334-14
Sodium Arsenite Solution	100 mL MDB	1047-32
StillVer Distillation Solution	500 mL	446-49

FLUORIDE, continued

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Cylinder, graduated, 100 mL	each	508-42
Cylinder, graduated, 250 mL	each	508-46
Distillation Heater and Support Apparatus Set, 115 V, 50/60 Hz	each	22744-00
Distillation Heater and Support Apparatus Set, 230 V, 50/60 Hz	each	22744-02
Distillation Apparatus General Purpose Accessories	each	22653-00
pH Meter, *sens**ion***™*1,* portable, with electrode	each	51700-10
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg	21997-96
Stopper	6/pkg	1731-06

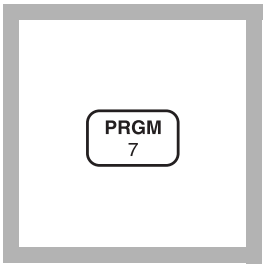
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

HARDNESS (0 to 4.00 mg/L Ca and Mg as $CaCO_3$) For water, wastewater, seawater

Calcium and Magnesium; Calmagite Colorimetric Method



1. Enter the stored program number for magnesium hardness (as $CaCO_3$).

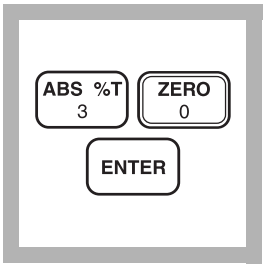
Press: **PRGM**

The display will show:

PRGM ?

Note: *Adjust the pH of stored samples before analysis.*

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



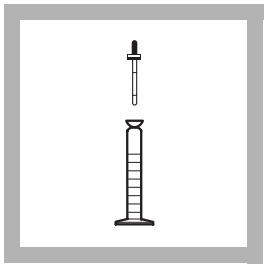
2. Press: **30 ENTER**

The display will show **mg/L, CaCO3** and the **ZERO** icon**.**

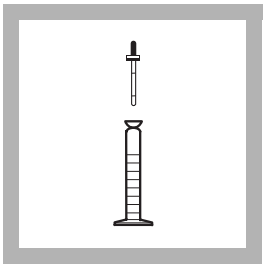
Note: *For alternate forms (Mg, $MgCO_3$), press the* **CONC** *key.*

3. Pour 100 mL of sample into a 100-mL graduated mixing cylinder.

Note: *The sample temperature should be 21-29 °C (70-84 °F).*

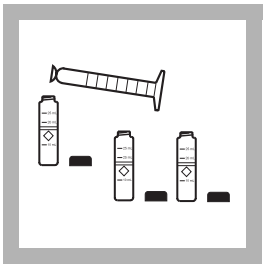


4. Add 1.0 mL of Calcium and Magnesium Indicator Solution using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.



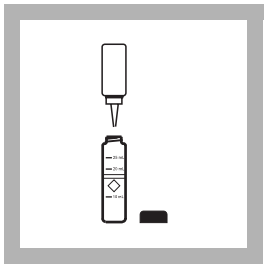
5. Add 1.0 mL of Alkali Solution for Calcium and Magnesium Test using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.

Note: *If the sample turns read after adding Alkali Solution, dilute sample 1:1 and repeat analysis.*

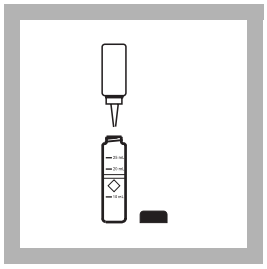


6. Pour 10 mL of the solution into each of three sample cells.

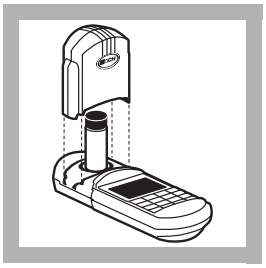
Note: *The test will detect any calcium or magnesium contamination in the mixing cylinder, measuring droppers or sample cells. To test cleanliness, repeat the test multiple times until you obtain consistent results.*



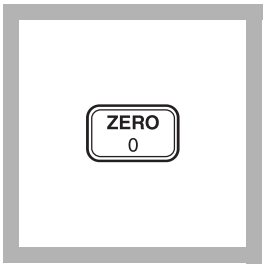
7. Add one drop of 1 M EDTA Solution to one cell (the blank). Swirl to mix.



8. Add one drop of EGTA Solution to another cell (the prepared sample). Swirl to mix.



9. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

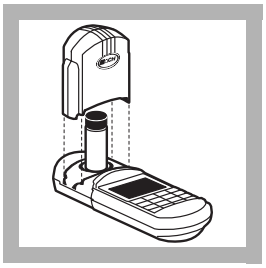


10. Press: **ZERO**

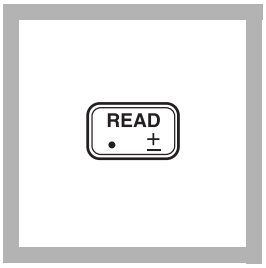
The cursor will move to the right, then the display will show:

0.00 mg/L CaCO3

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*

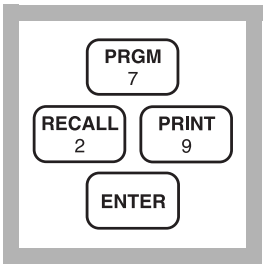


11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L magnesium hardness (as $CaCO_3$) will be displayed.



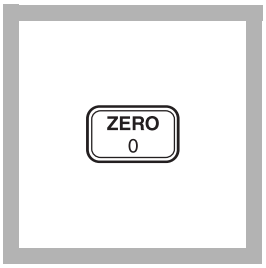
13. Without removing the cell, press:

PRGM 29 ENTER

The display will show:

PRGM ?

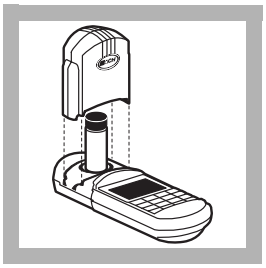
Note: *For alternate forms (Ca) press the* **CONC** *key.*



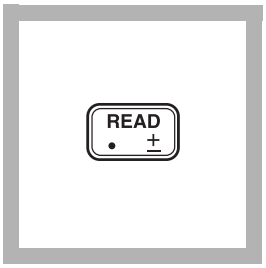
14. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L CaCO3



15. Place the third sample cell into the cell holder.



16. Press: **READ**

The cursor will move to the right, then the result in mg/L calcium hardness (as $CaCO_3$) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *mg/L total hardness = mg/L Ca as $CaCO_3$ + mg/L Mg as $CaCO_3$.*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months. Adjust the sample pH to

between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Correct the test results for volume additions; see *Correction for Volume Additions* in *Section 1* for more information.

Accuracy Check

Using a 2.00 mg/L (as $CaCO_3$) standard solution as sample, perform the hardness procedure described above. The results should be 2.00 mg/L calcium (as $CaCO_3$).

Method Performance

Precision

In a single laboratory using a standard solution of 2.00 mg/L Mg as $CaCO_3$ and 1.88 mg/L Ca as $CaCO_3$ with the instrument, a single operator obtained a standard deviation of ± 0.09 mg/L Mg as $CaCO_3$ and ± 0.08 mg/L Ca as $CaCO_3$.

Estimated Detection Limit

The estimated detection limit for program 30 is 0.13 mg/L magnesium hardness and 0.08 mg/L calcium hardness. For more information on the estimated detection limit, see *Section 1*.

Interferences

For the most accurate hardness test result, the test should be rerun on a diluted sample if the calcium is over 1.0 or the magnesium is over
0.25 mg/L as $CaCO_3$. No retesting is needed if either is below those respective concentrations.

The following cause a detectable error in test results.

Interfering Substance	Level at Which Substance Interferes
Cr^{3+}	0.25 mg/L
Cu^{2+}	0.75 mg/L
EDTA, chelated	0.2 mg/L as $CaCO_3$
Fe^{2+}	1.4 mg/L
Fe^{3+}	2.0 mg/L
Mn^{2+}	0.20 mg/L
Zn^{2+}	0.050 mg/L

Traces of EDTA or EGTA remaining in sample cells from previous tests will give erroneous results. Rinse cells thoroughly before use.

Summary of Method

The colorimetric method for measuring hardness supplements the conventional titrimetric method because it can measure very low levels of calcium and magnesium. Also some interfering metals (those listed above) in the titrimetric method are inconsequential in the colorimetric method when diluting the sample to bring it within the range of this test.

The indicator dye, calmagite, forms a purplish-blue color in a strongly alkaline solution and changes to red when it reacts with free calcium or magnesium. Calcium is chelated with EGTA to destroy any red color due to calcium and then the sample is chelated with EDTA to destroy the red color due to both calcium and magnesium. Measuring the red color in the different stages of chelation gives results as the calcium and magnesium hardness concentrations.

REQUIRED REAGENTS

	Cat. No.
Hardness Reagent Set (100 Tests)	23199-00
Includes: (1) 22417-32, (1) 22418-32, (1) 22419-26, (1) 22297-26	

Description	Quantity Required Per Test	Unit	Cat. No.
Alkali Solution for Calcium and Magnesium Test	1 mL	100 mL MDB	22417-32
Calcium and Magnesium Indicator Solution	1 mL	100 mL MDB	22418-32
EDTA Solution, 1 M	1 drop	50 mL	22419-26
EGTA Solution	1 drop	50 mL	22297-26

REQUIRED APPARATUS

Cylinder, 100-mL mixing	1	each	1896-42
Dropper, measuring, 0.5 and 1.0 mL	2	20/pkg	21247-20
Sample Cell, 10-20-25 mL, w/cap	3	6/pkg	24019-06

OPTIONAL REAGENTS

Calcium Standard Solution, 2.0 mg/L as $CaCO_3$	946 mL	20581-16
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Sodium Hydroxide Standard Solution 5.0 N	100 mL MDB	2450-32

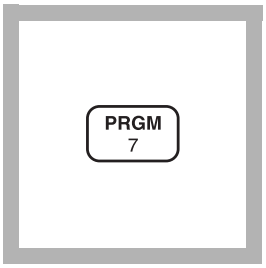
OPTIONAL APPARATUS

pH Meter, *sens**ion**™1*, portable, with electrode	each	51700-10
Thermometer, –20 to 110 °C	each	26357-02

HYDRAZINE (0 to 500 µg/L) For boiler water/feedwater, water and seawater

p-Dimethylaminobenzaldehyde Method*

Using Reagent Solution



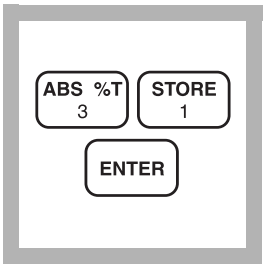
1. Enter the stored program number for hydrazine (N_2H_4).

Press: **PRGM**

The display will show:

PRGM ?

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



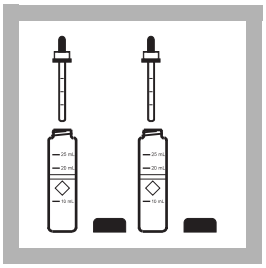
2. Press: **31 ENTER**

The display will show **µg/L, N2H4** and the **ZERO** icon**.**

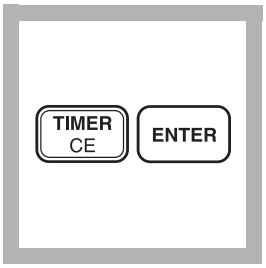
3. Pour 10.0 mL of deionized water into a sample cell (the blank) using a graduated cylinder.

4. Pour 10.0 mL of sample into a second sample cell (the sample) using a graduated cylinder.

Note: *The sample temperature should be 21 ± 4 °C (70 ± 7 °F).*



5. Add 0.5 mL of HydraVer 2 Hydrazine Reagent to each sample cell. Cap. Invert to mix.



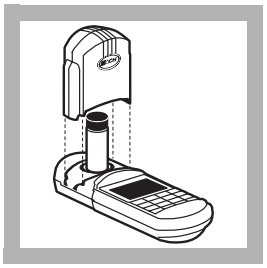
6. Press:

TIMER ENTER

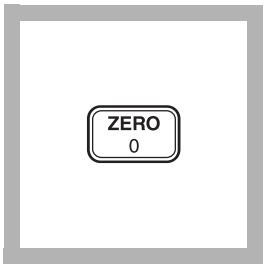
A 12-minute reaction period will begin.

Note: *Complete Steps 7-9 within 3 minutes.*

Note: *A yellow color will form if hydrazine is present. The blank will be a faint yellow color due to the HydraVer 2 reagent.*



7. Immediately after the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

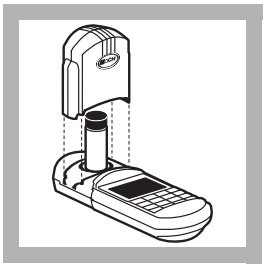


8. Press: **ZERO**

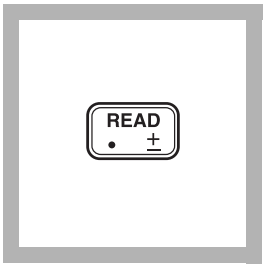
The cursor will move to the right, then the display will show:

0 µg/L N2H4

* Adapted from ASTM Manual of Industrial Water, D1385-78, 376 (1979)



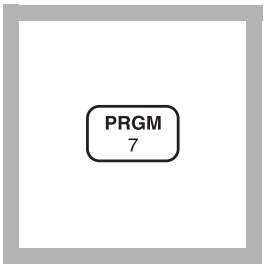
9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in µg/L hydrazine will be displayed.

Using AccuVac Ampuls



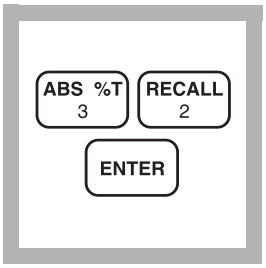
1. Enter the stored program number for hydrazine (N_2H_4)-AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

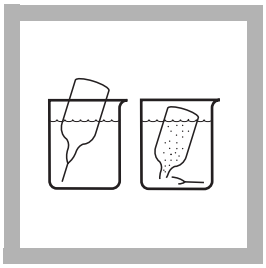
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*



2. Press: **32 ENTER**

The display will show **µg/L, N2H4** and the **ZERO** icon.

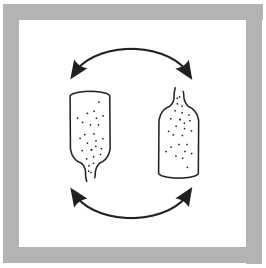
3. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second 50-mL beaker.



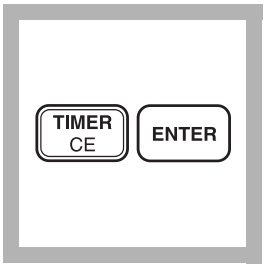
4. Fill a Hydrazine AccuVac Ampul with sample. Fill a second Hydrazine AccuVac Ampul with deionized water (the blank).

Note: *Keep the tip immersed while the ampul fills completely.*

Note: *The sample temperature should be 21 ± 4 °C (70 ± 7 °F).*



5. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.



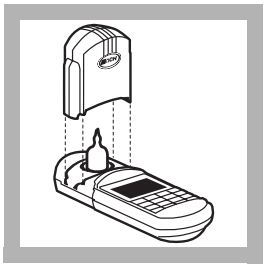
6. Press:

TIMER ENTER

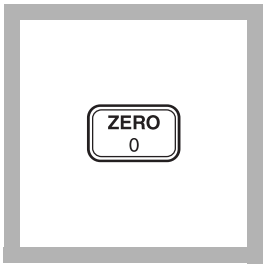
A 12-minute reaction period will begin.

Note: *Complete Steps 7-9 during this period.*

Note: *A yellow color will develop if hydrazine is present. The blank will be a faint yellow color due to the reagent.*



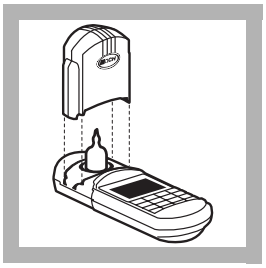
7. Insert the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



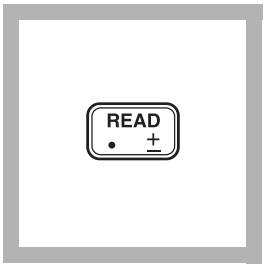
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 µg/L N2H4



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Immediately after the timer beeps, press **READ.**

The cursor will move to the right, then the result in µg/L hydrazine will be displayed.

Sampling and Storage

Collect samples in glass or plastic containers. Fill the containers completely and cap them tightly. Avoid excessive agitation or exposure to air. Samples must be analyzed immediately after collection and cannot be preserved for later analysis.

Accuracy Check

Standard Solution Method

To assure the accuracy of the test, prepare the following solutions:

a) Prepare a 25 mg/L hydrazine stock solution by dissolving 0.1016 g of hydrazine sulfate in 1000 mL of oxygen-free deionized water. Use Class A glassware. Prepare this stock solution daily.

b) Prepare a 100 µg/L hydrazine working solution by diluting 4.00 mL of the 25 mg/L stock solution to 1000 mL with deionized oxygen-free water. Prepare just before analysis.

c) Use the working solution in place of the sample in Step 4. The result should be 100 µg/L hydrazine.

Method Performance

Precision

In a single laboratory using a standard solution of 250 µg/L hydrazine (N_2H_4) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±9 µg/L hydrazine.

In a single laboratory using a standard solution of 250 µg/L hydrazine (N_2H_4) and two lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±3 µg/L hydrazine.

Estimated Detection Limit

The estimated detection limit for program 31 is 16 µg/L N_2H_4, and the estimated detection limit for program 32 is 10 µg/L N_2H_4. For more information on the estimated detection limit, see *Section 1*.

Interferences

For highly colored or turbid samples, prepare a blank by oxidizing the hydrazine in a portion of the sample. This can be accomplished with a
1:1 mixture of deionized water and household bleach. Add two drops of this mixture to 40 mL of sample contained in a graduated mixing cylinder and invert to mix. Use this solution in Step 3, in place of deionized water, to prepare the blank.

Ammonia has no effects up to 10 mg/L ammonia. At 20 mg/L, a positive interference occurs.

Morpholine does not interfere up to 10 mg/L.

HYDRAZINE, continued

Summary of Method

Hydrazine reacts with the p-dimethylaminobenzaldehyde from the HydraVer 2 Reagent to form a yellow color which is proportional to the hydrazine concentration.

REQUIRED REAGENTS (Using Reagent Solution)

Description	Quantity Required Per Test	Unit	Cat. No.
HydraVer 2 Hydrazine Reagent	1 mL	100 mL MDB	1790-32
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS (Using Reagent Solution)

Cylinder, graduated, 25 mL	1	each	508-40
Sample Cells, 10-, 20- and 25 mL, w/ caps	2	6/pkg	24019-06

REQUIRED REAGENTS (Using AccuVac Ampuls)

Hydrazine Reagent AccuVac Ampul	2	25/pkg	25240-25
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS (Using AccuVac Ampuls)

Beaker, 50 mL	2	each	500-41H

OPTIONAL REAGENTS

Hydrazine Sulfate, ACS		100 g	742-26

OPTIONAL APPARATUS

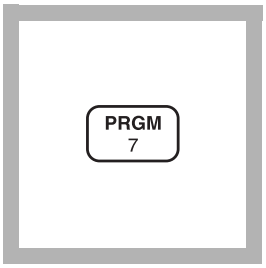
AccuVac Snapper Kit		each	24052-00
Balance, Analytical, 115 V, 0.1 mg		each	28014-01
Balance, Analytical, 220 V, 0.1 mg		each	28014-02
Cylinder, graduated, mixing, 25 mL		each	1896-40
Flask, volumetric, 100 mL, Class A		each	14574-42
Flask, volumetric, 1000 mL, Class A		each	14574-53
Pipet, serological, 1 mL		each	9190-02
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Pipet, volumetric, Class A, 4.00 mL		each	14515-04
Pipet Filler, safety bulb		each	14651-00
Thermometer, –20 to 110 °C, non-mercury		each	26357-02
Weighing Boat, 67/46 mm, 8.9 cm sq.		500/pkg	21790-00

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

IRON, FERROUS (0 to 3.00 mg/L)

1,10 Phenanthroline Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



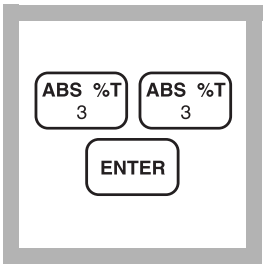
1. Enter the stored program number for Ferrous iron (Fe^{2+})-powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

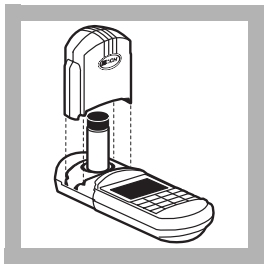
Note: *Analyze samples as soon as possible to prevent oxidation of ferrous iron to ferric iron, which is not determined.*



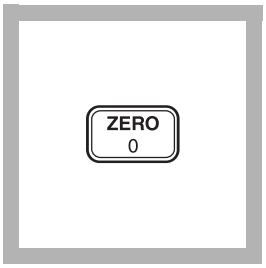
2. Press: **33 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon.

3. Fill a sample cell with 25 mL of sample (the blank).



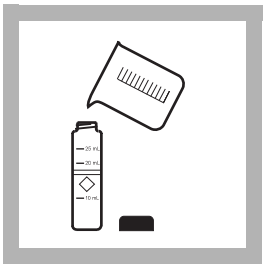
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

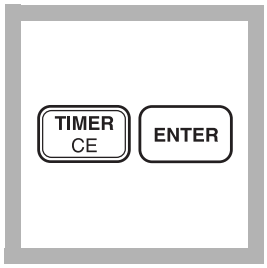
0.00 mg/L Fe



6. Fill another sample cell with 25 mL of sample.

7. Add the contents of one Ferrous Iron Reagent Powder Pillow to the sample cell (the prepared sample). Cap and invert to mix.

Note: *Undissolved powder does not affect accuracy.*



8. Press:

TIMER ENTER

A three-minute reaction period will begin.

Note: *An orange color will form if ferrous iron is present.*

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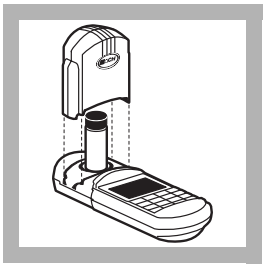
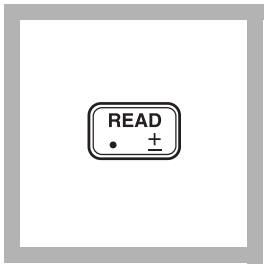
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

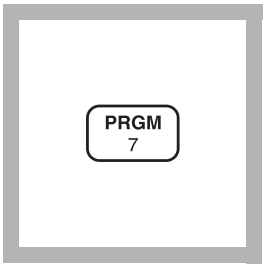


10. Press: **READ**

The cursor will move to the right, then the result in mg/L ferrous iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls



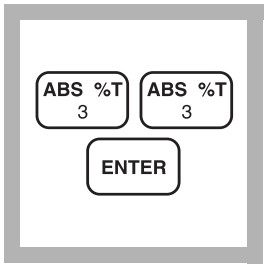
1. Enter the stored program number for ferrous iron (Fe^{2+}) AccuVac ampuls.

Press: **PRGM**

The display will show:

PRGM ?

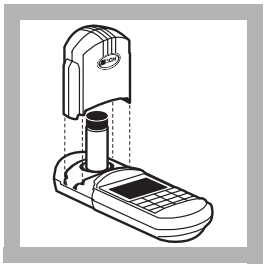
Note: *Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric, which is not determined.*



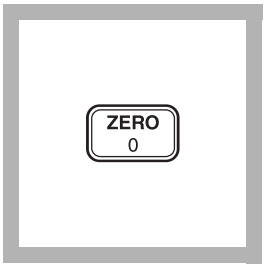
2. Press: **33 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



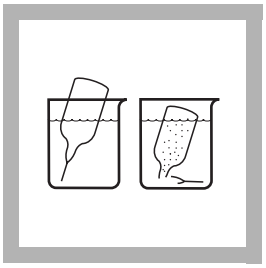
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

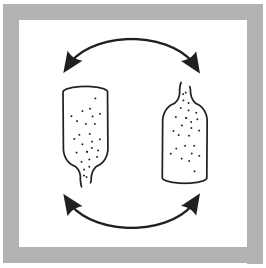
The cursor will move to the right, then the display will show:

0.00 mg/L Fe



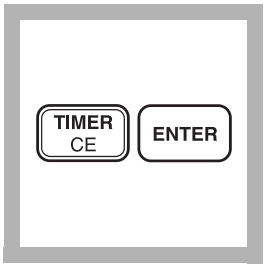
6. Fill a Ferrous Iron AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



7. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *Undissolved powder does not affect accuracy.*

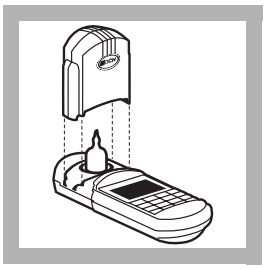


8. Press:

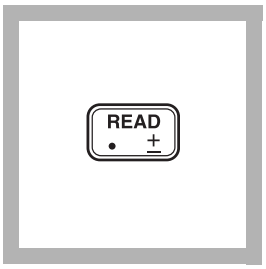
TIMER ENTER

A three-minute reaction period will begin.

Note: *An orange color will form if ferrous iron is present.*



9. Place the AccuVac ampul into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L ferrous iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Ferrous iron must be analyzed immediately and cannot be stored. Analyze samples as soon as possible to prevent oxidation of ferrous iron to ferric iron, which is not measured.

Accuracy Check

Standard Solution Method

Prepare a ferrous iron stock solution (100 mg/L Fe^{2+}) by dissolving 0.7022 grams of ferrous ammonium sulfate, hexahydrate, in deionized water. Dilute to 1 liter. Prepare immediately before use. Dilute 1.00 mL of this solution to 100 mL with deionized water to make a 1.00 mg/L standard solution. Prepare immediately before use.

Run the test using the 1.00 mg/L Fe^{2+} Standard Solution by following either the powder pillow or AccuVac procedure. Results should be between 0.90 mg/L and 1.10 mg/L Fe^{2+}.

Method Performance

Precision

In a single laboratory using an iron standard solution of 2.00 mg/L Fe^{2+} and two representative lots of powder pillow reagents with the instrument, a single operator obtained a standard deviation of ±0.017 mg/L Fe^{2+}.

In a single laboratory using a standard solution of 2.00 mg/L Fe^{2+} and two representative lots of AccuVac ampuls with the instrument, a single operator obtained a standard deviation of ±0.009 mg/L Fe^{2+}.

Estimated Detection Limit

The estimated detection limit for program 33 (powder pillows and AccuVac Ampuls) is 0.03 mg/L Fe. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

The 1,10-phenanthroline indicator in Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron (Fe^{3+}) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test.

REQUIRED REAGENTS & APPARATUS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Units	Cat. No.
Ferrous Iron Reagent Powder Pillows	1 pillow	100/pkg	1037-69
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (USING ACCUVAC AMPULS)

Ferrous Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25140-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Ferrous Ammonium Sulfate, hexahydrate, ACS		113 g	11256-14
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Balance, analytical, 115 V, 0.1 mg		each	28014-01
Balance, analytical, 230 V, 0.1 mg		each	28014-02
Clippers, for opening powder pillows		each	968-00
Flask, volumetric, 100 mL, Class A		each	14574-42
Flask, volumetric, 1000 mL, Class A		each	14574-53
Pipet, volumetric, Class A, 1.00 mL		each	14515-35
Pipet Filler, safety bulb		each	14651-00
Weighing Boat, 67/46 mm, 8.9 cm square		500/pkg	21790-00

For Technical Assistance, Price and Ordering

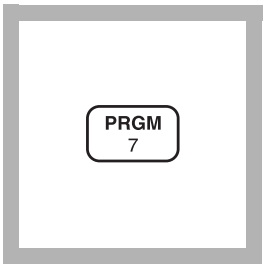
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

IRON, TOTAL (0 to 3.00 mg/L)

FerroVer Method (Powder Pillows or AccuVac Ampuls)

USEPA approved for reporting wastewater analysis (digestion is required; see Section 2*)



1. Enter the stored program number for iron (Fe) powder pillows.

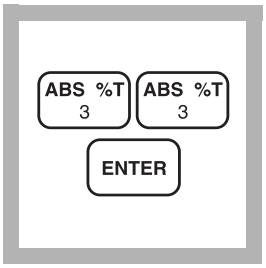
Press: **PRGM**

The display will show:

PRGM ?

Note: *Determination of total iron requires a digestion prior to analysis (see Section 2).*

Note: *Adjust pH of stored samples before analysis.*

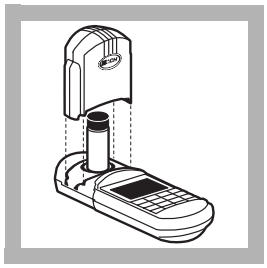


2. Press: **33 ENTER**

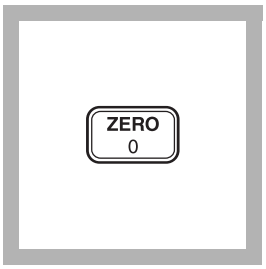
The display will show **mg/L, Fe** and the **ZERO** icon**.**

3. Fill a clean sample cell with 10 mL of sample (the blank).

Note: *For turbid samples, treat the blank with one 0.1-gram scoop of RoVer Rust Remover. Swirl to mix.*



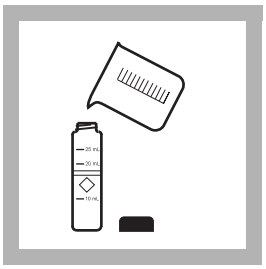
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

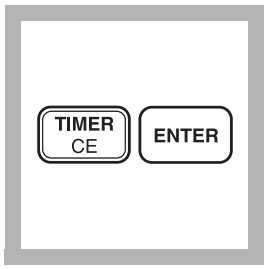
0.00 mg/L Fe



6. Fill another sample cell with 10 mL of sample.

7. Add the contents of one FerroVer Iron Reagent Powder Pillow to the sample cell (the prepared sample). Cap and invert to dissolve the reagent powder.

Note: *Accuracy is not affected by undissolved powder.*



8. Press:

TIMER ENTER

A three-minute reaction period will begin.

Note: *An orange color will form if iron is present.*

Note: *Samples containing visible rust should be allowed to react at least five minutes.*

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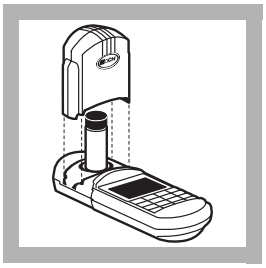
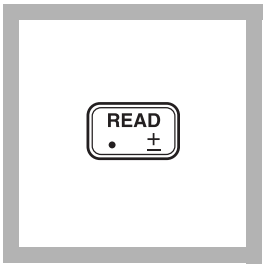
* *Federal Register*, 45 (126) 43459 (June 27, 1980). See also 40 CFR, part 136.3, Table IB.



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

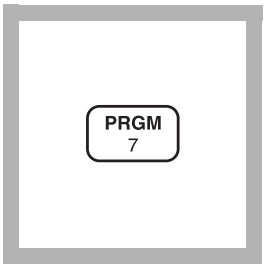


10. Press: **READ**

The cursor will move to the right, then the result in mg/L iron (Fe) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls



1. Enter the stored program number for iron (Fe), AccuVac ampuls.

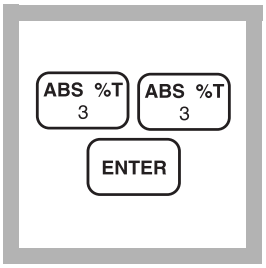
Press: **PRGM**

The display will show:

PRGM ?

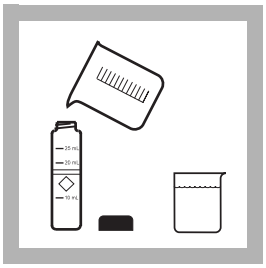
Note: *Adjust pH of stored samples before analysis.*

Note: *Determination of total iron requires a digestion prior to analysis (see Section 2).*



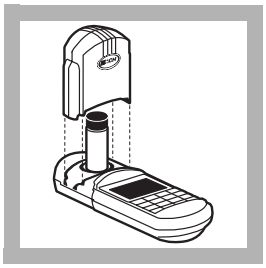
2. Press: **33 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon**.**

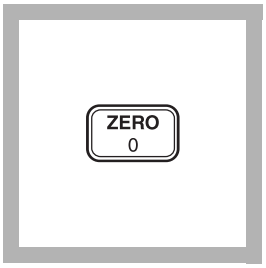


3. Fill a sample cell (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

Note: *For turbid samples, treat the blank with one 0.1 g scoop of RoVer Rust Remover. Swirl to mix.*



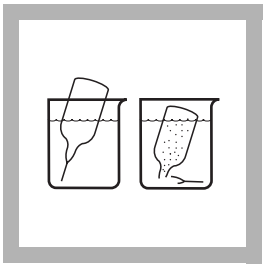
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

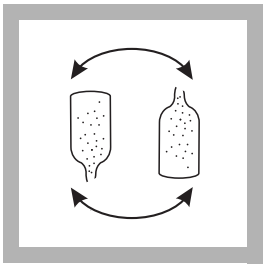
The cursor will move to the right, then the display will show:

0.00 mg/L Fe



6. Fill a FerroVer AccuVac Ampul with sample.

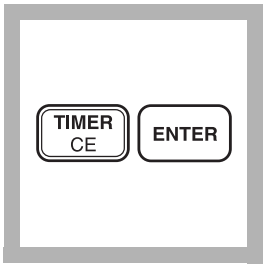
Note: *Keep the tip immersed while the ampul fills completely.*



7. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *An orange color will form if iron is present.*

Note: *Accuracy is not affected by undissolved powder.*

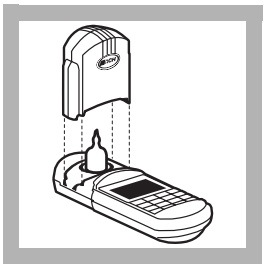


8. Press:

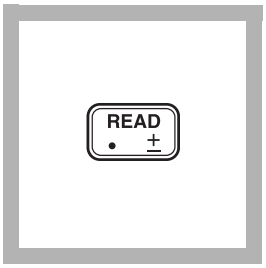
TIMER ENTER

A three-minute reaction period will begin.

Note: *Samples containing visible rust should be allowed to react at least five minutes.*



9. Place the AccuVac ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L iron (Fe) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-cleaned glass or plastic containers. No acid addition is necessary if analyzing the sample immediately. To preserve samples, adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to between 3 and 5 with 5.0 N Sodium Hydroxide Standard Solution before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1* for more information. If only dissolved iron is to be determined, filter the sample before adding the acid.

Accuracy Check

Standard Additions Method

a) Snap the neck off a 50 mg/L Iron PourRite Ampule Standard Solution.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to three 25-mL samples and mix thoroughly.

c) For analysis using AccuVac Ampuls, transfer solutions to dry, clean 50-mL beakers to facilitate filling of the ampuls. For analysis with powder pillows, transfer only 10 mL of solution to the 10-mL sample cells.

d) Analyze each standard addition sample as described above. The iron concentration should increase 0.2 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Standard Solution Method

Prepare a 1.0-mg/L iron standard by diluting 1.00 mL of Iron Standard Solution, 100 mg/L Fe, to 100 mL with deionized water. Or, dilute 1.00 mL of an Iron PourRite Ampule Standard Solution (50 mg/L) to 50 mL in a volumetric flask. Prepare this solution daily.

Run the test following the procedure for powder pillows or AccuVac Ampuls. Results should be between 0.90 mg/L and 1.10 mg/L Fe.

Method Performance

Precision

In a single laboratory, using a standard solution of 2.00 mg/L Fe and two representative lots of powder pillow reagents with the instrument, a single operator obtained a standard deviation of ±0.017 mg/L.

In a single laboratory, using a standard solution of 2.00 mg/L Fe and two representative lots of AccuVac ampuls with the instrument, a single operator obtained a standard deviation of ±0.009 mg/L Fe.

Estimated Detection Limit (EDL)

The EDL for program 33 is 0.03 mg/L Fe. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substances and Suggested Treatments

Interfering Substance	Interference Level and Treatment
Calcium, Ca^{2+}	No effect at less than 10,000 mg/L as $CaCO_3$
Chloride, Cl^-	No effect at less than 185,000 mg/L.
Copper, Cu^{2+}	No effect. Masking agent is contained in FerroVer Iron Reagent.
High Iron Levels	Inhibits color development. Dilute sample and retest to verify results.
Iron Oxide	Requires mild, vigorous or Digesdahl digestion (see Section 2). After digestion, adjust sample to pH 3-5 with sodium hydroxide, then analyze.
Magnesium	No effect at 100,000 mg/L as $CaCO_3$.
Molybdate, Molybdenum	No effect at 25 mg/L as Mo.
High Sulfide Levels, S^{2-}	**1.** Treat in fume hood or well-ventilated area. Add 5 mL HCl to 100 mL sample in a 250-mL Erlenmeyer flask. Boil 20 minutes. **2.** Cool. Adjust pH to 3-5 with NaOH. Re-adjust volume to 100 mL with deionized water. **3.** Analyze.

Interfering Substance	Interference Level and Treatment
Turbidity	**1.** Add 0.1 g scoop of RoVer Rust Remover to the blank in Step 3. Swirl to mix. **2.** Zero the instrument with this blank. **3.** If sample remains turbid, add three 0.2 g scoops of RoVer to a 75-mL sample. Let stand 5 minutes. **4.** Filter through a glass filter or centrifuge. **5.** Use filtered sample in Steps 3 and 6.
Sample pH (extreme)	Adjust pH to 3-5. See *Interferences* in *Section 1.*
Highly Buffered Samples	Adjust pH to 3-5. See *Interferences* in *Section 1.*

Summary of Method

FerroVer Iron Reagent reacts with all soluble iron and most insoluble forms of iron in the sample to produce soluble ferrous iron. This reacts with 1,10-phenanthroline indicator in the reagent to form an orange color in proportion to the iron concentration.

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat No.
FerroVer Iron Reagent Powder Pillows	1 pillow	100/pkg	21057-69
Sample cell, 10-20-25 mL, with screw cap	1	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (Using AccuVac Ampuls)

FerroVer Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25070-25
Beaker, 50 mL	1	each	500-41H

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Ammonium Hydroxide, ACS	500 mL	106-49
Drinking Water Standard, Metals, LR (Cu, Fe, Mn)	500 mL	28337-49
Drinking Water Standard, Metals, HR (Cu, Fe, Mn)	500 mL	28336-49
Hydrochloric Acid Standard Solution, 6 N	500 mL	884-49
Hydrochloric Acid, ACS	500 mL	134-49
Iron Standard Solution, 100 mg/L	100 mL	14175-42
Iron Ampule Standard, 50 mg/L	20/pkg	14254-20
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
RoVer Rust Remover	454 g	300-01
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each		24052-00
Ampule Breaker, PourRite Ampules	each		24846-00
Clippers, Shears $7^{1}/_{4}$ "	each		23694-00
Cylinder, graduated, poly, 25 mL	each		1081-40
Cylinder, graduated, poly, 100 mL	each		1081-42
Digesdahl Digestion Apparatus, 115 V	each		23130-20
Digesdahl Digestion Apparatus, 230 V	each		23130-21
Filter Discs, glass, 47 mm	100/pkg		2530-00
Filter Holder, membrane	each		2340-00
Filter Pump	each		2131-00
Flask, Erlenmeyer, 250 mL	each		505-46
Flask, filtering, 500 mL	each		546-49
Flask, volumetric, Class A, 50 mL	each		14574-41
Flask, volumetric, Class A, 100 mL	each		14574-42
Hot Plate, 4" diameter, 120 VAC	each		12067-01
Hot Plate, 4" diameter, 240 VAC	each		12067-02
pH Meter, *sens**ion***™*1*, portable, with electrode	each		51700-10
pH Indicator Paper, 1 to 11 pH	each		391-33
Pipet Filler, safety bulb	each		14651-00
Pipet, serological, 2 mL	each		532-36
Pipet, serological, 5 mL	each		532-37
Pipet, TenSette, 0.1 to 1.0 mL	each		19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg		21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg		21856-28
Pipet, volumetric, Class A, 1.00 mL	each		14515-35
Spoon, measuring, 0.1 g	each		511-00

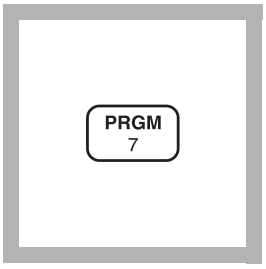
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

IRON (0 to 1.300 mg/L)

FerroZine Method*



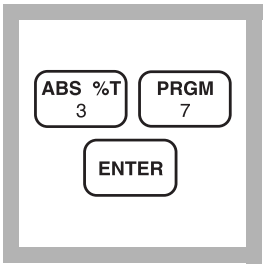
1. Enter the stored program number for iron (Fe).

Press: **PRGM**

The display will show:

PRGM ?

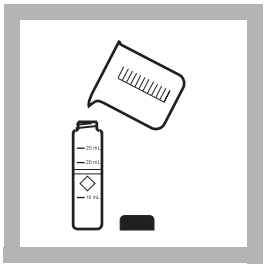
Note: *Adjust the pH of stored samples before analysis.*



2. Press: **37 ENTER**

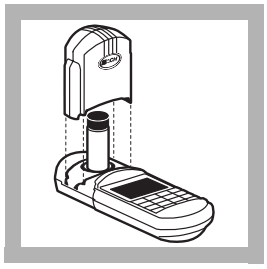
The display will show **mg/L, Fe** and the **ZERO** icon**.**

Note: *Total iron determinations need a prior digestion; use any of the three procedures given in Digestion (Section 2).*

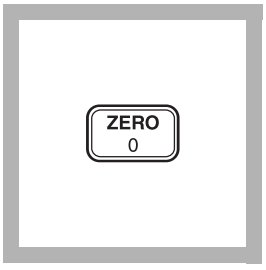


3. Fill a sample cell with 25-mL of sample (the blank).

Note: *Rinse glassware with a 1:1 Hydrochloric Acid Solution and deionized water before use to avoid errors due to iron deposits on the glass.*



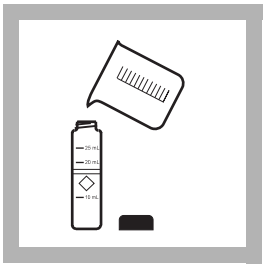
4. Insert the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

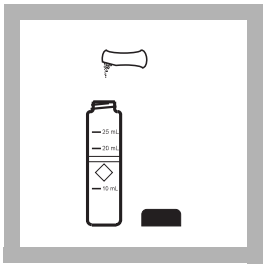
The cursor will move to the right, then the display will show:

0.000 mg/L Fe



6. Fill another sample cell with 25 mL of sample.

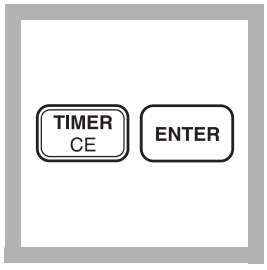
Note: *If the sample contains rust, see Interferences below.*



7. Add the contents of one FerroZine Iron Reagent Solution Pillow to the cell (the prepared sample). Cap and invert to mix.

Note: *Do not allow the clippers to come into contact with the contents of the pillow.*

Note: *If preferred , use 0.5 mL of FerroZine Iron Reagent Solution in place of the solution pillow.*



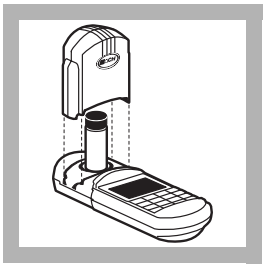
8. Press:

TIMER ENTER

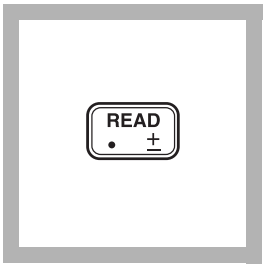
A five-minute reaction period will begin.

Note: *A violet color will develop if iron is present.*

* Adapted from Stookey, L.L., Anal. Chem., 42 (7) 779 (1970)



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-washed glass or plastic bottles. To preserve samples, adjust the sample pH to 2 or less with nitric acid (about 2 mL per liter). Samples preserved in this manner can be stored up to six months at room temperature. If only dissolved iron is to be reported, filter sample immediately after collection and before the addition of nitric acid.

Before testing, adjust the sample pH to 3–5 with ammonium hydroxide, ACS. Do not exceed pH 5 as iron may precipitate. Correct test results for volume additions; see *Correction for Volume Additions* in *Section 1* for more detailed information.

Accuracy Check

Standard Additions Method

a) Snap the neck off an Iron Voluette Ampule Standard, 25 mg/L Fe.

b) Use the TenSette Pipet to add 0.1 mL of standard to the prepared sample measured in Step 10.

c) Swirl to mix and allow another five-minute reaction period, then measure the iron concentration as in Step 10.

d) Add two additional 0.1-mL standard increments, taking a

concentration reading after allowing the five-minute reaction period for each increment.

e) Each 0.1 mL of standard added should cause a 0.1 mg/L increase in the concentration reading.

f) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Prepare a 0.4 mg/L iron working solution as follows:

a) Pipet 1.00 mL of Iron Standard Solution, 100 mg/L Fe, into a
250-mL volumetric flask.

b) Dilute to volume with deionized water. This solution should be prepared daily. Analyze the working solution according to the above procedure.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.80 mg/L iron and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.004 mg/L iron.

Estimated Detection Limit

The estimated detection limit for program 37 is 0.011 mg/L Fe. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Strong chelants, EDTA	Interfere at all levels. Use the FerroVer or TPTZ methods to test these samples. Use the TPTZ method for low iron concentrations.
Cobalt	May give slightly high results
Copper	May give slightly high results
Hydroxides	Boil the sample, with the FerroZine Iron Reagent from Step 7 added to it for 1 minute in a boiling water bath. Cool to 24 °C (75 °F) before proceeding with Step 8. Return the sample volume to 25 mL with deionized water. OR Use any of the digestions in *Section 2*.
Magnetite (black iron oxide) or Ferrites	**1.** Fill a 25-mL graduated cylinder with 25 mL of sample. **2.** Transfer this sample into a 125-mL erlenmeyer flask. **3.** Add the contents of one FerroZine Iron Reagent Solution Pillow and swirl to mix. **4.** Place the flask on a hot plate or over a flame and bring to a boil. **5.** Continue boiling gently for 20 to 30 minutes. ***Note:*** *Do not allow to boil dry.* ***Note:*** *A purple color will develop if iron is present.* **6.** Return the boiled sample to the 25-mL graduated cylinder. Rinse the erlenmeyer flask with small amounts of deionized water and empty into the graduated cylinder. **7.** Return the sample volume to the 25-mL mark with deionized water. **8.** Pour this solution into a sample cell. Swirl to mix. **9.** Proceed with Step 9. OR Use any of the digestions in *Section 2*.
Rust	Boil the sample, with the FerroZine Iron Reagent from Step 7 for 1 minute in a boiling water bath. Cool to 24 °C (75 °F) before proceeding with Step 8. Return the volume to 25 mL with deionized water. OR Use any of the digestions in *Section 2*.

Summary of Method

The FerroZine Iron Reagent forms a purple colored complex with trace amounts of iron in samples that are buffered to a pH of 3.5. This method is applicable for determining trace levels of iron in chemical reagents and glycols and can be used to analyze samples containing magnetite (black iron oxide) or ferrites after treatment as described in Interferences.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
FerroZine Iron Reagent Solution Pillows	1 pillow	50/pkg	2301-66
Clippers, for opening pillows	1	each	968-00
Sample Cell, 10-20-25, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Ammonium Hydroxide, ACS	500 mL	106-49	Drinking
Water Standard, Metals, LR (Cu, Fe, Mn)	500 mL		28337-49
Hydrochloric Acid Solution, 1:1 (6N)	500 mL		884-49
FerroZine Iron Reagent Solution	500 mL		2301-49
Iron Standard Solution, 100 mg/L Fe	100 mL		14175-42
Iron Standard Solution, Voluette Ampule, 25 mg/L Fe, 10 mL	16/pkg		14253-10
Nitric Acid, ACS	500 mL		152-49
Nitric Acid Solution, 1:1	500 mL		2540-49
Water, deionized	4 L		272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Clippers, shears, 7¼-inch	each	20658-00
Cylinder, graduated, 25 mL	each	508-40
Dropper, calibrated, 0.5-mL & 1.0-mL mark	6/pkg	23185-06
Flask, erlenmeyer, 125 mL	each	505-43
Flask, volumetric, 250 mL, Class A	each	14574-46
Hot plate, 3 ½" diameter, 120 V	each	12067-01
Hot plate, 3 ½" diameter, 240 V	each	12067-02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, serological, 2 mL	each	532-36
pH Meter, *sens**ion***™***1***, portable, with electrode	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96 Pipet
Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, 1.00 mL, Class A	each	14515-35
Thermometer, –20 to 110 °C, non-mercury	each	26357-02
Water Bath, with sample cell rack	each	1955-55

For Technical Assistance, Price and Ordering

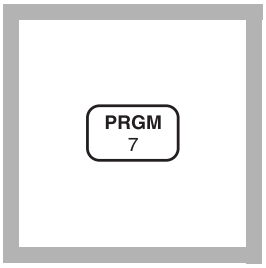
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

IRON, TOTAL (0 to 1.80 mg/L)

For cooling water with molybdenum-based treatment

FerroMo™ Method*



1. Enter the stored program number for iron (Fe).

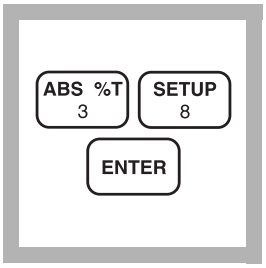
Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

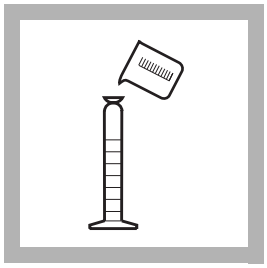
Note: *Adjust the pH of stored samples before analysis.*



2. Press: **38 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon**.**

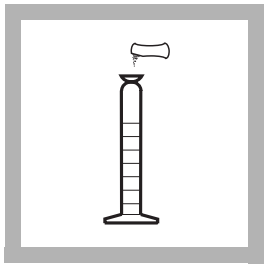
Note: *Determination of total iron requires digestion; see Section 2.*



3. Fill a 50-mL graduated mixing cylinder with 50 mL of sample.

Note: *Sample pH is important in the test; see Interferences.*

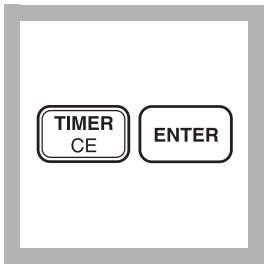
Note: *Rinse glassware with 1:1 Hydrochloric Acid Solution. Rinse again with deionized water. This removes iron deposits which can cause slightly high results.*



4. Add the contents of one FerroMo Iron Reagent 1 Powder Pillow to the graduated cylinder. Stopper and invert several times to mix. Remove the stopper. This is the prepared sample.

5. Transfer 25 mL of the prepared sample to a sample cell.

6. Add the contents of one FerroMo Iron Reagent 2 Powder Pillow to the sample cell. Cap the cell and shake for 30 seconds. This is the prepared sample.

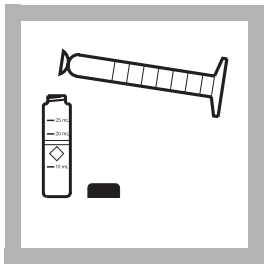


7. Press:

TIMER ENTER

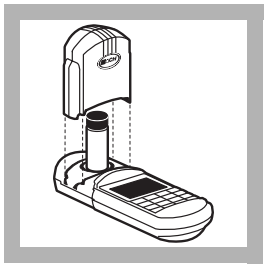
A three-minute reaction period will begin.

Note: *A blue color will develop if iron is present.*

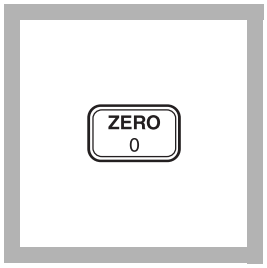


8. Fill a second sample cell with 25 mL of the prepared sample from Step 4 (the blank).

* Adapted from G. Frederic Smith Chemical Company, *The Iron Reagents*, 3rd ed. (1980).



9. Insert the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

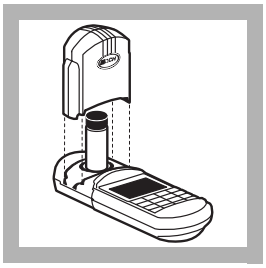


10. Press: **ZERO**

The cursor will move to the right, then the display will show:

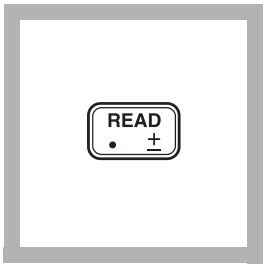
0.00 mg/L Fe

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



11. After the timer beeps, place the prepared sample in the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For samples containing high levels of molybdate (≥100 mg/L), read the sample immediately after zeroing the blank.*



12. Press: **READ**

The cursor will move to the right, then the result in mg/L iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-cleaned plastic or glass bottles. If prompt analysis is impossible, preserve the sample by adjusting to pH 2 or less with hydrochloric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. If reporting only dissolved iron, filter the sample immediately after collection and before adding the acid.

Before analysis, adjust the sample pH to between 3 and 4 with 5.0 N Sodium Hydroxide Standard Solution. Do not exceed pH 5 as iron may precipitate. Correct the test result for volume; see *Correction for Volume Additions* in *Section 1*.

Accuracy Check

Standard Additions Method

a) Snap the top off an Iron PourRite Ampule Standard Solution,
25 mg/L Fe.

b) Use the TenSette Pipet to add 0.2, 0.4 and 0.6 mL of standard to three 50-mL samples. Swirl gently to mix.

c) Analyze each sample as described above. The iron concentration should increase by 0.1 mg/L for each 0.2

mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more Information.

Standard Solution Method
Prepare a 0.4 mg/L iron working solution as follows:

a) Pipet 1.00 mL of Iron Standard Solution, 100 mg/L Fe, into a
250-mL volumetric flask.

b) Dilute to volume with deionized water. Prepare this solution daily. Analyze this working solution according to the above procedure. Results should be between 0.36 and 0.44 mg/L Fe.

Method Performance

Precision
In a single laboratory, using a standard solution of 1.00 mg/L Fe and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of ±0.006 mg/L Fe.

Estimated Detection Limit
The estimated detection limit for program 38 is 0.03 mg/L Fe. For more information on the estimated detection limit, see *Section 1*.

Interferences

A sample pH of less than 3 or greater than 4 after reagent addition may inhibit color formation, cause the developed color to fade, or result in turbidity. Adjust the sample pH before reagent addition to between 3 and 5 using a pH meter or pH paper. Drop by drop, add an appropriate amount of acid (1.0 N Sulfuric Acid Solution) or base (1.0 N Sodium Hydroxide Standard Solution). Make volume corrections if significant amounts of acid or base are used (see *Correction for Volume Additions* in *Section 1*).

Summary of Method

FerroMo Iron Reagent 1 contains a reducing agent combined with a masking agent. The masking agent eliminates interference from high levels of molybdate. The reducing agent converts precipitated or suspended iron (rust) to the ferrous state. FerroMo Iron Reagent 2 contains the indicator combined with a buffering

agent. The indicator reacts with the ferrous iron in the sample, buffered between pH 3-4, resulting in a deep blue-purple color.

REQUIRED REAGENTS

	Cat. No.
FerroMo Reagent Set (100 tests)	25448-00
Includes: (4) 25437-68, (2) 25438-66	

Description	Quantity Required Per Test	Unit	Cat. No
FerroMo Iron Reagent 1 Powder Pillows	1 pillow	25/pkg	25437-68
FerroMo Iron Reagent 2 Powder Pillows	1 pillow	50/pkg	25438-66

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, mixing, 50 mL	1	each	1896-41
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Hydrochloric Acid Solution, 6.0 N (1:1)	500 mL	884-49
Hydrochloric Acid, ACS	500 mL	134-49
Iron Standard Solution, 100 mg/L Fe	100 mL	14175-42
Iron Standard Solution, PourRite Ampule, 25 mg/L Fe, 2 mL	20/pkg	24629-20
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	1045-32
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfuric Acid Standard Solution, 1.0 N	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	24846-00
Flask, volumetric, Class A, 250 mL	each	14574-46
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *Sens**ion**™1*, portable, with electrode	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 1.00 mL	each	14515-35

For Technical Assistance, Price and Ordering

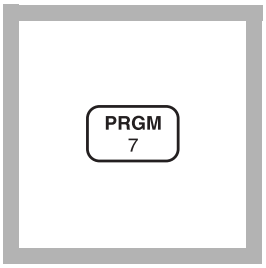
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

IRON, TOTAL (0 to 1.80 mg/L)

TPTZ Method* (Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



1. Enter the stored program number for iron (Fe)- powder pillows.

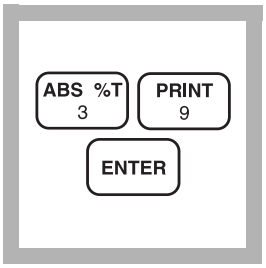
Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

Note: *Adjust the pH of stored samples before analysis.*



2. Press: **39 ENTER**

The display will show **mg/L, Fe** and the **ZERO** icon**.**

Note: *Total iron determination needs a prior digestion. Use any of the procedures in Digestion (Section 2).*

3. Fill a sample cell with 10 mL of sample.

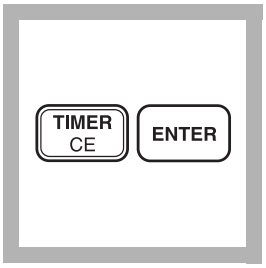
Note: *Sample pH is important in this test; see Interferences.*

Note: *Rinse glassware with a 1:1 hydrochloric acid and deionized water before use to avoid errors due to iron deposits on the glass.*

4. Add the contents of one TPTZ Iron Reagent Powder Pillow (the prepared sample). Cap and shake the cell for 30 seconds.

Note: *A blue color will develop if iron is present.*

* Adapted from G. Frederic Smith Chemical Co., *The Iron Reagents*, 3rd ed. (1980).

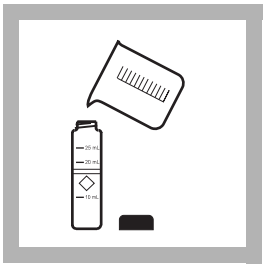


5. Press:

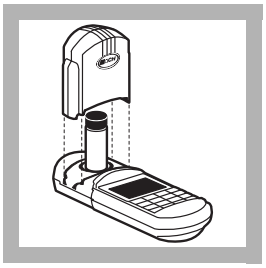
TIMER ENTER

A three-minute reaction period will begin.

Note: *Continue with Steps 6 to 8 while the timer is running.*

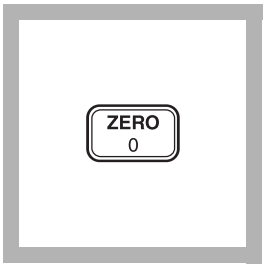


6. Fill a second sample cell with 10 mL of sample (the blank).



7. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Press* **EXIT** *to zero the instrument while the timer is running.*

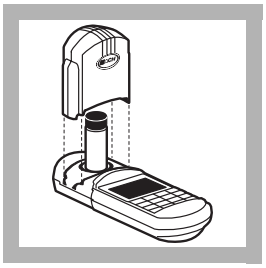


8. Press: **ZERO**

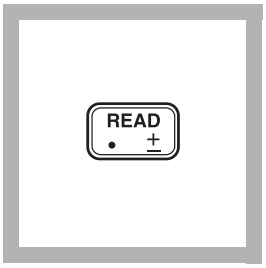
The cursor will move to the right, then the display will show:

0.00 mg/L Fe

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



9. After the timer beeps, place the prepared sample in the cell holder. Tightly cover the sample cell with the instrument cap.

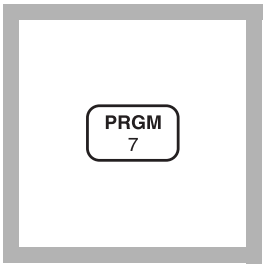


10. Press: **READ**

The cursor will move to the right, then the result in mg/L iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Using AccuVac Ampuls



1. Enter the stored program number for iron (Fe)- AccuVac Ampuls.

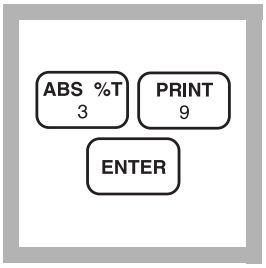
Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

Note: *Adjust the pH of stored samples before analysis.*



2. Press: **39 ENTER**

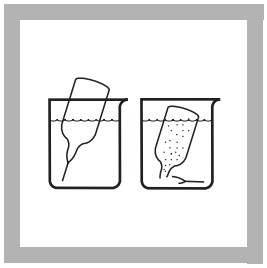
The display will show **mg/L, Fe** and the **ZERO** icon**.**

Note: *Total iron determination needs a prior digestion. Use any of the three procedures in Digestion (Section 2).*

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

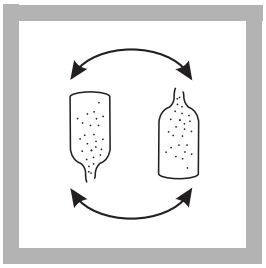
Note: *Sample pH is important in this test; see Interferences.*

Note: *Rinse glassware with a 1:1 hydrochloric acid and deionized water before use to avoid errors due to iron deposits on the glass.*



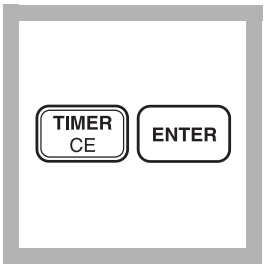
4. Fill a TPTZ Iron AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



5. Invert the ampul (the prepared sample) repeatedly to mix. Wipe off any liquid or fingerprints.

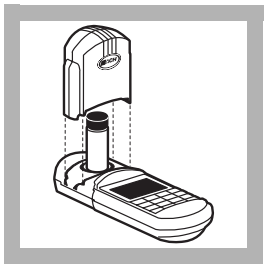
Note: *A blue color will develop if iron is present.*



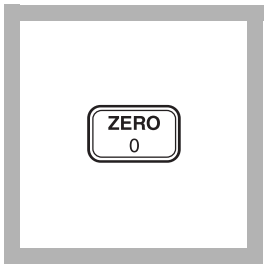
6. Press:

TIMER ENTER

A three-minute reaction period will begin.



7. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



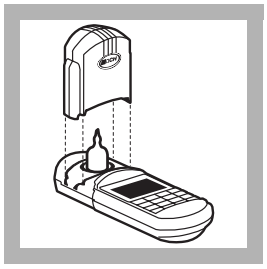
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

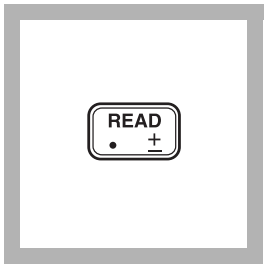
0.00 mg/L Fe

Note: *Press* **EXIT** *to zero the instrument while the timer is running.*

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



9. When the timer beeps, place the prepared sample into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L iron will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-washed glass or plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 2 mL per liter). Store samples preserved in this manner up to six months at room temperature. If reporting only dissolved iron, filter sample immediately after collection and before addition of nitric acid.

Before testing, adjust the pH of the stored sample to between 3 and 4 with 5.0 N Sodium Hydroxide Standard Solution. Do not exceed pH 5 as iron may precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1*.

Accuracy Check

Standard Additions Method (Powder Pillows)

a) Snap the neck off a PourRite Iron Ampule Standard, 25 mg/L Fe.

b) Use the TenSette Pipet to add 0.1 mL of standard to the prepared sample measured in Step 10. Swirl to mix.

c) Measure the iron concentration as in Step 10. The measurement does not require the three-minute waiting period.

d) Add two additional 0.1-mL aliquots of standard, measuring the concentration after each addition. The iron concentration should increase by 0.25 mg/L for each 0.1-mL addition of standard.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (AccuVac Ampuls)

a) Use a graduated cylinder to measure 25.0 mL of sample into each of three 50-mL beakers.

b) Snap the neck off an Iron Ampule Standard, 25 mg/L Fe.

c) Using a TenSette Pipet, add 0.1, 0.2 and 0.3 mL of standard, respectively, to the 50-mL beakers. Swirl to mix.

d) Fill a TPTZ AccuVac Ampul from each beaker.

e) Measure the concentration of each ampul according to the procedure. The iron concentration should increase by 0.1 mg/L for each 0.1 mL addition of standard.

f) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Prepare a 0.4 mg/L iron working solution as follows:

a) Using Class A glassware, pipet 1.00 mL of Iron Standard Solution, 100 mg/L Fe, into a 250-mL volumetric flask.

b) Dilute to volume with deionized water. Stopper and invert repeatedly to mix. Prepare this solution daily.

Method Performance

Precision

In a single laboratory using a standard solution of 1.00 mg/L Fe and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.017 mg/L Fe.

In a single laboratory using a standard solution of 1.00 mg/L Fe and one representative lot of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.022 mg/L Fe.

Estimated Detection Limit

The estimated detection limit for program 39 is 0.04 mg/L Fe. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Cadmium	Greater than 4.0 mg/L
Chromium ($^{3+}$)	Greater than 0.25 mg/L
Chromium ($^{6+}$)	Greater than 1.2 mg/L
Cobalt	Greater than 0.05 mg/L
Color or turbidity	If the sample is turbid, add one 0.1-g scoop of RoVer Rust Remover to the blank in Step 6 (Step 3 for AccuVac procedure). Swirl to mix.
Copper	Greater than 0.6 mg/L
Cyanide	Greater than 2.8 mg/L
Manganese	Greater than 50.0 mg/L
Mercury	Greater than 0.4 mg/L
Molybdenum	Greater than 4.0 mg/L
Nickel	Greater than 1.0 mg/L
Nitrite Ion	Greater than 0.8 mg/L
pH	A sample pH of < 3 or >4 after the addition of reagent may inhibit color formation, cause the developed color to fade quickly or result in turbidity. Adjust the sample pH to 3–5 before adding reagent using a pH meter or pH paper and adding (dropwise) an appropriate amount of iron-free acid or base (i.e., 1.0 N Sulfuric Acid Standard Solution or 1.0 N Sodium Hydroxide Standard Solution). Make a volume correction if significant volumes of acid or base are used.

Summary of Method

The TPTZ Iron Reagent forms a deep blue-purple color with ferrous iron. The indicator is combined with a reducing agent which converts precipitated or suspended iron, such as rust, to the ferrous state. The amount of ferric iron present can be determined as the difference between the results of a ferrous iron test and the concentration of total iron.

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
TPTZ Iron Reagent Powder Pillows,	1 pillow	100/pkg	26087-99
Sample Cell, 10-20-25 mL, w/cap	1	6/pkg	24019-06

REQUIRED REAGENTS (Using AccuVac Ampuls)

TPTZ Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25100-25

REQUIRED APPARATUS (Using AccuVac Ampuls)

Beaker, 50 mL	1	each	500-41H
Sample Cell, 10-20-25 mL, w/cap	1	6/pkg	24019-06

OPTIONAL REAGENTS

Drinking Water Standard, Metals, LR (Cu, Fe, Mn)	500 mL		28337-49
Drinking Water Standard, Metals, HR (Cu, Fe, Mn)	500 mL		28336-49
Hydrochloric Acid Solution, 1:1, 6.0 N	500 mL		884-49
Iron Standard Solution, 100 mg/L Fe	100 mL		14175-42
Iron Standard Solution, Ampule, 25 mg/L Fe, 2 mL	20/pkg		24629-20
Nitric Acid, ACS	500 mL		152-49
Nitric Acid Solution, 1:1	500 mL		2540-49
RoVer Rust Remover	454 g		300-01
Sodium Hydroxide Standard Solution, 1.0 N	100 mL	MDB	1045-32
Sodium Hydroxide Standard Solution, 5.0 N	100 mL	MDB	2450-32
Sulfuric Acid Standard Solution	100 mL	MDB	1270-32
Water, deionized	4 L		272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Ampule Breaker, Ampules	each	24846-00
Cylinder, graduated, 25 mL	each	1081-40
Dropper, graduated, 0.5 and 1.0 mL marks	20/pkg	21247-20
Flask, volumetric, Class A, 250 mL	each	14574-46
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sens**ion***™***1***, portable, with electrode	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00 mL	each	14515-35

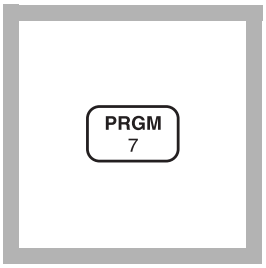
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

MANGANESE, High Range (0 to 20.0 mg/L)

Periodate Oxidation Method* USEPA approved for reporting wastewater analysis (digestion is required; see Section 2)**

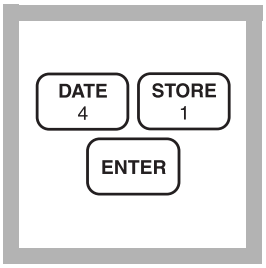


1. Enter the stored program number for manganese, periodate oxidation method.

Press: **PRGM**

The display will show:

PRGM ?



2. Press: **41 ENTER**

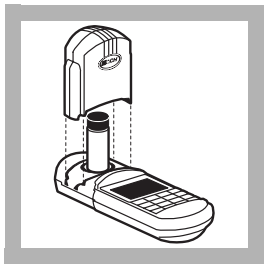
The display will show **mg/L, Mn** and the **ZERO** icon**.**

Note: *For alternate forms ($KMnO_4$, MnO_4), press the* **CONC** *key.*

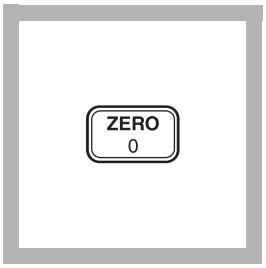
3. Fill a sample cell with 10 mL of sample (the blank).

Note: *For total manganese determination perform a digestion (see Section 2).*

Note: *Adjust the pH of stored samples before analysis.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



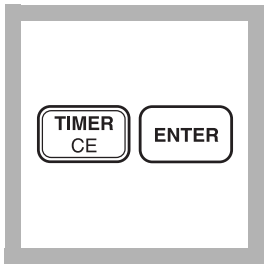
5. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.0 mg/L Mn

6. Remove the cell from the instrument. Add the contents of one Buffer Powder Pillow, citrate type, to the cell. Cap the cell and invert until the powder is dissolved. Remove cap.

7. Add the contents of one Sodium Periodate Powder Pillow to the sample cell (the prepared sample). Cap the sample cell. Invert for 10 seconds to mix.



8. Press:**TIMER ENTER**

A two-minute reaction period will begin.

Note: *A violet color will form if manganese is present.*

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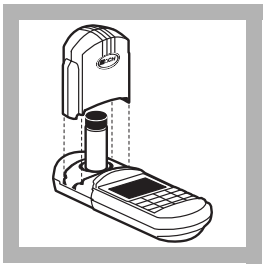
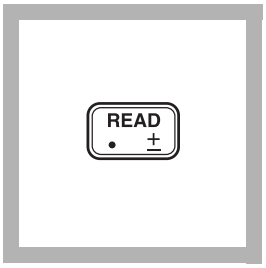
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** *Federal Register,* 44 (116) 34193 (June 14, 1979).



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L manganese will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Manganese may be lost by adsorption to glass container walls. Adjust the pH to less than 2 with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as manganese may be lost as a precipitate. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1* for more information. If only dissolved Mn is to be determined, filter before acid addition.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Manganese Voluette Ampule Standard Solution, 250 mg/L Mn.

b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three 25-mL water samples. Swirl to mix.

c) Transfer only 10 mL of each solution to the 10-mL sample cells.

d) Analyze each standard addition sample as described in the procedure. The manganese concentration should increase 1.0 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Standard Solution Method

Prepare a 5.0 mg/L manganese standard solution by pipetting (use a TenSette or Class A volumetric pipet) 5.00 mL of Manganese Standard Solution, 1000 mg/L Mn, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. Or, prepare this standard by diluting 1.00 mL of a High Range Manganese Standard Voluette Ampule, 250 mg/L, to 50 mL. Prepare these solutions daily. Use these solutions as the sample in the procedure.

Method Performance

Precision

In a single laboratory, using a standard solution of 10.00 mg/L Mn and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.18 mg/L Mn.

Estimated Detection Limit

The estimated detection limit for program 41 is 0.2 mg/L Mn. For more information on the estimated detection limit, see *Section 1*.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Calcium	700 mg/L
Chloride	70,000 mg/L
Iron	5 mg/L
Magnesium	100,000 mg/L

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section 1*.

Summary of Method

Manganese in the sample is oxidized to the purple permanganate state by sodium periodate, after buffering the sample with citrate. The purple color is directly proportional to the manganese concentration.

MANGANESE, High Range, continued

REQUIRED REAGENTS

	Cat. No.
High Range Manganese Reagent Set (100 tests) 10 mL	24300-00
Includes: (1) 21076-69, (1) 21077-69	

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Powder Pillows, citrate type for Manganese	1 pillow	100/pkg	21076-69
Sodium Periodate Powder Pillows for Manganese	1 pillow	100/pkg	21077-69

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Drinking Water Standard, Metals, HR (Cu, Fe, Mn)	500 mL	28336-49
Hydrochloric Acid, 6 N	500 mL	884-49
Manganese Standard Solution, 1000 mg/L Mn	100 mL	12791-42
Manganese Standard Solution, Voluette ampule, High Range, 250 mg/L Mn, 10 mL	16/pkg	14258-10
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution 1:1	500 mL	2540-49
Sodium Hydroxide Solution, 5.0 N	100 mL MDB	2450-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each		21968-00
Flask, Erlenmeyer, 250 mL	each		505-46
Flask, volumetric, Class A, 50 mL	each		14574-41
Flask, volumetric, Class A, 100 mL	each		14574-42
Flask, volumetric, Class A, 1000 mL	each		14574-53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg		391-33
pH Meter, *sens**ion***™*1*, portable, with electrode	each		51700-10
Pipet, serological, 5 mL	each		532-37
Pipet, TenSette, 0.1 to 1.0 mL	each		19700-01
Pipet, TenSette, 1.0 to 10.0 mL	each		19700-10
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg		21856-96Pipet
Tips, for 19700-01 TenSette Pipet	1000/pkg		21856-28
Pipet Tips, for 19700-10 TenSette Pipet	50/pkg		21997-96
Pipet, volumetric, Class A, 5.00 mL	each		14515-37
Pipet, volumetric, Class A, 1.00 mL	each		14515-35
Pipet Filler, safety bulb	each		14651-00

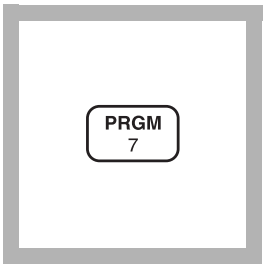
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

MANGANESE, Low Range (0 to 0.700 mg/L)

PAN Method*

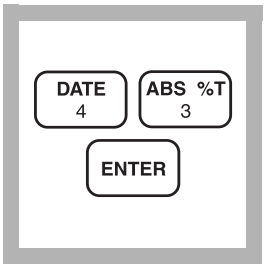


1. Enter the stored program number for low range manganese.

Press: **PRGM**

The display will show:

PRGM ?

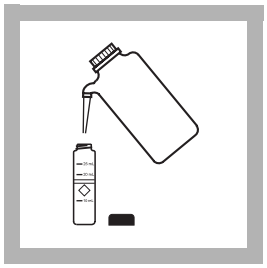


2. Press: **43 ENTER**

The display will show **mg/L, Mn** and the **ZERO** icon**.**

Note: *For alternate forms (MnO_4, $KMnO_4$), press the* **CONC** *key.*

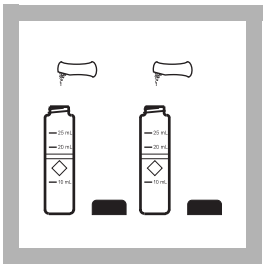
Note: *Total manganese determination requires a prior digestion; see Digestion (Section 2).*



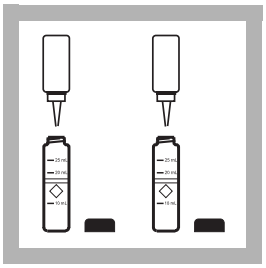
3. Fill a sample cell with 10 mL of deionized water (the blank).

Note: *Rinse all glassware with 1:1 Nitric Acid Solution. Rinse again with deionized water.*

4. Fill another sample cell with 10 mL of sample (the prepared sample).



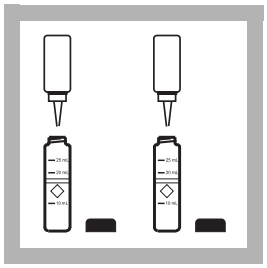
5. Add the contents of one Ascorbic Acid Powder Pillow to each cell. Swirl to mix.



6. Add 15 drops of Alkaline-Cyanide Reagent Solution to each cell. Swirl to mix.

Note: *A cloudy solution may form in some samples after reagent addition. The turbidity should dissipate after Step 8.*

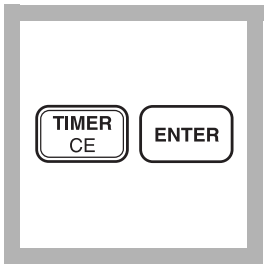
Note: *A Tensette Pipet may be used to dispense 0.4 mL of the Alkaline Cyanide Reagent.*



7. Add 21 drops of PAN Indicator Solution, 0.1%, to each sample cell. Swirl to mix.

Note: *An orange color will develop in the sample if manganese is present.*

Note: *A Tensette Pipet may be used to dispense 0.4 mL of the PAN Indicator Solution.*

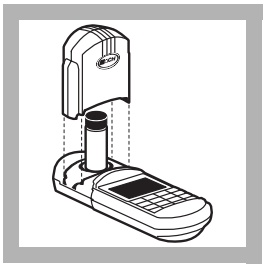


8. Press:

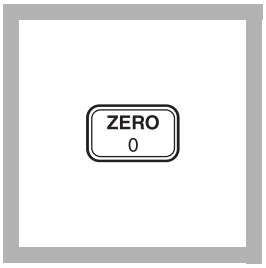
TIMER ENTER

A two-minute reaction period will begin.

* Adapted from Goto, K., et al., Talanta, 24, 752-3 (1977).



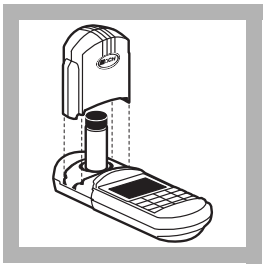
9. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



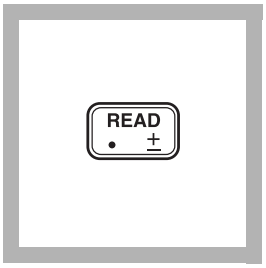
10. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.000 mg/L Mn



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L manganese will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Note: *See Waste Management below for proper disposal of cyanide wastes.*

Sampling and Storage

Collect samples in a clean glass or plastic container. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the pH to 4.0-5.0 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1*.

Accuracy Check

Standard Additions Method

Note: *Volume accuracy is very important when performing standard additions with 10-mL volumes. The fill mark on the 10-mL sample cell is not intended to measure standard addition volumes.*

a) Fill three 10-mL graduated mixing cylinders with 10.0 mL of sample.

b) Snap the neck off a Manganese Voluette Ampule Standard,
10 mg/L Mn.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper and mix each thoroughly.

d) Analyze each sample as described in the procedure. The manganese concentration should increase 0.1 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Note: *An alternative to the above procedure is to pipet 10.0 mL of sample into dry sample cells before performing standard additions. A volumetric pipet or a TenSette Pipet can be used to deliver the sample volume.*

Standard Solution Method

Prepare a 0.5 mg/L manganese standard solution as follows:

a) Pipet 5.00 mL of Manganese Standard Solution, 1000 mg/L Mn, into a 1000-mL volumetric flask.

b) Dilute to the mark with deionized water. Prepare this solution daily.

c) Pipet 10.00 mL of the solution from Step b into a 100-mL volumetric flask.

d) Dilute to the mark with deionized water. This second dilution is equivalent to 0.5 mg/L Mn.

Method Performance

Precision

In a single laboratory using a standard solution of 0.5 mg/L Mn and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.013 mg/L Mn.

Estimated Detection Limit

The estimated detection limit for program 43 is 0.020 mg/L Mn. For more information on the estimated detection limit, see *Section 1*.

Interferences

The following do not interfere up to the indicated concentrations:

Substance	Suggested Treatment For Levels That Interfere
Aluminum	20 mg/L
Cadmium	10 mg/L
Cobalt	20 mg/L
Copper	50 mg/L
Hardness	300 mg/L.
Iron	If the sample contains more than 5 mg/L iron, allow 10 minutes for complete color development. Instead of performing Step 8, set the timer for 10 minutes by pressing **TIMER** twice. Then press **1000**. Press **ENTER** to start the timer.
Lead	0.5 mg/L
Magnesium	For samples containing hardness greater than 300 mg/L $CaCO_3$, add four drops of Rochelle Salt Solution to the sample after addition of the Ascorbic Acid Powder Pillow.
Nickel	40 mg/L
Zinc	15 mg/L

Waste Management

The alkaline cyanide solution contains cyanide. Cyanide solutions should be collected for disposal as reactive (D003) waste. Store all cyanide solutions in a caustic solution with pH >11 to prevent release of hydrogen cyanide gas. In case of a spill, clean up the area as outlined below:

1. Use a fume hood or self-contained breathing apparatus.
2. While stirring, add the waste to a beaker containing a strong solution of sodium hydroxide and calcium hypochlorite or sodium hypochlorite (household bleach).
3. Maintain a strong excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.
4. Flush the solution down the drain with a large excess of water.

Summary of Method

The PAN method is a highly sensitive and rapid procedure for detecting low levels of manganese. An ascorbic acid reagent is used initially to reduce all oxidized forms of manganese to Mn^{2+}. An alkaline-cyanide reagent is added to mask any potential

interferences. PAN Indicator is then added to combine with the Mn^{2+} to form an orange-colored complex.

REQUIRED REAGENTS

	Cat. No.
Manganese Reagent Set (50 tests)	26517-00
Includes: (1) 21223-26, (1) 14577-99, (1) 21224-26	

Description	Quantity Required Per Test	Unit	Cat. No.
Alkaline-Cyanide Reagent	30 drops	50 mL SCDB	21223-26
Ascorbic Acid Powder Pillows	2 pillows	100/pkg	14577-99
PAN Indicator Solution, 0.1%	42 drops	50 mL SCDB	21224-26
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	1	each	508-40
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Drinking Water Standard, Metals, LR (Cu, Fe, Mn)		500 mL	28337-49
Hydrochloric Acid Solution, 1:1 (6 N)		500 mL	884-49
Manganese Standard Solution, 1000 mg/L Mn		100 mL	12791-42
Manganese Standard Sol'n, Ampule, 25 mg/L Mn, 2 mL		20/pkg.	21128-20
Nitric Acid Solution, 1:1		500 mL	2540-49
Rochelle Salt Solution.		29 mL DB	1725-33
Sodium Hydroxide Solution, 50%		500 mL	2180-49
Nitric Acid, ACS		500 mL	152-49

OPTIONAL APPARATUS

Ampule Breaker, Ampule		each	24846-00
Beaker, glass, 1000 mL		each	500-53
Cylinder, graduated, mixing, 10 mL		each	20886-38
Dropper, plastic, calibrated, 1.0 mL		20/pkg	21247-20
Flask, volumetric, Class A, 1000 mL		each	14574-53
Flask, volumetric, Class A, 100 mL		each	14574-42
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Pipet, volumetric, Class A, 10.0 mL		each	14515-38
Pipet, volumetric, Class A, 5.0 mL		each	14515-37
Pipet Filler, safety bulb		each	14651-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

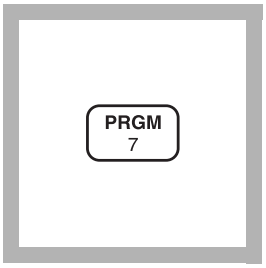
Outside the U.S.A.—Contact the Hach office or distributor serving you.

MOLYBDENUM, MOLYBDATE, High Range (0 to 40.0 mg/L)

Mercaptoacetic Acid Method*

For water and wastewater

Using Powder Pillows



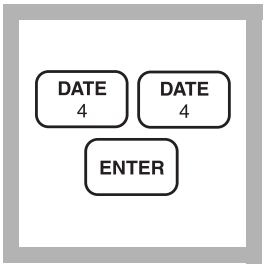
1. Enter the stored program number for high range molybdenum-powder pillows

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **44 ENTER**

The display will show **mg/L, Mo6** and the **ZERO** icon**.**

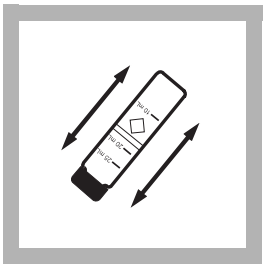
Note: *For alternate form (MoO_4), press the* **CONC** *key.*

3. Fill a sample cell with 10 mL of sample.

Note: *Filter turbid samples.*

Note: *Adjust pH of stored samples before analysis.*

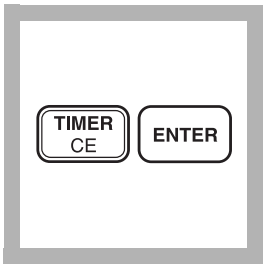
4. Add the contents of one MolyVer 1 Reagent Powder Pillow. Cap the cell and invert several times to mix.



5. Add the contents of one MolyVer 2 Reagent Powder Pillow. Cap the cell and invert several times to mix.

6. Add the contents of one MolyVer 3 Reagent Powder Pillow. Cap the cell and invert several times to mix. This is the prepared sample.

Note: *Accuracy is not affected by undissolved powder.*



7. Press:

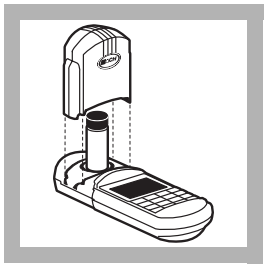
TIMER ENTER

A five-minute reaction period will begin.

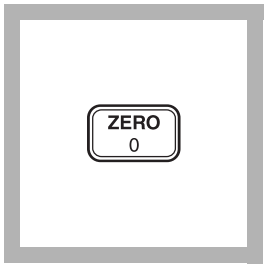
Note: *Molybdenum will cause a yellow color to form.*

8. After the timer beeps, fill a second sample cell with 10 mL of sample (the blank).

* Adapted from Analytical Chemistry, 25(9) 1363 (1953).



9. Insert the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

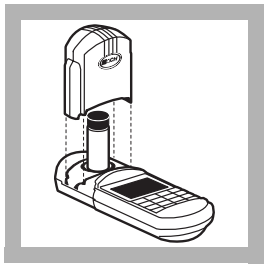


10. Press: **ZERO**

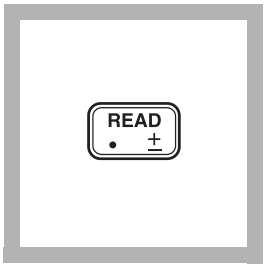
The cursor will move to the right, then the display will show:

0.0 mg/L Mo6

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



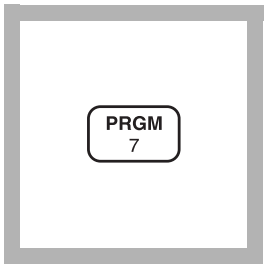
12. Press: **READ**

The cursor will move to the right, then the result in mg/L molybdenum (or alternate form) will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagents is highly recommended. See Accuracy Check.*

Using AccuVac Ampuls

Method 10046



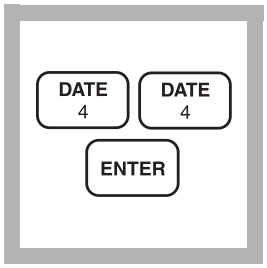
1. Enter the stored program number for high range molybdenum using AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **44 ENTER**

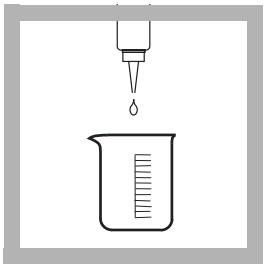
The display will show **mg/L, Mo6** and the **ZERO** icon.

Note: *For alternate form (MoO_4), press the* **CONC** *key.*

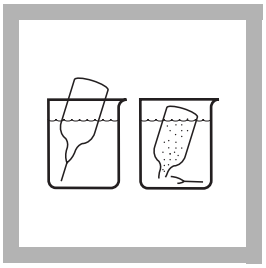
3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Filter turbid samples.*

Note: *Adjust the pH of stored samples before analysis.*

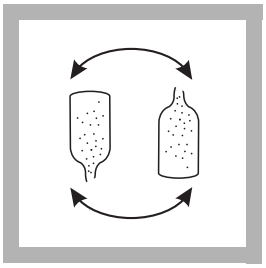


4. Add 4 drops of 0.4 M CDTA Solution to the beaker. Swirl to mix.



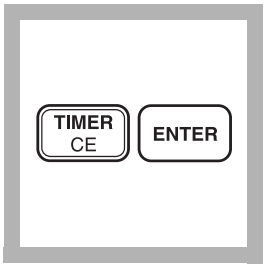
5. Fill a MolyVer 6 Reagent AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills.*



6. Invert the ampul repeatedly to mix. Wipe off any liquid or fingerprints.

Note: *Undissolved reagent will not affect the result.*

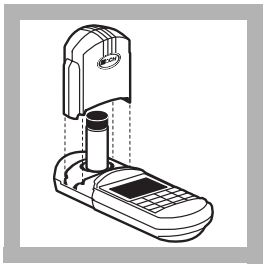


7. Press:

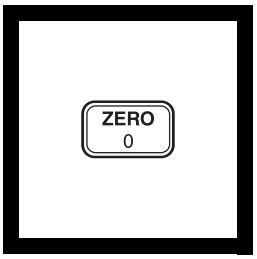
TIMER ENTER

A five-minute reaction period will begin.

Note: *If molybdenum is present a yellow color will develop.*



8. When the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

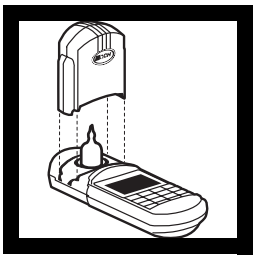


9. Press: **ZERO**

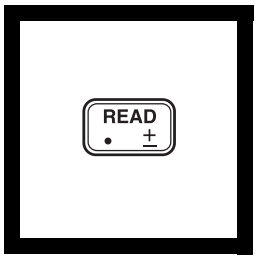
The cursor will move to the right, then the display will show:

0.0 mg/L Mo6

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



10. Place the AccuVac Ampul in the cell holder. Tightly cover the ampul with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L molybdenum will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Sampling and Storage

Collect samples in clean plastic bottles. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples can be stored up to 6 months at room temperature. Adjust the pH to 7 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Molybdenum Voluette Ampule Standard Solution, 500 mg/L Mo^{6+}.

c) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper each and mix thoroughly.

d) For analysis with AccuVac Ampuls, transfer solutions to dry, clean 50-mL beakers. For analysis with powder pillows, transfer only
10 mL of solution to the sample cells.

e) Analyze each standard addition sample as described in the procedure. The molybdenum concentration reading should increase 2.0 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Standard Solution Method

To assure the accuracy of the test, use a Molybdenum Standard Solution, 10.0 mg/L Mo^{6+}. Follow the procedure for powder pillows or AccuVac Ampuls. Results should be between 9.0 and 11.0 mg/L Mo^{6+}.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 10.0-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **10.0** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1*, *Standard Curve Adjustmen*t for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 20.0 mg/L Mo^{6+} and two representative lots of powder pillows with the instrument, a single operator obtained a standard deviation of ±0.3 mg/L Mo^{6+}.

In a single laboratory using a standard solution of 20.0 mg/L Mo^{6+} and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.1 mg/L Mo^{6+}.

Estimated Detection Limit

The estimated detection limit for program 44 is 0.2 mg/L Mo^{6+}. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Aluminum	Greater than 50 mg/L
Chromium	Greater than 1000 mg/L
Copper	Samples containing 10 mg/L copper or more will exhibit an increasing positive interference upon standing. Read these samples as soon as possible after the five-minute reaction period is complete.
Iron	Greater than 50 mg/L
Nickel	Greater than 50 mg/L
Nitrite	Interference from up to 2000 mg/L as NO_2^- can be eliminated by adding one Sulfamic Acid Powder Pillow to the sample.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; see *Section 1, pH Interferences*.

Summary of Method

Powder Pillows

MolyVer 1 and 2 Reagents are added to buffer and condition the sample. MolyVer 1 contains a buffer to control the pH in addition to a chelating agent to mask interferences. MolyVer 3 provides the mercaptoacetic acid, which reacts with molybdate molybdenum to form a yellow color proportional to the molybdenum concentration.

AccuVac Ampuls

The CDTA Solution masks metal interferences. The MolyVer 6 reagent provides the mercaptoacetic acid, which reacts with molybdate molybdenum to form a yellow color proportional to the molybdenum concentration.

MOLYBDENUM, MOLYBDATE, HR, continued

REQUIRED REAGENTS (for Powder Pillows)

	Cat. No.
Molybdenum Reagent Set, 10 mL (100 tests)	26041-00
Includes: (1) 26042-99, (1) 26043-99, (1) 26044-99	

Description	Quantity Required Per Test	Unit	Cat. No.
MolyVer 1 Reagent Powder Pillows	1 pillow	100/pkg	26042-99
MolyVer 2 Reagent Powder Pillows	1 pillow	100/pkg	26043-99
MolyVer 3 Reagent Powder Pillows	1 pillow	100/pkg	26044-99

REQUIRED REAGENTS (for AccuVac Ampuls)

MolyVer 6 Molybdenum AccuVac Reagent Set (25 tests)			25220-98
Includes: (1) 25220-25, (1) 26154-36			
CDTA Solution 0.4M	4 drops	15 mL SCDB	26154-36
MolyVer 6 Reagent AccuVac Ampuls	1 ampul	25/pkg	25220-25

REQUIRED APPARATUS (for Powder Pillows)

Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

REQUIRED APPARATUS (for AccuVac Ampuls)

Beaker, 50 mL	2	each	500-41H
Sample Cell, 10-20-25 mL, w/cap	1	6/pkg	24019-06

OPTIONAL REAGENTS

Molybdenum Standard Solution, 10 mg/L Mo^{6+}	100 mL	14187-42
Molybdenum Standard Solution, Voluette Ampule, 500 mg/L Mo^{6+}, 10 mL	16/pkg	14265-10
Nitric Acid, ACS	500 mL	152-49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfamic Acid Powder Pillows	100/pkg	1055-99
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, mixing, 25 mL	each	20886-40
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, Erlenmeyer, 250 mL	each	505-46
Funnel, poly, 65 mm	each	1083-67
Pipet, serological, 5 mL	each	532-37
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28

For Technical Assistance, Price and Ordering

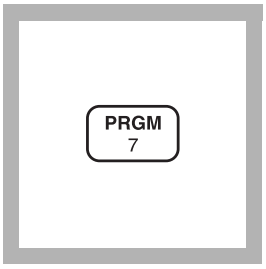
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

MOLYBDENUM, MOLYBDATE, Low Range (0 to 3.00 mg/L)

Ternary Complex Method

For boiler and cooling tower waters



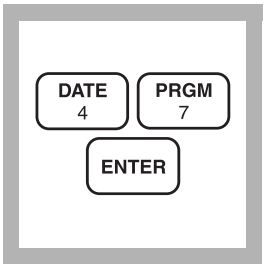
1. Enter the stored program number for molybdate molybdenum.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



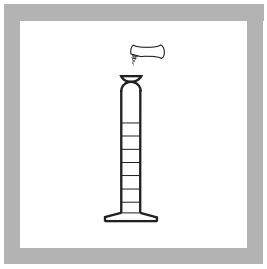
2. Press: **47 ENTER**

The display will show **mg/L, Mo6** and the **ZERO** icon**.**

Note: *For alternate forms (MoO_4), press the* **CONC** *key.*

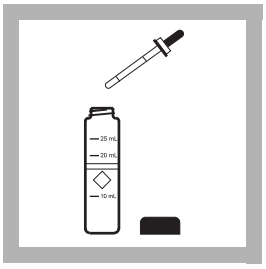
3. Fill a 25-mL mixing graduated cylinder with 20 mL of the sample.

Note: *Filter turbid samples using the labware listed under Optional Apparatus.*



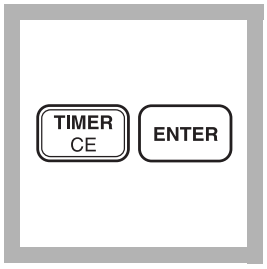
4. Add the contents of one Molybdenum 1 Reagent Powder Pillow to the graduated cylinder. Stopper. Invert the graduated cylinder several times to dissolve the reagents.

5. Pour 10 mL of the solution into a sample cell.



6. Add 0.5 mL of Molybdenum 2 Reagent to the sample cell. Swirl to mix. This is the prepared sample.

Note: *Molybdenum will cause a green color to form.*

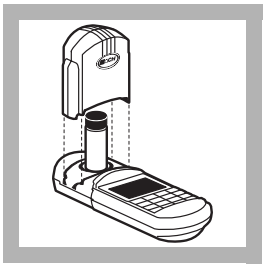


7. Press:

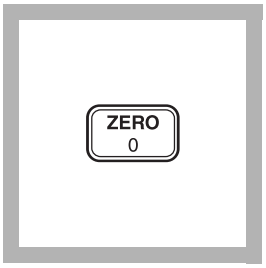
TIMER ENTER

A two-minute reaction period will begin.

8. Fill a second sample cell with 10 mL of solution from the graduated cylinder (the blank).



9. Insert the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

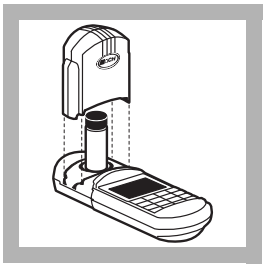


10. Press: **ZERO**

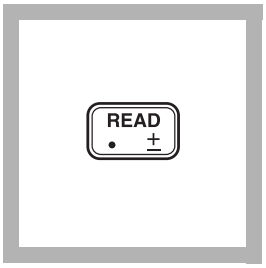
The cursor will move to the right, then the display will show:

0.00 mg/L Mo6

Note: *If Reagent Blank Correction is on, the display may flash "limit" (see Section 1).*



11. Place the developed sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L molybdate molybdenum will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in glass or plastic bottles.

Accuracy Check

Standard Addition Method

a) Add 25 mL of sample to three 25-mL mixing cylinders.

b) Snap the neck off a Molybdenum PourRite Ampule Standard Solution, 75 mg/L Mo^{6+}.

c) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard, respectively, to three 25-mL samples. Mix thoroughly.

d) Analyze 20 mL of each spiked sample as described in the procedure. The molybdenum concentration reading should increase by 0.3 mg/L for each 0.1 mL addition of standard.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Prepare a 2.0-mg/L molybdenum standard solution by pipetting 10 mL of a 10-mg/L Molybdenum Standard Solution into a 50-

mL graduated mixing cylinder. Dilute to the mark with deionized water and mix thoroughly. Analyze 20 mL of this solution according to the procedure.

Method Performance

Precision

In a single laboratory using standard solutions of 2.00 mg/L Mo^{6+} and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.009 mg/L Mo^{6+}.

Estimated Detection Limit

The estimated detection limit for program 47 is 0.07 mg/L Mo^{6+}. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interference studies were conducted by preparing a molybdenum standard solution (2 mg/L Mo^{6+}) as well as a solution of the potential interfering ion. When the standard solution concentration changed by ±5% with a given ion concentration, the ion was considered an interference.

Table 1 Negative Interferences

Ion	Level above which it interferes (mg/L)
Iron	200
Copper	98
Chromium (Cr^{6+})	4.5*
Chloride	1,400
AMP (Phosphonate)	15
Phosphonohydroxyacetic Acid	32
Bisulfate	3,300
Nitrite	350
Aluminum	2
Acrylates	790
Alum	7
Lignin Sulfonate	105
Orthophosphate	4,500
Bicarbonate	5,650
EDTA	1,500
Borate	5,250
Ethylene Glycol	2% (by volume)
Sulfite	6,500
Diethanoldithiocarbamate	32

Table 1 Negative Interferences (continued)

Ion	Level above which it interferes (mg/L)
Positive Interferences	
Carbonate	1,325
Silica	600
Benzotriazole	210
Morpholine	6

* Read molybdenum concentration immediately after the completion of the two-minute reaction period.

Table 2 No Interference

Ion	Highest Concentration Tested (mg/L)
Zinc	400
Calcium	720
Magnesium	8,000
Manganese	1,600
Chlorine	7.5
PBTC (phosphonate)	500
Sulfate	12,800
Bisulfite	9,600
Nickel	250

Phosphonate HEDP at concentrations up to 30 mg/L will increase the apparent molybdenum concentration reading by approximately 10% (positive interference). For these samples, multiply the value obtained in step 12 by 0.9 to obtain the actual molybdenum concentration. As the concentration of HEDP increases above 30 mg/L, a decrease in the molybdenum concentration reading occurs (negative interference).

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagent and require pretreatment. Adjust the sample pH to 3-5 (use a pH meter or pH paper) by adding drops of an acid or base such as 1.0 N Sulfuric Acid Standard Solution, or 1.0 N Sodium Hydroxide Standard Solution. If a significant volume of acid or base is used, correct the result by dividing the total volume (sample + acid + base) by the original volume and multiplying the test result by this factor.

Large interferences are caused by some biocides used in cooling tower samples. Hach recommends testing the ternary complex procedure on molybdenum standards containing the specific biocides in use to determine if the ternary complex method will work with these samples.

After many samples have been analyzed, the sample cells may show a slight blue color. Rinse with Hydrochloric Acid Solution, 1:1, to eliminate the build-up.

Summary of Method

The ternary complex method for molybdenum determination is a method in which molybdate molybdenum reacts with an indicator and sensitizing agent to give a stable blue complex.

MOLYBDENUM, MOLYBDATE, LR, continued

REQUIRED REAGENTS

Molybdenum Reagent Set, 20 mL sample (100 tests) 24494-00
Includes: (1) 23524-49, (1) 23525-12

Description	Quantity Required Per Test	Unit	Cat. No.
Molybdenum 1 Reagent for 20 mL sample size	1 pillow	100/pkg	23524-49
Molybdenum 2 Reagent Solution	0.5 mL	50 mL MDB	23525-12

REQUIRED APPARATUS

Cylinder, mixing, graduated, 25 mL	1	each	1896-40
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

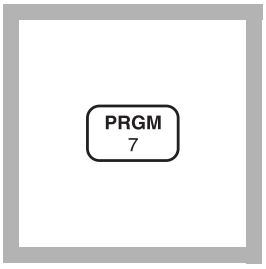
Hydrochloric Acid Solution, 1:1, 6.0 N		500 mL	884-49
Molybdenum Standard Solution, Ampule 75 mg/L Mo^{6+}, 2 mL		20/pkg	25575-20
Molybdenum Standard Solution, 10 mg/L Mo^{6+}		100 mL	14187-42
Sodium Hydroxide Standard Solution, 1.0 N		100 mL MDB	1045-32
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Cylinder, mixing, graduated, 50 mL		each	1896-41
Filter Paper, folded, 12.5 cm		100/pkg	1894-57
Funnel, poly, 65 mm		each	1083-67
pH Paper, 1-11 pH units		5 rolls/pkg	391-33
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet, volumetric, 10.00 mL, Class A		each	14515-38
Pipet Filler, safety bulb		each	14651-00
PourRite Ampule Breaker		each	24846-00

For Technical Assistance, Price and Ordering
In the U.S.A. call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

PAN Method*

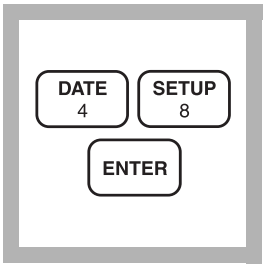


1. Enter the stored program number for nickel (Ni), PAN method.

Press: **PRGM**

The display will show:

PRGM ?

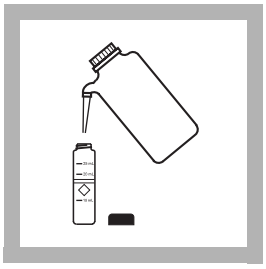


2. Press: **48 ENTER**

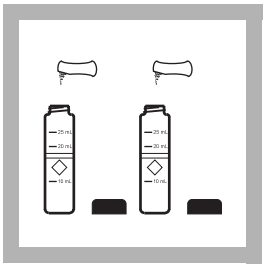
The display will show **mg/L, Ni** and the **ZERO** icon**.**

3. Fill a sample cell with 25 mL of sample (the prepared sample).

Note: *If sample is less than 10 °C (50 °F), warm to room temperature before analysis. Adjust the pH of stored samples.*

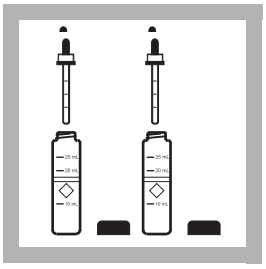


4. Fill a second sample cell with 25 mL of deionized water (the blank).



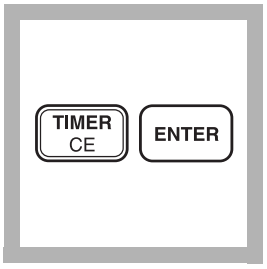
5. Add the contents of one Phthalate-Phosphate Reagent Powder Pillow to each cell. Cap. Invert several times to mix.

Note: *If sample contains iron (Fe^{3+}), all the powder must be dissolved completely before continuing with Step 6.*



6. Add 1.0 mL of 0.3% PAN Indicator Solution to each cell. Cap. Invert several times to mix.

Note: *Use the plastic dropper provided.*

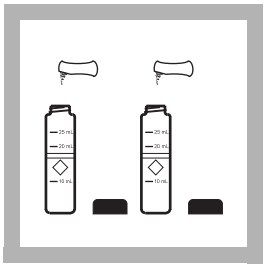


7. Press:

TIMER ENTER

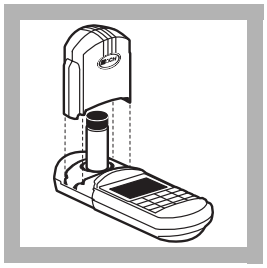
A 15-minute reaction period will begin.

Note: *The sample solution color may vary from yellowish-orange to dark red. The blank should be yellow.*

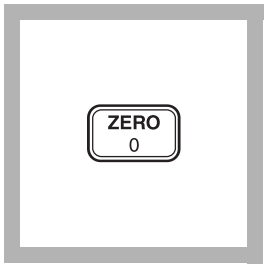


8. After the timer beeps, add the contents of one EDTA Reagent Powder Pillow to each cell. Cap. Invert several times to dissolve the reagent.

* Adapted from Watanabe, H., Talanta, 21 295 (1974)



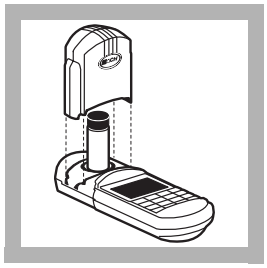
9. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



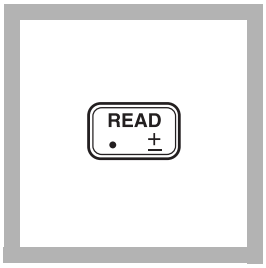
10. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.000 mg/L Ni



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L nickel will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the sample pH to between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Do not exceed pH 8 as this may cause some loss of nickel as a precipitate. Correct test results for volume additions, see *Correcting for Volume Additions*, (*Section 1*) for more information.

Accuracy Check

Standard Solution Method

Prepare a 0.5 mg/L nickel standard solution by diluting 10.0 mL of a 5 mg/L working stock solution to 100 mL in a 100-mL volumetric flask. The working stock solution should be prepared daily by diluting 5.00 mL of Nickel Standard Solution, 1000 mg/L as Ni, to 1000 mL with deionized water.

Or, using the TenSette Pipet, add 0.2 mL of a Nickel Voluette Ampule Standard Solution, 300 mg/L Ni, into a 100-mL volumetric flask. Dilute to volume with deionized water. This is a 0.6 mg/L standard solution.

Method Performance

Precision

In a single laboratory using a standard solution of 0.50 mg/L nickel and two representative lots of reagent with the instrument,

a single operator obtained a standard deviation of ±0.008 mg/L nickel.

Estimated Detection Limit

The estimated detection limit for program 48 is 0.013 mg/L Ni. For more information on the estimated detection limit, see *Section 1*.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Interfering Substance	Interference Level
Al^{3+}	32 mg/L
Ca^{2+}	1000 mg/L as ($CaCO_3$)
Cd^{2+}	20 mg/L
Cl^-	8000 mg/L
Co	Causes a positive interference at all levels.
Cr^{3+}	20 mg/L
Cr^{6+}	40 mg/L
Cu^{2+}	15 mg/L
F^-	20 mg/L
Fe^{3+}	10 mg/L
Fe^{2+}	Interferes directly and must not be present.
K^+	500 mg/L
Mg^{2+}	400 mg/L
Mn^{2+}	25 mg/L
Mo^{6+}	60 mg/L
Na^+	5000 mg/L
Pb^{2+}	20 mg/L
Zn^{2+}	30 mg/L

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and required sample pretreatment; see *pH Interferences (Section 1)*.

Chelating agents, such as EDTA, interfere. Use either the Digesdahl or vigorous digestion (*Section 2*) to eliminate this interference.

Summary of Method

After buffering the sample and masking any Fe^{3+} with pyrophosphate, the nickel is reacted with 1-(2-Pyridylazo)-2-Naphthol indicator.

The indicator forms complexes with most metals present. After color development, EDTA is added to destroy all metal-PAN complexes except nickel and cobalt.

REQUIRED REAGENTS

	Cat. No.
Nickel Reagent Set, 25 mL sample (100 tests)	22426-00
Includes: (2) 7005-99, (4) 21501-66, (2) 21502-32	

Description	Quantity Required Per Test	Unit	Cat. No.
EDTA Reagent Powder Pillows	2 pillows	100/pkg	7005-99
Phthalate-Phosphate Reagent Powder Pillows	2 pillows	50/pkg	21501-66
P.A.N. Indicator Solution, 0.3%	2 mL	100 mL MDB	21502-32
Water, deionized	10 mL	4 L	272-56

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, mixing, 25 mL	1	each	20886-40
Sample Cell, 10-20-25, w/caps	2	6/pkg	24019-06

OPTIONAL REAGENTS

Nickel Standard Solution, 1000 mg/L Ni		100 mL	14176-42
Nickel Standard Solution, Voluette Ampule, 300 mg/L Ni, 10 mL		16/pkg	14266-10
Nitric Acid, ACS		500 mL	152-49
Nitric Acid Solution, 1:1		500 mL	2540-49
Sodium Hydroxide Standard Solution, 5.0 N		100 mL MDB	2450-32

OPTIONAL APPARATUS

Ampule Breaker Kit		each	21968-00
Flask, volumetric, Class A, 100 mL		each	14574-42
Flask, volumetric, Class A, 1000 mL		each	14574-53
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable, with electrode		each	51700-10
Pipet, serological, 1 mL		each	9190-02
Pipet, serological, 5 mL		each	532-37
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Pipet, volumetric, Class A, 5.0 mL		each	14515-37
Pipet, volumetric, Class A, 10.0 mL		each	14515-38
Pipet Filler, safety bulb		each	14651-00
Thermometer, –20 to 110 °C, non-mercury		each	26357-02

For Technical Assistance, Price and Ordering

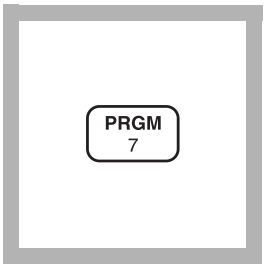
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITRATE, High Range (0 to 30.0 mg/L NO_3^--N) For water, wastewater, and seawater*

Cadmium Reduction Method (Using Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



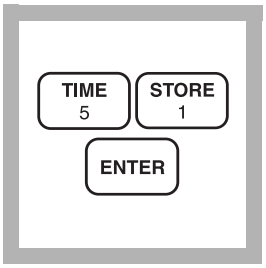
1. Enter the stored program number for high range nitrate nitrogen (NO_3^-–N) powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **51 ENTER**

The display will show **mg/L, NO3-N** and the **ZERO** icon**.**

Note: *For alternate forms (NO_3), press the* **CONC** *key.*

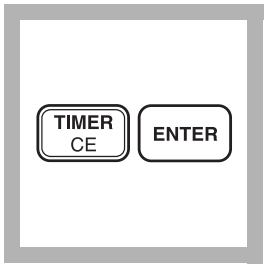
3. Fill a sample cell with 10 mL of sample.

Note: *Adjust the pH of stored samples before analysis.*

4. Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow to the sample cell (the prepared sample). Cap the sample cell.

Note: *It is important to remove all of the powder from the foil pillow. Tap the pillow until no more powder pours out.*

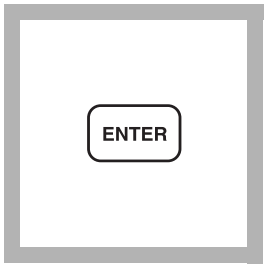
* Seawater requires a manual calibration; see Interferences.



5. Press:
TIMER ENTER

A one-minute reaction period will begin. Shake the sample cell vigorously until the timer beeps.

Note: *It is important to shake the cell vigorously. Shaking time and technique influence color development. For most accurate results, do successive tests on a standard solution and adjust the shaking time to obtain the correct result.*



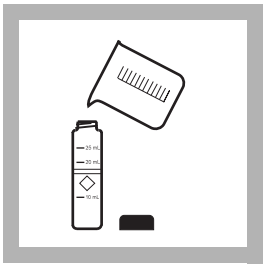
6. After the timer beeps, the display will show:
5:00 TIMER 2

Press: **ENTER**

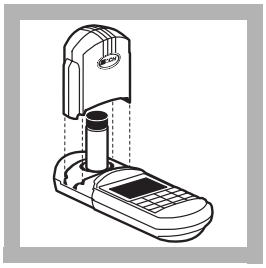
A five-minute reaction period will begin.

Note: *A deposit will remain after the reagent dissolves and will not affect test results.*

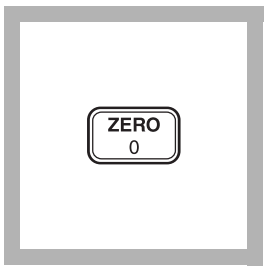
Note: *An amber color will develop if nitrate nitrogen is present.*



7. Fill another cell with 10 mL of sample (the blank). Wipe off any fingerprints or liquid.



8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

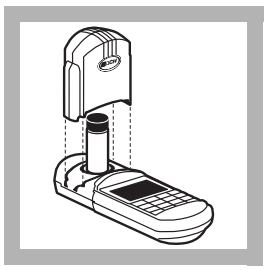


9. When the timer beeps, press **ZERO.**

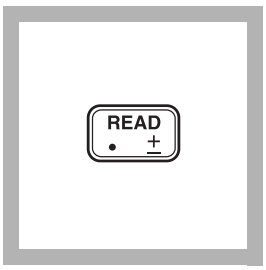
The cursor will move to the right, then the display will show:

0.0 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



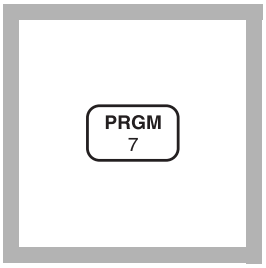
11. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3-N (or alternate form) will be displayed.

Note: *Use of the Standard Adjust feature for each new lot of reagent is highly recommended. See* Accuracy Check.

Note: *Rinse the sample cell immediately after use to remove all cadmium particles. Save the spent sample for proper hazardous waste disposal for cadmium.*

Using AccuVac Ampuls



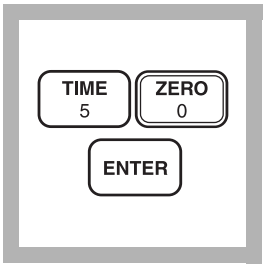
1. Enter the stored program number for high range nitrate nitrogen (NO_3^-–N) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

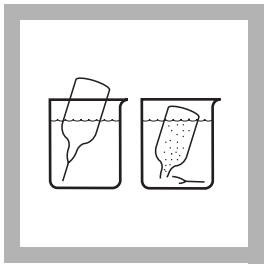
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **50 ENTER**

The display will show **mg/L, NO3-N** and the **ZERO** icon.

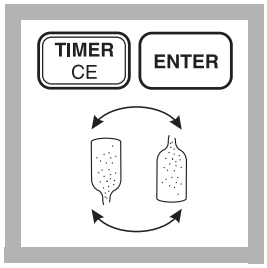
Note: *For alternate forms (NO_3), press the* **CONC** *key.*



3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitraVer 5 Nitrate AccuVac Ampul with sample. Place a stopper over the tip of the ampul.

Note: *Keep the tip immersed while the ampul fills. The ampul will not fill completely.*

Note: *Adjust the pH of stored samples before analysis.*

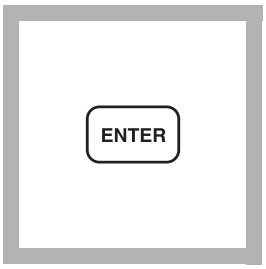


4. Press:

TIMER ENTER

A one-minute mixing period will begin. Invert the ampul repeatedly back and forth until the timer beeps. Wipe off any liquid or fingerprints.

Note: *Mixing time and technique influence color development. For most accurate results, do successive tests on a standard solution and adjust the mixing time to obtain the correct result.*



5. The display will show: **5:00 TIMER 2**

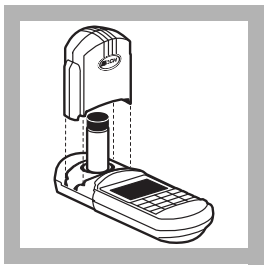
Press: **ENTER**

A five-minute reaction period will begin.

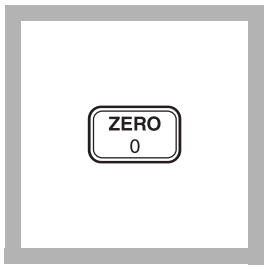
Note: *A deposit will remain after the reagent dissolves and will not affect results.*

Note: *An amber color will develop if nitrate nitrogen is present.*

6. Fill a sample cell with at least 10 mL of sample (the blank).



7. When the timer beeps, place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

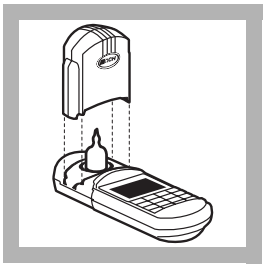


8. Press: **ZERO**

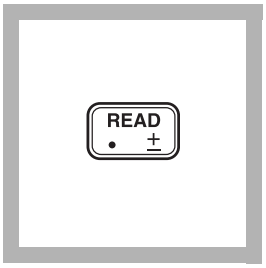
The cursor will move to the right, then the display will show:

0.0 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



9. Place the AccuVac Ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3-N (or alternate form) will be displayed.

Note: *Use of the Standard Adjust feature for each new lot of reagent is highly recommended. See* Accuracy Check.

Note: *See Pollution Prevention and Waste Management for proper disposal of cadmium.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution.

Do not use mercury compounds as preservatives.

Correct the test result for volume additions; see *Correction for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL mixing cylinders with 25 mL of sample.

b) Snap the neck off a Nitrate Nitrogen Ampule Standard,

500 mg/L nitrate nitrogen.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of Nitrate Nitrogen Standard Solution to the three samples. Stopper and
mix thoroughly.

d) For AccuVac analysis, transfer the solutions to clean, dry 50-mL beakers. For analysis with powder pillows, transfer only 10 mL of solution to clean, dry sample cells.

e) Analyze each sample as described above. The nitrate nitrogen (NO_3^--N) concentration should increase 2.0 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* (*Section 1*) for more information.

Standard Solution Method
Use a Hach Nitrate-Nitrogen Standard Solution, 10.0 mg/L NO_3^--N, listed under Optional Reagents as the sample and perform the procedure as described above.

Standard Adjust
To adjust the calibration curve using the reading obtained with the 10.0-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **10.0** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the curve adjustment. See *Section 1, Standard Curve Adjustmen*t for more information. If you are using a reagent blank correction, the blank correction should be entered before the Standard Adjust value is entered.

Method Performance

Precision
In a single laboratory using standard solutions of 25.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.3 mg/L nitrate nitrogen for program #50 and ±1.7 mg/L nitrate nitrogen for program # 51.

Estimated Detection Limit

The estimated detection limit for program 50 is 0.5 mg/L NO_3^--N and 0.8 mg/L NO_3^--N for program 51. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration.
Ferric iron	All levels
Nitrite	All levels Compensate for nitrite interference as follows: Add 30-g/L Bromine Water dropwise to the sample in Step 3 until a yellow color remains. Add one drop of 30-g/L Phenol Solution to destroy the color. Proceed with Step 4. Report the results as total nitrate and nitrite.
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels.

Summary Of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to gentisic acid to form an amber-colored product.

Pollution Prevention and Waste Management

NitraVer 5 contains cadmium metal. Both samples and reagent blanks will contain cadmium (D006) at a concentration regulated as hazardous wastes by the Federal RCRA. Do not pour these solutions down the drain. See *Section 3* for more information on proper disposal of these materials.

NITRATE, High Range, continued

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent Powder Pillows	1 pillow	100/pkg	21061-69
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

REQUIRED REAGENTS (Using AccuVac Ampuls)

NitraVer 5 Nitrate Reagent AccuVac Ampul	1 ampul	25/pkg	25110-25

REQUIRED APPARATUS (Using AccuVac Ampuls)

Beaker, 50 mL	1	each	500-41H
Stopper	1	6/pkg	1731-06

OPTIONAL REAGENTS

Bromine Water 30 g/L	29 mL*		2211-20
Nitrate Nitrogen Standard Solution, 10.0 mg/L as (NO_3^--N)	500 mL		307-49
Nitrate Nitrogen Standard Solution, 1000 mg/L as (NO_3^--N)	500 mL		12792-49
Nitrate Nitrogen Standard Solution, PourRite ampule, 500 mg/L as NO_3^--N, 2 mL		20/pkg	14260-20
Phenol Solution	29 mL		2112-20
Sodium Hydroxide Standard Solution, 5.0 N	50 mL*		2450-26
Sulfuric Acid, ACS	500 mL*		979-49
Water, deionized	4 L		272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Cylinder, graduated, mixing, 25 mL		each	1896-40
Dropper, for 29-mL bottle		each	2258-00
pH Indicator Paper, 1 to 11 pH		5 rolls/pkg	391-33
pH Meter, *sens**ion***™***1**, portable, with electrode		each	51700-10
Pipet Filler, safety bulb		each	14651-00
Pipet, serological, 2 mL		each	532-36
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
PourRite Ampule Breaker		each	24846-00
Thermometer, –20 to 110 °C, non-mercury		each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A. call 800-227-4224

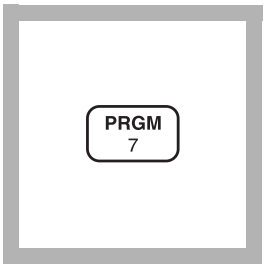
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes.

NITRATE, Mid Range (0 to 5.0 mg/L NO_3^--N) For water, wastewater and seawater*

Cadmium Reduction Method (Using Powder Pillows or AccuVac Ampuls)

Using Powder Pillows



1. Enter the stored program number for medium range nitrate nitrogen using powder pillows.

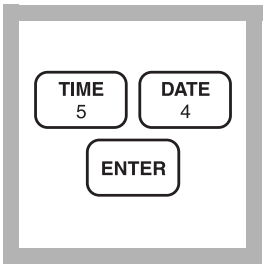
Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

Note: *Adjust the pH of stored samples before analysis.*

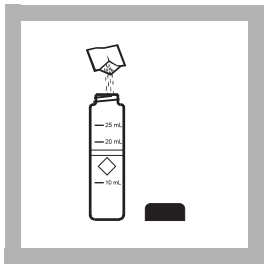


2. Press: **54 ENTER**

The display will show **mg/L, NO3-N** and the **ZERO** icon**.**

Note: *For alternate form (NO_3), press the* **CONC** *key.*

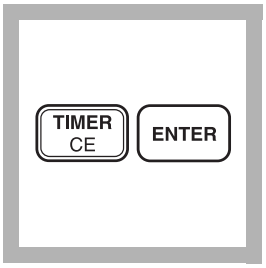
3. Fill two sample cells with 10 mL of sample each. One cell will be the prepared sample, the other is the blank. Set the blank aside.



4. Add the contents of one NitraVer 5 Nitrate Reagent Powder Pillow to one cell (the prepared sample). Cap the cell.

Note: *It is necessary to remove all the powder from the foil pouch by tapping repeatedly until no more powder comes out.*

* Seawater requires a manual calibration; see *Interferences*.

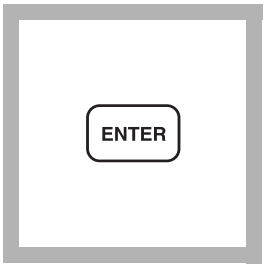


5. Press:

TIMER ENTER

A one-minute reaction period will begin. Shake the sample vigorously until the timer beeps.

Note: *Shaking time and technique influence color development. Low results usually occur if shaking is not vigorous enough. For most accurate results, do successive tests on a standard solution and adjust the shaking time by ±1 minute to obtain the correct result. See the Accuracy Check section for more information.*



6. After the timer beeps, the display will show:
5:00 TIMER 2

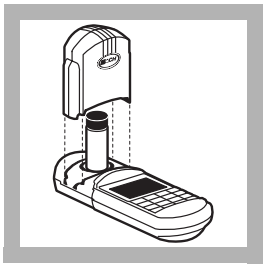
Press: **ENTER**

A five-minute reaction period will begin.

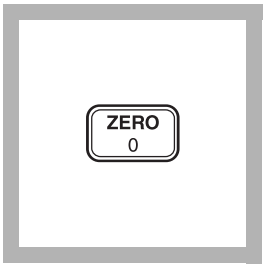
Note: *A cadmium deposit will remain after the NitraVer 5 Nitrate Reagent Powder dissolves and will not affect test results.*

Note: *An amber color will develop if nitrate nitrogen is present.*

7. After the timer beeps, wipe off any liquid or fingerprints.



8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

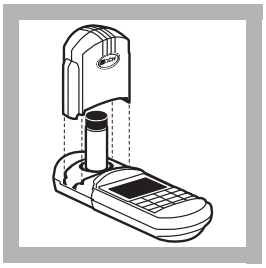


9. Press: **ZERO**

The cursor will move to the right, then the display will show:

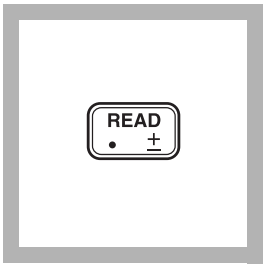
0.0 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit".*



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Read the sample within two minutes after the timer beeps.*



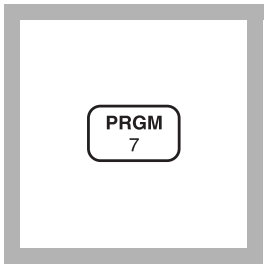
11. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3-N (or NO_3) will be displayed.

Note: *Use of the standard adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Note: *Rinse the sample cell immediately after use to remove all the cadmium particles. See Pollution Prevention and Waste Management following these steps for disposal of cadmium particles.*

Using AccuVac Ampuls



1. Enter the stored program number for medium range nitrate nitrogen using AccuVac Ampuls.

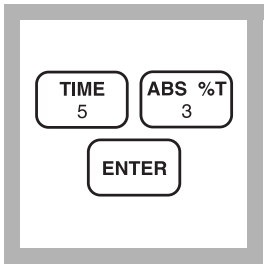
Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

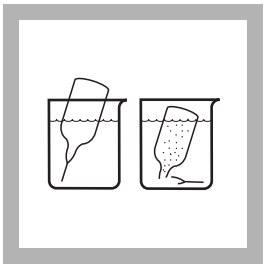
Note: *Adjust the pH of stored samples before analysis.*



2. Press: **53 ENTER**

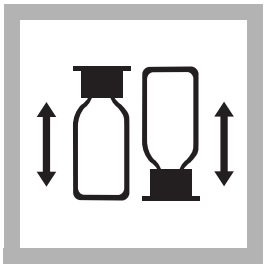
The display will show **mg/L, NO3-N** and the **ZERO** icon**.**

Note: *For alternate form (NO_3), press the* **CONC** *key.*



3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitraVer 5 Nitrate AccuVac Ampul with sample. Place a stopper over the tip of the ampul.

Note: *Keep the tip immersed while the ampul fills. The ampul will not fill completely to allow room for mixing.*

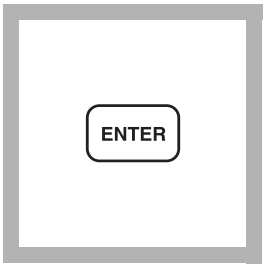


4. Press:

TIMER ENTER

A one-minute mixing period will begin. Invert the ampul repeatedly back and forth until the timer beeps. Wipe off any liquid or fingerprints after mixing.

Note: *Mixing speed and technique influence color development. For most accurate results, do successive tests on a standard solution and increase or decrease the mixing time to obtain the correct result. See Accuracy Check for more information.*



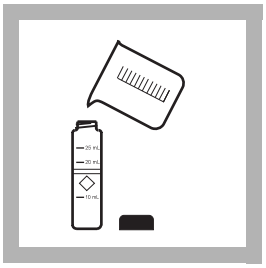
5. After the timer beeps, the display will show:
05:00 Timer 2

Press: **ENTER**

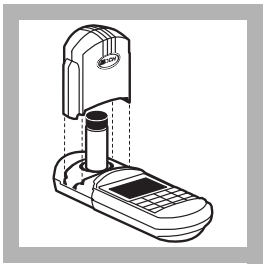
A five-minute reaction period will begin.

Note: *A cadmium deposit will remain after the NitraVer 5 Nitrate Reagent Powder dissolves and will not affect results.*

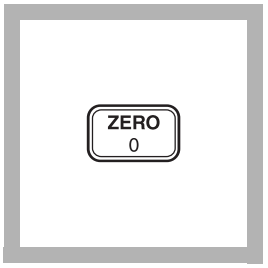
Note: *An amber color will develop if nitrate nitrogen is present.*



6. Fill a sample cell with at least 10 mL of sample (the blank).



7. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

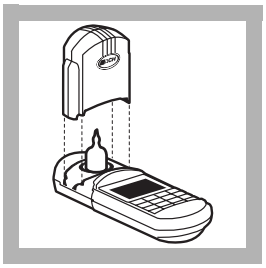


8. Press: **ZERO**

The cursor will move to the right, then the display will show:

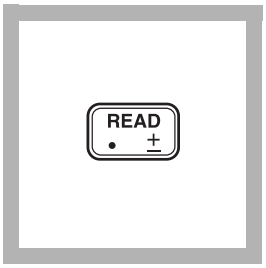
0.0 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



9. Place the AccuVac ampul into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Read the sample within two minutes after the timer beeps.*



10. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3-N (or NO_3) will be displayed.

Note: *Use of the standard adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution.

Do not use mercury compounds as preservatives.

Correct the test result for volume additions; see *Correction for Volume Additions*, (*Section 1)* for more information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Nitrate Nitrogen Ampule Standard Solution, 100 mg/L NO_3^--N.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the standard to the three samples. Stopper and mix well.

d) For analysis with AccuVac Ampuls, transfer the solutions to dry, clean 50 mL beakers. For analysis with powder pillows, transfer only 10 mL of the solution to dry, clean sample cells.

e) Analyze each sample as described above. The nitrate nitrogen (NO_3^--N) concentration should increase 0.4 mg/L for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* (*Section 1*) for more information.

Standard Solution Method

A 1.0 mg/L Nitrate Nitrogen Standard Solution is available from Hach. Use this standard in place of sample in the above procedure.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 1.00-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **1.0** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment . See *Section 1, Standard*

*Curve Adjustmen*t for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 3.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of powder pillows with the instrument, a single operator obtained a standard deviation of ±0.2 mg/L nitrate nitrogen.

In a single laboratory using a standard solution of 3.0 mg/L NO_3^--N and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.1 mg/L nitrate nitrogen.

Estimated Detection Limit

The estimated detection limit for programs 53 and 54 is 0.2 mg/L NO_3-N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration.
Ferric iron	All levels
Nitrite	All levels interfere. Compensate for nitrite interference as follows: **1.** Add 30-g/L Bromine Water dropwise to the sample in Step 3 until a yellow color remains. **2.** Add one drop of 30-g/L Phenol Solution to destroy the color. **3.** Proceed with Step 3. Report the results as total nitrate and nitrite.
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels.

Summary of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to gentisic acid to form an amber-colored product.

Pollution Prevention and Waste Management

NitraVer 5 contains cadmium metal. Both samples and reagent

blanks will contain cadmium (D006) at a concentration regulated as hazardous waste by the Federal RCRA. Do not pour these solutions down the drain. See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS AND APPARATUS (Using Powder Pillows)

Description	Qty/ Test	Unit	Cat. No.
NitraVer 5 Nitrate Reagent Powder Pillows	1 pillow	100/pkg	21061-69
Sample Cell, 10-20-25 mL, w/ caps	2	6/pkg	24019-06

REQUIRED REAGENTS (Using AccuVac Ampuls)

NitraVer 5 Nitrate Reagent AccuVac Ampul	1 ampul	25/pkg	25110-25

REQUIRED APPARATUS (Using AccuVac Ampuls)

Beaker, 50 mL	1	each	500-41
Stopper	1	6/pkg	1731-06

OPTIONAL REAGENTS

Bromine Water 30 g/L		29 mL*	2211-20
Drinking Water Standard, Inorganics, (Fe^{-}, NO_3^{-}, SO_4^{2-}, PO_4^{3-})		500 mL	28330-49
Nitrate Nitrogen Standard Solution, 1.0 mg/L as NO_3^{-}-N		500 mL	2046-49
Nitrate Nitrogen Standard Solution, 100 mg/L as NO_3^{-}-N		500 mL	1947-49
Nitrate Nitrogen Standard Solution, PourRite Ampule, 100 mg/L as NO_3^{-}-N, 2 mL		20/pkg	1947-20
Phenol Solution, 30 g/L		29 mL	2112-20
Sodium Hydroxide Standard Solution, 5.0 N		50 mL SCDB*	2450-26
Sulfuric Acid, ACS		500 mL*	979-49
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Cylinder, graduated, mixing, 25 mL		each	20886-40
Dropper, for 1-oz bottle		each	2258-00
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable, with electrode		each	51700-10
Pipet Filler, safety bulb		each	14651-00
Pipet, serological, 2 mL		each	532-36
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
PourRite Ampule Breaker		each	24846-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

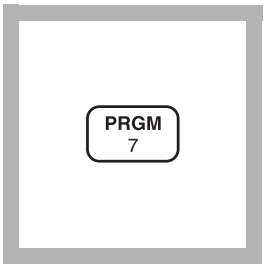
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes.

NITRATE, Low Range (0 to 0.50 mg/L NO_3^--N)

For water, wastewater and seawater*

Cadmium Reduction Method



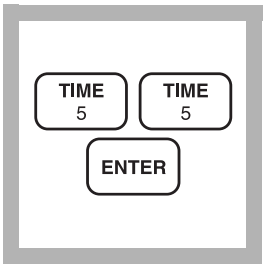
1. Enter the stored program number for low range nitrate nitrogen (NO_3^--N).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



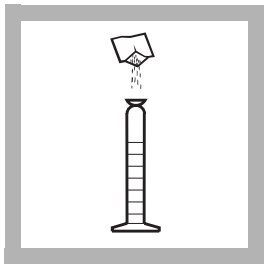
2. Press: **55 ENTER**

The display will show **mg/L, NO3-N** and the **ZERO** icon**.**

Note: *For alternate forms (NO_3), press the* **CONC** *key.*

3. Fill a 25-mL graduated mixing cylinder to the 15-mL mark with sample.

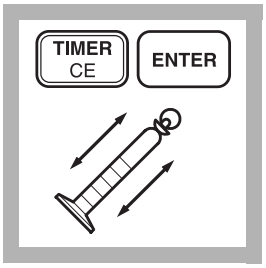
Note: *Adjust the pH of stored samples before analysis.*



4. Add the contents of one NitraVer 6 Nitrate Reagent Powder Pillow to the cylinder. Stopper.

Note: *It is necessary to remove* ***all*** *the powder from the foil pillow. Tap the pillow until no more powder pours out. Be sure to remove powder from the corners of the pillow.*

* Seawater requires a manual calibration; see Interferences.

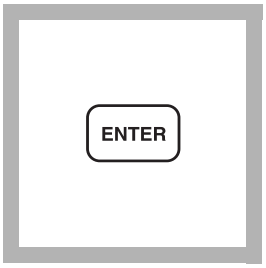


5. Press:

TIMER ENTER

A 3-minute reaction period will begin. Shake the cylinder vigorously throughout this three minute period.

Note: *Shaking time and technique influence color development. For most accurate results, analyze a standard solution several times and adjust the shaking time to obtain the correct result.*

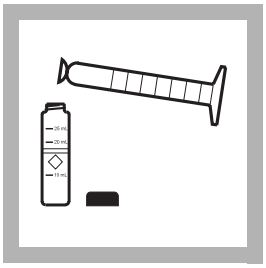


6. When the timer beeps, the display will show: **2:00 TIMER 2**

Press: **ENTER**

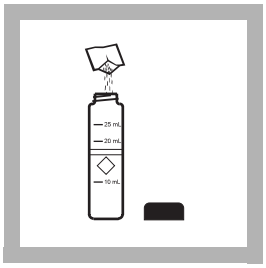
A 2-minute reaction period will begin.

Note: *A deposit will remain after the powder dissolves and will not affect results.*



7. When the timer beeps, pour 10 mL of the sample into a sample cell.

Note: *Do not transfer any cadmium particles.*



8. Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell (the prepared sample). Cap the cell and shake gently for 30 seconds.

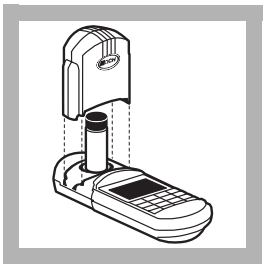
Note: *A pink color will form if nitrate is present.*

9. The display will show: **15:00 TIMER 3**

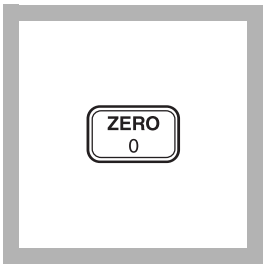
Press: **ENTER**

A 15-minute reaction period will begin.

Fill another sample cell (the blank) with 10 mL of sample.



10. When the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

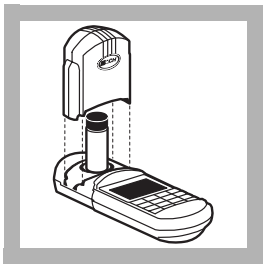


11. Press: **ZERO**

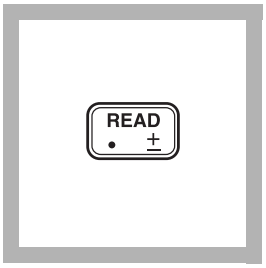
The cursor will move to the right, then the display will show:

0.00 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



12. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



13. Press: **READ**

The cursor will move to the right, then the result in mg/L NO_3^--N (or alternate form) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Note: *Rinse the sample cell and cylinder immediately after use to remove all cadmium particles.*

Note: *See Pollution Prevention and Waste Management for proper disposal of cadmium.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods, adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution. Do not use mercury compounds as preservatives. Correct the test result for volume additions; see *Correction for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard additions Method

a) Fill three 25-mL graduated mixing cylinders with 15 mL of sample.

b) Snap the neck off a Nitrate Nitrogen Ampule Standard Solution, 12.0 mg/L NO_3^--N.

c) Using the TenSette Pipet, add 0.1, 0.2, and 0.3 mL of the standard to the three samples. Stopper and mix well.

d) Analyze each sample as described above. The nitrate nitrogen concentration should increase 0.08 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* (Section 1) for more information.

Standard Solution Method

Prepare a 0.20 mg/L nitrate nitrogen standard by diluting 2.00 mL of a
10.0 mg/L Nitrate Nitrogen Standard Solution to 100.0 mL with deionized water. Use this standard in place of sample in Step 3.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 0.20-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **0.20** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the curve adjustment. If you are using a reagent blank correction, the blank correction should be entered before the Standard Adjust feature is entered. See *Section 1, Standard Curve Adjustmen*t for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 0.25 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of $\pm$0.03 mg/L nitrate nitrogen.

Estimated Detection Limit

The estimated detection limit for program 55 is 0.01 mg/L NO_3^--N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Calcium	100 mg/L
Chloride	Chloride concentrations above 100 mg/L will cause low results. The test may be used at high chloride concentrations (seawater) but a calibration must be done using standards spiked to the same chloride concentration.
Ferric iron	All levels
Nitrite	All levels: This method measures both the nitrate and nitrite in the sample. If nitrite is present, the nitrite nitrogen test Program 60 should be done on the sample. Pretreat the nitrate nitrogen sample with the following pretreatment. Then subtract the amount of nitrite found from the results of the LR nitrate nitrogen test using the pretreated sample. **1.** Add 30-g/L Bromine Water dropwise to the sample in Step 3 until a yellow color remains. Mix after each drop. **2.** Add one drop of 30-g/L Phenol Solution to destroy the yellow color. **3.** Proceed with the LR Nitrate procedure.
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.
Strong oxidizing and reducing substances	Interfere at all levels

Summary of Method

Cadmium metal reduces nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt which couples to chromotropic acid to form a pink-colored product.

Pollution Prevention and Waste Management

NitaVer 6 contains cadmium metal. Both samples and reagent blanks will contain cadmium (D006) at a concentration regulated as hazardous wastes by the Federal RCRA. Do not pour these solutions down the drain. See *Section 3* for more information on proper disposal of these materials.

NITRATE, Low Range, continued

REQUIRED REAGENTS

Low Range Nitrate Reagent Set (100 tests) 24298-00
Includes: (1) 21071-69, (1) 21072-49

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent Powder Pillows	1 pillow	100/pkg	21071-69
NitraVer 6 Nitrate Reagent Powder Pillows	1 pillow	100/pkg	21072-49

REQUIRED APPARATUS

Cylinder, graduated, mixing, 25 mL	1	each	1896-40
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Bromine Water, 30 g/L	29 mL*	2211-20
Nitrate Nitrogen Standard Solution, 10.0 mg/L as NO_3^--N	500 mL	307-49
Nitrate Nitrogen Standard Solution, Voluette ampule, 12 mg/L as NO_3^--N, 10 mL	16/pkg	14333-10
Phenol Solution, 30 g/L	29 mL	2112-20
Pretreatment Kit, contains: (1) 2112-20, (1) 2211-20	each	2268-00
Sodium Hydroxide Standard Solution, 5.0 N	50 mL* SCDB	2450-26
Sulfuric Acid, ACS	500 mL*	979-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker	each		21968-00
Dropper, for 29-mL bottle	each		2258-00
Flask, volumetric, Class A, 100 mL	each		14574-42
pH Indicator Paper, 1 to 11 pH	5-roll/pkg		391-33
pH Meter, *sens**ion**™1*, portable, with electrode	each		51700-10
Pipet, serological, 2 mL	each		532-36
Pipet, TenSette, 0.1 to 1.0 mL	each		19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg		21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg		21856-28
Pipet, volumetric, Class A, 2.00 mL	each		14515-36
Pipet Filler, safety bulb	each		14651-00
Thermometer, –20 to 110 °C	each		26357-02

Nitrate at these levels can also be determined directly using the Nitrate Ion Selective Electrode (Cat. No. 23488-00).

For Technical Assistance, Price and Ordering

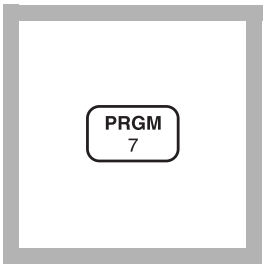
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Contact Hach for larger sizes

NITRATE, High Range, Test ‘N Tube (0 to 30.0 mg/L NO_3^--N)

Chromotropic Acid Method

For water and wastewater



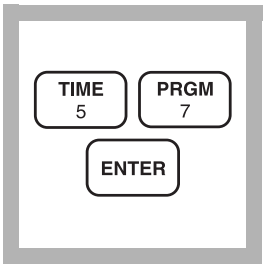
1. Enter the stored program number for Test ‘N Tube nitrate nitrogen (NO_3^--N).

Press: **PRGM**

The display will show:

PRGM ?

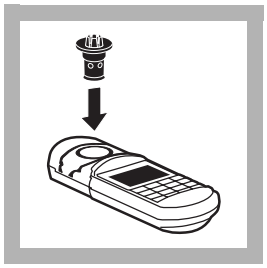
Note: *If samples cannot be analyzed immediately, see Sampling and Storage on page 321.*



2. Press: **57 ENTER**

The display will show **mg/L, NO3-N** and the **ZERO** icon**.**

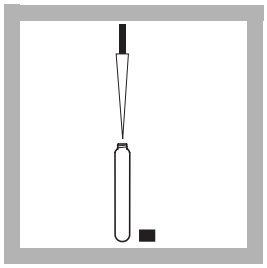
Note: *For alternate forms (NO_3) press the* **CONC** *key.*



3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

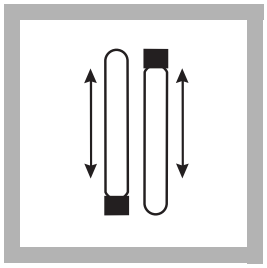
Note: *For proof of accuracy, use a 20 mg/L NO_3^--N standard in place of the sample.*

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



4. Remove the cap from a Nitrate Pretreatment Solution Vial and add 1 mL of sample (the blank).

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

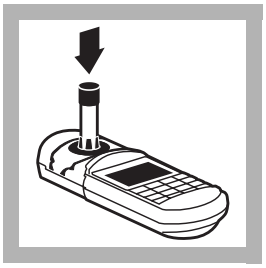


5. Cap the tube and invert 10 times to mix.

Note: *This test is technique-sensitive. Low results may occur if these instructions are not followed. Hold the vial vertical with the cap up. Invert the vial so the cap points down. Wait for all of the solution to flow to the cap end. Pause. Return the vial to the upright position. Wait for all the solution to flow to the vial bottom. This process equals 1 inversion. Do this 10 times.*

6. Clean the outside of the vial with a towel.

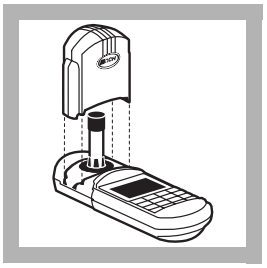
Note: *Wipe with a damp towel and follow with a dry one to remove fingerprints and other marks.*



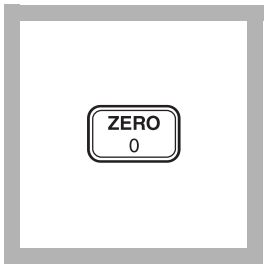
7. Place the blank in the vial adapter with the Hach logo facing the front of the instrument.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



8. Cover the vial tightly with the instrument cap.

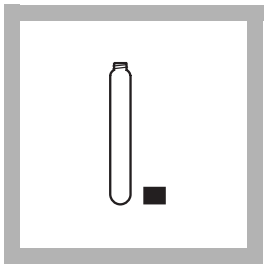


9. Press: **ZERO**

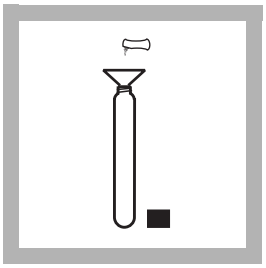
The cursor will move to the right, then the display will show:

0.0 mg/L NO3-N

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



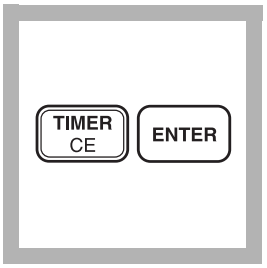
10. Remove the vial from the instrument. Remove the cap from the vial.



11. Using a funnel, add the contents of one NitraVer X Reagent B Powder Pillow to the vial. Cap. Invert 10 times to mix (this will be the prepared sample).

Note: *See Step 5 for inversion instructions*

Note: *Some solid matter will not dissolve.*



12. Press:

TIMER ENTER

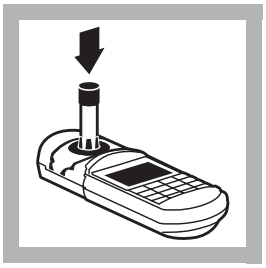
A five-minute reaction period will begin. Do not invert the vial again.

Note: *A yellow color will develop if nitrate nitrogen is present.*

Note: *Complete Steps 13-16 within five minutes after the timer beeps.*

NITRATE, High Range, Test 'N Tube, continued

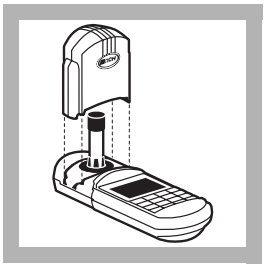
13. After the timer beeps, clean the outside of the vial with a damp towel and follow with a dry one to remove fingerprints and other marks.



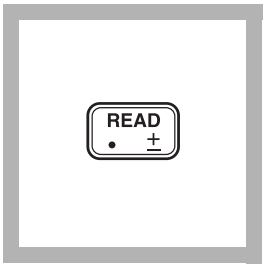
14. Place the prepared sample in the adapter with the Hach logo facing the front of the instrument.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



15. Cover the vial tightly with the instrument cap.



16. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrate nitrogen (NO_3-N) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Store at 4 °C (39 °F) or lower if the sample is to be analyzed within 24 to 48 hours. Warm to room temperature before running the test. For longer storage periods (up to 14 days), adjust sample pH to 2 or less with sulfuric acid, ACS (about 2 mL per liter). Sample refrigeration is still required.

Before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution.

Do not use mercury compounds as preservatives.

Correct the test result for volume additions; see *Correction for Volume Additions* in *Section 1* for more information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a fresh High Range Nitrate Nitrogen Voluette Ampule Standard, 500 mg/L NO_3^--N.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to the three mixing cylinders, respectively. Mix each thoroughly.

d) Analyze each sample as described in the procedure; use a 1-mL aliquot of the spiked sample in each test. The nitrogen concentration should increase 2.0 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* (*Section 1*) for more information.

Standard Solution Method

To test accuracy, prepare a 20.0 mg/L nitrate nitrogen standard solution by pipetting 2.00 mL of a High Range Nitrate Nitrogen Voluette Ampule Standard Solution, 500 mg/L NO_3^--N, into a 50 mL Class A volumetric flask. Dilute to the line with deionized water. Substitute this standard for the sample and perform the test as described in the procedure.

Method Performance

Precision

In a single laboratory, using a standard solution of 25.0 mg/L nitrate nitrogen (NO_3^--N) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ± 0.5 mg/L NO_3-N.

Estimated Detection Limit

The estimated detection limit for program 57 is 0.3 mg/L NO_3-N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level
Barium	A negative interference at concentrations greater than 1 mg/L.
Chloride	Does not interfere below 1000 mg/L.
Hardness	Does not interfere.
Nitrite	A positive interference at concentrations greater than 12 mg/L. Remove nitrite interference up to 100 mg/L by adding 400 mg of urea (one full 0.5 g Hach measuring spoon) to 10 mL of sample. Swirl to dissolve. Proceed with the nitrate test as usual.

Summary of Method

Nitrate in the sample reacts with chromotropic acid under strongly acidic conditions to yield a yellow product with a maximum absorbance at 410 nm.

NITRATE, High Range, Test 'N Tube, continued

REQUIRED REAGENTS

	Cat. No.
NitraVer X Nitrate, High Range Test 'N Tube Reagent Set (50 tests)	26053-45
Includes: (1) 26055-46, (1) 272-42, *(50) Nitrate Pretreatment Solution Vials	

Description	Quantity Required Per Test	Unit	Cat. No.
Nitrate Pretreatment Solution Vials	1	50/pkg	*
NitraVer X Reagent B Powder Pillows	1	50/pkg	26055-46

REQUIRED APPARATUS

COD Vial Adapter	1	each	48464-00
Funnel, micro	1	each	25843-35
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	varies	50/pkg	21856-96
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Nitrate-Nitrogen Standard Solution, Voluette Ampules, 500 mg/L N		16/pkg	14260-10
Sodium Hydroxide Standard Solution, 5.0 N		50 mL	2450-26
Sulfuric Acid, ACS, concentrated		500 mL	979-49
Urea, ACS		100 g	11237-26
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit		each	21968-00
Cylinder, graduated, mixing, 25-mL (3 required)		each	26363-40
Flask, volumetric, Class A, 50 mL		each	14574-41
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
Pipet, volumetric, Class A, 2 mL		each	14515-36
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Spoon, measuring, 0.5 g		each	907-00

For Technical Assistance, Price and Ordering

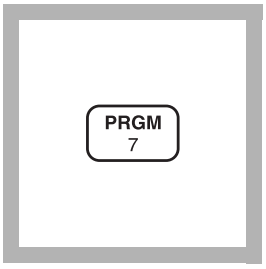
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Not available separately.

NITRITE, High Range (0 to 150 mg/L NO_2^-)

Ferrous Sulfate Method*



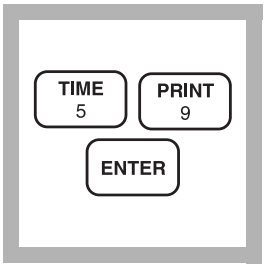
1. Enter the stored program number for high range nitrite (NO_2^-).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

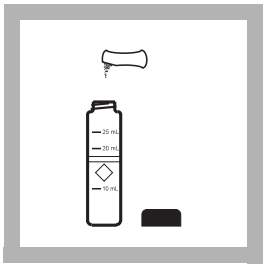


2. Press: **59 ENTER**

The display will show **mg/L, NO2** and the **ZERO** icon**.**

Note: *For alternate forms (NO_2-N, $NaNO_2$), press the* **CONC** *key.*

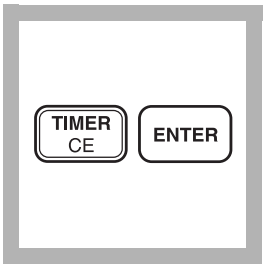
3. Fill a sample cell with 10 mL of sample.



4. Add the contents of one NitriVer 2 Nitrite Reagent Powder Pillow. Cap the cell and invert 5-7 times to mix (the prepared sample).

Note: *A greenish-brown color will develop if nitrite is present.*

Note: *Avoid excessive mixing or low results may occur. Accuracy is not affected by undissolved powder.*

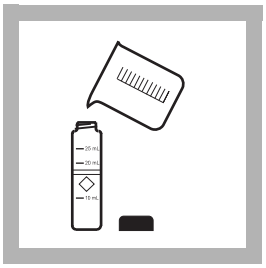


5. Press:

TIMER ENTER

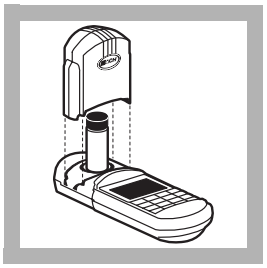
A ten-minute reaction period will begin.

Do not move or disturb the sample cell during this reaction period.

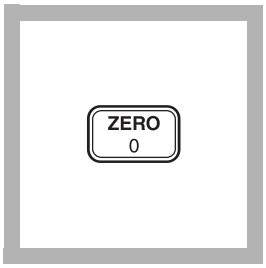


6. Fill another sample cell with 10 mL of sample (the blank). Clean the outside of the cells with a towel.

Note: *Wiping with a damp towel, followed by a dry one, removes fingerprints and other marks.*



7. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



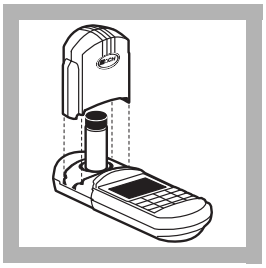
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L NO2

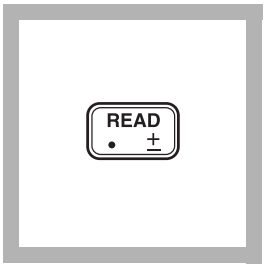
Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*

* Adapted from McAlpine, R. and Soule, B., *Qualitative Chemical Analysis*, New York, 476,575 (1933)



9. After the timer beeps, gently invert the prepared sample twice. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Avoid excessive mixing or low results may occur.*



10. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrite will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. If prompt analysis is impossible, store at 4 °C (39 °F) or lower if the sample is to be analyzed within 48 hours. Warm to room temperature before running the test. Do not use acid preservatives. Remove suspended solids by filtration.

Accuracy Check

Standard Solution Method

Dissolve 0.150 grams of fresh sodium nitrite and dilute to 1000 mL with deionized water to prepare a 100 mg/L nitrite standard solution. Prepare this solution daily.

Alternatively, make a dilution of a fresh Hach Nitrite Standard Solution, 821 mg/L NO_2^- (250 mg/L NO_2^--N) using Class A glassware. Dilute 10 mL of this standard to 100 mL with deionized water to give an
82 mg/L nitrite standard. Prepare this solution just before use. Using this solution as the sample, perform the nitrite procedure as described above.

NITRITE, High Range, continued

Method Performance

Precision

In a single laboratory using a standard solution of 123 mg/L nitrite and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of ±1 mg/L nitrite.

Estimated Detection Limit

The estimated detection limit for program 59 is 2 mg/L NO_2^-. For more information on the estimated detection limit, see *Section 1*.

Interferences

This test does not measure nitrates nor is it applicable to glycol based samples. Dilute glycol based samples and follow the Low Range Nitrite Procedure.

Summary of Method

The method uses ferrous sulfate in an acidic medium to reduce nitrite to nitrous oxide. Ferrous ions combine with the nitrous oxide to form a greenish-brown complex in direct proportion to the nitrite present.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 2 Nitrite Reagent Powder Pillows	1 pillow	100/pkg	21075-69
Sample cell, 10-20-25, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Nitrite Standard Solution, 821 mg/L NO_2 (250 mg/L NO_2^--N)	500 mL		23402-49
Sodium Nitrite, ACS	454 g		2452-01
Water, deionized	4 L		272-56

OPTIONAL APPARATUS

Balance, analytical, 110 V, Acculab UI Series, 120 g		each	26947-00
Flask, volumetric, 1000 mL		each	14547-53
Flask, volumetric, 100 mL, Class A		each	14574-42
Pipet, volumetric, 10.00 mL, Class A		each	14515-38
Pipet Filler, safety bulb		each	14651-00

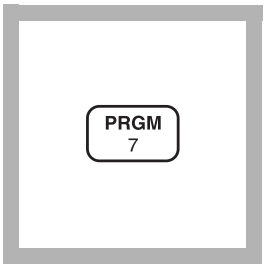
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITRITE, Low Range (0 to 0.350 mg/L NO_2^--N) For water, wastewater, seawater

Diazotization Method* (Powder Pillows or AccuVac Ampuls);
USEPA approved for reporting wastewater and drinking water analyses.



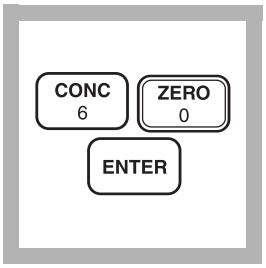
1. Enter the stored program number for nitrite nitrogen (NO_2^--N), powder pillows.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **60 ENTER**

The display will show **mg/L, NO2-N** and the **ZERO** icon.

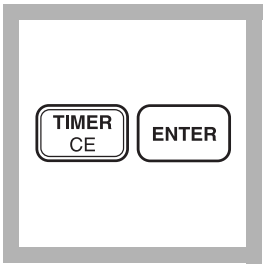
Note: *For alternate forms (NO_2^-, $NaNO_2$), press the* **CONC** *key.*

3. Fill a sample cell with 10 mL of sample.

4. Add the contents of one NitriVer 3 Nitrite Reagent Powder Pillow to the sample cell. Cap the cell and shake to dissolve.

Note: *Accuracy is not affected by undissolved powder.*

* *Federal Register*, 44(85) 25505 (May 1, 1979)

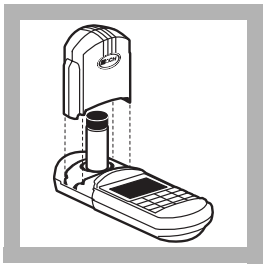


5. Press:
TIMER ENTER

A 15-minute reaction period will begin.

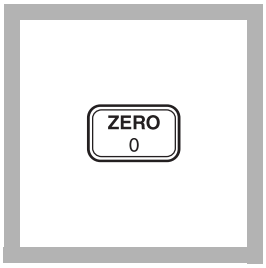
Note: *A pink color will develop if nitrite is present.*

6. When the timer beeps, fill an empty sample cell with 10 mL of sample (the blank).



7. Wipe the outside of the sample cell with a towel. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Wiping with a damp cloth, followed by a dry pne, removes fingerprints and other marks.*

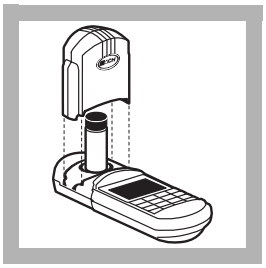


8. Press: **ZERO**

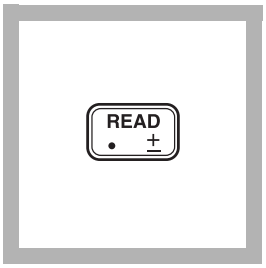
The cursor will move to the right, then the display will show:

0.000 mg/L NO2-N

Note: *If Reagent Blank Correction is on, the display may flash "limit." See Section 1.*



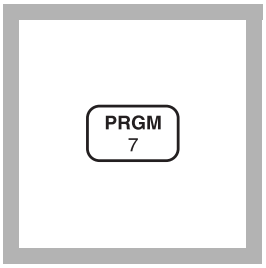
9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrite nitrogen (or an alternate form) will be displayed.

Using AccuVac Ampuls



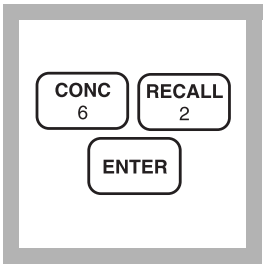
1. Enter the stored program number for nitrite nitrogen (NO_2^--N), AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

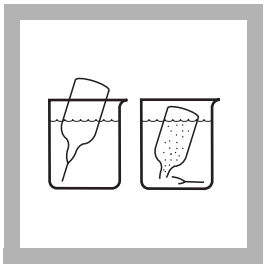
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **62 ENTER**

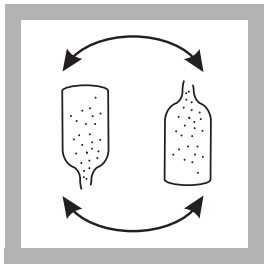
The display will show **mg/L, NO2-N** and the **ZERO** icon**.**

Note: *For alternate forms (NO_2^-, $NaNO_2$), press the* **CONC** *key.*



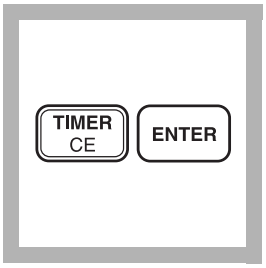
3. Collect at least 40 mL of sample in a 50-mL beaker. Fill a NitriVer 3 Nitrite AccuVac Ampul with the sample.

Note: *Keep the tip immersed while the ampul fills completely.*



4. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *Accuracy is not affected by undissolved powder.*

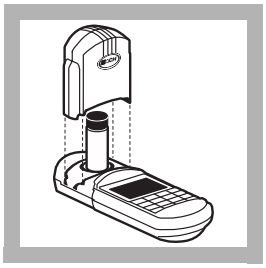


5. Press:
TIMER ENTER

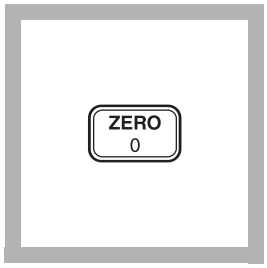
A 15-minute reaction period will begin.

Note: *A pink color will develop if nitrite is present.*

6. When the timer beeps, fill a sample cell with at least 10 mL of sample (the blank).



7. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

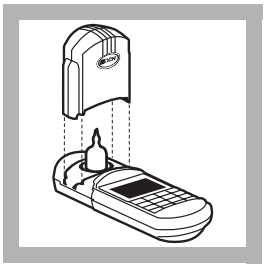


8. Press: **ZERO**

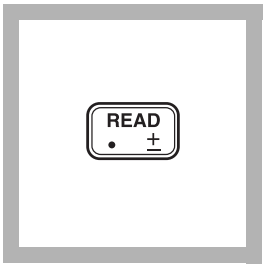
The cursor will move to the right, then the display will show:

0.000 mg/L NO2-N

Note: *If Reagent Blank Correction is on, the display may flash "limit." See Section 1.*



9. Place the AccuVac Ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrite nitrogen will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles.

Store at 4 °C (39 °F) or lower and analyze within 48 hours. Warm to room temperature before running the test.

Do not use acid preservatives.

Remove the suspended solids by filtration.

Accuracy Check

Standard Solution Method

Pipet 5.00 mL of a fresh 250 mg/L NO_2^--N standard into a 250.0 mL volumetric flask. Dilute to the mark with deionized water. This makes a 5.00-mg/L intermediate standard. To prepare a 0.100-mg/L NO_2^--N standard solution, dilute 10.00 mL of the 5.00-mg/L intermediate standard to 500 mL in a volumetric flask. Prepare this solution immediately before use.

Run the test using the 0.100 mg/L NO_2^--N standard in place of the sample. Results should be between 0.090 and 0.110 mg/L NO_2^--N.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.250 mg/L nitrite nitrogen and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.001 mg/L NO_2^--N for the powder pillow method and ±0.003 mg/L NO_2^--N for the
AccuVac method.

Estimated Detection Limit

The estimated detection limit for programs 60 and 62 is 0.005 mg/L NO_2^--N. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels
Antiminous ions	Interfere by causing precipitation
Auric ions	Interfere by causing precipitation
Bismuth ions	Interfere by causing precipitation
Chloroplatinate ions	Interfere by causing precipitation
Cupric ions	Cause low results
Ferric ions	Interfere by causing precipitation
Ferrous ions	Cause low results
Lead ions	Interfere by causing precipitation
Mercurous ions	Interfere by causing precipitation
Metavanadate ions	Interfere by causing precipitation
Nitrate	Very high levels of nitrate (>100 mg/L nitrate as N) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.
Silver ions	Interfere by causing precipitation
Strong oxidizing and reducing substances	Interfere at all levels

Summary of Method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present.

NITRITE, Low Range, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
NitriVer 3 Nitrite Reagent Powder Pillows	1 pillow	100/pkg	21071-69
or			
NitriVer 3 Nitrite Reagent AccuVac Ampuls	1 ampul	25/pkg	25120-25

REQUIRED APPARATUS

Beaker, 50 mL (for AccuVac procedure)	1	each	500-41H
or			
Sample Cells, 10-20-25 mL (powder pillow procedure)	2	6/pkg	24019-06

OPTIONAL REAGENTS

Nitrite Standard Solution, 250 mg/L as NO_2^--N	500	mL	23402-49
Water, deionized	4	L	272-56

OPTIONAL APPARATUS

Description	Unit	Cat. No.
AccuVac Snapper Kit	each	24052-00
Flask, volumetric, 250 mL	each	14574-46
Flask, volumetric, 500 mL	each	14574-49
Pipet, serological, 10 mL	each	532-38
Pipet, TenSette, 1 to 10 mL	each	19700-01
Pipet Tips for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00
Thermometer, –20 to 110 °C	each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A. call 800-227-4224

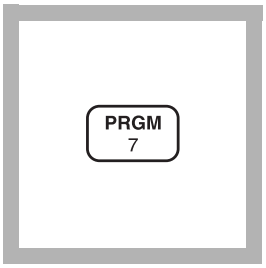
Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITRITE, Low Range, Test 'N Tube (0–0.500 mg/L NO_2^--N)

Diazotization Method

For water, wastewater, and seawater

USEPA approved for wastewater analysis*



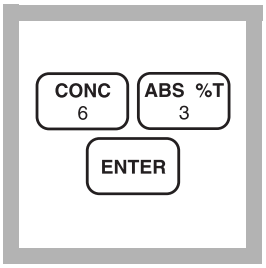
1. Enter the stored program number for nitrite nitrogen (NO_2^--N), Test 'N Tube.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



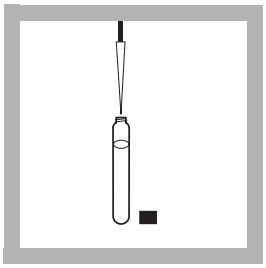
2. Press: **63 ENTER**

The display will show **mg/L, NO2-N** and the **ZERO** icon.

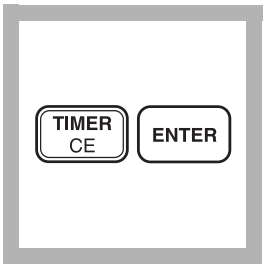
Note: *For alternate forms (NO_2^-, $NaNO_2$), press the* **CONC** *key.*

3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



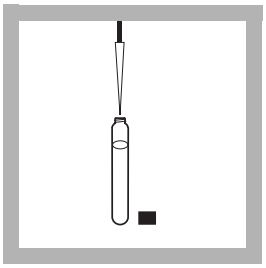
4. Fill a Test 'N Tube NitriVer® 3 Nitrite vial with 5 mL of sample. Cap and shake to dissolve powder. This is the prepared sample.



5. Press:
TIMER ENTER

A 20-minute reaction period will begin.

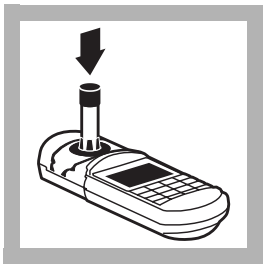
Note: *A pink color will develop if nitrite is present.*



6. When the timer beeps, fill an empty Test 'N Tube vial with 5 mL of sample (the blank).

7. Clean the outside of the vials with a towel.

Note: *Wipe with a damp towel and follow with a dry one to remove fingerprints and other marks.*

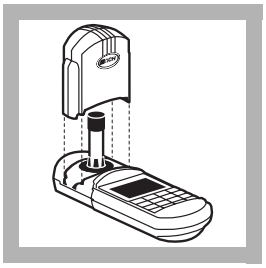


8. Place the blank in the vial adapter.

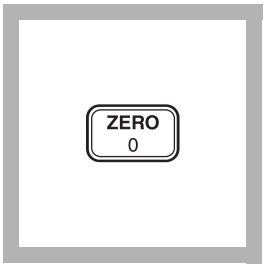
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*

* *Federal Register,* 44(85) 25505 (May 1, 1979).



9. Cover the sample cell tightly with the instrument cap.

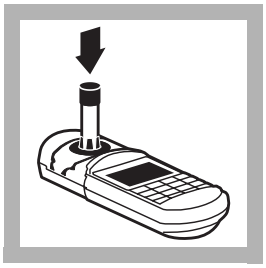


10. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.000 mg/L NO2-N

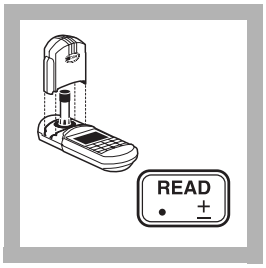
Note: *If the reagent blank correction is on, the display may flash "limit." See Section 1.*



11. Place the prepared sample in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Tightly cover the sample cell with the instrument cap.

Press: **READ**

The cursor will move to the right, then the result in mg/L nitrite nitrogen (or an alternate form) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles.

Store at 4 °C (39 °F) or lower and analyze within 48 hours. Warm to room temperature before running the test.

Do not use acid preservatives.

Remove suspended solids by filtration.

Accuracy Check

Standard Solution Method

Pipet 5.00 mL of a fresh Hach standard, 250 mg/L as NO_2^--N into a Class A 250-mL volumetric flask. Dilute to the line with deionized water to make a 5.00-mg/L intermediate standard. Pipet 10.00 mL of the 5.0-mg/L intermediate standard into a Class A 500-mL volumetric flask. Dilute to the line with deionized water to make a 0.100 mg/L NO_2^--N standard solution. Prepare immediately before use.

Run the test using the 0.100 mg/L NO_2^--N standard in place of the sample. Results should be between 0.090 and 0.110 mg/L NO_2^--N.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.250 mg/L nitrite nitrogen and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.004 mg/L NO_2^--N.

Estimated Detection Limit

The estimated detection limit for program 63 is 0.006 mg/L NO_2^--N. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels
Antiminous ions	Interfere by causing precipitation
Auric ions	Interfere by causing precipitation
Bismuth ions	Interfere by causing precipitation
Chloroplatinate ions	Interfere by causing precipitation
Cupric ions	Cause low results
Ferric ions	Interfere by causing precipitation
Ferrous ions	Cause low results
Lead ions	Interfere by causing precipitation
Mercurous ions	Interfere by causing precipitation
Metavanadate ions	Interfere by causing precipitation
Nitrate	Very high levels of nitrate (>100 mg/L nitrate as N) appear to undergo a slight amount of reduction to nitrite, either spontaneously or during the course of the test. A small amount of nitrite will be found at these levels.
Silver ions	Interfere by causing precipitation
Strong oxidizing and reducing substances	Interfere at all levels

Summary of Method

Nitrite in the sample reacts with sulfanilic acid to form an intermediate diazonium salt. This couples with chromotropic acid to produce a pink-colored complex directly proportional to the amount of nitrite present.

NITRITE, Test 'N Tube, continued

REQUIRED REAGENTS

Description	Cat. No.
NitriVer® 3 Nitrite, Low Range Test 'N Tube Reagent Set (50 tests)	26083-45
Includes:	
(50) NitriVer® 3 Nitrite Test 'N Tube Vials	*
Vials, 6 x 100 mm, 6/pkg	22758-06
Caps, for 22758-06 vials, 6/pkg	22411-06
Deionized water, 100-mL	272-42

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
COD/TNT Adapter	1	each	48464-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips for 19700-10 TenSette Pipet	1	50/pkg	21997-96

OPTIONAL REAGENTS

Nitrite Standard Solution, 250 mg/L as NO_2^--N	500	mL	23402-49
Water, deionized	4	L	272-56

OPTIONAL APPARATUS

Flask, volumetric, 250 mL		each	14574-46
Flask, volumetric, 500 mL		each	14574-49
Pipet, volumetric, Class A, 10.00 mL		each	14515-38

For Technical Assistance, Price and Ordering

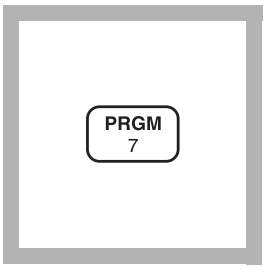
In the U.S.A. call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Not available separately.

NITROGEN, AMMONIA (0 to 0.50 mg/L NH_3-N) For water, wastewater, seawater

Salicylate Method*

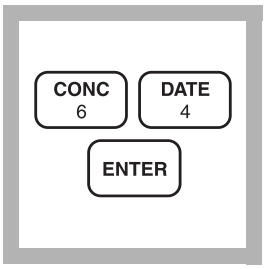


1. Enter the stored program number for ammonia nitrogen (NH_3-N).

Press: **PRGM**

The display will show:

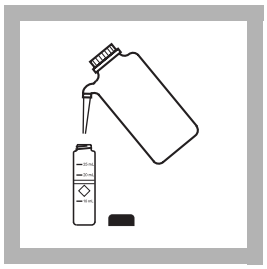
PRGM ?



2. Press: 64 ENTER

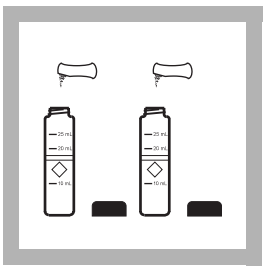
The display will show **mg/L, NH3-N** and the **ZERO** icon**.**

Note: *For alternate forms (NH_3, NH_4), press the* **CONC** *key.*

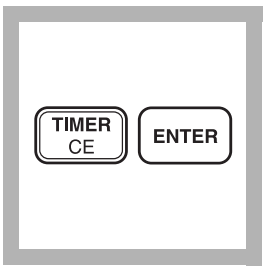


3. Fill a sample cell with 10 mL of deionized water (the blank).

4. Fill a second sample cell with 10 mL of the sample.



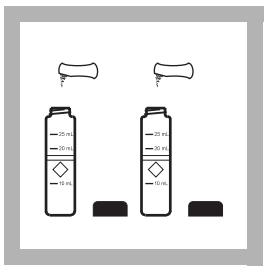
5. Add the contents of one Ammonia Salicylate Reagent Powder Pillow to each sample cell. Cap both cells and shake to dissolve.



6. Press:

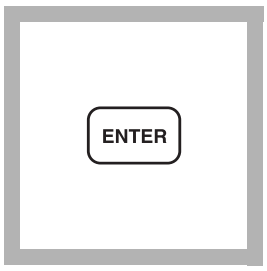
TIMER ENTER

A three-minute reaction period will begin.



7. After the timer beeps add the contents of one Ammonia Cyanurate Reagent Powder Pillow to each sample cell. Cap the cells and shake to dissolve the reagent.

Note: *A green color will develop if ammonia nitrogen is present.*

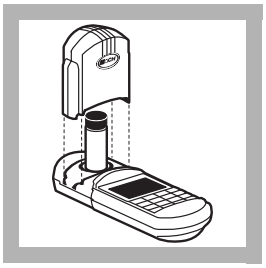


8. The display will show: **15:00 TIMER 2**

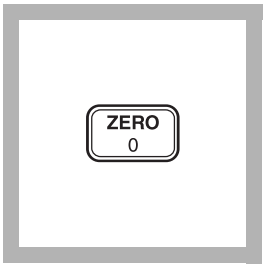
Press: **ENTER**

A 15-minute reaction period will begin.

* Adapted from Clin. Chim. Acta., 14 403 (1966)



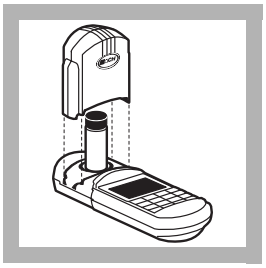
9. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



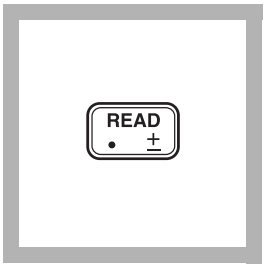
10. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L NH3-N



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L ammonia nitrogen will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Most reliable results are obtained when samples are analyzed as soon as possible after collection.

If chlorine is known to be present, the sample must be treated immediately with sodium thiosulfate. Add one drop of Sodium Thiosulfate Standard Solution, 0.1 N, for each 0.3 mg of chlorine present in a one liter sample.

To preserve the sample, adjust the pH to 2 or less with concentrated sulfuric acid (about 2 mL per liter). Store samples at 4 °C or less. Samples preserved in this manner can be stored up to 28 days. Just before testing the stored sample, warm to room temperature and neutralize with 5.0 N Sodium Hydroxide Standard Solution. Correct the test result for volume additions; see *Correction for Volume Additions,* in *Section 1* for more detailed information.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL mixing cylinders with 20 mL of sample.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of Ammonium Nitrogen Standard, 10 mg/L as NH_3-N to the three samples. Stopper the cylinders and mix well.

c) Analyze a 10-mL portion of sample as described above. The ammonia nitrogen concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions (Section 1)* for more information.

Standard Solution Method

Prepare a 0.40 mg/L ammonia nitrogen standard by diluting 4.00 mL of the Ammonia Nitrogen Standard Solution, 10 mg/L, to 100 mL with deionized water. Or, using the TenSette Pipet, prepare a 0.40 mg/L ammonia nitrogen standard by diluting 0.8 mL of a Ammonia Nitrogen Voluette Standard Solution, 50 mg/L as NH_3-N, to 100 mL with
deionized water.

Method Performance

Precision

In a single laboratory using a standard solution of 0.40 mg/L ammonia nitrogen (NH_3-N) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of $\pm$0.02 mg/L ammonia nitrogen.

Estimated Detection Limit

The estimated detection limit for program 64 is 0.02 mg/L NH_3-N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substances and Suggested Treatments.

Interfering Substance	Interference Level and Treatments
Calcium	Greater than 1000 mg/L as $CaCO_3$
Glycine, hydrazine	Less common. Will cause intensified colors in the prepared sample.
Iron	All levels. Correct for iron interference as follows: **1.** Determine the amount of iron present in the sample using one of the Total Iron procedures. **2.** Prepare a deionized water sample containing the same iron concentration as the original sample. Run the procedure on this solution to determine the interference due to iron. Subtract this value from the result in Step 12 obtained on the original sample.
Magnesium	Greater than 6000 mg/L as $CaCO_3$
Nitrate	Greater than 100 mg/L as NO_3^--N
Nitrite	Greater than 12 mg/L as NO_2^--N
Phosphate	Greater than 100 mg/L as PO_4^{3-}-P
Sulfate	Greater than 300 mg/L as SO_4^{2-}
Sulfide	Sulfide will intensify the color. Eliminate sulfide interference as follows: **1.** Measure about 350 mL of sample in a 500-mL erlenmeyer flask. **2.** Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix. **3.** Filter the sample through a folded filter paper. **4.** Use the filtered solution in Step 3.
Turbidity, sample color	Turbidity and sample color will give erroneous high values. Samples with severe interferences require distillation. Albuminoid nitrogen samples also require distillation. Hach recommends the distillation procedure using the Hach General Purpose Distillation Set. See the Optional Apparatus list.

Summary of Method

Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The
5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution.

REQUIRED REAGENTS AND APPARATUS

	Cat. No.
Ammonia Nitrogen Reagent Set for 10-mL samples (100 tests) Includes: (2) 26531-99, (2) 26532-99	26680-00

Description	Quantity Required Per Test	Unit	Cat. No.
Ammonia Cyanurate Reagent Powder Pillows	2 pillows	100/pkg	26531-99
Ammonia Salicylate Reagent Powder Pillows	2 pillows	100/pkg	26532-99
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Ammonia Nitrogen Standard Solution, 10 mg/L as NH_3-N	500 mL	153-49
Ammonia Nitrogen, PourRite Ampules, 50 mg/L as NH_3-N, 2 mL	20/pkg	14791-20
Cylinder, graduated, mixing, 25 mL	each	20886-40
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	1045-32
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB	323-32
Sulfide Inhibitor Reagent Powder Pillows	100/pkg	2418-99
Sulfuric Acid, concentrated, ACS	500 mL	979-49
Sulfuric Acid Standard Solution, 1.0 N	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Cylinder, graduated, polypropylene, 500 mL	each	1081-49
Distillation Heater and Support Apparatus, 115 V	each	22744-00
Distillation Heater and Support Apparatus, 230 V	each	22744-02
Distillation Set, General Purpose	each	22653-00
Filter Paper, folded, 12.5 cm	100	1894-57
Flask, Erlenmeyer, polypropylene, 500 mL	each	1082-49
Flask, volumetric, Class A, 100 mL	each	14574-42
Funnel, poly, 65 mm	each	1083-67
pH Meter, *sens**ion***™***1***, portable, with electrode	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 2.0 mL	each	14515-36
PourRite Ampule Breaker Kit	each	24846-00
Thermometer, –20 to 110 °C	each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

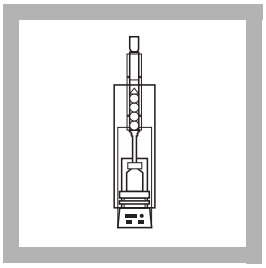
Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITROGEN, TOTAL KJELDAHL (0 to 150 mg/L)

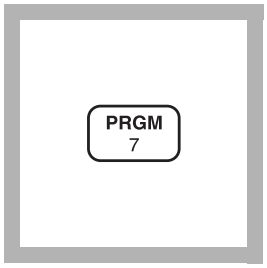
Nessler Method* (digestion required)

For water, wastewater and sludge

1. A User-Entered Calibration is necessary to obtain the most accurate results. See the User Calibration section following these steps.



2. Digest the sample as described in the Digesdahl Apparatus Instruction manual. Digest an equal amount of deionized water as the blank.

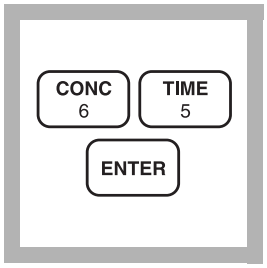


3. Enter the stored program number for total Kjeldahl nitrogen.

Press: **PRGM**

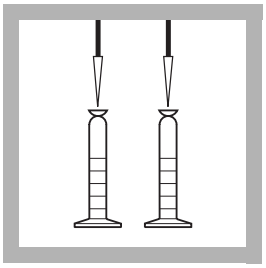
The display will show:

PRGM ?

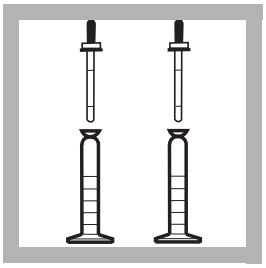


4. Press: **65 ENTER**

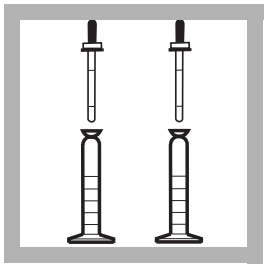
The display will show **mg/L, TKN** and the **ZERO** icon**.**



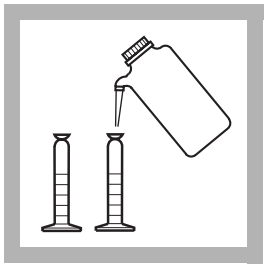
5. Select the appropriate analysis volume of the digested sample given in *Table 1* on page *347*. Pipet the analysis volume from the sample and the digested blank into separate 25-mL mixing graduated cylinders.



6. Add one drop of TKN Indicator to each cylinder. Add 8.0 N KOH dropwise to each cylinder, mixing after each addition. Continue until the first apparent blue color is visible.



7. Add 1.0 N KOH to each cylinder, one drop at a time, mixing after each addition. Continue until the first permanent blue color appears.



8. Fill both mixing cylinders to the 20-mL mark with deionized water. Add 3 drops of Mineral Stabilizer to each cylinder. Invert several times to mix. Add 3 drops of Polyvinyl Alcohol Dispersing Agent to each cylinder. Invert several times to mix.

Note: *Hold the dropping bottles upright while dispensing.*

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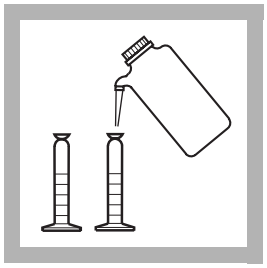
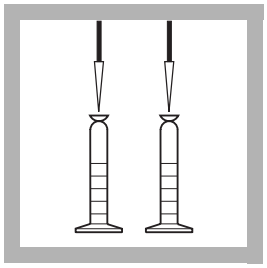
* Adapted from: Hach et al., *Journal of Association of Official Analytical Chemists*, 70 (5) 783-787 (1987); Hach et al., *Journal of Agricultural and Food Chemistry,* 33 (6) 1117-1123 (1985); *Standard Methods for the Examination of Water and Wastewater.*

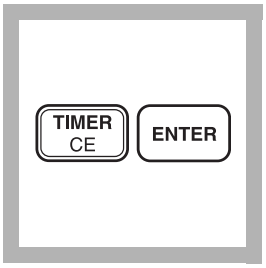


9. Fill both cylinders to the 25-mL mark with deionized water.



10. Pipet 1 mL of Nesslers Reagent to each cylinder. Stopper, invert repeatedly. The solution should not be hazy.

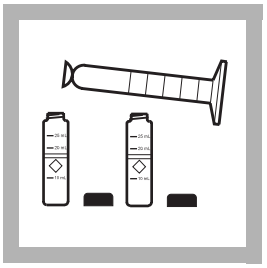
Note: *Any haze (turbidity) will cause incorrect results.*



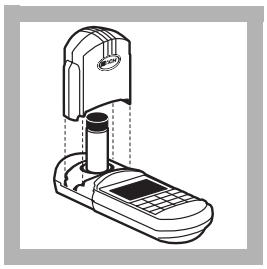
11. Press:

TIMER ENTER

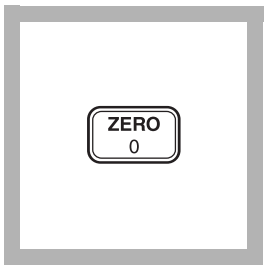
A two-minute reaction period will begin.



12. When the timer beeps, pour the contents of each cylinder into a separate labeled sample cell.



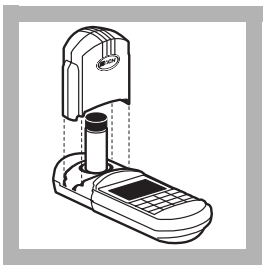
13. Place the blank into a cell holder. Tightly cover the sample cell with the instrument cap.



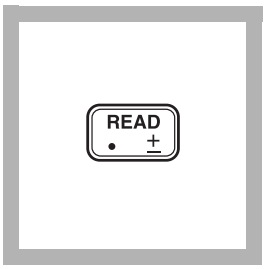
14. Press: **ZERO**

The cursor will move to the right, then the display will show:

0. mg/L TKN



15. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



16. Press: **READ**

The cursor will move to the right, then the result in mg/L total Kjeldahl nitrogen will be displayed.

Note: *Standard Adjust may be performed using a prepared ammonia standard (see Standard Adjust in Section 1).*

$$\text{ppm TKN} = \frac{75 \times A}{B \times C}$$

17. Use the formula shown to calculate the final TKN value.

Where:

A = mg/L displayed

B = g (or mL of water) sample taken for digest

C = mL analysis volume of digested sample (step 5).

Note: *For water samples ppm TKN = mg/L TKN.*

Note: *For maximum accuracy, the reagent blank value may be determined by repeating procedure using reagents only. Subtract the reagent blank value from the reading on the display.*

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Table 1 Analysis Volumes Based on Concentration

AQUEOUS SAMPLES (Solutions of suspensions in water- less than 1% solids)	
Expected Nitrogen Concentration (mg/L)	**Analysis Volume (mL)**
0.5-28	10.00
2-112	5.00
11-560	2.00
45-2250	1.00
425-22500	0.50
DRY SAMPLES	
Expected Nitrogen Concentration (mg/L)	**Analysis Volume (mL)**
42-2200	10.0
106-5600	5.00
350-18000	2.00
1000-56000	1.00
4200-220000	0.50
OILS AND FATS	
Expected Nitrogen Concentration (mg/L)	**Analysis Volume (mL)**
85-4500	10.0
210-11000	5.00
2100-11000	1.00

Sampling and Storage

Collect samples in a cleaned glass or plastic container. Adjust the pH to 2 or less with sulfuric acid (about 2 mL per liter) and cool to 4 °C. Preserved samples can be stored up to 28 days.

Accuracy Check

Kjeldahl Nitrogen Standard Method
This procedure checks digestion efficiency and indicates that amount of bound nitrogen that is freed during digestion. The methods and standards available to check digestion technique are found in the Accuracy Check section following the procedures in the Digesdahl Digestion Apparatus Instruction Manual. Using the digested Kjeldahl standard, perform the above TKN analysis on the colorimeter. The TKN value should come within about ±3% of the value of the prepared Kjeldahl standard.

Standard Solution Method (to check calibration accuracy only)
Add one drop of TKN Indicator to each of two 25-mL graduated mixing cylinders. Fill one cylinder to the 20-mL mark with deionized water. Fill the other cylinder to the 20-mL mark with a 1.0 mg/L Ammonia Nitrogen Solution. Add 3 drops of Mineral Stabilizer to each cylinder. Invert several times to mix. Add 3 drops of Polyvinyl Alcohol Dispersing agent to each cylinder. Perform the TKN procedure as described in Steps 9 to 16. This display should show 26-27 mg/L TKN.

User Calibration

For most accurate results, use a user-calibrated program. The Standard Adjust feature should not be used with a user-entered calibration; it will hinder performance.

A one-time setup of a program for TKN is recommended for each new lot of reagents. A new calibration may be performed for each lot of Nessler Reagent by following these instructions:

Standard Preparation
Use the following standards to make a calibration curve. See *Preparing a User-Entered Calibration Curve* on page *49*, for more information and instructions. Prepare standards representing concentrations of 20, 60, 80, 100, 140 and 160 mg/L NH_3-N as follows:

a) Using volumetric pipets, transfer 5.0, 15.0, 20.0, 25.0,

35.0, and 40.0 mL of 100 mg/L NH_3-N standard solution into six separate 100-mL volumetric flasks. Dilute to volume with deionized water, stopper, and invert to mix.

b) Begin at step 4 of the procedure using a 3-mL aliquot for the sample volume. Also prepare a blank solution by substituting a 3 mL aliquot of deionized water for sample in Step 4.

Note: *Standard solutions are prepared as if a 25-mL volume was used for the digestion. Actual concentrations prepared in Step 1 are 5, 15, 20, 25, 35, and 40 mg/L NH_3-N. These represent original concentrations of 20, 60, 80, 100, 140, and 160 mg/L NH_3-N, based on the 25 to 100 mL dilution in the digestion.*

User Entered Calibration Settings For TKN
Program # = 101 to 105
Wavelength = 420 nm
Resolution = 0 mg/L

Method Performance

Precision
In a single laboratory using a standard solution of 64 mg/L TKN and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±1.0 mg/L TKN.

Estimated Detection Limit
The estimated detection limit for program 65 is 2 mg/L TKN. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

"Total Kjeldahl Nitrogen" (also called crude protein) refers to the combination of ammonia and organic nitrogen. Organically-bound in the trinegative state, it is converted into ammonium salts by the action of sulfuric acid and hydrogen peroxide. The ammonia is then analyzed by a modified nessler method test. The Mineral Stabilizer complexes calcium and magnesium. The Polyvinyl Alcohol Dispersing Agent aids the color formation in the reaction of Nessler Reagent with ammonium ions. A yellow color forms, proportional to the ammonia concentration.

Pollution Prevention And Waste Management

Nessler reagent contains mercuric iodide. Both the sample and blank will contain mercury (D009) at concentrations regulated as

a hazardous waste by the Federal RCRA. Do not pour these solutions down the drain. See Section *3* for more information on proper disposal of these materials.

REQUIRED REAGENTS

Total Kjeldahl Nitrogen Reagent Set 24953-00
Includes: (1) 21196-49, (1) 23766-26, (1) 21194-49, (1) 23765-26, (1) 282-32H, (1) 23144-26, (1) 979-49, (1) 22519-26

Description	Quantity Required Per Test	Unit	Cat. No.
Hydrogen Peroxide, 50%	20 mL	490 mL	21196-49
Mineral Stabilizer	6 drops	50 mL SCDB	23766-26
Nesslers Reagent	2 mL	500 mL	21194-49
Polyvinyl Alcohol Dispersing Agent	6 drops	50 mL SCDB	23765-26
Potassium Hydroxide Standard Solution, 8.0 N	varies	100 mL MDB	282-32H
Potassium Hydroxide Standard Solution, 1.0 N	varies	50 mL SCDB	23144-26
Sulfuric Acid, ACS	6 mL	500 mL	979-49
TKN Indicator Solution	2 drops	50 mL SCDB	22519-26
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Boiling Chips, silicon carbide	2-3	500 g	20557-34
Cylinder, graduated, mixing, tall-form, 25 mL	2	each	20886-40
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	2	50/pkg	21856-96
Safety Shield, for Digesdahl	1	each	50040-00
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

Select one based on available voltage:

Digesdahl Digestion Apparatus, 115 V	1	each	23130-20
Digesdahl Digestion Apparatus, 230 V	1	each	23130-21

OPTIONAL REAGENTS

Ammonia Nitrogen Standard Solution, 1 mg/L NH_3-N		500 mL	1891-49
Ammonia Nitrogen Standard Solution, Voluette Ampule, 150 mg/L NH_3-N, 10 mL		16/pkg	21284-10
Ammonia Nitrogen Standard Solution, 100 mg/L NH_3-N		500 mL	24065-49
Nitrogen Standard, Primary		3/set	22778-00

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit	each	21968-00
Balance, AccuLab Pocket Pro 250B	each	27969-00
Bottle, glass dispenser, 118 mL	each	591-00
Bottle, plastic wash, 1000 mL	each	620-16
Cylinder, graduated, 50 mL	each	508-41
Flask, volumetric, 100 mL, Class A	each	14574-42
Mini Grinder, 120 V	each	20991-00
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 0.50 mL	each	14515-34
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet, volumetric, Class A, 15.00 mL	each	14515-39
Pipet, volumetric, Class A, 20.00 mL	each	14515-20
Pipet, volumetric, Class A, 25.00 mL	each	14515-40
Safety Glasses	each	18421-00

For Technical Assistance, Price and Ordering

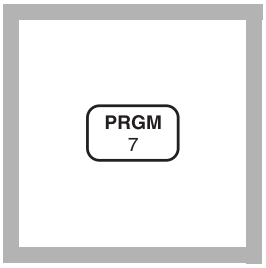
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITROGEN, AMMONIA, Low Range, Test 'N Tube (0 to 2.50 mg/L NH_3-N)

Salicylate Method*

For water, wastewater, and seawater

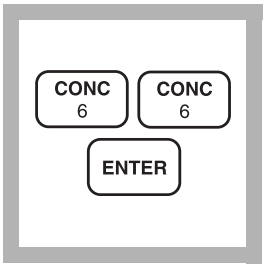


1. Enter the stored program number for low range nitrogen, ammonia Test 'N Tube.

Press: **PRGM**

The display will show:

PRGM ?



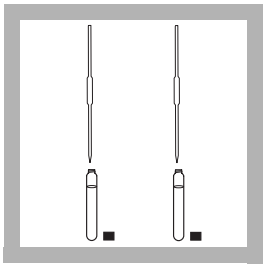
2. Press: **66 ENTER**

The display will show **mg/L, NH3-N** and the **ZERO** icon**.**

Note: *For alternate forms (NH_3), press the* **CONC** *key.*

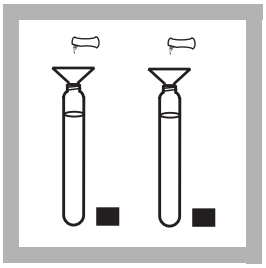
3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*

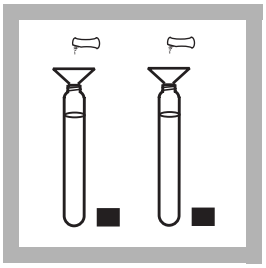


4. Remove the caps from 2 AmVer Diluent Reagent vials. Add 2 mL of sample to one vial (the sample). Add 2 mL of deionized water to the other vial (the blank).

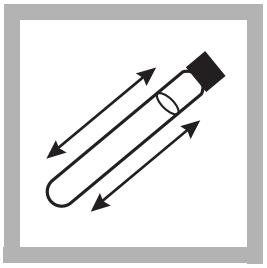
Note: *Adjust the pH of stored samples before analysis. See Interferences on page 355.*



5. Using a funnel, add the contents of one Ammonia Salicylate Reagent Powder Pillow for 5 mL sample to each vial.

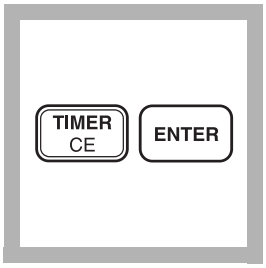


6. Using a funnel, add the contents of one Ammonia Cyanurate Reagent Powder Pillow for 5 mL sample to each vial.



7. Cap the vials tightly and shake thoroughly to dissolve the powder.

Note: *A green color will develop if ammonia is present.*



8. Press:

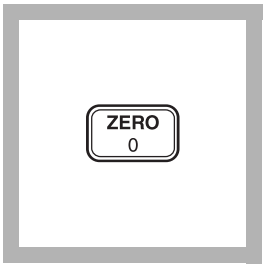
TIMER ENTER

A 20-minute reaction period will begin.

* Adapted from *Clin. Chim. Acta,* 14 403 (1966).

9. Wipe the outside of the vials with a towel. After the timer beeps, place the blank into the adapter. Tightly cover the vial with the instrument cap.

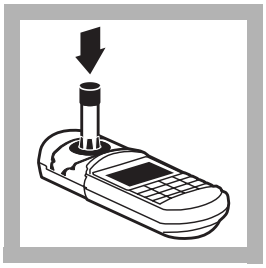
Note: *Wipe with a damp cloth followed by a dry one to remove fingerprints and other marks.*



10. Press: **ZERO**

The cursor will move to the right, then the display will show:

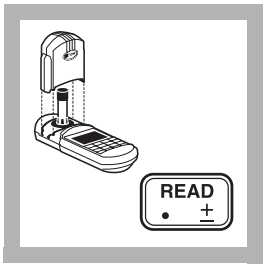
0.00 mg/L NH3-N



11. Place the prepared sample in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Tightly cover the sample cell with the instrument cap.

Press: **READ**

The cursor will move to the right, then the result in mg/L ammonia nitrogen will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust (Adjusting the Standard Curve) on page 47).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis. If chlorine is known to be present, add one drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a one liter sample. Preserve the sample by reducing the pH to 2 or less with hydrochloric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Before analysis, warm samples to room temperature and neutralize with 5.0 N sodium hydroxide. Correct the test result for volume additions. See *Correcting for Volume Additions on page 22* for more information.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Nitrogen, Ammonia Ampule Standard Solution, 50 mg/L NH_3-N.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25 mL samples. Mix thoroughly.

c) Analyze each sample as described above. The nitrogen concentration should increase 0.20 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions, Section 1*, for more information.

Standard Solution Method

To check accuracy, use a 1.0 mg/L Nitrogen, Ammonia Standard Solution listed under Optional Reagents. Or, dilute 1 mL of solution from a
50 mg/L Ampule Standard for Nitrogen, Ammonia to 50 mL with deionized water using a 50-mL volumetric flask.

Method Performance

Precision

In a single laboratory, using a standard solution of 1.0 mg/L ammonia nitrogen and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of $\pm$0.02 mg/L NH_3-N.

Estimated Detection Limit

The estimated detection limit for program 66 is 0.08 mg/L NH_3-N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Level and Treatment
Calcium	2500 mg/L as $CaCO_3$
Iron	**1.** Determine the amount of iron present in the sample following one of the total iron procedures. **2.** Add the same iron concentration to the deionized water in step 4. The interference will then be successfully blanked out.
Magnesium	5000 mg/L as $CaCO_3$
Nitrite	30 mg/L as NO_2^--N
Nitrate	250 mg/L as NO_3^--N
Orthophosphate	250 mg/L as PO_4^{3-}-P
pH	Acidic or basic samples should be adjusted to about pH 7. Use 1 N Sodium Hydroxide Standard Solution for acidic samples and 1 N Hydrochloric Acid Standard Solution for basic samples.
Sulfate	300 mg/L as SO_4^{2-}

Interfering Substance	Interference Level and Treatment
Sulfide	**1.** Measure about 350 mL of sample in a 500 mL erlenmeyer flask. **2.** Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix. **3.** Filter the sample through a folded filter paper. **4.** Use the filtered solution in step 4.
Other	Less common interferences such as **hydrazine** and **glycine** will cause intensified colors in the prepared sample. **Turbidity** and **color** will give erroneous high values. Samples with severe interferences require distillation. Hach recommends the distillation procedure using the Hach General Purpose Distillation Set. See Optional Apparatus at the end of this procedure.

Summary of Method

Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution.

Pollution Prevention And Waste Management

The ammonia salicylate reagent contains sodium nitroferricyanide. Cyanide solutions are regulated as hazardous wastes by the Federal RCRA. Collect cyanide solutions for disposal as reactive (D001) waste. Be sure cyanide solutions are stored in a caustic solution with pH >11 to prevent release of hydrogen cyanide gas. See *Section 3* for further information in proper disposal of these materials.

REQUIRED REAGENTS

	Cat. No.
AmVer Reagent Set for Nitrogen, Ammonia, Low Range TNT (25 tests) Includes: (1) 23952-66, (1) 23954-66, (1) 272-42, *(50) AmVer Low Range Vials	26045-45

Description	Quantity Required Per Test	Unit	Cat. No.
AmVer Diluent Reagent, Low Range Test 'N Tube	2 vials	50/pkg	*
Salicylate Reagent Powder Pillows, 5 mL sample	2 pillows	50/pkg	23952-66
Cyanurate Reagent Powder Pillows, 5 mL sample	2 pillows	50/pkg	23954-66

* Not available separately.

NITROGEN, AMMONIA, Low Range, Test 'N Tube, continued

REQUIRED APPARATUS

Vial Adapter, COD	1	each	48464-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette, 0-10 mL	1	each	19700-10
Pipet Tips for 19700-10	2	50/pkg	21997-96
Funnel, micro (for reagent addition)	1	each	25843-35

OPTIONAL REAGENTS

Nitrogen, Ammonia Standard Solution, 1.0 mg/L NH_3-N	500 mL		1891-49
Nitrogen, Ammonia Standard Solution, 10 mL Voluette ampules, 50 mg/L NH_3-N	16/pkg		14791-10
Nitrogen, Ammonia Standard Solution, 2 mL PourRite ampules, 50 mg/L NH_3-N	20/pkg		14791-20
Hydrochloric Acid, ACS	500 mL		134-49
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB		2450-26
Sodium Hydroxide, 1.000 N	100 mL MDB		1045-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL MDB		323-32
Sulfide Inhibitor Reagent Powder Pillows	100/pkg		2418-99
Sulfuric Acid, 1.00 N	100 mL MDB		1270-32
Wastewater Effluent Standard, Inorganics (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL		28332-49
Water, deionized	4 L		272-56

OPTIONAL APPARATUS

Ampule Breaker Kit		each	21968-00
Cylinder, graduated, mixing, 25 mL, Class A		each	508-40
Distillation Apparatus Set		each	22653-00
Heater and Support Apparatus (for distillation), 115 Vac		each	22744-00
Heater and Support Apparatus (for distillation), 230 Vac		each	22744-02
Filter Paper, folded		100/box	1894-57
Flask, Erlenmeyer, 500 mL		each	505-49
Flask, volumetric, 50 mL, Class A		each	14547-41
Funnel, analytical (for filtering)		each	1083-68
Jack, laboratory (use with distillation apparatus)		each	22743-00
pH Indicator Paper, 1 to 11 pH		5 rolls/pkg	391-33
Ampule Breaker Kit, PourRite		each	24846-00
Thermometer, –20 to 110 °C, non-mercury		each	26357-02
Thermometer, –10 to 260 °C, non-mercury		each	26357-01

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

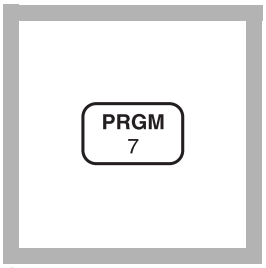
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Nitrogen, Free Ammonia and Chloramine (Mono) Method 10200

Indophenol Method* (0–4.50 mg/L Cl_2 and 0–0.50 mg/L NH_3–N)

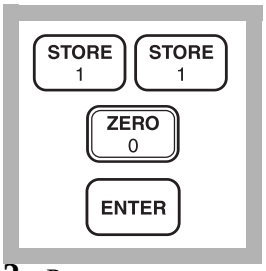
For finished chloraminated drinking water

Note: *For the most accurate chloramine results, determine a reagent blank for each new lot of reagent using deionized water instead of sample. Subtract the blank value from the final chloramine result.*



1. Enter the user program number for monochloramine.

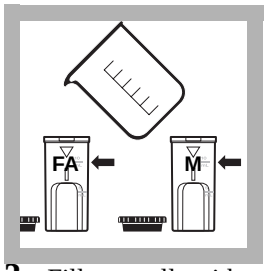
Press: **PRGM**
The display will show:
PRGM?



2. Press:
110 ENTER

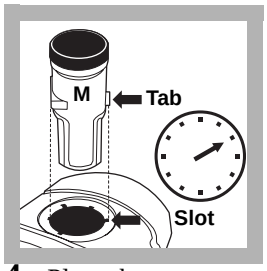
The display will show
mg/L Cl_2
and the zero icon.

Note: *For alternate forms, press the* **CONC** *key.*



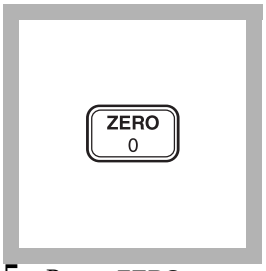
3. Fill two cells with 10 mL of sample

Label one cell "Free Ammonia" and one cell "Monochloramine".



4. Place the Monochloramine cell into the instrument so that the cell tab is at the two-o'clock position. Make sure the sample cell tab is completely seated in the cell holder slot.

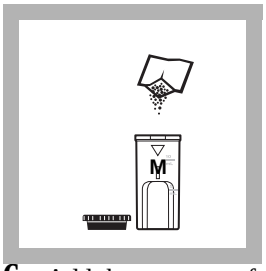
Tightly cover the sample cell with the instrument cap.



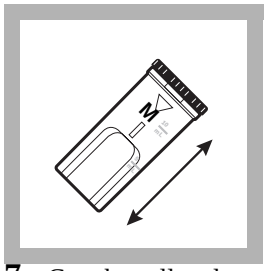
5. Press: **ZERO**

The cursor will move to the right, then the display will show:
0.00 mg/L Cl_2

Remove the cell from the instrument.

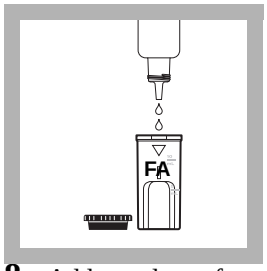


6. Add the contents of one pillow of Monochlor F to the cell for the Monochloramine measurement.



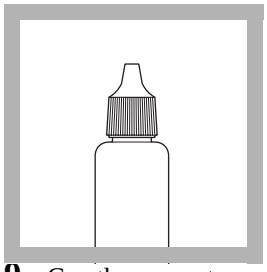
7. Cap the cell and shake for 20 seconds to dissolve the reagent.

A green color will form if monochloramine is present.

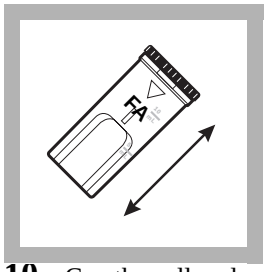


8. Add one drop of Free Ammonia Reagent Solution to the cell for Free Ammonia measurement.

* U.S. Patent 6,315,950

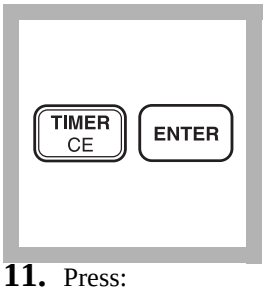


9. Cap the reagent bottle to maintain reagent performance and stability.



10. Cap the cell and mix.

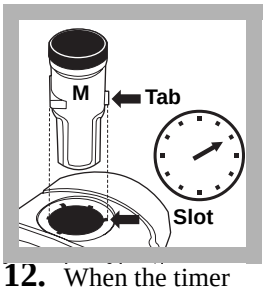
Note: *If the sample becomes cloudy by the end of the reaction period, pretreat the sample and retest. See Interferences on page 362.*



11. Press:
TIMER ENTER

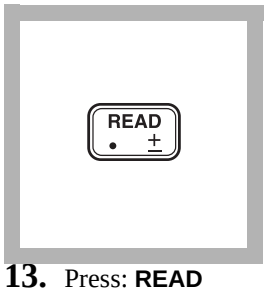
A five-minute reaction period will begin.

Note: *The color development time depends on the sample temperature. See Table 1. For accurate results allow the full reaction period to occur.*



12. When the timer expires, place the Monochloramine cell into the instrument so that the cell tab is in the two-o'clock position. Make sure the sample cell tab is completely seated in the cell holder slot.

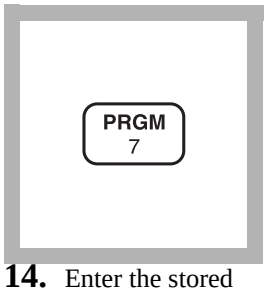
Tightly cover the sample cell with the instrument cap.



13. Press: **READ**

The cursor will move to the right, then the result in mg/L Monochloramine (as Cl_2 or chosen units) will be displayed.

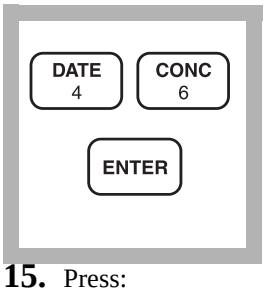
Leave the cell in the instrument.



14. Enter the stored program number for Free Ammonia.

Press: **PRGM**

The display will show PRGM?



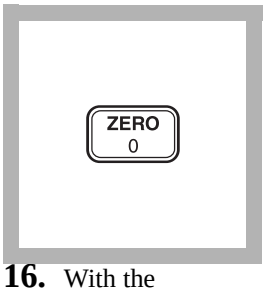
15. Press:
46 ENTER

The display will show

NH_3–N

and the zero icon.

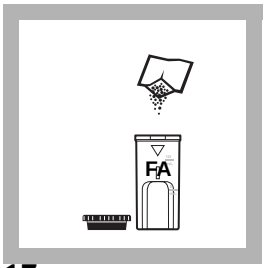
Note: *For alternate forms, press the* **CONC** *key.*



16. With the Monochloramine sample still in the cell holder, press **ZERO**.

The cursor will move to the right, then the display will show: 0.00 mg/L NH_3–N.

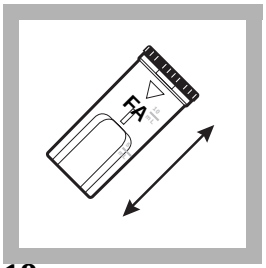
Remove the cell from the instrument.



17. Add the contents of one pillow of Monochlor F to the cell for the Free Ammonia measurement.

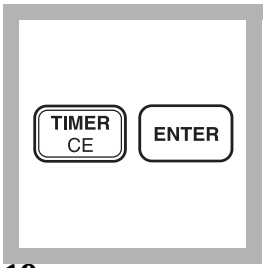
Cap and shake the cell about 20 seconds to dissolve the reagent.

Note: *The reaction period indicated in step 11 must be complete before the addition of Monochlor F to the cell for free ammonia measurement.*



18. Cap and shake the cell about 20 seconds to dissolve the reagent.

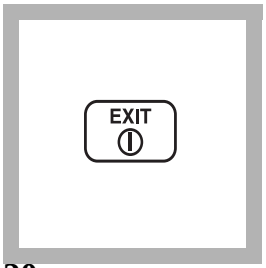
A green color will form if ammonia or monochloramine is present.



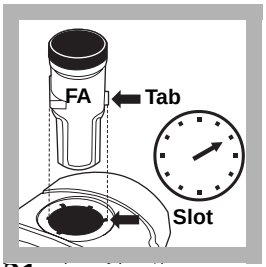
19. Press:
TIMER ENTER

A five-minute reaction period will begin.

Note: *The color development time depends on the sample temperature. See Table 1.*

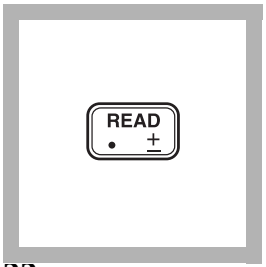


20. After the timer has expired, press: **EXIT**



21. Place the Free Ammonia cell into the instrument so that the cell tab is at the two-o'clock position. Make sure the sample cell tab is completely seated in the cell holder slot.

Tightly cover the sample cell with the instrument cap.



22. Press: **READ**

The cursor will move to the right, then the result in mg/L free ammonia as nitrogen (NH_3–N) or chosen units will be displayed.

Sampling and Storage

Collect samples in clean glass bottles. Most reliable results are obtained when samples are analyzed as soon as possible after collection.

Color Development Time

Test results are strongly influenced by sample temperature. **Both reaction periods in the procedure are the same and depend on the temperature of the sample.** The reaction periods indicated in the procedure are for a sample temperature of 18–20 °C (68–73 °F). Adjust both reaction periods according to Table 2.

Table 2 Reaction Period

Sample Temperature		Reaction Periods (Minutes)
° C	° F	
5	40	10
7	42	9
9	48	8
10	50	8
12	54	7
14	58	7
16	61	6
18	68	5
20	73	5
23	75	2.5
25	77	2
>25	>77	2

Interferences

This method is intended for finished, chloraminated drinking water samples that have a measurable combined (total) chlorine disinfectant residual. Samples where the disinfectant residual has disappeared and samples which exhibit a chlorine demand may produce low ammonia test results. Blanks and ammonia standards analyzed without a disinfectant residual must be prepared using high quality, reagent grade water.

The following do not interfere in free ammonia determination when at or below the stated concentration.

Substance	Level Tested
Aluminum	0.2 mg/L Al

Substance	Level Tested
Chloride	1200 mg/L Cl
Copper	1 mg/L Cu
Iron	0.3 mg/L Fe
Manganese	0.05 mg/L Mn
Nitrate	10 mg/L NO_3–N
Nitrite	1 mg/L NO_2–N
Phosphate	2 mg/L –PO_4
Silica	100 mg/L SiO_2
Sulfate	1600 ppm as $CaCO_3$
Zinc	5 ppm Zn

Samples containing high levels of both Total Hardness and Alkalinity may become turbid (cloudy) after the addition of the Free Ammonia Reagent Solution. If this occurs by the end of the first reaction period, the sample for Free Ammonia measurement must be pretreated as follows:

Note: *The sample for Monochloramine measurement does not need pretreatment.*

1. Measure 10 mL of sample into the cell for Free Ammonia measurement.
2. Add the contents of one Hardness Treatment Reagent Powder Pillow (Cat. No. 28823-46) to the sample.
3. Cap the cell and invert until the reagent is dissolved.
4. Remove the cap.

Continue with the analysis at step 2 using the pretreated sample as the Free Ammonia cell.

Accuracy Check (Monochloramine, Program 110)

1. Prepare the following monochloramine standard fresh before use.
2. Add the contents of one Buffer Powder Pillow, pH 8.3 to about 50-mL of organic-free water in a clean 100-mL Class A volumetric flask. Swirl to dissolve the powder.
3. Using a Class A volumetric pipet, transfer 2.00 mL of Nitrogen, Ammonia Standard Solution, 100 mg/L as NH_3–N into the flask.
4. Dilute to volume with organic-free water, cap and mix thoroughly. This is a 2.00 mg/L buffered ammonia standard.

5. Pipet 50.0 mL of the buffered ammonia standard into a clean 100-mL beaker. Add a stir bar.

6. Obtain a recent lot of Chlorine Solution Ampules, 50–70 mg/L, and note the actual free chlorine concentration for this lot.

7. Calculate the amount of Chlorine Solution to be added to the ammonia standard using the following equation:

$$\text{mL chlorine solution required} = \frac{455}{\text{free chlorine concentration}}$$

8. Open an ampule and, using a glass Mohr pipet, add the calculated amount of Chlorine Solution slowly to the ammonia standard, while mixing at medium speed on a stir plate.

9. Allow the monochloramine solution to mix for 1 minute after all Chlorine Solution is added.

Important Note: *Because of the strong buffer used in the preparation of this standard, it cannot be used for accuracy verification of the Free Ammonia test.*

10. Quantitatively transfer the monochloramine solution to a clean 100-mL Class A volumetric flask. Dilute to the mark with organic-free water, cap, and mix thoroughly. This is a nominal 4.5 mg/L (as Cl_2) monochloramine standard.

Use this standard within 1 hour of preparation.

Accuracy Check (Free Ammonia Test, Program 46)

Dilution water is required when testing a diluted sample and preparing standard solutions. Dilution water must be free of ammonia, chlorine and chlorine demand. A convenient source is a recirculating, deionizer system with carbon filtration which produces 18 megaohm-cm water.

Standard Additions Method

1. Measure 50 mL of sample into three 50-mL mixing cylinders.

2. Use the TenSette Pipet to add 0.3, 0.6, and 1.0 mL of Ammonium Nitrogen Standard, 10 mg/L as NH_3-N to the three samples. Mix well.

3. Analyze each spiked sample, following all steps of the Monochloramine and Free Ammonia procedure. The ammonia nitrogen concentration should increase 0.02 mg/L for each 0.1 mL of standard added.

4. If these increases do not occur, see *Standard Additions (Section 1 of the DR/890 Procedures Manual)* for more information.

Standard Solution Method
Prepare a 0.20 mg/L ammonia nitrogen standard by diluting 2.00 mL of the Ammonia Nitrogen Standard Solution, 10 mg/L, to 100 mL with dilution water. Or, using the TenSette Pipet, prepare a 0.20 mg/L ammonia nitrogen standard by diluting 0.4 mL of a Ammonia Nitrogen Voluette Standard Solution, 50 mg/L as NH_3–N, to 100 mL with dilution water. Analyze the standard solution, following all steps of the Monochloramine and Free Ammonia procedure.

Method Performance

Monochloramine Test

Precision
In a single laboratory, using a monochloramine standard solution of 2.10 mg/L Cl_2 and representative lots of reagent, a single operator obtained a standard deviation of ± 0.12 mg/L Cl_2.

Estimated Detection Limit
The estimated detection limit for Method 10171 is 0.05 mg/L Cl_2.

Free Ammonia Test

Precision
In a single laboratory using a solution containing 1.80 mg/L Cl_2 plus 0.20 mg/L ammonia nitrogen (NH_3–N) and two representative lots of reagent with the DR/890, a single operator obtained a standard deviation of ± 0.01 mg/L N for seven replicates.

Estimated Detection Limit
The estimated detection limit for program 46 is 0.02 mg/L N.

For more information on the estimated detection limit, see *Section 1* of the *DR/850 or DR/890 Procedure Manual*.

Summary of Method

Monochloramine (NH_2Cl) and "free ammonia" (NH_3 and NH_4^+) can exist in the same water sample. Added hypochlorite combines with free ammonia to form more monochloramine. In the presence

of a cyanoferrate catalyst, monochloramine in the sample reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green-colored indophenol, which is proportional to the amount of monochloramine present in the sample. Free ammonia is determined by comparing the color intensities, with and without added hypochlorite.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet (MSDS) for information specific to the reagent used.

Nitrogen, Free Ammonia and Chloramine (Mono), continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Free Ammonia Reagent Set (50 tests) Includes: (1) 28022-99, (1) 28773-36			28797-00
Free Ammonia Reagent Solution	1 drop	4 mL SCDB	28773-36
Monochlor F Reagent Pillows	2 pillows	100/pkg	28022-99

REQUIRED APPARATUS

Sample Cell, 1-cm/10-mL, with cap	2	2/pkg	48643-02

OPTIONAL REAGENTS

Buffer, pH 8.3, Powder Pillows		25/pkg	898-68
Chlorine Solution, Voluette® Ampule		16/pkg	14268-10
Hardness Treatment Reagent Pillows (1 per test)		50/pkg	28823-46
Nitrogen Ammonia Standard Solution, 10 mg/L as NH_3–N		500 mL	153-49
Nitrogen Ammonia Standard Ampule, 50 mg/L as NH_3–N, 10 mL		16/pkg	14791-10
Nitrogen Ammonia Standard Solution, 100 mg/L as NH_3–N		500 mL	24065-10

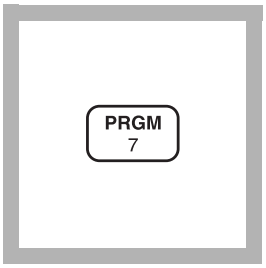
OPTIONAL APPARATUS

Ampule Breaker Kit		each	21968-00
Beaker, 100 mL, Polypropylene		each	1080-42
Beaker, 100 mL, Glass		each	500-42H
Cylinder, 50 mL, mixing		each	20886-41
Flask, Volumetric, Class A, 100 mL		each	14574-42
Pipet Filler, Safety Bulb		each	14651-00
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet, Mohr, Glass, 10 mL		each	20934-38
Pipet, Volumetric, Class A, 2.0 mL		each	14515-36
Pipet, Volumetric, Class A, 50.00 mL		each	14515-41
Scissors		each	28831-00
Stir Bar, Octagonal		each	20953-53
Stirrer, Magnetic		each	23436-00
Thermometer, –10 to 110 °C		each	1877-01
Wipers, Disposable Kimwipes®, 30 x 30 cm, 280/box		box	20970-01

NITROGEN, AMMONIA, High Range, Test 'N Tube

(0 to 50 mg/L NH_3-N) **For water, wastewater, and seawater**

Salicylate Method*

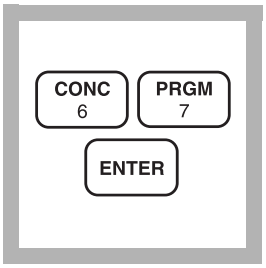


1. Enter the stored program number for nitrogen, ammonia, high range Test 'N Tube (NH_3-N) method.

Press: **PRGM**

The display will show:

PRGM ?



2. Press: **67 ENTER**

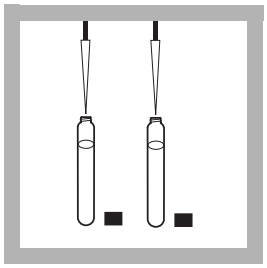
The display will show **mg/L, NH3-N** and the **ZERO** icon**.**

Note: *For alternate forms (NH_3), press the* **CONC** *key.*

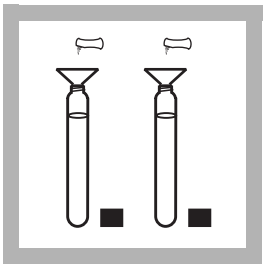
Note: *For proof of accuracy, use a 10-mg/L nitrogen, ammonia standard in place of the sample.*

3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

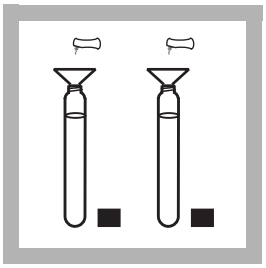
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



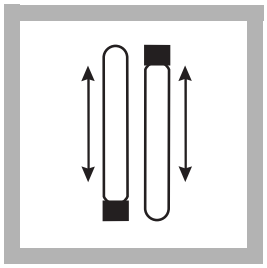
4. Remove the caps from 2 AmVer Diluent Reagent High Range Vials. Add 0.1 mL of sample to one vial (the sample). Add 0.1 mL of deionized water to the other (the blank).



5. Add the contents of 1 Ammonia Salicylate Reagent Powder Pillow for 5 mL Sample to each vial.

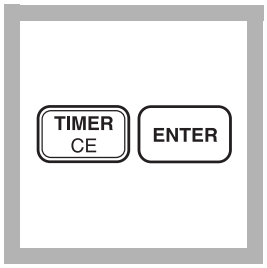


6. Add the contents of 1 Ammonia Cyanurate Reagent Powder Pillow for 5 mL Sample to each vial.



7. Cap the vials tightly and shake thoroughly to dissolve the powder.

Note: *A green color will develop if ammonia is present.*



8. Press:

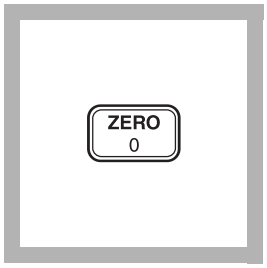
TIMER ENTER

A 20-minute reaction period will begin.

* Adapted from *Clin. Chim. Acta*, **14** 403 (1966).

9. Clean the outside of the vial with a towel. After the timer beeps, place the blank into the vial adapter. Tightly cover the vial with the instrument cap.

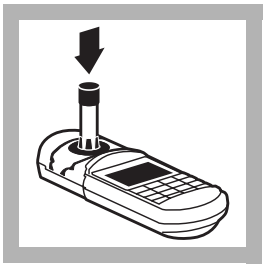
Note: *Wipe with a damp cloth and follow with a dry one to remove fingerprints and other marks.*



10. Press: **ZERO**

The cursor will move to the right, then the display will show:

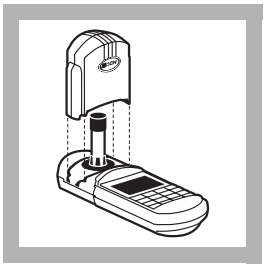
0 mg/L NH3-N



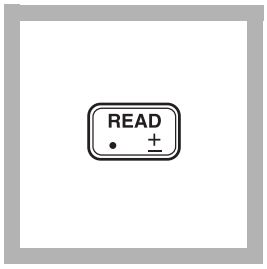
11. Place the prepared sample in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Tightly cover the vial with the instrument cap.



13. Press: **READ**

The cursor will move to the right, then the result in mg/L NH_3-N will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis. If chlorine is known to be present, add one drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a one liter sample. Preserve the sample by reducing the pH to 2 or less with hydrochloric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Before analysis, warm samples to room temperature and neutralize with 5.0 N sodium hydroxide. Correct the test result for volume additions.

Accuracy Check

Standard Additions Method

a) Snap the top off an Ammonia PourRite Ampule Standard, 150 mg/L NH_3-N.

b) Use the TenSette Pipet to add 0.2, 0.4 and 0.6 mL of standard to three 25-mL samples. Swirl to mix.

c) Analyze each sample as described above. The ammonia concentration should increase approximately 1.2 mg/L NH_3-N for each 0.2 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

To check accuracy, use a 10 or 50 mg/L Nitrogen, Ammonia Standard Solution or use a Nitrogen, Ammonia Voluette Ampule Standard, 50 mg/L.

Method Performance

Precision

In a single laboratory, using a standard solution of 50 mg/L ammonia nitrogen (NH_3-N) and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of $\pm$5 mg/L NH_3-N.

Estimated Detection Limit

The estimated detection limit for program 67 is 1 mg/L NH_3-N. For more information on the estimated detection limit, see *Section 1*.

Interferences

The following ions may interfere when present in concentrations exceeding those listed below.

In some lab environments, airborne cross contamination of the blank is possible. Complete preparation of the blank before opening or handling any samples or standards to avoid transfer of ammonia. If sample or standard containers have already been open, move to a separate area of the lab to prepare the blank.

Substance	Concentration and Suggested Treatments
Acidic or basic samples	Adjust to approximately pH 7. Use 1 N Sodium Hydroxide Standard Solution for acidic samples and 1 N Hydrochloric Acid Standard Solution for basic samples.
Calcium	50,000 mg/L as $CaCO_3$
Glycine, hydrazine	Will cause intensified colors in the prepared sample.
Magnesium	300,000 mg/L as $CaCO_3$
Iron	Eliminate iron interference as follows: **1.** Determine the amount of iron present in the sample using one of the total iron procedures. **2.** Add the same iron concentration to the deionized water in step 4. **3.** The interference will then be successfully blanked out.
Nitrite	600 mg/L as NO_2^--N
Nitrate	5,000 mg/L as NO_3^--N
Orthophosphate	5,000 mg/L as PO_4^{3-}-P
Sulfate	6,000 mg/L as SO_4^{2-}
Sulfide	Sulfide will intensify the color. Eliminate sulfide interference as follows: **1.** Measure about 350 mL of sample in a 500 mL Erlenmeyer flask. **2.** Add the contents of one Sulfide Inhibitor Reagent Powder Pillow. Swirl to mix. **3.** Filter the sample through folded filter paper. Use the filtered solution in step 4.
Turbidity and color	Give erroneous high values. Samples with severe interferences require distillation. Hach recommends the distillation procedure using the Hach General Purpose Distillation Set.

Summary of Method

Ammonia compounds combine with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a

sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a green-colored solution.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheets* for information specific to the reagents used. For additional information, refer to *Section 3*.

Pollution Prevention And Waste Management

The ammonia salicylate reagent contains sodium nitroferricyanide. Cyanide solutions are regulated as hazardous wastes by the Federal RCRA. Collect cyanide solutions for disposal as reactive (D001) waste. Be sure cyanide solutions are stored in a caustic solution with pH >11 to prevent release of hydrogen cyanide gas. See *Section 3* for further information in proper disposal of these materials.

REQUIRED REAGENTS

AmVer™ Reagent Set for Nitrogen, Ammonia, High Range, TNT (25 tests) 26069-45
Includes: (1) 23952-66, (1) 23954-66, (1) 272-42, *(50) AmVer HR Vials

Description	Quantity Required Per Test	Unit	Cat. No.
AmVer™ HR Reagent Test 'N Tube™ Vials	2 vials	50/pkg	*
Ammonia Salicylate Reagent Powder Pillows	2 pillows	50/pkg	23952-66
Ammonia Cyanurate Reagent Powder Pillows	2 pillows	50/pkg	23954-66

REQUIRED APPARATUS

COD/TNT Adapter	1	each	48464-00
Pipet, TenSette®, 0-1 mL	1	each	19700-01
Pipet Tips for 19700-01	varies	50/pkg	21856-96
Test Tube Rack	1-3	each	18641-00
Funnel, micro (for reagent addition)	1	each	25843-35

OPTIONAL REAGENTS

Nitrogen, Ammonia Standard Solution, 50 mg/L NH_3-N	500 mL		14791-50
Nitrogen, Ammonia Standard Solution, 10 mg/L NH_3-N	500 mL		153-49
Ammonia Standard Solution, PourRite™ ampules, 150 mg/L NH_3-N, 2 mL	20/pkg		21284-20
Hydrochloric Acid, ACS	500 mL		134-49
Sodium Hydroxide Standard Solution, 5.0 N	50 mL		2450-26

* Not available separately.

Sodium Hydroxide Standard Solution, 1.0 N	100 mL	1045-32
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL	323-32
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3, PO_4, COD, SO_4, TOC)	500 mL	28331-49

OPTIONAL REAGENTS (continued)

Description	Quantity Required Per Test	Unit	Cat. No.
Sulfide Inhibitor Powder Pillows		100/pkg	2418-99
Sulfuric Acid, 1.00 N		100 mL MDB	1270-32
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Cylinder, 25 mL, graduated, mixing	each	20886-40
Distillation Apparatus Set, general purpose	each	22653-00
Heater and Support Apparatus (for distillation), 115 VAC	each	22744-00
Heater and Support Apparatus (for distillation), 230 VAC	each	22744-02
Filter Paper, folded	100/pkg	1894-57
Flask, Erlenmeyer, 500 mL	each	505-49
Funnel, analytical (for filtering)	each	1083-68
Jack, laboratory (use with distillation apparatus)	each	22743-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
PourRite™ Ampule Breaker	each	24846-00
Sample Cell, 10-20-25 mL, w/cap	6/pkg	24019-06

For Technical Assistance, Price and Ordering

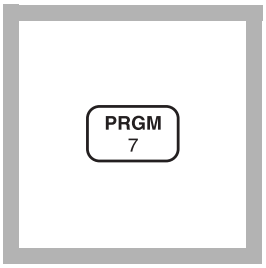
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITROGEN, Total Inorganic, Test 'N Tube™ (0 to 25.0 mg/L N)

Titanium Trichloride Reduction Method **For water, wastewater, and seawater**

Requires Centrifuge

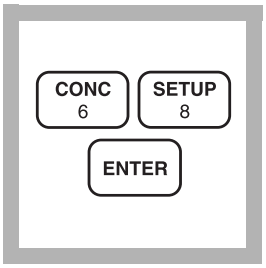


1. Enter the stored program number for Test 'N Tube Total Inorganic Nitrogen.

Press: **PRGM**

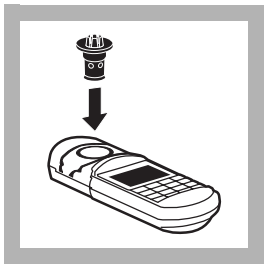
The display will show:

PRGM ?



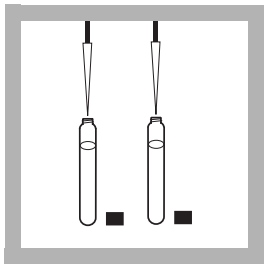
2. Press: **68 ENTER**

The display will show **mg/L, N** and the **ZERO** icon**.**

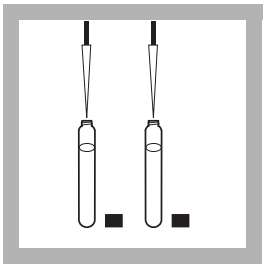


3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert.

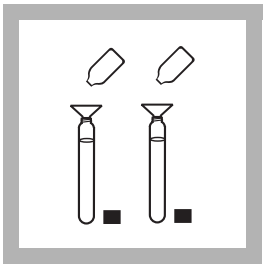
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



4. Pipet 1 mL of Total Inorganic Nitrogen Pretreatment Base Concentrate into each of 2 Total Inorganic Nitrogen Pretreatment Diluent Vials.



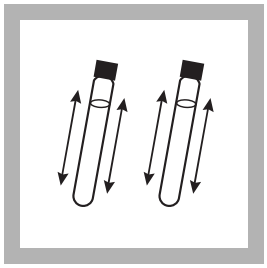
5. Pipet 1 mL of sample into 1 TIN Diluent Vial (the sample). Pipet 1 mL of deionized water into the other vial (the blank). Cap the vials and shake for 30 seconds to mix.



6. Snap the necks off two Total Inorganic Nitrogen Reductant ampules and pour the contents of one into the TIN Diluent Vial containing sample. Repeat for the second vial, the blank.

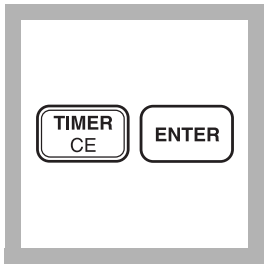
Note: *For safety, wear gloves while breaking the ampules.*

Note: *A black precipitate will form immediately.*



7. Cap the vials. Shake gently for 30 seconds to mix the reagents. Allow the vials to sit for at least one minute.

Note: *The precipitate should remain black after shaking. Excessive shaking will cause a white precipitate and low results.*

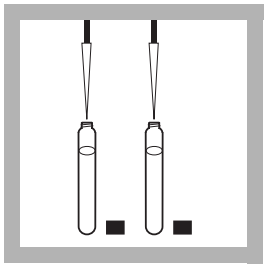


8. Centrifuge the vials for 3 minutes or until the solids settle to the bottom of the vial.

Press: **TIMER ENTER**

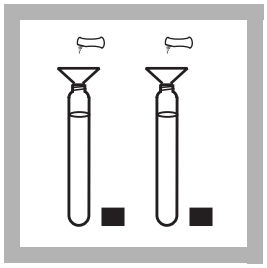
immediately after starting the centrifuge.

Note: *The precipitate will settle without using a centrifuge, but it may take up to 30 minutes.*

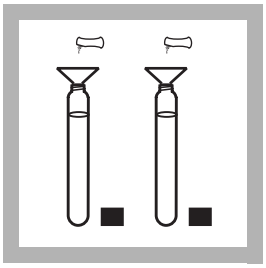


9. Remove the caps from 2 AmVer Diluent Reagent Test ‘N Tubes for Low Range Ammonia Nitrogen. Using a pipet, add 2 mL of centrifuged sample into 1 vial. Add 2 mL of centrifuged blank to the other vial. Label the vials appropriately.

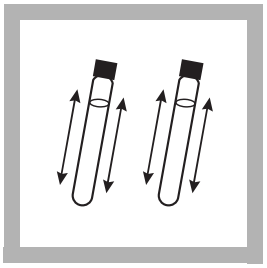
Note: *Pipet carefully to avoid disturbing the sediment.*



10. Using a funnel, add the contents of one Ammonia Salicylate Reagent Powder Pillow to each vial.

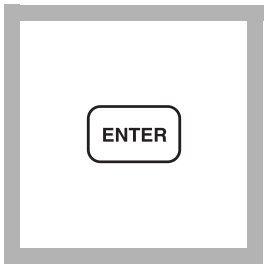


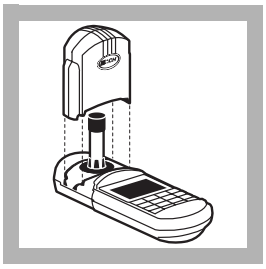
11. Using a funnel, add the contents of one Ammonia Cyanurate Reagent Powder Pillow to each vial.

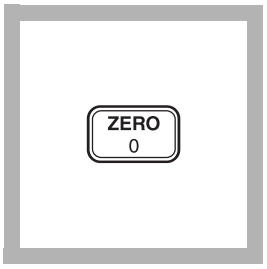


12. Cap the vials tightly and shake thoroughly to dissolve the powder.

Note: *A green color will develop if inorganic nitrogen is present.*







13. The display will show: **15:00 TIMER 2**

Press: **ENTER**

A 15-minute reaction period will begin.

14. After the timer beeps, clean the outside of the vials with a towel. Place the blank in the adapter. Push straight down on the top of the vial until it seats solidly into the adapter. Do not move the vial from side to side as this can cause errors.

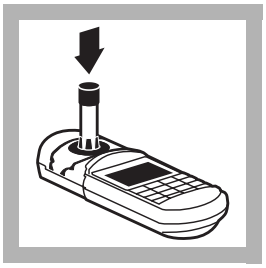
Note: *Wipe with a damp cloth and follow with a dry one to remove fingerprints and other marks.*

15. Tightly cover the sample cell with the instrument cap.

16. Press: **ZERO**

The cursor will move to the right, then the display will show:

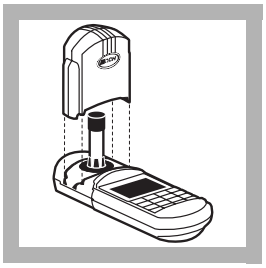
0.0 mg/L N



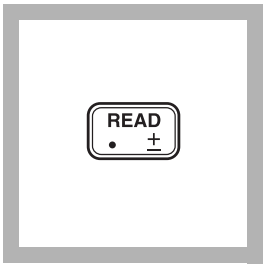
17. Place the prepared sample in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



18. Tightly cover the sample cell with the instrument cap.



19. Press: **READ**

The cursor will move to the right, then the result in mg/L total inorganic nitrogen will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling And Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis.

If chlorine is known to be present, add 1 drop of 0.1 N sodium thiosulfate for each 0.3 mg/L Cl_2 in a 1 liter sample.

Preserve the sample by reducing the pH to 2 or less with concentrated hydrochloric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N Sodium

Hydroxide before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1*.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a fresh High Range Nitrate Nitrogen PourRite Ampule Standard, 500 mg/L NO_3^--N.

c) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to 3 25-mL mixing cylinders. Mix thoroughly.

d) Analyze each sample as described in the procedure; use a 1-mL aliquot of the prepared sample in Step 5. The nitrogen concentration should increase about 1.8 to 1.9 mg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

To check accuracy, use a 10.0 mg/L Nitrate Nitrogen Standard Solution listed under Optional Reagents. Alternatively, a 20.0 mg/L nitrate nitrogen standard can be prepared by diluting 2 mL of solution from a PourRite Ampule Standard for High Range Nitrate Nitrogen, 500 mg/L NO_3^--N, to 50 mL with deionized water. Substitute this standard for the sample and perform the test as described. The recovery of the standards should be about 90-95%.

Method Performance

Precision/Accuracy

The total inorganic nitrogen test provides an estimate of the total nitrite, nitrate, and ammonia nitrogen load in water or wastewater samples. This test is most applicable for monitoring an industrial process stream or a wastewater treatment stream where it is important to track the inorganic nitrogen load as it passes through the treatment process. The test exhibits different recoveries of each of the three nitrogen species, as summarized below. This test is not recommended for quantifying only one of the three species. In that case, use a specific procedure for each particular analyte.

Ammonia Nitrogen

In a single laboratory, using a standard solution of 20.0 mg/L NH_3-N and 2 representative lots of reagent with the instrument, a single operator obtained a mean recovery of 21.3 mg/L with a standard deviation of
± 0.77 mg/L N (replicate number = 7 per reagent lot).

Nitrate Nitrogen
In a single laboratory, using a standard solution of 20.0 mg/L NO_3-N and 2 representative lots of reagent with the instrument, a single operator obtained a mean recovery of 18.9 mg/L with a standard deviation of
± 0.55 mg/L N (replicate number = 7 per reagent lot).

Nitrite Nitrogen
In a single laboratory, using a standard solution of 20.0 mg/L NO_2-N and 2 representative lots of reagent with the instrument, a single operator obtained a mean recovery of 14.6 mg/L with a standard deviation of
± 0.77 mg/L N (replicate number = 7 per reagent lot).

Estimated Detection Limit

The estimated detection limit for program 68 is 0.7 mg/L N. For more information on the estimated detection limit, *see Section 1*.

Interferences

The following ions may interfere when present in concentrations exceeding those listed below:

Species	Level	Effect
Calcium	1000 mg/L as $CaCO_3$	Positive
Manganese (IV)	3 mg/L	Negative
Magnesium	1000 mg/L as $CaCO_3$	Positive
Sulfide	3 mg/L	Negative
Sulfate	250 mg/L	Negative

The following do not interfere below the levels listed:

Species	Level
Al^{3+}	8 mg/L
Ba^{2+}	40 mg/L
Cu^{2+}	40 mg/L
Fe^{3+}	8 mg/L
Zn^{2+}	80 mg/L
F^-	40 mg/L
PO_4^{3-}-P	8 mg/L
SiO_2	80 mg/L
EDTA	80 mg/L

Summary of Method

Titanium (III) ions reduce nitrate and nitrite to ammonia in a basic environment. After centrifugation to remove solids, the ammonia is combined with chlorine to form monochloramine. Monochloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue-colored compound. The blue color is masked by the yellow color from the excess reagent present to give a final green-colored solution.

NITROGEN, TOTAL INORGANIC, Test 'N Tube, continued

REQUIRED REAGENTS

Total Inorganic Nitrogen Pretreatment Reagent Set ($TiCl_3$ Reduction) (25 tests) 26049-45
Includes: (1) 26051-50, (1) 2040-59, *(50) TIN Pretreatment Diluent Vials

AmVer™ Reagent Set for Nitrogen, Ammonia, Low Range (25 tests)..... 26045-45
Includes: (1) 23952-66, (1) 23954-66 , (1) 272-42, *(50) AmVer™ Diluent LR Vials

Description	Quantity Required Per Test	Unit	Cat. No.
Total Inorganic Nitrogen Pretreatment Diluent Vials	2 vials	50/pkg	*
Total Inorganic Nitrogen Reductant Ampules	2 ampules	50/pkg	26051-50
Total Inorganic Nitrogen Pretreatment Base Concentrate	2 mL	50 mL	2040-59
AmVer™ Diluent Reagent, Low Range Vials	2 vials	50/pkg	*
Ammonia Salicylate Reagent Powder Pillows for 5-mL sample	2 pillows	50/pkg	23952-66
Ammonia Cyanurate Reagent Powder Pillows for 5-mL sample	2 pillows	50/pkg	23954-66

REQUIRED APPARATUS

Centrifuge, 115V	1	each	26765-00
Centrifuge, 230V	1	each	26765-02
COD/TNT Vial Adapter	1	each	48464-00
Funnel, micro	1	each	25843-35
Pipet, TenSette®, 0.1 to 1.0	1	each	19700-01
Pipet Tips for 19700-01	2	50/pkg	21856-96
Test Tube Rack	1	each	18641-00

OPTIONAL REAGENTS

Hydrochloric Acid, ACS	500 mL		134-49
Nitrate Nitrogen Standard Solution, 10 mg/L NO_3^--N	500 mL		307-49
Nitrate Nitrogen Standard Solution, PourRite Ampules, 500 mg/L NO_3^--N, 2 mL	20/pkg		14260-20
Sodium Hydroxide Standard Solution, 5.0 N	50 mL	SCDB	2450-26
Sodium Thiosulfate Standard Solution, 0.1 N	100 mL	MDB	323-32
Wastewater Effluent Standard, Inorganics (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL		28332-49
Water, deionized	4 L		272-56

* These items are not sold separately. Please order the complete set (cat. no. 26049-45 or 26045-45).

NITROGEN, TOTAL INORGANIC, Test 'N Tube, continued

OPTIONAL APPARATUS

Cylinder, graduated, mixing, 25 mL	each	20886-40
Flask, volumetric, Class A, 50.0 mL	each	14574-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
Pipet, volumetric, Class A, 2.0 mL	each	14515-36
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28

PourRite Ampule Breaker	each	24846-00

For Technical Assistance, Price and Ordering

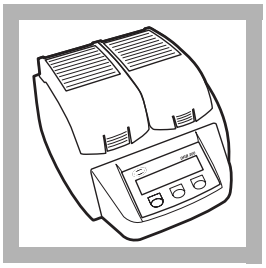
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

NITROGEN, TOTAL, Test 'N Tube (0.0 to 25.0 mg/L N)

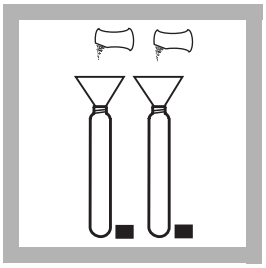
TNT Persulfate Digestion Method

For water and wastewater



1. Turn on the DRB 200 Reactor. Heat to 103-106 °C (optimum temperature is 105 °C).

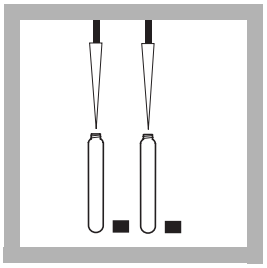
Note: *For proof of accuracy, run a 20 mg/L NH_3-N standard through digestion and analysis.*



2. Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to each of two Total Nitrogen Hydroxide Reagent vials.

Note: *Wipe off any reagent that may get on the lid or the tube threads.*

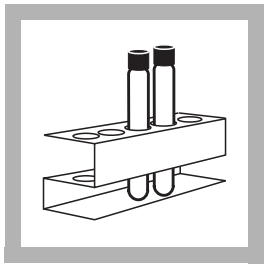
Note: *One reagent blank is sufficient for each set of samples.*



3. Add 2 mL of sample to one vial. Add 2 mL of organic-free water to another vial (the reagent blank). Cap both vials and shake vigorously (about 30 seconds). Place the vials in the Reactor. Heat for 30 minutes.

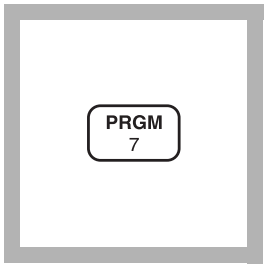
Note: *The reagent may not dissolve completely after shaking.*

Note: *Alternate water must be free of all nitrogen-containing species.*



4. Using finger cots or gloves, remove the hot vials from the reactor and allow to cool to room temperature.

Note: *It is very important to remove the vials from the Reactor after exactly 30 minutes.*

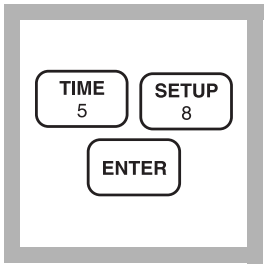


5. Enter the stored program number for Test ‘N Tube Total Nitrogen.

Press: **PRGM**

The display will show:

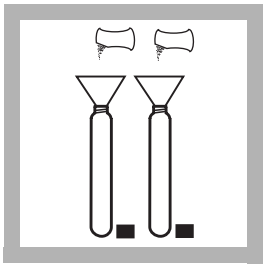
PRGM ?



6. Press: **58 ENTER**

The display will show **mg/L, N** and the **ZERO** icon**.**

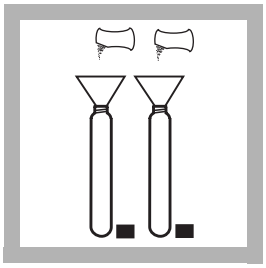
Note: *For alternate forms (NH_3, NO_3), press the* **CONC** *key.*



7. Remove the caps from the digested vials and add the contents of one TN Reagent A Powder Pillow to each vial. Cap the vials and shake for 15 seconds.

Press: **TIMER ENTER** after shaking.

A three-minute reaction period will begin.



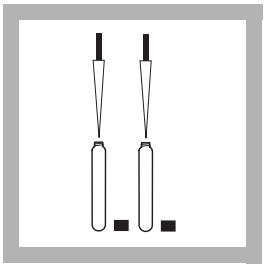
8. After the timer beeps, remove the caps from the vials and add one TN Reagent B Powder Pillow to each vial. Cap the vials and shake for 15 seconds. The display will show:

02:00 Timer 2

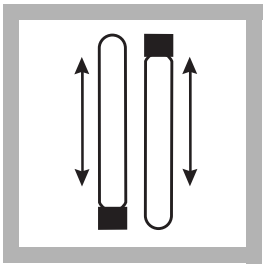
Press **ENTER** after shaking.

A two-minute reaction period will begin.

Note: *The reagent will not completely dissolve. The solution will begin to turn yellow.*

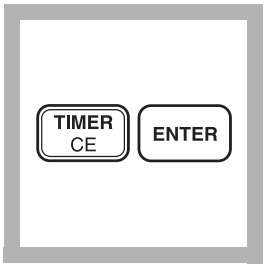


9. After the timer beeps, remove the caps from two TN Reagent C Vials. Add 2 mL of digested, treated sample to one vial. Add 2 mL of the digested, treated reagent blank to the second TN Reagent C Vial.



10. Cap and invert 10 times to mix. Use slow, deliberate inversions for complete recovery. The vials will be warm.

Note: *Follow these instructions for inversion or low results may occur. Hold the vial vertical with the cap up. Invert the vial and wait for all of the solution to flow to the cap end. Pause. Return the vial to the upright position and wait for all of the solution to flow to the vial bottom. This is one inversion (10 inversions = 30 seconds).*



11. The display will show: **05:00 Timer 3**

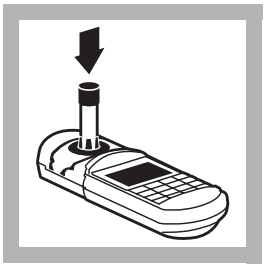
Press: **ENTER**

A five-minute reaction period will begin.

Note: *The yellow color will intensify.*

12. During the reaction period, insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

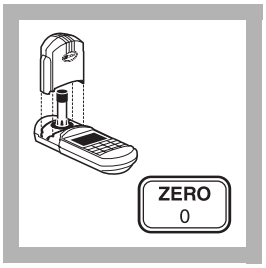
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



13. After the timer beeps, wipe the TN Reagent C vial containing the reagent blank. Place the vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



14. Tightly cover the vial with the instrument cap.

Press: **ZERO**

The cursor will move to the right, then the display will show:

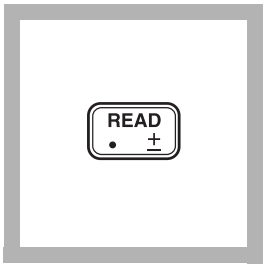
0.0 mg/L N

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*

Note: *The reagent blank is stable when stored in the dark; see* Blanks For Colorimetric Measurement *following these steps.*

15. Wipe the TN Reagent C vial containing the sample and place it into the adapter. Tightly cover the vial with the instrument cap.

Note: *Multiple samples may be read after zeroing on one reagent blank.*



16. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrogen (N) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Note: *If the display flashes "limit", dilute the sample and repeat the digestion and the colorimetric finish. The digestion must be repeated for accurate results; diluting and repeating the color finish does not yield complete results. Multiply the result by the dilution factor; see Section 1.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis.

Preserve the sample by reducing the pH to 2 or less with concentrated sulfuric acid (at least 2 mL). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1*.

Accuracy Check

This method generally yields 95-100% recovery on organic nitrogen standards. For proof of accuracy Hach offers a set of three Primary Standards for Kjeldahl Nitrogen.

1. Prepare one or more of the following three solutions. Each preparation is for an equivalent 25 mg/L N standard. Use water that is free of all organic and nitrogen-containing species.

   a) Weigh 0.3379 g of Ammonium p-Toluenesulfonate (PTSA). Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

   b) Weigh 0.4416 g of Glycine p-Toluenesulfonate. Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

   c) Weigh 0.5274 g of Nicotinic p-Toluenesulfonate. Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

2. Analyze each of these solutions using the test procedure above. Calculate the percent recovery for each using this formula:

$$\% \text{ recovery} = \frac{\text{measured concentration}}{25} \times 100$$

The percent recovery should be:

Compound	Lowest Expected % Recovery
Ammonia-PTSA	95%
Glycine-PTSA	95%
Nicotinic-PTSA	95%

Hach analysts have found Ammonia-PTSA to be the most difficult to digest. Other compounds may yield different percent recoveries.

Standard Solution Method

Substitute 2 mL of a 20 mg/L ammonia nitrogen standard solution for the sample. To prepare a 20-mg/L standard, use a 20-mL Class A pipet to transfer 20 mL of a 100-mg/L Ammonia Nitrogen Standard (see *Optional Reagents*) to a 100-mL Class A volumetric flask. Dilute to the line with organic-free water. A single analyst should obtain less than 5% variation on replicates. Comparison of the user-obtained value with the standard concentration is an indication of test performance for this user.

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off an Ammonia Nitrogen Voluette Ampule Standard Solution, 160 mg/L as NH_3-N.

c) Use the TenSette Pipet to add 0.3 mL, 0.6 mL, and 0.9 mL of standard, respectively, to the three mixing cylinders.

d) Stopper each cylinder and mix thoroughly.

e) Add 2 mL of each prepared solution, respectively, to three TN Hydroxide Reagent Sample Digestion Vials.

f) Analyze each standard addition sample as described in the procedure. The nitrogen concentration should increase 2 mg/L for each 0.3 mL of standard added.

g) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Blanks for Colorimetric Measurement

The reagent blank may be used up to 7 days for measurements using the same lots of reagents. Store the reagent blank in the dark at room temperature (18-25 °C). If a small amount of white floc appears prior to the end of one week, discard the reagent blank and prepare a new one.

Method Performance

Precision

A Hach chemist analyzed two independent nutrient standards. The lowest average percent recovery was 95% with a standard deviation of ±2%.

In a single laboratory, using a standard solution of 15.0 mg/L N and two lots of reagent with the instrument, a single operator obtained a standard deviation of less than ±0.5 mg/L N. For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit

The estimated detection limit for program 58 is 2 mg/L N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering substances that resulted in a concentration change of

±10%:

Substance	Level and Effect
Bromide	>60 ppm; positive interference
Chloride	>1000 ppm; positive interference

The substances in the following table have been tested and found **not** to interfere up to the indicated levels (in mg/L):

Substance	Maximum Level Tested (mg/L)
Barium	2.6
Calcium	300
Chromium (3+)	0.5
Iron	2
Lead	6.6 ppb
Magnesium	500
Organic Carbon	150
pH	13 pH units
Phosphorus	100
Silica	150
Silver	0.9
Tin	1.5

Hach chemists tested this chemistry on standard nitrogen solutions prepared from the following compounds and obtained ≥95% recovery:

- Ammonium chloride
- Ammonium sulfate
- Ammonium acetate
- Urea
- Glycine

Ammonium chloride or nicotinic-PTSA spikes in domestic influent, effluent and the ASTM standard specification for substitute wastewater (D 5905-96) also resulted in ≥95% recovery.

Large amounts of nitrogen-free organic compounds in some samples may decrease digestion efficiency by consuming some of

the persulfate reagent. Samples known to contain high levels of organics should be diluted and re-run to verify digestion efficiency.

Summary of Method

An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after the digestion to eliminate halogen oxide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum near 420 nm.

REQUIRED REAGENTS

Description	Cat. No.
Test 'N Tube Total Nitrogen Reagent Set (50 vials)	26722-45
Includes:	
TN Reagent C Vials, Acid Solution*, 50/pkg	26721-45
TN Hydroxide Reagent Sample Digestion Vials*, 50/pkg	26717-45

Description	Quantity Required Per Test	Unit	Cat. No.
TN Persulfate Reagent Powder Pillows	2 pillows	100/pkg	26718-49
TN Reagent A, Bisulfite Powder Pillows	2 pillows	100/pkg	26719-49
TN Reagent B, Indicator Powder Pillows	2 pillows	100/pkg	26720-49

REQUIRED APPARATUS

DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
COD/TNT Adapter	1	each	48464-00
Funnel, micro	1	each	25843-35
Pipet, TenSette, 1.0-10.0 mL	1	each	19700-10
Pipet Tips for 19700-10	1	50/pkg	21997-96
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips for 19700-01	2	50/pkg	21856-96
Test Tube Cooling Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Nitrogen, Ammonia, 100 mg/L NH_3-N	500 mL	24065-49
Nitrogen, Ammonia, Voluette Ampule, 160 mg/L NH_3–N, 10 mL	16/pkg	21091-10
Sulfuric Acid, ACS	500 mL	979-49
Primary Standards for Kjeldahl Nitrogen	set of 3	22778-00
Ammonium p-Toluenesulfonate	25 g	22779-24
Glycine p-Toluenesulfonate	25 g	22780-24
Nicotinic Acid p-Toluenesulfonate	25 g	22781-24

* Not available separately.

NITROGEN, TOTAL, Test 'N Tube, continued

Sodium Hydroxide Standard Solution, 5.0 N ..... 50 mL MDB 2450-26
Wastewater Effluent Standard, Inorganics
(NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC) ..... 500 mL 28332-49
Water, organic-free ..... 500 mL 26415-49

OPTIONAL APPARATUS

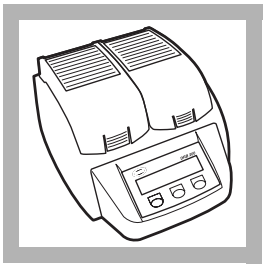
Ampule Breaker Kit ..... each 21968-00
Balance, analytical, 115 VAC ..... each 28014-01
Balance, analytical, 230 VAC ..... each 28014-02
Cots, finger 2/pkg 14647-02
Cylinder, graduated, mixing, 25 mL (3 required) ..... each 26363-40
Flask, volumetric, Class A, 1000 mL (3 required) ..... each 14574-53
Flask, volumetric, Class A, 100 mL ..... each 14574-42
Pipet, volumetric, Class A, 20 mL ..... each 14515-20
Pipet Tips, for 19700-01 TenSette Pipet 1000/pkg 21856-28
pH Paper, 1 to 11 pH units ..... 5 rolls/pkg 391-33

DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm LTV082.52.30001

NITROGEN, TOTAL, HR, Test 'N Tube™ (10.0 to 150.0 mg/L N)

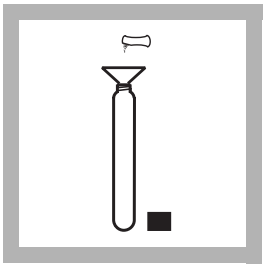
TNT Persulfate Digestion Method

For water and wastewater



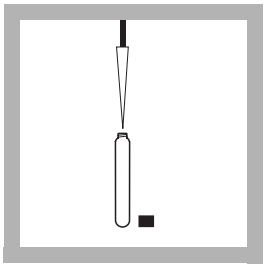
1. Turn on the DRB 200 Reactor. Heat to 103-106 °C (optimum temperature is 105 °C).

Note: *For proof of accuracy, run a 125 mg/L NH_3-N standard through digestion and analysis.*



2. Prepare a reagent blank: Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to one HR Total Nitrogen Hydroxide Digestion Vial.

Note: *Wipe off any reagent that gets on the lid or the tube threads.*



3. Add 0.5 mL of organic-free water to the vial. Cap the vial and shake vigorously for about 30 seconds.

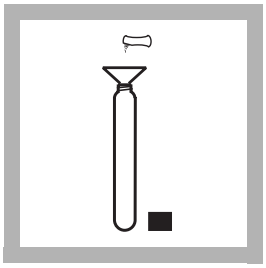
Process this reagent blank exactly the same as the sample, including digestion and color finish. Proceed to *step 6.*

Note: *Alternate water must be free of all nitrogen-containing species.*

Note: *The persulfate reagent may not dissolve completely after shaking.*

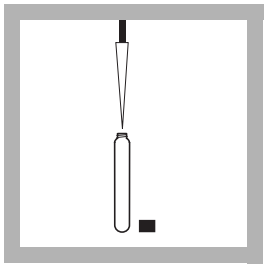
Note: *One reagent blank is sufficient for each set of samples using the same lots of reagents.*

Note: *The reagent blank is stable for as long as seven days when stored in the dark; see* Blanks for Colorimetric Measurement *following this procedure.*



4. Prepare a sample: Using a funnel, add the contents of one Total Nitrogen Persulfate Reagent Powder Pillow to one HR Total Nitrogen Hydroxide Digestion Vial.

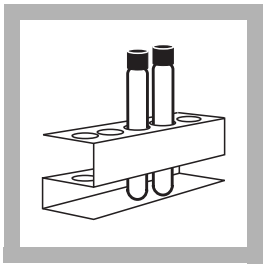
Note: *Wipe off any reagent that gets on the lid or the tube threads.*



5. Add 0.5 mL of sample to the vial. Cap the vial and shake vigorously for about 30 seconds.

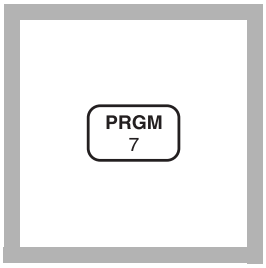
Note: *The persulfate reagent may not dissolve completely after shaking.*

6. Place the vials in the Reactor. Heat for 30 minutes.



7. Using finger cots or gloves, remove the hot vials from the reactor and allow to cool to room temperature.

Note: *It is very important to remove the vials from the Reactor after exactly 30 minutes.*

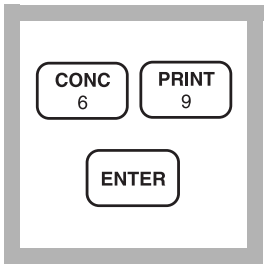


8. Enter the stored program number for Test 'N Tube HR Total Nitrogen.

Press: **PRGM**

The display will show:

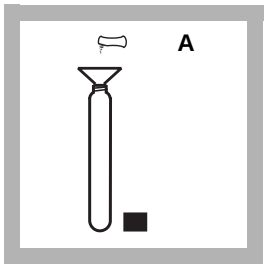
PRGM ?



9. P**ress: 69 ENTER**

The display will show **mg/L, N** and the **ZERO** icon**.**

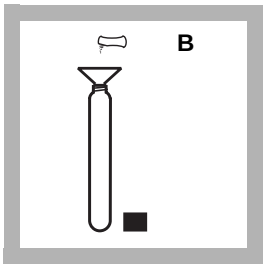
Note: *For alternate forms (NH_3, NO_3), press the* **CONC** *key.*



10. Add the contents of one Total Nitrogen Reagent A Powder Pillow to the vial containing the digested blank or sample. Cap the vial and shake for 15 seconds.

Press: **TIMER ENTER** after shaking.

A three-minute reaction period will begin.



11. After the timer beeps, add one Total Nitrogen Reagent B Powder Pillow to the vial. Cap the vial and shake for 15 seconds.

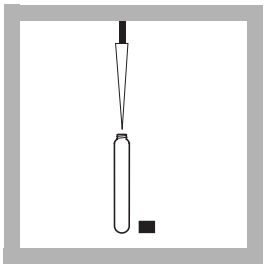
The display will show:

02:00 Timer 2

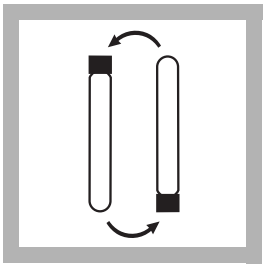
Press **ENTER** after shaking.

A two-minute reaction period will begin.

Note: *The reagent will not completely dissolve. The solution will begin to turn yellow.*

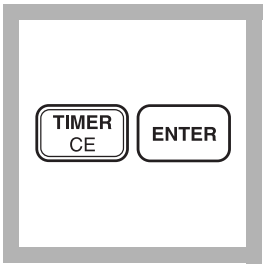


12. After the timer beeps, remove the cap from one Total Nitrogen Reagent C Vial. Add 2 mL of digested, treated sample (or reagent blank) to the vial. The vial will be warm.



13. Cap and invert slowly 10 times to mix. The vial will be warm.

Note: *Proper mixing is important for complete recovery. Hold the vial vertical with the cap up. Invert the vial and wait for all of the solution to flow to the cap end. Pause. Return the vial to the upright position and wait for all of the solution to flow to the vial bottom. This is one inversion (10 inversions = 30 seconds).*



14. The display will show: **05:00 Timer 3**

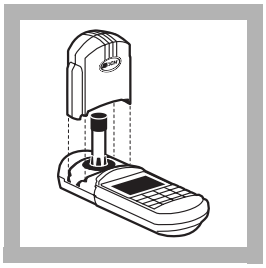
Press: **ENTER**

A five-minute reaction period will begin. Do not invert the vial again.

Note: *The yellow color will intensify.*

15. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



16. When the timer beeps, wipe the outside of the Total Nitrogen Reagent C vial containing the reagent blank.

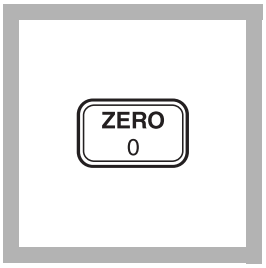
Place the vial into the adapter with the Hach logo facing the front of the instrument.

Push straight down on the top of the vial until it seats solidly into the adapter.

Tightly cover the vial with the instrument cap.

Note: *Do not move the vial from side to side during insertion, as this can cause errors.*

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*



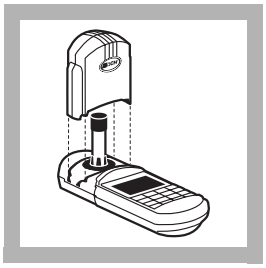
17. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L N

18. Wipe the Total Nitrogen Reagent C vial containing the sample.

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*



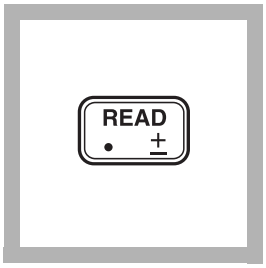
19. Place the vial into the adapter with the Hach logo facing the front of the instrument.

Push straight down on the top of the vial until it seats solidly into the adapter.

Tightly cover the vial with the instrument cap.

Note: *Do not move the vial from side to side during insertion, as this can cause errors.*

Note: *Multiple samples may be read after zeroing on one reagent blank.*



20. Press: **READ**

The cursor will move to the right, then the result in mg/L nitrogen (N) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see* Standard Adjust *in* Section1 *of the Procedures Manual).*

Note: *If the display flashes* **Limit**, *dilute the sample and repeat the digestion and the colorimetric finish. The digestion must be repeated for accurate results; diluting and repeating the color finish does not yield complete results. Multiply the result by the dilution factor; see SECTION 1.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Best results are obtained with immediate analysis.

Preserve the sample by reducing the pH to 2 or less with concentrated sulfuric acid (at least 2 mL/L). Store at 4 °C (39 °F) or less. Preserved samples may be stored up to 28 days. Warm samples to room temperature and neutralize with 5 N sodium hydroxide before analysis. Correct the test result for volume additions; see *Correcting for Volume Additions* in *Section 1*.

Accuracy Check

This method generally yields 95-100% recovery on organic nitrogen standards. For proof of accuracy Hach offers a set of three Primary Standards for Kjeldahl Nitrogen.

1. Prepare one or more of the following three solutions. Each preparation is for an equivalent 120 mg/L N standard. Use water that is free of all organic and nitrogen-containing species.

   a) Weigh 1.6208 g of Ammonium p-Toluenesulfonate (PTSA). Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

   b) Weigh 2.1179 g of Glycine p-Toluenesulfonate. Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

   c) Weigh 2.5295 g of Nicotinic p-Toluenesulfonate. Dissolve in a 1000-mL volumetric flask with deionized water. Add deionized water to the 1000-mL mark.

2. Analyze each of these solutions using the test procedure above. Calculate the percent recovery for each using this formula:

$$\%\ \text{recovery} = \frac{\text{measured concentration}}{120} \times 100$$

The percent recovery should be:

Compound	Lowest Expected % Recovery
Ammonia-PTSA	95%
Glycine-PTSA	95%
Nicotinic-PTSA	95%

Hach analysts have found Ammonia-PTSA to be the most difficult to digest. Other compounds may yield different percent recoveries.

Standard Solution Method

For proof of accuracy, substitute 0.5 mL of a 125 mg/L ammonia nitrogen standard solution for the sample in the procedure. To prepare a 125-mg/L standard, use a 25-mL Class A pipet to transfer 25.00 mL of a 1000-mg/L Ammonia Nitrogen Standard

(see *OPTIONAL REAGENTS* on page *400*) to a 200-mL Class A volumetric flask. Dilute to the line with organic-free water.

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off an Ammonia Nitrogen Voluette™ Ampule Standard Solution, 1000 mg/L as NH_3-N.

c) Use the TenSette® Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to the three mixing cylinders.

d) Stopper each cylinder and mix thoroughly.

e) Add 0.5 mL of each prepared solution, respectively, to three HR Total Nitrogen Hydroxide Digestion Vials.

f) Analyze each standard addition sample as described in the procedure. The nitrogen concentration should increase 4 mg/L N for each 0.1 mL of standard added.

g) If these increases do not occur, see *Standard Additions* in *Section 1* for troubleshooting information.

Blanks for Colorimetric Measurement

The reagent blank may be used repeatedly for measurements using the same lots of reagents. Store the reagent blank in the dark at room temperature (18–25 °C) for a maximum of seven days. If a small amount of white floc appears prior to the end of one week, discard the reagent blank and prepare a new one.

Method Performance

Precision

In a single laboratory, using a standard solution of 125 mg/L N and two lots of reagent with the instrument, a single operator obtained a standard deviation of less than 3 mg/L N. For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit

The estimated detection limit for program 69 is 7 mg/L N. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering substances that resulted in a concentration change of ±10%:

Substance	Level and Effect
Bromide	> 240 ppm; positive interference
Chloride	≥3000 ppm; positive interference

The substances in the following table have been tested and found **not** to interfere up to the indicated levels:

Substance	Maximum Level Tested (mg/L)
Barium	10.4
Calcium	1200
Chromium (3+)	2
Iron	8
Lead	26.4 ppb
Magnesium	2000
Organic Carbon	600
pH	13 pH units
Phosphorus	400
Silica	600
Silver	3.6
Tin	6.0

The large amounts of nitrogen-free organic compounds in some samples may decrease digestion efficiency by consuming some of the persulfate reagent. Samples known to contain high levels of organics should be diluted and re-run to verify digestion efficiency.

Summary of Method

An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after the digestion to eliminate halogen oxide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex with an absorbance maximum near 420 nm.

NITROGEN, TOTAL, HR, Test 'N Tube, continued

REQUIRED REAGENTS

Test 'N Tube HR Total Nitrogen Reagent Set (50 vials) 27141-00
Includes: (1) 26718-46, (1) 26719-46, (1) 26720-46, *(50) Hydroxide Digestion Vials, *(50) Acid Solution Vials

Description	Quantity Required Per Test	Unit	Cat. No.
HR Total Nitrogen Hydroxide Digestion Vials	1 vial	50/pkg	*
Total Nitrogen Persulfate Reagent Powder Pillows	1 pillow	50/pkg	26718-46
Total Nitrogen Reagent A, Bisulfite Powder Pillows	1 pillow	50/pkg	26719-46
Total Nitrogen Reagent B, Indicator Powder Pillows	1 pillow	50/pkg	26720-46
Total Nitrogen Reagent C Vials, Acid Solution	1 vial	50/pkg	*

REQUIRED APPARATUS

DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
COD/TNT Adapter	1	each	48464-00
Funnel, micro	1	each	25843-35
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips for 19700-01	2	50/pkg	21856-96
Test Tube Rack, for cooling vials	1-3	each	18641-00

OPTIONAL REAGENTS

Nitrogen, Ammonia, 1000 mg/L NH_3-N		1 L	23541-53
Nitrogen, Ammonia, Voluette Ampule, 1000 mg/L NH_3-N, 10 mL		16/pkg	23541-10
Sulfuric Acid, ACS		500 mL	979-49
Primary Standards for Kjeldahl Nitrogen		set of 3	22778-00
Ammonium p-Toluenesulfonate		25 g	22779-24
Glycine p-Toluenesulfonate		25 g	22780-24
Nicotinic Acid p-Toluenesulfonate		25 g	22781-24
Sodium Hydroxide Standard Solution, 5.0 N		50 mL MDB	2450-26
Wastewater Influent Standard, Inorganics (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28331-49
Water, organic-free		500 mL	26415-49

* These items are not sold separately. Please order the complete set (Cat. No. 27141-00) as a replacement.

NITROGEN, TOTAL, HR, Test 'N Tube, continued

OPTIONAL APPARATUS

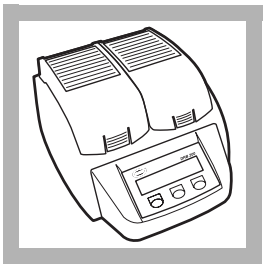
Description		Unit	Cat. No.
Ampule Breaker Kit		each	21968-00
Balance, analytical, 115 Vac		each	28014-01
Balance, analytical, 230 Vac		each	28014-02
Cots, finger		2/pkg	14647-02
Cylinder, graduated, mixing, 25 mL	3	each	26363-40
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm			LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm			LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm			LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm			LTV082.52.30001
Flask, volumetric, Class A, 1000 mL	3	each	14574-53
Flask, volumetric, Class A, 200 mL		each	14574-45
Pipet, volumetric, Class A, 25 mL	2	each	14515-40
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224. Out side the U.S.A— Contact the Hach office or distributor serving you.
Outside the U.S.A.—Contact the Hach office or distributor serving you.

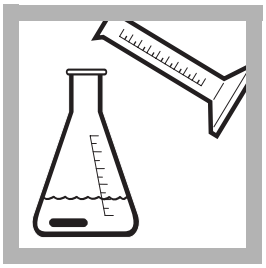
ORGANIC CARBON, TOTAL, Low Range (0.0–20.0 mg/L C)

Direct Method* **For water, drinking water, and wastewater**



1. Turn on the DRB 200 reactor. Heat to 103-105 °C.

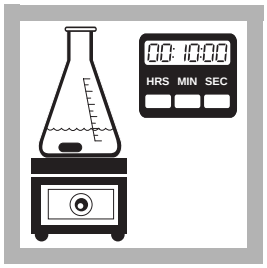
Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*



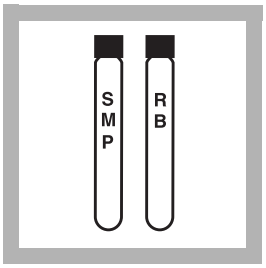
2. Use a graduated cylinder to add 10 mL of sample to a 50-mL erlenmeyer flask containing a stir bar.

3. Add 0.4 mL of Buffer Solution, pH 2.0.

Note: *Use pH paper to make sure the sample pH is 2.*

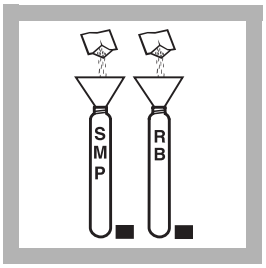


4. Place the flask on a stir plate and stir at a moderate speed for 10 minutes.

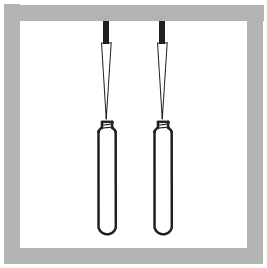


5. Label two Low Range Acid Digestion vials: **sample** and **reagent blank**.

Note: *A reagent blank is required for each series of samples.*



6. Using a funnel, add the contents of one TOC Persulfate Powder Pillow to each Acid Digestion vial (colorless liquid).

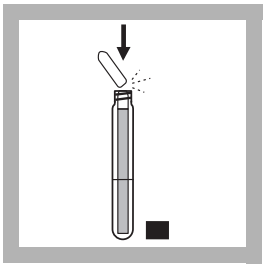


7. Use a TenSette® Pipet to add 3.0 mL of **organic-free water** to the **reagent blank** vial and 3.0 mL of **prepared sample** to the **sample** vial. Swirl to mix.

8. Rinse two blue Indicator Ampules with deionized water and wipe them with a soft, lint-free wipe.

Note: Do not touch the ampules on the sides after wiping. Pick them up by the top.

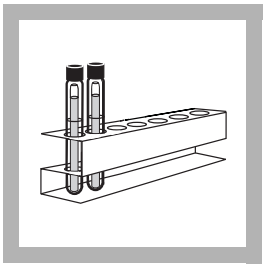
* Patent pending



9. Lower one unopened ampule into each Acid Digestion vial. When the score mark on the ampule is level with the top of the Acid Digestion vial, snap the top off the ampule and allow it to drop into the Acid Digestion vial.

Note: Do not invert or tilt the vial after inserting the ampule to prevent the Indicator Reagent from mixing with the contents of the acid digestion vial.

10. Cap the vial assemblies tightly and place them in the reactor for 2 hours at 103-105 °C.

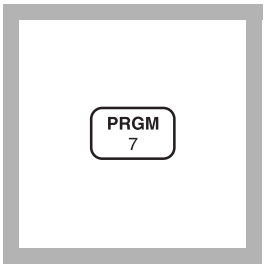


11. Carefully remove the vial assemblies from the reactor. Place them in a test tube rack.

Allow the vials to cool for **one hour** for accurate results.

12. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

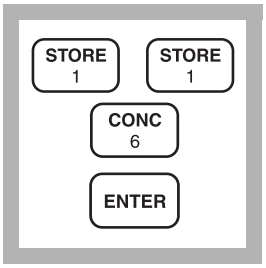
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



13. Enter the stored program number for Low Range TOC.

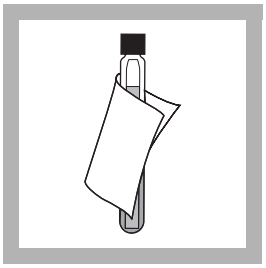
Press: **PRGM**

The display will show:
PRGM?



14. Press: **116 ENTER**

The display will show **mg/L** and the **ZERO** icon.

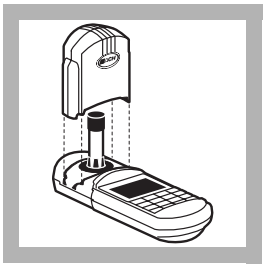


15. Wipe the reagent blank vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.

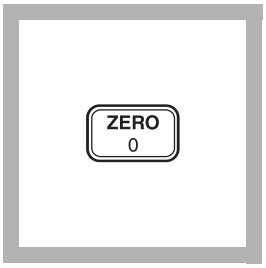
Note: *The liquid in the reagent blank vial should be dark blue.*

16. Place the **reagent blank** vial assembly in the adapter.

Push straight down on the top of the vial until it seats solidly in the adapter.



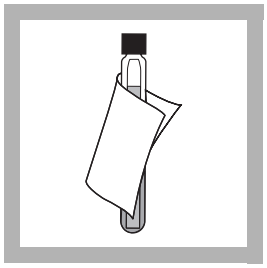
17. Tightly cover the vial assembly with the instrument cap.



18. Press: **ZERO**

The cursor will move to the right, then the display will show:

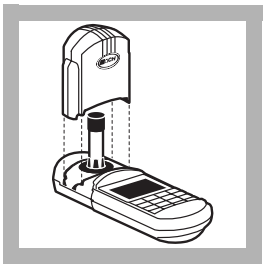
0.0 mg/L C



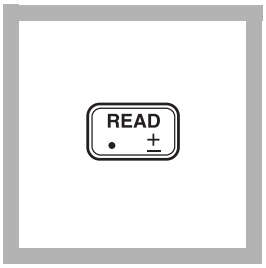
19. Wipe the sample vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.

20. Place the **sample** vial assembly in the adapter.

Push straight down on the top of the vial assembly until it seats solidly in the adapter.



21. Tightly cover the vial assembly with the instrument cap.



22. Press: **READ**

The cursor will move to the right, then the result in mg/L C will be displayed.

Sampling and Storage

Collect samples in clean glass bottles. Rinse the sample bottle several times with the sample to be collected. Fill the bottle with minimum headspace before capping. Test samples as soon as possible. Acid preservation is not recommended. Homogenize samples containing solids to assure representative samples.

Accuracy Check

Standard Solutions Method

a. Prepare a 1000 mg/L organic carbon stock standard by dissolving 2.1254 g dry primary standard Potassium Acid Phthalate in Organic-Free Reagent Water and dilute to 1000 mL. This stock standard is stable for about 1 month at room temperature.

Alternatively, open one ampule of TOC Standard Solution (Cat. No. 27915-05).

b. Prepare a 10.0 mg/L C standard by transferring 1.00 mL of the stock standard to a 100-mL Class A volumetric flask. Dilute to volume using Organic-Free Reagent Water. Stopper and mix thoroughly. Prepare this standard fresh daily.

Standard Additions Method

a. Prepare a 150 mg/L C standard by transferring 15.00 mL of 1000 mg/L C stock solution to a 100-mL Class A volumetric flask. Dilute to volume with organic-free water. Mix.

b. Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 150 mg/L C standard to each of three Acid Digestion vials.

c. Add the contents of one TOC Persulfate powder pillow to each vial.

d. Add 3.0 mL of sample to each vial. Swirl to mix.

e. Proceed with the procedure starting at *step 8*.

f. The mg/L C concentration should increase by 5.0 mg/L for each 0.1 mL increment.

Method Performance

Precision
In a single laboratory, using a standard solution of 9.0 mg/L C and one lot of reagents, a single operator obtained a standard deviation of ±0.5 mg/L C.

Estimated Detection Limit
The estimated detection limit for Method 10129 is 0.3 mg/L C.

Sensitivity
At mid-range, the sensitivity, expressed as the concentration change per 0.010 absorbance change, is 0.2 mg/L C.

Interferences

The following have been tested for interference and found not to interfere up to the indicated levels:

Table 1 Non-interfering Substances

Substance	Maximum Level Tested
Aluminum	10 mg/L
Ammonia Nitrogen	1000 mg/L as N
ASTM Wastewater	No effect
Bromide	500 mg/L Br^-
Bromine	25 mg/L Br_2
Calcium	2000 mg/L as $CaCO_3$
Chloride	500 mg/L
Chlorine	10 mg/L Cl_2
Chlorine Dioxide	6 mg/L ClO_2
Copper	10 mg/L
Cyanide	10 mg/L CN^-
Iodide	50 mg/L
Iron (II)	10 mg/L
Iron (III)	10 mg/L
Magnesium	2000 mg/L as $CaCO_3$
Manganese (VII)	1 mg/L
Monochloramine	14 mg/L NH_2Cl as Cl_2
Nitrite	500 mg/L NO_2^-
Ozone	2 mg/L O_3
Phosphate	3390 mg/L PO_4^{2-}

Table 1 Non-interfering Substances (Continued)

Substance	Maximum Level Tested
Silica	100 mg/L SiO_2
Sulfate	5000 mg/L SO_4^{2-}
Sulfide	20 mg/L S^{2-}
Sulfite	50 mg/L SO_3^{2-}
Zinc	5 mg/L

If the sample contains greater than 600 mg/L $CaCO_3$ alkalinity, lower the sample pH to less than 7 before testing by adding sulfuric acid solution.

Most sample turbidity is either dissolved during the digestion stage or settled during the cooling period. Sample turbidities up to 50 NTU have been tested without interference.

Summary of Method

The total organic carbon (TOC) is determined by first sparging the sample under slightly acidic conditions to remove the inorganic carbon. In the outside vial, organic carbon in the sample is digested by persulfate and acid to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in the inner ampule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the color. The amount of color change is related to the original amount of carbon present in the sample.

REQUIRED REAGENTS

Description	Qty/Test	Unit	Cat. No.
Total Organic Carbon Direct Method Low Range Test 'N Tube Reagent Set	50	vials	27603-45
Includes:			
Acid Digestion Solution Vials, Low Range TOC	1	50/pkg	*
Buffer Solution, Sulfate	0.4 mL	25 mL	452-33
Funnel, micro	1	each	25843-35
Indicator Ampules, Low Range TOC	1	10/pkg	*
TOC Persulfate Powder Pillows	1	50/pkg	*
Water, organic-free**	3.0 mL	500 mL	26415-49

REQUIRED APPARATUS

Cylinder, graduated, 10-mL	1	each	508-38
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Flask, Erlenmeyer, 50-mL	1	each	505-41
Magnetic Stirrer, 115 V, 4" x 4"	1	each	28812-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet, TenSette®, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-01 TenSette® Pipet	2	50/pkg	21856-96
Pipet Tips, for 19700-10 TenSette® Pipet	2	50/pkg	21997-96
Stir Bar, Magnetic	1	each	45315-00
Wipes, Disposable, Kimwipes	1	280/pkg	20970-00

OPTIONAL REAGENTS

Potassium Acid Phthalate	500 g		315-34
Sulfuric Acid Reagent Solution, 5.25 N	100 mL	MDB	2449-32
TOC Standard Solution Ampules (KHP Standard, 1000 mg/L C)	5/pkg		27915-05
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL		28332-49

* These items are not sold separately.

** This item must be purchased separately.

OPTIONAL APPARATUS

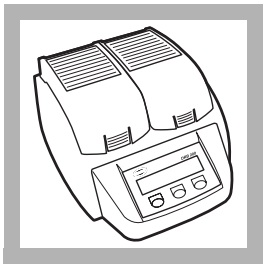
Description	Unit	Cat. No.
Analytical Balance	each	28014-01
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001
Flask, volumetric, 100-mL	each	14574-42
Pipet, Class A, 200-mL	each	14515-35
Pipet, Class A, 15.00-mL	each	14515-39

Method 10173

ORGANIC CARBON, TOTAL, Mid Range

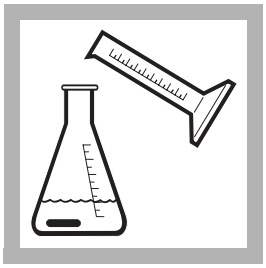
(15–150 mg/L C)

Direct Method* **For wastewater and industrial waters**

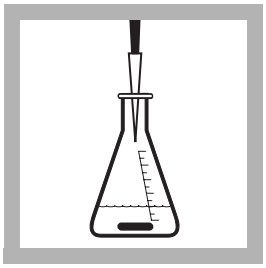


1. Turn on the DRB 200 reactor. Heat to 103–105 °C.

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*

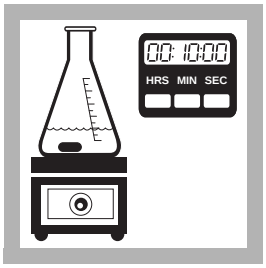


2. Use a graduated cylinder to add 10 mL of sample to a 50-mL erlenmeyer flask containing a stir bar.

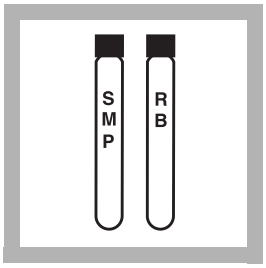


3. Add 0.4 mL of Buffer Solution, pH 2.0.

Note: *Use pH paper to make sure the sample pH is 2.*

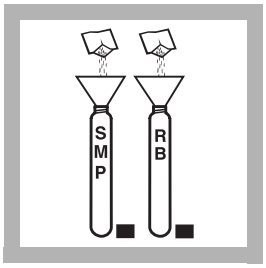


4. Place the flask on a stir plate and stir at a moderate speed for 10 minutes.

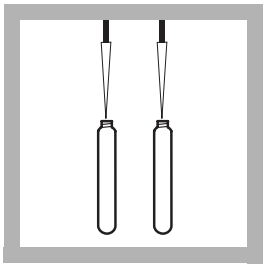


5. Label two Mid Range Acid Digestion vials: **sample** and **reagent blank**.

Note: *A reagent blank is required for each series of samples.*



6. Using a funnel, add the contents of one TOC Persulfate Powder Pillow to each Acid Digestion vial (colorless liquid).

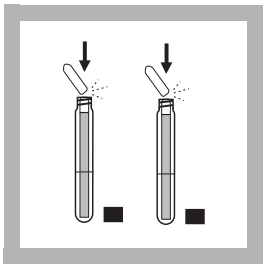


7. Use a TenSette® Pipet to add 1.0 mL of **organic-free water** to the **reagent blank** vial and1.0 mL of **prepared sample** to the **sample** vial. Do not cap the vial; swirl gently to mix.

8. Rinse two blue Indicator Ampules with deionized water and wipe them with a soft, lint-free wipe.

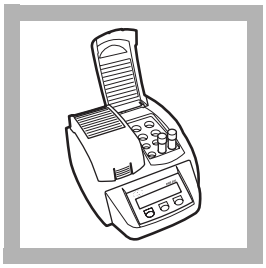
Note: Do not touch the ampules on the sides after wiping. Pick them up by the top.

* Patent pending

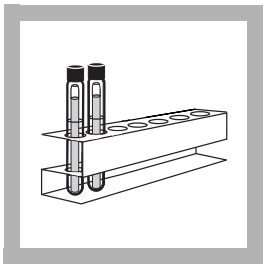


9. Lower one unopened ampule into each Acid Digestion vial. When the score mark on the ampule is level with the top of the Acid Digestion vial, snap the top off the ampule and allow it to drop into the Acid Digestion vial.

Note: Do not invert or tilt the vial after inserting the ampule to prevent the Indicator Reagent from mixing with the contents of the acid digestion vial.

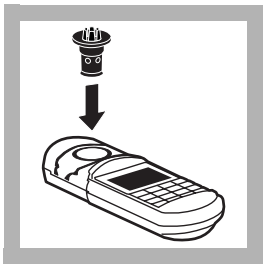


10. Cap the vial assemblies tightly and place them in the reactor for 2 hours at 103–105 °C.



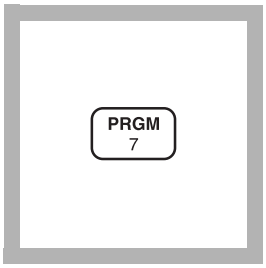
11. Carefully remove the vial assemblies from the reactor. Place them in a test tube rack.

Allow the vials to cool for **one hour** for accurate results.



12. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

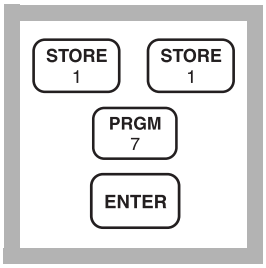
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



13. Enter the stored program number for Mid Range TOC.

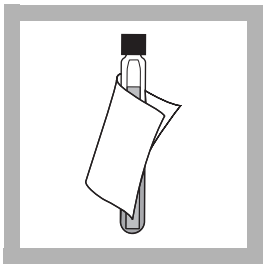
Press: **PRGM**

The display will show:
PRGM?



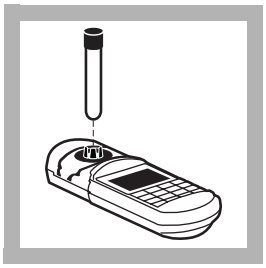
14. Press: **117 ENTER**

The display will show **mg/L** and the **ZERO** icon.



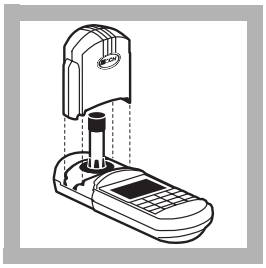
15. Wipe the reagent blank vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.

Note: *The liquid in the reagent blank vial should be dark blue.*

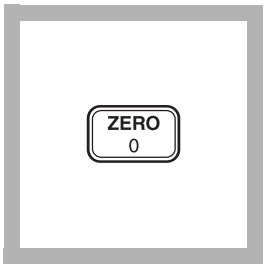


16. Place the **reagent blank** vial assembly in the adapter.

Push straight down on the top of the vial until it seats solidly in the adapter.



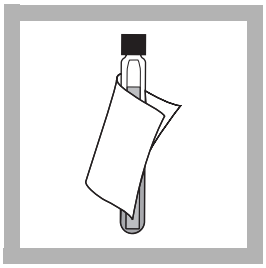
17. Tightly cover the vial assembly with the instrument cap.



18. Press: **ZERO**

The cursor will move to the right, then the display will show:

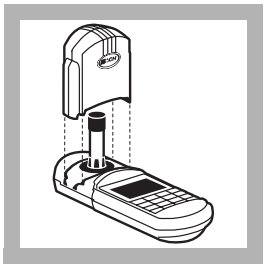
0 mg/L C



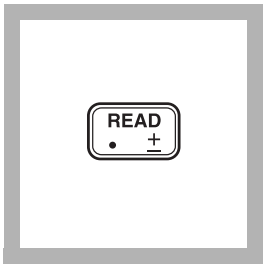
19. Wipe the sample vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.

20. Place the **sample** vial assembly in the adapter.

Push straight down on the top of the vial assembly until it seats solidly in the adapter.



21. Tightly cover the vial assembly with the instrument cap.



22. Press: **READ**

The cursor will move to the right, then the result in mg/L C will be displayed.

Sampling and Storage

Collect samples in clean glass bottles. Rinse the sample bottle several times with the sample to be collected. Fill the bottle with minimum headspace before capping. Test samples as soon as possible. Acid preservation is not recommended. Homogenize samples containing solids to assure representative samples.

Accuracy Check

Standard Solutions Method

a. Prepare a 1000 mg/L organic carbon stock standard by dissolving 2.1254 g dry primary standard Potassium Acid Phthalate in Organic-Free Reagent Water and dilute to 1000 mL. This stock standard is stable for about 1 month at room temperature. Alternatively, open one ampule of TOC Standard Solution (Cat. No. 27915-05).

b. Prepare a 100 mg/L C standard by transferring 5.00 mL of the stock standard to a 50-mL Class A volumetric flask. Dilute to volume using Organic-Free Reagent Water. Stopper and mix thoroughly. Prepare this standard fresh weekly.

Standard Additions Method

a. Prepare a 300 mg/L C standard by transferring 15.00 mL of 1000 mg/L C stock solution to a 50-mL Class A volumetric flask. Dilute to volume with Organic-Free Water. Mix.

b. Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 300 mg/L C standard to each of three Acid Digestion vials.

c. Add the contents of one TOC Persulfate powder pillow to each vial.

d. Add 1.0 mL of sample to each vial. Swirl to mix.

e. Proceed with the procedure starting at *step 8*.

f. The mg/L C concentration should increase by 30 mg/L for each 0.1 mL increment.

Method Performance

Precision

mg/L C	95% Confidence Limits
15	± 5 mg/L C
50	± 6 mg/L
75	± 7 mg/L
115	± 4 mg/L
150	± 6 mg/L

Estimated Detection Limit
Use Method Number 10173 to test TOC levels below 15 mg/L C.

Sensitivity
At mid-range, the sensitivity, expressed as the concentration change per 0.010 absorbance change, is 1.9 mg/L C.

Interferences
The following have been tested for interference and found not to interfere up to the indicated levels:

Table 1 Non-interfering Substances

Substance	Maximum Level Tested
Aluminum	10 mg/L
Ammonia Nitrogen	1000 mg/L as N
ASTM Wastewater	No effect
Bromide	500 mg/L Br
Bromine	25 mg/L Br_2
Calcium	2000 mg/L as $CaCO_3$
Chloride	1500 mg/L
Chlorine	10 mg/L Cl_2
Chlorine Dioxide	6 mg/L ClO_2
Copper	10 mg/L
Cyanide	10 mg/L CN
Iodide	50 mg/L
Iron (II)	10 mg/L
Iron (III)	10 mg/L
Magnesium	2000 mg/L as $CaCO_3$
Manganese (VII)	1 mg/L

Table 1 Non-interfering Substances (Continued)

Substance	Maximum Level Tested
Monochloramine	14 mg/L NH_2Cl as Cl_2
Nitrite	500 mg/L NO_2^-
Ozone	2 mg/L O_3
Phosphate	3390 mg/L PO_4^{3-}
Silica	100 mg/L SiO_2
Sulfate	5000 mg/L SO_4^{2-}
Sulfide	20 mg/L S^{2-}
Sulfite	50 mg/L SO_3^{2-}
Zinc	5 mg/L

Note: *If the sample contains greater than 1000 mg/L $CaCO_3$ alkalinity, lower the sample pH to less than 7 before testing by adding sulfuric acid solution.*

Note: *Most sample turbidity is either dissolved during the digestion stage or settled during the cooling period. Sample turbidities up to 50 NTU have been tested without interference.*

Summary of Method

The total organic carbon (TOC) is determined by first sparging the sample under slightly acidic conditions to remove the inorganic carbon. In the outside vial, organic carbon in the sample is digested by persulfate and acid to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in the inner ampule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the color. The amount of color change is related to the original amount of carbon present in the sample.

Instrument Setup

This procedure will add the current method as a new Hach program to your DR/850 or DR/890.

1. Turn the instrument on by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the down arrow key until the prompt line shows **USER**.
4. Press the **ENTER** key.
5. Enter **8138**, followed by **ENTER**.
6. Enter each of the numbers in the right column, followed by **ENTER**. The line numbers in the left column relate to the line number on the display. At any time you may use the arrow keys to scroll back to review or change a number already entered.

Line Number	Entry	Line Number	Entry
1	117	29	0
2	42	30	0
3	72	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	0
8	66	36	0
9	36	37	0
10	92	38	0
11	40	39	0
12	195	40	0
13	89	41	0
14	74	42	0
15	61	43	0
16	0	44	165
17	0	45	128
18	0	46	0
19	0	47	10
20	67	48	0
21	0	49	0
22	0	50	0
23	0	51	0
24	0	52	0
25	0	53	0
26	0	54	25
27	0	55	0
28	0	56	255

ORGANIC CARBON, TOTAL, Mid Range, continued

REQUIRED REAGENTS

Total Organic Carbon Direct Method Mid Range
Test 'N Tube Reagent Set ..... 50 vials 28159-45

Includes:

Description	Quantity Required Per Test	Unit	Cat. No.
Acid Digestion Solution Vials, Mid Range TOC	1	50/pkg	*
Buffer Solution, Sulfate	0.4 mL	25 mL	452-33
Funnel, micro	1	each	25843-35
Indicator Ampules, Mid/High Range TOC	1	50/pkg	*
TOC Persulfate Powder Pillows	1	50/pkg	*
Water, organic-free**	1.0 mL	500 mL	26415-49

REQUIRED APPARATUS

DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Cylinder, graduated, 10-mL	1	each	508-38
Flask, Erlenmeyer, 50-mL	1	each	505-41
Magnetic Stirrer, 115 V, 4" x 4"	1	each	28812-00
Test Tube Rack	1–3	each	18641-00
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet	2	50/pkg	21856-96
Stir Bar, Magnetic	1	each	45315-00
Wipes, Disposable, Kimwipes	1	280/pkg	20970-00

OPTIONAL REAGENTS

Description	Per Test	Unit	Cat. No.
TOC Standard Solution (KHP Standard, 1000 mg/L C)		5/pkg	27915-05
Potassium Acid Phthalate		500 g	315-34
Sulfuric Acid Reagent Solution, 5.25 N		100 mL MDB	2449-32

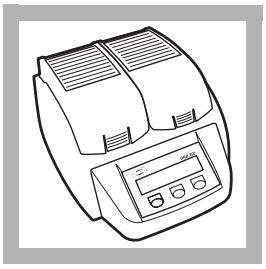
OPTIONAL APPARATUS

Analytical Balance		each	28014-01
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm			LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm			LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm			LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm			LTV082.52.30001
Flask, volumetric, 100-mL		each	14574-42
Pipet, Class A, 10.00-mL		each	14515-38
Pipet, Class A, 15.00-mL		each	14515-39
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28

* These items are not sold separately.
** This item must be purchased separately.

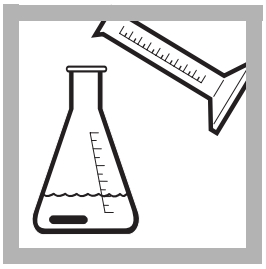
ORGANIC CARBON, TOTAL, High Range (20–700 mg/L C)

Direct Method* **For wastewater and industrial waters**



1. Turn on the DRB 200 reactor. Heat to 103-105 °C.

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*

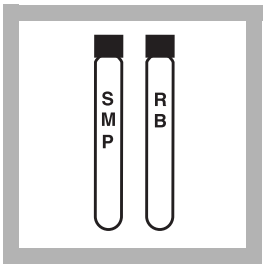


2. Use a graduated cylinder to add 10 mL of sample to a 50-mL erlenmeyer flask containing a stir bar.

3. Add 0.4 mL of Buffer Solution, pH 2.0.

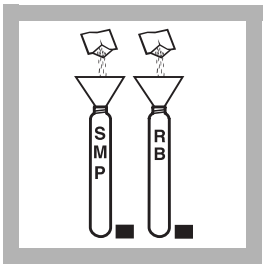
Note: *Use pH paper to make sure the sample pH is 2.*

4. Place the flask on a stir plate and stir at a moderate speed for 10 minutes.

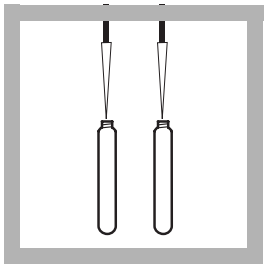


5. Label two High Range Acid Digestion vials: **sample** and **reagent blank**.

Note: *A reagent blank is required for each series of samples.*



6. Using a funnel, add the contents of one TOC Persulfate Powder Pillow to each Acid Digestion vial (colorless liquid).

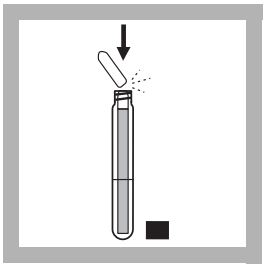


7. Use a TenSette® Pipet to add 0.3 mL of **organic-free water** to the **reagent blank** vial and 0.3 mL of **prepared sample** to the **sample** vial. Swirl to mix.

8. Rinse two blue Indicator Ampules with deionized water and wipe them with a soft, lint-free wipe.

Note: Do not touch the ampules on the sides after wiping. Pick them up by the top.

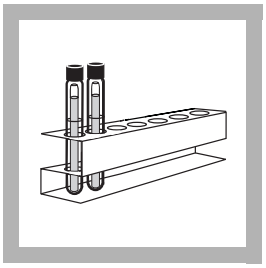
* Patent pending



9. Lower one unopened ampule into each Acid Digestion vial. When the score mark on the ampule is level with the top of the Acid Digestion vial, snap the top off the ampule and allow it to drop into the Acid Digestion vial.

Note: Do not invert or tilt the vial after inserting the ampule to prevent the Indicator Reagent from mixing with the contents of the acid digestion vial.

10. Cap the vial assemblies tightly and place them in the reactor for 2 hours at 103–105 °C.

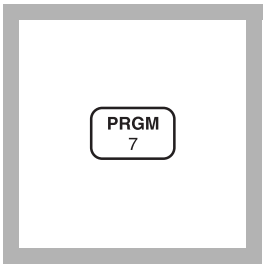


11. Carefully remove the vial assemblies from the reactor. Place them in a test tube rack.

Allow the vials to cool for **one hour** for accurate results.

12. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

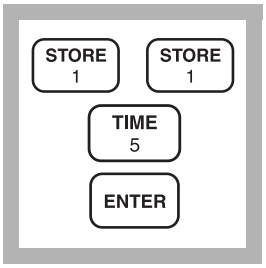
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



13. Enter the stored program number for High Range TOC.

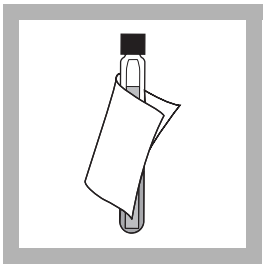
Press: **PRGM**

The display will show:
PRGM?



14. Press: **115 ENTER**

The display will show **mg/L** and the **ZERO** icon.

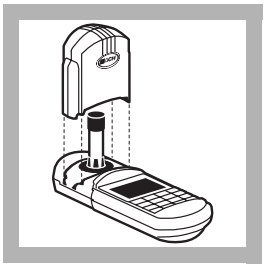


15. Wipe the reagent blank vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.

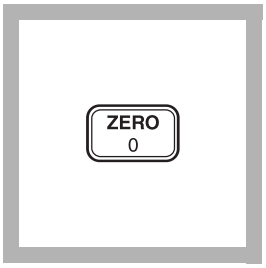
Note: *The liquid in the reagent blank vial should be dark blue.*

16. Place the **reagent blank** vial assembly in the adapter.

Push straight down on the top of the vial until it seats solidly in the adapter.



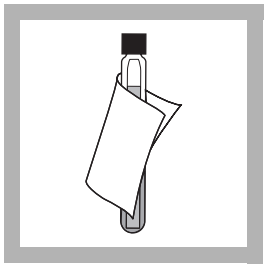
17. Tightly cover the vial assembly with the instrument cap.



18. Press: **ZERO**

The cursor will move to the right, then the display will show:

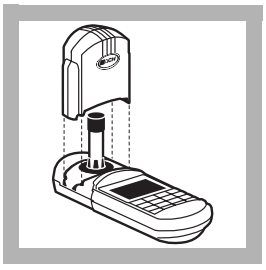
0 mg/L C



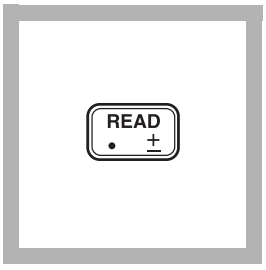
19. Wipe the sample vial assembly with a damp towel, followed by a dry one, to remove fingerprints or other marks.

20. Place the **sample** vial assembly in the adapter.

Push straight down on the top of the vial assembly until it seats solidly in the adapter.



21. Tightly cover the vial assembly with the instrument cap.



22. Press: **READ**

The cursor will move to the right, then the result in mg/L C will be displayed.

Sampling and Storage

Collect samples in clean glass bottles. Rinse the sample bottle several times with the sample to be collected. Fill the bottle with minimum headspace before capping. Test samples as soon as possible. Acid preservation is not recommended. Homogenize samples containing solids to assure representative samples.

Accuracy Check

Standard Solutions Method

a. Prepare a 1000 mg/L organic carbon stock standard by dissolving 2.1254 g dry primary standard Potassium Acid Phthalate in Organic-Free Reagent Water and dilute to 1000 mL. This stock standard is stable for about 1 month at room temperature.
Alternatively, open one ampule of TOC Standard Solution (Cat. No. 27915-05).

b. Prepare a 300 mg/L C standard by transferring 15.00 mL of the stock standard to a 50-mL Class A volumetric flask. Dilute to volume using Organic-Free Reagent Water. Stopper and mix thoroughly. Prepare this standard fresh weekly.

Standard Additions Method

a. Prepare a 300 mg/L C standard by transferring 18.00 mL of 1000 mg/L C stock solution to a 50-mL Class A volumetric flask. Dilute to volume with Organic-Free Water. Mix.

b. Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of the 300 mg/L C standard to each of three Acid Digestion vials.

c. Add the contents of one TOC Persulfate powder pillow to each vial.

d. Add 0.3 mL of sample to each vial. Swirl to mix.

e. Proceed with the procedure starting at *step 8*.

f. The mg/L C concentration should increase by 100 mg/L for each 0.1 mL increment.

Method Performance

Precision
In a single laboratory, using a standard solution of 360 mg/L C and one lot of reagents, a single operator obtained a standard deviation of ±8 mg/L C.

Estimated Detection Limit
Use Method Number 10129 to test TOC levels below 20 mg/L C.

Sensitivity
At mid-range, the sensitivity, expressed as the concentration change per 0.010 absorbance change, is 6 mg/L C.

Interferences

The following have been tested for interference and found not to interfere up to the indicated levels:

Table 1 Non-interfering Substances

Substance	Maximum Level Tested
Aluminum	10 mg/L
Ammonia Nitrogen	1000 mg/L as N
ASTM Wastewater	No effect
Bromide	500 mg/L Br
Bromine	25 mg/L Br_2
Calcium	2000 mg/L as $CaCO_3$
Chloride	5000 mg/L
Chlorine	10 mg/L Cl_2
Chlorine Dioxide	6 mg/L ClO_2
Copper	10 mg/L
Cyanide	10 mg/L CN
Iodide	50 mg/L
Iron (II)	10 mg/L
Iron (III)	10 mg/L
Magnesium	2000 mg/L as $CaCO_3$
Manganese (VII)	1 mg/L
Monochloramine	14 mg/L NH_2Cl as Cl_2
Nitrite	500 mg/L NO_2^-
Ozone	2 mg/L O_3
Phosphate	3390 mg/L PO_4^{3-}

Table 1 Non-interfering Substances (Continued)

Substance	Maximum Level Tested
Silica	100 mg/L SiO_2
Sulfate	5000 mg/L SO_4^{2-}
Sulfide	20 mg/L S^{2-}
Sulfite	50 mg/L SO_3^{2-}
Zinc	5 mg/L

If the sample contains greater than 600 mg/L $CaCO_3$ alkalinity, lower the sample pH to less than 7 before testing by adding sulfuric acid solution.

Most sample turbidity is either dissolved during the digestion stage or settled during the cooling period. Sample turbidities up to 900 NTU have been tested without interference.

Summary of Method

The total organic carbon (TOC) is determined by first sparging the sample under slightly acidic conditions to remove the inorganic carbon. In the outside vial, organic carbon in the sample is digested by persulfate and acid to form carbon dioxide. During digestion, the carbon dioxide diffuses into a pH indicator reagent in the inner ampule. The adsorption of carbon dioxide into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the color. The amount of color change is related to the original amount of carbon present in the sample.

ORGANIC CARBON, TOTAL, High Range, continued

REQUIRED REAGENTS

Total Organic Carbon Direct Method High Range
Test 'N Tube Reagent Set ..... 50 vials 27604-45

Includes:

Description	Qty/Test	Unit	Cat. No.
Acid Digestion Solution Vials, High Range TOC	1	50/pkg	*
Buffer Solution, Sulfate	0.4 mL	25 mL	452-33
Funnel, micro	1	each	25843-35
Indicator Ampules, High Range TOC	1	10/pkg	*
TOC Persulfate Powder Pillows	1	50/pkg	*
Water, organic-free**	0.3 mL	500 mL	26415-49

REQUIRED APPARATUS

Cylinder, graduated, 10-mL	1	each	508-38
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Flask, Erlenmeyer, 50-mL	1	each	505-41
Magnetic Stirrer, 115 V, 4" x 4"	1	each	28812-00
Safety Shield, laboratory bench	1	each	50030-00
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	19700-01
Pipet, TenSette®, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-01 TenSette® Pipet	2	50/pkg	21856-96
Pipet Tips, for 19700-10 TenSette® Pipet	2	50/pkg	21997-96
Stir Bar, Magnetic	1	each	45315-00
Wipes, Disposable, Kimwipes	1	280/pkg	20970-00

OPTIONAL REAGENTS

Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules		16/pkg	28335-10
Potassium Acid Phthalate		500 g	315-34
Sulfuric Acid Reagent Solution, 5.25 N		100 mL MDB	2449-32
TOC Standard Solution Ampules (KHP Standard, 1000 mg/L C)		5/pkg	27915-05
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28331-49

* These items are not sold separately.
** This item must be purchased separately.

OPTIONAL APPARATUS

Analytical Balance	each	28014-01
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001
Flask, volumetric, 1000-mL	each	14574-53
Flask, volumetric, 100-mL	each	14574-42
Pipet, Class A, 10.00-mL	each	14515-38
Pipet, Class A, 15.00-mL	each	14515-39

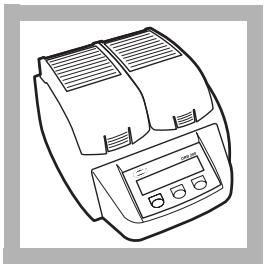
OXYGEN DEMAND, CHEMICAL

For water, wastewater and seawater

Reactor Digestion Method* USEPA approved for reporting wastewater analysis**
Digestion

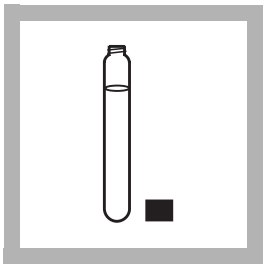
1. Homogenize 500 mL of sample for 2 minutes in a blender.

Note: For the 0-15,000 mg/L range, *homogenize 100 mL of sample. Pour the blended sample into a 250-mL beaker. Stir with a magnetic stirrer while withdrawing a sample aliquot. This improves accuracy and reproducibility.*



2. Turn on the DRB 200 Reactor. Preheat to 150 °C.

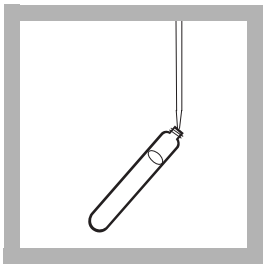
Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*



3. Remove the cap of a COD Digestion Reagent Vial for the appropriate range:

Sample Conc. Range (mg/L)	COD Digestion Reagent Vial Type
0 to 150	Low Range
0 to 1500	High Range
0 to 15,000	High Range Plus

Note: *The reagent mixture is light-sensitive. Keep unused vials in the opaque shipping container, in a refrigerator if possible. The light striking the vials during the test will not affect results.*



4. Hold the vial at a 45-degree angle. Pipet 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) of sample into the vial.

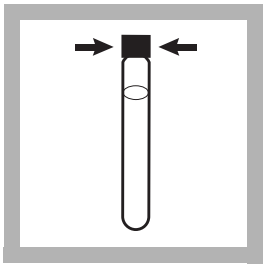
Note: For the 0-15,000 mg/L range, *pipet only 0.20 mL of sample, not 2.00 mL of sample, using a TenSette Pipet. For greater accuracy analyze a minimum of three replicates and average the results.*

Note: *Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Do not run tests with vials which have been spilled. If spills occur, wash with running water.*

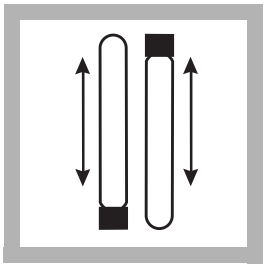
Caution: Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and clothing. If contact occurs, flush the affected area with running water. Follow all instructions carefully.

* Jirka, A.M.; Carter, M.J. *Analytical Chemistry*, 1975, 47(8). 1397.

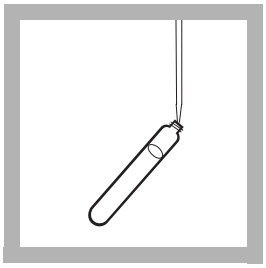
** *Federal Register*, April 21, 1980, 45(78), 26811-26812. The 0-15,000 mg/L range is **not** USEPA approved.



5. Replace the vial cap tightly. Rinse the outside of the COD vial with deionized water and wipe the vial clean with a paper towel.

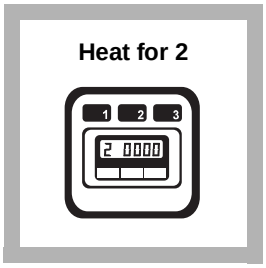


6. Hold the vial by the cap and over a sink. Invert gently several times to mix the contents. Place the vial in the preheated DRB 200 Reactor.
Note: *The vial will become very hot during mixing.*

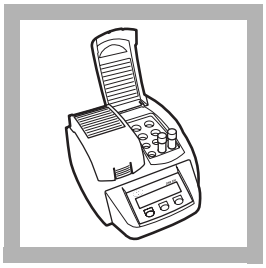


7. Prepare a blank by repeating Steps 3 to 6, substituting 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) deionized water for the sample.
Note: *Be sure the pipet is clean.*

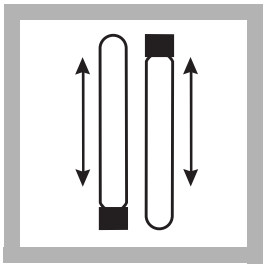
Note: *One blank must be run with each set of samples. Run samples and blanks with vials from the same lot number (lot # is on the container label).*



8. Heat the vials for 2 hours.
Note: *Many samples are digested completely in less than two hours. If desired, measure the concentration (while still hot) at 15 minute intervals until the reading remains unchanged. Cool vials to room temperature for final measurement.*



9. Turn the reactor off. Wait about 20 minutes for the vials to cool to 120 °C or less.

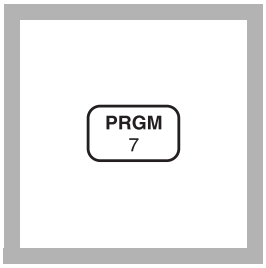


10. Invert each vial several times while still warm. Place the vials into a rack. Wait until the vials have cooled to room temperature.
Note: *If a pure green color appears in the reacted sample, measure the COD and, if necessary, repeat the test with a diluted sample.*

11. Use one of the following analytical techniques to measure the COD:

- Colorimetric method, 0-150 mg/L COD
- Colorimetric method, 0-1,500 mg/L COD
- Colorimetric method, 0-15,000 mg/L COD

Colorimetric Determination, 0 to 150 mg/L COD

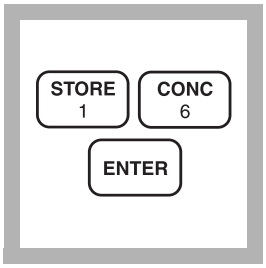


1. Enter the stored program number for chemical oxygen demand (COD), low range.

Press: **PRGM**

The display will show:

PRGM ?



2. Press: **16 ENTER**

The display will show **mg/L, COD** and the **ZERO** icon**.**

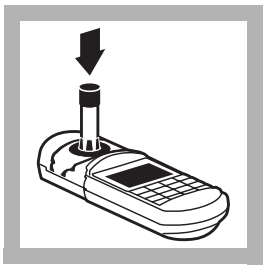
Note: *For alternate form (O_2), press the* **CONC** *key.*

3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*

4. Clean the outside of the blank with a towel.

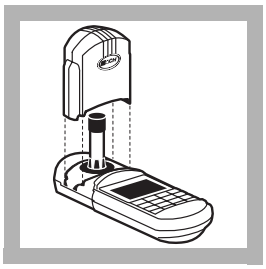
Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



5. Place the blank in the adapter.

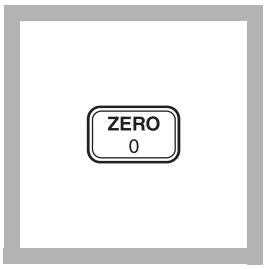
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



6. Tightly cover the vial with the instrument cap.

Note: *The blank is stable when stored in the dark. See Blanks for Colorimetric Determination following these procedures.*

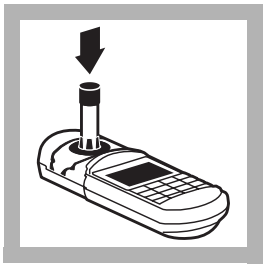


7. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L COD

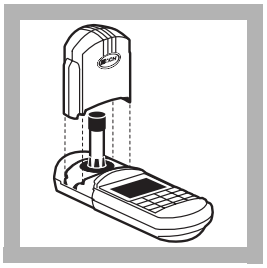
8. Clean the outside of the sample vial with a towel.



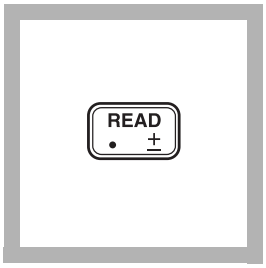
9. Place the sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



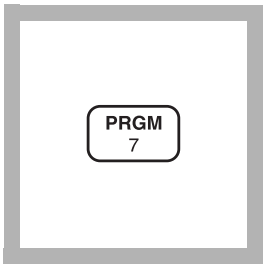
10. Tightly cover the vial with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

Colorimetric Determination, 0 to 1,500 and 0 to 15,000 mg/L COD

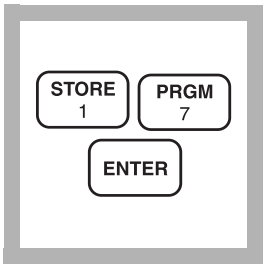


1. Enter the stored program number for chemical oxygen demand, high range.

Press: **PRGM**

The display will show:

PRGM ?



2. Press: **17 ENTER**

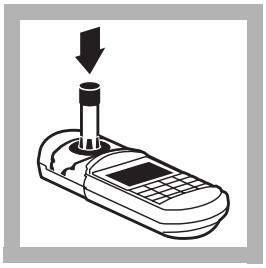
The display will show **mg/L, COD** and the **ZERO** icon.

Note: *For alternate form (O_2), press the* **CONC** *key.*

3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

4. Clean the outside of the blank with a towel.

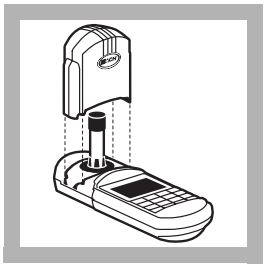
Note: *Wiping with a damp towel followed by a dry one will remove fingerprints or other marks.*



5. Place the blank in the adapter.

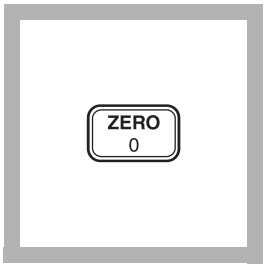
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



6. Tightly cover the sample cell with the instrument cap.

The blank is stable when stored in the dark. See Blanks for Colorimetric Determination following these procedures.

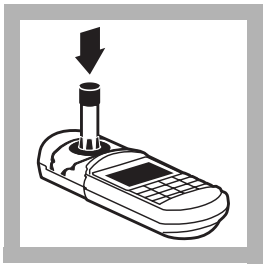


7. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L COD

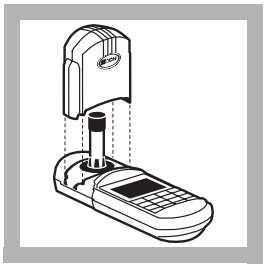
8. Clean the outside of the sample vial with a towel.



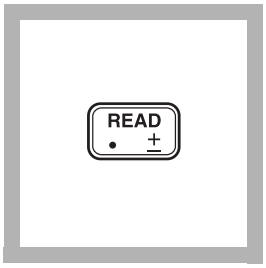
9. Place the sample in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



10. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

Note: *When using High Range Plus COD Digestion Reagent Vials, multiply the reading by 10.*

Note: *For most accurate results with samples near 1,500 or15,000 mg/L COD, repeat the analysis with a diluted sample.*

Sampling and Storage

Collect samples in glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C can be stored up to 28 days. Correct results for volume additions; see *Correction for Volume Additions* (Section 1) for more information.

Accuracy Check

Standard Solution Method

Check the accuracy of the 0 to 150 mg/L range with a 100 mg/L standard. Prepare by dissolving 85 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1 liter of deionized water. Use 2.0 mL as the sample volume. The expected result will be 100 mg/L COD. As an alternative, dilute 10 mL of 1000-mg/L COD Standard Solution to 100 mL to make a 100-mg/L standard.

Check the accuracy of the 0 to 1,500 mg/L range by using either a 300 mg/L or 1000 mg/L COD Standard Solution. Alternatively, prepare a 500 mg/L standard by dissolving 425 mg of dried (120 °C, overnight) KHP. Dilute to 1 liter with deionized water. Use 2.0 mL of one of these solutions as the sample volume.

Check the accuracy of the 0 to 15,000 mg/L range by using a 10,000 mg/L COD standard solution. Prepare the 10,000 mg/L solution by dissolving 8.500 g of dried (120 °C, overnight) KHP in 1 liter of deionized water. Use 0.2 mL of this solution as the sample volume; the expected result will be 10,000 mg/L COD.

Method Performance

Precision

Program #16: In a single laboratory, using a standard solution of 100 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±2 mg/L COD.

Program #17: In a single laboratory, using a standard solution of 1000 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ± 16 mg/L COD. For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit (EDL)

The EDL for program 16 is 4 mg/L COD. The EDL for program 17 is 30 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Alternate reagents

Mercury-free COD2 Reagents can provide a mercury-free testing option for non-reporting purposes. For process control applications, COD2 reagents will eliminate mercury waste and save on disposal costs. These reagents are fully compatible with test procedures and calibration curves programmed into the DR/2400 spectrophotometer. Determine chloride and ammonia for accurate results.

Note: *Mercury-free COD2 reagents are not approved for USEPA reporting. Request a copy of the COD Reagent Vial Information Brochure, Lit. No. 1356, for more information about specific applications.*

Interferences

Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to the level specified in column 1 in *Table 1*. Samples with higher chloride concentrations should be diluted. Dilute the sample enough to reduce the chloride concentration to the level given in column 2.

If sample dilution will cause the COD concentration to be too low for accurate determination, add 0.50 g of mercuric sulfate ($HgSO_4$) to each COD vial before the sample is added. The additional mercuric sulfate will raise the maximum chloride concentration allowable to the level given in column 3.

Table 1

	Column 1	Column 2	Column 3
Vial Type Used	Maximum Cl^- concentration in sample (mg/L)	Maximum Cl^- concentration of diluted samples (mg/L)	Maximum Cl^- concentration in sample when 0.50 $HgSO_4$ added (mg/L)
Low Range	2000	1000	8000
High Range	2000	1000	4000
High Range Plus	20,000	10,000	40,000

Blanks for Colorimetric Determination

The blank may be used repeatedly for measurements using the same lot of vials. Store it in the dark. Monitor decomposition by measuring the absorbance at the appropriate wavelength (420 or 610 nm). Zero the instrument in the absorbance mode, using a vial containing 5 mL of deionized water and measure the absorbance of the blank. Record the value. Prepare a new blank when the absorbance has changed by about 0.01 absorbance units.

Summary of Method

The mg/L COD results are defined as the mg of O_2 consumed per liter of sample under conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). When the 0-150 mg/L colorimetric method is used, the amount of Cr^{6+} remaining is determined. When the 0-1,500 mg/L or 0-15,000 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex the chloride interference.

Pollution Prevention and Waste Management

Final samples will contain mercury (D009), silver (D011), and chromium (D007) at concentration levels regulated by the Federal RCRA. Please see *Section 3* for further information on proper disposal of these materials.

REQUIRED REAGENTS

Description	Qty/Test	Unit	Cat. No.
Select the appropriate COD Digestion Reagent Vial:			
Low Range, 0 to 150 mg/L COD	1 to 2 vials	25/pkg	21258-25
High Range, 0 to 1,500 mg/L COD	1 to 2 vials	25/pkg	21259-25
High Range Plus, 0 to 15,000 mg/L COD	1 to 2 vials	25/pkg	24159-25
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Blender, Osterizer, 120 V, 14 speed	1	each	26160-00
Blender, Osterizer, 240 V, 14 speed	1	each	26160-02
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
COD/TNT Adapter	1	each	48464-00

REQUIRED APPARATUS, Cont.

Description	Qty/Test	Unit	Cat. No.
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	1	50/pkg	21856-96
Pipet, volumetric, Class A, 2.00 mL	1	each	14515-36
Pipet Filler, safety bulb	1	each	14651-00
Test Tube Rack	1 to 2 racks	each	18641-00

ALTERNATE REAGENTS*

COD2, LR, 0 to 150 mg/L COD	1–2 vials	25/pkg	25650-25
COD2, HR, 0 to 1500 mg/L COD	1–2 vials	25/pkg	25651-25
COD2, HR, 0 to 1500 mg/L COD	1–2 vials	150/pkg	25651-15
COD2, HR, 0 to 15,000 mg/L COD	1–2 vials	25/pkg	28343-25

OPTIONAL REAGENTS

Description	Unit	Cat. No.
COD Digestion Reagent Vials, 0 to 150 mg/L COD	150/pkg	21258-15
COD Digestion Reagent Vials, 0 to 1,500 mg/L COD	150/pkg	21259-15
COD Standard Solution, 300 mg/L	200 mL	12186-29
COD Standard Solution, 1000 mg/L	200 mL	22539-29
Mercuric Sulfate	28.3 grams	1915-20
Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules	16/pkg	28335-10
Potassium Acid Phthalate, ACS	500 g	315-34
Potassium Dichromate Standard Solution, 0.25 N	1000 mL*	1809-53
Sulfuric Acid, ACS	500 mL**	979-49
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28332-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49

* Mercury-free COD2 reagents are not approved for USEPA reporting. Request a copy of the COD Reagent Vial Information Brochure, Lit. No. 1356, for more information about specific applications.

** Contact Hach for larger sizes.

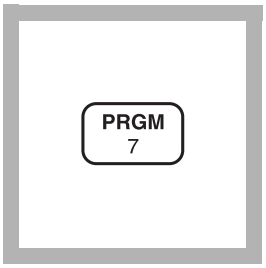
OPTIONAL APPARATUS

Description	Unit	Cat. No.
Balance, analytical, 115 V	each	28014-01
Balance, analytical, 230 V	each	28014-02
Beaker, 250 mL	each	500-46H
Cylinder, graduated, 5 mL	each	508-37
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001
Electromagnetic Stirrer, 120 V, with electrode stand	each	45300-01
Electromagnetic Stirrer, 230 V, with electrode stand	each	45300-02
Flask, volumetric, Class A, 1000 mL	each	14574-53
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Paper, 1 to 11 pH units	5 rolls/pkg	391-33
Pipet, serological, 5 mL	each	532-37
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 10 mL	each	14515-38
Spoon, measuring, 0.5 g	each	907-00
Stir Bar, 22.2 x 4.76 mm (7/8" x 3/16")	each	45315-00
Stir Bar Retriever	each	15232-00
Timer	each	26304-00

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L) For water and wastewater

Manganese III Digestion Method* (without chloride removal)



1. Enter the stored program number for Manganese III COD.

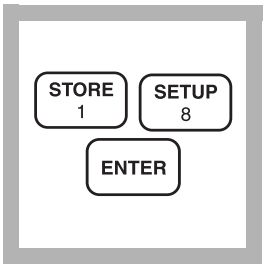
Press: **PRGM**

The display will show:

PRGM ?

Note: *If samples cannot be analyzed immediately, see Sampling and Storage following these steps.*

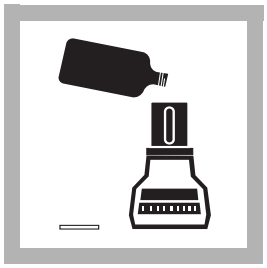
Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



2. Press: **18 ENTER**

The display will show **mg/L, COD** and the **ZERO** icon**.**

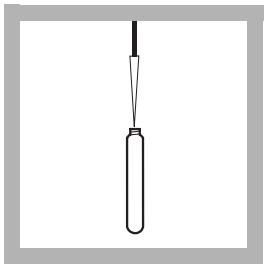
Note: *For alternate forms (O_2), press the* **CONC** *key.*



3. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: *Blending promotes even distribution of solids and improves accuracy and reproducibility.*

Note: *Continue mixing the sample while pipetting if suspended solids are present.*



4. If chloride is not present in significant amounts†, pipet 0.50 mL of homogenized sample into a Mn III COD vial. Cap and invert several times to mix.

Note: *If the sample COD value is not between 20-1000 mg/L dilute the sample with deionized water to obtain a range of 20-1000 mg/L COD. Multiply the final result by the dilution factor.*

† To determine if chloride will interfere, run the sample with and without the chloride removal procedure and compare the results.

Caution: Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and appropriate clothing. If contact occurs, flush the affected area with running water. Follow all instructions carefully.

* U.S. Patent 5,556,787

5. Prepare a blank (see note) by substituting 0.50 mL of deionized water for the sample. Continue with Step 19 of this procedure.

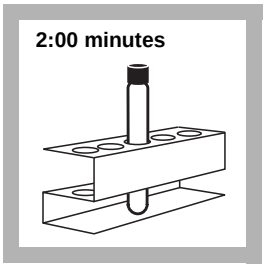
Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range should be about 1.36-1.43.*

6. Place the vials in the DRB 200 Reactor that is preheated to 150 °C. Digest for 1 hour.

Note: *Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.*

Note: *Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.*

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*



7. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about three minutes.

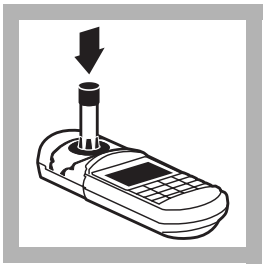
Note: *Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed. This will not affect test results.*

8. Remove the vials from the water and wipe with a clean, dry paper towel.

Invert the vials several times to mix.

9. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

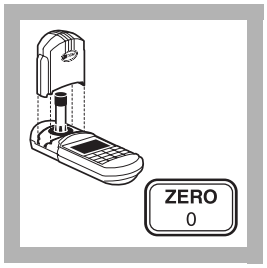
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



10. Place the blank in the sample cell adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



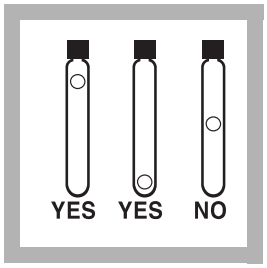
11. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*

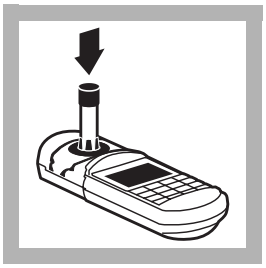
Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L COD



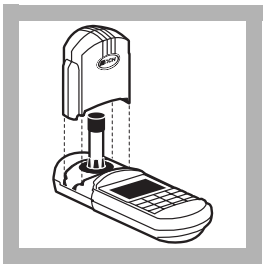
12. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



13. Place the sample in the adapter.

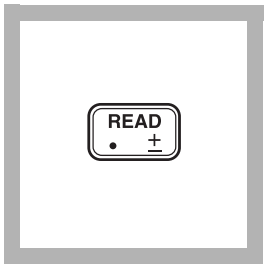
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



14. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*



15. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Note: *Adjust the result for any sample dilution in Steps 4 or 6.*

Sampling and Storage

Collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with concentrated sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C may be stored up to 28 days. Correct results for volume additions; see *Correcting for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard Solution Method

Prepare an 800 mg/L COD standard solution by adding 0.6808 g of
dried (103 °C, overnight) potassium acid phthalate (KHP) to 1 liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be
800 ±26 mg/L COD.

An 800 mg/L COD solution can also be purchased directly from Hach (see *Optional Reagents*).

Method Performance (for Manganic III COD without the chloride removal procedure)

Precision

In a single laboratory, using a standard solution of 800 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±23 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 18 is 14 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Inorganic materials may also be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. If chloride is known to be absent or present in insignificant levels, the pretreatment can be omitted. A simple way to determine if chloride will affect test results is to run

routine samples with and without the chloride removal, then compare results. Other inorganic interferences (i.e., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. If necessary, these interferences can be corrected for after determining their concentrations with separate methods and adjusting the final COD test results accordingly.

Ammonia nitrogen is known to interfere in the presence of chloride; it does not interfere if chloride is absent.

Summary of Method

Chemical oxygen demand (COD) is defined as "... a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" (APHA Standard Methods, 19th ed., 1995). Trivalent manganese is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colorless when it reacts with organic matter. It typically oxidizes about 80% of the organic compounds. Studies have shown that the reactions are highly reproducible and test results correlate closely to Biochemical Oxygen Demand (BOD) values and hexavalent chromium COD tests. None of the oxygen demand tests provide 100% oxidation of all organic compounds.

A calibration is provided which is based on the oxidation of Potassium Acid Phthalate (KHP). A different response may be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy is obtained when test results are correlated to a standard reference method such as BOD or one of the chromium COD methods. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The sample digestion time can be extended up to 4 hours for samples which are difficult to oxidize.

OXYGEN DEMAND, CHEMICAL, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Manganese III COD Reagent Vials, 20-1000 mg/L	1	25/pkg	26234-25
Sulfuric Acid, concentrated	1 mL	4 Kg	979-09
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Adapter, COD/TNT	1	each	48464-00
Blender, Osterizer, 120 Vac, 14-speed	1	each	26747-00
Blender Container, 118 mL	1	2/pkg	26748-00
Cap, with inert Teflon liner, for mixing bottle	varies	12/pkg	24018-12
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Forceps, extra fine point	1	each	26696-00
Mixing Bottle, glass, for sample + acid	1	each	24276-06
Pipet, TenSette, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette	2	250/pkg	21997-25
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette	2	1000/pkg	21856-28
Test Tube Rack, stainless steel	1	each	18641-00

OPTIONAL REAGENTS

COD Standard Solution, 800 mg/L COD	200 mL	26726-29
Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules	16/pkg	28335-10
Potassium Acid Phthalate	500 g	315-34
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28332-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49

OPTIONAL APPARATUS

Dispenser for sulfuric acid	each	25631-37
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001

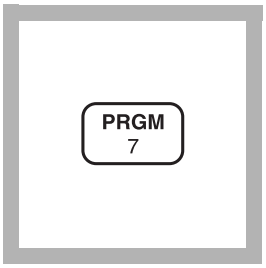
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L) For water and wastewater

Manganese III Digestion Method* (with chloride removal)



1. Enter the stored program number for Manganese III COD.

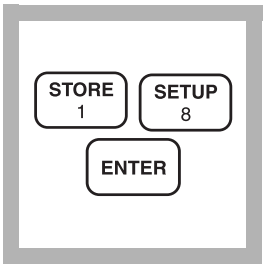
Press: **PRGM**

The display will show:

PRGM ?

Note: *If samples cannot be analyzed immediately, see Sampling and Storage following these steps.*

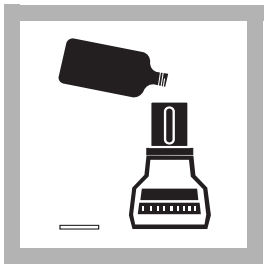
Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



2. Press: **18 ENTER**

The display will show **mg/L, COD** and the **ZERO** icon**.**

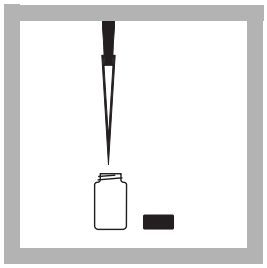
Note: *For alternate forms (O_2), press the* **CONC** *key.*



3. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: *Blending promotes even distribution of solids and improves accuracy and reproducibility.*

Note: *Continue mixing the sample while pipetting if suspended solids are present.*



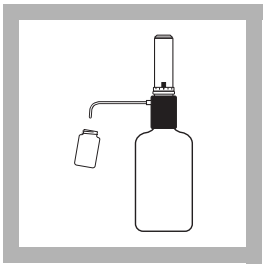
Chloride Removal Procedure

4. Using a TenSette Pipet or a pipet and safety bulb, pipet 9.0 mL of homogenized sample into an empty glass mixing cell. If the sample COD exceeds 1000 mg/L, dilute the sample as described in *Table 1*.

Note: *If suspended solids are present, continue mixing the sample while pipetting.*

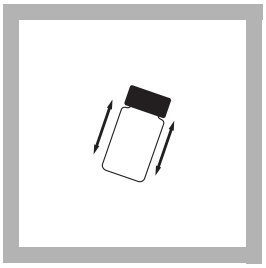
Caution: Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and appropriate clothing. If contact occurs, flush the affected area with running water. Follow all instructions carefully.

* U.S. Patent 5,556,787



5. Using an automatic dispenser or TenSette Pipet, add 1.0 mL of concentrated sulfuric acid to the mixing cell.

Note: *Mixing concentrated sulfuric acid and water is not additive. Adding 1.0 mL of concentrated sulfuric acid to 9.0 mL of sample does not result in a final volume of 10.0 mL. This factor is built into the calibration curve.*



6. Cap the cell tightly and invert it several times. The solution will become hot. Cool to room temperature before proceeding.

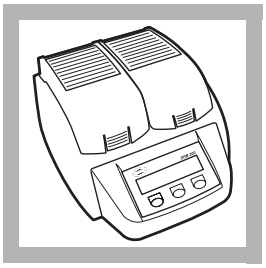
Note: *Acidified samples are stable for several months when refrigerated at 4 °C.*

7. Prepare a blank (see note) by repeating Steps 4-6, substituting 9.0 mL of deionized water for the sample.

Note: *The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range, when using chloride removal, should be about 1.31-1.36.*

Note: *Use a clean pipet or rinse it thoroughly.*

Note: *One blank must be run with each lot of reagents. Run all samples and blanks with the same lot of vials (lot number is on the container label).*



8. If not already on, turn on the DRB 200 Reactor and heat to 150 °C.

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*

Table 1 Dilution Table (for use with Chloride Removal Procedure Only)

Sample (mL)	Deionized Water (mL)	Range (mg/L COD)	Multiplication Factor
6.0	3.0	30-1500	1.5
3.0	6.0	60-3000	3
1.0	8.0	180-9000	9
0.5	8.5	360-18000	18

All dilutions require that the ratio of sample to sulfuric acid remain at 9:1. For other dilutions that are not listed in Table 1, simply add the sample volume + deionized water and divide by the sample volume to obtain the multiplication factor.

Example:

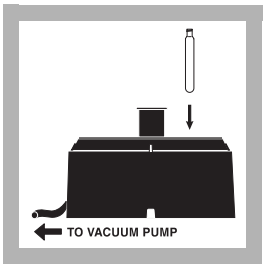
Dilute the sample to a range of 90-4500 mg/L COD

Sample Volume (2.0 mL) + Deionized water (7.0 mL) = Total Volume (9.0 mL)

$$\text{Multiplication Factor} = \frac{\text{Total Volume}}{\text{Sample Volume}} = \frac{9.0\ \text{mL}}{2.0\ \text{mL}} = 4.5$$

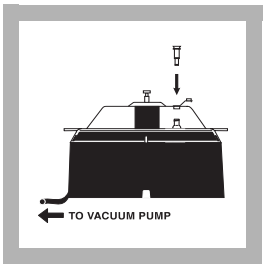
Standard test range is 20-1000 mg/L COD. Example Test Range = 4.5 (20) to 4.5 (1000) = 90-4500 mg/L COD

It is best to use 0.5 mL or more of sample for diluting. If sample values exceed 18,000 mg/L COD, use a separate sample dilution before the sample chloride removal procedure.

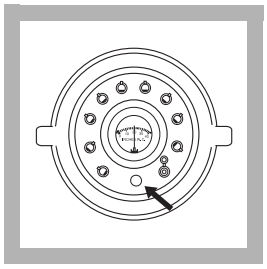


9. Label each Mn III COD vial and remove the cap. Place the vial in one of the numbered holes in the Vacuum Pretreatment Device (VPD)* base.

Note: *The VPD must be attached to a vacuum pump (not an aspirator-type vacuum) that can create a vacuum of 20 to 25 inches of mercury.*

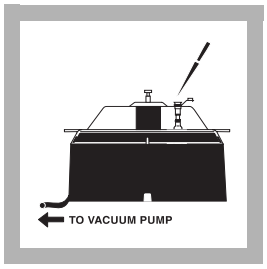


10. Place the VPD top on the base. Insert a fresh Chloride Removal Cartridge (CRC)** directly above each Mn III COD Reagent Vial. Plug any open holes in the VPD top using the stoppers provided.



11. Turn the vacuum pump on and adjust the vacuum regulator valve on top of the VPD until the internal gauge reads 20 inches of water.

Note: *The optimum setting allows the sample to flow through the CRC in about 30 to 45 seconds.*

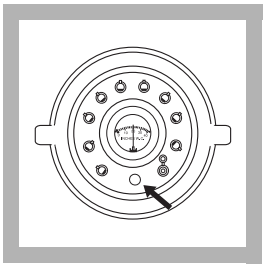


12. Pipet 0.60 mL of acidified sample (made in Steps 4-6) into the CRC. Pipet 0.60 mL of acidified blank into another CRC.

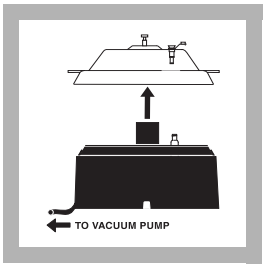
Note: *If the sample does not flow through the CRC, increase the vacuum until flow starts, then reduce the vacuum to 20 inches of water. Proceed as usual.*

* Patent Pending.

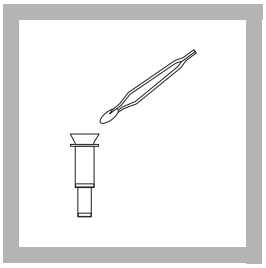
** U.S. patents 5,667,754 and 5,683,914.



13. Close the vacuum regulator valve completely to achieve full vacuum. After one minute under full vacuum, slide the VPD back and forth several times to dislodge any drops clinging to the cartridge.



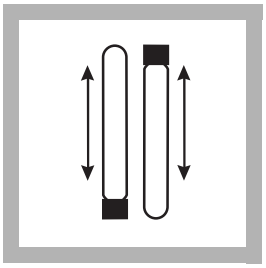
14. Open the VPD regulator valve to release the vacuum. Turn the pump off. Remove the VPD top and set it beside the base.



15. Use forceps to remove the filter from the top of each CRC. Place each filter in the corresponding Mn III COD Vial (use the numbers on the VPD as a guide).

Note: *If the sample does not contain suspended solids, it is not necessary to transfer the filter to the digestion vial.*

Note: *To avoid cross contamination, clean forceps tips between samples by wiping with a clean towel or rinsing with deionized water.*



16. Remove the Mn III COD vial from the vacuum chamber and replace the original cap. Screw the cap on tightly. Invert several times to mix.

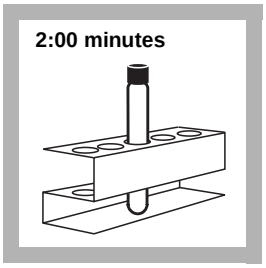
Note: *Dispose of the used Chloride Removal Cartridge. Do not reuse it.*

17. Place the vials in the DRB 200 Reactor that is preheated to 150 °C. Digest for 1 hour.

Note: *Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.*

Note: *Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.*

Note: *See DRB 200 user manual for selecting pre-programmed temperature applications.*

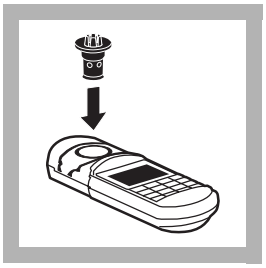


18. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about three minutes.

Note: *Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed. This will not affect test results.*

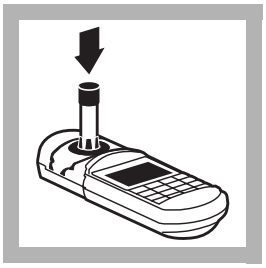
19. Remove the vials from the water and wipe with a clean, dry paper towel.

Invert the vials several times to mix.



20. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

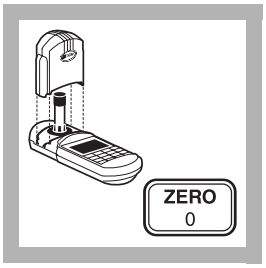
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



21. Place the blank in the sample cell adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



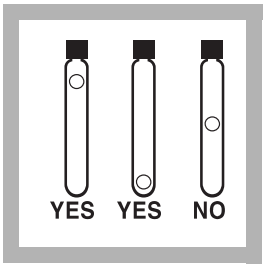
22. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*

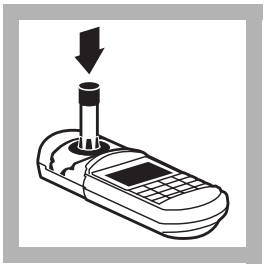
Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L COD



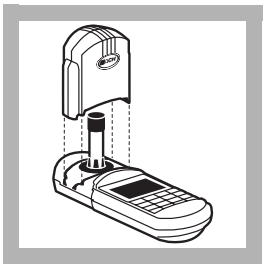
23. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



24. Place the sample in the adapter.

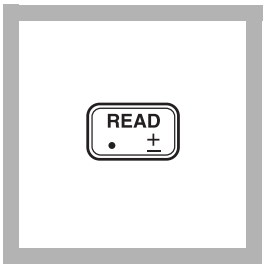
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



25. Tightly cover the sample cell with the instrument cap.

Note: *Clean the COD vial with a towel to remove fingerprints or other marks.*



26. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Note: *Adjust the result for any sample dilution.*

Sampling and Storage

Collect samples in clean glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with concentrated sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C may be stored up to 28 days. Correct results for volume additions; see *Correcting for Volume Additions* (*Section 1*) for more information.

Accuracy Check

Standard Solution Method

Prepare an 800 mg/L COD standard solution by adding 0.6808 g of
dried (103 °C, overnight) potassium acid phthalate (KHP) to 1 liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be
800 ±26 mg/L COD.

An 800 mg/L COD solution can also be purchased directly from Hach (see *Optional Reagents*).

Method Performance (for Manganic III COD without the chloride removal procedure)

Precision

In a single laboratory, using a standard solution of 800 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±23 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 18 is 14 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Inorganic materials may also be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. If chloride is known to be absent or present in insignificant levels, the pretreatment can be omitted. A simple way to determine if chloride will affect test results is to run

routine samples with and without the chloride removal, then compare results. Other inorganic interferences (i.e., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. If necessary, these interferences can be corrected for after determining their concentrations with separate methods and adjusting the final COD test results accordingly.

Ammonia nitrogen is known to interfere in the presence of chloride; it does not interfere if chloride is absent.

Summary of Method

Chemical oxygen demand (COD) is defined as "... a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" (APHA Standard Methods, 19th ed., 1995). Trivalent manganese is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colorless when it reacts with organic matter. It typically oxidizes about 80% of the organic compounds. Studies have shown that the reactions are highly reproducible and test results correlate closely to Biochemical Oxygen Demand (BOD) values and hexavalent chromium COD tests. None of the oxygen demand tests provide 100% oxidation of all organic compounds.

A calibration is provided which is based on the oxidation of Potassium Acid Phthalate (KHP). A different response may be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy is obtained when test results are correlated to a standard reference method such as BOD or one of the chromium COD methods. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The sample digestion time can be extended up to 4 hours for samples which are difficult to oxidize.

OXYGEN DEMAND, CHEMICAL, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Chloride Removal Cartridges (CRC)	1	25/pkg	26618-25
Manganese III COD Reagent Vials, 20-1000 mg/L	1	25/pkg	26234-25
Sulfuric Acid, concentrated	1 mL	4 Kg	979-09
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Adapter, COD/TNT	1	each	48464-00
Blender, Osterizer, 120 Vac, 14-speed	1	each	26747-00
Blender Container, 118 mL	1	2/pkg	26748-00
Cap, with inert Teflon liner, for mixing bottle	varies	12/pkg	24018-12
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Forceps, extra fine point	1	each	26696-00
Mixing Bottle, glass, for sample + acid	1	each	24276-06
Pipet, TenSette, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette	2	250/pkg	21997-25
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette	2	1000/pkg	21856-28
Test Tube Rack, stainless steel	1	each	18641-00
Vacuum Pretreatment Device (VPD)	1	each	49000-00
Vacuum Pump, 115 V	1	each	14697-00
Vacuum Pump, 230V	1	each	14697-02

OPTIONAL REAGENTS

COD Standard Solution, 800 mg/L COD	200 mL		26726-29
Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules	16/pkg		28335-10
Potassium Acid Phthalate	500 g		315-34
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL		28332-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL		28331-49

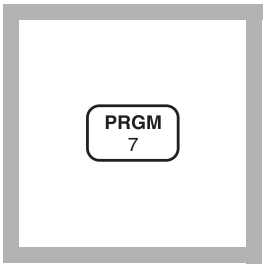
OPTIONAL APPARATUS

Dispenser for sulfuric acid		each	25631-37
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm			LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm			LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm			LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm			LTV082.52.30001

OXYGEN, DISSOLVED, High Range (0 to 15.0 mg/L O_2)

HRDO Method

For water and wastewater

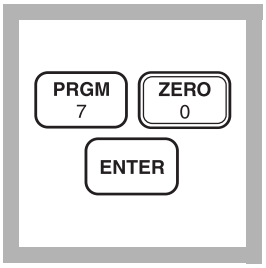


1. Enter the stored program number for dissolved oxygen, high range.

Press: **PRGM**

The display will show:

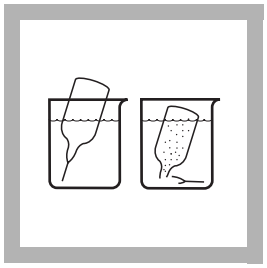
PRGM ?



2. Press: **70 ENTER**

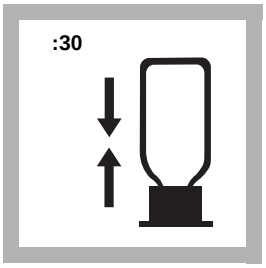
The display will show **mg/L, O2** and the **ZERO** icon.

3. Fill a sample cell (the blank) with at least 10 mL of sample. Fill a blue ampul cap with sample. Collect at least 40 mL of sample in a 50-mL beaker.



4. Fill a High Range Dissolved Oxygen AccuVac Ampul with sample.

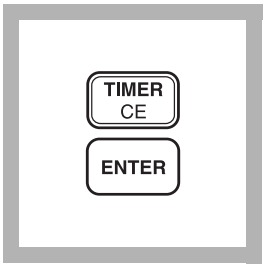
Note: *Keep the tip immersed while the ampul fills completely.*



5. Without inverting the ampul, immediately place the ampul cap that has been filled with sample securely over the tip of the ampul. Shake for about 30 seconds.

Note: *Accuracy is not affected by undissolved powder.*

Note: *The cap prevents contamination with atmospheric oxygen.*

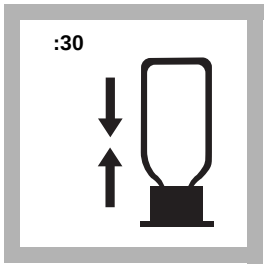


6. Press:

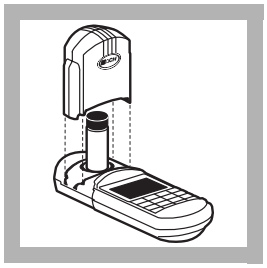
TIMER ENTER

A 2-minute reaction period will begin.

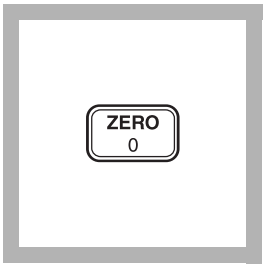
Note: *The two-minute period allows oxygen which was degassed during aspiration to redissolve in the sample and react.*



7. When the timer beeps, shake the ampul for 30 seconds.



8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

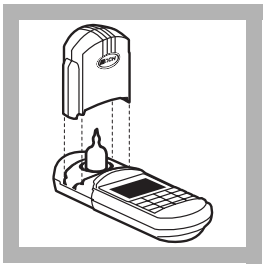


9. Press: **ZERO**

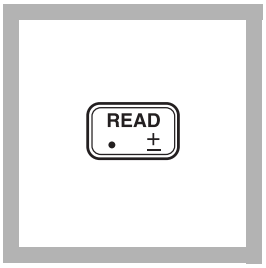
The cursor will move to the right, then the display will show:

0.0 mg/L O2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



10. Place the AccuVac ampul into the cell holder. Tightly cover the ampul with the instrument cap. Wait approximately 30 seconds for the air bubbles to disperse from the light path.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L O_2 will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

The main consideration in sampling with the High Range Dissolved Oxygen AccuVac Ampul is to prevent the sample from becoming contaminated with atmospheric oxygen. This is accomplished by capping the ampul with an ampul cap in the interval between breaking open the ampul and reading the absorbance. If the ampul is securely capped, it should be safe from contamination for several hours. The absorbance will decrease by approximately 3% during the first hour and will not change significantly afterwards.

Sampling and sample handling are important considerations in obtaining meaningful results. The dissolved oxygen content of the water being tested can be expected to change with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time and other factors. A single dissolved oxygen test rarely reflects the accurate over-all condition of a body of water. Several samples taken at different times, locations and depths are recommended for most reliable results. Samples must be tested immediately upon collection although only a small error results if the absorbance reading is taken several hours later.

Accuracy Check

The results of this procedure may be compared with the results of a dissolved oxygen meter (Cat. No. 51815-01).

Method Performance

Precision

In a single laboratory, using a standard solution of 8.0 mg/L O_2 determined by the Winkler method and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of
±0.41 mg/L O_2.

Estimated Detection Limit

The estimated detection limit for program 70 is 0.10 mg/L O_2. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Cr^{3+}	Greater than 10 mg/L
Cu^{2+}	Greater than 10 mg/L
Fe^{2+}	Greater than 10 mg/L
Mg^{2+}	Magnesium is commonly present in seawater and causes a negative interference. If the sample contains more than 50% seawater, the oxygen concentration obtained by this method will be 25% less than the true oxygen concentration. If the sample contains less than 50% seawater, the interference will be less than 5%.
Mn^{2+}	Greater than 10 mg/L
Ni^{2+}	Greater than 10 mg/L
NO_2^-	Greater than 10 mg/L

Summary of Method

The High Range Dissolved Oxygen AccuVac Ampul contains reagent vacuum sealed in a 12-mL ampul. When the AccuVac ampul is broken open in a sample containing dissolved oxygen, a yellow color forms, which turns purple as the oxygen reacts with the reagent. The color developed is proportional to the concentration of dissolved oxygen.

OXYGEN, DISSOLVED, High Range, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
High Range Dissolved Oxygen AccuVac Ampuls, with 2 reusable ampul caps	1 ampul	25/pkg	25150-25

REQUIRED APPARATUS

Beaker, 50 mL	1	each	500-41H
Caps, ampul, blue	varies	25/pkg	1731-25
Sample Cell, 10-20-25 mL, w/ cap	1	6/pkg	24019-06

OPTIONAL REAGENTS AND APPARATUS

AccuVac Dissolved Oxygen Sampler	each	24051-00
AccuVac Snapper Kit	each	24052-00
AccuVac Drainer	each	41036-00
BOD bottle and stopper, 300 mL	each	621-00
Dissolved Oxygen Meter, Portable HQ 10	each	51815-01
Dissolved Oxygen Reagent Set (Buret Method)	100 tests	23514-00
Dissolved Oxygen Reagent Set (Digital Titrator Method)	50 tests	22722-00

Dissolved oxygen may also be determined by titrimetric methods. Request Publication 8042 for additional information.

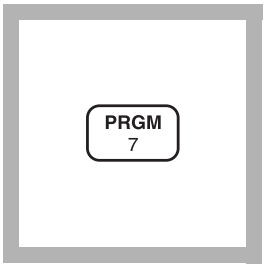
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

OXYGEN, DISSOLVED, Low Range (0 to 1000 µg/L O_2) For boiler feedwater

Indigo Carmine Method (Using AccuVac Ampuls)



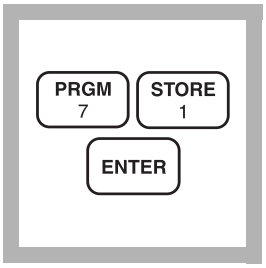
1. Enter the stored program number for low range dissolved oxygen (O_2).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*

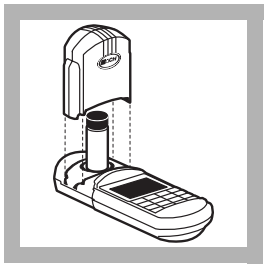


2. Press: **71 ENTER**

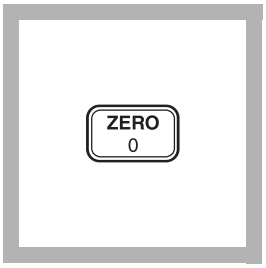
The display will show **µg/L, O2** and the **ZERO** icon**.**

3. Fill a sample cell with at least 10 mL of sample (the blank).

Note: *Samples must be analyzed immediately and cannot be stored.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

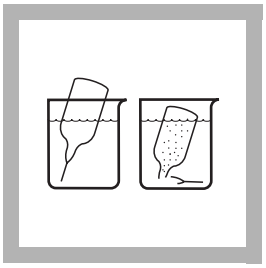


5. Press: **ZERO**

The cursor will move to the right, then the display will show:

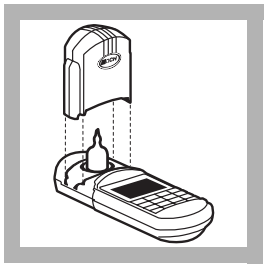
0 µg/L O2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



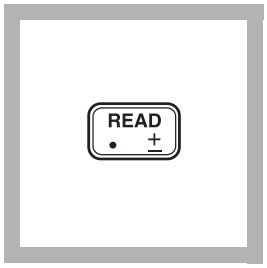
6. Collect at least 40 mL of sample in a 50-mL beaker. Fill a Low Range Dissolved Oxygen AccuVac Ampul with sample.

Note: *Keep the tip immersed while the ampul fills completely.*



7. Immediately place the AccuVac ampul into the cell holder. Tightly cover the ampul with the instrument cap.

Note: *The ampuls will contain a small piece of wire to maintain reagent quality. The solution color will be yellow.*



8. Press: **READ**

The cursor will move to the right, then the result in µg/L dissolved oxygen will be displayed.

Note: *Use the initial reading. The reading is stable for 30 seconds. After 30 seconds, the ampul solution will absorb oxygen from the air.*

Sampling and Storage

The main consideration in this procedure is to prevent contaminating the sample with atmospheric oxygen. Sampling from a stream of water that is hard plumbed to the sample source is ideal. Use a funnel to maintain a continual flow of sample and yet collect enough sample to immerse the ampul. It is important not to introduce air in place of the sample. Rubber tubing, if used, will introduce unacceptable amounts of oxygen into the sample unless the length of tubing is minimized and the flow rate is maximized. Flush the sampling system with sample for at least 5 minutes.

Accuracy Check

The reagent blank for this test can be checked by following these steps:

a) Fill a 50-mL beaker with sample and add approximately 50 mg sodium hydrosulfite.

b) Immerse the tip of a Low Range Dissolved Oxygen AccuVac Ampul in the sample and break the tip. Keep the tip immersed while the ampul fills completely.

c) Determine the dissolved oxygen concentration according to the preceding procedure. The result should be 0 ±1 µg/L.

Method Performance

Precision

In a single laboratory, using a standard solution of 500 µg/L O_2 and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±2 µg/L O_2. For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit

The estimated detection limit for program #71 is 10 µg/L O_2. For more information on the estimated detection limit, see *Section 1*.

OXYGEN, DISSOLVED, Low Range, continued

Interferences

Interfering Substance	Interference Levels and Treatments
Hydrazine	100,000 fold excess will begin to reduce the oxidized form of the indicator solution.
Sodium hydrosulfite	Reduces the oxidized form of the indicator solution and will cause a significant interference.

Excess amounts of sodium thioglycolate, sodium ascorbate, sodium ascorbate + sodium sulfite, sodium ascorbate + cupric sulfate, sodium nitrite, sodium sulfite, sodium thiosulfate, and hydroquinone do not cause significant interference.

Summary of Method

When the vacuum-sealed AccuVac ampul is broken open in a sample containing dissolved oxygen, the yellow reagent solution turns blue. The blue color is proportional to the dissolved oxygen concentration.

REQUIRED REAGENTS & APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Low Range Dissolved Oxygen AccuVac Ampuls	1 ampul	25/pkg	25010-25
Beaker, 50 mL	1	each	500-41H
Sample Cell, 10-20-25 mL, w/cap	1	6/pkg	24019-06

OPTIONAL REAGENTS AND APPARATUS

AccuVac Snapper Kit		each	24052-00
Sodium Hydrosulfite, technical grade		500 g	294-34

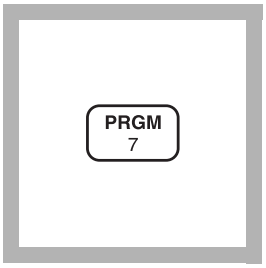
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

OZONE (0 to 0.25 mg/L O_3, 0 to 0.75 mg/L O_3 or 0 to 1.50 mg/L O_3) For water

Indigo Method (Using AccuVac Ampuls)

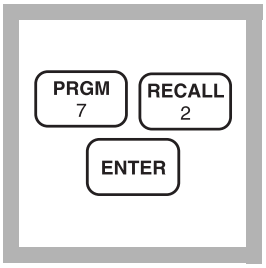


1. Enter the stored program number for Ozone (O_3) AccuVac ampuls.

Press: **PRGM**

The display will show:

PRGM ?

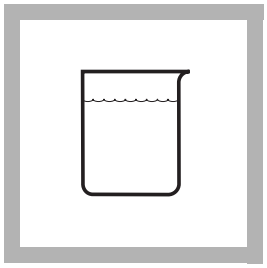


2. Press: **72 ENTER** for low range ozone

Press: **73 ENTER** for mid range ozone

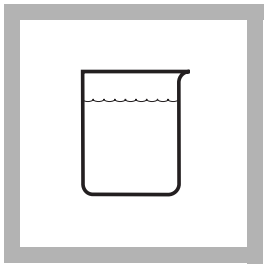
Press: **74 ENTER** for high range ozone.

The display will show **mg/L, O3** and the **ZERO** icon**.**



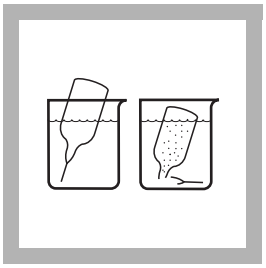
3. Gently collect at least 40 mL of sample in a 50-mL beaker.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis. See* Sampling and Storage *following these steps for proper collection.*



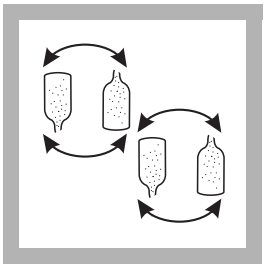
4. Collect at least 40 mL of ozone-free water (blank) in another 50-mL beaker.

Note: *Ozone-free water used for the blank may be deionized water or tap water.*



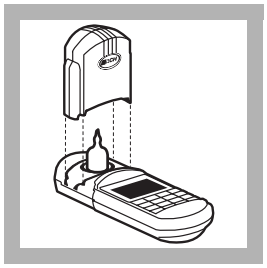
5. Fill one Indigo Ozone Reagent AccuVac Ampul with the sample and one ampul with the blank.

Note: *Keep the tip immersed while the ampul fills.*



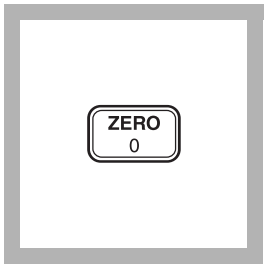
6. Quickly invert both ampuls several times to mix. Wipe off any liquid or fingerprints.

Note: *Part of the blue color will be bleached if ozone is present. (The sample will be lighter than the blank.)*



7. Place the **sample** AccuVac ampul into the cell holder. Tightly cover the ampul with the instrument cap.

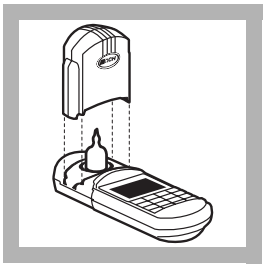
Note: *Standardization for this procedure is intentionally reversed.*



8. Press: **ZERO**

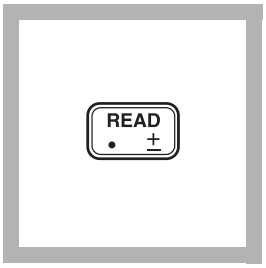
The cursor will move to the right, then the display will show:

0.00 mg/L O3



9. Place the AccuVac ampul containing the **blank** into the cell holder. Tightly cover the ampul with the instrument cap.

Note: *Standardization for this procedure is intentionally reversed.*



10. Press: **READ**

The cursor will move to the right, then the result in mg/L ozone will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling

The chief consideration when collecting a sample is to prevent the escape of ozone from the sample. The sample should be collected gently and analyzed immediately. Warming the sample or disturbing the sample by stirring or shaking will result in ozone loss. After collecting the sample, do not transfer it from one container to another unless absolutely necessary.

Stability of Indigo Reagent

Indigo is light-sensitive. Therefore, the AccuVac Ampuls should be kept in the dark at all times.

However, the indigo solution decomposes slowly under room light after filling with sample. The blank ampul can be used for multiple measurements during the same day.

Method Performance

Precision

In a single laboratory, using standard solutions of 0.15, 0.28 and 0.96 mg/L ozone for the low, mid and high range, respectively, and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.01, ±0.02 and ±0.02 mg/L O_3 for the low, mid and high range tests, respectively. For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit

The estimated detection limit for the programs #72, #73, and #74 is 0.02 mg/L O_3. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

The reagent formulation adjusts the sample pH to 2.5 after the ampul has filled. The indigo reagent reacts immediately and quantitatively with ozone. The blue color of indigo is bleached in proportion to the amount of ozone present in the sample. Other reagents in the formulation prevent chlorine interference. No transfer of sample is needed in the procedure. Therefore, ozone loss due to sampling is eliminated.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Ozone AccuVac Ampuls			
Select one or more based on range:			
0-0.25 mg/L	2 ampuls	25/pkg	25160-25
0-0.75 mg/L	2 ampuls	25/pkg	25170-25
0-1.50 mg/L	2 ampuls	25/pkg	25180-25
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Beaker, 50 mL	2	each	500-41H

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
AccuVac Ampule sampler		each	24051-00

For Technical Assistance, Price and Ordering

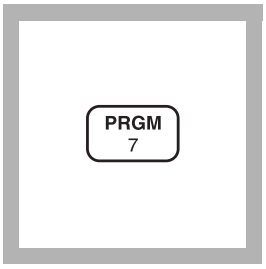
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

pH (6.5 to 8.5 pH units)

Colorimetric pH Determination Using Phenol Red

For water and wastewater

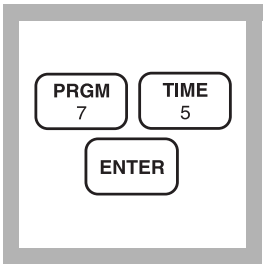


1. Enter the stored program number for the pH method.

Press: **PRGM**

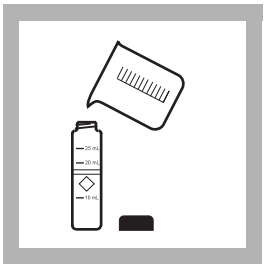
The display will show:

PRGM ?

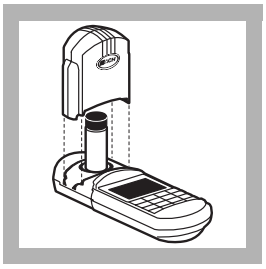


2. Press: **75 ENTER**

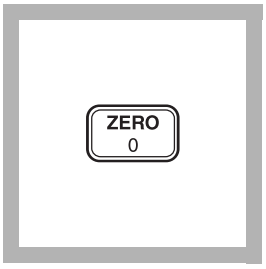
The display will show **PH** and the **ZERO** icon.



3. Fill a sample cell with 10 mL of sample (the blank).



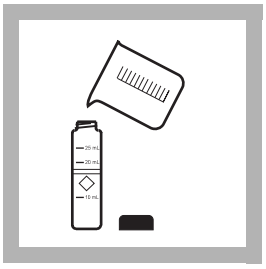
4. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

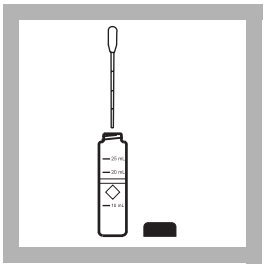
The cursor will move to the right, then the display will show:

6.0 PH

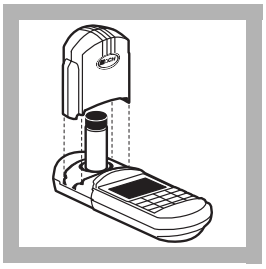


6. Fill another cell with 10 mL of sample.

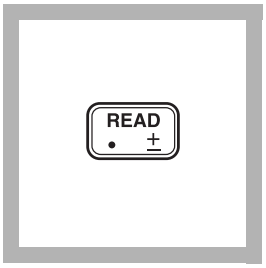
Note: *Sample temperature must be 21-29 °C.*



7. Using a disposable dropper, add 1 mL of Phenol Red Indicator Solution to the cell (the prepared sample). Cap the sample cell and invert twice to mix.



8. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



9. Press: **READ**

The cursor will move to the right, then the result in pH units will be displayed.

Note: *Use of the Standard Adjust feature is highly recommended. See* Accuracy Check.

Note: *Any reading below 6.5 pH units will be erroneous.*

Sampling and Storage

Analyze samples immediately for best results.

Accuracy Check

Standard Solution Method
Using a clear pH 7.0 buffer solution as the sample, perform the pH procedure as described above.

Method Performance

Precision
In a single laboratory using a standard solution of pH 7.0 and two lots of reagent with the instrument, a single operator obtained a standard deviation of less than 0.1 pH units.

Estimated Detection Limit
The estimated detection limit for program 75 is a pH of 6.5.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 7.0 buffer solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **7.0** to edit the standard concentration to match that of the standard used. See *Section 1*, *Standard Curve Adjustmen*t for more information. Press **ENTER** to complete the curve adjustment.

Interferences

Chlorine does not interfere at levels of 6 mg/L or lower.

Salt water (sea water) will interfere and cannot be analyzed using this method.

Summary of Method

This method uses a sulfonphthalein indicator (Phenol Red) to determine pH colorimetrically. Phenol Red has a working range of pH 6.8 (yellow) to 8.2 (red).

REQUIRED REAGENTS & APPARATUS

Description	Quantity Required Per Test	Units	Cat. No.
Dropper, 0.5 & 1.0 mL marks	1	20/pkg	21247-20
Phenol Red Indicator Solution, spec grade	1.0 mL	50 mL	26575-12
Sample Cells, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

pH 7.0 Buffer Solution		500 mL	12222-49

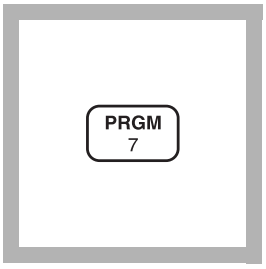
OPTIONAL APPARATUS

Description	Units	Cat. No.
Thermometer, -20 to 110 °C, Non-Mercury	each	26357-02

For Technical Assistance, Price and Ordering
In the U.S.A. call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHONATES (0-2.5 to 0-125 mg/L)

Persulfate UV Oxidation Method*



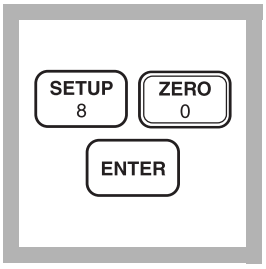
1. Enter the stored program number for phosphonates.

Press: **PRGM**

The display will show:

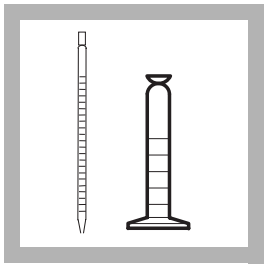
PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **80 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon**.**



3. Choose the appropriate sample size from *Table 1* below. Pipet the chosen sample volume into a 50-mL graduated mixing cylinder. Dilute the sample to 50 mL with deionized water. Mix well.

Note: *Clean glassware with 1:1 hydrochloric acid, followed by a deionized water rinse. Do not use commercial detergents containing phosphates to clean glassware.*

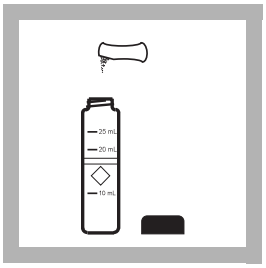
4. Fill a sample cell to the 10-mL mark with diluted sample from Step 3 (label this as the blank).

Fill another sample cell to the 25-mL mark with diluted sample from Step 3 (label this as the sample).

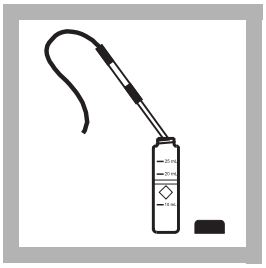
Table 1

Expected Range (mg/L phosphonate)	Sample Volume (mL)
0-2.5	50
0-5	25
0-12.5	10
0-25	5
0-125	1

* Adapted from Blystone, P.; Larson, P., *A Rapid Method for Analysis of Phosphonate Compounds*, International Water Conference, Pittsburgh, Pa. (Oct. 26-28, 1981).



5. Add the contents of one Potassium Persulfate for Phosphonate Powder Pillow to the cell labeled as "sample". Swirl to mix. This cell contains the prepared sample.

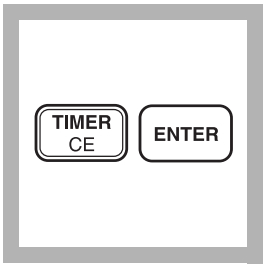


6. Insert the ultraviolet (UV) lamp into the prepared sample.

Note: *Wear UV safety goggles while the lamp is on.*

Note: *Do not handle the lamp surface. Fingerprints will etch the glass. Wipe lamp with a soft, clean tissue between samples. Do not use detergents with phosphates to wash glassware.*

Note: *A specially designed cord adapter is available for performing two digestions with a single power supply. A second UV lamp is required.*



7. Turn on the UV lamp to digest the prepared sample.

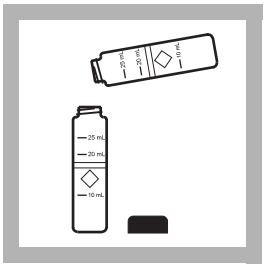
Press: **TIMER ENTER**

A 10-minute reaction period will begin.

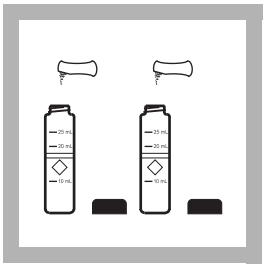
Note: *Phosphonates are converted to ortho-phosphate in this step.*

Note: *The digestion step may take less time. Contaminated samples or a weak lamp could result in incomplete digestion. Check efficiency by running a longer digestion to see if readings increase.*

8. When the timer beeps, turn off the UV lamp. Remove it from the sample cell.

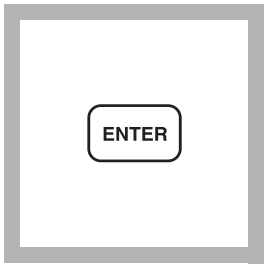


9. Pour 10 mL of sample from the cell labeled as "sample" into a second clean, dry sample cell. This is the prepared sample.



10. Add the contents of one PhosVer 3 Phosphate Reagent Powder Pillow for 10-mL samples to each sample cell. Swirl immediately to mix.

Note: *A blue color will form if phosphate is present. Sample and blank cells may develop color.*

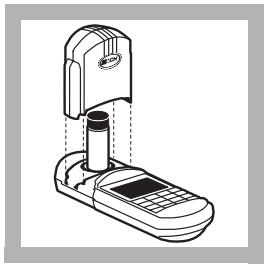


11. The display will show: **2:00 TIMER 2**

Press: **ENTER**

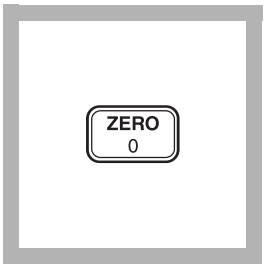
A two-minute reaction period will begin.

Note: *If sample is colder than 15 °C, 4 minutes are required for color development.*



12. When the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Perform Steps 12-15 within three minutes after the timer beeps.*

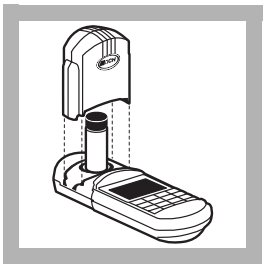


13. Press: **ZERO**

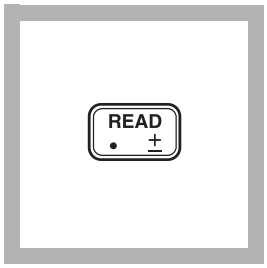
The cursor will move to the right, then the display will show:

0.0 mg/L PO4

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



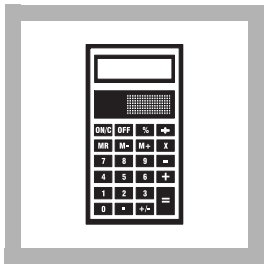
14. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



15. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate will be displayed. Multiply this value by the appropriate multiplier from *Table 2* to obtain the actual concentration of phosphonates as phosphate in the sample.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*



16. Results may be expressed in terms of a specific active phosphonate by using the appropriate conversion factor and the equation found in *Table 3*.

Table 2

Sample Volume (mL) (chosen in Step 3)	Multiplier
50	0.1
25	0.2
10	0.5
5	1.0
1	5.0
Phosphate concentration = Instrument Reading x Multiplier	

Table 3

Phosphonate Type	Conversion Factor
PBTC	2.84
NTP	1.050
HEDPA	1.085
EDTMPA	1.148
HMDTMPA	1.295
DETPMPA	1.207
HPA	1.49
Active Phosphonate (mg/L) = Phosphate concentration from Step 15 x Conversion Factor	

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water.
Do not use a commercial detergent. If prompt analysis is impossible, adjust the pH to 2 or less with about 2 mL of sulfuric acid, ACS, per liter of sample. Store at 4 °C (39 °F) or below. Preserved samples can be stored at least 24 hours. See *Section 1* for more information on dilution factors, cleaning instructions, etc.

Accuracy Check

Ideally, a solution containing a known amount of the phosphonate product being used should be prepared. This will check the UV conversion of phosphonate to orthophosphate.

Interferences

When testing a 5-mL sample volume, the following may interfere when present in concentrations exceeding those listed below:

The interference levels will decrease as the sample size increases. For example, copper does not interfere at or below 100 mg/L for a 5.00 mL sample. If the sample volume is increased to 10.00 mL, copper will begin to interfere above 50 mg/L.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *pH Interferences* in *Section 1*.

Phosphites and organophosphorus compounds other than phosphonates react quantitatively. Meta and polyphosphates do not interfere.

Interfering Substance	Level	Interfering Substance	Level
Aluminum	100 mg/L	EDTA	100 mg/L
Arsenate	all levels	Iron	200 mg/L
Benzotriazole	10 mg/L	Nitrate	200 mg/L
Bicarbonate	1000 mg/L	NTA	250 mg/L
Bromide	100 mg/L	Orthophosphate	15 mg/L
Calcium	5000 mg/L	Silica	500 mg/L
CDTA	100 mg/L	Silicate	100 mg/L
Chloride	5000 mg/L	Sulfate	2000 mg/L
Chromate	100 mg/L	Sulfide	All levels
Copper	100 mg/L	Sulfite	100 mg/L
Cyanide*	100 mg/L	Thiourea	10 mg/L
Diethanoldithiocarbamate	50 mg/L		

* Increase the UV digestion to 30 minutes.

Summary of Method

This method is directly applicable to boiler and cooling tower samples. The procedure is based on a UV catalyzed oxidation of phosphonate to orthophosphate. Range may be as low as 0 to 2.5 mg/L or as high
as 0 to 125 mg/L.

Phosphonate is converted to orthophosphate during the UV digestion. Both the sample and the blank will develop color if orthophosphate is present in the sample. The increase in color in the sample is proportional to the phosphate produced in the digestion.

PHOSPHONATES, continued

REQUIRED REAGENTS

Phosphonates Reagent Set (100 tests) 24297-00
Includes: (2) 21060-69, (1) 20847-69

Description	Quantity Required Per Test	Unit	Cat. No
PhosVer 3 Phosphate Reagent Powder Pillows	2 pillows	100/pkg	21060-69
Potassium Persulfate Pillow for Phosphonate	1 pillow	100/pkg	20847-69
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Cylinder, mixing, graduated, 50 mL	1	each	1896-41
Goggles, UV safety	1	each	21134-00
Pipet, serological, 25 mL	1	each	2066-40
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06
UV Lamp with power supply, 115 V, with goggles	1	each	20828-00
OR			
UV Lamp with power supply, 230 V	1	each	20828-02

OPTIONAL REAGENTS

Hydrochloric Acid, 6.0 N (1:1)		500 mL	884-49
Sulfuric Acid, ACS		500 mL	979-49

OPTIONAL APPARATUS

pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
Pipet, serological, 2 mL		each	532-36
Pipet, TenSette, 1-10 mL		each	19700-10
Pipet Tips, for 19700-10 Tensette Pipet		50/pkg	21997-96
Thermometer, -20 to 110 °C, Non-Mercury		each	1877-01

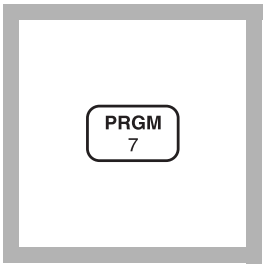
For Technical Assistance, Price and Ordering
In the U.S.A. call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHORUS, REACTIVE (0 to 45.0 mg/L PO_4^{3-}) For water and wastewater

(Also called Orthophosphate) Molybdovanadate Method*

(Reagent Solution or AccuVac Ampuls)

Using Reagent Solution

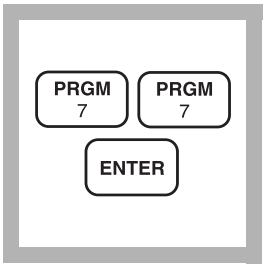


1. Enter the stored program number for high range phosphate (PO_4^{3-}) reagent solution.

Press: **PRGM**

The display will show:

PRGM ?



2. Press: **77 ENTER**

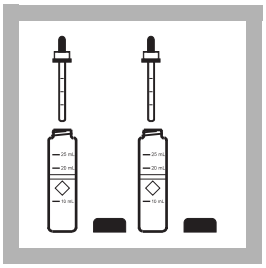
The display will show **mg/L, PO4** and the **ZERO** icon**.**

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*

3. Fill a sample cell with 25 mL of deionized water (the blank).

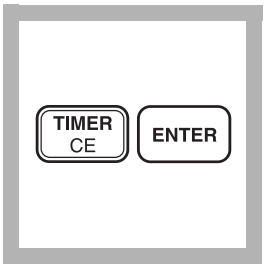
4. Fill another sample cell with 25 mL of sample (the prepared sample).

Note: *For best results, the sample temperature should be 20-25 °C.*



5. Add 1.0 mL of Molybdovanadate Reagent to each sample cell. Cap the cells and invert to mix.

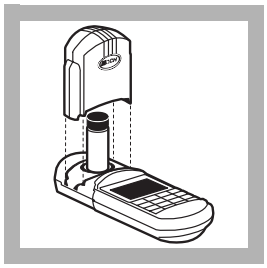
Note: *A yellow color will form if phosphate is present. A small amount of yellow will be present in the blank, because of the reagent.*



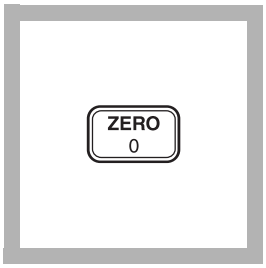
6. Press:

TIMER ENTER

A five-minute reaction period will begin.



7. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

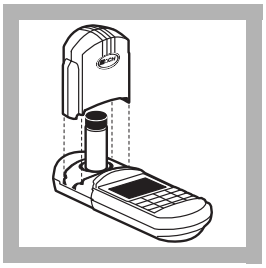


8. Press: **ZERO**

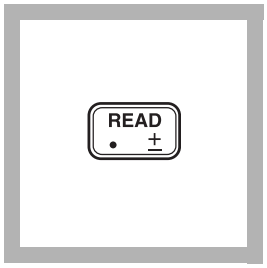
The cursor will move to the right, then the display will show:

0.0 mg/L PO4

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

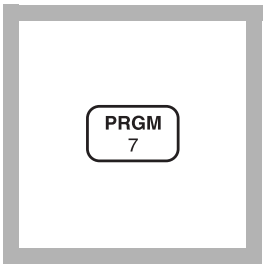


10. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (or alternate form) will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Using AccuVac Ampuls

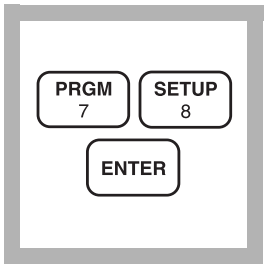


1. Enter the stored program number for high range phosphate (PO_4^{3-})-AccuVac Ampuls.

Press: **PRGM**

The display will show:

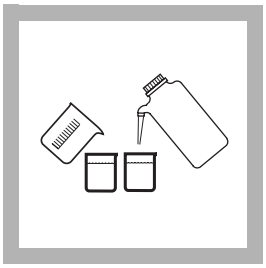
PRGM ?



2. Press: **78 ENTER**

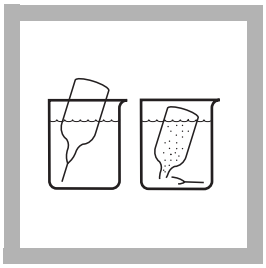
The display will show **mg/L, PO4** and the **ZERO** icon**.**

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*



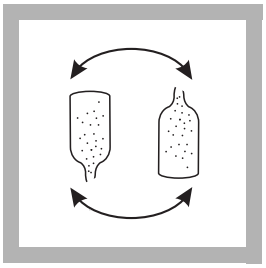
3. Collect at least 40 mL of sample in a 50-mL beaker. Pour at least 40 mL of deionized water into a second beaker.

Note: *For best results, sample temperature should be 20-25 °C.*



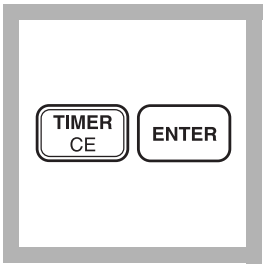
4. Fill a Molybdo-vanadate Reagent AccuVac Ampul with sample. Fill a second AccuVac Ampul with deionized water (the blank).

Note: *Keep the tip immersed while the ampul fills completely.*



5. Invert the ampul several times to mix, then wipe off any liquid or fingerprints.

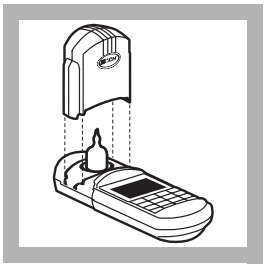
Note: *A yellow color will form if phosphate is present. A small amount of yellow will be present in the blank because of the reagent.*



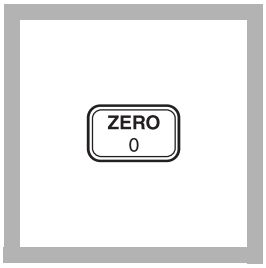
6. Press:

TIMER ENTER

A five-minute reaction period will begin.



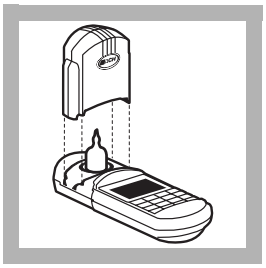
7. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



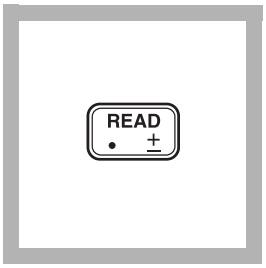
8. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.0 mg/L PO4



9. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (or alternate form) will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water.

Do not use a commercial detergent containing phosphate for

cleaning glassware used in this test.

Analyze samples immediately for best results. If prompt analysis is impossible, preserve samples by filtering immediately and storing at 4 °C for up to 48 hours.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate Voluette Ampule Standard Solution, 500 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper and invert to mix well.

d) For analysis with AccuVac Ampuls, transfer the spiked samples to clean, dry 50-mL beakers to facilitate filling of the ampuls. For analysis with reagent solution, transfer the spiked samples to
25-mL sample cells.

e) Analyze each sample as described in the procedure. Each 0.1-mL addition of standard should cause an increase of 2.0 mg/L PO_4^{3-}.

f) If these increases do not occur, see *Standard Additions* (Section 1) for more information.

Standard Solution Method

Obtain a Hach Phosphate Standard Solution, 10.0 mg/L as phosphate. Using this solution as the sample, perform the phosphate procedure as described above.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 10.0 mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **10.0** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Standard Curve Adjustment*, *Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 30.0 mg/L PO_4^{3-}, two lots of reagent, and the instrument, a single operator obtained a standard deviation of ±0.1 mg/L PO_4^{3-} for the reagent solution method and a standard deviation of ±0.2 for the AccuVac Ampul method.

Estimated Detection Limit

The estimated detection limit for program 77 is 0.3 mg/L PO_4^{3-} and
0.4 mg/L PO_4^{3-} for program 78. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substances and Suggested Treatment

Interfering Substance	Interference Level and Treatment
Arsenate	Only interferes if sample is heated.
Iron, ferrous	Blue color caused by ferrous iron does not interfere if iron concentration is less than 100 mg/L.
Molybdate	Causes negative interference above 1000 mg/L.
Silica	Only interferes if sample is heated.
Sulfide	Causes a negative interference. Remove interference as follows: **1.** Measure 50 mL of sample into an erlenmeyer flask. **2.** Add Bromine Water drop-wise with constant swirling until a permanent yellow color develops. **3.** Add Phenol Solution drop-wise until the yellow color just disappears. Proceed with step 4 of the procedure (step 3 if using the AccuVac procedure).
Extreme pH or highly buffered samples	May exceed buffering capacity of reagents. See Section 1, *pH Interferences*. Samples may require pretreatment. Sample pH should be about 7.
Fluoride, thorium, bismuth, thiosulfate or thiocyanate	Cause negative interference
The following do not interfere in concentrations up to 1000 mg/L: Pyrophosphate, tetraborate, selenate benzoate, citrate, oxalate, lactate, tartrate, formate, salicylate, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Mn^{2+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, SO_3^{2-}, Pb^{2+}, Hg^{+}, Hg^{2+}, Sn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, U^{4+}, Zr^{4+}, AsO_3^{-}, Br^{-}, CO_3^{2-}, $Cl0_4^{-}$, CN^{-}, IO_3^{-}, SiO_4^{4-}.	

Summary of Method

In the molybdovanadate method, orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. In the presence of vanadium, yellow vanadomolybdophosphoric acid is formed. The intensity of the yellow color is proportional to the phosphate concentration.

REQUIRED REAGENTS AND APPARATUS (using Reagent Solution)

Description	Quantity Required Per Test	Units	Cat. No.
Molybdovanadate Reagent	2.0 mL	100 mL* MDB	20760-32
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06
Water, deionized	25 mL	4 L	272-56

REQUIRED REAGENTS AND APPARATUS (using AccuVac Ampuls)

Molybdovanadate Reagent AccuVac Ampuls	2	25/pkg	25250-25
Beaker, 50 mL	2	each	500-41H
Water, deionized	25 mL	4 L	272-56

OPTIONAL REAGENTS

Description	Units	Cat. No.
Bromine Water, 30 g/L	29 mL*	2211-20
Hydrochloric Acid Solution, 1:1 (6.0 N)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, 10.0 mg/L as PO_4^{3-}	946 mL	14204-16
Phosphate Standard Solution, Voluette Ampule, 500 mg/L as PO_4^{3-}, 10 mL	16/pkg	14242-10
Sodium Hydroxide Standard Solution, 5.0 N	100 mL* MDB	2450-32
Sulfuric Acid, ACS	500 mL*	979-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49

OPTIONAL APPARATUS

AccuVac Snapper Kit	each		24052-00
Ampule Breaker Kit	each		21968-00
Cylinder, graduated, 25 mL	each		508-40
Cylinder, graduated, mixing, 25-mL	each		20886-40
Dispenser, fixed volume, 1.0 mL Repipet Jr.	each		21113-02
Flask, erlenmeyer, 50 mL	each		505-41
Flask, volumetric, Class A, 50 mL	each		14574-41
pH Paper, 1 to 11 pH units	5 rolls/pkg		391-33
pH Meter, *Sens**ion**™1*, portable with electrode	each		51700-10

* Contact Hach for larger sizes.

Pipet, serological, 2.0 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg	21856-28
Thermometer, -20 to 110 °C	each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

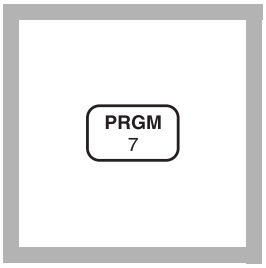
Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHORUS, REACTIVE (0 to 2.50 mg/L PO_4^{3-}) For water, wastewater, seawater

(Also called Orthophosphate) PhosVer 3 (Ascorbic Acid) Method*

(Powder Pillows or AccuVac Ampuls) USEPA Accepted for wastewater analysis reporting**

Using Powder Pillows



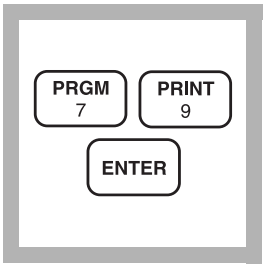
1. Enter the stored program number for reactive phosphorus, ascorbic acid method.

Press: **PRGM**

The display will show:

PRGM ?

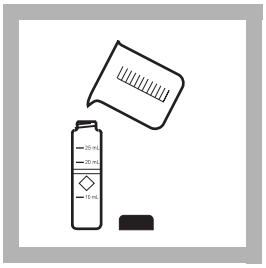
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **79 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon**.**

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*



3. Fill a sample cell with 10 mL of sample.

Note: *For samples with extreme pH, see* Interferences *following these steps.*

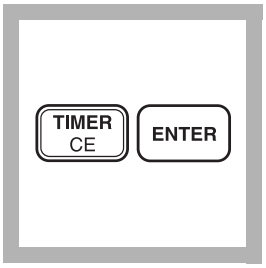
Note: *Clean glassware with 1:1 HCl. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

4. Add the contents of one PhosVer 3 Phosphate Powder Pillow for 10-mL sample to the cell (the prepared sample). Shake for 15 seconds.

Note: *A blue color will form if phosphate is present.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater*.

** Procedure is equivalent to USEPA method 365.2 and Standard Method 4500-PE for wastewater.



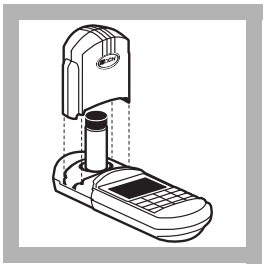
5. Press:

TIMER ENTER

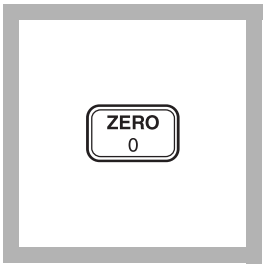
A two-minute reaction period will begin. Perform Steps 6-8 during this period.

Note: *If the acid-persulfate digestion was used, an 8-10 minute reaction period is required.*

6. Fill another sample cell with 10 mL of sample (the blank).



7. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

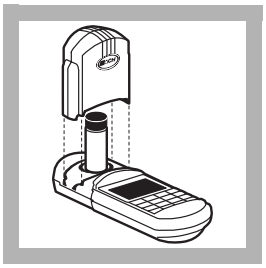


8. Press: **ZERO**

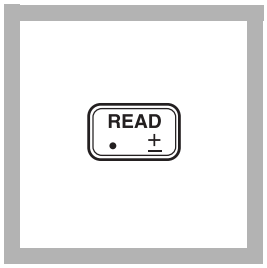
The cursor will move to the right, then the display will show:

0.00 mg/L PO4

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



9. After the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

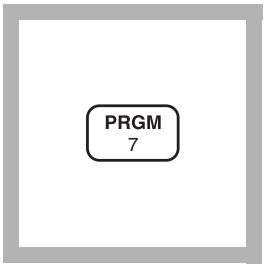


10. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (PO_4^{3-}) will be displayed.

Note: *Standard Adjust may be performed using a 2.0-mg/L PO_4^{3-} standard; see Section 1.*

Using AccuVac Ampuls



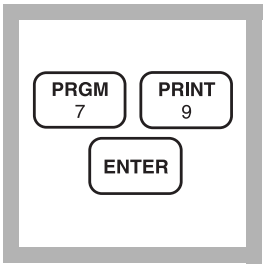
1. Enter the stored program number for reactive phosphorus-ascorbic acid method.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **79 ENTER**

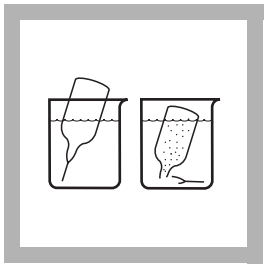
The display will show **mg/L, PO4** and the **ZERO** icon**.**

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*

3. Fill a sample cell (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50-mL beaker.

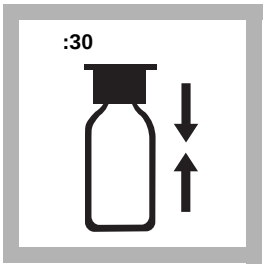
Note: *For samples with extreme pH, see* Interferences.

Note: *Clean glassware with 1:1 HCl. Rinse again with deionized water. Do not use detergent containing phosphates to clean glassware.*



4. Fill a PhosVer 3 Phosphate AccuVac Ampul with sample.

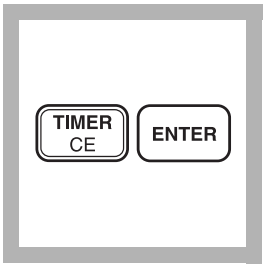
Note: *Keep the tip immersed while the ampul fills completely.*



5. Place an ampul cap securely over the tip of the ampul. Shake the ampul for about 30 seconds. Wipe off any liquid or fingerprints.

Note: *A blue color will form if phosphate is present.*

Note: *Accuracy is not affected by undissolved powder.*

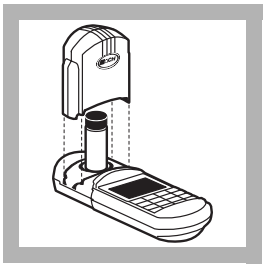


6. Press:

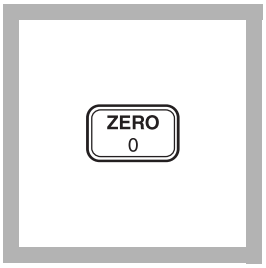
TIMER ENTER

A two-minute reaction period will begin. Perform Steps 7-8 during this period.

Note: *Use an 8-10 minute reaction period if determining total phosphorus following the acid-persulfate digestion.*



7. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

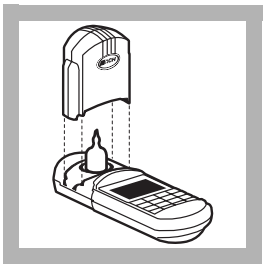


8. Press: **ZERO**

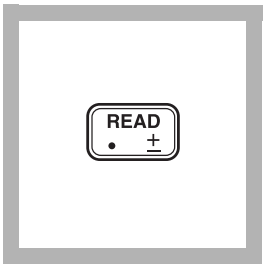
The cursor will move to the right, then the display will show:

0.00 mg/L PO4

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



9. After the timer beeps, place the AccuVac ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (PO_4^{3-}) will be displayed.

Note: *Standard Adjust may be performed using a 2.0-mg/L PO_4^{3-} standard; see Section 1.*

Sampling and Storage

Collect sample in plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve samples for up to 48 hours by filtering immediately and storing samples at 4 °C. Warm to room temperature before testing.

Accuracy Check

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate PourRite Ampule Standard Solution, 50 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to the three mixing cylinders. Stopper each and mix thoroughly.

d) For analysis with AccuVacs, transfer solutions to dry, clean 50 mL beakers to fill the AccuVac ampules. For analysis with powder pillows, transfer only 10 mL of solution to the sample cells.

e) Analyze each standard addition sample as described in the procedure. The phosphate concentration should increase 0.2 mg/L PO_4^{3-} for each 0.1 mL of standard added.

f) If these increases do not occur, see *Standard Additions* in *Section 1*.

Standard Solution Method

Prepare a 2.0 mg/L PO_4^{3-} standard solution by pipetting 4.0 mL of Phosphate Standard Solution, 50 mg/L as PO_4^{3-}, into an acid-washed Class A 100-mL volumetric flask. Dilute to volume with deionized water. Stopper and invert to mix. Use this solution in place of the sample in the procedure to insure the accuracy of the test. The mg/L PO_4^{3-} reading should be 2.00 mg/L.

Method Performance

Precision

In a single laboratory using a standard solution of 1.00 mg/L PO_4^{3-} and two lots of reagents with the instrument, a single operator obtained a standard deviation of ±0.05 mg/L PO_4^{3-}.

In a single laboratory using a standard solution of 1.00 mg/L PO_4^{3-} and two representative lots of AccuVac ampuls with the instrument, a single operator obtained a standard deviation of ±0.03 mg/L PO_4^{3-}.

Estimated Detection Limit (EDL)

The EDL for program 79 is 0.05 mg/L PO_4. For more information on the estimated detection limit, see *Section 1*.

Interference

Interfering Substance	Interference Levels and Treatments
Aluminum	Greater than 200 mg/L
Arsenate	All levels
Chromium	Greater than 100 mg/L
Copper	Greater than 10 mg/L
Hydrogen sulfide	All levels
Iron	Greater than 100 mg/L
Nickel	Greater than 300 mg/L
Silica	Greater than 50 mg/L
Silicate	Greater than 10 mg/L
Turbidity or color	Large amounts may cause inconsistent results in the test because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles. For highly turbid or colored samples, add the contents of one Phosphate Pretreatment Pillow to 25 mL of sample. Mix well. Use this solution to zero the instrument.
Zinc	Greater than 80 mg/L
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment. pH 2 to 10 is recommended.

Summary of Method

Orthophosphate reacts with molybdate in an acid medium to produce a Phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

PHOSPHORUS, REACTIVE, continued

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows			
10 mL sample size	1 Pillow	100/pkg	21060-69
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (Using AccuVac Ampuls)

PhosVer 3 Phosphate Reagent AccuVac Ampuls	1 ampul	25/pkg	25080-25
Beaker, 50 mL	1	each	500-41
Cap, ampul, blue	1	25/pkg	1731-25
Sample Cell, 10-20-25 mL, w/cap	1	6/pkg	24019-06

OPTIONAL REAGENTS

Drinking Water Standard, Inorganic, F^-, NO_3^{-N}, PO_4^{3-}, SO_4^{2-}		500mL	28330-49
Hydrochloric Acid Standard Solution, 6.0 N (1:1)		500 mL	884-49
Phosphate Standard Solution, 1mg/L		500mL	2569-49
Phosphate Standard Solution, PourRite ampule, 50 mg/L as PO_4^{3-}, 2 mL		20/pkg	171-20
Phosphate Standard Solution, Voluette Ampul, 50 mg/L, 10 mL		16/pkg	171-10
Sodium Hydroxide Standard Solution, 5.0 N		100 mL* MDB	2450-32
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28332-49
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Ampule Breaker Kit for 10-ml ampules		each	21968-00
Aspirator, vacuum		each	2131-00
Cylinder, graduated, mixing, 25 mL, tall (3 required)		each	20886-40
Filter Holder, 47 mm, 300 mL, graduated		each	13529-00
Filter, membrane, 47 mm, 0.45 microns		100/pkg	13530-00
Flask, filtering, 500 mL		each	546-49
Flask, volumetric, Class A, 100 mL		each	14574-42
pH Indicator Paper, 1 to 11 pH		5 rolls/pkg	391-33
pH Meter, *Sens**ion**™1*, portable with electrode		each	51700-10
Pipet, 2 mL serological		each	532-36
Pipet, TenSette, 0.1 to 1.0 mL TenSette Pipet		each	19700-01
Pipet Tips, for 19700-01		50/pkg	21856-96
Pipet Tips, for 19700-01		1000/pkg	21856-28
Pipet Filler, safety bulb		each	14651-00
Pipet, volumetric, Class A, 4.00 mL		each	14515-04
PourRite Ampule Breaker Kit		each	24846-00

Outside the U.S.A.—Contact the Hach office or distributor serving you.

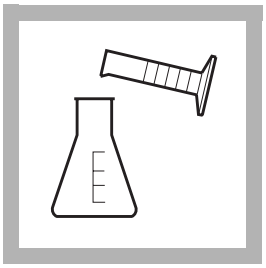
* Larger sizes available.

PHOSPHORUS, TOTAL

For water, wastewater, and seawater

(Also called Organic and Acid Hydrolyzable) Acid Persulfate Digestion Method*

USEPA Accepted for reporting wastewater analysis**

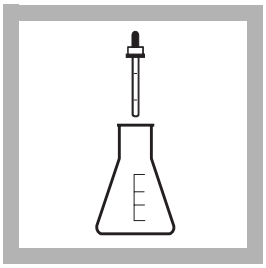


1. Measure 25 mL of sample into a 50-mL erlenmeyer flask using a graduated cylinder.

Note: *Rinse all glassware with 1:1 Hydrochloric Acid Solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

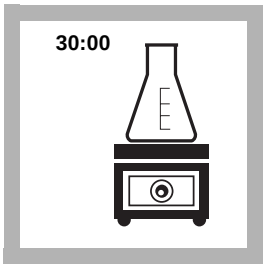
Note: *Adjust the pH of stored samples before digestion.*

2. Add the contents of one Potassium Persulfate Powder Pillow. Swirl to mix.



3. Add 2.0 mL of 5.25 N Sulfuric Acid Solution.

Note: *Use the 1-mL calibrated dropper provided.*



4. Place the flask on a hot plate. Boil gently for 30 minutes.

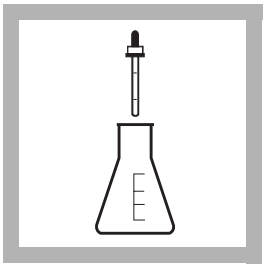
Note: *Samples should be concentrated to less than 20 mL for best recovery. After concentration, maintain the volume near 20 mL by adding small amounts of deionized water. Do not exceed 20 mL.*

---

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

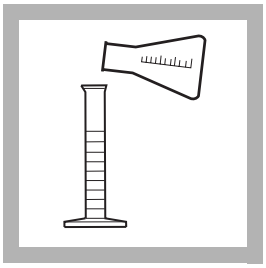
** Procedure is equivalent to USEPA Method 365.2 and Standard Method 4500-P B,5 & P E.

5. Cool the sample to room temperature.



6. Add 2.0 mL of 5.0 N Sodium Hydroxide Solution. Swirl to mix.

Note: *Use the 1-mL calibrated dropper provided.*



7. Pour the sample into a 25-mL graduated cylinder. Return the volume to 25 mL. Proceed with a reactive phosphorus test of the expected total phosphorus concentration range.

Note: *Use deionized water rinsings from the flask to adjust the volume.*

Note: *Results of the reactive phosphorus test at this point will include the organic phosphate plus the orthophosphate and the acid-hydrolyzable (condensed) phosphate. The organic phosphate concentration is determined by subtracting results of an acid hydrolyzable phosphorus test from this result. Make sure that both results are in the same units before taking the difference.*

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid-washed with 1:1 HCl and rinsed with deionized water. Do not use detergents containing phosphates for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve samples up to 28 days by adjusting the pH to 2 or less with concentrated sulfuric acid (about 2 mL per liter) and storing at 4 °C. Warm to room temperature before testing. Correct results for volume additions; see *Volume Additions* (Section 1) for more information.

Interferences

For turbid samples, use 50 mL of sample and double the reagent quantities. Use digested sample to zero the instrument in the reactive phosphorus procedure. This compensates for any color or turbidity destroyed by this procedure. For alkaline or highly buffered samples it may be necessary to add additional acid in Step 3 to drop the pH of the solution below 1.

Summary of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphate by heating with acid and persulfate. Organically bound phosphates are thus determined indirectly by subtracting the result of an acid hydrolyzable phosphorus test from the total phosphorus result.

This procedure must be followed by one of the reactive phosphorus (orthophosphate) analysis methods for determination of the phosphorus content of the sample. If the ascorbic acid (PhosVer 3) method is used to measure the reactive phosphorus, this method is EPA approved for NPDES reporting.

The following reagents and apparatus are required in addition to those required for the reactive phosphorus test.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Potassium Persulfate Powder Pillows	1 pillow	100/pkg	2451-99
Sodium Hydroxide Solution, 5.0 N	2 mL	100 mL* MDB	2450-32
Sulfuric Acid Solution, 5.25 N	2 mL	100 mL* MDB	2449-32

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	2	each	508-40
Flask, erlenmeyer, 50 mL	1	each	505-41
Sample Cell, 10-20-25 mL, w/caps	2	6/pkg	24019-06

OPTIONAL REAGENTS

Drinking Water Standard, Inorganic, F^-, $NO_3^{-N,}$ PO_4^{3-}, SO_4^{2-}		500mL	28330-49
Hydrochloric Acid, 6 N		500 mL	884-49
Sodium Hydroxide Solution, 5.0 N		1 L	2450-53
Sulfuric Acid		500 mL	979-49
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28332-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28331-49
Water, deionized		4 L	272-56

* Marked Dropper Bottle - Contact Hach for larger sizes.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Cylinder, graduated, 50 mL	each	508-41
Flask, erlenmeyer, 125 mL	each	505-43
Hot Plate, 4" diameter, 120 Vac	each	12067-01
Hot Plate, 4" diameter, 240 Vac	each	12067-02
Pads, cooling, 4 x 4"	each	18376-00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *Sens**ion**™1*, portable with electrode	each	51700-10

For Technical Assistance, Price and Ordering

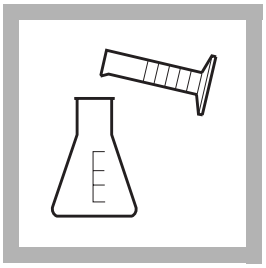
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHORUS, ACID HYDROLYZABLE

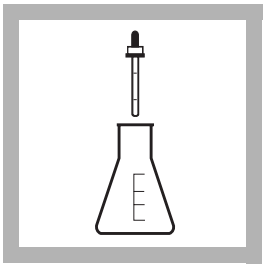
Hydrolysis to Orthophosphate Method*

For water, wastewater, seawater



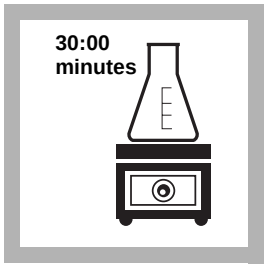
1. Measure 25 mL of sample into a 50-mL erlenmeyer flask using a graduated cylinder.

Note: *Wash all glassware with 6 N hydrochloric acid. Rinse with deionized water. Do not use detergents containing phosphate to clean glassware.*



2. Add 2.0 mL of 5.25 N Sulfuric Acid Solution.

Note: *Use the 1-mL calibrated dropper provided.*

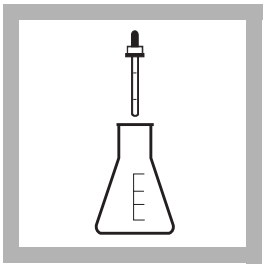


3. Place the flask (the prepared sample) on a hot plate. Boil gently for 30 minutes.

Note: *Samples should be concentrated to less than 20 mL for best recovery. After concentration, maintain the volume near 20 mL by adding small amounts of deionized water. Do not exceed 20 mL.*

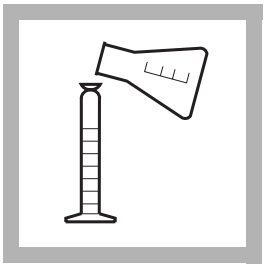
4. Cool the hot prepared sample to room temperature.

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



5. Add 2.0 mL of 5.0 N Sodium Hydroxide Solution to the prepared sample. Swirl to mix.

Note: *Use the 1-mL calibrated dropper provided.*



6. Pour the prepared sample into a graduated cylinder. Add deionized water rinsings from the flask to return the volume to 25 mL. Proceed with the appropriate reactive phosphorus test.

Note: *Results of the reactive phosphorus test at this point will include the orthophosphate plus the acid-hydrolyzable (condensed) phosphate. The condensed phosphate concentration is determined by subtracting the results of a reactive phosphorus test on an untreated sample from this result. Make sure both results are in the same chemical form and units.*

PHOSPHORUS, ACID HYDROLYZABLE, continued

Sampling and Storage

Analyze samples immediately after collection for best results. If prompt analysis is not possible, samples may be preserved up to 48 hours by cooling to 4 °C (39 °F). Warm to room temperature before testing.

Interferences

If the sample is turbid, use 50 mL of sample and double the reagent volumes. Use the hydrolyzed sample to zero the instrument in the reactive phosphorus procedure. This compensates for any turbidity dissolved by this procedure.

Summary of Method

This procedure lists the necessary steps to convert condensed phosphate forms (meta-, pyro- or other polyphosphates) to reactive orthophosphate before analysis. The procedure uses acid and heat to hydrolyze the sample. Organic phosphates are not converted to orthophosphate by this process, but a very small fraction may be unavoidably included in the result. Thus, the "acid hydrolyzable" phosphate results are primarily a measure of inorganic phosphorus. This procedure must be followed by one of the reactive phosphorus (orthophosphate) analysis methods for determination of the phosphorous content of the sample.

The following reagents and apparatus are required in addition to those required for the reactive phosphorus test.

PHOSPHORUS, ACID HYDROLYZABLE, continued

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Drinking Water Standard, Inorganic, F^-, $NO_3^{-N,}$ PO_4^{3-}, SO_4^{2-}		500 mL	28330-49
Sodium Hydroxide Solution, 5.0 N	2 mL	100 mL* MDB	2450-32
Sulfuric Acid Solution, 5.25 N	2 mL	100 mL* MDB	2449-32
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28332-49
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28331-49

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	2	each	508-40
Flask, erlenmeyer, 50 mL	1	each	505-41

OPTIONAL REAGENTS

Hydrochloric Acid, 6 N		500 mL	884-49
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

Cylinder, graduated, 50 mL		each	508-41
Flask, erlenmeyer, 125 mL		each	505-43
Hot Plate, 4" diameter, 120 Vac		each	12067-01
Hot Plate, 4" diameter, 240 Vac		each	12067-02
Pad, cooling, 4" x 4"		each	18376-00
pH indicator Paper, 1 to 11 pH		5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable with electrode		each	51700-10
Thermometer, -20 to 110 °C, Non-Mercury		each	26357-02

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

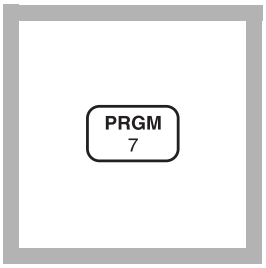
* Contact Hach for larger sizes.

PHOSPHORUS, REACTIVE (0.00 to 5.00 mg/L PO_4^{3-})

PhosVer 3 Method, Test 'N Tube Procedure

For water, wastewater, and seawater

USEPA accepted for reporting wastewater analysis*



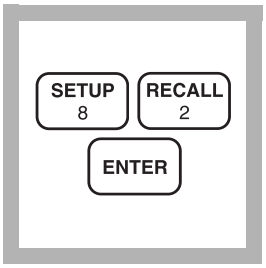
1. Enter the stored program number for reactive phosphorus (PO_4^{3-}), Test 'N Tube.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



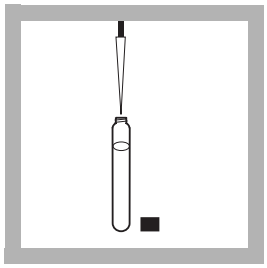
2. Press: **82 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon**.**

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*

3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *A diffuser band covers the light path holes on the adapter to give increased performance.The band should NOT be removed.*



4. Use a TenSette Pipet to add 5.0 mL of sample to a Reactive Phosphorus Test 'N Tube Dilution Vial. Cap and mix.

Note: *For samples with extreme pH, see the* Interference *section.*

* Procedure is equivalent to USEPA Method 365.2 and Standard Method 4500-P E for wastewater.

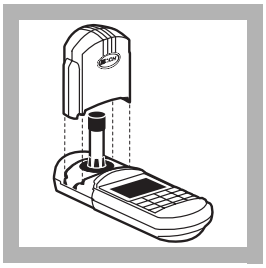
5. Clean the outside of the vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*

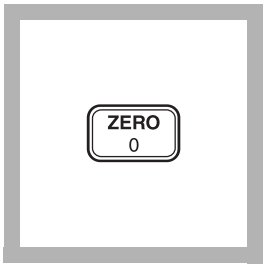
6. Place the sample vial into the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



7. Tightly cover the sample vial with the instrument cap.

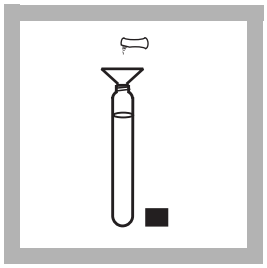


8. Press: **ZERO**

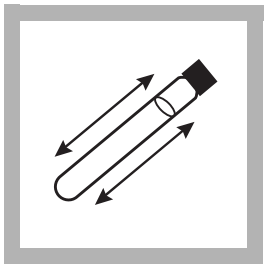
The cursor will move to the right, then the display will show:

0.00 mg/L PO4

Note: *For multiple samples, zero only on the first sample. Read the remaining samples after adding the PhosVer 3 Reagent.*

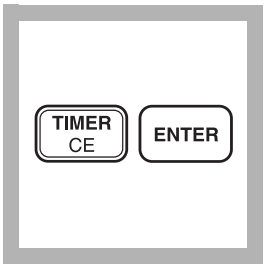


9. Using a funnel, add the contents of one PhosVer 3 Phosphate Powder Pillow to the vial.



10. Cap the vial tightly and shake for 10-15 seconds.

Note: *The powder will not completely dissolve.*



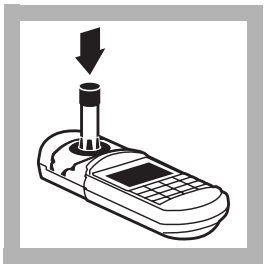
11. Press:

TIMER ENTER

A 2-minute reaction time will begin.

Note: *Read samples between 2 and 8 minutes after the addition of the PhosVer 3 reagent.*

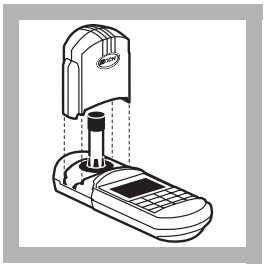
Note: *A blue color will develop if phosphate is present.*



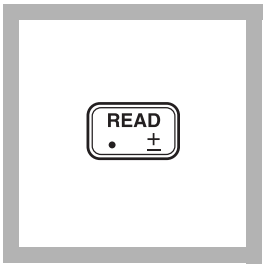
12. Immediately after the timer beeps, place the sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



13. Tightly cover the vial with the instrument cap.



14. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (PO_4^{3-}) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve samples for up to 48 hours by filtering immediately and storing at 4 °C. Warm to room temperature before analyzing the sample.

Accuracy Check

Note: *Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate PourRite Ampule Standard, 50 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 25-mL aliquots of sample prepared in *step a*. Mix well.

d) Analyze each sample as described in the procedure; use 5.0 mL of the prepared standard additions for each test. The concentration should increase as follows: 0.2 mg/L, 0.4 mg/L, 0.6 mg/L PO_4^{3-}, respectively.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

To check accuracy, use a 1.0 mg/L Phosphate Standard Solution listed under *Optional Reagents*. Or, prepare a 1.0-mg/L PO_4^{3-} standard by pipetting 2 mL of solution from a Phosphate Voluette Ampule Standard for Phosphate, 50 mg/L as PO_4^{3-}, into an acid-washed, Class A 100-mL volumetric flask. Dilute to the mark with deionized water. Substitute this standard for the sample and perform the procedure as described.

Method Performance

Precision

In a single laboratory, using a standard solution of 5.00 mg/L PO_4^{3-} and two lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.08 mg/L PO_4^{3-}.

Estimated Detection Limit (EDL)

The EDL for program 82 is 0.07 mg/L PO_4^{3-}. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

The following may interfere when present in concentrations exceeding these listed below:

Substance	Interference Level and Treatment
Aluminum	200 mg/L
Arsenate	Interferes at any level
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Sulfide	6 mg/L. Sulfide interference may be removed by oxidation with Bromine Water as follows: 1. Measure 25 mL of sample into a 50-mL beaker. 2. Swirling constantly, add Bromine Water dropwise until a permanent yellow color develops. 3. Swirling constantly, add Phenol Solution dropwise until the yellow color just disappears. Proceed with *step 1*.
Turbidity (large amounts)	May cause inconsistent results because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.
Zinc	80 mg/L
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interferences (Section 1).

The PhosVer 3 Phosphate Reagent Powder Pillows should be stored in a cool, dry environment.

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA.

Summary of Method

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

REQUIRED REAGENTS

Reactive Phosphorus Test 'N Tube Reagent Set ..... 50 tests 27425-45
Includes: (1) 21060-46, (50) Orthophosphate Dilution Vials*

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows	1	50/pkg	21060-46
50 Orthophosphate Test 'N Tube Dilution Vials	1	50/pkg	*

REQUIRED APPARATUS

COD/TNT Adapter	1	each	48464-00
Funnel, micro	1	each	25843-35
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	1	50/pkg	21997-96
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L	29 mL	2211-20
Drinking Water Standard, Inorganic, F^-, $NO_3^{-N,}$ PO_4^{3-}, SO_4^{2-}	500mL	28330-49
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, 1 mg/L as PO_4^{3-}	500 mL	2569-49
Phosphate Standard Solution, Voluette ampule, 50 mg/L as PO_4^{3-}, 10 mL	16/pkg	171-10
Phosphate Standard Solution, PourRite ampule, 50 mg/L as PO_4^{3-}, 2 mL	20/pkg	171-20H
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28332-49
Water, deionized	4 L	272-56

* These items are not sold separately.

OPTIONAL APPARATUS

Ampule Breaker, Pour Rite (2-mL ampule)	each	24846-00
Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, mixing, 25 mL (3 required)	each	20886-40
Dispenser, Repipet Jr., 2 mL	each	22307-01
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	100/pkg	13530-00
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sens**ion***™*1*, portable with electrode	each	51700-10
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01	50 pkg	21856-96
Pipet Tips, for 19700-01	1000/pkg	21856-28
Pipet Filler, Safety Bulb	each	14651-00
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 2.00 mL	each	14515-36

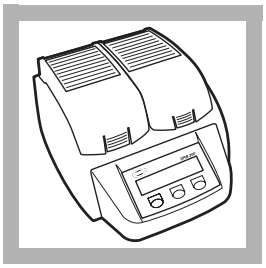
For Technical Assistance, Price and Ordering

In the U.S.A. call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

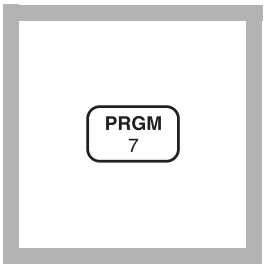
PHOSPHORUS, TOTAL (0.00 to 3.50 mg/L PO_4^{3-}) For water, wastewater and seawater

PhosVer 3 with Acid Persulfate Digestion* USEPA Accepted for reporting wastewater analysis** Test 'N Tube Procedure



1. Turn on the DRB200 Reactor. Heat the reactor to 150 °C.

Note: *See DRB200 instrument manual for selecting preprogrammed temperature applications.*



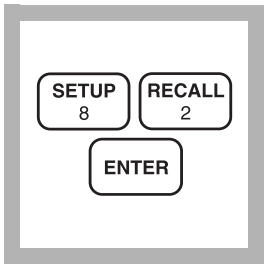
2. Enter the stored program number for total phosphorus, (PO_4^{3-}), Test 'N Tube.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



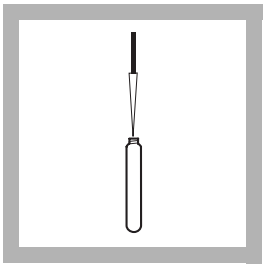
3. Press: **82 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon**.**

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*

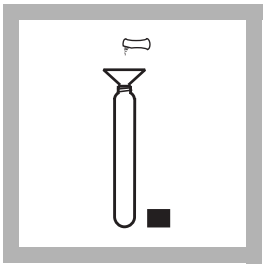
4. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *A diffuser band covers the light path holes on the adapter to give increased performance. The band should NOT be removed.*

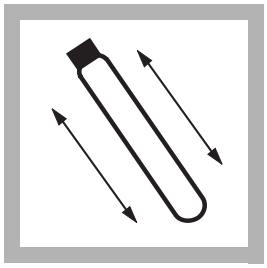


5. Use a TenSette Pipet to add 5.0 mL of sample to a Total and Acid Hydrolyzable Test Vial.

Note: *Adjust the pH of stored samples to 6-8 before analysis.*



6. Using a funnel, add the contents of one Potassium Persulfate Powder Pillow for Phosphonate to the vial.

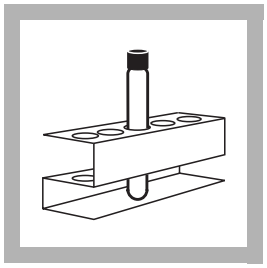


7. Cap tightly and shake to dissolve.

8. Place the vial in the DRB200 Reactor. Heat the vial for 30 minutes.

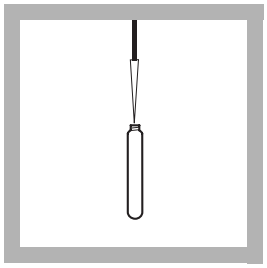
* Adapted from *Standard Methods for the Examination of Water and Wastewater*.

** Procedure is equivalent to USEPA Method 365.2 and Standard Method 4500-P B, 5 and P.E.

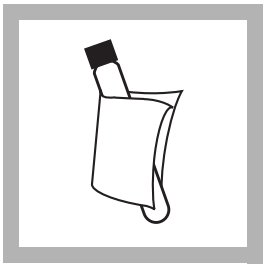


9. Carefully remove the vial from the reactor. Place it in a test tube rack and allow to cool to room temperature.

Note: *Vials will be hot.*

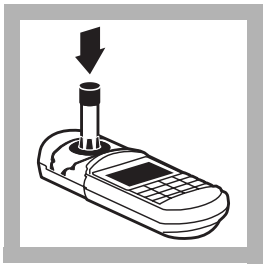


10. Use a TenSette Pipet to add 2.0 mL of 1.54 N sodium hydroxide to the vial. Cap and mix.



11. Clean the outside of the vial with a towel.

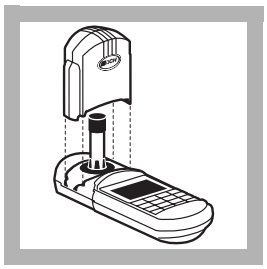
Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



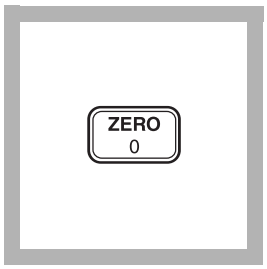
12. Place the sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



13. Tightly cover the vial with the instrument cap.

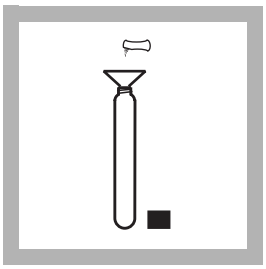


14. Press: **ZERO**

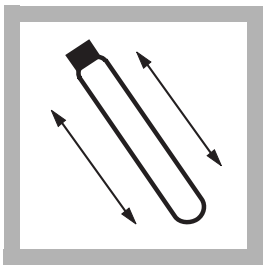
The cursor will move to the right, then the display will show:

0.00 mg/L PO4

Note: *For multiple samples, zero only on the first sample. Read the remaining samples after adding the PhosVer 3 reagent.*

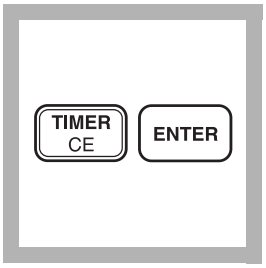


15. Remove the cap from the vial. Using a funnel, add the contents of one PhosVer 3 Phosphate Reagent Powder Pillow to the vial.



16. Cap tightly and shake for 10-15 seconds.

Note: *The powder will not completely dissolve.*



17. Press:

TIMER ENTER

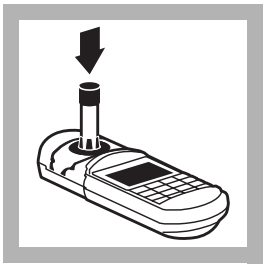
A 2-minute waiting period will begin.

Note: *Read samples between 2 and 8 minutes after the addition of the PhosVer 3 reagent.*

Note: *A blue color will form if phosphate is present.*

18. After the timer beeps, clean the outside of the sample vial with a towel.

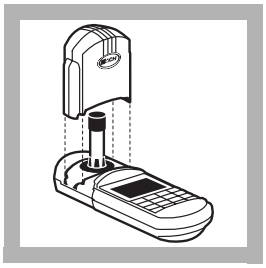
Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



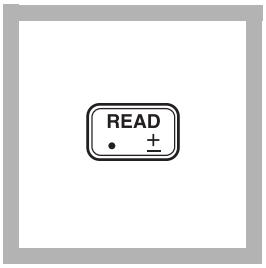
19. Place the prepared sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



20. Tightly cover the vial with the instrument cap.



21. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (PO_4^{3-}) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

IMPORTANT NOTE:

The test range for total phosphate is limited to 0 to 3.5 mg/L PO_4^{3-}. Values above 3.5 mg/L may be used to estimate dilution ratios, but should NOT be used for reporting purposes. If a value above 3.5 mg/L PO_4^{3-} is obtained, dilute the sample and repeat the digestion and the colorimetric test.

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphates for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve the sample for up to 28 days by adjusting the pH to 2 or less with concentrated sulfuric acid (about 2 mL per liter) and storing at 4 °C. Neutralize and warm the sample to room temperature before analysis. Correct test results for volume additions; see *Volume Additions* in *Section 1*.

Accuracy Check

Note: *Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

Standard Additions Method

a) Fill three 25 mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate PourRite Ampule Standard, 50 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 25-mL aliquots of sample prepared in *step a*. Mix well.

d) Analyze each sample as described in the procedure using 5.0 mL of the prepared standard additions for each test. The concentration should increase 0.2 mg/L, 0.4 mg/L, and 0.6 mg/L PO_4^{3-}, respectively.

e) If these increases do not occur, see *Standard Additions* (Section 1).

Standard Solution Method

To check accuracy, use a 1.0 mg/L Phosphate Standard Solution (see Optional Reagents). Or, prepare a standard by pipetting 2 mL of solution a Voluette Ampule Standard for Phosphate Standard, 50 mg/L as PO_4^{3-}, into an acid-cleaned Class A 100-mL volumetric flask. Dilute to the mark with deionized water. Substitute this standard for the sample and perform the procedure as described. The mg/L PO_4^{3-} reading should be 1.0 mg/L.

OR

Prepare a 2.5 mg/L standard solution by pipetting 5 mL of a 50-mg/L Phosphate Voluette Ampule Standard into an

acid-washed 100-mL Class A volumetric flask. Dilute to the mark with deionized water.

Method Performance

Precision

In a single laboratory, using a standard solution of 3.00 mg/L PO_4^{3-} and two lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.06 mg/L PO_4^{3-}.

Estimated Detection Limit

The estimated detection limit for program 82 is 0.07 mg/L PO_4^{3-}. For more information on the estimated detection limit, see *Section 1*.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Substance	Interference Level and Treatment
Aluminum	200 mg/L
Arsenate	Interferes at any level.
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Sulfide	90 mg/L
Turbidity (large amounts)	May cause inconsistent results because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.
Zinc	80 mg/L
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interferences (Section 1).

Store PhosVer 3 Reagent Powder Pillows in a cool, dry environment.

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA.

Summary of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphate by heating with acid and persulfate.

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

REQUIRED REAGENTS

Total Phosphorus Test 'N Tube Reagent Set ..... 50 tests 27426-45
Includes: (1) 272-42, (1) 20847-66, (1) 21060-46, (1) 27430-42, (50) Acid Dilution Vials*

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows	1	50/pkg	21060-46
Potassium Persulfate powder Pillows	1	50/pkg	20847-66
Sodium Hydroxide Solution, 1.54 N	2 mL	100 mL	27430-42
Test 'N Tube Acid Dilution Vials	1	50/pkg	*
Water, deionized for reagent blank	5 mL	100 mL	272-42

REQUIRED APPARATUS

COD/TNT Adapter	1	each	48464-00
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Funnel, micro	1	each	25843-35
Test Tube Rack	1-3	each	18641-00
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	varies	50/pkg	21997-96

* These items are not sold separately.

OPTIONAL REAGENTS

Description	Unit	Cat. No.
Drinking Water Standard, Inorganic, F^-, $NO_3^{-N,}$ PO_4^{3-}, SO_4^{2-}	500mL	28330-49
Total and Acid Hydrolyzable Test 'N Tube Reagent Set	each	27427-45
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phosphate Standard Solution, 1 mg/L as PO_4^{3-}	500 mL	2569-49
Phosphate Standard Solution, PourRite ampule, 50 mg/L as PO_4^{3-}, 2 mL	20/pkg	171-20H
Phosphate Standard Solution, Voluette ampule, 50 mg/L as PO_4^{3-}, 10 mL	16/pkg	171-10
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Total and Acid Hydrolyzable Test 'N Tube Reagent Set	each	27427-45
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28332-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Ampule Breaker, PourRite ampules	each	24846-00
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001
Cylinder, graduated, mixing, 25 mL (3 required)	each	20886-40
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *Sens**ion**™1*, portable with electrodes	each	51700-10
Pipet Filler, safety bulb	each	14651-00
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet, TenSette, 0.1-1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01	1000/pkg	21856-28

For Technical Assistance, Price and Ordering

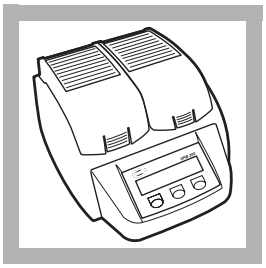
In the U.S.A. call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHORUS, ACID HYDROLYZABLE (0.00 to 5.00 mg/L PO_4^{3-})

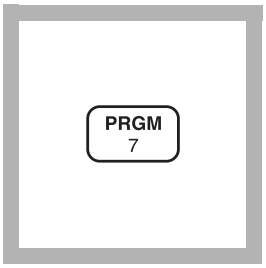
PhosVer 3 with Acid Hydrolysis Test 'N Tube™ Procedure

For water, wastewater, and seawater



1. Turn on the COD Reactor. Heat to 150 °C.

Note: *See DRB200 instrument manual for selecting preprogrammed temperature applications.*



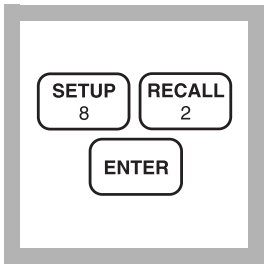
2. Enter the stored program number for acid hydrolyzable phosphorus (PO_4^{3-}), Test 'N Tube.

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



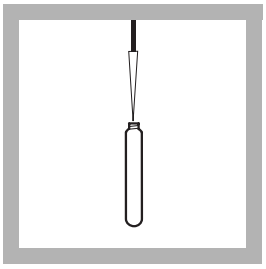
3. Press: **82 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon**.**

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*

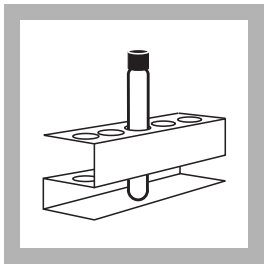
4. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *A diffuser band covers the light path holes on the adapter to give increased performance. The band should NOT be removed.*



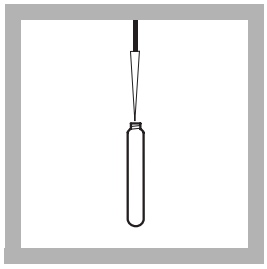
5. Use a TenSette Pipet to add 5.0 mL of sample to a Total and Acid Hydrolyzable Test Vial. Cap and mix.

6. Heat the vial in the DRB200 Reactor for 30 minutes.



7. Carefully remove the vial from the reactor. Place it in a test tube rack and allow to cool to room temperature.

Note: *Vials will be hot.*



8. Remove the cap from the vial. Use a TenSette Pipet to add 2.0 mL of 1.00 N sodium hydroxide to the vial. Cap and mix.

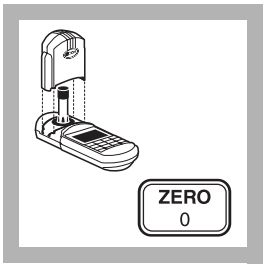
9. Clean the outside of the vial with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*

10. Place the sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



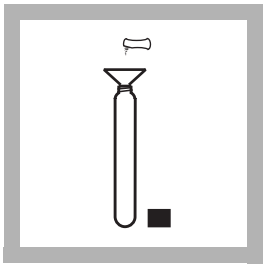
11. Tightly cover the vial with the instrument cap.

Press: **ZERO**

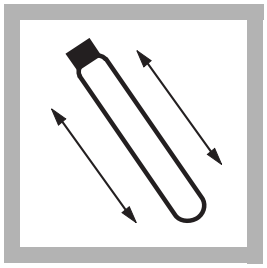
The cursor will move to the right, then the display will show:

0.00 mg/L PO4

Note: *For multiple samples, zero on the first sample. Read the remaining samples after adding the PhosVer 3 reagent. Subtract the reagent blank value from each reading.*

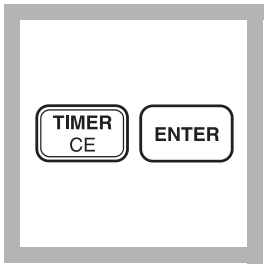


12. Remove the cap from the vial. Using a funnel, add the contents of one PhosVer 3 Phosphate Reagent Powder Pillow to the vial.



13. Cap tightly and shake for 10-15 seconds.

Note: *The powder will not completely dissolve.*



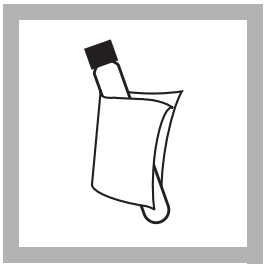
14. Press:

TIMER ENTER

A 2-minute reaction period will begin.

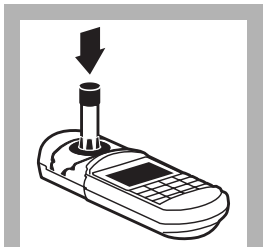
Note: *Read samples between 2 and 8 minutes after adding the PhosVer 3 reagent.*

Note: *A blue color will form if phosphate is present.*



15. After the timer beeps, clean the outside of the sample vial with a towel.

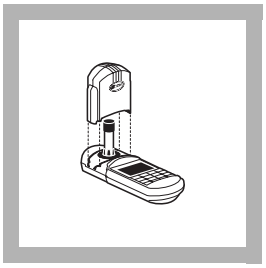
Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*



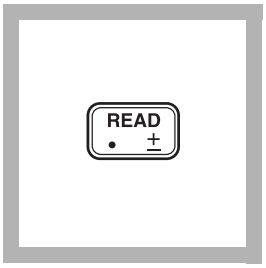
16. Place the prepared sample in the adapter

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



17. Tightly cover the vial with the instrument cap.



18. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (PO_4^{3-}) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water.
Do not use commercial detergents containing phosphate for cleaning glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, the sample may be preserved up to 48 hours by cooling to 4 °C (39 °F). Warm to room temperature before testing.

Accuracy Check

Note: *Clean glassware with 1:1 hydrochloric acid solution. Rinse with deionized water. Do not use detergents containing phosphate to clean glassware.*

Standard Additions Method

a) Fill three 25-mL graduated mixing cylinders with 25 mL of sample.

b) Snap the neck off a Phosphate PourRite Ampule Standard, 50 mg/L as PO_4^{3-}.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 25-mL aliquots of sample prepared in *step a*. Mix well.

d) Analyze each sample as described in the procedure. Use

5.0 mL of the prepared standard additions for each test; the concentration should increase as follows: 0.2 mg/L, 0.4 mg/L, and 0.6 mg/L PO_4^{3-}, respectively.

e) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Obtain a 1.0 mg/L Phosphate Standard Solution listed under *Optional Reagents*. Or, this can be prepared by pipetting 2 mL of a Voluette Ampule Standard for Phosphate, 50 mg/L as PO_4^{3-}, into an acid washed Class A 100-mL volumetric flask. Dilute to the mark with deionized water. Substitute this standard for the sample and perform the procedure as described.

Interferences

The following may interfere when present in concentrations exceeding those listed below:

Substance	Interference Level and Treatment
Aluminum	200 mg/L
Arsenate	Interferes at any level.
Chromium	100 mg/L
Copper	10 mg/L
Iron	100 mg/L
Nickel	300 mg/L
Silica	50 mg/L
Silicate	10 mg/L
Sulfide	9 mg/L. Sulfide interference may be removed by oxidation with Bromine Water as follows: 1. Measure 25 mL of sample into a 50-mL beaker. 2. Swirling constantly, add Bromine Water dropwise until a permanent yellow color develops. 3. Swirling constantly, add Phenol Solution dropwise until the yellow color just disappears. Proceed with *step 1*.
Turbidity (large amounts)	May cause inconsistent results because the acid present in the powder pillows may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

Zinc	80 mg/L
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; see pH Interferences (Section 1).

The PhosVer 3 Phosphate Reagent Powder Pillows should be stored in a cool, dry environment.

Method Performance

Precision

In a single laboratory, using a standard solution of 3.00 mg/L PO_4^{3-} and two lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.06 mg/L PO_4^{3-}.

Estimated Detection Limit

The estimated detection limit for program 82 is 0.07 mg/L PO_4^{3-}. For more information on the estimated detection limit, see *Section 1*.

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA.

Summary of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphate by heating with acid and persulfate.

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color.

REQUIRED REAGENTS

Total and Acid Hydrolyzable Test 'N Tube Reagent Set .....50 tests 27427-45
Includes: (1) 272-42, (1) 1045-42, (1) 20847-66, (1) 21060-46, (50) Total and Acid Hydrolyzable Test Vials* (1) 27430-42

PHOSPHORUS, ACID HYDROLYZABLE, continued

Description	Quantity Required Per Test	Unit	Cat. No.
PhosVer 3 Phosphate Reagent Powder Pillows	1	50/pkg	21060-46
Potassium Persulfate powder Pillows	1	50/pkg	20847-66
Sodium Hydroxide Solution, 1.0 N	2 mL	100 mL	1045-42
Total and Acid Hydrolyzable Test Vials	1	50/pkg	*
Water, deionized for reagent blanks	5 mL	100 mL	272-42

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
COD/TNT Adapter	1	each	48464-00
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes			LTV082.52.40001
Funnel, micro	1	each	25843-35
Pipet, TenSette, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet		50/pkg	21997-96
Test Tube Rack	1-3	each	18641-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L		29 mL	2211-20
Drinking Water Standard, Inorganic, F^-, $NO_3^{-N,}$ PO_4^{3-}, SO_4^{2-}		500mL	28330-49
Hydrochloric Acid Standard Solution, 6.0 N (1:1)		500 mL	884-49
Phenol Solution, 30 g/L		29 mL	2112-20
Phosphate Standard Solution, 1 mg/L as PO_4^{3-}		500 mL	2569-49
Phosphate Standard Solution, PourRite ampule, 50 mg/L as PO_4^{3-}, 2 mL		20/pkg	171-20H
Phosphate Standard Solution, Voluette ampule, 50 mg/L as PO_4^{3-}, 10 mL		16/pkg	171-10
Sodium Hydroxide Standard Solution, 5.000 N		1000 mL	2450-53
Sulfuric Acid Standard Solution, 1.000 N		1 L	1270-53
Wastewater Effluent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)		500 mL	28332-49
Water, deionized		4 L	272-56

* These items are not sold separately.

OPTIONAL APPARATUS

Description	Units	Cat. No.
Ampule Breaker Kit, Voluette	each	21968-00
Ampule Breaker, PourRite	each	24846-00
Cylinder, graduated, mixing, 25 mL (3 required)	each	20886-40
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001
Flask, volumetric, Class A, 100 mL	each	14574-42
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable with electrode	each	51700-10
Pipet, TenSette, 0.1-1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01	1000/pkg	21856-28
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 2.00 mL	each	14515-36
Pipet Filler, safety bulb	each	14651-00

For Technical Assistance, Price and Ordering

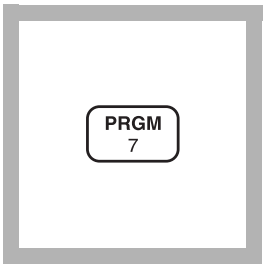
In the U.S.A. call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHORUS, REACTIVE (0 to 30.0 mg/L PO_4^{3-})

Amino Acid Method*

For water, wastewater, seawater



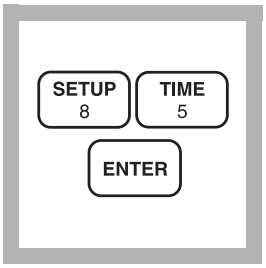
1. Enter the stored program number for reactive phosphate (PO_4^{3-}), amino acid method.

Press: **PRGM**

The display will show:

PRGM ?

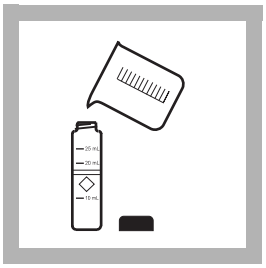
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



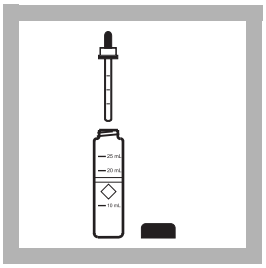
2. Press: **85 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon.

Note: *For alternate forms (P, P_2O_5), press* **CONC**.

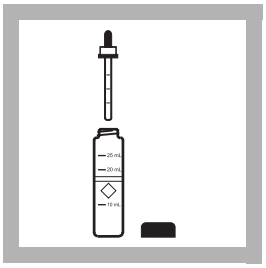


3. Fill a 25-mL sample cell with 25 mL of sample.



4. Add 1 mL of Molybdate Reagent using a 1-mL calibrated dropper.

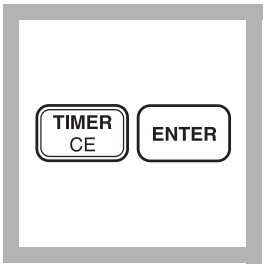
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



5. Add 1 mL of Amino Acid Reagent Solution. Cap and invert several times to mix (the prepared sample).

Note: *A blue color will form if phosphate is present.*

Note: *You may substitute the contents of one Amino Acid Reagent Powder Pillow for 1 mL of Amino Acid Reagent Solution.*

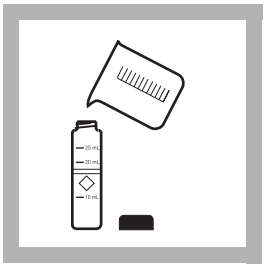


6. Press:

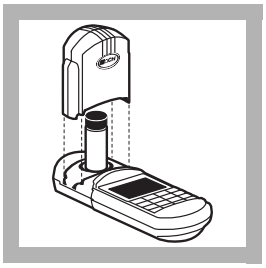
TIMER ENTER

A 10-minute reaction period will begin.

Note: *Perform Step 7 while the timer is running.*



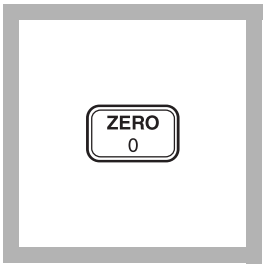
7. Pour 25 mL of sample (the blank) into a sample cell.



8. When the timer beeps, the display will show:

mg/L PO4

Place the blank into the cell holder. Cover the sample cell with the instrument cap.

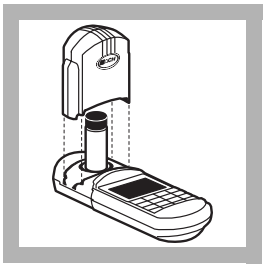


9. Press: **ZERO**

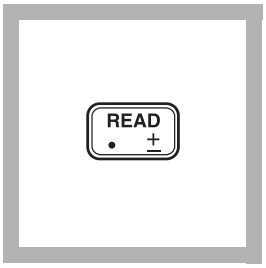
The cursor will move to the right, then the display will show:

0.0 mg/L PO4

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L PO_4 will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles that have been cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use a commercial detergent containing phosphate for cleaning glassware used in this test.

Analyze samples immediately for best results. If prompt analysis is not possible, preserve samples by filtering immediately and storing the sample at 4 °C (39 °F) for up to 48 hours.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Phosphate PourRite Ampule Standard Solution, 500 mg/L as PO_4^{3-}.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to three 25-mL samples. Mix well.

c) Analyze each sample as described in the procedure. Each 0.1-mL addition of standard should cause an increase of 2.0 mg/L orthophosphate (PO_4^{3-}).

d) If these increases do not occur, see *Standard Additions* (*Section 1*) for more information.

Standard Solution Method

Prepare a 10.0-mg/L phosphate standard by pipetting 10.0 mL of a Phosphate Standard Solution, 50 mg/L as PO_4^{3-} into a 50-mL volumetric flask. Dilute to volume with deionized water.

Or, prepare a 10.0-mg/L PO_4^{3-} standard solution by using the TenSette Pipet to add 1.00 mL of Phosphate PourRite Ampule Standard,
500 mg/L as PO_4^{3-}, into a 50-mL volumetric flask. Dilute to volume
with deionized water.

Substitute this standard for the sample and perform the test as described. The mg/L PO_4^{3-} reading should be 10 mg/L.

Method Performance

Precision

In a single laboratory using a standard solution of 15.0 mg/L PO_4^{3-} and two lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.12 mg/L PO_4^{3-}.

Estimated Detection Limit

The estimated detection limit for program 85 is 0.14 mg/L PO_4^{3-}. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Calcium (Ca^{2+})	Greater than 10,000 mg/L as $CaCO_3$
Chloride	Greater than 150,000 mg/L as Cl^-
Colored samples	Add 1 mL of 10 N Sulfuric Acid Standard Solution to another 25-mL sample. Use this instead of untreated sample as the blank to zero the instrument. Use a pipet and pipet filler to measure the sulfuric acid standard.
High salt levels (Na^+)	May cause low results. To eliminate this interference, dilute the sample until two successive dilutions yield about the same result.
Magnesium	Greater than 40,000 mg/L as $CaCO_3$
Nitrites (NO_2^-)	Bleach the blue color. Remove nitrite interference by adding 0.05 g of sulfamic acid to the sample. Swirl to mix. Continue with Step 4.
Phosphates, high levels (PO_4^{3-})	As the concentration of phosphate increases, the color changes from blue to green, then to yellow and finally to brown. The brown color may suggest a concentration as high as 100,000 mg/L PO_4^{3-}. If a color other than blue is formed, dilute the sample and retest.
Sulfide (S^{2-})	Sulfide interferes. For samples with sulfide concentration less than 5 mg/L, sulfide interference may be removed by oxidation with Bromine Water as follows: **1.** Measure 50mL of sample into a 125-mL flask. **2.** Add Bromine Water dropwise with constant swirling until permanent yellow color develops. **3.** Add Phenol Solution dropwise until the yellow color just disappears. Use this sample in Steps 3 and 7.
Temperature	For best results, sample temperature should be 21 ±3 °C (70 ±5 °F).
Turbidity	May give inconsistent results for two reasons. Some suspended particles may dissolve because of the acid used in the test. Also, desorption of orthophosphate from particles may occur. For highly turbid samples, add 1 mL of 10 N Sulfuric Acid Standard Solution to another 25-mL sample. Use this instead of untreated sample as the blank to zero the instrument. Use a pipet and pipet filler to measure the sulfuric acid standard.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment.

Summary of Method

In a highly acidic solution, ammonium molybdate reacts with orthophosphate to form molybdophosphoric acid. This complex is then reduced by the amino acid reagent to yield an intensely colored molybdenum blue compound.

PHOSPHORUS, REACTIVE, continued

REQUIRED REAGENTS

	Cat. No.
High Range Reactive Phosphorus Reagent Set (100 Test) Includes: (1) 1934-32, (1) 2236-32	22441-00

Description	Quantity Required Per Test	Units	Cat. No.
Amino Acid Reagent	1 mL	100 mL MDB*	1934-32
Molybdate Reagent	1 mL	100 mL MDB*	2236-32

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Description	Units	Cat. No.
Amino Acid Reagent Powder Pillow	100/pkg	804-99
Bromine Water, 30 g/L	29 mL	2211-20
Hydrochloric Acid Solution, 1:1 (6 N)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, 50 mg/L PO_4^{3-}	500 mL	171-49
Phosphate Standard Solution, PourRite ampule, 500 mg/L PO_4^{3-}, 2 mL	20/pkg	14242-20
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450-32
Sulfamic Acid	113 g	2344-14
Sulfuric Acid Standard Solution, 10 N	1 L	931-53
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49
Water, deionized	4 L	272-56

* Larger sizes available.

OPTIONAL APPARATUS

Description	Unit	Cat. No.
Ampule Breaker Kit, PourRite	each	24846-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, 50 mL	each	508-41
Cylinder, graduated, mixing, 25 mL	each	20886-40
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	100/pkg	13530-00
Flask, filtering, 500 mL	each	546-49
Flask, erlenmeyer, 125 mL	each	505-43
Flask, volumetric, Class A, 50 mL	each	14574-41
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable with electrode	each	51700-10
Pipet, serological, 2.0 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01	1000/pkg	21856-28
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet Filler, safety bulb	each	12189-00
Spoon, measuring, 0.05 g	each	492-00
Thermometer, -20 to 110 °C, Non-Mercury	each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

PHOSPHORUS, REACTIVE, HR (0.0 to 100.0 mg/L PO_4^{3-})

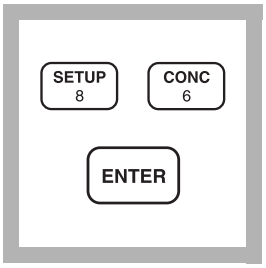
Molybdovanadate Method*, Test 'N Tube™ Procedure **For water and wastewater**

1. Enter the stored program number for phosphorus, reactive, high range, Test 'N Tube.

Press: **PRGM**

The display will show:

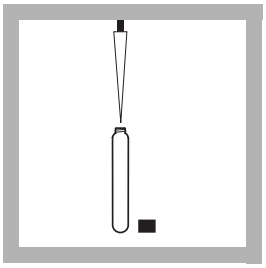
PRGM ?



2. Press: **86 ENTER**

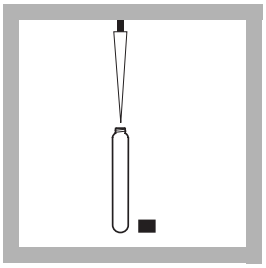
The display will show **mg/L, PO4** and the **ZERO** icon.

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*



3. Use a TenSette® Pipet to add 5.0 mL of deionized water to a Reactive High Range Phosphorus Test 'N Tube Vial (the blank).

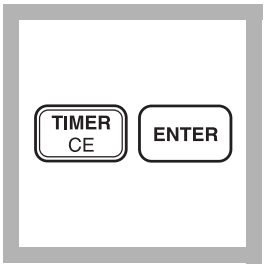
Cap and invert to mix.



4. Use a TenSette Pipet to add 5.0 mL of sample to a Reactive High Range Phosphorus Test 'N Tube Vial (the sample).

Cap and invert to mix.

Note: *For samples with extreme pH, see the Interference section.*



5. Press:

TIMER ENTER

A 7-minute reaction period will begin.

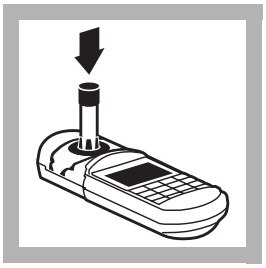
Note: *This reaction time is for samples at 23 °C (73 °F). If the sample temperature is 13 °C (55 °F), wait 15 minutes. If the sample temperature is 33 °C (91 °F), wait two minutes.*

6. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: *A diffuser band covers the light path holes on the adapter to give increased performance. The band should NOT be removed.*

7. Clean the outside of the vials with a towel.

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*

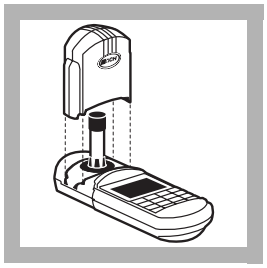


8. When the timer sounds, place the blank vial into the adapter.

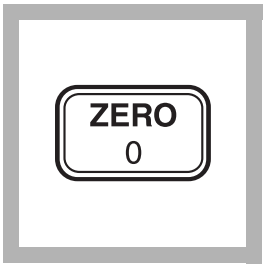
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater*.



9. Tightly cover the sample cell with the instrument cap.

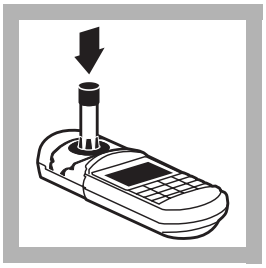


10. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.0 mg/L PO4

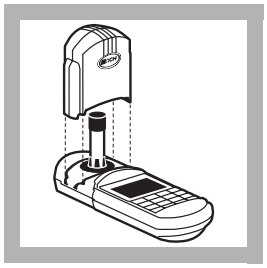
Note: *Reagent blanks for each lot of reagent may be used more than once. At room temperature, the reagent blank is stable for as long as three weeks; then prepare a new one.*



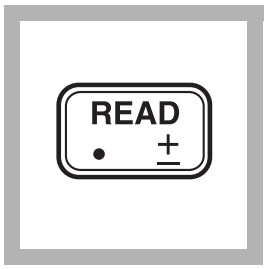
11. Place the sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



12. Tightly cover the vial with the instrument cap.



13. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (PO_4^{3-}) will be displayed.

Note: *For best results, use Standard Adjust with each new lot of reagent. (See* Accuracy Check.*)*

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphate for cleaning the glassware used in this test.

For best results, analyze the samples immediately after collection. If prompt analysis is impossible, preserve the samples for up to 748 hours by filtering immediately and storing at 4 °C. The sample should have a neutral (6–8) pH and be at room temperature before analysis.

Accuracy Check

Note: *Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

Standard Additions Method

a. Fill three 10-mL graduated mixing cylinders with 10 mL of sample.

b. Snap the neck off a Voluette™ Ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-} (Cat. No. 14242-10).

c. Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 10-mL aliquots of sample prepared in *step a*. Mix well.

d. Analyze each sample from *step c* as described in the procedure; use 5.0 mL of the prepared sample for each test. The concentration should increase as follows: 5 mg/L, 10 mg/L, and 15 mg/L PO_4^{3-}, respectively.

e. If these increases do not occur, see *Standard Additions* in *Section 1* of the *DR/890 Procedures Manual* for more information.

Standard Solution Method

To check accuracy, prepare an 80 mg/L PO_4^{3-} standard by pipetting 8.0 mL of solution from a 10-mL Voluette Ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-}, into an acid-cleaned 50-mL Class A volumetric flask. Fill to the line with deionized water. Substitute this standard for the sample and perform the procedure as described.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 80 mg/mL PO_4^{3-} standard solution, press the **SETUP** key and

scroll, using the arrow keys, to the **STO** option. Press **ENTER** to activate the standard adjust option. Then enter 80.0 to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Standard Curve Adjustment, Section 1* of the *Procedures Manual* for more information.

Interferences

Large amounts of sample turbidity may cause inconsistent results in the test because the acid present in the reagents may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The following may interfere when present in concentrations exceeding these listed below:

Substance	Interference Level and Treatment
Arsenate	Causes positive interference if the sample is heated.*
Iron, ferrous	Blue color caused by ferrous iron does not interfere if the iron concentration is less than 100 mg/L.
Molybdate	Causes negative interference above 1000 mg/L.
Silica	Causes positive interference if the sample is heated.*
Sulfide	Causes a negative interference. Remove interference as follows: **1.** Measure 50 mL of sample into an Erlenmeyer flask. **2.** Add Bromine Water drop-wise with constant swirling until a permanent yellow color develops. **3.** Add Phenol Solution drop-wise until the yellow color just disappears. Proceed with *step 1* of the procedure.
Extreme pH or highly buffered samples	May exceed buffering capacity of the reagents. See *pH Interferences* in *Section 1* of the *DR/890 Procedure Manual*. Samples may require pretreatment. Sample pH should be about 7.
Fluoride, thorium, bismuth, thiosulfate or thiocyanate	Cause a negative interference.
Temperature, cold (less than 20 °C)	Causes a negative interference.
Temperature, hot (greater than 25 °C)	Causes a positive interference.
The following do not interfere in concentrations up to 1000 mg/L: Pyrophosphate, tetraborate, selenate, benzoate, citrate, oxalate, lactate, tartrate, formate, salicylate, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Mn^{2+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, SO_3^{2-}, Pb^{2+}, Hg^{+}, Hg^{2+}, Sn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, U^{4+}, Zr^{4+}, AsO_3^{-}, Br^{-}, CO_3^{2-}, ClO_4^{-}, CN^{-}, IO_3^{-}, SiO_4^{4-}.	

* Gentle warming of the sample to reach room temperature will not cause this substance to interfere.

Method Performance

Precision

In a single laboratory, using a standard solution of 80.0 mg/L PO_4^{3-} and two lots of reagent with the instrument, a single operator obtained a standard deviation of ±3.0 mg/L PO_4^{3-}.

Estimated Detection Limit (EDL)

The EDL for program 86 is 7.0 mg/L PO_4^{3-}. For more information on derivation and use of Hach's estimated detection limit, see *Section 1* of the *DR/890 Procedures Manual*.

Sample Disposal Information

Final samples will contain molybdenum. In addition, final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA. Consult the Material Safety Data Sheet for information specific to the reagent used.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

Summary of Method

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. In the presence of vanadium, yellow vanadomolybdophosphoric acid forms. The intensity of the yellow color is proportional to the phosphate concentration.

Installing this Program on the DR/800

This procedure will add the current method as a new Hach program to your DR/800.

1. Turn the DR/800 on by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the down arrow key two times so that the prompt line shows **USER**.
4. Press the **ENTER** key.
5. Enter **8138**, followed by **ENTER**.

6. Enter each of the numbers in the right column, each followed by **ENTER**. The line numbers in the left column relate to the line number on the display. At any time you may use the arrow keys to scroll back to review or change any number you have already entered.

Line Number	Entry	Line Number	Entry
1	86	29	0
2	4	30	80
3	73	31	50
4	0	32	79
5	0	33	53
6	0	34	0
7	0	35	62
8	65	36	166
9	56	37	246
10	217	38	148
11	21	39	63
12	66	40	63
13	157	41	78
14	197	42	252
15	30	43	4
16	0	44	76
17	0	45	128
18	0	46	0
19	0	47	15
20	80	48	1
21	79	49	164
22	52	50	0
23	0	51	0
24	0	52	0
25	80	53	0
26	0	54	80
27	0	55	0
28	0	56	255

PHOSPHORUS, REACTIVE, HR, continued

REQUIRED REAGENTS

High Range Reactive Phosphorus Test 'N Tube™ Reagent Set .....50 vials 27673-45
Includes: (50) Reactive High Range Phosphorus Test 'N Tube™ Vials*, (2) 272-42

Description	Quantity Required Per Test	Unit	Cat. No.
Reactive High Range Phosphorus Test 'N Tube™ Vials	1	50/pkg	*
Water, deionized		100 mL	272-42

REQUIRED APPARATUS

COD/TNT Adapter for DR/800 Series	1	each	48464-00
Pipet, TenSette®, 1 to 10 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette® Pipet	1	50/pkg	21997-96
Test Tube Rack	1–3	each	18641-00

OPTIONAL REAGENTS

Bromine Water, 30 g/L	29 mL**	2211-20
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phenol Solution, 30 g/L	29 mL	2112-20
Phosphate Standard Solution, PourRite ampule, 500 mg/L as PO_4^{3-}, 2 mL	20/pkg	14242-20
Phosphate Standard Solution, Voluette ampule, 500 mg/L as PO_4^{3-}, 10 mL	16/pkg	14242-10
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49

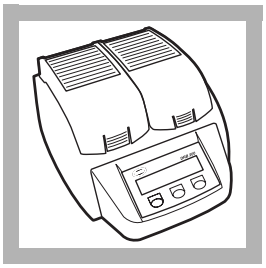
OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, mixing, 10 mL, 3 required	each	20886-38
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	200/pkg	13530-00
Flask, filtering, 500 mL	each	546-49
Flask, volumetric, Class A, 50-mL	each	14574-41
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable with electrode	each	51700-10
Pipet, TenSette®, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette® Pipet	1000/pkg	21856-28
Pipet Tips, for 19700-10 TenSette® Pipet	250/pkg	21997-25
Pipet, volumetric, Class A, 5.00-mL	each	14515-37
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
PourRite™ Ampule Breaker	each	24846-00

* These items are not sold separately.
** Larger sizes available.

PHOSPHORUS, TOTAL, HR (0.0 to 100.0 mg/L PO_4^{3-})

Molybdovanadate Method with Acid Persulfate Digestion*
Test 'N Tube™ Procedure **For water and wastewater**



1. Turn on the DRB200 Reactor. Heat to 150 °C.

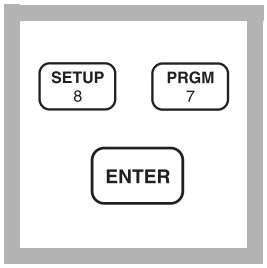
Note: *See DRB200 instrument manual for selecting preprogrammed temperature applications*

2. Enter the stored program number for phosphorus total high range, Test 'N `Tube.

Press: **PRGM**

The display will show:

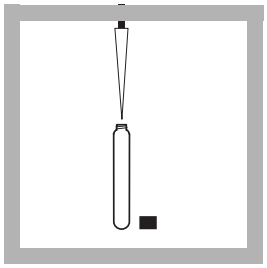
PRGM ?



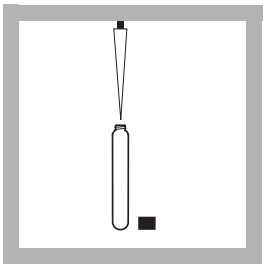
3. Press: **87 ENTER**

The display will show **mg/L, PO4** and the **ZERO** icon.

Note: *For alternate forms (P, P_2O_5), press the* **CONC** *key.*

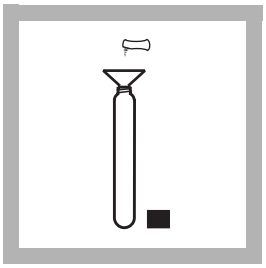


4. Use a TenSette® Pipet to add 5.0 mL of deionized water to a Total Phosphorus Test 'N Tube Vial (the blank).

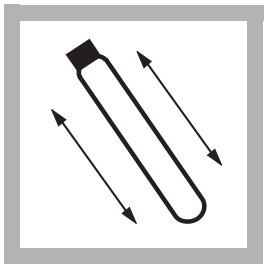


5. Use a TenSette Pipet to add 5.0 mL of sample to a Total Phosphorus Test 'N Tube Vial (the sample).

Note: *Adjust the pH of stored samples to 6–8 before analysis.*



6. Use a funnel to add the contents of one Potassium Persulfate Powder Pillow for Phosphonate to each vial.

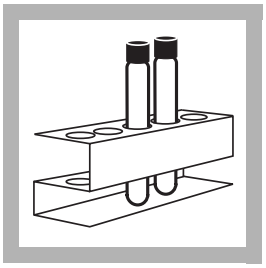


7. Cap tightly and shake to dissolve.

8. Place the vials in the DRB200 Reactor. Heat for 30 minutes.

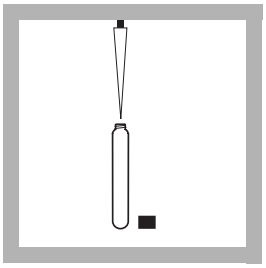
Press: **TIMER ENTER** to time the heating period.

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



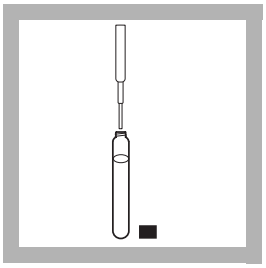
9. Carefully remove the vials from the reactor. Place them in a test tube rack and allow to cool to room temperature (18–25 °C).

Note: *Vials will be hot.*



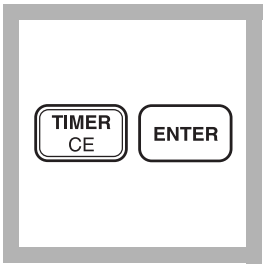
10. Use a TenSette Pipet to add 2.0 mL of 1.54 N sodium hydroxide to each vial.

Cap and invert to mix.



11. Use a polyethylene dropper to add 0.5 mL of Molybdovanadate Reagent to each vial.

Cap and invert to mix.



12. Press:

TIMER ENTER

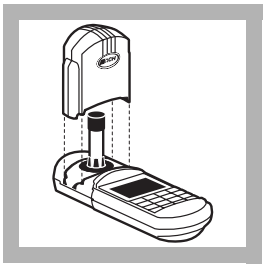
A 7-minute reaction period will begin.

Note: *Read the samples between 7 and 9 minutes.*

13. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

14. Clean the outside of the vials with a towel.

Note: *Wipe with a damp towel, followed by a dry one, to remove fingerprints or other marks.*

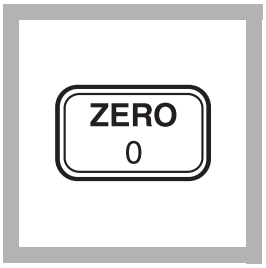


15. When the timer sounds, place the blank vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Tightly cover the vial with the instrument cap.

Note: *Do not move the vial from side to side as this can cause errors.*

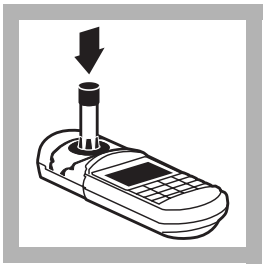


16. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.0 mg/L PO4

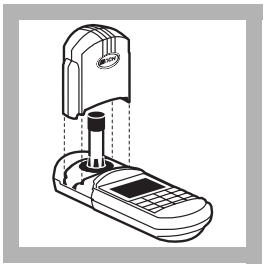
Note: *Reagent blanks for each lot of reagents may be used more than once, but should not be used for longer than one day.*



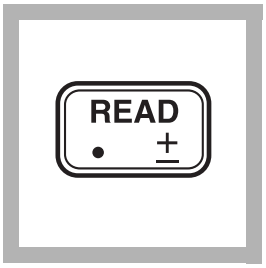
17. Place the prepared sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: *Do not move the vial from side to side as this can cause errors.*



18. Tightly cover the vial with the instrument cap.



19. Press: **READ**

The cursor will move to the right, then the result in mg/L phosphate (PO_4^{3-}) will be displayed.

Note: *For best results, use Standard Adjust with each new lot of reagent. (See* Accuracy Check.*)*

Sampling and Storage

Collect samples in plastic or glass bottles that have been acid cleaned with 1:1 Hydrochloric Acid Solution and rinsed with deionized water. Do not use commercial detergents containing phosphates for cleaning the glassware used in this test.

Analyze samples immediately after collection for best results. If prompt analysis is impossible, preserve the sample for up to 28 days by adjusting the pH to 2 or less with concentrated H_2SO_4 (about 2 mL per liter) and storing at 4 °C. Warm the sample to room temperature and neutralize with 5.0 N NaOH before analysis.

Correct test results for volume additions; see *Volume Additions* in *Section 1*of the *DR/890 Procedures Manual*.

Accuracy Check

Note: *Clean glassware with 1:1 hydrochloric acid solution. Rinse again with deionized water. Do not use detergents containing phosphates to clean glassware.*

Standard Additions Method

a. Fill each of three 10-mL graduated mixing cylinders with 10 mL of sample.

b. Snap the neck off a 10-mL Voluette® Ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-} (Cat. No. 14242-10).

c. Use a TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL, respectively, to the three 10-mL aliquots of the water sample prepared in *step a*. Mix well.

d. Analyze samples from *step c* as described in the procedure. Use 5.0 mL of the prepared sample for each test. The concentration should increase: 5 mg/L, 10 mg/L, and 15 mg/L PO_4^{3-}, respectively.

e. If these increases do not occur, see *Standard Additions (Section 1 of the DR/890 Procedures Manual*) for more information.

Standard Solution Method

To check accuracy, prepare an 80 mg/L standard by pipetting 8.0 mL of solution from a 10-mL Voluette® Ampule of Phosphate Standard Solution, 500 mg/L as PO_4^{3-} into an acid-cleaned, Class A, 50-mL volumetric flask. Dilute to the mark with deionized water. Substitute this standard for the sample and perform the procedure as described.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 80 mg/L PO_4^{3-} standard solution, press the **SETUP** key and scroll, using the arrow keys, to the **STO** option. Press **ENTER** to activate the standard adjust option. Then enter 80.0 to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Standard Curve Adjustment, Section 1* of the *Procedures Manual* for more information.

Interferences

Large amounts of sample turbidity may cause inconsistent results in the test because the acid present in the reagents may dissolve some of the suspended particles and because of variable desorption of orthophosphate from the particles.

The following may interfere when present in concentrations exceeding those listed below:

Interfering Substance	Interference Level and Treatment
Arsenate	Causes positive interference if the sample is heated.*
Iron, ferrous	Blue color caused by ferrous iron does not interfere if iron concentration is less than 100 mg/L.
Molybdate	Causes negative interference above 1000 mg/L.
Silica	Causes positive interference if the sample is heated.*
Extreme pH or highly buffered samples	May exceed buffering capacity of the reagents. See *pH Interferences* in *Section 1* of the *DR/890 Procedures Manual*. Samples may require pretreatment. Sample pH should be about 7.
Fluoride, thorium, bismuth, thiosulfate or thiocyanate	Cause a negative interference.
Temperature, Cold (less than 18 °C)	Causes a negative interference.
Temperature, Hot (greater than 25 °C)	Causes a positive interference. Post-digestion samples should be brought to room temperature (18–25 °C) before the addition of the Molybdovanadate Reagent or sodium hydroxide.
The following do not interfere in concentrations up to 1000 mg/L: Pyrophosphate, tetraborate, selenate, benzoate, citrate, oxalate, lactate, tartrate, formate, salicylate, Al^{3+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Li^{+}, Na^{+}, K^{+}, NH_4^{+}, Cd^{2+}, Mn^{2+}, NO_3^{-}, NO_2^{-}, SO_4^{2-}, SO_3^{2-}, Pb^{2+}, Hg^{+}, Hg^{2+}, Sn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, U^{4+}, Zr^{4+}, AsO_3^{-}, Br^{-}, CO_3^{2-}, ClO_4^{-}, CN^{-}, IO_3^{-}, SiO_4^{4-}.	

* Gentle warming of the sample to reach room temperature will not cause this substance to interfere.

Method Performance

Precision

In a single laboratory, using a standard solution of 80.0 mg/L PO_4^{3-} and two lots of reagent with the instrument, a single operator obtained a standard deviation of ±3.0 mg/L PO_4^{3-}.

Estimated Detection Limit

The estimated detection limit for program 87 is 7.0 mg/L PO_4^{3-}. For more information on the estimated detection limit, see *Section 1* of the *DR/890 Procedures Manual*.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the Material Safety Data Sheet for information specific to the reagents used.

Sample Disposal Information

The final samples will contain molybdenum. In addition, the final samples will have a pH less than 2 and are considered corrosive (D002) by the Federal RCRA. Consult the Material Safety Data Sheet for information specific to the reagent used.

Summary of Method

Phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analysis. Pretreatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphate by heating with acid and persulfate.

Orthophosphate reacts with molybdate in an acid medium to produce a phosphomolybdate complex. In the presence of vanadium, yellow vanadomolybdophosphoric acid forms. The intensity of the yellow color is proportional to the phosphate concentration.

Installing this Program on the DR/800

This procedure will add the current method as a new Hach program to your DR/800.

1. Turn the DR/800 on by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the down arrow key two times so that the prompt line shows **USER**.
4. Press the **ENTER** key.
5. Enter **8138**, followed by **ENTER**.
6. Enter each of the numbers in the right column, each followed by **ENTER**. The line numbers in the left column relate to the line number on the display. At any time you may use the arrow keys to scroll back to review or change any number you have already entered.

Line Number	Entry	Line Number	Entry
1	87	18	0
2	4	19	0
3	73	20	80
4	0	21	79
5	0	22	52
6	0	23	0
7	0	24	0
8	0	25	80
9	0	26	0
10	0	27	0
11	0	28	0
12	66	29	0
13	175	30	80
14	48	31	50
15	32	32	79
16	0	33	53
17	0	34	0
35	62	46	0

Line Number	Entry	Line Number	Entry
36	166	47	15
37	246	48	7
38	148	49	8
39	63	50	1
40	63	51	164
41	78	52	0
42	252	53	0
43	4	54	40
44	76	55	0
45	128	56	255

REQUIRED REAGENTS

Total High Range Phosphorus Test 'N Tube™ Reagent Set ..... 50 vials 27672-45
Includes: (50) Total Phosphorus Test 'N Tube™ Vials*, (2) 272-42, (1) 20847-66
(1) 20760-26, (1) 27430-42

Description	Quantity Required Per Test	Unit	Cat. No.
Molybdovanadate Reagent	0.5 mL	25 mL	20760-26
Potassium Persulfate Powder Pillows	1	50/pkg	20847-66
Sodium Hydroxide Solution, 1.54 N	2 mL	100 mL	27430-42
Total Phosphorus Test 'N Tube™ Vials	1	50/pkg	*
Water, deionized		100 mL	272-42

REQUIRED APPARATUS

DRB 200 Reactor, 110 V, 15 x 16 mm tubes LTV082.53.40001
DRB 200 Reactor, 220 V, 15 x 16 mm tubes LTV082.52.40001
COD/TNT Adapter, DR/800 series ..... 1 ..... each 48464-00
Dropper, LDPE, 0.5 to 1.0 mL ..... 1 ..... 20/pkg 21247-20
Pipet, TenSette®, 1 to 10 mL ..... 1 ..... each 19700-10
Pipet Tips, for 19700-10 TenSette® Pipet ..... varies .. 50/pkg 21997-96
Test Tube Rack ..... 1–3 ..... each 18641-00

* These items are not sold separately.

PHOSPHORUS, TOTAL, HR, continued

OPTIONAL REAGENTS

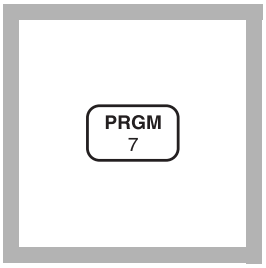
Description	Unit	Cat. No.
Hydrochloric Acid Standard Solution, 6.0 N (1:1)	500 mL	884-49
Phosphate Standard Solution, PourRite™ ampule, 500 mg/L as PO_4^{3-}, 2-mL	20/pkg	14242-20
Phosphate Standard Solution, Voluette™ ampule, 500 mg/L as PO_4^{3-}, 10-mL	16/pkg	14242-10
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450-53
Sulfuric Acid, ACS, concentrated	500 mL	979-491
Wastewater Influent Standard, Inorganic (NH_3–N, NO_3–N, PO_4, COD, SO_4, TOC)	500 mL	28331-49

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Aspirator, vacuum	each	2131-00
Cylinder, graduated, mixing, 10 mL (3 required)	each	20886-38
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm		LTV082.53.42001
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm		LTV082.52.42001
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm		LTV082.53.30001
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001
Filter Holder, 47 mm, 300 mL, graduated	each	13529-00
Filter, membrane, 47 mm, 0.45 microns	200/pkg	13530-01
Flask, filtering, 500-mL	each	546-49
Flask, volumetric, Class A, 50-mL	each	14574-41
pH Indicator Paper, 1 to 11 pH units	5 rolls/pkg	391-33
pH Meter, *sension™1*, portable with electrode	each	51700-10
Pipet Filler, Safety Bulb	each	14651-00
Pipet, TenSette®, 0.- to 1.0-mL	each	19700-01
Pipet Tips, for 19700-01	50/pkg	21856-96
Pipet Tips, for 19700-01	1000/pkg	21856-28
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
Stopper, No. 7 one hole	6/pkg	2119-07
Tubing, rubber	12 feet	560-19

SILICA, Low Range (0 to 1.60 mg/L)

Heteropoly Blue Method*

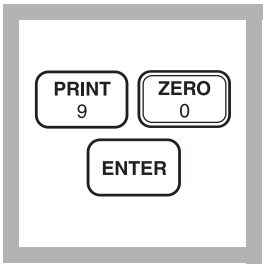


1. Enter the stored program number for low range silica (SiO_2).

Press: **PRGM**

The display will show:

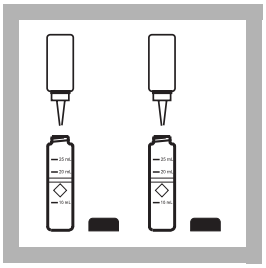
PRGM ?



2. Press: **90 ENTER**

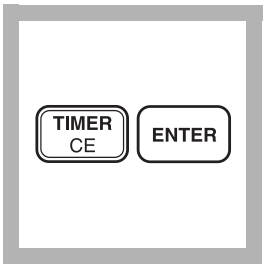
The display will show **mg/L, SiO2** and the **ZERO** icon**.**

3. Fill two sample cells to the 10-mL line with sample.



4. Add 15 drops of Molybdate 3 Reagent to each sample cell. Swirl to mix.

Note: *For greatest accuracy, hold dropping bottle vertical.*

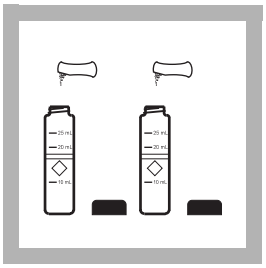


5. Press:

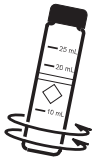
TIMER ENTER

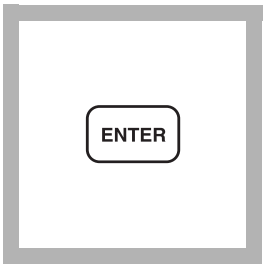
A 4-minute reaction period will begin.

Note: *Reaction time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait 8 minutes. If the sample temperature is 30 °C (86 °F), wait 2 minutes.*



6. After the timer beeps, add the contents of one Citric Acid Reagent Powder Pillow to each sample cell. Swirl to mix.





7. The display will show:

1:00 TIMER 2

Press: **ENTER**

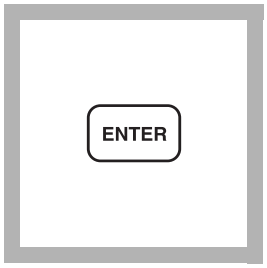
A 1-minute reaction period will begin. Phosphate interference is eliminated during this period.

Note: *The time given is for samples at 20 °C (68 °F). If the sample temperature is 10 °C (50 °F), wait two minutes. If the sample is 30 °C (86 °F), wait 30 seconds.*

8. After the timer beeps, add the contents of one Amino Acid F Reagent Powder Pillow to one of the sample cells (the prepared sample). Invert to mix.

Note: *The sample cell without the Amino Acid F Reagent is the blank.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*



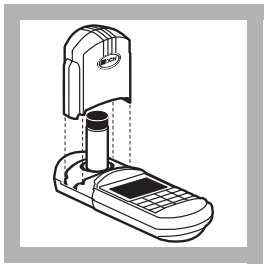
9. The display will show:

2:00 TIMER 3

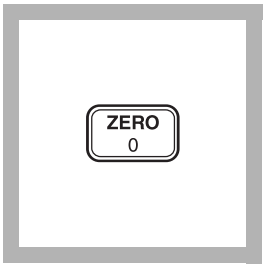
Press: **ENTER**

A 2-minute reaction period will begin.

Note: *A blue color will develop if silica is present.*



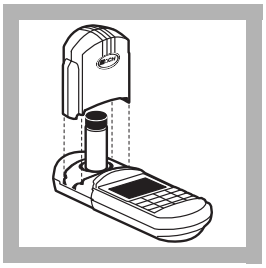
10. After the timer beeps, place the blank (solution without Amino Acid F Reagent) into the cell holder. Tightly cover the sample cell with the instrument cap.



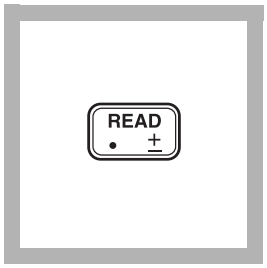
11. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L SiO2



12. Place the sample into the cell holder. Tightly cover the sample cell with the instrument cap.



13. Press: **READ**

The cursor will move to the right, then the result in mg/L SiO2 will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Sampling and Storage

Collect samples in clean plastic bottles. Analyze samples as soon as possible after collection. If prompt analysis is not possible, store samples for up to 28 days by cooling to 4 °C (39 °F) or below. Warm samples to room temperature before analysis.

Accuracy Check

Standard Additions Method

a) Open a Silica Standard Solution Bottle, 25 mg/L SiO_2.

b) Using the TenSette Pipet, add 0.1, 0.2, and 0.3 mL of standard to three 10-mL samples. Mix thoroughly.

c) Analyze each sample as described above. The silica concentration should increase 0.25 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 1.00-mg/L Standard Solution (see *Optional Reagents*), press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **1.00** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1*, *Standard Curve Adjustment* for more information.

Method Performance

Precision

In a single laboratory, using standard solutions of 1.00 mg/L silica and two representative lots of reagent and a instrument, a single operator obtained a standard deviation of ±0.025 mg/L silica.

Estimated Detection Limit (EDL)

The estimated detection limit for program 90 is 0.020 mg/L SiO2. For more information on the estimated detection limit, see *Section 1*. If testing for very low levels of silica, use the ultra-low range silica method on the Hach DR/2010 or DR/4000 Spectrophotometers.

Interferences

Interfering Substance	Interference Levels and Treatments
Color	Eliminated by zeroing the instrument with the original sample.
Phosphate	Phosphate does not interfere at levels less than 50 mg/L PO_4. At 60 mg/L PO_4, an interference of -2% occurs. At 75 mg/L PO_4 the interference is -11%.
Iron	Large amounts of iron interfere.
Slow reacting forms of silica	Occasionally a sample contains silica which reacts very slowly with molybdate. The nature of these "molybdate-unreactive" forms is not known. A pretreatment with sodium bicarbonate, then sulfuric acid will make these forms reactive to molybdate. The pretreatment is given in *Standard Methods for the Examination of Water and Wastewater* under Silica-Digestion with Sodium Bicarbonate. A longer reaction time with the sample and the molybdate and acid reagents (before adding citric acid) may help in lieu of the bicarbonate pretreatment.
Sulfides	Interfere at all levels
Turbidity	Eliminated by zeroing the instrument with the original sample.

Reagent Preparation

To prepare Amino Acid F Reagent Solution, dissolve 11.4 grams of Amino Acid F Reagent Powder in 100 mL of 1.0 N Sodium Hydroxide Solution. The solution is stable for at least one month if stored in a plastic bottle.

Summary of Method

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Acid reduces the yellow silicomolybdic acid to an intense blue color, which is proportional to the silica concentration.

SILICA, Low Range, continued

REQUIRED REAGENTS

	Cat. No.
Low Range Silica Reagent Set, 10 mL sample (100 tests) Includes: (1) 22540-69, (1) 21062-69 (2) 1995-26	24593-00

Description	Quantity Required Per Test	Units	Cat. No.
Amino Acid F Reagent Powder Pillows	1 pillow	100/pkg	22540-69
Citric Acid Powder Pillows	2 pillows	100/pkg	21062-69
Molybdate 3 Reagent	28 drops	50 mL SCDB	1995-26

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Silica Standard Solution, 1.00 mg/L SiO_2		500 mL	1106-49
Silica Standard Solution, 25 mg/L SiO_2		236 mL	21225-31
Sodium Bicarbonate, ACS		454 g	776-01
Sodium Hydroxide Standard Solution, 1.000 N		900 mL	1045-53
Sulfuric Acid Standard Solution, 1.0 N		1000 mL	1270-53

OPTIONAL APPARATUS

Bottle, 118 mL, polyethylene, oblong		6/pkg	23184-06
Dropper, 0.5- & 1.0-mL marks		6/pkg	23185-06
Pipet, serological, 2 mL, poly		each	2106-36
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 Pipet		1000/pkg	21856-28
Standard Methods for the Examination of Water and Wastewater		each	22708-00
Thermometer, - 20 to 110 °C, Non-Mercury		each	26357-02

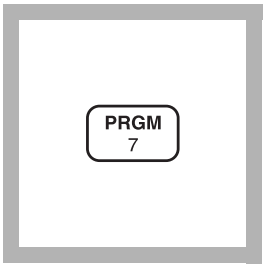
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SILICA, High Range (0 to 75.0 mg/L)

Silicomolybdate Method



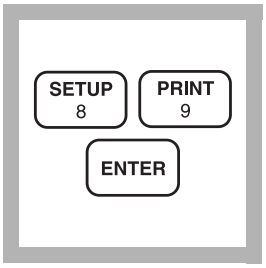
1. Enter the stored program number for high range silica (SiO_2).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **89 ENTER**

The display will show **mg/L, SiO2** and the **ZERO** icon**.**

Note: *For alternate form (Si), press the* **CONC** *key.*

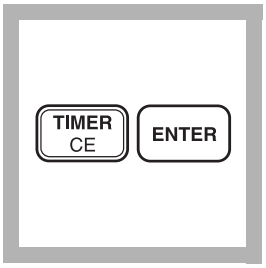
3. Fill two sample cells with 10 mL of sample. Set one aside as the blank.

Note: *Sample temperature should be 15 to 25 °C (59 to 77 °F).*

4. To the other cell, add the contents of one Molybdate Reagent Powder Pillow for High Range Silica (the prepared sample). Cap and invert to mix.

5. Add the contents of one Acid Reagent Powder Pillow for High Range Silica. Cap and invert to mix.

Note: *Silica or phosphate will cause a yellow color to develop.*



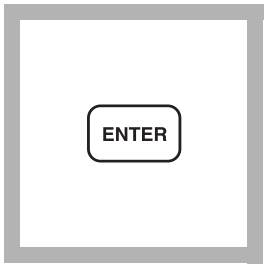
6. Press:

TIMER ENTER

A 10-minute reaction period will begin.

7. When the timer beeps, add the contents of one Citric Acid Powder Pillow to the prepared sample. Cap and invert to mix.

Note: *The yellow color due to phosphate will disappear.*

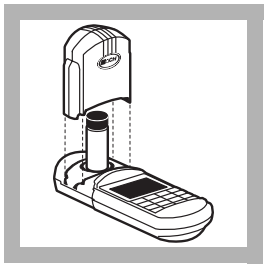


8. The display will show: **2:00 Timer 2**

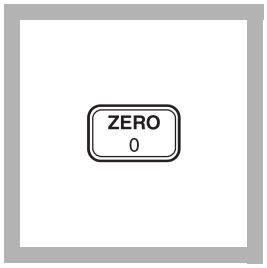
Press: **ENTER**

A two-minute reaction period will begin.

Note: *Perform Steps 9-12 within three minutes after the timer beeps.*



9. When the timer beeps, place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

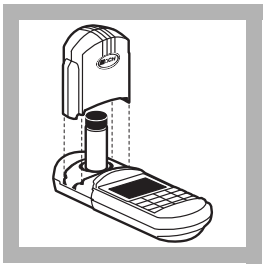


10. Press: **ZERO**

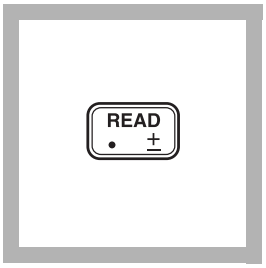
The cursor will move to the right, then the display will show:

0.0 mg/L SiO2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L silica (SiO_2) will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible after collection. Store samples up to 28 days at 4 °C (39 °F) or below. Warm samples to room temperature before analyzing.

Accuracy Check

Standard Additions Method

a) Open a High Range Silica Standard Solution, 1000 mg/L SiO_2.

b) Use the TenSette Pipet to add 0.1 mL, 0.3 mL, and 0.5 mL of the standard to three 10-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The silica concentration should increase 10.0 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

To check the accuracy of the method, use the Silica Standard Solutions, 25 and 50 mg/L as SiO_2, listed under Optional Reagents. Analyze according to the above procedure using deionized water as the blank.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 50.0 mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **50.0** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1, Standard Curve Adjustmen*t for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 50.0 mg/L SiO_2 and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±1.0 mg/L silica.

Estimated Detection Limit

The estimated detection limit for program 89 is 1.00 mg/L SiO_2. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Color	Eliminated by zeroing the instrument with the original sample.
Iron	High levels of Fe^{2+} and Fe^{3+} interfere.
Phosphate	Does not interfere below 50 mg/L PO_4^{3-}. At 60 mg/L PO_4^{3-}, a negative 2% interference occurs. At 75 mg/L PO_4^{3-} the interference is negative 11%.
Sulfides (S^{2-})	High levels interfere.
Turbidity	Eliminated by zeroing the instrument with the original sample.

Occasionally a sample contains silica which reacts very slowly with molybdate. The nature of these “molybdate-unreactive” forms is not known. A pretreatment with sodium bicarbonate, then sulfuric acid will make these forms reactive to molybdate. The pretreatment is given in *Standard Methods for the Examination of Water and Wastewater* under Silica-Digestion

with Sodium Bicarbonate. A longer reaction time with the sample and the molybdate and acid reagents (before adding citric acid) may help in lieu of the bicarbonate treatment.

Summary of Method

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. Silica is then determined by measuring the remaining yellow color.

REQUIRED REAGENTS

	Cat. No.
High Range Silica Reagent Set, 10-mL sample (100 tests)	24296-00
Includes: (1) 21074-69, (1) 21062-69, (1) 21073-69	

Description	Quantity Required Per Test	Units	Cat. No.
Acid Reagent Powder Pillows for High Range Silica	1	100/pkg	21074-69
Citric Acid Powder Pillows	1	100/pkg	21062-69
Molybdate Reagent Powder Pillows for HR Silica	1	100/pkg	21073-69

REQUIRED APPARATUS

Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

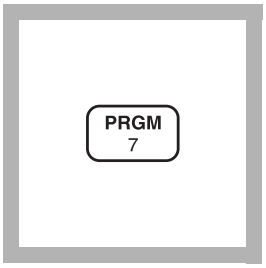
Silica Standard Solution, 10 mg/L	500 mL	1403-49
Silica Standard Solution, 25 mg/L	236 mL	21225-31
Silica Standard Solution, 50 mg/L	200 mL	1117-29
Silica Standard Solution, 1000 mg/L	500 mL	194-49
Sodium Bicarbonate, ACS	454 g	776-01
Sulfuric Acid Standard Solution, 1.000 N	100 mL MDB	1270-32
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 Pipet	1000/pkg	21856-28
Standard Methods for the Examination of Water and Wastewater	each	22708-00
Thermometer, -20 to 110 ˚C, Non-Mercury	each	26357-02

SILICA, Ultra High Range (0 to 200 mg/L)

Silicomolybdate Method



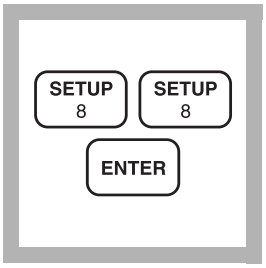
1. Enter the stored program number for ultra high range silica (SiO_2).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



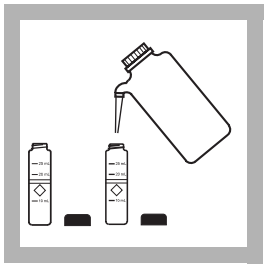
2. Press: **88 ENTER**

The display will show **mg/L, SiO2** and the **ZERO** icon**.**

Note: *For alternate form (Si), press the* **CONC** *key.*

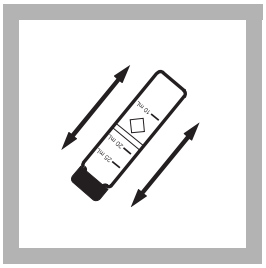
3. Fill 2 sample cells with 10 mL of sample.

Note: *Sample temperature should be 15 to 25 °C (59 to 77 °F).*



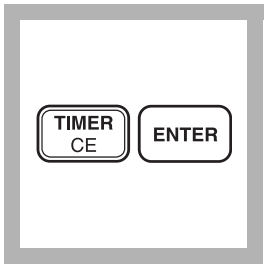
4. Fill both sample cells to the 25-mL line with deionized water. Set one sample cell aside as the blank.

5. To the other cell, add the contents of one Molybdate Reagent Powder Pillow for High Range Silica (the prepared sample). Cap and invert to mix.



6. Add the contents of one Acid Reagent Powder Pillow for High Range Silica to the prepared sample. Cap and invert to mix.

Note: *Silica or phosphate will cause a yellow color to develop.*



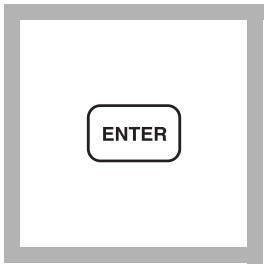
7. Press:

TIMER ENTER

A 10-minute reaction period will begin.

8. When the timer beeps, add the contents of one Citric Acid Powder Pillow to the prepared sample. Cap and invert to mix.

Note: *The yellow color due to phosphate will disappear.*

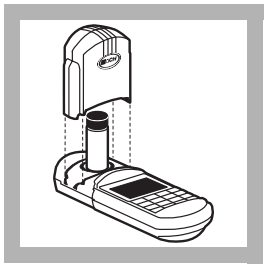


9. The display will show: **2:00 Timer 2**

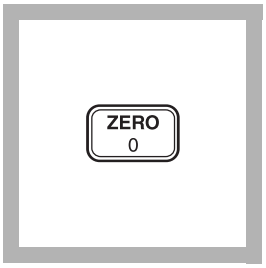
Press: **ENTER**

A two-minute reaction period will begin.

Note: *Perform Steps 10-13 within three minutes after the timer beeps.*



10. When the timer beeps, place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

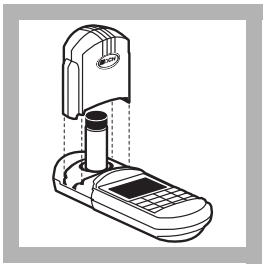


11. Press: **ZERO**

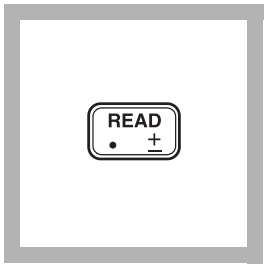
The cursor will move to the right, then the display will show:

0 mg/L SiO2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



12. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



13. Press: **READ**

The cursor will move to the right, then the result in mg/L silica (SiO_2) will be displayed.

Note: *Use of the Standard Adjust feature with each new lot of reagent is highly recommended. See Accuracy Check.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible after collection. Store samples up to 28 days at 4 °C (39 °F) or below. Warm samples to room temperature before analyzing.

Accuracy Check

Standard Additions Method

a) Open a High Range Silica Standard Solution, 1000 mg/L SiO_2.

b) Use the TenSette Pipet to add 0.1 mL, 0.3 mL, and 0.5 mL of the standard to three 10-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The silica concentration should increase 4 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

To prepare a 160-mg/L silica standard, pipet 40.0 mL of a 1000-mg/L Silica Standard Solution into a 250-mL volumetric flask. Dilute to the line with deionized water. Analyze according to the above procedure using deionized water as the blank.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 160-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **160.** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1, Standard Curve Adjustmen*t for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 100.0 mg/L SiO_2 and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±2.0 mg/L silica.

Estimated Detection Limit

The estimated detection limit for program 88 is 3.0 mg/L SiO_2. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Color	Eliminated by zeroing the instrument with the original sample.
Iron	High levels of Fe^{2+} and Fe^{3+} interfere.
Phosphate	Does not interfere below 50 mg/L PO_4^{3-}. At 60 mg/L PO_4^{3-}, a negative 2% interference occurs. At 75 mg/L PO_4^{3-} the interference is negative 11%.
Sulfides (S^{2-})	High levels interfere.
Turbidity	Eliminated by zeroing the instrument with the original sample.

Occasionally a sample contains silica which reacts very slowly with molybdate. The nature of these "molybdate-unreactive" forms is not known. A pretreatment with sodium bicarbonate, then sulfuric acid will make these forms reactive to molybdate. The pretreatment is given in *Standard Methods for the Examination of Water and Wastewater* under Silica-Digestion with Sodium Bicarbonate. A longer reaction time with the sample and the molybdate and acid reagents (before adding citric acid) may help in lieu of the bicarbonate treatment.

Summary of Method

Silica and phosphate in the sample react with molybdate ion under acidic conditions to form yellow silicomolybdic acid complexes and phosphomolybdic acid complexes. Addition of citric acid destroys the phosphate complexes. Silica is then determined by measuring the remaining yellow color.

SILICA, Ultra High Range, continued

REQUIRED REAGENTS

	Cat. No.
High Range Silica Reagent Set, 25-mL sample (100 tests)	22443-00
Includes: (1) 1042-99, (1) 14548-99, (1) 1041-99	

Description	Quantity Required Per Test	Units	Cat. No.
Acid Reagent Powder Pillows for High Range Silica	1	100/pkg	1042-99
Citric Acid Powder Pillows	1	100/pkg	14548-99
Molybdate Reagent Powder Pillows for HR Silica	1	100/pkg	1041-99
Water, deionized	30 mL	4 L	272-56

REQUIRED APPARATUS

Sample 10-20-15 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Silica Standard Solution, 10 mg/L		500 mL	1403-49
Silica Standard Solution, 25 mg/L		236 mL	21225-31
Silica Standard Solution, 50 mg/L		200 mL	1117-29
Silica Standard Solution, 1000 mg/L		500 mL	194-49
Sodium Bicarbonate, ACS		454 g	776-01
Sulfuric Acid Standard Solution, 1.000 N		100 mL MDB	1270-32

OPTIONAL APPARATUS

Flask, volumetric, 250 mL, Class A		each	14574-46
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 Pipet		50/pkg	21856-96
Pipet, volumetric, Class A, 100 mL		each	14515-42
Pipet Filler, safety bulb		each	14651-00
Standard Methods for the Examination of Water and Wastewater		each	22708-00
Thermometer, -20 to 110 °C, Non-Mercury		each	26357-02

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

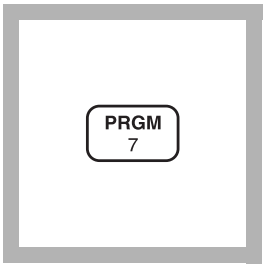
SULFATE (0 to 70 mg/L)

SulfaVer 4 Method* (Powder Pillows or AccuVac Ampuls); USEPA accepted for reporting wastewater analysis**

Using Powder Pillows

1. A User-Entered Calibration is necessary to obtain the most accurate results. See the *User Calibration* section at the back of this procedure. Program 91 can be used for process control or applications where a high degree of accuracy is not needed.

Note: *The nature of turbidimetric tests and reagent lot variation requires user calibration for best results.*

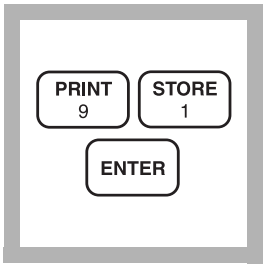


2. Enter the stored program number for sulfate (SO_4^{-}).

Press: **PRGM**

The display will show:

PRGM ?



3. Press: **91 ENTER** or the program number selected for a user-entered calibration.

The display will show **mg/L, SO4** and the **ZERO** icon.

4. Fill a clean sample cell with 10 mL of sample.

Note: *Filter highly turbid or colored samples. Use filtered sample in this step and as the blank.*

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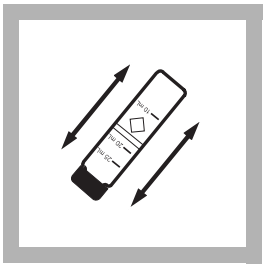
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

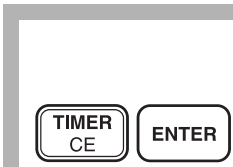
** Procedure is equivalent to USEPA method 375.4 for wastewater.



5. Add the contents of one SulfaVer 4 Sulfate Reagent Powder Pillow to the sample cell (the prepared sample). Cap the cell and invert several times to mix.

Note: *A white turbidity will develop if sulfate is present in the sample.*

Note: *Accuracy is not affected by undissolved powder.*

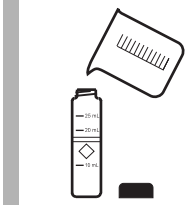


6. Press:

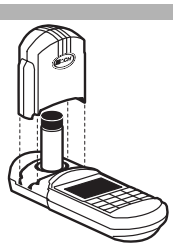
TIMER ENTER

A 5-minute reaction period will begin.

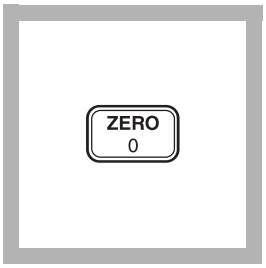
Allow the cell to stand undisturbed.



7. After the timer beeps, fill a second sample cell with 10 mL of sample (the blank).



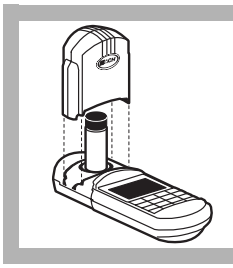
8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



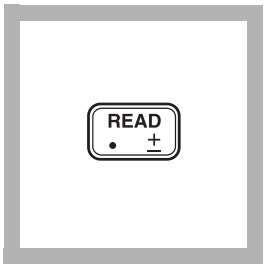
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L SO4



10. Within five minutes after the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

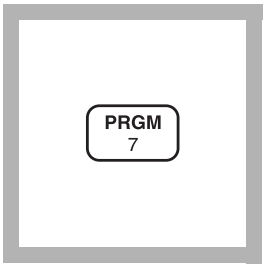
The cursor will move to the right, then the result in mg/L sulfate will be displayed.

Note: *If Program 91 is used, use of the Standard Adjust is highly recommended. See Accuracy Check.*

Note: *Clean the sample cells with soap and a brush.*

Using AccuVac Ampuls

1. A User-Entered Calibration is necessary to obtain the most accurate results. See User Calibration Section at the back of this procedure. Program 92 can be used for process control or applications where a high degree of accuracy is not needed.

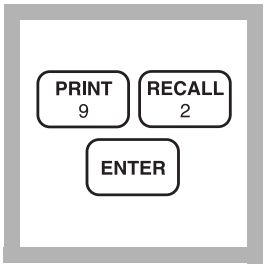


2. Enter the stored program number for sulfate (SO_4^{-})-AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

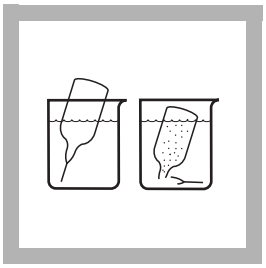


3. Press: **92 ENTER**

The display will show **mg/L, SO4** and the **ZERO** icon**.**

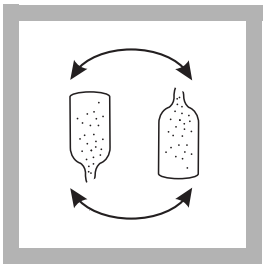
4. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

Note: *Filter highly turbid or colored samples. Use filtered sample in this step and as the blank.*



5. Fill a SulfaVer 4 Sulfate AccuVac Ampul with sample.

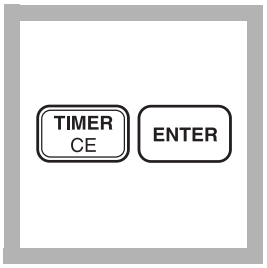
Note: *Keep tip immersed until the ampul fills completely.*



6. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A white turbidity will develop if sulfate is present.*

Note: *Accuracy is not affected by undissolved powder.*

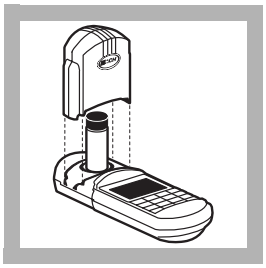


7. Press:

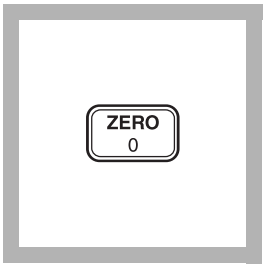
TIMER ENTER

A 5-minute reaction period will begin.

Note: *Allow the ampul to stand undisturbed.*



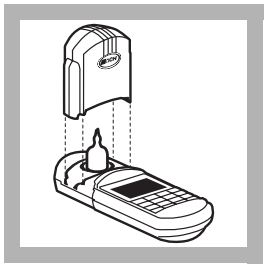
8. After the timer beeps, place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



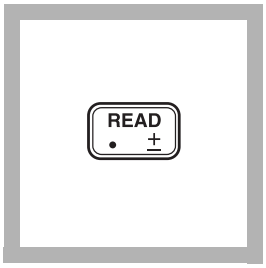
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L SO4



10. Within five minutes after the timer beeps, place the AccuVac ampul into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L sulfate will be displayed.

Note: *If Program 92 is used, use of the Standard Adjust is highly recommended. See Accuracy Check.*

User- Entered Calibration

There are various programs to determine sulfate, each with a different level of accuracy. Best results are obtained by performing a user-entered calibration with each new lot of reagent. Programs 91 and 92 can be run when a high degree of accuracy is not needed. Use of the Standard Adjust feature will improve performance when using programs 91 and 92. It should NOT be used with a user calibration, as it will hinder performance.

Using Class A glassware, prepare standards of 10, 20, 30, 40, 50, 60, and 70 mg/L sulfate by pipetting 1, 2, 3, 4, 5, 6, and 7 mL of a 1000-mg/L sulfate standard into 100-mL volumetric flasks. Dilute to the mark with deionized water and mix well.

Zero the instrument with water. The user-entered settings for sulfate are:

Program number: #101 to 105
Wavelength: 520 nm
Resolution: 0 mg/L

See *Creating User-Entered Program* in the instrument manual for specific instructions on entering a user-entered program.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Samples may be stored up to 28 days by cooling to 4 °C (39 °F) or lower. Warm to room temperature before analysis.

Accuracy Check

Standard Additions Method- Powder Pillows

a) Snap the neck off a Sulfate Standard PourRite Ampule, 1000 mg/L SO_4^{2-} .

b) Use a TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to the three 10-mL samples. Mix thoroughly.

c) Analyze each sample as described above. The sulfate concentration should increase 10 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method- AccuVac Ampuls

a) Snap the neck off a Sulfate Standard PourRite Ampule, 2500 mg/L SO_4^{2-} .

b) Fill three 25- mL graduated cylinders with 25 mL of sample. Use a TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to the three cylinders. Mix thoroughly. For AccuVac Ampuls, transfer to a 50-mL beaker.

c) Analyze each sample as described above. The sulfate concentration should increase 10 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Check the accuracy of the test by using the Sulfate Standard Solution, 50 mg/L, listed under Optional Reagents. Or, prepare this solution by pipetting 1.0 mL of a PourRite Ampule Standard for Sulfate (2500 mg/L) into a 50-mL volumetric flask. Dilute to volume with deionized water. The final concentration is 50 mg/L sulfate. Substitute this standard for the sample and proceed with the test as described in the procedure.

Standard Adjust

Standard adjust is recommended when using stored programs 91 or 92. It **should not** be used with a user-entered calibration.

To adjust the calibration curve using the reading obtained with the 50-mg/L standard solution, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **50** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1*, *Standard Curve Adjustmen*t for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 50 mg/L sulfate and two representative lots of powder pillows with the instrument, a single operator obtained a standard deviation of ±0.5 mg/L sulfate.

In a single laboratory, using a standard solution of 50 mg/L sulfate and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±3 mg/L sulfate.

Estimated Detection Limit (EDL)

The EDL for program 91 is 4.9 mg/L SO_4 and the EDL for program 92 is 3 mg/L SO_4. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

The following interfere at levels above those concentrations listed:

Calcium: 20,000 mg/L as $CaCO_3$	Magnesium: 10,000 mg/L as $CaCO_3$
Chloride: 40,000 mg/L as Cl^-	Silica: 500 mg/L as $CaCO_3$

Summary of Method

Sulfate ions in the sample react with barium in the SulfaVer 4 Sulfate Reagent to form insoluble barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. The SulfaVer 4 also contains a stabilizing agent to hold the precipitate in suspension.

REQUIRED REAGENTS AND APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Units	Cat. No.
SulfaVer 4 Sulfate Reagent Powder Pillows	1 pillow	100/pkg	21067-69
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS AND APPARATUS (Using AccuVac Ampuls)

SulfaVer 4 Sulfate AccuVac Ampuls	1 ampul	25/pkg	25090-25
Beaker, 50-mL	1	each	500-41H

OPTIONAL REAGENTS

Standard, Drinking Water Inorganics, F^-, NO_3^{-N}, PO_4^{-3}, SO_4^{-2}		500 mL	28330-49
Standard, Wastewater Effluent Inorganics, NH_3^{-N}, NO_3^{-N}, PO_4^{-3}, COD, SO_4^{-2}, TOC		500 mL	28332-49
Sulfate Standard Solution, 50 mg/L		500 mL	2578-49
Sulfate Standard Solution, 1000 mg/L		500 mL	21757-49
Sulfate Standard Solution, PourRite Ampule, 2500 mg/L, 10 mL		16/pkg	14252-10
Sulfate Standard Solution, PourRite Ampule, 1000 mg/L, 2 mL		20/pkg	21757-20
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit		each	24052-00
Cylinder, graduated mixing, 25 mL		each	20886-40
Filter Paper, folded, 12.5 cm		100/pkg	1894-57
Flask, volumetric, 50 mL, Class A		each	14574-41
Funnel, poly, 65 mm		each	1083-67
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 Pipet		50/pkg	21856-96
Pipet, volumetric, 1.00 mL, Class A		each	14515-35
Pipet, volumetric, 2.00 mL, Class A		each	14515-36
Pipet, volumetric, 3.00 mL, Class A		each	14515-03
Pipet, volumetric, 4.00 mL, Class A		each	14515-04
Pipet, volumetric, 5.00 mL, Class A		each	14515-37
Pipet, volumetric, 6.00 mL, Class A		each	14515-06
Pipet, volumetric, 7.00 mL, Class A		each	14515-07
Pipet Filler, safety bulb		each	14651-00
PourRite Ampule Breaker		each	24846-00

For Technical Assistance, Price and Ordering

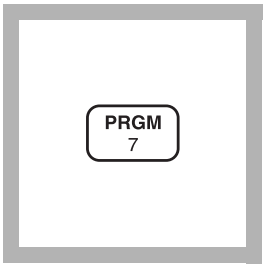
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SULFIDE (0 to 0.70 mg/L S^{2-})

For water, wastewater and seawater

Methylene Blue Method* USEPA accepted for reporting wastewater analysis**

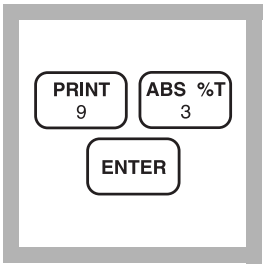


1. Enter the stored program number for sulfide (S).

Press: **PRGM**

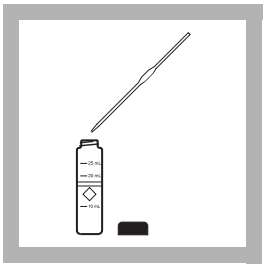
The display will show:

PRGM ?



2. Press: **93 ENTER**

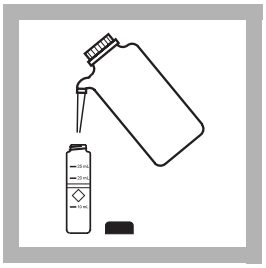
The display will show **mg/L, S** and the **ZERO** icon**.**



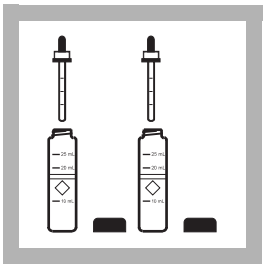
3. Pipet 25 mL of sample into a clean sample cell. This will be the prepared sample.

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis. Use a pipet to avoid agitation.*

Note: *For field testing, a 25-mL graduated cylinder may be used.*

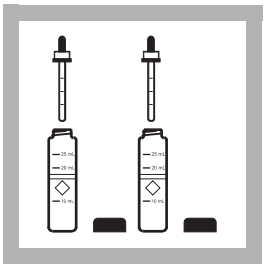


4. Fill a second sample cell with 25 mL of deionized water (the blank).



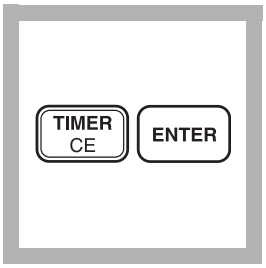
5. Add 1.0 mL of Sulfide 1 Reagent to each cell. Swirl to mix.

Note: *Use the calibrated 1-mL dropper.*



6. Add 1.0 mL of Sulfide 2 Reagent to each cell. Immediately swirl to mix.

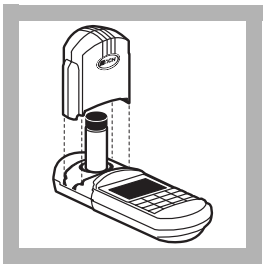
Note: *A pink color will develop, then the solution will turn blue if sulfide is present.*



7. Press:

TIMER ENTER

A 5-minute reaction period will begin.



8. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

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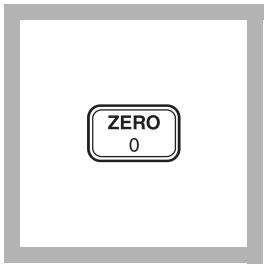
* Adapted from *Standard Methods for the Examination of Water and Wastewater*.

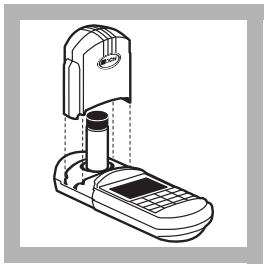
** Procedure is equivalent to USEPA method 376.2 or Standard Method 4500-S^{2-} D for wastewater.



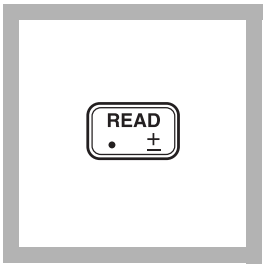
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.00 mg/L S



10. After the timer beeps, place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L sulfide will be displayed.

Note: *Some sulfide loss may occur if dilution is necessary.*

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples immediately.

Accuracy Check

Sulfide standards are unstable and must be user prepared. See Sandard Methods, 4500S^{-} for preparation and standardization directions.

Method Performance

Precision

In a single laboratory, using standard solutions of 0.73 mg/L sulfide and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ± 0.02 mg/L sulfide.

Estimated Detection Limit (EDL)

The EDL for program 93 is 0.01 mg/L S^{2-}. For more information on derivation and use of Hach's estimated detection limit, see

Section 1.

Interferences

Interfering Substance	Interference Levels and Treatments
Strong reducing substances (sulfite, thiosulfate and hydrosulfite)	Interfere by reducing the blue color or preventing its development.
Sulfide, high levels	High concentrations of sulfide may inhibit full color development and require sample dilution. Some sulfide loss may occur when the sample is diluted.
Turbidity	For turbid samples, prepare a sulfide-free blank as follows. Use it in place of the deionized water blank in the procedure. **1.** Measure 25 mL of sample into a 50-mL erlenmeyer flask. **2.** Add Bromine Water dropwise with constant swirling until a permanent yellow color just appears. **3.** Add Phenol Solution dropwise until the yellow color just disappears. Use this solution in Step 4 in place of deionized water.

Soluble Sulfides

Determine soluble sulfides by centrifuging the sample in completely filled, capped tubes and analyzing the supernatant. Insoluble sulfides are then estimated by subtracting the soluble sulfide concentration from the total sulfide result.

Summary of Method

Hydrogen sulfide and acid-soluble metal sulfides react with N, N-dimethyl-p-phenylenediamine oxalate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after dilution.

Pollution Prevention and Waste Management

Sulfide 2 Reagent contains potassium dichromate. The final solution will contain hexavalent chromium (D007) at a concentration regulated as a hazardous waste by Federal RCRA. See *Section 3* for more information on proper disposal of these materials.

SULFIDE, continued

REQUIRED REAGENTS

	Cat. No.
Sulfide Reagent Set (100 tests)	22445-00
Includes: (2) 1816-42, (2) 1817-42	

Description	Quantity Required Per Test	Units	Cat. No.
Sulfide 1 Reagent	2 mL	100 mL MDB	1816-32
Sulfide 2 Reagent	2 mL	100 mL MDB	1817-32
Water, deionized	25 mL	4 L	272-56

REQUIRED APPARATUS

Cylinder, graduated, 25 mL	1	each	508-40
Pipet, volumetric, Class A, 25.00 mL	1	each	14515-40
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Description	Units	Cat. No.
Bromine Water, 30 g/L	29 mL	2211-20
Phenol Solution, 30 g/L	29 mL	2112-20
Sodium Sulfide, hydrate	114 g	785-14

OPTIONAL APPARATUS

Bottle, Wash, 250 mL	each	620-31
Dropper, for 1 oz. bottle	each	2258-00
Flask, erlenmeyer, 50 mL	each	505-41
Standard Methods for the Examination of Water and Wastewater	each	22708-00

For Technical Assistance, Price and Ordering

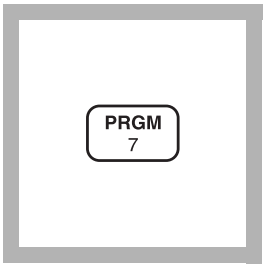
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SURFACTANTS, ANIONIC (0 to 0.300 mg/L)

For water, wastewater, and seawater

(Also called: Detergents) Crystal Violet Method*

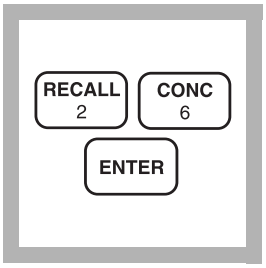


1. Enter the stored program number for Surfactants, anionic (LAS).

Press: **PRGM**

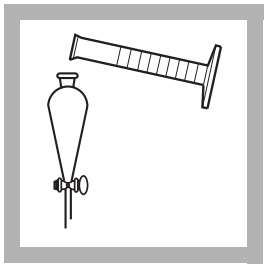
The display will show:

PRGM ?

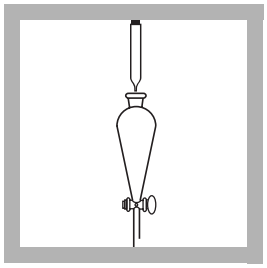


2. Press: **26 ENTER**

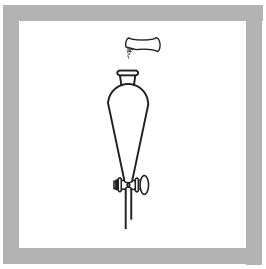
The display will show **mg/L, LAS** and the **ZERO** icon**.**



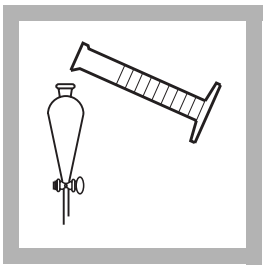
3. Fill a clean 500-mL graduated cylinder to the 300-mL mark with sample. Pour the sample into a clean 500-mL separatory funnel.



4. Add 10 mL of Sulfate Buffer Solution. Stopper the funnel. Shake the funnel for five seconds.



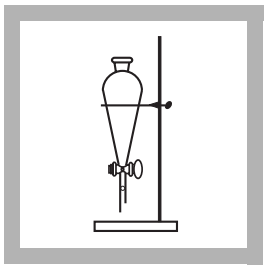
5. Add the contents of one Detergents Reagent Powder Pillow to the funnel. Stopper the funnel and shake to dissolve the powder.



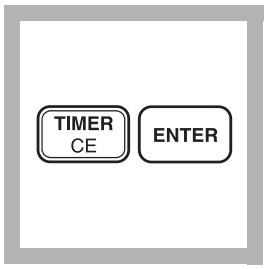
6. Add 30 mL of benzene to the funnel. Stopper the funnel and shake gently for one minute.

Note: *Spilled reagent will affect test accuracy and is hazardous to the skin and other materials.*

Note: *Use benzene only in a well-ventilated area.*



7. Place the separatory funnel in a support stand.



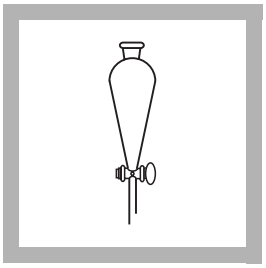
8. Press:

TIMER ENTER

A 30-minute reaction period will begin.

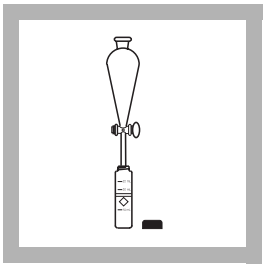
Note: *Excessive agitation may cause an emulsion, requiring a longer time for phase separation. If this occurs, remove most of the water layer, then gently agitate the funnel with a clean inert object in the funnel such as a Teflon-coated magnetic stirring bar.*

* *Analytical Chemistry*, 38, 791(1966).



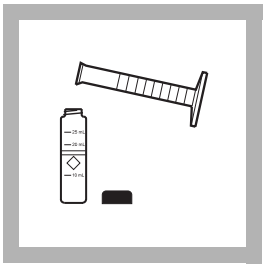
9. After the timer beeps, remove the stopper and drain the bottom water layer. Discard this layer.

Note: *Benzene solutions are a regulated waste and cannot be poured down the drain. See Section 3 for proper disposal of these materials.*

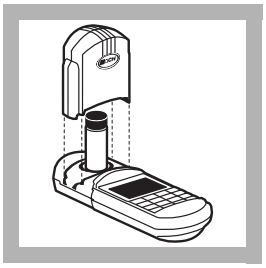


10. Drain the top benzene layer into a clean sample cell (the prepared sample).

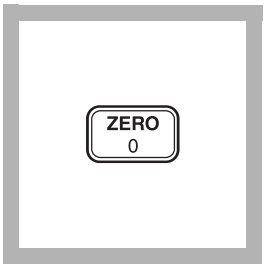
Note: *The benzene layer cannot be filtered before color measurement. Filtration removes the blue color.*



11. Fill another sample cell to the 25-mL mark with pure benzene (the blank).



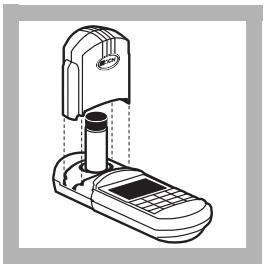
12. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.



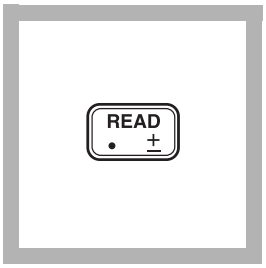
13. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.000 mg/L LAS



14. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



15. Press: **READ**

The cursor will move to the right, then the result in mg/L anionic surfactants (LAS) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Note: *Acetone may be used to clean benzene from glassware.*

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible, but they may be stored at least 24 hours by cooling to 4 °C
(39 °F). Warm to room temperature before testing.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Detergent Voluette Ampule Standard Solution, 60 mg/L as LAS (The molecular weight of linear alkylate sulfonate used to make the standard is 342).

b) Using the TenSette Pipet, add 0.1, 0.2, and 0.3 mL of standard to three 300-mL samples. Mix thoroughly.

c) Analyze each as described above. The anionic surfactants reading should increase 0.02 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* (Section 1) for more information.

Method Performance

Precision

In a single laboratory, using a standard solution of 0.150 mg/L LAS, two lots of reagent, and the instrument, a single operator obtained a standard deviation of ±0.010 mg/L LAS as anionic surfactant.

Estimated Detection Limit

The estimated detection limit for program 26 is 0.020 mg/L LAS. For more information on the estimated detection limit, see *Section 1*.

Interferences

Perchlorate and periodate ions will interfere. High amounts of chloride, such as those levels found in brines and seawater, will cause low results.

Summary of Method

Detergents, ABS (alkyl benzene sulfonate) or LAS (linear alkylate sulfonate) are determined by association with crystal violet dye and extraction of the ion-pair complex into benzene.

Pollution Prevention and Waste Management

Benzene (D018) solutions are regulated as hazardous waste by Federal RCRA. Do not pour these materials down the drain. Collect water saturated with benzene solutions for disposal with laboratory solvent wastes. See *Section 3* for more information on proper disposal of these materials.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Benzene, ACS	55 mL	500 mL	14440-49
Buffer Solution, sulfate type	10 mL	500 mL	452-49
Detergent Reagent Powder Pillow	1 pillow	25/pkg	1008-68

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968-00
Cylinder, graduated, 25 mL	1	each	508-40
Cylinder, graduated, 50 mL	1	each	508-41
Cylinder, graduated, 500 mL	1	each	508-49
Funnel, separatory, 500 mL	1	each	520-49
Ring, support, 4 inch	1	each	580-01
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06
Stand, support, 127 x 203 mm (5 x 8")	1	each	563-00

OPTIONAL REAGENTS

Acetone, ACS	500 mL	14429-49
Detergent Standard Solution, Voluette ampule, 60 mg/L as LAS, 10 mL	16/pkg	14271-10

OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 Pipet	1000/pkg	21856-28
Thermometer, -20 to 110 °C, Non-Mercury	each	26357-02

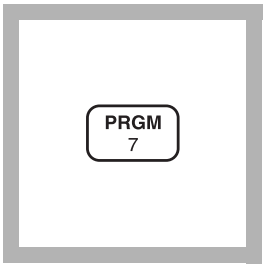
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SUSPENDED SOLIDS (0 to 750 mg/L)

Photometric Method* (Also called Nonfilterable Residue)

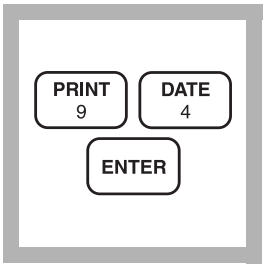


1. Enter the stored program number for suspended solids.

Press: **PRGM**

The display will show:

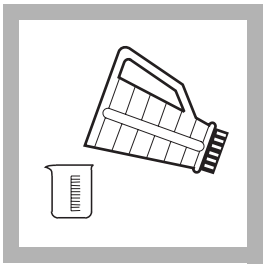
PRGM ?



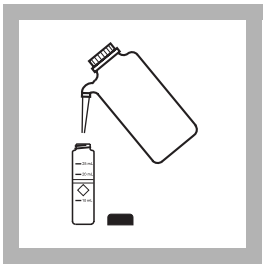
2. Press: **94 ENTER**

The display will show **mg/L, SuSld** and the **ZERO** icon**.**

3. Blend 500 mL of sample in a blender at high speed for exactly 2 minutes.

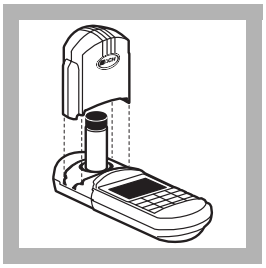


4. Pour the blended sample into a 600-mL beaker.

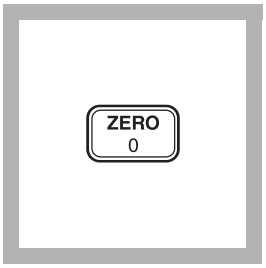


5. Fill a sample cell with 25 mL of tap water or deionized water (the blank).

Note: *Remove gas bubbles in the water by swirling or tapping the bottom of the cell on a table.*



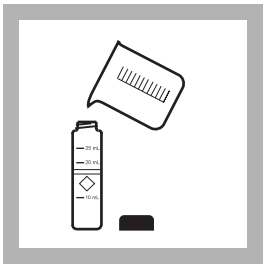
6. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.



7. Press: **ZERO**

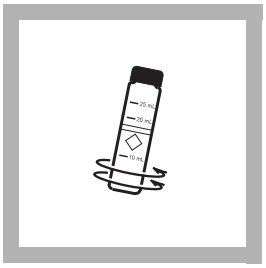
The cursor will move to the right, then the display will show:

0 mg/L SuSld

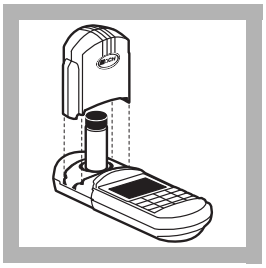


8. Stir the sample thoroughly and immediately pour 25 mL of the blended sample into a sample cell (the prepared sample).

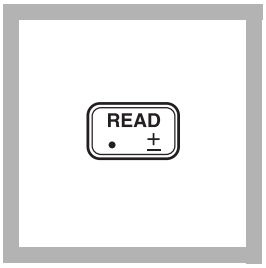
* Adapted from *Sewage and Industrial Wastes*, 31, 1159 (1959).



9. Swirl the prepared sample cell to remove any gas bubbles and uniformly suspend any residue.



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L suspended solids will be displayed.

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible after collection. The sample may be stored seven days by cooling to 4 °C (39 °F).

Method Performance

Precision

In a single laboratory, using a standard solution of 847.4 mg/L Suspended Solids with the instrument, a single operator obtained a standard deviation of ±18.2 mg/L Suspended Solids.

For more information on Hach's precision statement, see *Section 1*.

Estimated Detection Limit

The estimated detection limit for program 94 is 22.1 mg/L Suspended Solids. For more information on the estimated detection limit, see *Section 1*.

Interferences

Calibration for this test is based on parallel samples using the gravimetric technique on sewage samples from a municipal sewage plant. For most samples, this calibration will provide satisfactory results. When higher accuracy is required, run parallel photometric and gravimetric determinations with portions of the same sample. The new calibration should be made on your particular sample using a gravimetric technique as a basis.

Summary of Method

This method of determining suspended solids is a simple, direct measurement which does not require the filtration or ignition and weighing steps that gravimetric procedures do. The USEPA specifies the gravimetric method for solids determinations, while this method is often used for checking in-plant processes.

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Beaker, 600 mL, low form	1	each	1080-52
Blender, 1.2 L, 120 V	each	each	26161-00
Blender, 1.2 L, 240 V	each	each	26161-02
Cylinder, graduated, 500 mL, poly	1	each	1081-49
Pipet, serologic, 25 mL	1	each	2066-40
Pipet, Filler, safety bulb	1	each	14651-00

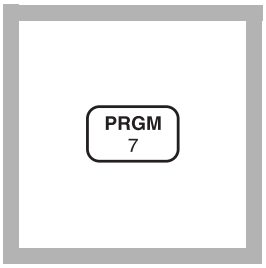
OPTIONAL APPARATUS

Stirring Rod, glass		3/pkg	1770-01
Wash Bottle, 250 mL		each	620-31

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

TANNIN AND LIGNIN (0 to 9.0 mg/L)

Tyrosine Method*

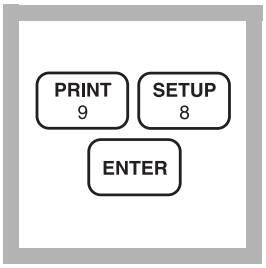


1. Enter the stored program number for tannin and lignin.

Press: **PRGM**

The display will show:

PRGM ?



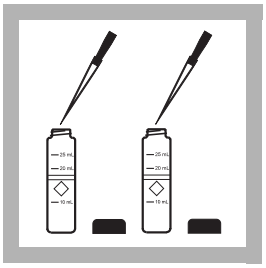
2. Press: **98 ENTER**

The display will show **mg/L, tanic** and the **ZERO** icon**.**

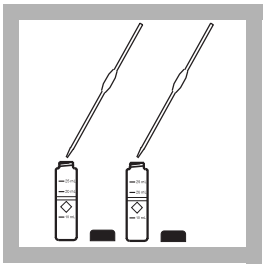
3. Fill a clean sample cell to the 25-mL mark with deionized water (the blank).

4. Fill a clean sample cell to the 25-mL mark with sample (the prepared sample).

Note: *Filter turbid samples and report results as mg/L soluble tannic acid.*

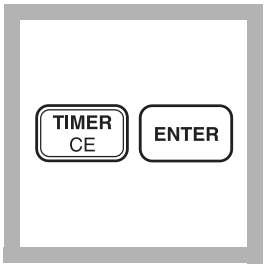


5. Pipet 0.5 mL of TanniVer 3 Tannin-Lignin Reagent into each cell. Swirl to mix.



6. Pipet 5.0 mL of Sodium Carbonate Solution into each cell. Swirl to mix.

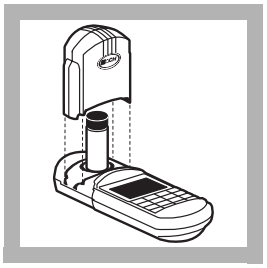
Note: *A blue color will develop if tannins and/or lignins are present.*



7. Press:

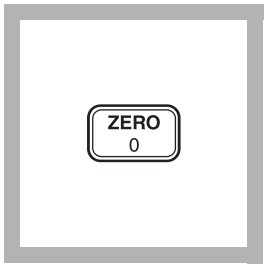
TIMER ENTER

A 25-minute reaction period will begin.



8. Place the blank in the cell holder. Tightly cover the sample cell with the instrument cap.

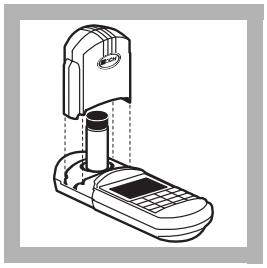
* Adapted from Kloster, M.B., *Journal American Water Works Association*, Vol. 66, No. 1, p. 44 (1974).



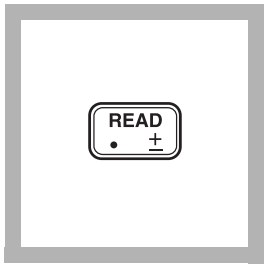
9. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.0 mg/L tanic



10. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L tannic acid will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

Sampling and Storage

Collect samples in clean plastic or glass bottles.

Accuracy Check

Standard Solution Method

Prepare a 200-mg/L tannic acid standard solution by dissolving 0.200 grams of tannic acid in deionized water and diluting to 1000 mL. Prepare this solution monthly. A 2.0 mg/L tannic acid standard is prepared by diluting 10.00 mL of the stock solution to 1000 mL with deionized water. Prepare this standard daily.

Method Performance

Precision

In a single laboratory, using standard solutions of 4.0 mg/L tannic acid and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.1 mg/L tannic acid.

Estimated Detection Limit

The estimated detection limit for program 98 is 0.1 mg/L tannin and lignin. For more information on the estimated detection limit, see *Section 1*.

TANNIN AND LIGNIN, continued

Interferences

Substance	Interference Level and Treatment
Ferrous iron	Causes a positive interference. Two mg/L of ferrous iron produces a color equivalent to about 1 mg/L of tannic acid. To eliminate interference of ferrous iron up to 20 mg/L, add one 0.2-g scoop of sodium pyrophosphate to the sample before testing.
Sulfide	Eliminated by adding 1 mL of formaldehyde to the sample before testing the sample.

Summary of Method

This test measures all hydroxylated aromatic compounds, including tannin, lignin, phenol and cresol. This method produces a blue color proportional to the amount of these compounds present in the sample. Report results as total tannin and lignin expressed as mg/L tannic acid.

REQUIRED REAGENTS

	Cat. No.
Tannin and Lignin Reagent Set (up to 100 tests)	22446-00
Includes: (2) 675-49, (1) 2560-42	

Description	Quantity Required Per Test	Unit	Cat. No
Sodium Carbonate Solution	10 mL	500 mL	675-49
TanniVer 3 Tannin-Lignin Reagent	1 mL	100 mL	2560-42
Water, deionized	25 mL	4 L	272-56

REQUIRED APPARATUS

Pipet Filler, safety bulb	1	each	14651-00
Pipet, volumetric, Class A, 5.0 mL	1	each	14515-37
Pipet, volumetric, Class A, 0.5 mL	1	each	14515-34
Sample Cell, 10-20-25-mL, w/ cap	2	6/pkg	24019-06

OPTIONAL REAGENTS

Formaldehyde	100 mL	2059-32
Sodium Pyrophosphate, ACS	50 g	14295-25
Tannic Acid	113 g	791-14

OPTIONAL APPARATUS

Description	Unit	Cat. No
Balance, analytical, 115 V	each	28014-01
Balance, analytical, 230 V	each	28014-02
Cylinder, graduated, 25 mL	each	508-40
Filter Paper, folded, 12.5 cm	100/pkg	1894-57
Flask, volumetric, 1000 mL	each	14547-53
Funnel, poly, 65 mm	each	1083-67
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 Pipet	50/pkg	21856-96
Pipet Tips, for 19700-01 Pipet	1000/pkg	21856-28
Pipet, volumetric, Class A, 10.00 mL	each	14515-38
Pipet, Filler, safety bulb	each	14651-00
Spoon, measuring, 0.2 g	each	638-00
Weighing Boat, 67/47 mm	500/pkg	21790-00

For Technical Assistance, Price and Ordering

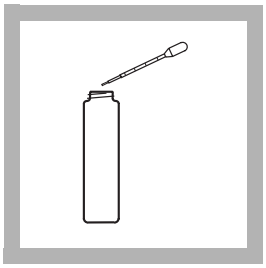
In the U.S.A.—Call 800-227-4224

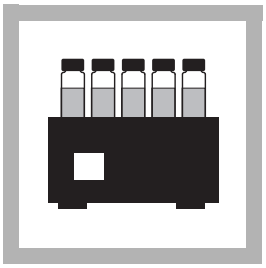
Outside the U.S.A.—Contact the Hach office or distributor serving you.

TOXTRAK™ TOXICITY TEST*

Colorimetric Method**

Inoculum Development



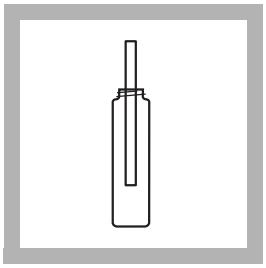


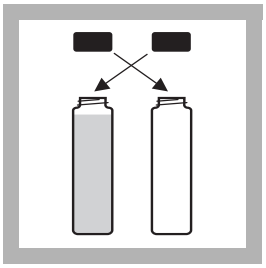
Using Indigenous Biomass

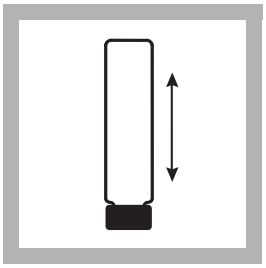
1. Using one of the dropper pipets provided, add 1.0 mL of source culture to a Tryptic Soy Broth Tube.

2. Incubate at 37 °C until the vial contents are visibly turbid (turbidity indicates bacterial growth).

Inoculum Development Using Aqua QC-Stiks







1. Inoculate a Lauryl Tryptose broth tube with an *E. coli* Aqua QC-Stik™ according to the instructions that come with the stick.

2. Incubate the Lauryl Tryptose Broth Tube at 35°C (95°F) until the medium is visibly turbid (approxamately 12 hours). Turbidity develops much faster in an incubator than at room temperature.

3. Inoculate a new Lauryl Tryptose Broth Tube by first inverting the tube and switching the caps of the two tubes.

In this way, several medium vials can be inoculated from one Aqua–QC Stick™.

4. Invert the new tube. After incubation, this new vial may be used in subsequent tests.

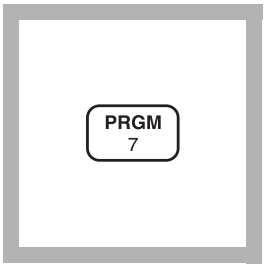
If toxicity tests will be run on consecutive days, inoculum may be kept several days at room temperature.

Cultures 10 to 72 hours old give best results.

* U.S. Patent number 5,413,916.

** Liu, D., *Bull. Environ. Contam. Toxicol.* 26, 145-149 (1981).

Colorimetric Reaction

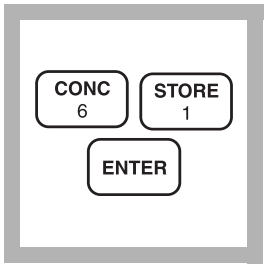


1. Enter the stored program number for toxicity.

Press: **PRGM**

The display will show:

PRGM ?

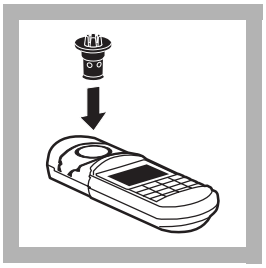


2. Press: **61 ENTER**

The display will show:

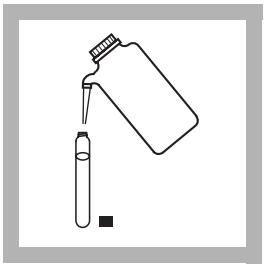
ABS 610 nm

and the zero icon.

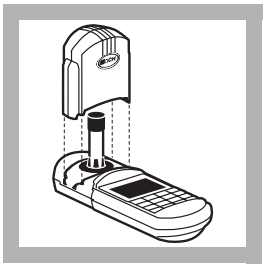


3. Insert the TNT/COD Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

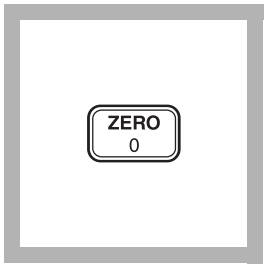
Note: *A diffuser band covers the light path holes on the adapter to give increased performance. The band should NOT be removed.*



4. Fill a Test 'N Tube vial with deionized water. Label this vial as the "blank". Wipe the outside of all the vials with a tissue to remove fingerprints and smudges.



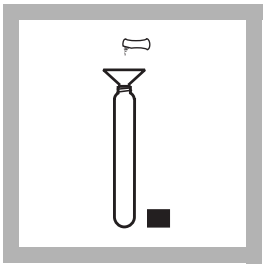
5. Place the blank in the adapter. Tightly cover the vial with the instrument cap.



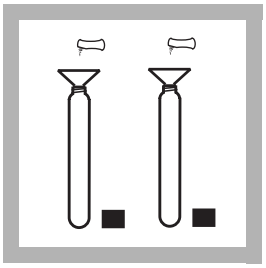
6. Press: **ZERO**

The cursor will move to the right, then the display will show:

0.000 ABS

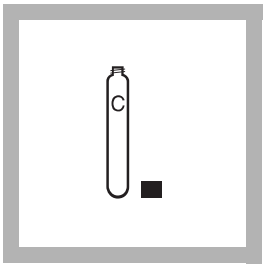


7. Label a vial "control." Open one ToxTrak Reagent Powder Pillow and add the contents to the empty reaction vial.

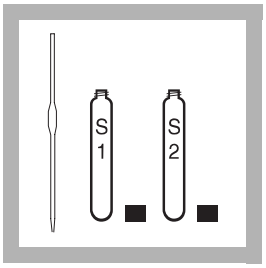


8. Label each sample or dilution vial clearly. Add the contents of one ToxTrak Reagent Powder Pillow to each labeled vial.

TOXTRAK TOXICITY TEST, continued

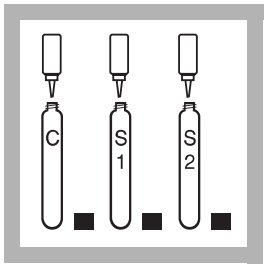


9. Add 5.0 mL of deionized water to the control tube.

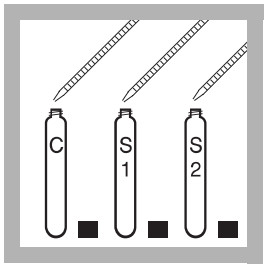


10. Add 5.0 mL of the sample (or dilution) to each sample vial.

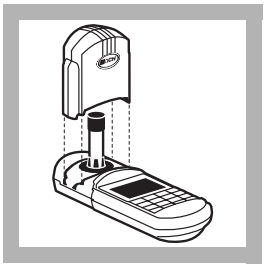
Note: *To determine the approximate threshold level of toxicity for a sample, dilute 1 mL of sample to 10 mL of deionized water and run the test. Continue to make serial 1:10 dilutions until a level is reached which gives a 0% Inhibition in Step 18.*



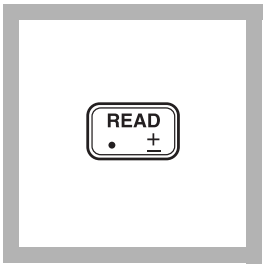
11. Add 2 drops of Accelerator Solution to each vial. Cap and invert to mix.



12. Add 0.5 mL of inoculum (previously prepared) to each vial. Cap and invert to mix.



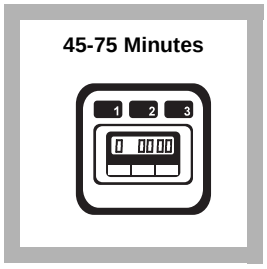
13. Place the control vial in the cell holder. Tightly cover the vial with the instrument cap.



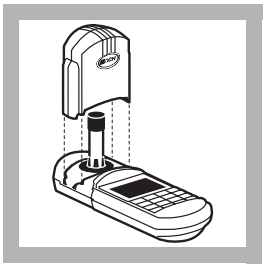
14. Press: **READ**

The cursor will move to the right, then the result in ABS will be displayed. Record the absorbance of the "control" vial.

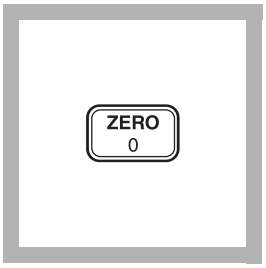
15. Repeat Steps 13-14 for all samples and dilutions. Be sure to record each absorbance.



16. Allow the solutions in the tubes to react until the absorbance of the **control tube** decreases 0.60 ±0.10.
This should take about 45-75 minutes.



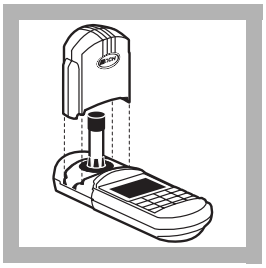
17. After the absorbance of the "control" vial has decreased 0.60 ±0.10 absorbance units, place the blank in the adapter. Tightly cover the vial with the instrument cap.



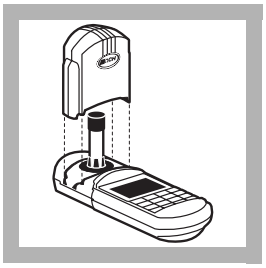
18. Press: **ZERO**

The cursor will move to the right, then the display will show:

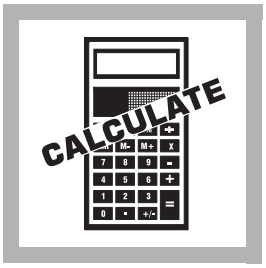
0.000 ABS



19. Place the "control" vial in the cell holder. Tightly cover the vial with the instrument cap. Record the absorbance value of the control.



20. Place each sample or dilution vial in the cell holder. Tightly cover the vial with the instrument cap. Record each absorbance value.



21. Calculate the % Inhibition as follows:

$$\%I = \left[1 - \left(\frac{\Delta Abs\ sample}{\Delta Abs\ control}\right)\right] \times 100$$

ΔA is the initial absorbance value minus the final absorbance value.

See the example following this step.

Note: *Some toxins increase respiration and will give a negative % inhibition on all respiration-based toxicity tests. After repeated testing, samples which always give a % inhibition in Step 21 that is more negative than –10% should be considered toxic.*

Example

The control tube (C) has an initial absorbance of 1.6 and decreases to 1.0 Abs. The sample tube has an initial absorbance of 1.7 and decreases to 1.3 Abs.

$\Delta Abs.\ Sample = 1.7 - 1.3 = 0.4$ $\Delta Abs.\ Control = 1.6 - 1.0 = 0.6$

$$\%I = \left(1 - \left(\frac{0.4}{0.6}\right)\right) \times 100$$

$\%I = 33.3$

Interpreting Results

The Percent Inhibition results obtained are only a relative measurement. They do not represent a true quantitative measurement of toxic concentration. The Percent Inhibition does not necessarily increase in direct proportion to the concentration of toxins. To determine the minimum inhibition concentration of a toxin, it is possible to make tenfold dilutions of the sample and determine the Percent Inhibition for the dilutions. When the sample is diluted so that no inhibition is observed, this is the No Observed Effect Concentration (NOEC).

Due to the many variables involved in the test, the limits of detection are on the order of 10% Inhibition. This would correlate to the Lowest Observable Effect Concentration (LOEC). If a sample shows less that 10% Inhibition, repeat the test. After several repetitions, look at the series of data to determine the likelihood of toxicity. Results below 10% are not reliable, but can be used to surmise some presence of toxicity if they are consistent. See the table below.

Toxicity Results

Data Points: Percent Inhibition	Conclusion
7%, 9%, 5%, 8%, 5%	May be slightly toxic
7%, –4%, 5%, 5%, 1%	Most likely not toxic
–7%, –9%, 5%, –8%, –5%	May be slightly toxic

Some toxins will increase respiration and will give a negative Percent Inhibition on this and all other respiration-based toxicity tests. After repeated testing, samples that always give a Percent Inhibition that is more negative than –10% should be considered toxic.

Disposal of Test Cultures

Dispose of active bacterial cultures by using one of these methods:

1. Autoclave used test containers at 121 °C for 15 minutes at 15 pounds of pressure. Once the containers are sterile, pour the contents down the drain with running water. The reaction tubes may be washed
and re-used.

2. Sterilize test containers by using a 1:10 dilution of commercial

laundry bleach. Pour the test container contents and test containers into the bleach solution. Allow 10-15 minutes of contact time with the bleach solution. Then pour the liquid down the drain and wash the reaction tubes for re-use.

Summary of Method

Resazurin is a redox-active dye, which changes from pink to blue when it is reduced. Bacterial respiration occurring in the sample reduces resazurin. If toxic substances are present, they inhibit the rate of resazurin reduction. The sample color is compared to a toxin-free control tube to determine how toxic the sample is to an indigenous culture or a culture of *E. coli*. A chemical accelerant reduces the reaction time of the procedure.

TOXTRAK TOXICITY TEST, continued

REQUIRED REAGENTS

Description	Cat. No.
ToxTrak Reagent Set (25 tests)	25972-00
Includes: (1) 25607-66, (1) 25608-36, (1) 22777-00, (1) 24092-32	

Description	Quantity Required Per Test	Unit	Cat. No.
Aqua QC–Stiks, Escherichia Coli	1	3 cultures	27063-03
Sodium Thiosulfate Standard Solution	varies	100 mL	24092-32
ToxTrak Reagent Powder Pillows	1 pillow	50/pkg	25607-66
ToxTrak Accelerator Solution	2 drops	15 mL SCDB	25608-36
Tryptic Soy Broth Tubes	1	15/pkg	22777-00
Tube, culture, with cap	1	10/pkg	20962-08
Water, deionized	varies	200 mL	272-29

REQUIRED APPARATUS

Cap, White	1	6/pkg	22411-06
Clippers, to open powder pillows	1	each	936-00
COD/TNT Adapter	1	each	48464-00
Dropper Pipet, 1 mL	varies	10/pkg	21247-20
Forceps, flat square tip	1	each	14537-00
Pipet, volumetric, 5.00 mL, Class A	1	each	14515-37
Pipet Filler, Safety Bulb	1	each	14651-00
Vial, Test ‘N Tube	1	6/pkg	25831-25

OPTIONAL APPARATUS

Burner, Alcohol, 60 mL	each	20877-42
Burner, Bunsen	each	21627-00
Germicidal Cloth	50/pkg	24632-00
Incubator, Dri Bath, 25 well, 120/230 V	each	45900-00
Incubator, Dri Bath, 25 well, 120/230 V, with European power cord	each	45900-02
Pipet, Sterile Transfer	15/pkg	22325-12
Timer	each	26305-00

For Technical Assistance, Price and Ordering

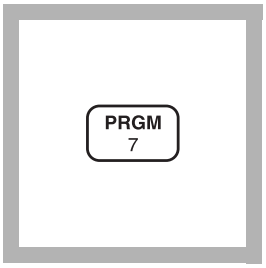
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

TURBIDITY (0 to 1000 FAU)

For water, wastewater, and seawater

Absorptometric Method*



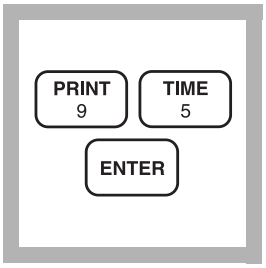
1. Enter the stored program number for turbidity.

Press: **PRGM**

The display will show:

PRGM ?

Note:
1 FAU=1 NTU=1 FTU when measuring formazin. These are not equivalent when measuring other types of standards or samples.

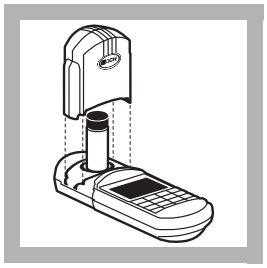


2. Press: **95 ENTER**
The display will show **FAU** and the **ZERO** icon.

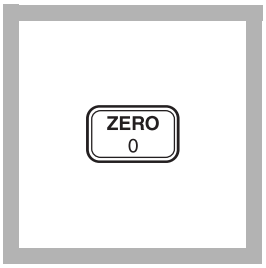
3. Fill a sample cell with 10 mL of deionized water (the blank).

Note: *Wipe the surface of the cell with a soft cloth.*

Note: *For highly colored samples, use a filtered portion of sample in place of the deionized water.*



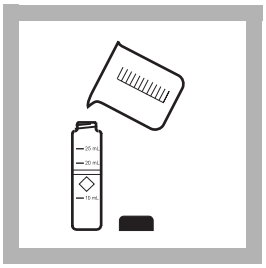
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**

The cursor will move to the right, then the display will show:

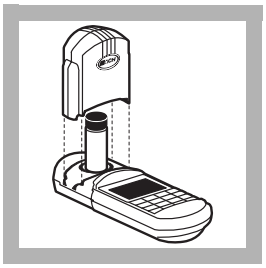
0 FAU



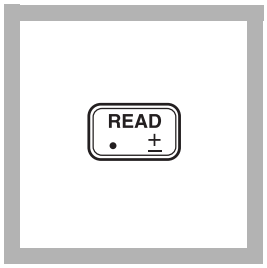
6. Fill another sample cell with 10 mL of sample.

Note: *Mix the sample well before transferring it to the sample cell.*

Note: *Wipe the surface of the cell with a soft cloth.*



7. Place the sample cell into the cell holder. Tightly cover the sample cell with the instrument cap.



8. Press: **READ**

The cursor will move to the right, then the result in Formazin Attenuation Units (FAU) will be displayed.

Note: *Standard Adjust may be performed using a prepared standard (see Section I).*

* Adapted from FWPCA *Methods for Chemical Analysis of Water and Wastes*, 275 (1969)

Sampling and Storage

Collect samples in clean plastic or glass bottles. Analyze samples as soon as possible. Store samples up to 48 hours by cooling to 4 °C (39 °F). Analyze the sample at the same temperature as it was collected.

Accuracy Check

Standard Solution Method

The stored program has been calibrated using formazin, the primary standard for turbidity. A 200 FAU formazin solution for checking the accuracy of the test can be prepared using the following procedure.

1. Pipet 5.00 mL of a 4000 NTU Formazin stock solution into a 100-mL volumetric flask.

2. Dilute to the mark with deionized water. Prepare this daily.

Convenient stabilized turbidity stock solution (200 NTU StablCal™ Standard) is available from Hach.

Standard Adjust

To adjust the calibration curve using the reading obtained with the 200 FAU formazin standard, press the **SETUP** key and scroll (using the arrow keys) to the STD setup option. Press **ENTER** to activate the standard adjust option. Then enter **200** to edit the standard concentration to match that of the standard used. Press **ENTER** to complete the adjustment. See *Section 1, Standard Curve Adjustment* for more information.

Method Precision

Precision

In a single laboratory, using a turbidity standard solution of 200 FAU with the instrument, a single operator obtained a standard deviation of ±2 FAU.

Estimated Detection Limit

The estimated detection limit for program 95 is 21 FAU. For more information on the estimated detection limit, see *Section 1*.

Interferences

Interfering Substance	Interference Levels and Treatments
Air Bubbles	Interfere at all levels. Degass samples using the Degassing Kit or an ultrasonic bath.
Color	Interferes if the color absorbs light at 520 nm.
Temperature extremes	May interfere by changing the turbidity of the sample. Analyze samples as soon as possible after collection. Analyze at the same temperature as the original sample.

Summary of Method

This turbidity test measures an optical property of the sample which results from scattering and absorption of light by particles in the sample. The amount of turbidity measured depends on variables such as the size, shape, color, and refractive properties of the particles.

This procedure is calibrated using formazin turbidity standards and the readings are in terms of Formazin Attenuation Units (FAU). This test cannot be used for USEPA reporting purposes, but it may be used for daily in-plant monitoring. One FAU is equivalent to one Nephelometric Turbidity Unit (NTU) of Formazin. However, the optical method of measurement for FAU is very different than the NTU method (1 NTU = 1 FTU = 1 FAU when traced to formazin primary standards.)

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06

REQUIRED REAGENTS

Description	Units	Cat. No.
Formazin Stock Solution, 4000 NTU	500 mL	2461-49
Silicone Oil	15 mL DB	1269-36
StablCal Stabilized Turbidity Standard, 200 NTU	500 mL	26604-49
Water, deionized	4 L	272-56

OPTIONAL APPARATUS

Description	Units	Cat. No.
Bath, ultrasonic	each	24895-00
Bottle, wash, 250 mL	each	620-31
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, filter, 500 mL	each	546-49
Filter Holder	each	13529-00
Filter Pump, aspirator	each	2131-00
Oiling cloth, for applying silicone oil	each	26873-00
Pipet Filler, safety bulb	each	14651-00
Pipet, volumetric, Class A, 5.0 mL	each	14515-37
Sample Degassing Kit	each	43975-00
Stopper, rubber, one-hole, No. 7	6/pkg	2119-07
Tubing, rubber, 5/16” I.D.	12 feet	560-19
Tweezers, plastic	each	14282-00

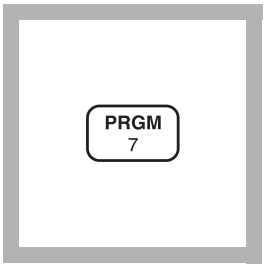
For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

VOLATILE ACIDS (0 to 2800 as mg/L HOAc)

Esterification Method*



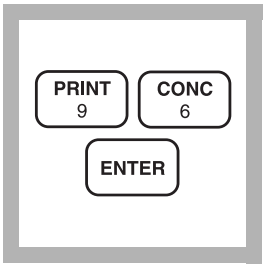
1. Enter the stored program number for Volatile Acids as acetic acid (HOAc).

Press: **PRGM**

The display will show:

PRGM ?

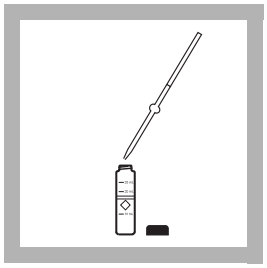
Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **96 ENTER**

The display will show **mg/L, HOAc** and the **ZERO** icon**.**

Note: *If high levels of dissolved solids or mineral acids are present, distill as described in the Hach Distillation Apparatus manual.*



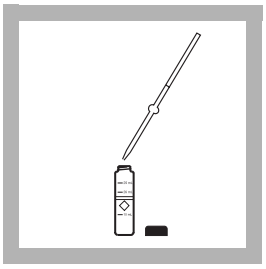
3. Pipet 0.5 mL of deionized water into a dry 25-mL sample cell (the blank).

Note: *Use a Class A or TenSette Pipet.*

Note: *Adjust the pH of stored samples before analysis.*

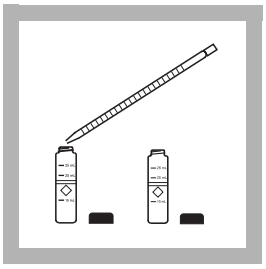
4. Filter or centrifuge 25 mL of the sample.

Note: *Centrifugation is faster than filtration.*

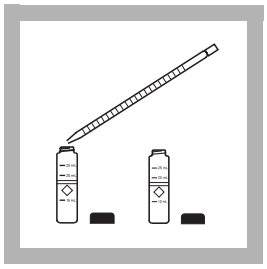


5. Pipet 0.5 mL of the filtrate or supernatant into another dry 25-mL sample cell (the prepared sample).

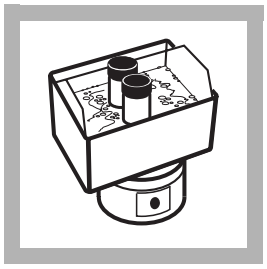
Note: *Use a Class A or TenSette Pipet.*



6. Pipet 1.5 mL of ethylene glycol into each sample cell. Swirl to mix.



7. Pipet 0.2 mL of 19.2 N Sulfuric Acid Standard Solution into each cell. Swirl to mix.

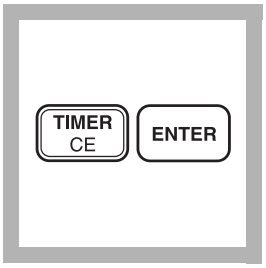


8. Place both cells into a boiling water bath.

Note: *Samples may be boiled in a 600-mL beaker.*

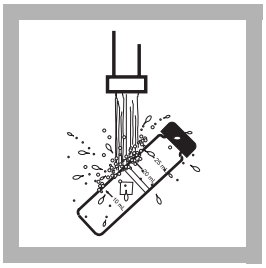
* Adapted from *The Analyst*, 87, 949 (1962)

VOLATILE ACIDS, continued

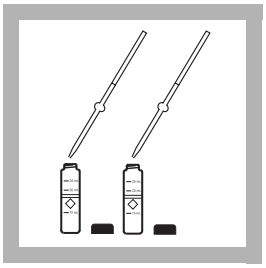


9. Press: **TIMER ENTER**

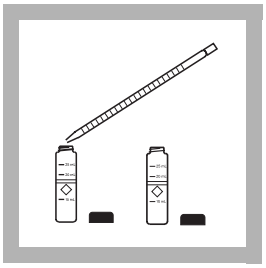
A 3-minute reaction period will begin.



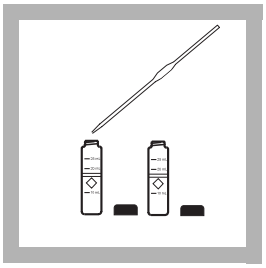
10. When the timer beeps, cool solutions to 25 °C (until cells feel cool) with running tap water. Then dry the cells with a soft cloth.



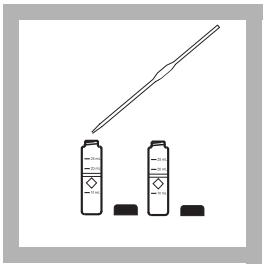
11. Pipet 0.5 mL of Hydroxylamine Hydrochloride Solution into each cell. Swirl to mix.



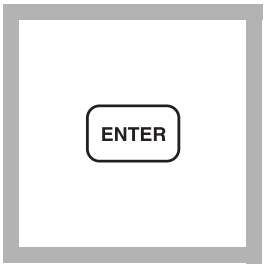
12. Pipet 2.0 mL of 4.5 N Sodium Hydroxide Standard Solution into each cell. Cap and invert to mix.



13. Add 10 mL of Ferric Chloride Sulfuric Acid Solution to each cell. Cap and invert to mix.



14. Add 10 mL of deionized water to each cell. Cap and invert to mix.

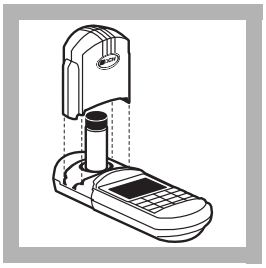


15. The display will show: **3:00 TIMER 2**

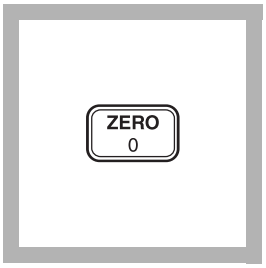
Press: **ENTER**

A 3-minute reaction period will begin.

Note: *After this three-minute reaction period, proceed immediately through steps 16-19.*



16. When the timer beeps, immediately place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

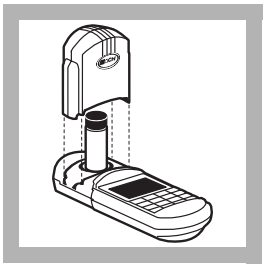


17. Press: **ZERO**

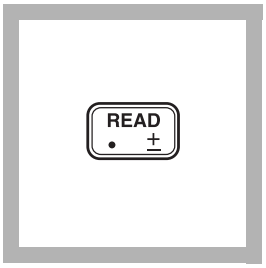
The cursor will move to the right, then the display will show:

0 mg/L HOAc

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



18. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



19. Press: **READ**

The cursor will move to the right, then the result in mg/L Volatile Acids as acetic acid will be displayed.

Sampling and Storage

Collect samples in plastic or glass bottles. Analyze samples as soon as possible after collection. Samples can be stored up to 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before testing.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Volatile Acids PourRite Ampule Standard Solution, 62,500 mg/L as acetic acid.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard, respectively, to three 25-mL graduated mixing cylinders, each containing 25 mL of filtered sample. Stopper. Shake well to mix.

c) Remove a 0.5 mL aliquot of sample from each cylinder; add to three dry sample cells. Analyze all three samples along with the original test sample beginning with Step 5 of the procedure. The volatile acid concentration should increase 250 mg/L volatile acids as acetic acid for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1*.

Standard Solution Method

Prepare a 500 mg/L volatile acid standard by using the TenSette Pipet to add 0.8 mL of a Volatile Acids PourRite Ampule Standard Solution (62,500 mg/L as acetic acid) to a 100-mL volumetric flask. Dilute to volume with deionized water. Stopper and invert to mix.

Method Performance

Precision

In a single laboratory, using a standard solution of 500 mg/L volatile acids as acetic acid and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±8 mg/L.

Estimated Detection Limit

The estimated detection limit for program 96 is 17 mg/L HOAc. For more information on the estimated detection limit, see *Section 1*.

Summary of Method

The volatile acids test is designed specifically for the determination of volatile acids in digestor sludges. The method is based on esterification of the carboxylic acids present and determination of the esters by the ferric hydroxamate reaction. All volatile organic acids present are reported as their equivalent mg/L acetic acid.

REQUIRED REAGENTS

	Cat. No.
Volatile Acids Reagent Set (90 tests)	22447-00
Includes: (1) 2039-53, (2) 2042-53, (1) 818-42, (1) 2040-53, (1) 2038-32	

Description	Quantity Required Per Test	Units	Cat. No.
Ethylene Glycol	3 mL	1000 mL	2039-53
Ferric Chloride-Sulfuric Acid Solution	20 mL	1000 mL	2042-53
Hydroxylamine Hydrochloride Solution, 100 g/L	1 mL	100 mL	818-42
Sodium Hydroxide Standard Solution, 4.5 N	4 mL	1000 mL	2040-53
Sulfuric Acid Standard Solution, 19.2 N	0.4 mL	100 mL	2038-32
Water, deionized	20.5 mL	4 L	272-56

VOLATILE ACIDS, continued

REQUIRED APPARATUS

Description	Quantity Required Per Test	Units	Cat. No.
Cots, finger	2	2/pkg	14647-02
Cylinder, graduated, 10 mL	1	each	508-38
Filter Paper, folded, 12.5 cm	1	100/pkg	1894-57
Flask, erlenmeyer, 50 mL	1	each	505-41
Funnel, poly, 65 mm	1	each	1083-67
Hot Plate, circular, 3.5-inch diameter	1	each	12067-01
Pipet Filler, safety bulb	1	each	14651-00
Pipet, serological, 2 mL	2	each	532-36
Pipet, volumetric, Class A, 0.5 mL	3	each	14515-34
Pipet, volumetric, Class A, 10.00 mL	3	each	14515-38
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06
Water Bath and Rack	1	each	1955-55

OPTIONAL REAGENTS

Volatile Acids Standard Solution, PourRite ampule, 62,500 mg/L as acetic acid, 10 mL		16/pkg	14270-10

OPTIONAL APPARATUS

Ampule Breaker, PourRite		each	24846-00
Beaker, 600 mL		each	500-52
Bottle, wash, 500 mL		each	620-11
Centrifuge, laboratory, 115 Vac		each	26765-00
Centrifuge, laboratory, 230 Vac		each	26765-02
Centrifuge Tubes, 15 mL		10/pkg	22787-39
Centrifuge Tube Caps		20/pkg	25852-20
Cylinder, graduated, mixing, 25 mL		each	1896-40
Cylinder, graduated, plastic, 250 mL		each	1081-46
Distillation Apparatus		each	22653-00
Distillation Heater and Support Apparatus		each	22744-00
Flask, volumetric, Class A, 100 mL		each	14574-42
Pipet, TenSette, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette Pipet		1000/pkg	21856-28
Pipet, TenSette, 1.0 to 10.0 mL		each	19700-10
Pipet Tips, for 19700-10		50/pkg	21997-96

For Technical Assistance, Price and Ordering

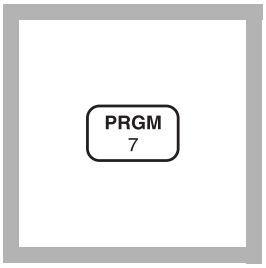
In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

ZINC (0 to 3.00 mg/L Zn)

For water and wastewater

Zincon Method* USEPA approved for wastewater analysis (digestion needed; see Section 2)**



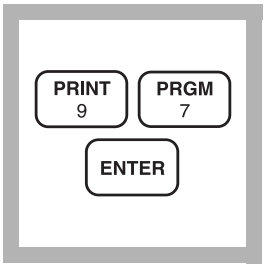
1. Enter the stored program number for zinc (Zn).

Press: **PRGM**

The display will show:

PRGM ?

Note: *For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).*



2. Press: **97 ENTER**

The display will show **mg/L, Zn** and the **ZERO** icon**.**

Note: *Total zinc requires a prior digestion; use either the Digesdahl or mild digestion (Section 2).*

Note: *Adjust the sample to pH 4-5; see Sampling and Storage following these steps.*

3. Fill a 25-mL sample cell with 20 mL of sample.

Note: *Rinse glassware with 1:1 hydrochloric acid and deionized water before use.*

Note: *If samples cannot be analyzed immediately, see Sampling and Storage.*

4. Add the contents of one ZincoVer 5 Reagent Powder Pillow. Cap. Invert several times to completely dissolve the powder. If the sample does not turn orange, see the note below.

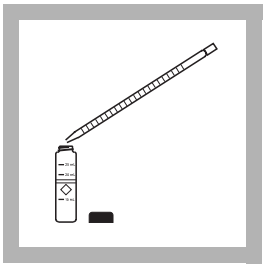
Note: *Powder must be completely dissolved or inconsistent results may occur.*

Note: *The sample should be orange. If it is brown or blue, dilute the sample and repeat the test. Either the zinc concentration is too high or an interference is present.*

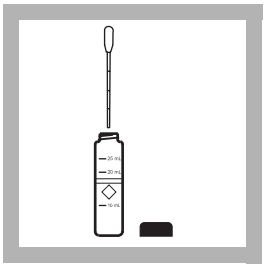
Caution: **ZincoVer 5 contains cyanide and is very poisonous if taken internally or inhaled. Do not add to an acidic sample. Store away from water and acids.**

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*

** *Federal Register,* 45 (105) 36166 (May 29, 1980).

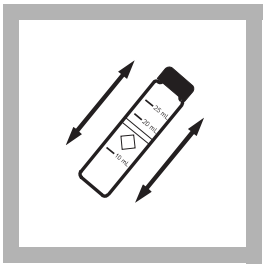


5. Measure 10 mL of the orange solution into another sample cell (the blank).



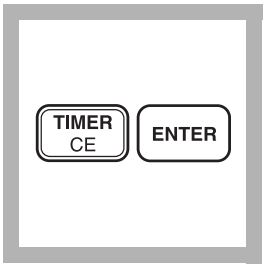
6. Add 0.5 mL of cyclohexanone to the remaining orange solution in the first sample cell (the prepared sample).

Note: *Use a plastic squeezer. Rubber bulbs may contaminate the cyclohexanone.*



7. Tightly cap the cell. Shake vigorously for 30 seconds (the prepared sample).

Note: *The sample will be red-orange, brown or blue, depending on the zinc concentration.*

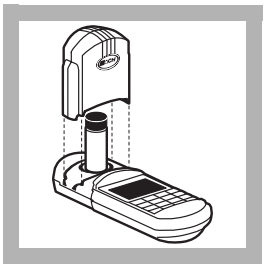


8. Press:

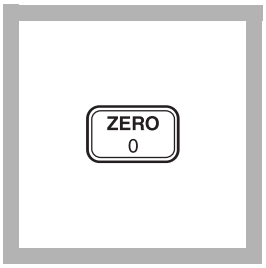
TIMER ENTER

A 3-minute reaction period will begin.

Note: *Steps 9-11 must be completed within 10 minutes after the timer beeps.*



9. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

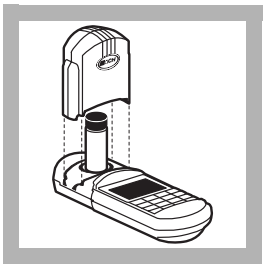


10. Press: **ZERO**

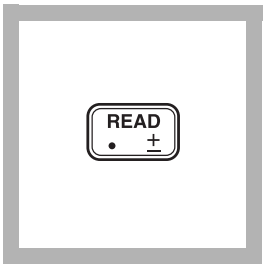
The cursor will move to the right, then the display will show:

0.00 mg/L Zn

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1.*



11. Immediately place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**

The cursor will move to the right, then the result in mg/L Zn will be displayed.

Note: *Standard Adjust may be performed using a prepared 0.50 mg/L standard. See Section 1.*

Sampling and Storage

Collect samples in acid-washed plastic bottles. For storage, adjust the pH to 2 or less with nitric acid (about 2 mL per liter). The preserved samples can be stored up to six months at room temperature.

Adjust the pH to 4 to 5 with 5.0 N sodium hydroxide before analysis. Do not exceed pH 5, as zinc may be lost as a precipitate. Correct the test result for volume additions; see *Sampling and Storage, Volume Additions*, in *Section 1* for more information.

If only dissolved zinc is to be determined, filter the sample before the
acid addition.

Accuracy Check

Standard Additions Method

a) Snap the neck off a Zinc PourRite Ampule Standard, 25 mg/L Zn.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25-mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The zinc concentration should increase 0.1 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section 1* for more information.

Standard Solution Method

Prepare a 0.50 mg/L zinc standard solution by diluting 5.00 mL of Zinc Standard Solution, 100 mg/L as Zn, to 1000 mL with deionized water in a Class A 1000-mL volumetric flask. Prepare this solution daily. Use this solution as the sample and perform the zinc procedure as described above.

Method Performance

Precision

In a single laboratory, using a standard solution of 1.50 mg/L Zn and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±0.02 mg/L Zn.

Estimated Detection Limit (EDL)

The EDL for program 97 is 0.02 mg/L Zn. For more information

on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

The following may interfere when present in concentrations exceeding those listed below.

Interfering Substance	Interference Level and Treatments
Aluminum	6 mg/L
Cadmium	0.5 mg/L
Copper	5 mg/L
Iron (ferric)	7 mg/L
Manganese	5 mg/L
Nickel	5 mg/L
Organic material	Large amounts may interfere. Perform the mild digestion (Section 2) to eliminate this interference.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment (see pH Interference in Section 1). Adjust pH to 4-5.

Pollution Prevention and Waste Management

ZincoVer 5 reagent contains potassium cyanide. Cyanide solutions are regulated as hazardous wastes by the Federal RCRA. Cyanide should be collected for disposal as reactive (D003) waste. Be sure that cyanide solutions are stored in a caustic solution with pH >11 to prevent the release of hydrogen cyanide gas.

In the event of a spill or release, clean up the area by following these steps:

a) Use a fume hood or supplied-air or self-contained breathing apparatus.

b) While stirring, add the waste to a beaker containing a strong solution of sodium hydroxide and calcium hypochlorite or sodium hypochlorite (household bleach).

c) Maintain a strong excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.

d) Neutralize and flush the solution down the drain with a

large excess of water.

Summary of Method

Zinc and other metals in the sample complex with cyanide. Adding cyclohexanone selectively releases zinc. The zinc then reacts with the 2-carboxy-2'-hydroxy-5'-sulfoforamazyl benzene (zincon) indicator and forms a blue color that is proportional to the zinc concentration.

REQUIRED REAGENTS

Zinc Reagent Set, 20 mL size (100 tests) 24293-00
Includes: (1) 14033-32, (1) 21066-69

Description	Quantity Required Per Test	Units	Cat. No.
Cyclohexanone	0.5 mL	100 mL MDB	14033-32
ZincoVer 5 Reagent Powder Pillows	1 pillow	100/pkg	21066-69

REQUIRED APPARATUS

Pipet, serological, 10 mL	1	each	532-38
Pipet Filler, safety bulb	1	each	14651-00
Sample Cell, 10-20-25 mL, w/cap	2	6/pkg	24019-06
Squeezers, plastic dropper	1	20/pkg	21247-20

OPTIONAL REAGENTS

Bleach, household	1 gal	buy locally	
Cylinder, graduated, mixing, 25mL	each	20886-40	
Hydrochloric Acid Standard Solution, 6 N	500 mL	884-49	
Nitric Acid, ACS	500 mL	152-49	
Nitric Acid 1:1	500 mL	2540-49	
Sodium Hydroxide Standard Solution, 5.0 N	50 mL SCDB	2450-26	
Water, deionized	4 L	272-56	
Zinc Standard Solution, 100 mg/L Zn	100 mL	2378-42	
Zinc Standard Solution, PourRite ampule, 25 mg/L as Zn, 2mL	20/pkg	14246-20	

OPTIONAL APPARATUS

Ampule Breaker, PourRite ampules	each	24846-00	
Aspirator, vacuum	each	2131-00	
Beaker, glass, 1000 mL	each	500-53	
Cylinder, graduated, 100 mL	each	508-42	
Cylinder, graduated, mixing, 250 mL	each	26362-46	
Filter discs, glass, 47 mm	100/pkg	2530-00	
Filter holder, 47 mm	each	2340-00	

Flask, erlenmeyer, 250 mL	each	505-46
Flask, filtering, 500 mL	each	546-19

OPTIONAL APPARATUS (continued)

Description	Units	Cat. No.
Flask, volumetric, Class A, 100 mL	each	14574-42
Flask, volumetric, Class A, 1000 mL	each	14574-53
Hot plate, micro 115 V	each	12067-01
Hot plate, micro 230 V	each	12067-02
pH paper, 1 to 11 pH	5 rolls/pkg	391-33
pH meter, *Sens**ion***™*1*, portable with electrode	each	51700-10
Pipet filler, safety bulb	each	14651-00
Pipet, serological, 2 mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet, TenSette, tips for 19700-01	50/pkg	21856-96
Pipet, TenSette, 1.0 to 10.0 mL	each	19700-10
Pipet, TenSette, tips for 19700-01	1000/pkg	21856-28
Pipet, TenSette, tips for 19700-10	50/pkg	21997-96
Pipet, TenSette, tips for 19700-10	250/pkg	21997-25
Pipet, volumetric, Class A, 5.00 mL	each	14515-37
Pipet, volumetric, Class A, 0.5 mL	each	14515-34

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

SECTION 5 ORDERING INFORMATION

HOW TO ORDER

By Phone:
6:30 a.m. to 5:00 p.m. MST
Monday through Friday
800-227-HACH (800-227-4224)

By Mail:
Hach Company
P. O. Box 389
Loveland, Colorado 80539-0389 U.S.A.

By FAX:
970-669-2932 (Hach Loveland)

Information Required:

- Hach account number (if available)
- Billing address
- Shipping address
- Your name and phone number
- Purchase order number
- Catalog number
- Brief description or model number
- Quantity

Technical and Customer Service

Hach Technical and Customer Service Department personnel are eager to answer questions about our products and their use and to take your orders. Specialists in analytical methods, they are happy to put their talents to work for you. Call **1-800-227-4224**.

HOW TO ORDER, continued

International Customers

Hach maintains a network of dealers and distributors throughout the world.

In Canada
Hach Sales and Service Canada Ltd.
1313 Border Street, Unit 34
Winnipeg, Manitoba R3H 0X4
Telephone: (204) 632-5598
FAX: (204) 694-5134

In other countries, contact:
Hach Company World Headquarters
P. O. Box 389
Loveland, Colorado, U.S.A. 80539-0389
Telephone: (1) (970) 669-3050
FAX: (1) (970) 669-2932

Information presented on these pages applies only to Hach products manufactured for use within the United States. Exportation of these products renders these terms void.

Prices and Terms

Prices are subject to change without notice. All prices are FOB from the shipping point (usually Ames, Iowa). Hach offers instant credit up to $200 on Net 30 Day terms. Larger orders are subject to credit review. Customers may send remittance with orders or we can ship C.O.D. if you prefer.

Warranty

Hach warrants its products to be of high quality, to be free of material defects on the date of shipment and to be as specified. Full warranty information is on the back of Hach invoices.

ADDITIONAL INFORMATION

Limits of Usage

Our chemicals and reagents are offered for laboratory and manufacturing use ONLY. They may not be used as drugs, cosmetics or food additives.

MSDS

Hach Material Safety Data Sheets, among the most complete and informative in the industry, provide comprehensive safety data essential for day-to-day operations and safety training.

An MSDS accompanies all Hach chemical products including test kits. For an additional $15.00 per item, we will print MSDSs on your own forms.

Label Information

Labels on Hach chemicals and reagents supply the following:

- Product Name -- In French, German, Italian and Spanish as well as English is printed on all but the smallest-size labels.
- Hach Catalog Number -- Makes reordering easy and helps match the appropriate MSDS.
- Storage Information and Lot Numbers -- Lot numbers made up of letters and numbers indicate an extended shelf life; a four-digit number indicates items should be rotated and checked with a standard to confirm performance. The lot number is essential if you call for technical assistance or with questions about reagent performance.

Shipping

Our experienced warehouse staff packages your orders for safe arrival. Unless we are instructed otherwise, the best and most efficient mode of transportation is selected. Motor freight shipments will be sent freight collect unless you specify otherwise at the time you order.

If you have questions about methods for shipment and availability of special packaging, please ask when you place your order.

ADDITIONAL INFORMATION, continued

Claims and Returns

We take extreme care to fill, check, re-check and pack orders properly. If errors or damages should occur, please report details to our Loveland Customer Service Department and to the carrier immediately. Be sure to keep all containers and packing materials.

AUTHORIZATION MUST BE OBTAINED from Hach when returning items for any reason. Call 1-800-227-4224 toll free. **ALL "FREIGHT COLLECT" SHIPMENTS OR MERCHANDISE RETURNED WITHOUT PROPER AUTHORIZATION FROM HACH WILL BE REFUSED.**

Newsletter

News & Notes for the Analyst, Hach's informative newsletter, contains updates on federal regulations, in-depth discussions of chemical reactions, application notes and information about new products. Contact Hach for your free subscription.

MAIL ORDER FORM

Send order to: HACH COMPANY, P.O. Box 608, Loveland, CO 80539-0608

Use this convenient form, your own purchase orders, or for PROMPT PHONE SERVICE CALL 1-800-227-4224. If ordering by phone, please have information related to items 1 - 4 (below) ready.

☐ Check box if "Ship To" information is identical to "Bill To".

BILL TO

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DIVISION OF
ADDRESS
CITY **STATE** **ZIP**
ATTENTION
PHONE NO. (_____) _____ **EXTENSION** _____

SHIP TO

COMPANY
DIVISION OF
ADDRESS
CITY **STATE** **ZIP**
ATTENTION
HACH ACCOUNT NO. (If available) ❶

PAYMENT METHOD: ☐ **Check** ☐ **MasterCard** ☐ **Visa** ☐ **Purchase Order**

Card Account or Purchase Order No. | Card Exp. Date | Signature

❷ ❸ ❹ ❺

QUANTITY	CAT. NO.	DESCRIPTION	UNIT SIZE	UNIT PRICE	TOTAL

❻ **Shipping Charge**

Prices are subject to change without notice

❼ **TAXABLE?** ☐ Yes ☐ No*

*If no, tax exempt document is: ☐ Enclosed ☐ On file at Hach

TOTAL ORDER

❶ If Hach account number is not known, leave the space blank.

❷ Most chemicals and apparatus are sold separately ("each"), but others are sold in units. Powder pillows, for example, are available in packages of 100. To purchase 100 powder pillows, order 1 unit, not 100 pillows. Be sure to order the number of units (packages) you need.

❸ Include all numbers given in the products listing.

❹ A one- or two-word description of the item.

❺ If more than one size of an item is offered, state the size you want.

❻ Unless otherwise instructed, Hach will choose the best and most efficient mode of transportation and calculate the amount.

❼ Check one box. Tax exempt status must be substantiated with documentation identifying your tax exempt number. If taxable, sales tax will be added.

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P.O. Box 608
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Send order to: HACH COMPANY, P.O. Box 608, Loveland, CO 80539-0608

Use this convenient form, your own purchase orders, or for PROMPT PHONE SERVICE CALL 1-800-227-4224. If ordering by phone, please have information related to items 1 - 4 (below) ready.

☐ Check box if "Ship To" information is identical to "Bill To".

BILL TO

COMPANY
DIVISION OF
ADDRESS
CITY **STATE** **ZIP**
ATTENTION
PHONE NO. (_____) _____ **EXTENSION** _____

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DIVISION OF
ADDRESS
CITY **STATE** **ZIP**
ATTENTION
HACH ACCOUNT NO. (If available) ❶

PAYMENT METHOD: ☐ **Check** ☐ **MasterCard** ☐ **Visa** ☐ **Purchase Order**

Card Account or Purchase Order No. | Card Exp. Date | Signature

❷ ❸ ❹ ❺

QUANTITY	CAT. NO.	DESCRIPTION	UNIT SIZE	UNIT PRICE	TOTAL

❻ **Shipping Charge**

Prices are subject to change without notice

❼ **TAXABLE?** ☐ Yes ☐ No*

*If no, tax exempt document is: ☐ Enclosed ☐ On file at Hach

TOTAL ORDER

❶ If Hach account number is not known, leave the space blank.

❷ Most chemicals and apparatus are sold separately ("each"), but others are sold in units. Powder pillows, for example, are available in packages of 100. To purchase 100 powder pillows, order 1 unit, not 100 pillows. Be sure to order the number of units (packages) you need.

❸ Include all numbers given in the products listing.

❹ A one- or two-word description of the item.

❺ If more than one size of an item is offered, state the size you want.

❻ Unless otherwise instructed, Hach will choose the best and most efficient mode of transportation and calculate the amount.

❼ Check one box. Tax exempt status must be substantiated with documentation identifying your tax exempt number. If taxable, sales tax will be added.

TAPE HERE

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NO POSTAGE
NECESSARY
IF MAILED
IN THE
UNITED STATES

BUSINESS REPLY MAIL
FIRST CLASS MAIL PERMIT NO. 100 LOVELAND, CO

POSTAGE WILL BE PAID BY ADDRESSE

HACH COMPANY—SALES DEPT.
P.O. Box 608
Loveland, CO 80539-0608

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