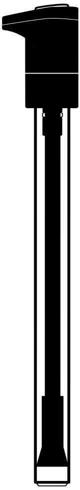
User Guide

Potassium
Ion Selective
Electrode



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ORION Series A meters and 900A printer are protected by U.S. patents 5,198,093, D334,208 and D346,753.

ionplus electrodes and Optimum Results solutions are protected by US Patent 5,830,338.

ROSS Ultra electrodes are protected by US patents 6,793,787.

Orion ORP Standard is protected by US Patent 6,350,367.

Orion NoCal electrodes are protected by US Patent 7,276,142.

This publication supersedes all previous publications on this subject.

TABLE OF CONTENTS

GENERAL INFORMATION

Introduction

This user guide contains information on the preparation, operation and maintenance for the potassium ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Potassium electrodes measure potassium ions in aqueous solutions quickly, simply, accurately and economically.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com/contactwater.

For more information on our full product offering, visit www.thermo.com/water.

Potassium ionplus® Sure-Flow® Plastic Membrane Combination ISE

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Sure-Flow reference junction prevents electrode clogging and provides fast and stabile readings. The potassium ionplus combination ISE is available with a waterproof BNC connector, Cat. No. 9719BNWP.

Potassium Plastic Membrane Half-Cell ISE

The potassium half-cell electrode must be used with the double junction reference electrode, Cat. No. 900200. The potassium half-cell is available with a BNC connector, Cat. No. 9319BN.

Required Equipment

Meter– Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter. Potassium electrodes can be used on any ISE meter with a BNC connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used.

Reference Electrode– The 9319BN half-cell potassium electrode requires the Thermo Scientific Orion double junction reference electrode, Cat. No. 900200. Do not use the outer chamber filling solution, Cat. No. 900003, that is supplied with the reference electrode. Instead, use a dilute ISA solution as the outer filling solution. Use the inner chamber filling solution, Cat. No. 900002, that is supplied with the reference electrode.

Stirrer– Magnetic stirrer or stir probe, Cat. No. 096019. The stir probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.

Labware– Volumetric flasks, graduated cylinders and beakers.

Required Solutions

Distilled or Deionized Water

Electrode Filling Solution

Use Optimum Results E filling solution, Cat. No. 900065, with the 9719BNWP combination potassium electrode.

Use the inner chamber filling solution, Cat. No. 900002, that is supplied with the double junction reference electrode that is used with the 9319BN half-cell potassium electrode.

Use a dilute ISA solution as the outer filling solution in the double junction reference electrode that is used with the 9319BN half-cell potassium electrode. Do not use the outer chamber filling solution that is supplied with the double junction reference electrode, as it contains interferences. Prepared the dilute ISA solution by adding 2 mL of ISA, Cat. No. 931911, to a 100 mL volumetric flask and diluting to the mark with distilled water.

Potassium Calibration Standards

0.1 M Potassium Standard, Cat. No. 921906

1000 ppm Potassium Standard– Prepare a 1000 ppm potassium standard by transferring 25.6 mL of the 0.1 M potassium standard, Cat. No. 921906, to a 100 mL volumetric flask and dilute to the mark with distilled water.

Ionic Strength Adjustor (ISA), Cat No. 931911– To adjust ionic strength of samples and standards

BEFORE USING THE ELECTRODE

Electrode Assembly and Preparation

9319BN Potassium Half-Cell Electrode:

Remove the sensing module from the vial. Make sure the rubber electrode washer on the sensing module is in place. See **Figure 1**. Screw the sensing module into the electrode body until finger tight. To ensure electrical continuity, shake down the electrode like a clinical thermometer. Rinse the potassium electrode with distilled water, then soak in Potassium Standard, 100 ppm or 10^{-2} M for 1 to two hours prior to initial use. **Do not immerse the electrode past the rubber electrode washer.** See **Figure 1.**

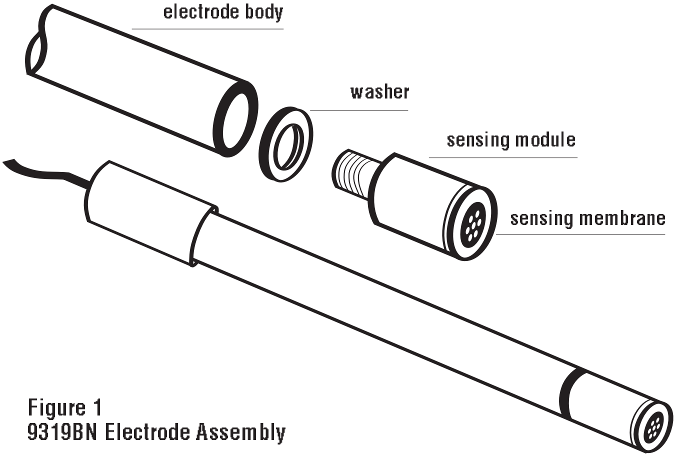


Figure 1
9319BN Electrode Assembly

900200 Double Junction Reference Electrode:

Required for use with 9319BN potassium half-cell electrode. Fill the reference electrode according to instructions in the reference electrode user guide, using Cat. No. 900002 filling solution in the inner chamber. Substitute diluted ISA for the Outer Chamber Filling Solution provided with the electrode. **Do not use the outer chamber filling solution shipped with the 900200 reference electrode because it will interfere with your potassium measurements.**

9719BNWP ionplus Potassium Combination Electrode:

This electrode consists of two parts, the sensing module and the electrode handle. See **Figure 2**.

Note: Be careful not to touch the sensing membrane or reference pellet during assembly!

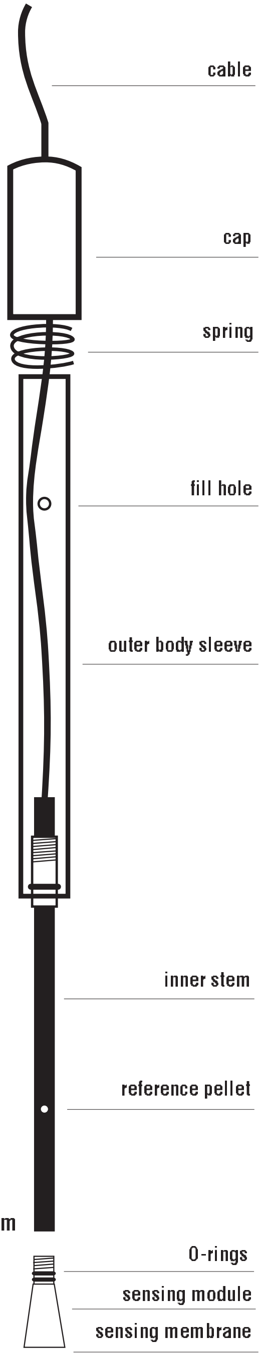


Figure 2

9719BNWP ionplus Potassium Combination Electrode

1

Remove the sensing module from the vial. Make sure both O-rings are in place. Take the handle from the box.

2

Take the outer body sleeve, with the fill hole end towards the white cap, and gently push the inner stem through the outer body.

3

Slide the outer body sleeve, spring, and cap down the electrode cable until the outer body sleeve is beyond the inner stem.

4

With one hand grasp the middle of the inner stem **without touching the reference pellet**. With your other hand, screw the sensing module onto the stem until it stops and the module is flush against the stem. Then tighten an additional one-quarter turn and stop. **Do not continue to over tighten**. The module should be firmly attached to the stem.

5

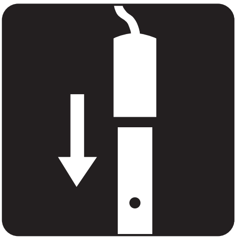
Holding the electrode cable, slide the outer body, spring and cap over the inner stem.

6

Grasp the outer body sleeve, ***do not touch the sensing membrane***. With your other hand, pull on the cable and gently screw the cap onto the inner stem. **Stop** when an opposite force is felt. **Do not over tighten or continue to turn the cap**! The cap will not completely stop! If the inner body turns at all, the cap is too tight. Remove the cap and reassemble.

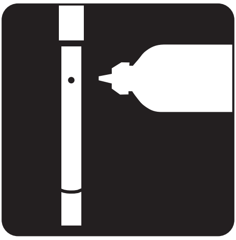
7

Hold the electrode with one hand. Press on the top of the cap with your thumb to make sure the electrode has a smooth flushing motion and reseats back onto the module.



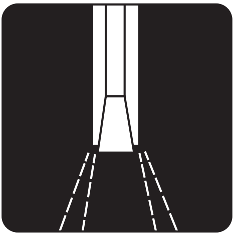
8

Fill the outer body with Optimum Results E filling solution, Cat. No. 900065, to approximately 1/4 full.



9

Press cap to flush out the solution. Release the cap and ensure that the outer body sleeve returns to its original position.



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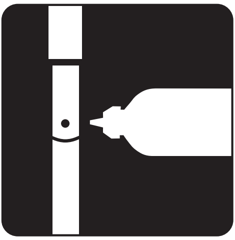
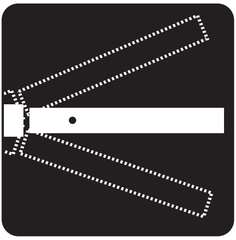
Refill the electrode with Optimum Results E filling solution until the fluid level is just below the fill hole.



11

To ensure electrical continuity, grasp the outer body and cap and shake the sensing module end firmly. Check to make sure the membrane surface is dark and homogeneous with no bubbles on the inner surface.



Electrode reference filling solution should be added each day before use. The filling solution should be no lower than 1 inch from the fill hole and must be above the reference pellet. The filling solution level should always remain 1 inch above the sample level to ensure proper flow rate. Rinse the potassium electrode with distilled water, then soak in Potassium Standard, 100 ppm or 10^{-2} M, for 1 to 2 hours prior to initial use.

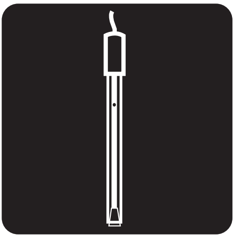
Checking Electrode Operation (Slope)

Use these general instructions to check electrode operation. See the meter user guide for more specific information.

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every tenfold (decade) change in concentration. Obtaining the slope value provides the best means for checking electrode operation.

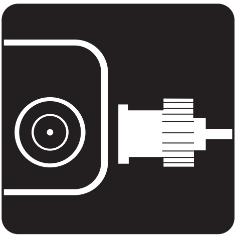
1

If electrode(s) has been stored dry, prepare the electrode(s) as described under the section entitled **Electrode Assembly and Preparation.**



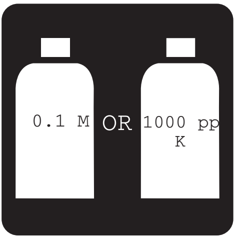
2

Connect the electrode(s) to the meter as described in the meter user guide.



3

Select either 0.1 M or 1000 ppm potassium standard.



4

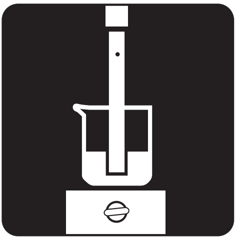
Place 100 mL distilled water into a 150 mL beaker. Add 2 mL ISA, Cat. No. 931911.
Stir thoroughly.

5

Set the meter to the mV mode.

6

Rinse the electrode(s) with distilled water, shake dry, and place in the solution prepared in step 4 above.



7

Pipet 1.0 mL of the standard into the beaker. Stir thoroughly.

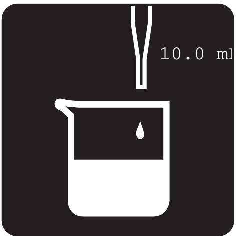
8

When a stable reading is displayed, record the electrode potential in millivolts.

mV

9

Pipet 10.0 mL of the same standard into the same beaker.
Stir thoroughly.



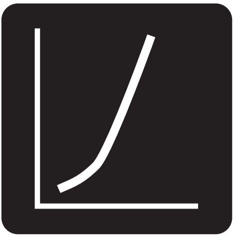
10

When a stable reading is displayed, record the electrode potential in millivolts.

mV

11

The difference between the first and second potential reading is defined as the slope of the electrode. The difference should be in the range of 54 to 60 mV/decade when the solution temperature is 25 ± 5 °C. If the slope is not within this range, resoak the electrode as described under the section entitled **Electrode Assembly and Preparation**. For other troubleshooting techniques refer to the **Troubleshooting** section.



Recommendations for Optimum Results

Units of Measurement

Measure potassium in units of moles per liter, parts per million as potassium, parts per million as potassium chloride or any other convenient unit (see **Table 1**).

Table 1

Concentration Unit Conversion Factors

moles per liter	ppm as K^+	ppm as KCl
10^{-4}	3.91	7.46
10^{-3}	39.1	74.6
10^{-2}	391	746

Sample Requirements

Samples must be aqueous and must not contain organic solvents. Consult Technical Support for using the electrode in specific applications.

Sample temperature must be less than 40°C, with samples and standards at the same temperature. At the 10^{-3} M level, a 1°C difference in temperature produces about a 2.5% error. For highly accurate results, use a water bath to control temperature variances.

Interferences should be absent. See section entitled **Interferences** for a list of possible interferences.

Important ISE Measurement Techniques

- Stir all standards and samples at a uniform rate during measurement. Magnetic stirrers may generate sufficient heat to change solution temperature. Place a piece of insulating material such as cork, cardboard or Styrofoam between the stir plate and sample beaker.

- Always use fresh standards for calibration.

- Always rinse electrode(s) thoroughly with distilled water between measurements. Shake electrode after rinsing to prevent solution carryover, then shake dry. **Do not wipe or rub the sensing membrane, as you may contaminate and damage the surface.**

- Allow all standards and samples to come to room temperature for precise measurements.

- After immersion in solution, check the potassium electrode for any air bubbles on the membrane surface. Remove air bubbles at the electrode surface by gently tapping the electrode.

- The 9319BN potassium half-cell electrode should be submerged approximately half the length of the potassium module. **Do not submerge the potassium electrode above the rubber electrode washer.** Submerge the reference electrode to the same depth as the potassium electrode.

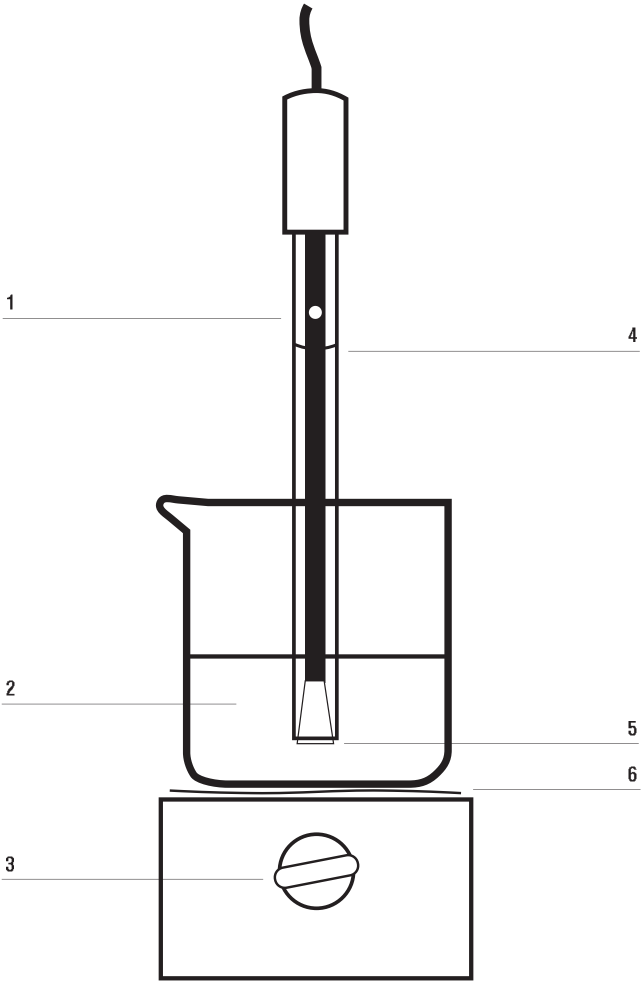


Figure 3

1. Uncover fill hole during measurements.
2. Use fresh standard.
3. Stir all samples and standards.
4. Filling solution level must be higher than sample level, and at least one inch above the reference pellet.
5. Immerse reference junction.
6. Place insulation between stirrer and beaker.

NOTE: Do not submerge potassium module past the rubber electrode washer (9319BN only).

Roadway to ionplus Success!

Guide to measuring techniques

	Direct Measurement	Small Volume Direct Measurement	Low-Level Measurement	Known Addition
Recommended Concentration Range	0.04 to 39000 ppm K^+	0.04 to 39000 ppm K^+	< 0.39 ppm K^+	0.39 to 39000 ppm K^+
Large # of samples	X	X (9719BNWP only)	X	X
Small sample volume		X (9719BNWP only)		X
Reduced chemical usage		X (9719BNWP only)		
Field Measurements	X	X (9719BNWP only)		X
Ionic Strength >0.1 M				X
Occasional sampling				X
see page #	18	24	29	34

A variety of analytical techniques are available to the analyst. The best technique is dependent upon the sample matrix. The following section describes the recommended techniques for potassium determination.

Direct Measurement is a simple procedure for measuring a large number of samples. This method requires only one meter reading for each sample. Calibration is performed in a series of standards. The concentration of the samples is determined by comparison to the standards. Addition of ISA to all solutions ensures that samples and standards have similar ionic strength, proper pH, and reduces the effect of interfering ions. When measuring small sample volumes or to reduce chemical usage, follow the **Small Volume Direct Measurement** method, using the 9719BNWP potassium combination electrode.

Low-Level Measurement is similar to **Direct Measurement**. Use this method when the expected sample concentration is less than 10^{-5} M or 0.39 ppm. Using a minimum of three calibration standards compensates for the electrode's non-linear response at low concentrations. This procedure describes the best means of preparing low-level calibration standards.

Known Addition is an alternate method useful when measuring only a few samples, when samples have a high (>0.1 M) ionic strength, or have a complicated background matrix. Refer to **Theory of Operation** for an explanation of these effects. The electrodes are immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined. As in direct calibration, any convenient concentration unit can be used.

MEASUREMENT PROCEDURES

Direct Measurement

The following direct measurement procedures are recommended for moderate to high level measurements, when all samples fall within the electrode's linear range, greater than 0.39 ppm or 10^{-5} M potassium. A two-point calibration is sufficient, though more points can be used if desired. Using ISE meters, read sample concentrations directly from the meter. Refer to the meter's user guide for calibration details. When using a mV meter, prepare a calibration curve on semi-logarithmic graph paper, or a linear regression can be performed at the user's discretion using a spreadsheet or graphing program.

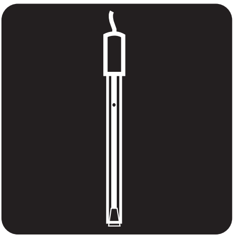
For Improved Accuracy

- Bracket standard concentrations around the expected sample concentration.
- Always dilute samples and standards in a 50:1 ratio with ISA. For example, 100 mL of sample and 2 mL of ISA.
- Verify this procedure by measuring a standard of known concentration as an unknown or by spiking a sample with potassium standard.
- For high ionic strength samples, having an ionic strength of 0.1 M or greater, prepare standards with a composition similar to that of the samples, measure the samples using the known addition method, or dilute the samples.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated.
- The best method for preparation of standards is serial dilution. This procedure involves preparing an initial standard that is diluted to prepare a second standard solution using volumetric glassware. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.
- Review section entitled **Important ISE Measurement Techniques**.

Direct Measurement Procedure using an ISE meter or a mV meter
See the meter user guide for more specific calibration information.

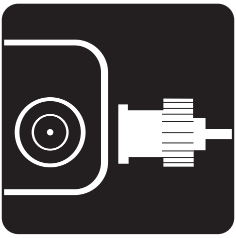
1

Prepare the electrode(s) as described in **Electrode Assembly and Preparation**.



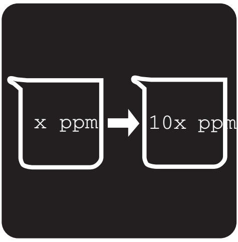
2

Connect electrode(s) to the meter, and adjust the meter to measure concentration for an ISE meter or mV for a mV meter.



3

Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to **Temperature Effects**.



4

Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 2 mL ISA to each standard and sample.

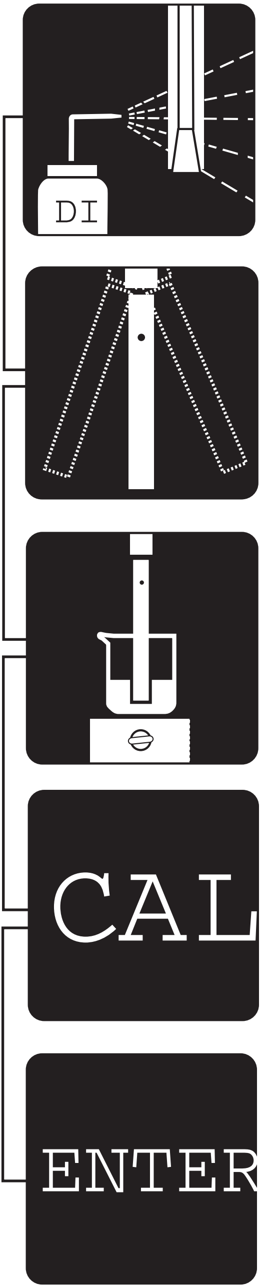
NOTE: Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.

Stir thoroughly.

5

For an ISE meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker containing the most dilute standard. Wait for a stable reading, then calibrate the meter to display the value of the standard as described in the meter user guide.

For a mV meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker containing the least concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.



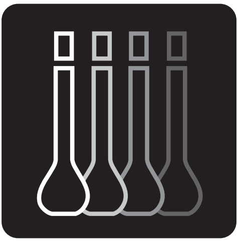
6

For an ISE meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker with the next standard. Wait for a stable reading, then adjust the meter to display the value of the second standard, as described in the meter user guide.

For a mV meter: Rinse electrode(s) with distilled water, shake dry, and place into the beaker containing the next standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

7

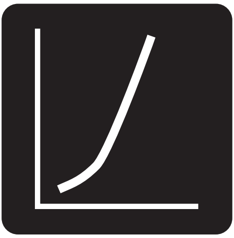
Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.



8

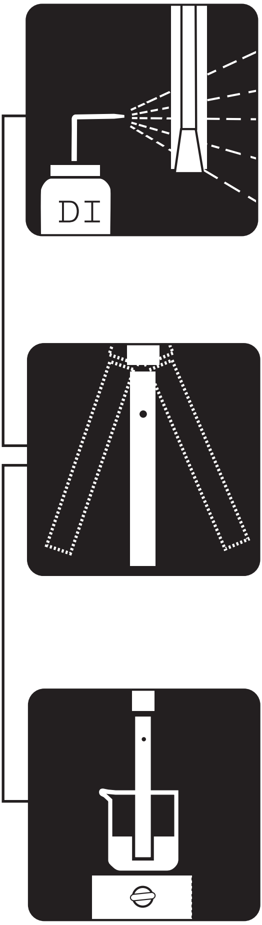
For an ISE meter: Calibration information will be calculated and stored automatically.

For a mV meter: Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis. See **Figure 4**.



9

Rinse electrode(s) with distilled water, shake dry, and place into sample.



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For an ISE meter: When the electrode stabilizes, the meter will display the sample concentration.

For a mV meter: When the electrode stabilizes, the meter will display the mV value for the sample. Using the calibration curve prepared in step 8, determine the unknown sample concentration.

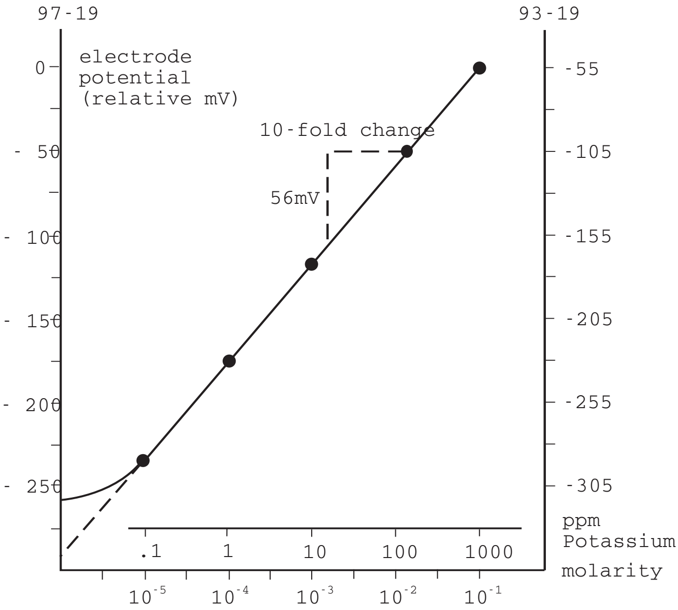


Figure 4
Typical Potassium Electrode Calibration Curve

During the direct measurement procedure, a calibration curve is constructed automatically by the ISE meter. Alternately, a calibration curve may be plotted by hand using semi-logarithmic paper. Measured electrode potentials of standard solutions are plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken for accurate results. The direct measurement procedures in the user guide are given for concentrations in the region of linear electrode response. When measuring in the non-linear region follow the low-level measurement procedure. This curve serves as an example only. Actual mV values may differ.

Small Volume Direct Measurement (9719BNWP Potassium Combination Electrode Only)

Using the Sure-Flow reference design, the 9719BNWP potassium combination electrode allows measurement of sample volumes as small as 5 mL with a modified direct measurement procedure. This technique is applicable to any sample where reduced chemical usage of standards and ISA is important. This small volume measurement is well-suited for field testing as the combination reference electrode conveniently reduces equipment, setup and sampling time. All samples should be greater than 0.39 ppm or 10^{-5} M potassium. As with the previously described **Direct Measurement** procedure, a two point calibration is sufficient, though more points can be used if desired. Use a direct concentration meter (ISE meter) or a pH/mV meter with 0.1 mV resolution. The following procedure recommends using 25 mL of sample. Smaller sample volumes can be used, as long as the final volume of solution is sufficient to cover the reference junction of the 9719BNWP electrode. Do not allow the sensing membrane to touch the sample container.

For Improved Accuracy

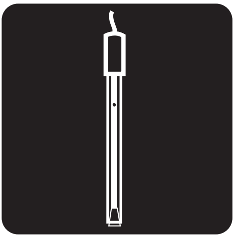
- Use the 9719BNWP potassium combination electrode.
- Bracket standard concentrations around the expected sample concentration.
- Always dilute samples and standards in a 50:1 ratio with ISA.
- Verify this procedure by measuring a standard of known concentration as an unknown or by spiking a sample with potassium standard.
- For high ionic strength samples, having an ionic strength of 0.1 M or greater, prepare standards with a composition similar to that of the samples, measure the samples using the known addition method, or dilute the samples.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated.
- The best method for preparation of standards is serial dilution. This procedure involves preparing an initial standard that is diluted to prepare a second standard solution using volumetric glassware. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.
- Review section entitled **Important ISE Measurement Techniques**.

Small Volume Direct Measurement Procedure using ISE Meter or mV meter and 9719BNWP Potassium Combination Electrode

See the meter user guide for more specific calibration information.

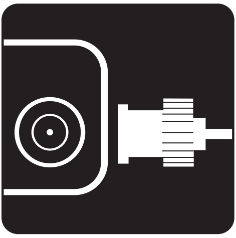
1

Prepare the 9719BNWP potassium combination electrode as described in **Electrode Assembly and Preparation**.



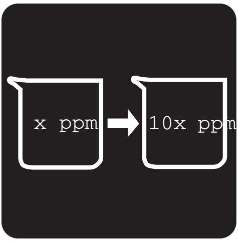
2

Connect the electrode to the meter, and adjust the meter to measure concentration for an ISE meter or mV for a mV meter.



3

Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to **Temperature Effects**.



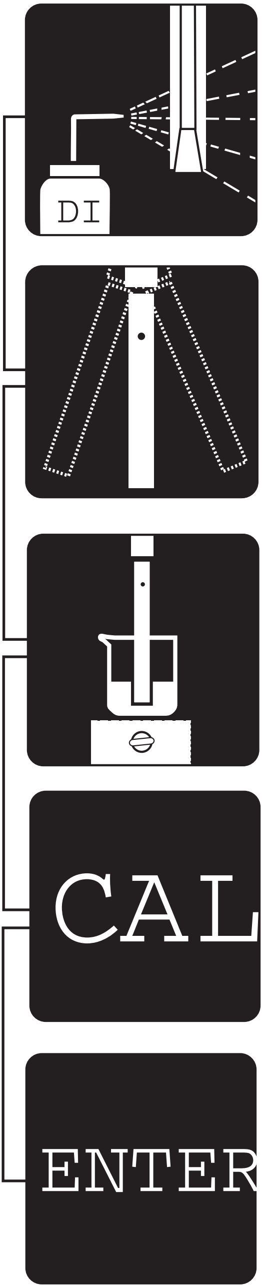
4

Measure 25 mL of each standard and sample into separate 150 mL beakers. Add 0.5 mL ISA to each standard and sample.

NOTE: Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.

Stir thoroughly.

5



For an ISE meter: Rinse the 9719BNWP potassium combination electrode with distilled water, shake dry, and place into the beaker containing the most dilute standard. Wait for a stable reading, calibrate the meter to display the value of the standard as described in the meter user guide.

For a mV meter: Rinse the 9719BNWP potassium electrode with distilled water, shake dry, and place into the beaker containing the most dilute standard. Wait for a stable reading, record the mV value and corresponding standard concentration.

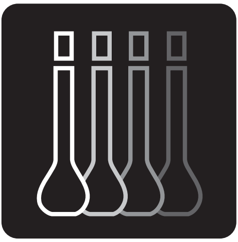
6

For an ISE meter: Rinse the 9719BNWP electrode with distilled water, shake dry, and place into the beaker with the next standard. Wait for a stable reading, then adjust the meter to display the value of the second standard, as described in the meter user guide.

For a mV meter: Rinse the 9719BNWP electrode with distilled water, shake dry, and place into the beaker containing the next concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

7

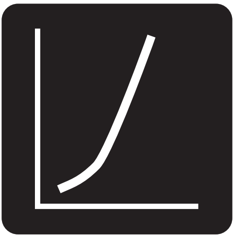
Repeat step 6 for all standards, working from the least concentrated to most concentrated standard.



8

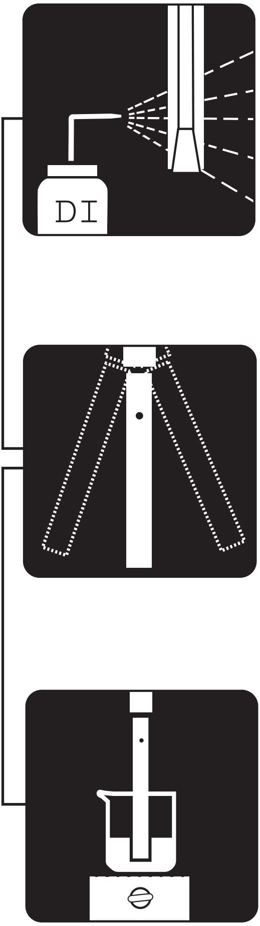
For an ISE meter: Calibration information will be calculated and stored automatically.

For a mV meter: Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis. See **Figure 4**.



9

Rinse the 9719BNWP electrode with distilled water, shake dry, and place into the sample.



10

For an ISE meter: When the electrode stabilizes, the meter will display the sample concentration.

For a mV meter: When the electrode stabilizes, the meter will display the mV value for the sample. Using the calibration curve prepared in step 8, determine the unknown sample concentration.

Low-Level Measurements By Direct Measurement

Use this method when measuring solutions with a potassium concentration of less than 0.39 ppm or 10^{-5} M potassium, those within the non-linear range of the potassium electrode. Low-level measurements require at least three standards to compensate for the electrode's non-linearity.

For Improved Accuracy

- If some samples have low-level concentrations, and some have higher concentrations, dilute the higher concentrations down to the low-level range. The electrode's response time at low-levels is faster when it is not also exposed to high concentrations.
- The choice of calibration standard concentrations is important for obtaining the best electrode performance and most rapid analysis time. Here are some guidelines:

  Ideally, calibration standard concentrations should bracket the expected sample concentrations.

  The best results are obtained when the ratio of the highest to the lowest calibration standard is between ten to 100 times the lowest calibration standard concentration. Space additional standards equally within the range.

  If the expected sample concentrations fall within a narrow range (less than one order of magnitude), a ratio of highest to lowest standard concentration of ten should be used.

  When measuring sub-ppm levels an ISE meter, take advantage of the autoblank feature. It does not require a zero standard, but can perform blank correction as long as the lowest standard concentration is in the non-linear range of the electrode. Electrodes are very slow in the absence of a measurable concentration and a multipoint calibration generally will be less accurate when "zero" is included as a standard. Standard concentrations should be chosen such that the lowest standard value is larger than the blank value obtained, and the second lowest standard should be at least twice that of the lowest. See the ISE meter user guide for additional information on blank correction.

  When not using an ISE meter, a calibration curve can be drawn on semi-logarithmic graph paper or the data can be processed by means of a spreadsheet or graphing program with a non-linear curve fitting feature.

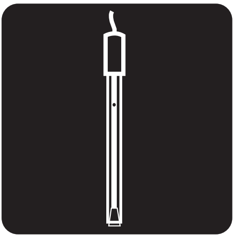
  When using an ISE meter with the autoblank feature, three calibration points are sufficient. If a calibration curve is prepared manually, additional points may be helpful to facilitate drawing the curve.

- Remember to stir all standards and samples at a uniform rate.
- Review section entitled **Important ISE Measurement Techniques**.

Low-Level Measurement Procedure using an ISE meter or a mV meter

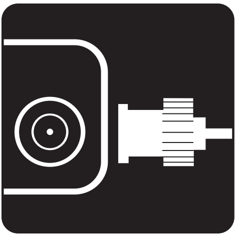
1

Prepare electrode(s) as described in **Electrode Assembly and Preparation**.



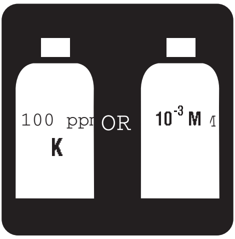
2

Connect the electrode(s) to the meter. Set the meter to read concentration for an ISE meter or mV for a mV meter.



3

Select a standard solution. Use either 100 ppm potassium or dilute the 0.1 M Potassium standard, Cat. No. 921906, to 10^{-3} M.

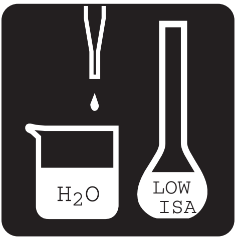


4

Prepare a low-level ISA solution by diluting 20 mL of the potassium ISA, Cat. No. 931911, to 100 mL with distilled water. **Use this low-level ISA for low-level measurements only.**

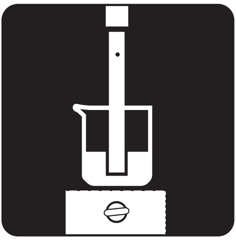
5

Measure 100 mL distilled water into 150 mL beaker. Add 1 mL low-level ISA.



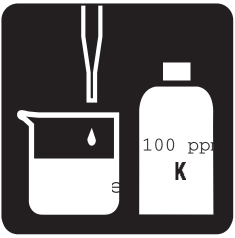
6

Rinse the electrode(s) with distilled water, place into beaker.
Stir thoroughly.



7

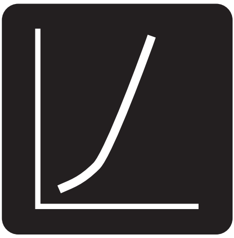
Add increments of the standard to the beaker using steps outlined in **Table 2**.



8

For an ISE meter. Follow meter user guide for detailed calibration instructions.

For a mV meter: Record stable millivolt reading after each increment. On semi-logarithmic paper, plot the concentration on the log axis against the millivolt potential on the linear axis, see **Figure 4**. Prepare a new low-level calibration curve with fresh standards each day.

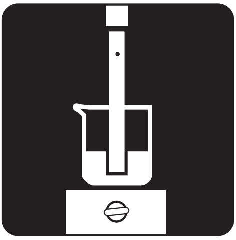


9

Measure 100 mL of sample into a beaker. Add 1 mL of low-level ISA.

10

Rinse the electrode(s) with distilled water, shake dry, and place into the sample. Stir thoroughly.



11

For an ISE meter: When the electrode stabilizes, the meter will display the sample concentration.

For a mV meter: When the electrode stabilizes, the meter will display the sample mV value. Determine the sample concentration corresponding to the measured potential using the low-level calibration curve prepared in step 8.

Table 2

Preparing a Calibration Curve For Low-Level Measurements Using a Meter with mV Readout

Step	Graduated Pipette Size	Added Volume	Concentration ppm K	Molarity
1	1 mL	0.1 mL	0.1	1.0×10^{-6}
2	1 mL	0.1 mL	0.2	2.0×10^{-6}
3	1 mL	0.2 mL	0.4	3.9×10^{-6}
4	1 mL	0.2 mL	0.6	5.9×10^{-6}
5	1 mL	0.4 mL	1.0	9.8×10^{-6}
6	2 mL	2.0 mL	2.9	2.9×10^{-5}
7	2 mL	2.0 mL	4.7	4.7×10^{-5}

Additions of 100 ppm K or 10^{-3} M standards to 100 mL distilled water, plus 1 mL low-level ISA.

Known Addition

Known addition, KA, is a convenient technique for measuring samples in the linear response range, greater than 0.39 ppm or 10^{-5} M potassium, because no calibration curve is needed. Use this method to verify the results of a direct measurement or to minimize existing matrix effects. The sample potential is measured before and after addition of a standard solution. Many meters have the known addition algorithms preprogrammed. This programming makes multiple standard additions to the sample, resulting in more precise results. These direct reading meters provide a great convenience. Accurate measurement requires that the following conditions be met.

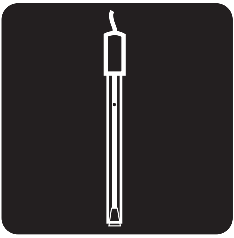
For Improved Accuracy

- Sample concentration should be known to within a factor of three.
- Concentration should approximately double as a result of the addition.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- All samples and standards should be at the same temperature.
- In general, either no complexing agents or a large excess of the complexing agents may be present.
- Standard addition volume should be less than 10% of the sample volume, or standard should be pre-treated with ISA in a 50:1 ratio.
- Dilute samples in a 50:1 ratio of sample to ISA before analysis.
- Review section entitled **Important ISE Measurement Techniques**.

Setup for Known Addition with all meters

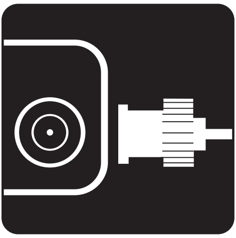
1

Prepare electrode(s) as described in **Electrode Assembly and Preparation**.



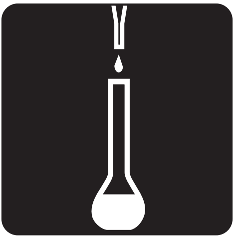
2

Connect electrode(s) to the meter.



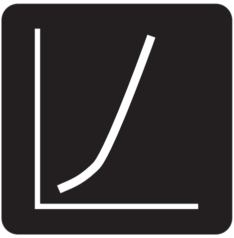
3

Prepare a standard solution that, upon addition to the sample, will cause the concentration of the potassium to double. Refer to **Table 3** as a guideline.



4

Determine the slope of the potassium electrode by performing the procedure under **Checking Electrode Operation (Slope)**.



Single Known Addition Measurement Procedure using an ISE meter with KA program

See the meter user guide for more specific information.

1

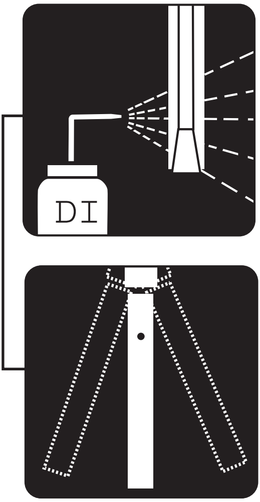
Set up the meter to measure in the known addition mode.

2

Measure 100 mL of the sample into a beaker. Add 2 mL ISA.
Stir thoroughly.

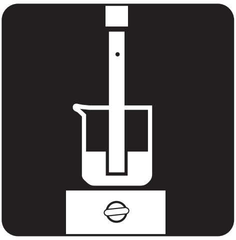
3

Rinse electrode(s) with distilled water, shake dry, and place into sample solution.



4

When a stable reading is displayed, program the meter as described in the meter user guide.



5

Pipet the appropriate amount of the standard solution into the beaker. Stir thoroughly.

6

When a stable reading is displayed, record the sample concentration.

Known Addition Measurement Procedure using a mV meter

1. Set the meter to millivolt mode.
2. Measure 100 mL of the sample into a 150 mL beaker. Add 2 mL ISA. Stir thoroughly.
3. Rinse electrode(s) with distilled water, shake dry and place into sample solution.
4. When a stable reading is displayed, record the mV value as E_1.
5. Pipet the appropriate amount of standard solution into the beaker. See **Table 3**. Stir thoroughly.
6. When a stable reading is displayed, record the mV value as E_2. Subtract the first reading from the second to find ΔE.
7. From **Table 5**, find the Q value that corresponds to the change in potential, ΔE. To determine the original sample concentration, multiply Q by the concentration of the added standard:

   $$\mathbf{C_{sam} = QC_{std}}$$

   where:

   C_{std} = standard concentration

   C_{sam} = sample concentration

   Q = reading from known addition table

The table of Q values is calculated for a 10% total volume change for electrodes with slopes of 57.2, 58.2, 59.2, and 60.1 mV/decade.

The equation for the calculation of Q for different slopes and volume changes is given below:

$$Q = \frac{p * r}{((1 + p)10^{\Delta E/S}) - 1}$$

where:

ΔE = $E_2 - E_1$

S = slope of the electrode

p = (volume of standard) / (volume of sample & ISA)

r = (volume of sample & ISA) / (volume of sample)

Table 3

Volume of Addition	Concentration of Standard Before Adding ISA
1 mL	100 x sample concentration
5 mL	20 x sample concentration
10 mL*	10 x sample concentration

*Most convenient volume to use, valid for Q Tables

If it is more convenient, a simple spreadsheet can be set up to calculate known addition results, using any ratios of sample and addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 4

Calculating known addition for potassium samples using Lotus, Excel or Quattro Spreadsheet

A	B	C
1		Enter Values
2	VOL. OF SAMPLE & ISA, ML	102
3	VOL. OF ADDITION, ML	10
4	CONCENTRN. OF ADDITION	10
5	VOL. OF SAMPLE	100
6	INITIAL MV READING	-45.3
7	FINAL MV READING	-63.7
8	ELECTRODE SLOPE	59.2
9		
10		DERIVED VALUES
11	DELTA E	+C7-C6
12	p-TERM	+C3/C2
13	ANTILOG TERM	+10^(C11/C8)
14	r TERM	+C2/C5
15	Q TERM	+C12*C14/(((1+C12)*C13)-1)
16	CALCULATED INITIAL CONC. IN SAME UNIT AS ADDITION	+C15*C4

NOTE: for Excel, use = instead of + at start of formula

Table 5

Known Addition for an added volume one-tenth the sample volume. Slopes (in the column headings) are in units of mV/decade

ΔE	Q, Concentration Ratio			
		Slope		
Monovalent	**57.2**	**58.2**	**59.2**	**60.1**
5.0	0.2917	0.2957	0.2996	0.3031
5.2	0.2827	0.2867	0.2906	0.2940
5.4	0.2742	0.2781	0.2820	0.2854
5.6	0.2662	0.2700	0.2738	0.2772
5.8	0.2585	0.2623	0.2660	0.2693
6.0	0.2512	0.2550	0.2586	0.2619
6.2	0.2443	0.2480	0.2516	0.2548
6.4	0.2377	0.2413	0.2449	0.2480
6.6	0.2314	0.2349	0.2384	0.2416
6.8	0.2253	0.2288	0.2323	0.2354
7.0	0.2196	0.2230	0.2264	0.2295
7.2	0.2140	0.2174	0.2208	0.2238
7.4	0.2087	0.2121	0.2154	0.2184
7.6	0.2037	0.2070	0.2102	0.2131
7.8	0.1988	0.2020	0.2052	0.2081
8.0	0.1941	0.1973	0.2005	0.2033
8.2	0.1896	0.1927	0.1959	0.1987
8.4	0.1852	0.1884	0.1914	0.1942
8.6	0.1811	0.1841	0.1872	0.1899
8.8	0.1770	0.1801	0.1831	0.1858
9.0	0.1732	0.1762	0.1791	0.1818
9.2	0.1694	0.1724	0.1753	0.1779
9.4	0.1658	0.1687	0.1716	0.1742
9.6	0.1623	0.1652	0.1680	0.1706
9.8	0.1590	0.1618	0.1646	0.1671
10.0	0.1557	0.1585	0.1613	0.1638
10.2	0.1525	0.1553	0.1580	0.1605
10.4	0.1495	0.1522	0.1549	0.1573
10.6	0.1465	0.1492	0.1519	0.1543
10.8	0.1437	0.1463	0.1490	0.1513
11.0	0.1409	0.1435	0.1461	0.1485
11.2	0.1382	0.1408	0.1434	0.1457
11.4	0.1356	0.1382	0.1407	0.1430
11.6	0.1331	0.1356	0.1381	0.1404
11.8	0.1306	0.1331	0.1356	0.1378

ΔE	**Q, Concentration Ratio**			
		Slope		
Monovalent	**57.2**	**58.2**	**59.2**	**60.1**
12.0	0.1282	0.1307	0.1331	0.1353
12.2	0.1259	0.1283	0.1308	0.1329
12.4	0.1236	0.1260	0.1284	0.1306
12.6	0.1214	0.1238	0.1262	0.1283
12.8	0.1193	0.1217	0.1240	0.1261
13.0	0.1172	0.1195	0.1219	0.1239
13.2	0.1152	0.1175	0.1198	0.1218
13.4	0.1132	0.1155	0.1178	0.1198
13.6	0.1113	0.1136	0.1158	0.1178
13.8	0.1094	0.1117	0.1139	0.1159
14.0	0.1076	0.1098	0.1120	0.1140
14.2	0.1058	0.1080	0.1102	0.1121
14.4	0.1041	0.1063	0.1084	0.1103
14.6	0.1024	0.1045	0.1067	0.1086
14.8	0.1008	0.1029	0.1050	0.1069
15.0	0.0992	0.1012	0.1033	0.1052
15.5	0.0953	0.0973	0.0994	0.1012
16.0	0.0917	0.0936	0.0956	0.0974
16.5	0.0882	0.0902	0.0921	0.0938
17.0	0.0850	0.0869	0.0887	0.0904
17.5	0.0819	0.0837	0.0856	0.0872
18.0	0.0790	0.0808	0.0825	0.0841
18.5	0.0762	0.0779	0.0797	0.0813
19.0	0.0736	0.0753	0.0770	0.0785
19.5	0.0711	0.0727	0.0744	0.0759
20.0	0.0687	0.0703	0.0719	0.0734
20.5	0.0664	0.0680	0.0696	0.0710
21.0	0.0642	0.0658	0.0673	0.0687
21.5	0.0621	0.0637	0.0652	0.0666
22.0	0.0602	0.0617	0.0631	0.0645
22.5	0.0583	0.0597	0.0612	0.0625
23.0	0.0564	0.0579	0.0593	0.0606
23.5	0.0547	0.0561	0.0575	0.0588
24.0	0.0530	0.0544	0.0558	0.0570
24.5	0.0514	0.0528	0.0541	0.0553
25.0	0.0499	0.0512	0.0525	0.0537
25.5	0.0484	0.0497	0.0510	0.0522

ΔE	Q, Concentration Ratio			
		Slope		
Monovalent	**57.2**	**58.2**	**59.2**	**60.1**
26.0	0.0470	0.0483	0.0495	0.0507
26.5	0.0456	0.0469	0.0481	0.0492
27.0	0.0443	0.0455	0.0468	0.0479
27.5	0.0431	0.0443	0.0455	0.0465
28.0	0.0419	0.0430	0.0442	0.0452
28.5	0.0407	0.0418	0.0430	0.0440
29.0	0.0395	0.0407	0.0418	0.0428
29.5	0.0385	0.0396	0.0407	0.0417
30.0	0.0374	0.0385	0.0396	0.0406
30.5	0.0364	0.0375	0.0385	0.0395
31.0	0.0354	0.0365	0.0375	0.0384
31.5	0.0345	0.0355	0.0365	0.0374
32.0	0.0335	0.0345	0.0356	0.0365
32.5	0.0327	0.0336	0.0346	0.0355
33.0	0.0318	0.0328	0.0337	0.0346
33.5	0.0310	0.0319	0.0329	0.0337
34.0	0.0302	0.0311	0.0320	0.0329
34.5	0.0294	0.0303	0.0312	0.0321
35.0	0.0286	0.0295	0.0305	0.0313
35.5	0.0279	0.0288	0.0297	0.0305
36.0	0.0272	0.0281	0.0290	0.0298
36.5	0.0265	0.0274	0.0282	0.0290
37.0	0.0258	0.0267	0.0275	0.0283
37.5	0.0252	0.0260	0.0269	0.0276
38.0	0.0246	0.0254	0.0262	0.0270
38.5	0.0240	0.0248	0.0256	0.0263
39.0	0.0234	0.0242	0.0250	0.0257
39.5	0.0228	0.0236	0.0244	0.0251
40.0	0.0223	0.0230	0.0238	0.0245
40.5	0.0217	0.0225	0.0232	0.0239
41.0	0.0212	0.0219	0.0227	0.0234
41.5	0.0207	0.0214	0.0221	0.0228
42.0	0.0202	0.0209	0.0216	0.0223
42.5	0.0197	0.0204	0.0211	0.0218
43.0	0.0192	0.0199	0.0206	0.0213
43.5	0.0188	0.0195	0.0202	0.0208
44.0	0.0183	0.0190	0.0197	0.0203
44.5	0.0179	0.0186	0.0192	0.0198

ΔE	Q, Concentration Ratio			
		Slope		
Monovalent	**57.2**	**58.2**	**59.2**	**60.1**
45.0	0.0175	0.0181	0.0188	0.0194
45.5	0.0171	0.0177	0.0184	0.0190
46.0	0.0167	0.0173	0.0179	0.0185
46.5	0.0163	0.0169	0.0175	0.0181
47.0	0.0159	0.0165	0.0171	0.0177
47.5	0.0156	0.0162	0.0168	0.0173
48.0	0.0152	0.0158	0.0164	0.0169
48.5	0.0148	0.0154	0.0160	0.0166
49.0	0.0145	0.0151	0.0157	0.0162
49.5	0.0142	0.0147	0.0153	0.0158
50.0	0.0139	0.0144	0.0150	0.0155
50.5	0.0135	0.0141	0.0146	0.0151
51.0	0.0132	0.0138	0.0143	0.0148
51.5	0.0129	0.0135	0.0140	0.0145
52.0	0.0126	0.0132	0.0137	0.0142
52.5	0.0124	0.0129	0.0134	0.0139
53.0	0.0121	0.0126	0.0131	0.0136
53.5	0.0118	0.0123	0.0128	0.0133
54.0	0.0116	0.0120	0.0125	0.0130
54.5	0.0113	0.0118	0.0123	0.0127
55.0	0.0110	0.0115	0.0120	0.0125
55.5	0.0108	0.0113	0.0118	0.0122
56.0	0.0106	0.0110	0.0115	0.0119
56.5	0.0103	0.0108	0.0113	0.0117
57.0	0.0101	0.0106	0.0110	0.0114
57.5	0.0099	0.0103	0.0108	0.0112
58.0	0.0097	0.0101	0.0105	0.0110
58.5	0.0095	0.0099	0.0103	0.0107
59.0	0.0093	0.0097	0.0101	0.0105
59.5	0.0091	0.0095	0.0099	0.0103
60.0	0.0089	0.0093	0.0097	0.0101

ELECTRODE STORAGE

9319BN Potassium Half-Cell Electrode

The potassium sensing module should be kept in the glass vial until used. The assembled electrode can be stored in potassium standard. For long periods of time (over 2-3 days), disassemble the potassium electrode, rinse thoroughly with distilled water, blot dry, and store the module in its vial.

9719BNWP ionplus Potassium Combination Electrode

The solution in the potassium combination electrode should not be allowed to evaporate and crystallize around the junction.

For short periods of time (2-3 days):

Store the assembled electrode in potassium standard, such as 10^{-2} M.

For storage longer than 2-3 days:

Drain the reference compartment of the electrode and flush it with distilled water. Disassemble the electrode, see **Figure 2**, as follows to remove the potassium sensing module:

1. Grasp the outer body sleeve. With your other hand, unscrew the electrode cap. Allow cap and spring assembly to slide down the electrode cable.
2. Push the inner stem of the electrode handle out through the outer electrode sleeve, exposing the sensing module.
3. Rinse the inner stem and module well with distilled water. Blot dry gently in order not to damage the sensing membrane.
4. Carefully unscrew the sensing module from the inner stem, **taking care not to touch the sensing membrane**.
5. Place the potassium sensing module in the glass vial until it is to be used again.
6. Gently dry the inside of the inner stem and O-ring area with a lint-free tissue and reassemble the electrode handle. Store dry.

900200 Double Junction Reference Electrode

The double junction reference electrode may be stored in air between sample measurements (up to 1 hour).

For short periods of time (up to one week):

The double junction reference electrode may be stored in its filling solution or distilled water. Do not allow the solution inside the electrode to evaporate and crystallize.

For long periods of time (over one week):

Drain the reference electrode completely, rinse with distilled water, and store dry.

TROUBLESHOOTING

Troubleshooting Checklist

Symptom	Possible Causes
Off-scale or Over-range reading	Defective meter Defective sensing module Electrodes not plugged in properly Module not installed properly Reference electrode junction is dry (9719BNWP and 900200) No reference electrode (9319BN) Reference electrode chamber not filled (9719BNWP and 900200) Interior of membrane not thoroughly wetted Air bubble on membrane Electrodes not in solution
Noisy or unstable readings (readings continuously or rapidly changing)	Defective meter Meter or stirrer improperly grounded Module not installed properly Air bubble on membrane Interior of the membrane not thoroughly wetted Wrong reference electrode ISA not used 9719BNWP electrode cap on too tight
Drift (Reading slowly changing in one direction)	Samples and standards at different temperatures Electrode exposed to interference Incorrect reference filling solution Membrane may contain a surface layer of contaminants 9719BNWP electrode cap on too tight

Solution
Check meter with shorting cap (See meter user guide) Refer to **Troubleshooting Guide** Unplug electrodes and reseat Check **Before Using the Electrode** Through the reference junction, expel a few drops of filling solution Use the 900200 reference electrode (with 9319BN potassium electrode) Be sure reference electrode is filled with correct solution. See **Electrode Assembly and Preparation**. Tap module gently or shake down like a clinical thermometer Remove air bubble by gently tapping electrode Put electrodes in solution
Check meter with shorting cap. (See meter user guide) Check meter and stirrer for grounding Check **Before Using the Electrode** Remove air bubble by gently tapping electrode Tap module gently or shake down like a clinical thermometer Use the 900200 double junction reference electrode (with 9319BN potassium electrode) Do not use calomel or Ag/AgCl (frit-or fiber-type) reference electrode Use recommended ISA, Cat. No. 931911 Reassemble electrode. See **Electrode Assembly and Preparation**.
Allow solutions to come to room temperature before measurement, See **Interferences** Use recommended filling solution. See **Electrode Assembly and Preparation** Rinse electrode with distilled water and soak in potassium standard (10^{-2} M) for 1 hour Reassemble electrode. See **Electrode Assembly and Preparation**.

Troubleshooting Checklist (cont.)

Symptom	Possible Causes
Low slope or No slope	Electrodes not properly conditioned
	Standards contaminated or incorrectly made
	ISA not used
	Standard used as ISA
	9719BNWP electrode cap on too tight
	Defective sensing module
	Electrode exposed to interferences
"Wrong Answer" (But calibration curve is OK)	Incorrect scaling of semi-log paper
	Incorrect standards
	Incorrect sign
	Wrong units used

Solution
See **Electrode Assembly and Preparation**
Prepare fresh standards
Use recommended ISA, Cat. No. 931911
Use ISA!
Reassemble electrode. See **Electrode Assembly and Preparation**.
Refer to **Troubleshooting Guide**
See **Interferences**.
Plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
Prepare fresh standards
Be sure to note sign of millivolt value correctly
Apply correct conversion factor: 10^{-3} M = 39.1 ppm as K^+ = 74.6 ppm as KCl
For additional information on blank correction, see the meter user guide.

Troubleshooting Guide

The most important principle in troubleshooting is to isolate the components of the system and check each in turn. The components of the system are: 1) Meter 2) Electrodes 3) Standard 4) Sample and 5) Technique. See also **Important ISE Measurement Techniques** and **For Improved Accuracy** sections.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters are provided with an instrument checkout procedure in the user guide and a shorting cap for convenience in troubleshooting. Consult the user guide for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Electrodes

1. Rinse electrodes thoroughly with distilled water.
2. Check electrode operation (slope), see **Checking Electrode Operation**.
3. If electrode fails this procedure, resoak potassium electrode as directed in **Electrode Assembly and Preparation**.

   Clean reference electrode as described in reference electrode user guide (used with 9319BN only).
4. Repeat step 2.

5a. For the 9319BN Potassium Half-Cell Electrode:
If the electrodes still do not perform as described, determine whether the potassium or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the slope check.

5b. For the 9719BNWP Potassium Combination Electrode:
Disassemble and reassemble the electrode, taking care not to overtighten the cap. If the electrode still does not perform as described, replace the sensing module and repeat the slope check. If the slope check still fails, replace the electrode handle.

6. If the stability and slope check out properly, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error. See **Standard**, **Sample**, and **Technique** sections.
7. Before replacing a “faulty” electrode, or if another electrode is not available for test purposes, review the user guide and be sure to:

   - Clean the electrode thoroughly
   - Prepare the electrode properly
   - Check that the 9719BNWP electrode cap is not too tight
   - Use proper filling solution, ISA, and standards
   - Measure correctly
   - Review **Troubleshooting Checklist**

Standard

The quality of results depends greatly upon the quality of the standards. Always prepare fresh standards when problems arise as it could save hours of frustrating troubleshooting! Error may result from contamination of prepared standards, quality of dilution, distilled water, or a numerical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. This procedure involves preparing an initial standard that is diluted to prepare a second standard solution using volumetric glassware. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

Sample

If the electrodes work properly in standards but not in sample, look for possible interferences, complexing agents, or substances that could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Sample Requirements, Interferences,** and **Specifications**.

Technique

Check the method of analysis for compatibility with your sample. Direct measurement may not always be the method of choice. If the ionic strength varies markedly from sample to sample, known addition may be best. If working at low levels, be sure to follow the low level measurement technique. Also, be sure that the expected concentration of the ion of interest is within the electrode's limits of detection. If problems persist, review operational procedures and user guides to be sure that proper technique has been followed. Read **Important ISE Measurement Techniques** and **Measurement Procedures**.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com/contactwater.

Warranty

For the most current warranty information, visit www.thermo.com/water.

ELECTRODE CHARACTERISTICS

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 54 to 60 mV per decade until concentration reaches 10^{-5} M. See **Figure 4**.

The electrode exhibits good time response (99% in one minute or less) for potassium concentrations above 10^{-5} M K^+. Below this value response times vary from 2 to 5 minutes. See **Figure 5**.

Limits of Detection

In pure potassium chloride solutions, the upper limit of detection is 1 M. When possible, dilute the sample into the linear working range of the electrode. If this is not possible, the possibility of a liquid junction potential at the reference electrode and the "salt extraction effect", need to be considered. At high salt concentrations, some salts may be extracted into the electrode membrane, causing deviation from theoretical response. To measure samples between 10^{-1} and 1 M, calibrate the electrode at 4 or 5 intermediate points, or dilute the sample.

The lower limit of detection is determined by the slight water solubility of the ion exchanger, which causes deviation from theoretical response. **Figure 4** shows the theoretical response at low levels of potassium chloride compared to the actual response. If potassium measurements are made below 10^{-5} M (0.39 ppm as K^+), a low-level measurement procedure is recommended.

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the electrode operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements reproducible to ± 2% can be obtained.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1°C (± 2°F) of each other. At the 10^{-3} M level, a 1°C difference in temperature results in a 2.5% error. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the potassium electrode also varies with temperature, as indicated by the factor “S” in the Nernst equation. Values for the change in slope for potassium ion are given in **Table 6**. If temperature changes occur, meter and electrodes should be recalibrated.

The electrode can be used at temperatures from 0 to 40 °C, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, equilibriation times of up to one hour are recommended.

The isopotential concentration, C_{iso}, of the 9719BNWP potassium combination electrode is approximately 1.54 M.

Table 6
Values of Electrode Slope vs. Temperature

T °C	S	T °C	S
0	54.20	30	60.15
10	56.18	40	62.13
20	58.16	50	64.11
25	59.16		

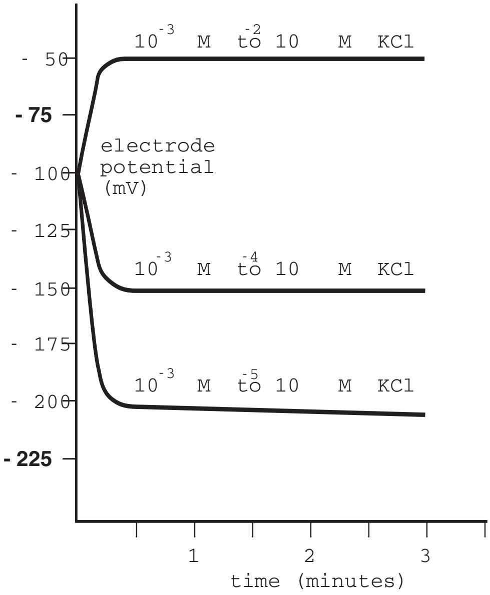


Figure 5
Typical Electrode Response to KCl

Interferences

Cations, if present at high enough levels, are electrode interferences and will cause measurement errors. **Table 7** indicates levels of common cations that will cause 10% errors at different concentrations of potassium.

If the electrode is exposed to high levels of interfering ions, it may become drifty and sluggish in response. When this happens, restore normal performance by soaking for an hour in distilled water, then for a few hours in potassium standard solution.

When the level of interferences in samples is constant, it is sometimes possible to measure potassium accurately when interference levels are higher than those in **Table 7**. Call Thermo Electron's Technical Edge for more information. See **Assistance**.

pH Effects

Although the electrode can be used over a wide pH range, hydrogen ion interferes with measurements of low levels of potassium ion. Refer to **Table 7** to determine the minimum pH at which low level potassium measurements can be made without more than a 10% error due to hydrogen ion interference.

Electrode Life

Each sensing module should last at least six months in normal laboratory use. In time, electrode slope will decrease and readings will start to drift, indicating that the module should be changed. Before replacement, refer to **Troubleshooting Checklist**, to make sure that the difficulties are caused by the sensing module.

Table 7
Levels of Possible Interferences Causing a 10% Error Interferences to Potassium Chloride with a Background Ionic Strength of 0.12 M Sodium Chloride

Moles/Liter	10^{-4} M	10^{-3} M	10^{-2} M
Cs^+	3×10^{-5}	3×10^{-4}	3×10^{-3}
NH_4^+	6×10^{-4}	6×10^{-3}	6×10^{-2}
Tl^+	6×10^{-4}	6×10^{-3}	6×10^{-2}
H^+	1×10^{-3}	1×10^{-2}	0.1
Ag^+	0.1	1.0	10
*$Tris^+$	0.1	1.0	10
Li^+	0.2	2.0	20
Na^+	0.2	2.0	20

* Tris is the cation of tris(hydroxymethyl) aminomethane.

Interferences

ppm	1 ppm	10 ppm	100 ppm
Cs^+	1.0	10	100
NH_4^+	2.7	27	270
Tl^+	31.4	314	3140
H^+	3.6 pH	2.6 pH	1.6 pH
Ag^+	2,765	27,650	276,500
*$Tris^+$	3,105	31,050	310,500
Li^+	356	3,560	35,600
Na^+	1,179	11,790	117,900

* Tris is the cation of tris(hydroxymethyl) aminomethane.

Theory of Operation

The potassium electrode consists of an electrode body and a replaceable pretested sensing module. The sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a potassium selective ion exchanger. See **Figure 6**.

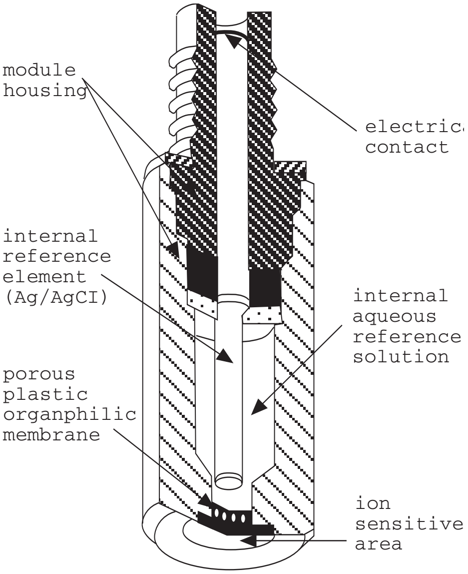


Figure 6
Example of Ion Sensing Module

When the membrane is in contact with a potassium solution, an electrode potential develops across the membrane. This potential, which depends on the level of free potassium ion in solution, is measured against a constant reference potential with a pH/mV meter or specific ion meter. The measured potential corresponding to the level of potassium ion in solution is described by the Nernst equation:

$$\mathbf{E = E_o + S \log (A)}$$

where:

E = measured electrode potential

E_o = reference potential (a constant)

A = potassium ion level in solution

S = electrode slope (about 57 mV per decade)

The level of potassium ion, A, is the activity or "effective concentration" of free potassium ion in solution. The total potassium concentration, C_t, includes some bound or complexed ions as well as free ions, whose concentration is:

$$\mathbf{C_t = C_f + C_b}$$

where:

C_b = concentration of potassium ions in all
bound or complexed forms

C_f = concentration of free potassium ions

The potassium ion activity is related to free potassium ion concentration by the activity coefficient:

$$\mathbf{A = \gamma C_f}$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ion strength is defined as:

$$\textbf{Ionic strength} = \mathbf{1/2\Sigma(C_i Z_i^2)}$$

C_i = concentration of ion i

Z_i = charge of ion i

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration.

Ionic strength adjustor (ISA) is added to all potassium standards and samples so that the background ionic strength is high and constant relative to variable concentrations of potassium ion. For the potassium electrode, NaCl is the recommended ISA. Other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to potassium ion.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, the electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements, it is important that this potential be the same when the reference is in the standardizing solution as well as in the sample solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable which analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result. Using the Optimum Results E filling solution in the 9719BNWP will minimize junction potential in most samples.

ORDERING INFORMATION

Cat. No.	**Description**
9719BNWP	Potassium ionplus Sure-Flow combination electrode, waterproof BNC connector
9319BN	Potassium half-cell electrode, BNC connector
900200	Double junction reference electrode
900002	Inner chamber filling solution for the double junction reference electrode, 5 x 60 mL bottles
900065	Optimum Results E filling solution for 9719BNWP potassium electrode, 5 x 60 mL bottles
921906	0.1 M potassium standard solution, 475 mL bottle
931911	Ionic Strength Adjustor solution, 475 mL bottle
971901	Replacement Sensing Module for Orion 97-19 ***ionplus*** Potassium Electrode, 1 each
971901	(1) Replacement sensing module for 9719BNWP potassium combination electrode
931901	(1) Replacement sensing module for 9319BN potassium half-cell electrode
900060	ionplus stirring accessory

SPECIFICATIONS

Concentration Range

1×10^{-6} M to 1 M K^+
0.04 ppm to 39,000 ppm K^+

pH Range

2.5 to 11 pH
Low level measurements may be influenced by hydrogen or hydroxide ion interferences.

Temperature Range

0 to 40°C

Electrode Resistance

Less than 50 megohms

Reproducibility

± 2%

Sample

Aqueous solutions only

Module Life

Six months under normal laboratory conditions

Size	**9319BN**	**9719BNWP**
Electrode Length (Body with Module)	135 mm	110 mm
Cap Length	30 mm	30 mm
Cap Diameter	16 mm	16 mm
Electrode Diameter	12 mm	13 mm
Cable Length	1 meter	1 meter
Maximum Immersion Depth	22 mm	Up to fill hole

Thermo Fisher Scientific

Environmental Instruments
Water Analysis Instruments

166 Cummings Center
Beverly, MA 01915 USA
Tel: 978-232-6000
Toll Free: 800-225-1480
Dom. Fax: 978-232-6015
Int’l. Fax: 978-232-6031

www.thermo.com/water

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