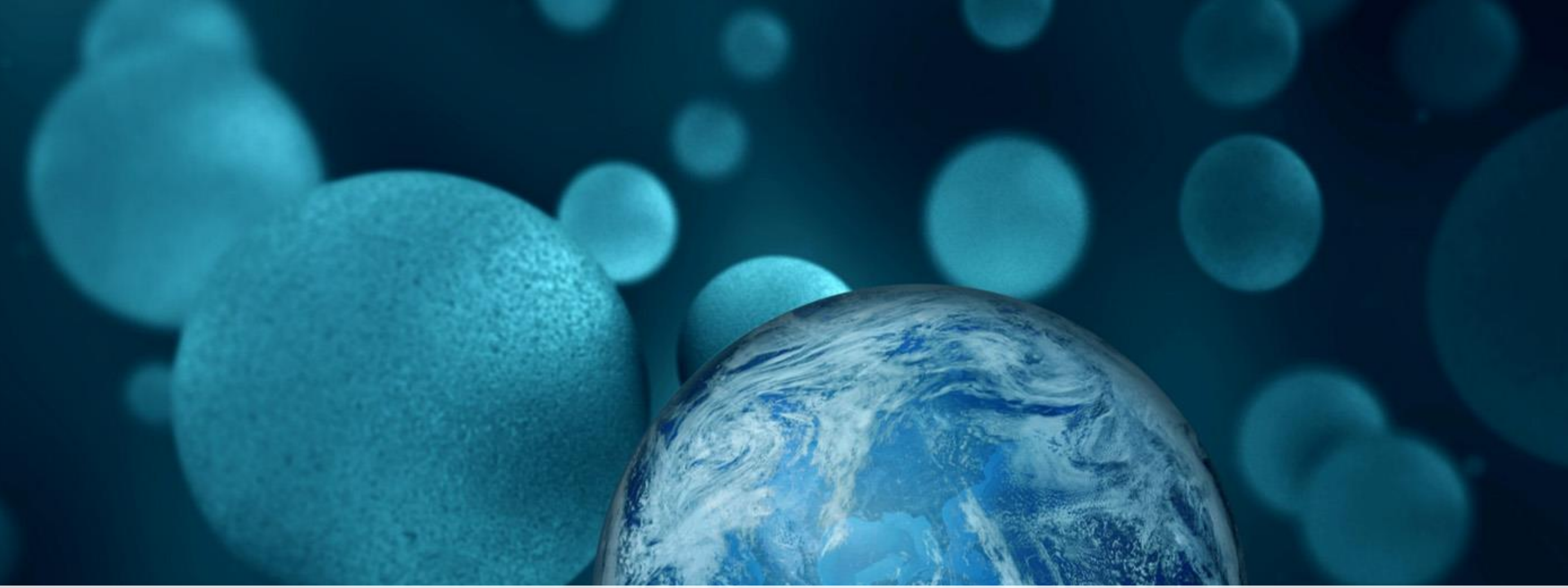

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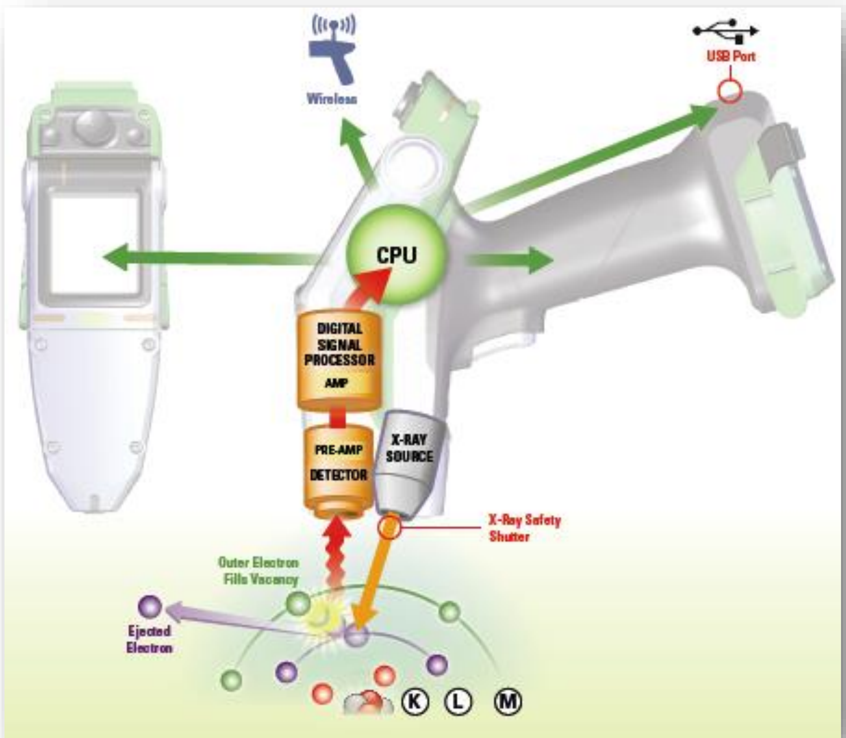
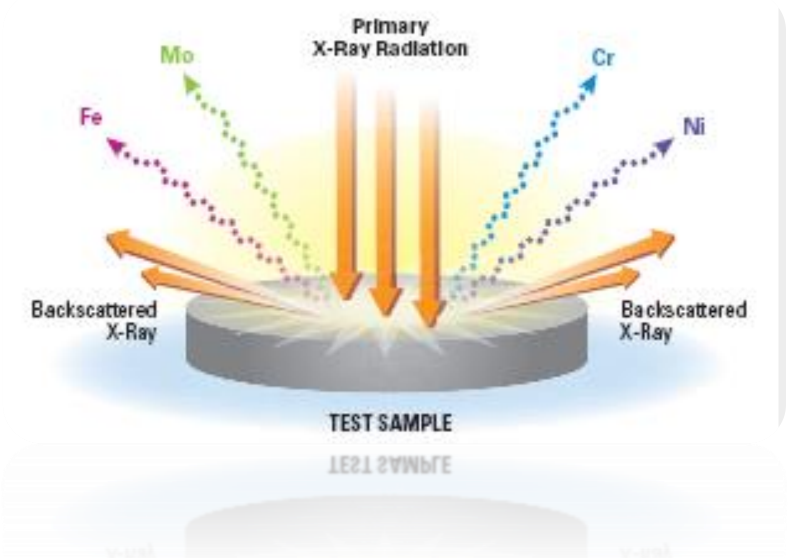
X선 형광분석 소개

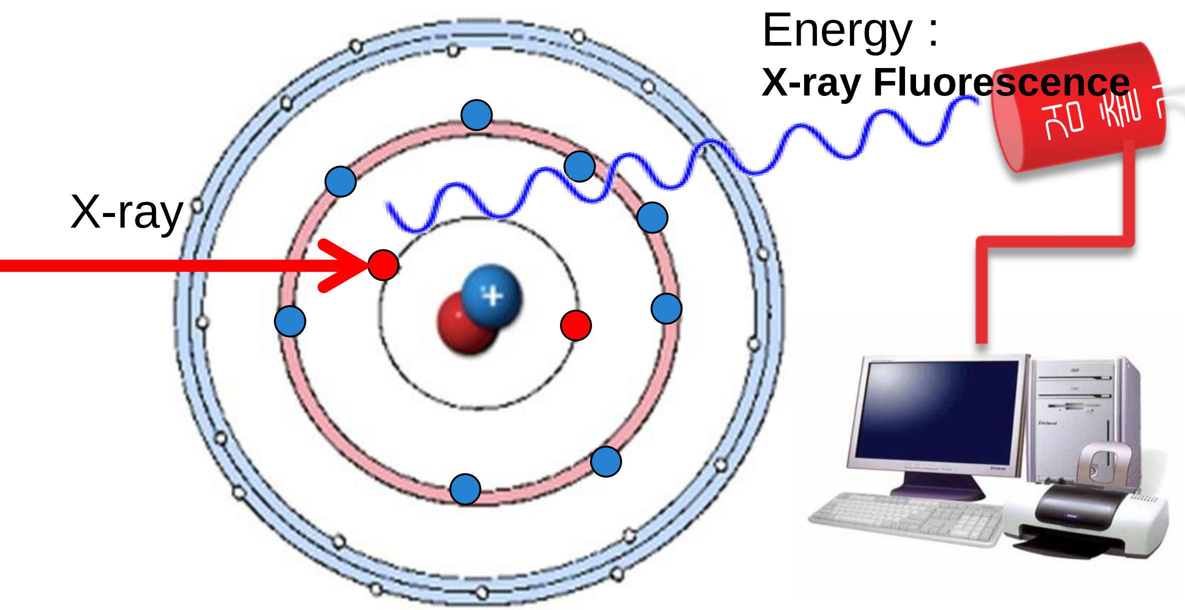
Introduction to X-Ray Fluorescence

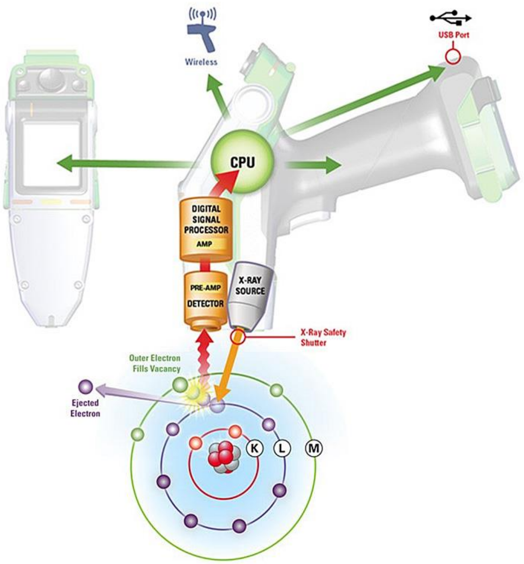
How the XRF Works



- Each individual element produces its own set of characteristic x-rays; the basis for **qualitative** analysis
- By counting the number of characteristic x-rays of a given element we can determine its concentration; the basis for **quantitative** analysis





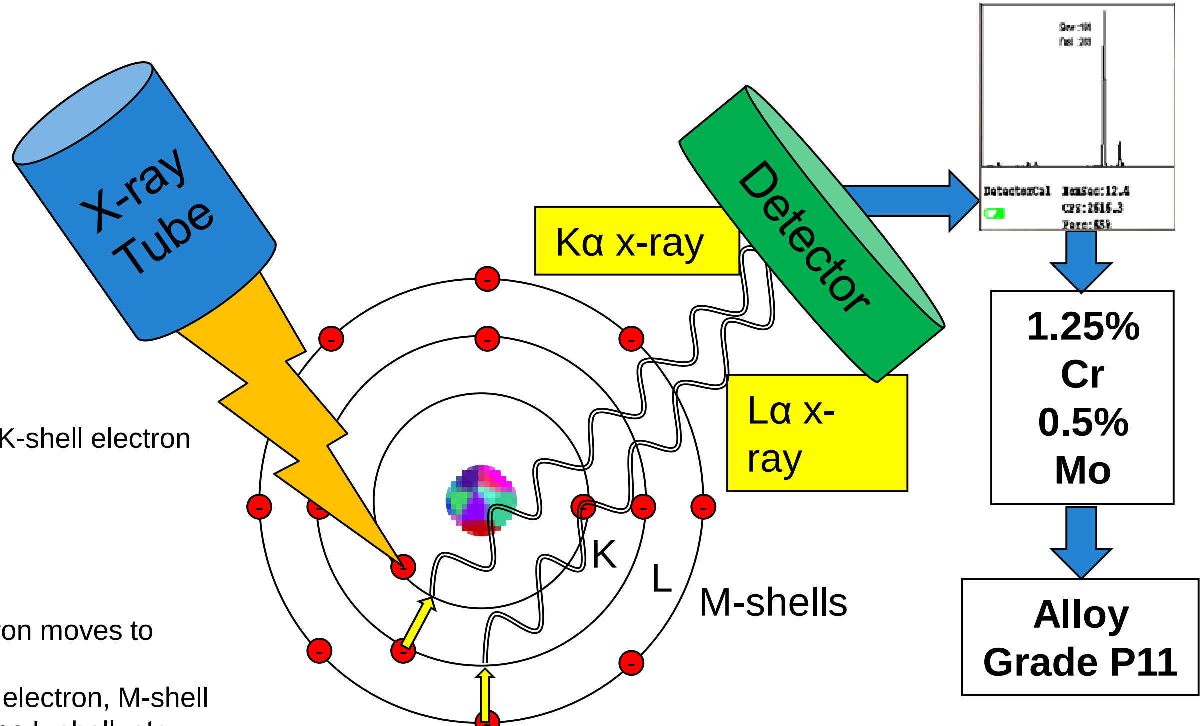


엑스선 입사 (광원) → 엑스선 형광 (샘플) → 각 원소별 분석 (검출기) → 정성 및 정량 분석 (내장 PC)

Technology Basics

1. X-ray ejects K-shell electron

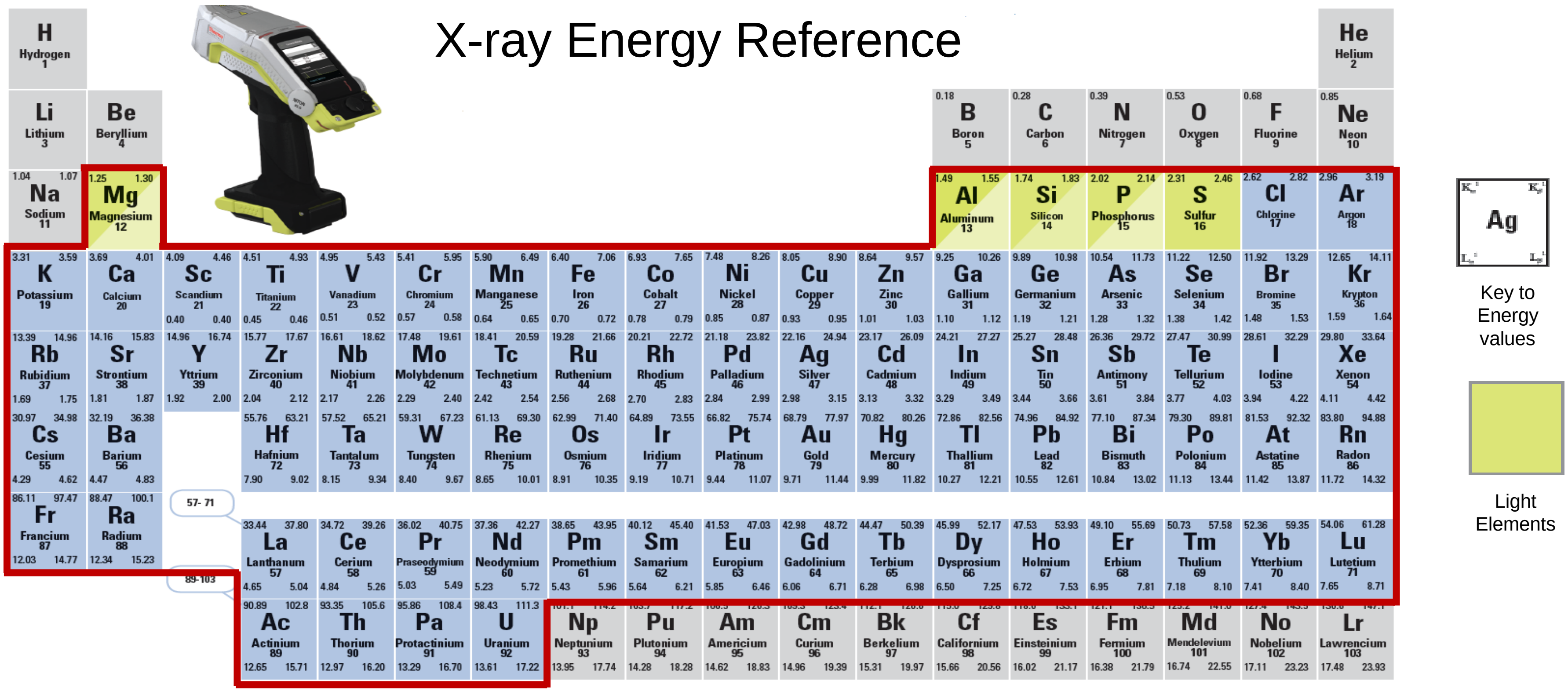
2. L-shell electron moves to replace
ejected K-shell electron, M-shell electron replaces L-shell, etc…



3. Reduced energy state is given off as a "Kα", "Lα", etc. x-rays, the energies of which are read by the detector

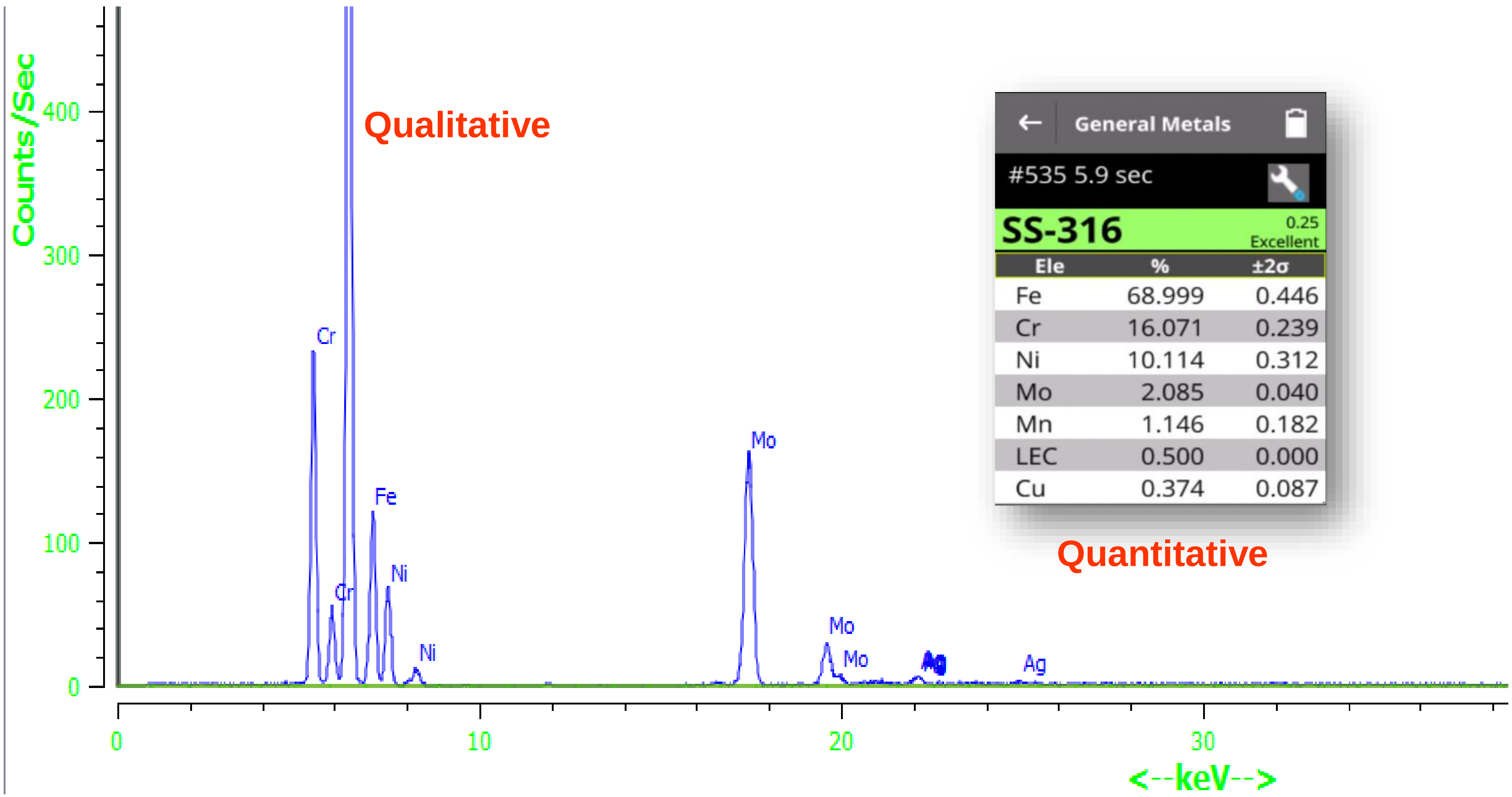
4. The x-ray energies and fluxes are interpreted by the analyzer into the corresponding elements, concentrations, and resultant alloy grade

Total 분석 범위



X-ray Energy Reference
H Hydrogen 1
He Helium 2
Li Lithium 3
Be Beryllium 4
0.18 B Boron 5
0.28 C Carbon 6
0.39 N Nitrogen 7
0.53 O Oxygen 8
0.68 F Fluorine 9
0.85 Ne Neon 10
1.04 1.07 Na Sodium 11
1.25 1.30 Mg Magnesium 12
1.49 1.55 Al Aluminum 13
1.74 1.83 Si Silicon 14
2.02 2.14 P Phosphorus 15
2.31 2.46 S Sulfur 16
2.62 2.82 Cl Chlorine 17
2.96 3.19 Ar Argon 18
3.31 3.59 K Potassium 19
3.69 4.01 Ca Calcium 20
4.09 4.46 Sc Scandium 21 0.40 0.40
4.51 4.93 Ti Titanium 22 0.45 0.46
4.95 5.43 V Vanadium 23 0.51 0.52
5.41 5.95 Cr Chromium 24 0.57 0.58
5.90 6.49 Mn Manganese 25 0.64 0.65
6.40 7.06 Fe Iron 26 0.70 0.72
6.93 7.65 Co Cobalt 27 0.78 0.79
7.48 8.26 Ni Nickel 28 0.85 0.87
8.05 8.90 Cu Copper 29 0.93 0.95
8.64 9.57 Zn Zinc 30 1.01 1.03
9.25 10.26 Ga Gallium 31 1.10 1.12
9.89 10.98 Ge Germanium 32 1.19 1.21
10.54 11.73 As Arsenic 33 1.28 1.32
11.22 12.50 Se Selenium 34 1.38 1.42
11.92 13.29 Br Bromine 35 1.48 1.53
12.65 14.11 Kr Krypton 36 1.59 1.64
13.39 14.96 Rb Rubidium 37 1.69 1.75
14.16 15.83 Sr Strontium 38 1.81 1.87
14.96 16.74 Y Yttrium 39 1.92 2.00
15.77 17.67 Zr Zirconium 40 2.04 2.12
16.61 18.62 Nb Niobium 41 2.17 2.26
17.48 19.61 Mo Molybdenum 42 2.29 2.40
18.41 20.59 Tc Technetium 43 2.42 2.54
19.28 21.66 Ru Ruthenium 44 2.56 2.68
20.21 22.72 Rh Rhodium 45 2.70 2.83
21.18 23.82 Pd Palladium 46 2.84 2.99
22.16 24.94 Ag Silver 47 2.98 3.15
23.17 26.09 Cd Cadmium 48 3.13 3.32
24.21 27.27 In Indium 49 3.29 3.49
25.27 28.48 Sn Tin 50 3.44 3.66
26.36 29.72 Sb Antimony 51 3.61 3.84
27.47 30.99 Te Tellurium 52 3.77 4.03
28.61 32.29 I Iodine 53 3.94 4.22
29.80 33.64 Xe Xenon 54 4.11 4.42
30.97 34.98 Cs Cesium 55 4.29 4.62
32.19 36.38 Ba Barium 56 4.47 4.83
55.76 63.21 Hf Hafnium 72 7.90 9.02
57.52 65.21 Ta Tantalum 73 8.15 9.34
59.31 67.23 W Tungsten 74 8.40 9.67
61.13 69.30 Re Rhenium 75 8.65 10.01
62.99 71.40 Os Osmium 76 8.91 10.35
64.89 73.55 Ir Iridium 77 9.19 10.71
66.82 75.74 Pt Platinum 78 9.44 11.07
68.79 77.97 Au Gold 79 9.71 11.44
70.82 80.26 Hg Mercury 80 9.99 11.82
72.86 82.56 Tl Thallium 81 10.27 12.21
74.96 84.92 Pb Lead 82 10.55 12.61
77.10 87.34 Bi Bismuth 83 10.84 13.02
79.30 89.81 Po Polonium 84 11.13 13.44
81.53 92.32 At Astatine 85 11.42 13.87
83.80 94.88 Rn Radon 86 11.72 14.32
86.11 97.47 Fr Francium 87 12.03 14.77
88.47 100.1 Ra Radium 88 12.34 15.23
57- 71
89-103
33.44 37.80 La Lanthanum 57 4.65 5.04
34.72 39.26 Ce Cerium 58 4.84 5.26
36.02 40.75 Pr Praseodymium 59 5.03 5.49
37.36 42.27 Nd Neodymium 60 5.23 5.72
38.65 43.95 Pm Promethium 61 5.43 5.96
40.12 45.40 Sm Samarium 62 5.64 6.21
41.53 47.03 Eu Europium 63 5.85 6.46
42.98 48.72 Gd Gadolinium 64 6.06 6.71
44.47 50.39 Tb Terbium 65 6.28 6.98
45.99 52.17 Dy Dysprosium 66 6.50 7.25
47.53 53.93 Ho Holmium 67 6.72 7.53
49.10 55.69 Er Erbium 68 6.95 7.81
50.73 57.58 Tm Thulium 69 7.18 8.10
52.36 59.35 Yb Ytterbium 70 7.41 8.40
54.06 61.28 Lu Lutetium 71 7.65 8.71
90.89 102.8 Ac Actinium 89 12.65 15.71
93.35 105.6 Th Thorium 90 12.97 16.20
95.86 108.4 Pa Protactinium 91 13.29 16.70
98.43 111.3 U Uranium 92 13.61 17.22
Np Neptunium 93 13.95 17.74
Pu Plutonium 94 14.28 18.28
Am Americium 95 14.62 18.83
Cm Curium 96 14.96 19.39
Bk Berkelium 97 15.31 19.97
Cf Californium 98 15.66 20.56
Es Einsteinium 99 16.02 21.17
Fm Fermium 100 16.38 21.79
Md Mendelevium 101 16.74 22.55
No Nobelium 102 17.11 23.23
Lr Lawrencium 103 17.48 23.93
Ag
Key to Energy values
Light Elements

XRF Spectrum



Qualitative

General Metals

#535 5.9 sec

SS-316 0.25 Excellent

Ele	%	±2σ
Fe	68.999	0.446
Cr	16.071	0.239
Ni	10.114	0.312
Mo	2.085	0.040
Mn	1.146	0.182
LEC	0.500	0.000
Cu	0.374	0.087

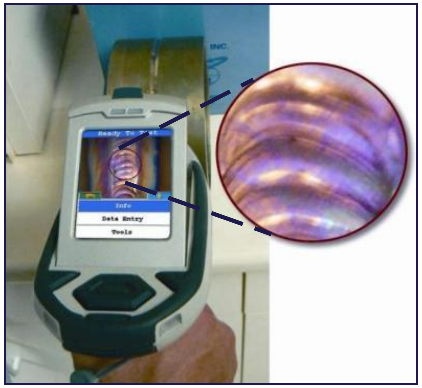
Quantitative

Application for HHXRF

Energy Markets / Positive Material Identification (PMI)

Fabrication and Metals QC/QA

Scrap Recycling



Weld analysis

Thermo Fisher SCIENTIFIC

XL5 Coatings Mode

Mathieu Bauer, Senior Application Scientist
SEATW Sales Meeting, Bali May 9-11 2018

Coatings Mode Overview

- Designed to determine the coat weight or the coating thickness of metal coatings
- Enables testing of large or irregularly shaped samples, as well as small-diameter wiring or tubing and direct testing of coated samples at the plating line
- Enables analysis of up to four coating layers
- Layer can be pure element, alloy or compound
- Substrate can be pure element, alloy, plastic or wood.
- Optional 3mm small spot analysis
- Element suite - 30 elements including:

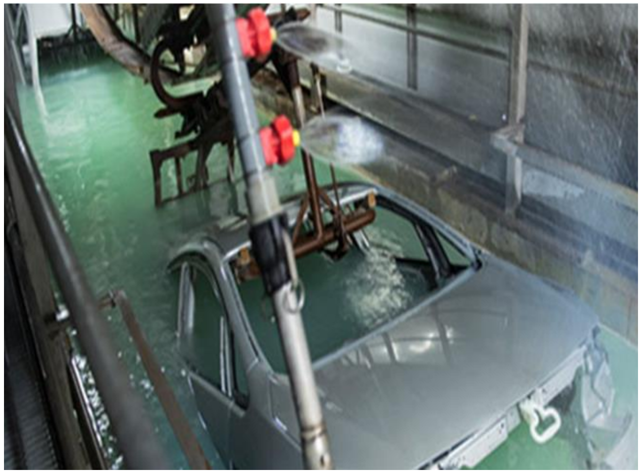
  Pb, **Hg**, Au, Pt, **W**, Sb, Sn, Cd, Ag, Pd, **Rh, Ru**, Mo, Nb, Zr, **Y**, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Ti, S, P, Si, Al, Mg

- Multi point standardization feature enables user to easily optimize calibration with known standards.

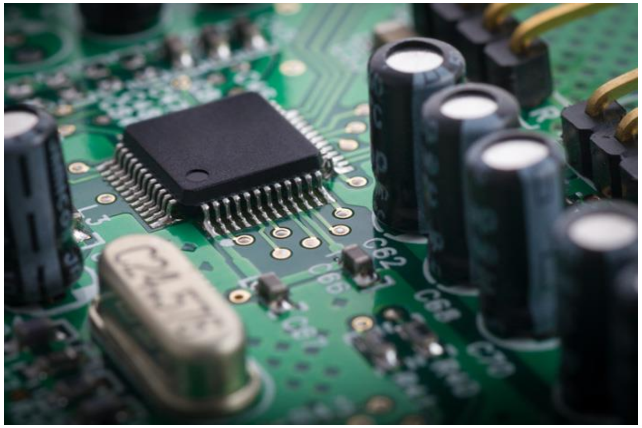
Markets and applications

Coatings generally applied for decorative purpose of for improving corrosion wear and heat resistance solderability or electrical conductivity.

- Metal Finishing (40% of total avail. market)
  - Automotive (Cr/Ni/Cu/Plastics, ZnNi/LAS, passivation coatings)
  - Aerospace (ZnNi/LAS, Cd/LAS, etc.)
  - Fasteners (NiP/LAS, Zn/LAS, etc.)
  - Fixtures (Cr/Ni/Brass, Cr/Ni/Cu/ABS etc.)
  - Cutting Tools (WC/TS etc.)
  - Electrical appliances (Zn/Fe NiP/LAS etc.)
  - Accessories, apparel (Au/Ni/Cu/Zn etc.)
  - Jewelry & Watchmaking (Rh/Brass etc.)
  - Electrification products (Ag/Cu etc.)



- Electronics (60% of total avail. market)
  - PCB
  - Connectors
  - Hard drives

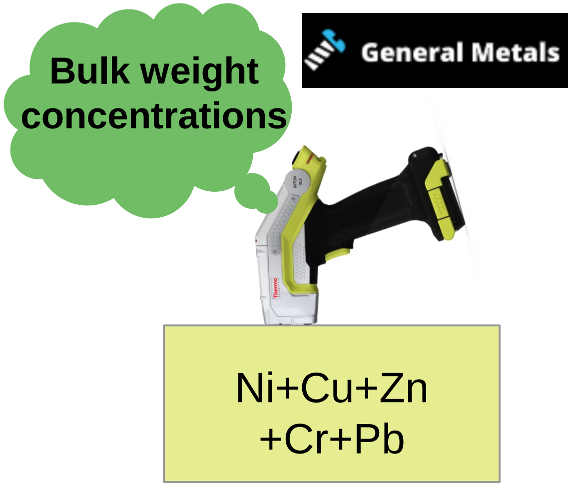


Handheld XRF suitable for metal finishing but not in electronics

Coating Mode Basics

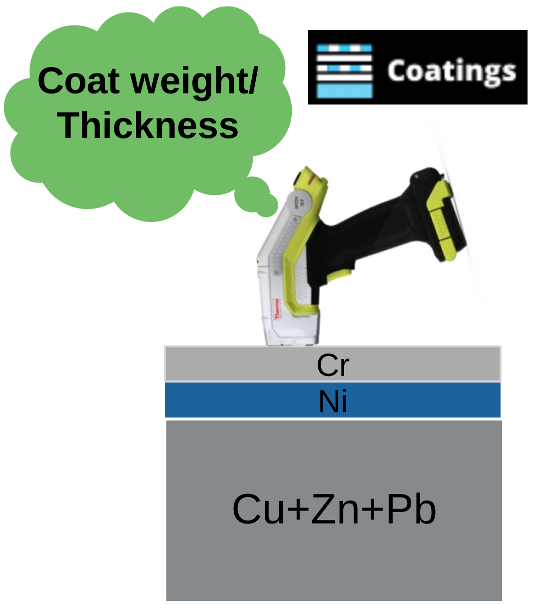
- Using General Metal Mode assumes to analyze homogeneous metals and alloys. Units of the measure is wt.%, ppm, etc.
- Coated materials are heterogeneous: composition at the surface is different from composition of the core. General Metal Mode not accurate

Coatings Mode conceived to measure coat weight or layer thicknesses applied on a substrate, not to measure the composition of layer or substrate

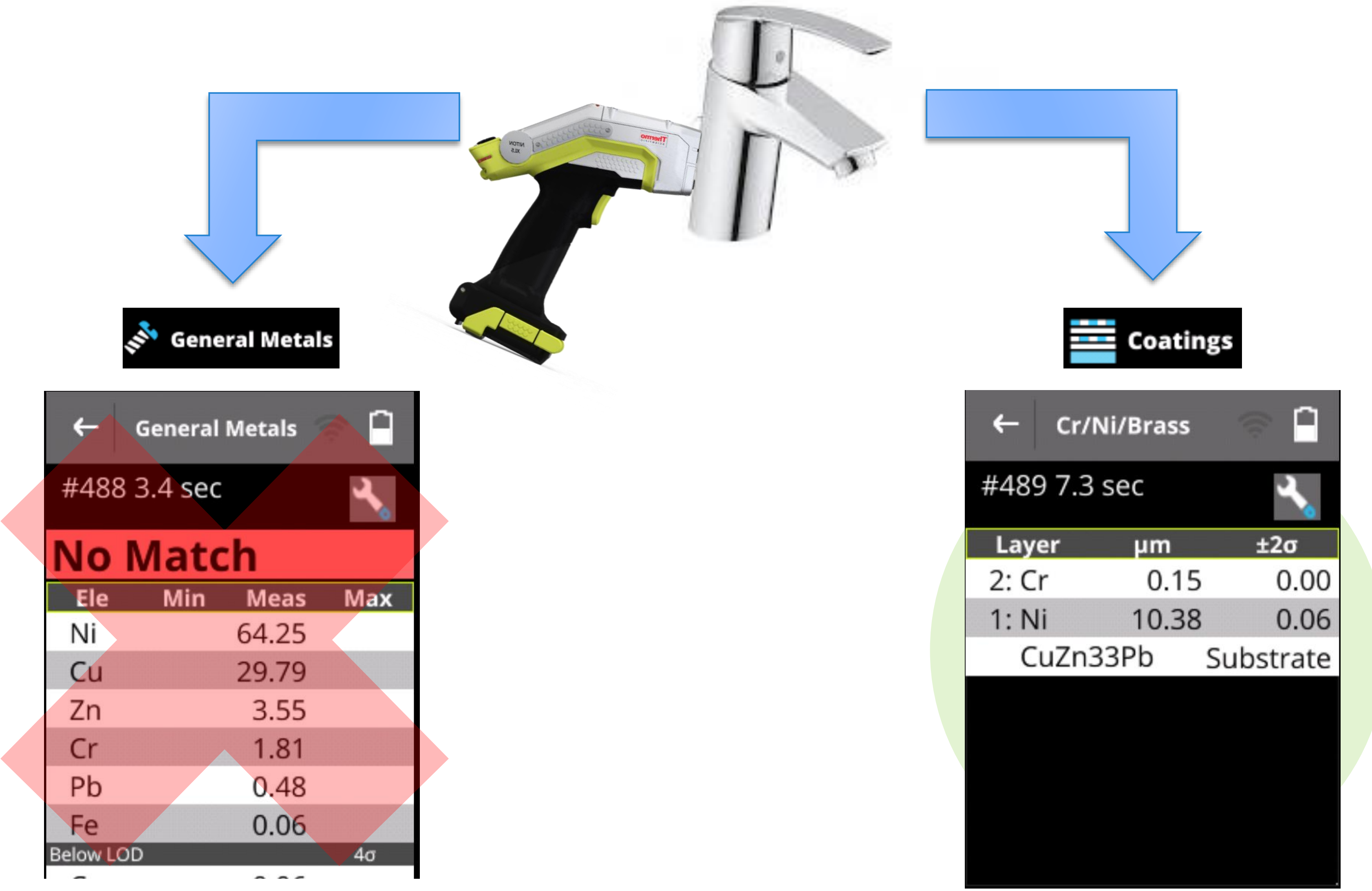


- Units designating quantity of coating: applicable to surface, not to bulk composition.
  - Layer Thickness: unit of length e.g. µm
  - Coat Weight: mass per unit of area, e.g. g/m^2

In coatings analysis, the user needs to define substrate material and the sequence of layers



Example

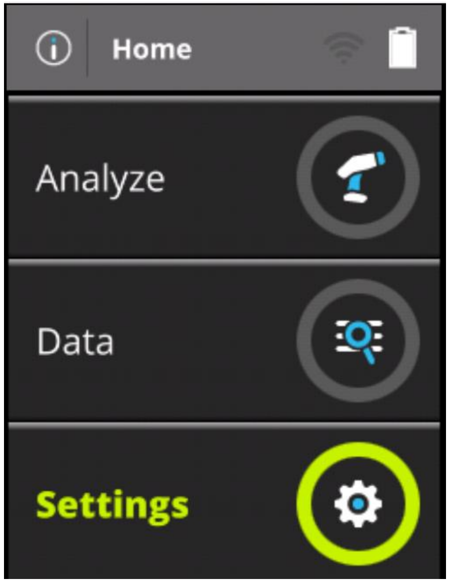


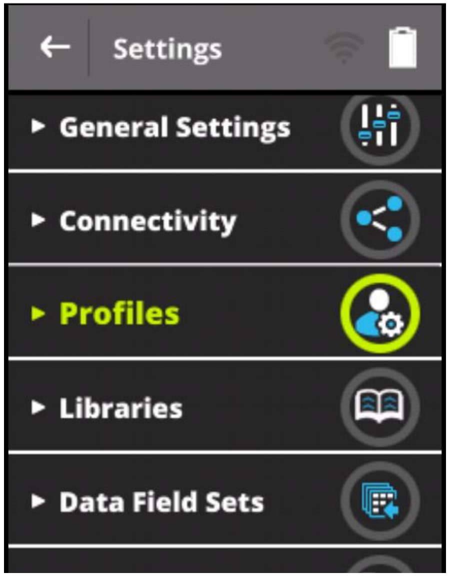
General Metals
Coatings
General Metals
#488 3.4 sec
No Match
Ele Min Meas Max
Ni 64.25
Cu 29.79
Zn 3.55
Cr 1.81
Pb 0.48
Fe 0.06
Below LOD 4σ
Cr/Ni/Brass
#489 7.3 sec
Layer µm ±2σ
2: Cr 0.15 0.00
1: Ni 10.38 0.06
CuZn33Pb Substrate

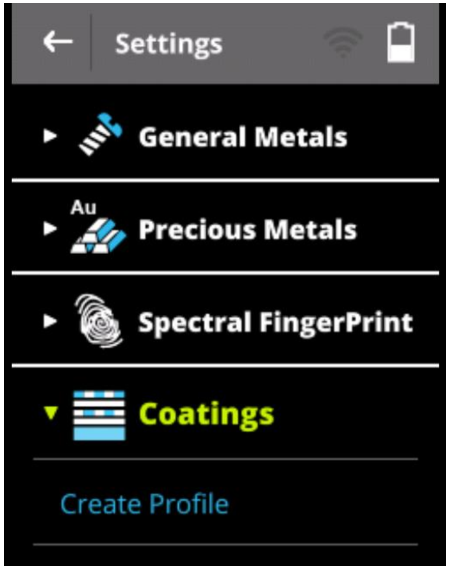
Coatings Mode Profile. Get Started!

- Unlike General Metals and other Modes, Coatings Mode can't operate without defining the substrate and the sequence of layers

Create a profile to describe coated material

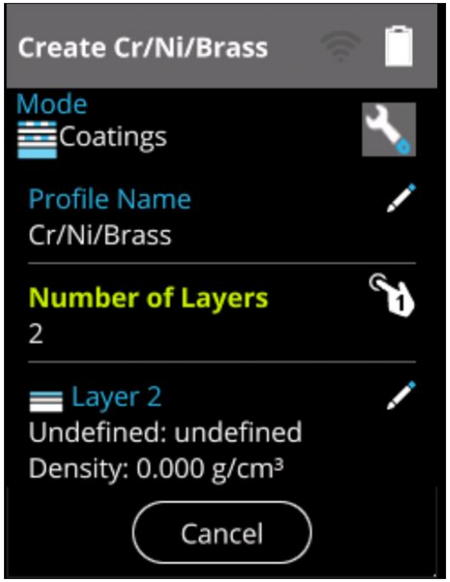




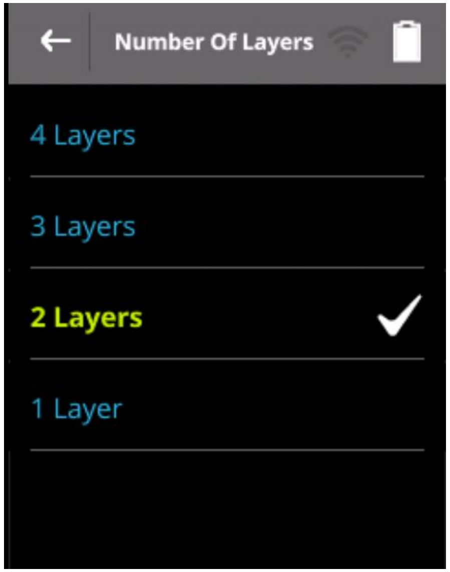


Example of Cr/Ni/Brass substrate

- Assign name to the profile
- Select number of layers



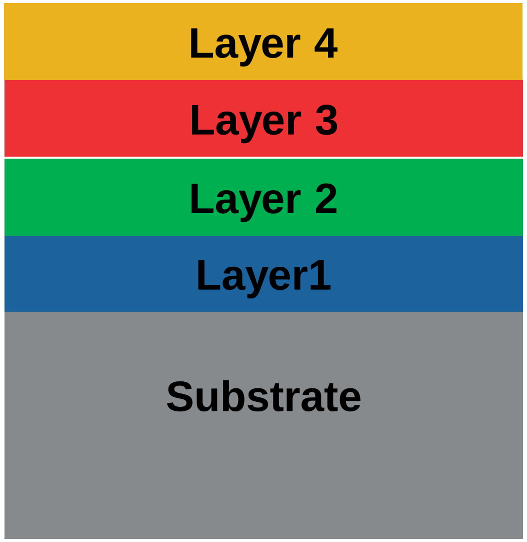
Enter Profile Name



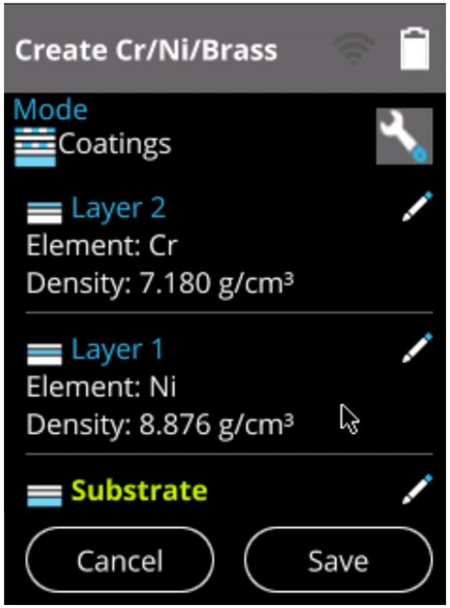
Select the number of layers (up to 4)

Define sequence and nature of layers

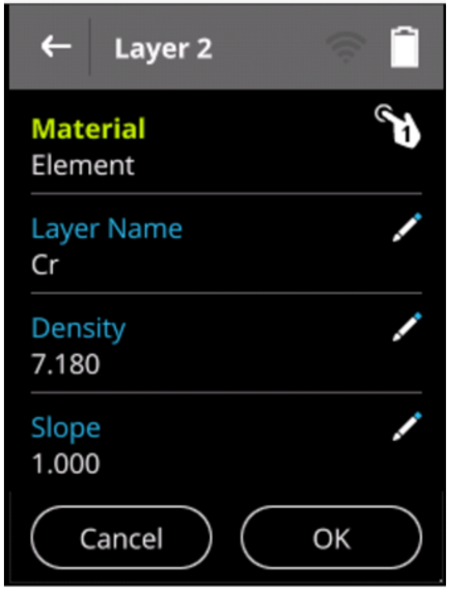
- Layer 1: the closest to the substrate, layer with highest # (up to 4) at the surface
- Select layer material
- Density of the layer (default value of pure metal or alloy) can be edited in case an element is mixed with some compound
- Slope of the layer can be adjusted to match values of available reference samples



Select layer to edit

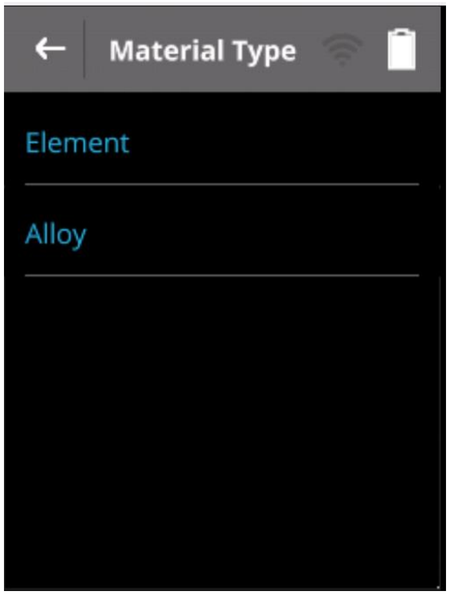


Layer Edit

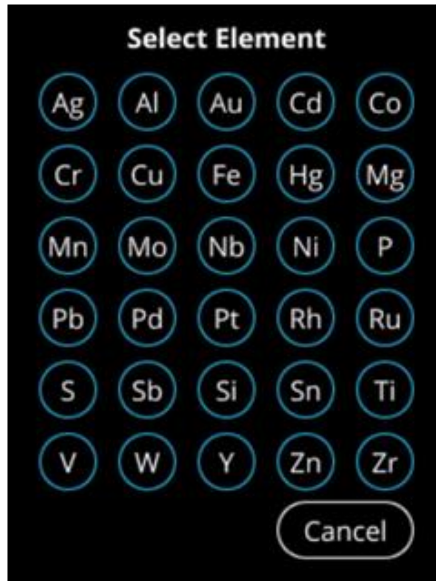


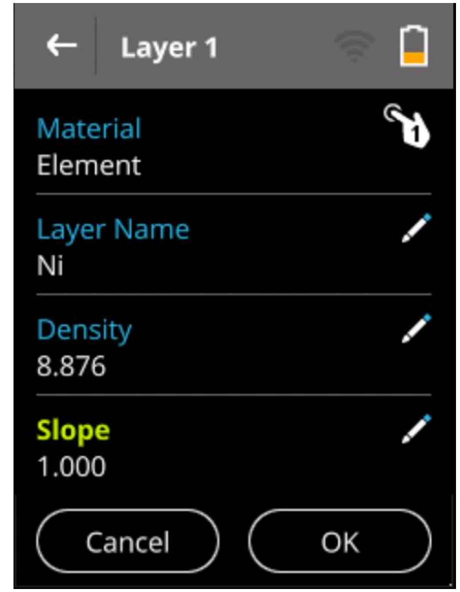
Selection of layer material

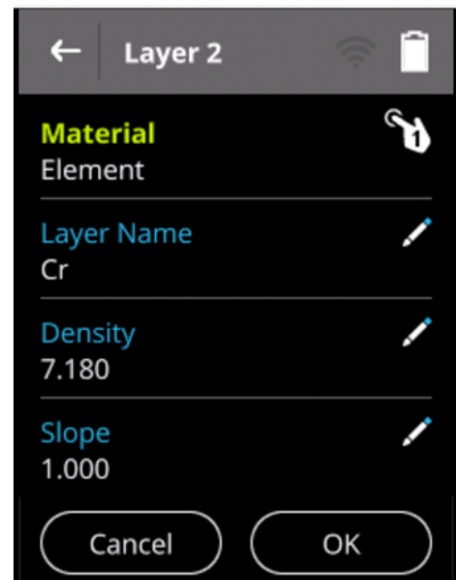
Layers: pure elements. Ni, Cr



Select among list

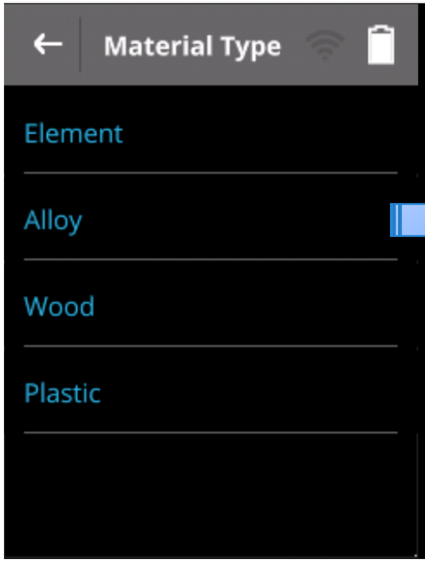




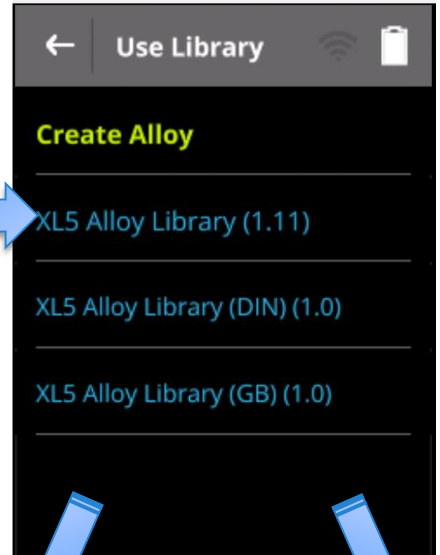


Define the material of the substrate

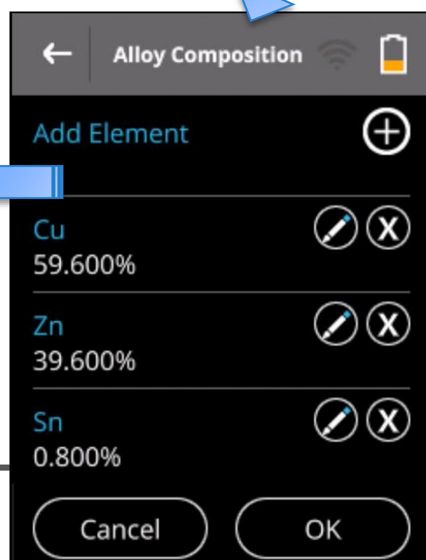
Select type of Material: Alloy



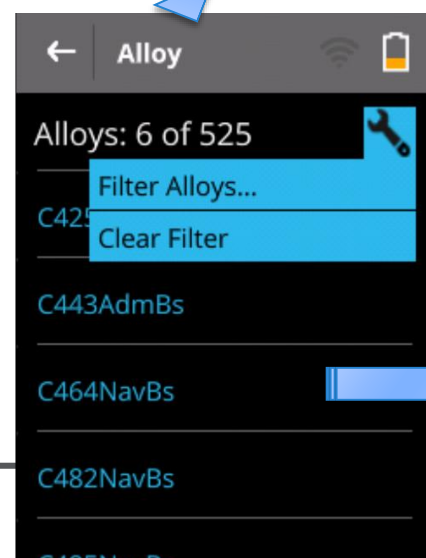
Define Alloy Composition <u>or</u> select library



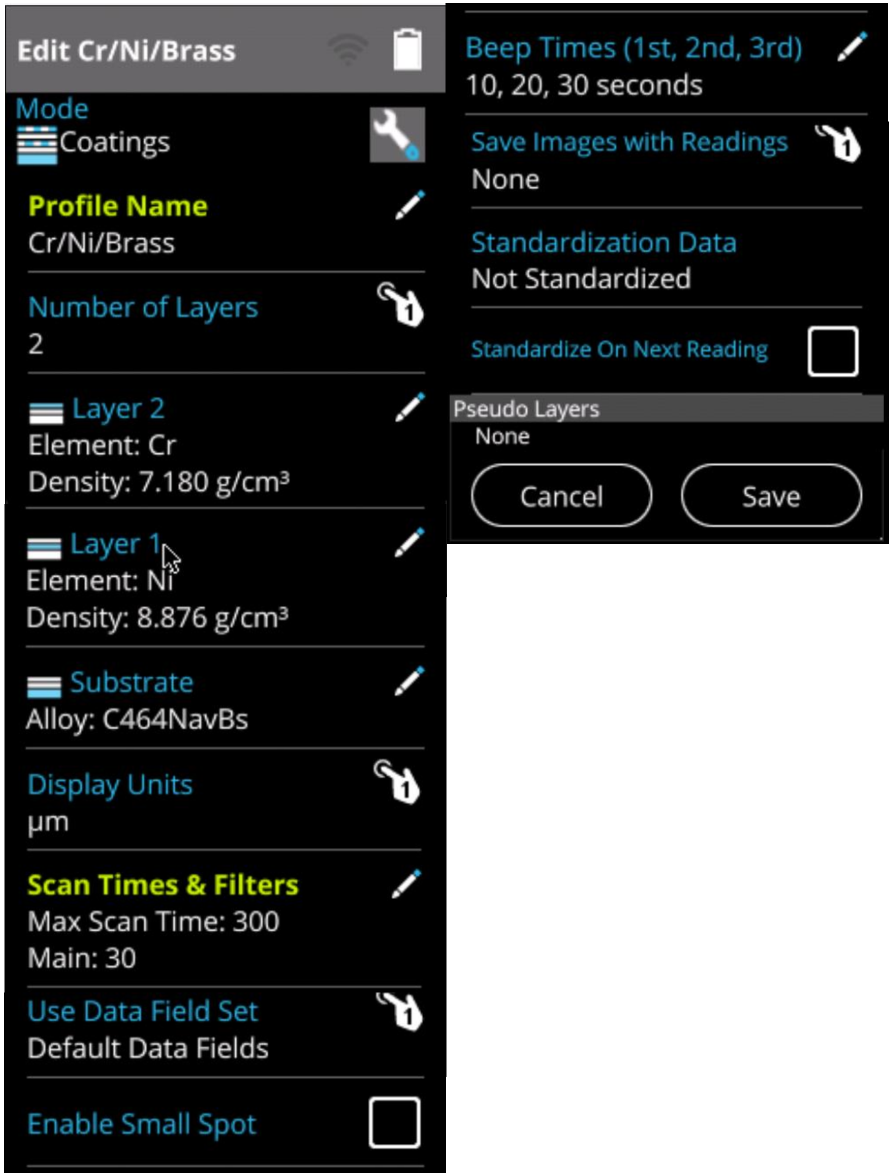
Nominal or measured chemistry



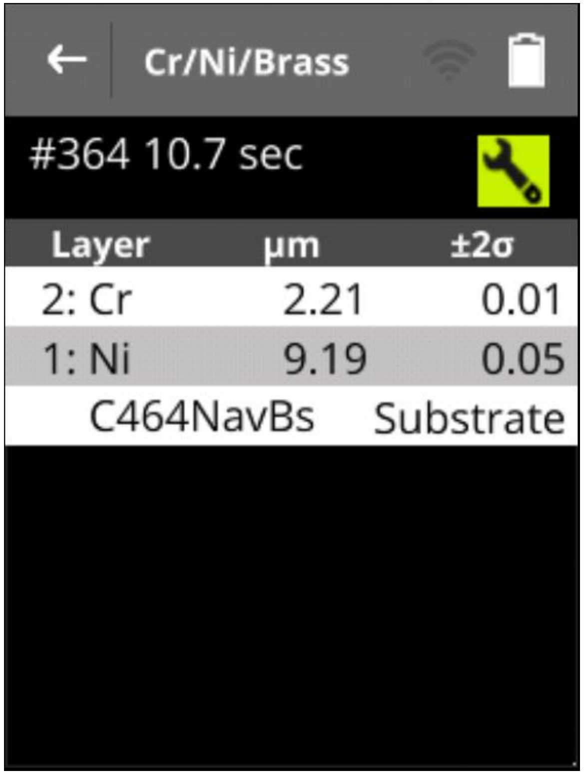
Pick alloy & avg. chemistry from library



Review of the profile, analysis of sample



Results of analysis
2 µm Cr foil/ 10µmNi Foil/
C464 substrate



Result "Out of the Box"

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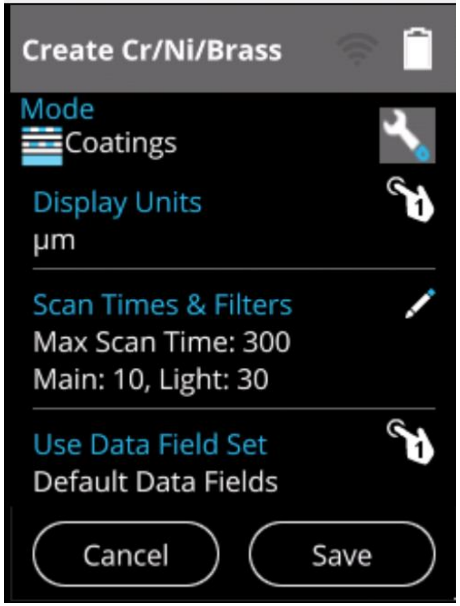
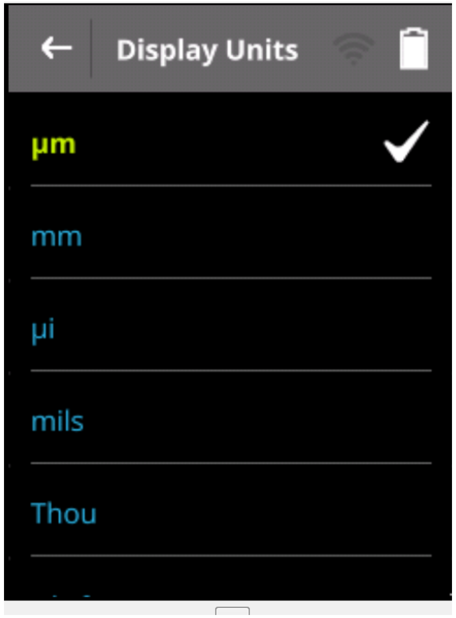
Measurement units

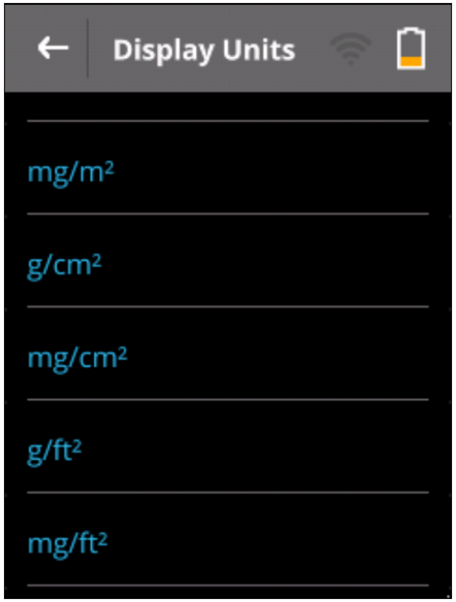
- Layer Thickness: Ang, µm, mm, µi, mils, thou
- Coat Weight: µg/cm2 g/m^2, mg/m^2, g/cm^2, mg/cm^2, g/ft^2, mg/ft^2, µg/ft^2, oz/ft^2
- Coat weight mostly used when coating material is not pure metal but compound (metal passivation, etc.)

$$Th = \frac{CW}{d}$$

Th: layer thickness
CW: coat weight
d: density



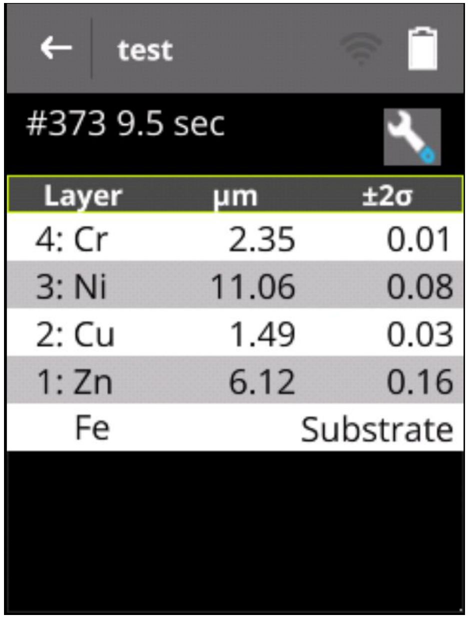




Selectable units

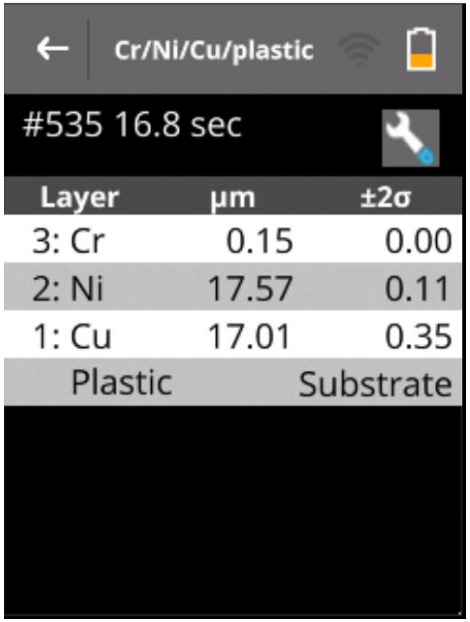
Analyzing up to 4 layers

2µmCr/10µmNi/1.5µmCu/
6.3µmZn/Fe substrate



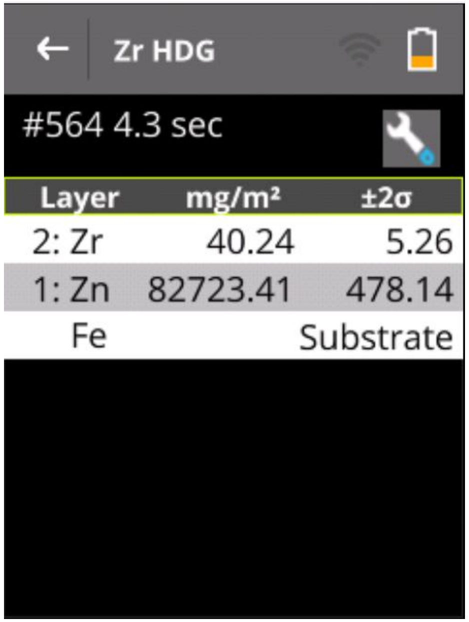
Analyzing multiple layers over Plastics

Common decorative coating



Analyzing thin layers

Passivation coating
38mg/m2 Zr/HDG

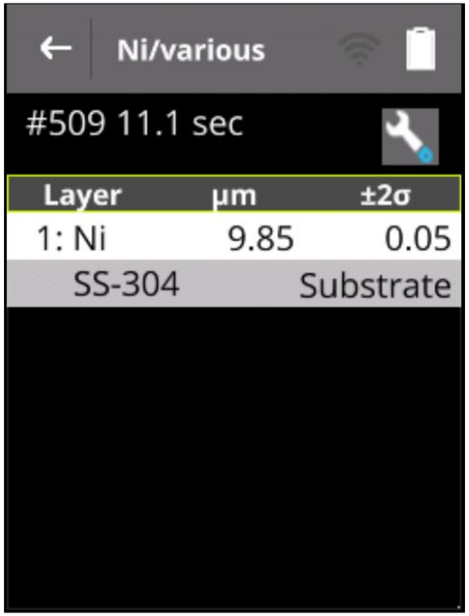


Accurate Determination of Multilayer Coat Weight & Thickness

Capabilities of coatings Mode. Alloy substrates

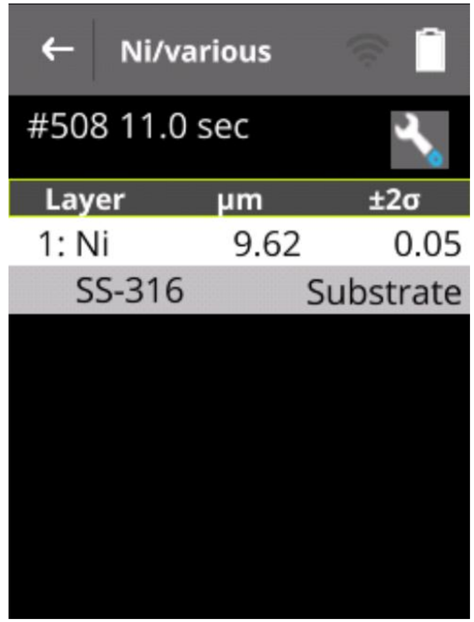
Determination of Ni Monolayers over Stainless steel

10µm Ni/ SS 304



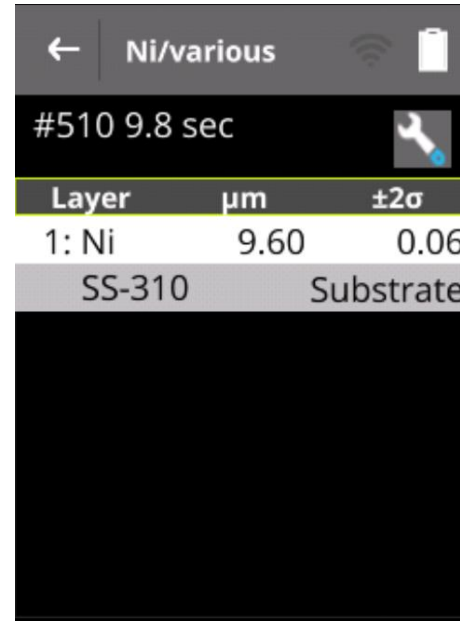
SS-304: Cr:17.9%, Ni:8.36%, Mn:1.6%, Mo:0.29%, Fe:Bal

10µm Ni/SS 316



SS-316: Cr:16.7%, Ni:10.2%, Mn:1.6%, Mo:2.14%, Fe:Bal

10µm Ni/SS 310



SS-310: Cr:24.9%, Ni:19.7%, Mn:1.6%, Mo:0.39%, Fe:Bal

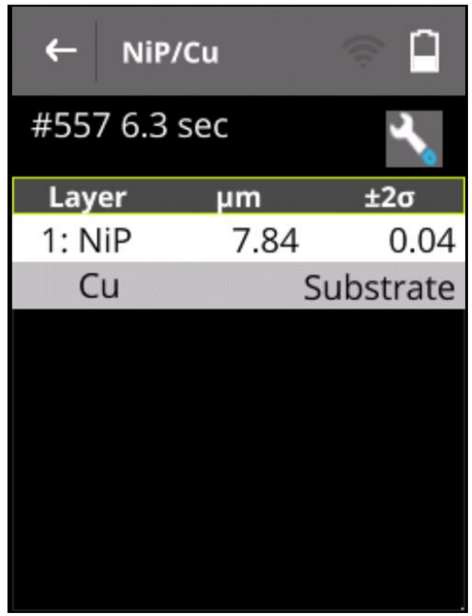
Accurate determination of layer thickness over alloy substrates containing the same element

Determination of Alloy layers over pure elements and alloys

10.14µm NiZn/ Fe

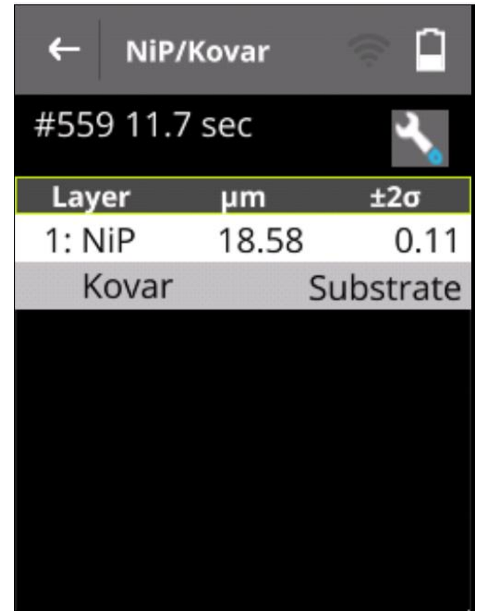
NiZn: Ni:6% Zn:94%

8.0 µm NiP/Cu



Electroless Ni plating
NiP: 88%Ni 12%P

20 µm NiP/Kovar

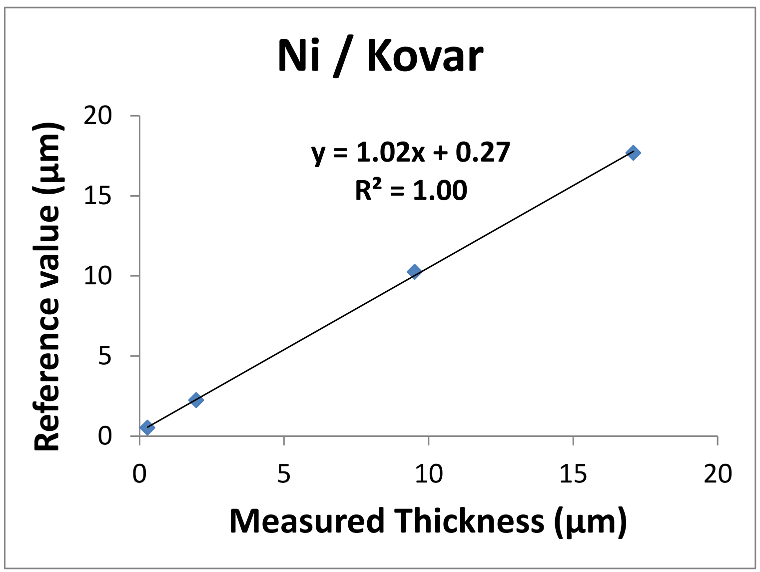


Electroless Ni plating
NiP: 92%Ni 8%P
Kovar: 29%Ni%,17%Co, Bal Fe

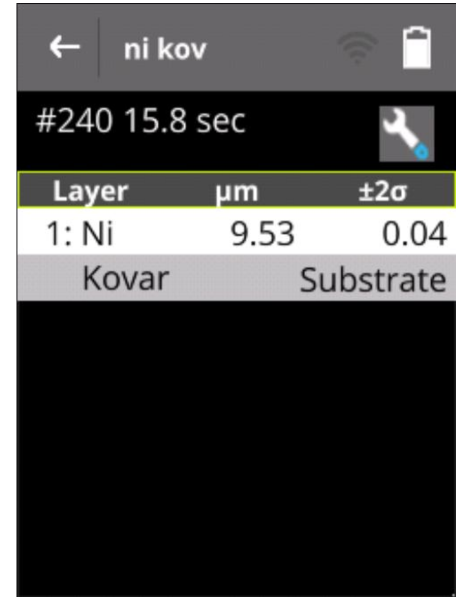
Accurate determination of thickness of alloy layers over pure metals or alloys substrates

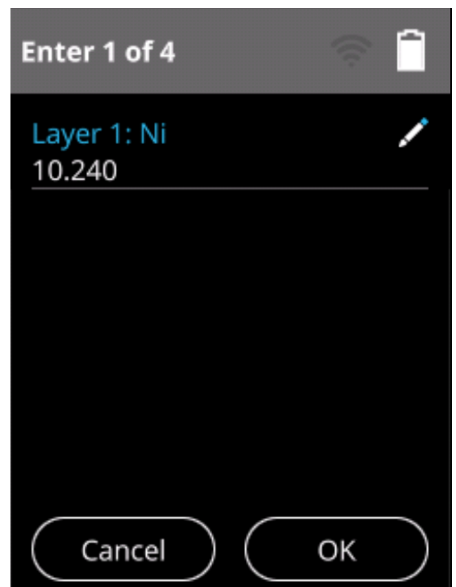
Standardization

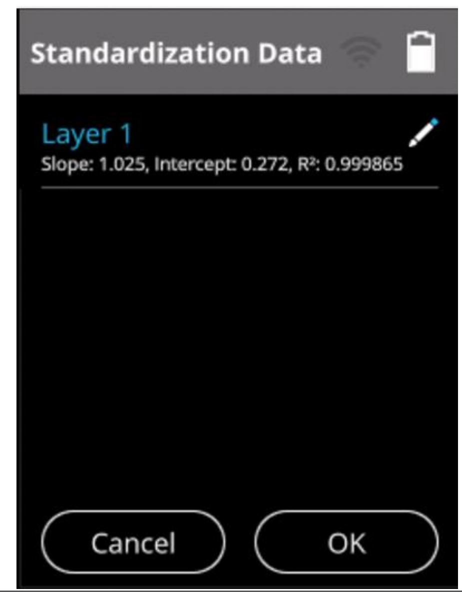
- Check Standardization on next reading, enter # of standards (max.5)
- When prompted, enter reference value for each standard
- Perform the measurement
- After last measurement, linear correction is calculated and applied



Kovar: Ni:29%, Co:17%, Fe:Bal

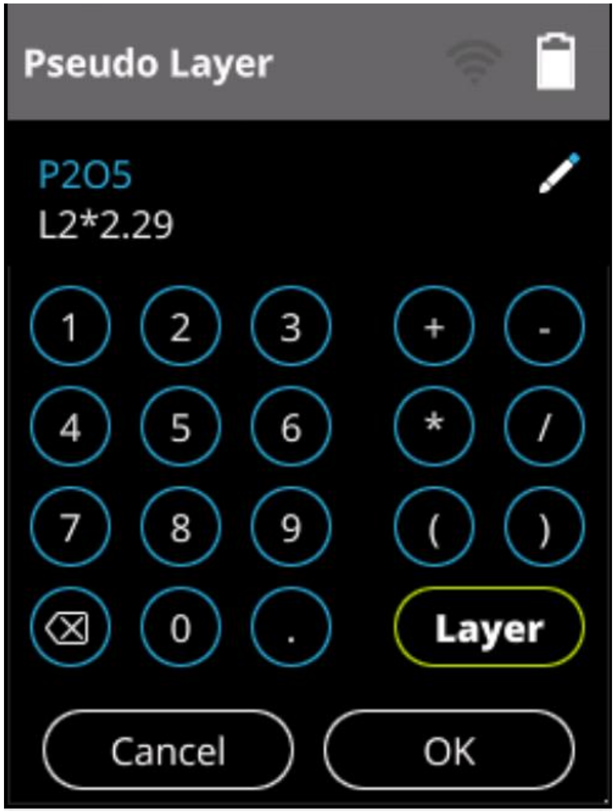






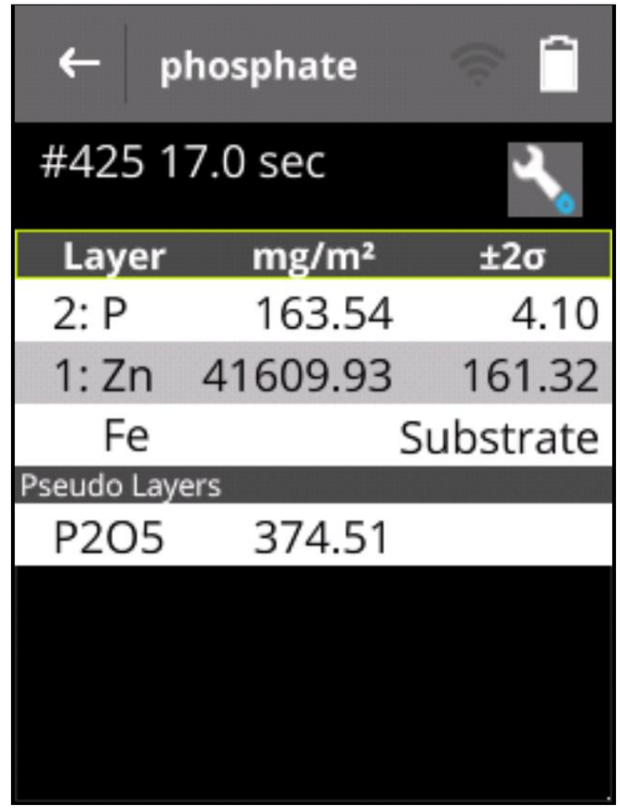
Pseudo Layers: compounds as coating

Define Pseudo Layer as function of existing layers



Example P as P2O5/ Galvanized steel

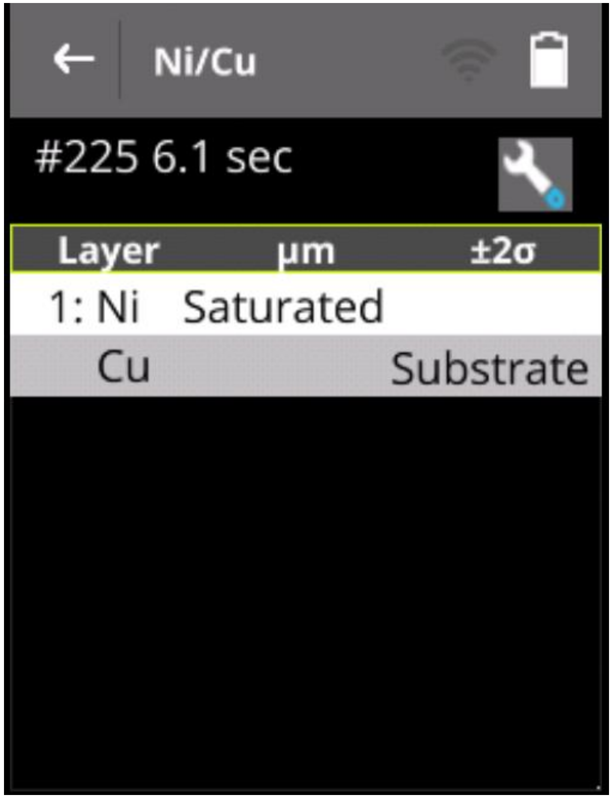
340mg/m2 P2O5/Galvanized

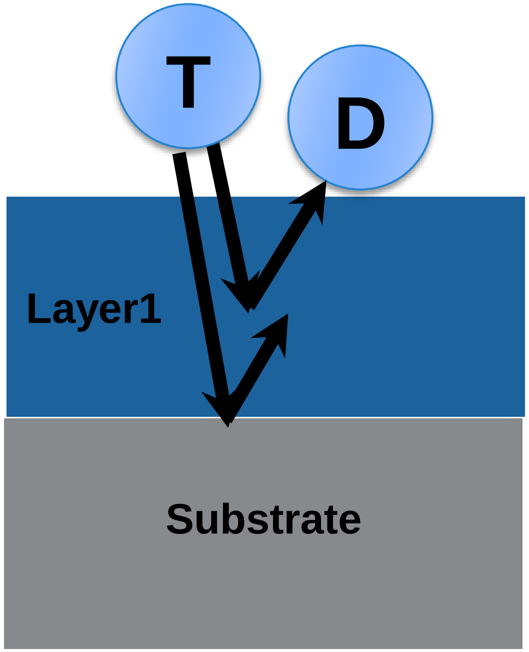


Determination of Compounds Coat Weight

Infinite Thickness – Saturation

50µm Ni /Cu substrate



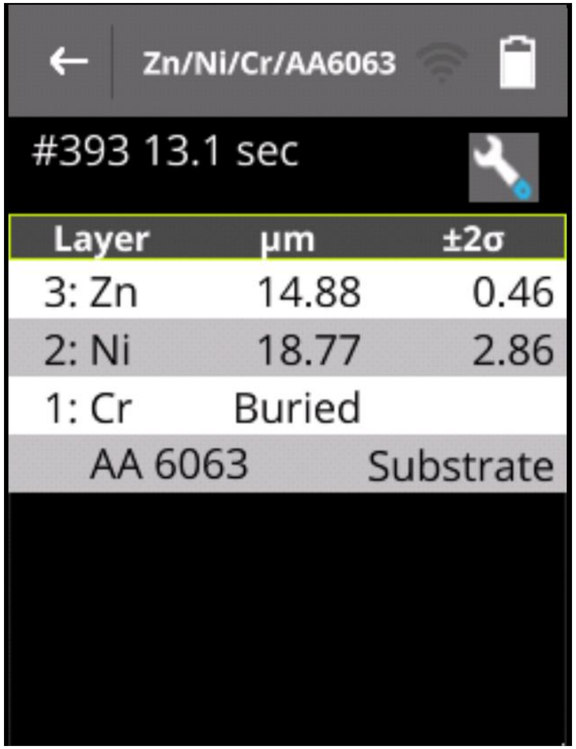


T: Tube
D: Detector

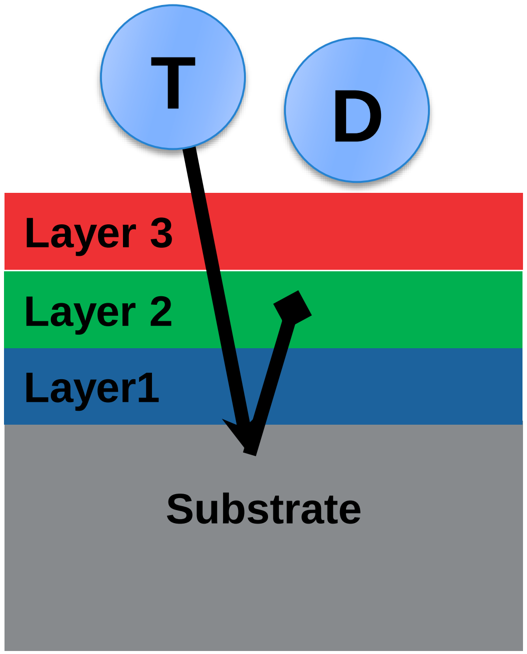
Saturation: no signal increase at increasing thickness

Infinite Thickness – Buried Layer

15µm Zn/20µmNi/2µmCr/AA6063



Layer	µm	±2σ
3: Zn	14.88	0.46
2: Ni	18.77	2.86
1: Cr	Buried	
AA 6063	Substrate	



T: Tube
D: Detector

Buried layer: signal from substrate & deep layer(s) not detected

Infinite Thickness – examples

Calculated values of infinite thicknesses (80% absorption) for different coating/substrate

Coating	Substrate	Infinite thickness of the coating element (µm).	Infinite thickness of the coating for the substrate element (µm)
Ag	Cu	59	6.0
Au	Ni	8.0	2.9
Au	Cu	8.0	3.5
Cd	Fe	73	4.0
Cr	Fe	22	4.0
Cr	Ni	22	6.2
Cu	Al	29	0.3
Cu	ABS	29	N/A
Ni	Al	26	0.4
Ni	Cu	26	31
Ni	Fe	26	17
Pb	Cu	22	7.7
Pd	Ni	51	4.7
Rh	Cu	48	5.8
Sn	Al	89	0.6
Sn	Cu	89	7.5
Ti	Fe	28	8.7
Zn	Fe	39	18
Zr	Al	79	1.3