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Real Time Analysis of Copper Alloys using Handheld X-Ray Fluorescence Spectrometry

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The purpose of this presentation is to guide programs benefiting the copper industry and to provide attendees with information to make independent business decisions.

Who is Thermo Fisher Scientific?

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The world leader in serving science

thermo scientific | applied biosystems | invitrogen | fisher scientific | unity lab services

130,000 employees

5,300 R&D scientists/engineers

>$1.5B invested in R&D

$39B in revenues

Our Mission: we enable our customers to make the world healthier, cleaner and safer

Thermo Fisher Scientific Portfolio

Agenda

1 Importance of metal analysis

2 Metal and Alloy Testing Methods

3 Handheld X-Ray Fluorescence Spectrometry

4 Alloy grade identification

5 Accuracy, Precision, Detection limits

6 Examples

The Importance of Material Verification

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Mission Critical

- Dangerous Equipment Failures
- Excessive Downtime

Loss of Profit

- Rework Products
- Downgrade Incorrectly Identified Materials

Poor Reputation

- QA/ QC Issues
- Negative Standing w/ Customers

Deploy a "trust but verify" method to ensure proper material verification.

Metal and Alloy Material Testing Methods

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Qualitative Material Testing Methods				Elemental Analysis / Spectroscopy		
Visual/ Hand Sorting	Magnet Tests	Spark Tests	Chemical Acid Tests	Stationary Spectrometers OES, XRF	Mobile OES	Handheld XRF/ LIBS

Qualitative Material Testing Methods:

- Not all methods are applicable to every metal base
- Inaccurate Results / (compared to spectroscopy)
- Time Consuming (must combine multiple methods)
- Difficult to Separate Alloy Grades
- OSHA Restrictions/ Safety Liabilities
- Mostly Obsolete

Stationary Spectrometers OES, XRF:

- Lab / field lab use
- Need highly Skilled Operator
- Low Throughput (sampling needed)
- Best accuracy & precision

Mobile OES:

- “Mobile” Technology (difficult to maneuver)
- Moderately Skilled Operator
- Medium Throughput

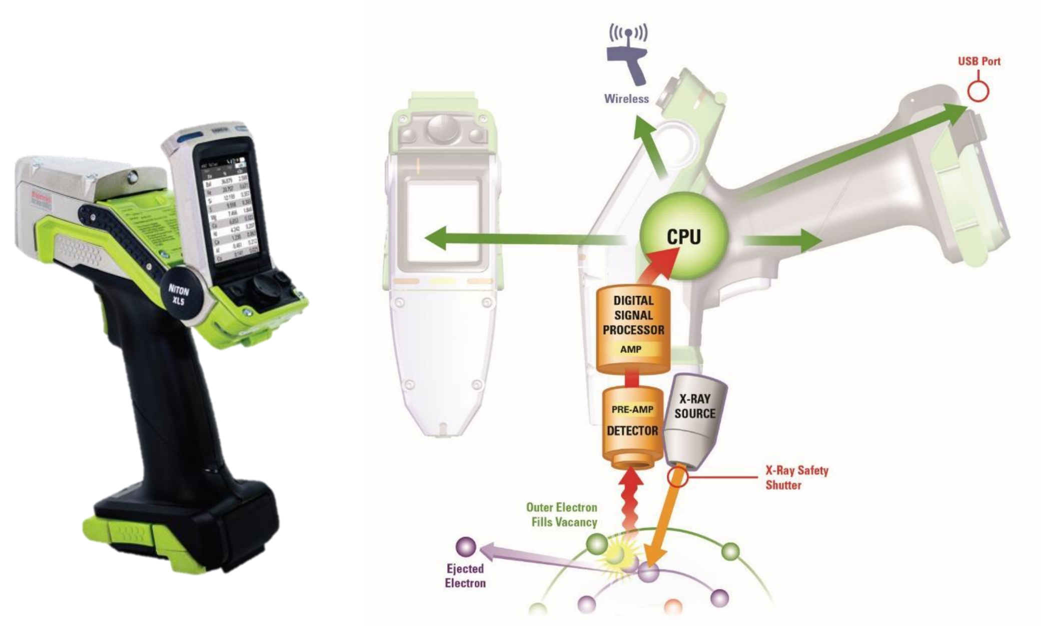
Handheld XRF/ LIBS:

- Handheld Technology (easy to maneuver)
- Pre-calibrated instruments
- Point-and-Shoot
- High Throughput

OES: optical emission spectrometry - XRF: x-ray fluorescence spectrometry - LIBS: Laser induced breakdown spectrometry

How Do Handheld XRF & LIBS Work?

XRF: X-Ray Fluorescence spectrometry



- A miniaturized tube irradiates the sample surface
- One electron from inner atom shell is ejected
- Electron from outer shell fill the vacancy
- An element-specific x-ray photon (fluorescence) is emitted
- Photon is detected in a semi conductor detector

LIBS: Laser Induced Breakdown Spectrometry

- A focused laser pulse ablates the sample surface and forms a plasma
- The plasma atomizes the sample material
- Atoms change from ground to excited state
- Getting back to ground state, atoms emit element-specific photons in UV-Visible range
- Photons are detected using an optical spectrometer

Handheld Metal Analysis

Handheld-XRF

- Ready to use, pre-calibrated analyzers.
- “Point-and-shoot” analysis
- Element range: magnesium (Mg) to uranium (U)
- Large spot size (8mm diameter)

+ Near laboratory grade results
+ Non-destructive testing Method
+ No or little sample preparation required

- Unable to detect carbon (C) and beryllium (Be)
- Longer testing time needed to detect light elements

Handheld-LIBS

- Ready to use, pre-calibrated analyzers.
- ”Point-and-shoot” analysis
- Element range: theoretically entire periodic system
- Small spot size (50µm diameter)

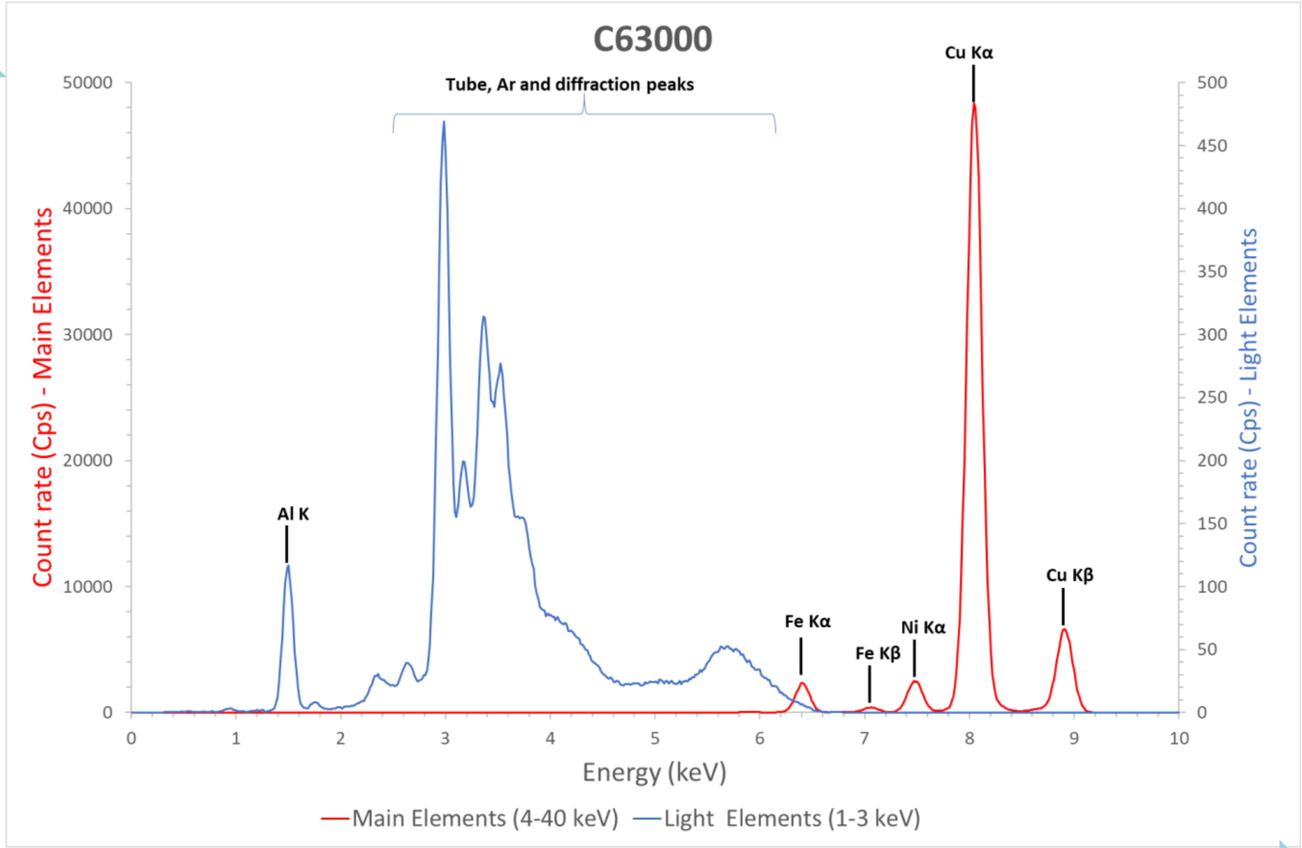
+ Near laboratory grade results
+ Including carbon (C), and beryllium (Be) detection

- Sample Preparation (grinding) required
- Periodic setup procedures required
- Unable to measure low levels of sulphur (S) and phosphorus (P) in steel or copper alloys

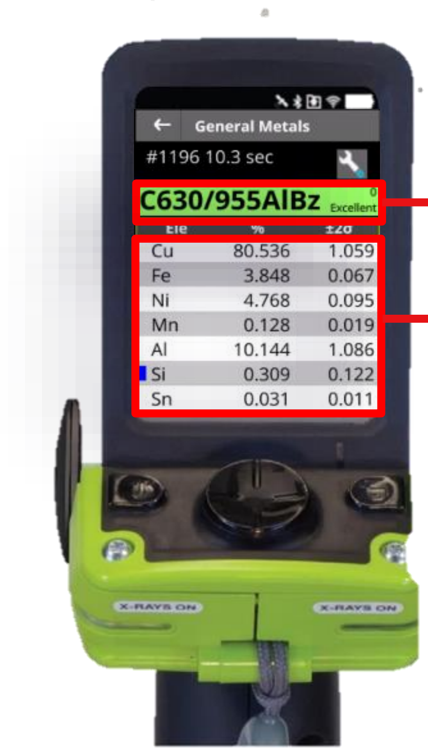
HH-LIBS: suitable for low alloy steel & stainless steel that needs carbon analysis
HH-XRF: more suitable for non-ferrous metals including copper-based alloy analysis

XRF Spectrum

Information for quantitative analysis



Information for qualitative analysis



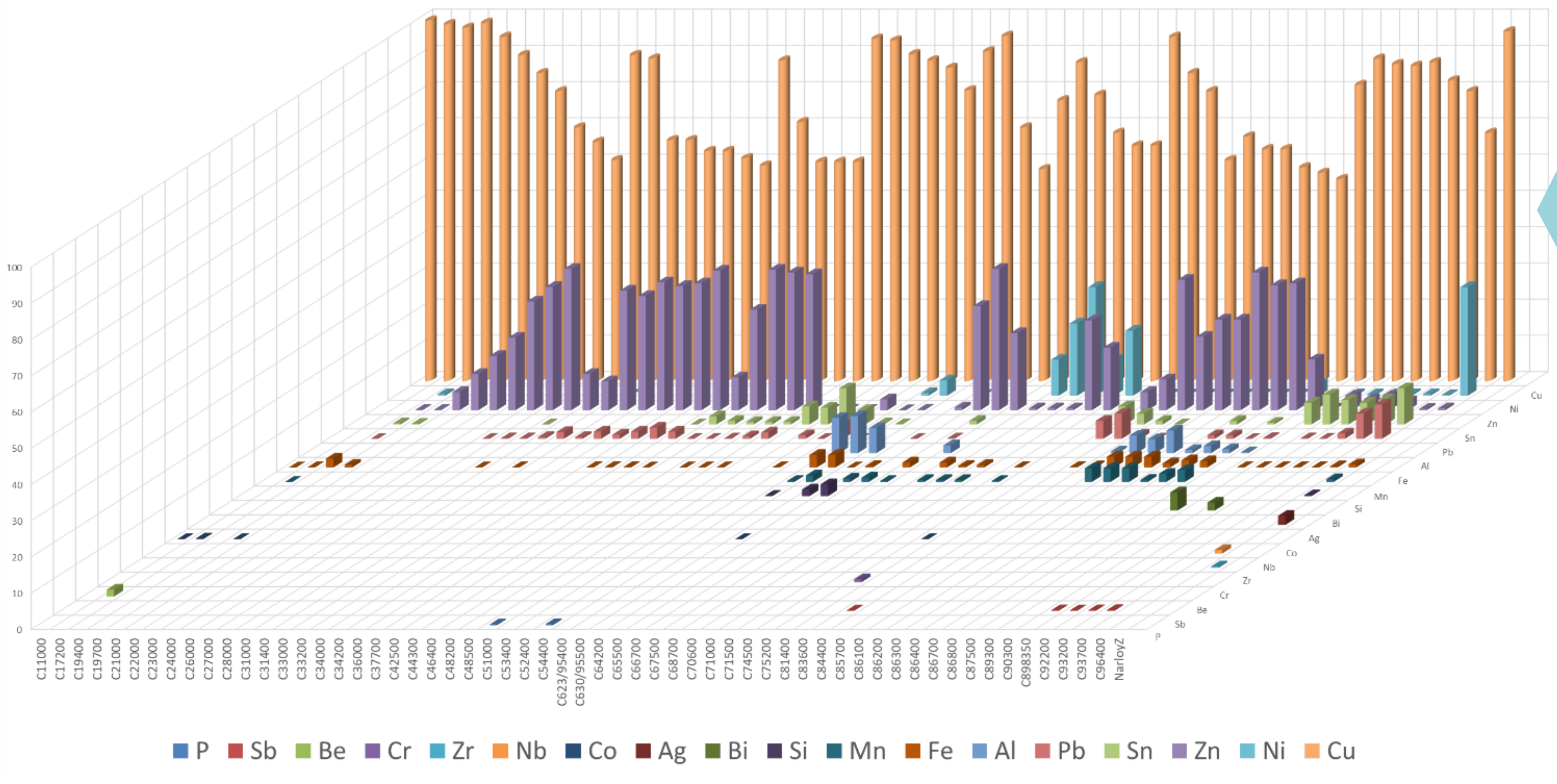
Alloy Grade ID

Quantitative analysis

Alloy Library for Copper Grades

Standard Alloy Library includes 60 common grades according CDA + 450 alloys from different bases

Copper Grades Average Composition



- Library can be augmented by user
  - but composition of added alloys defined should not overlap with existing entries
- Customized library can be created
- Libraries available
  - ASTM/SAE
  - DIN standard
  - GB standard

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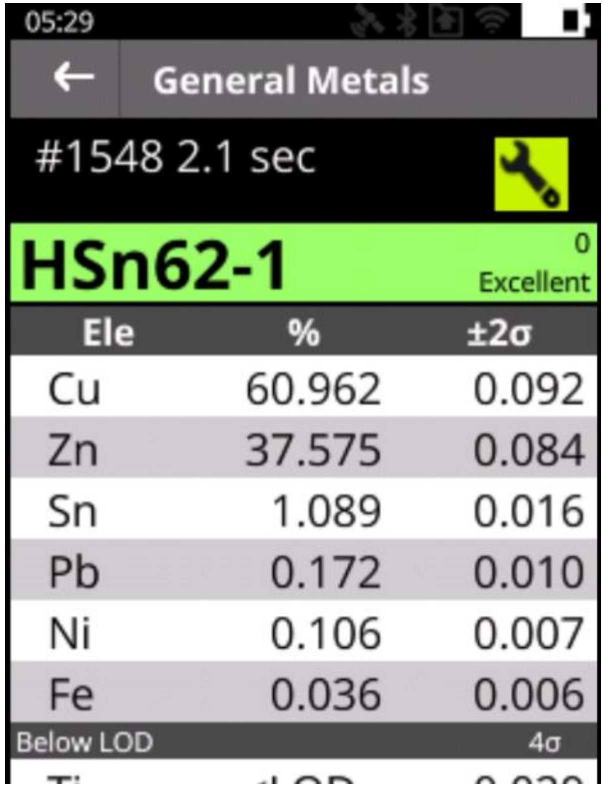
Copper Grade ID According to Different Standards

USA – CDA

Copper Dev. Association

China

GB Guobiao

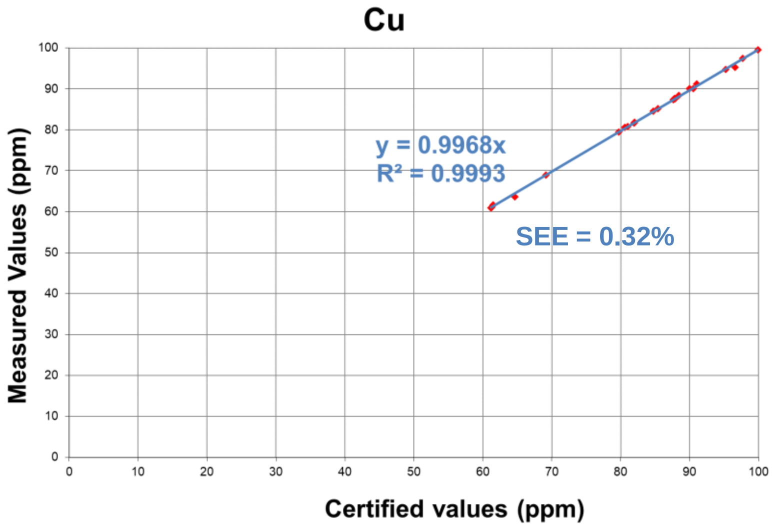


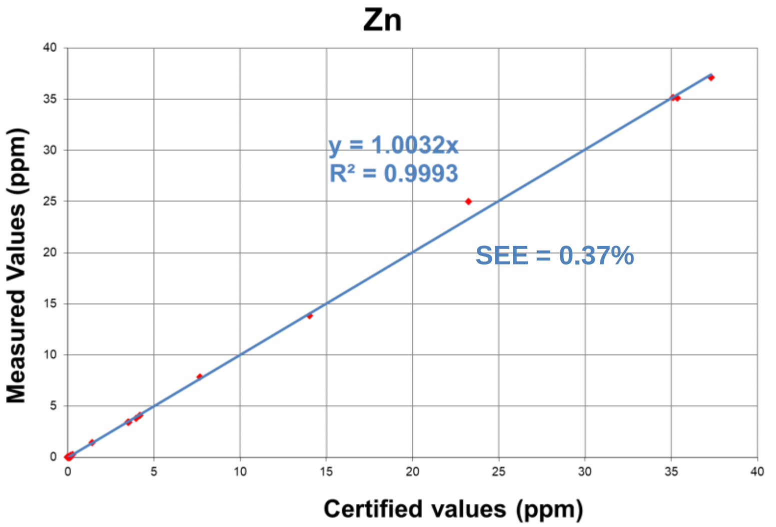
Germany

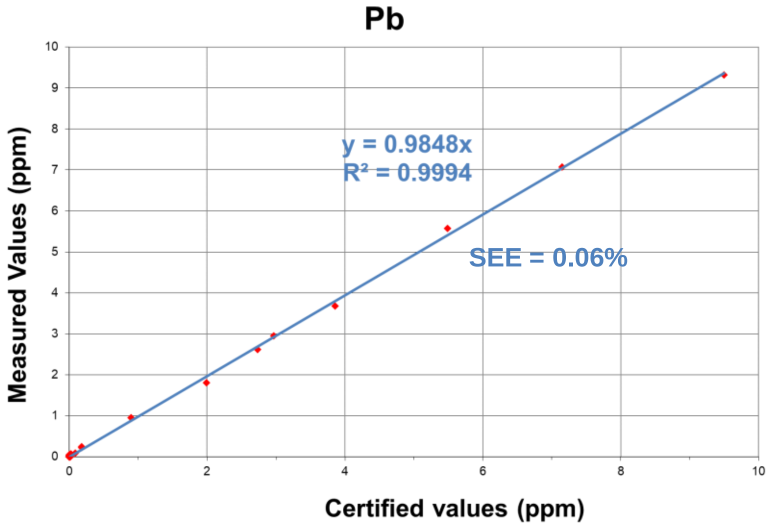
DIN standard

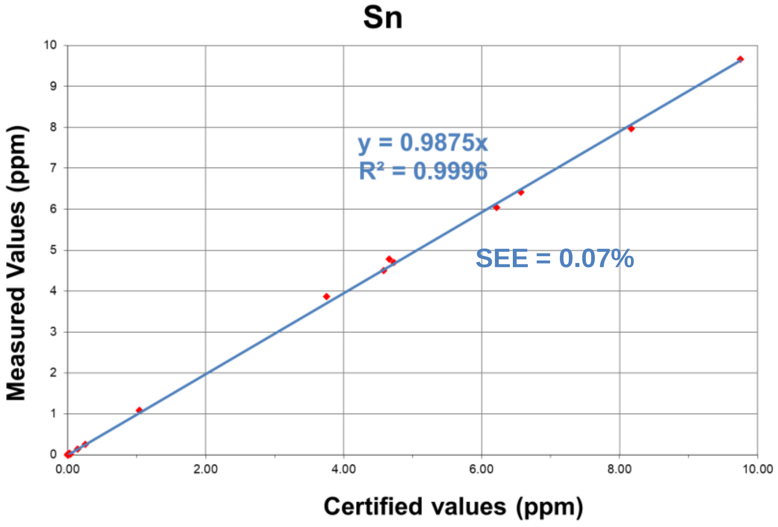
Measurement Accuracy

Measured vs. Reference Values 40s test time (10s/main elements, 30s light elements)









Parameters reflecting accuracy

- R^2: reflects linearity of the response. Shall be close to 1
- Slope: reflects systematic error when different from 1 & good linearity
- SEE: standard error of estimate (average difference between refence and measure value)

Accuracy depends on algorithm

- Model of line overlaps (additive matrix effect)
- Model of absorption & enhancement effect from concomitant elements (multiplicative matrix effect)

Measurement Precision & Limits of Detection

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Precision for different testing time

LODs on XL5 Plus* (60s per beam)

Element	LOD (%)
Al	0.028
Si	0.0082
P	0.0070
Mn	0.012
Fe	0.0104
Ni	0.0083
Zn	0.0176
Sn	0.0022
Pb	0.0033
Bi	0.0028

Precision expressed as multiple of standard deviation σ

LOD is defined as the signal equivalent to 3 σ of the background

Precision and LOD depend on

- Tube (Power, max voltage, max current)
- Detector (technology, Surface, Window Material)
- Measurement time

$$LOD\ \alpha\ \sigma\ \alpha\ \frac{1}{\sqrt{t}}$$

Qudrupling measurement time will provide 2-times better precision and cut in half the limits of detections

*5W-50kV-500µA max, SDD 20mm2, Graphene Window,

Example 1: Rapid Separation of Copper Alloys

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1-2 s measurement. Approach used in metal scrap sorting.

Copper Alloy Classification

Wrought Alloys

- Coppers C10100-C15999
- High-copper Alloys C16200-C19999
- Brasses C20000-C49999
- Bronzes C50000-C69999
- Cupronickel C70000-C73499
- Nickel Silvers C73500-C79999

Cast Alloys

- Coppers C80000-C81399
- High-copper Alloys C81400-C83299
- Brasses C83300-C89999
- Bronzes C90000-C95999
- Cupronickel C96000-C96999
- Nickel Silvers C97000-C97999
- Leaded Coppers C98000-C98999
- Special Alloys C99000-C99999

Cartridge brass

04:53 — Alloy

#1153 2.3 sec

C260CartBs 0 Excellent

Ele	%	±2σ
Cu	68.919	0.410
Zn	31.081	0.332
Below LOD		4σ
Se	<LOD=	0.025
Al	<LOD=	0
Ti	<LOD=	0.257
V	<LOD=	0.149

Free Cutting brass

04:23 — General Metals

#1215 1.4 sec

360FrCutBs 0.05 Excellent

Ele	%	±2σ
Pb	2.546	0.198
Cu	61.639	0.523
Zn	35.465	0.457
Fe	0.156	0.046
Sn	0.155	0.045
Below LOD		4σ
Au	<LOD=	0

Naval Brass

05:32 — General Metals

#1545 1.7 sec

C464NavBs 0.44 Excellent

Ele	%	±2σ
Cu	60.860	0.094
Zn	37.650	0.085
Sn	1.095	0.016
Pb	0.177	0.011
Ni	0.098	0.007
Fe	0.040	0.006
Below LOD		4σ

Phos.-Lead Bronze

04:42 — General Metals

#1241 1.3 sec

C544PBzB2 0.05 Excellent

Ele	%	±2σ
LEC	0.280	0
Pb	3.450	0.223
Cu	87.990	0.555
Zn	3.634	0.188
Sn	4.563	0.177
Below LOD		4σ
Au	<LOD=	0

Aluminum Bronze

04:48 — General Metals

#1257 3.1 sec

C630/955AlBz 0 Excellent

Ele	%	±2σ
LEC	10.250	0
Cu	81.658	0.481
Fe	3.826	0.130
Ni	4.146	0.144
Mn	0.059	0.029
Below LOD		4σ
Pb	<LOD=	0.023

Cupronickel

04:25 — General Metals

#1220 1.4 sec

C715(70-30) 0 Excellent

Ele	%	±2σ
Cu	69.058	0.886
Fe	0.620	0.079
Ni	29.731	0.521
Mn	0.534	0.087
Below LOD		4σ
Pb	<LOD=	0.035
Al	<LOD=	0

Leaded Red brass

04:45 — General Metals

#1244 0.5 sec

836(85-555) 0.29 Excellent

Ele	%	±2σ
Pb	5.014	0.423
Cu	85.042	0.877
Zn	4.182	0.327
Ni	0.733	0.166
Sn	4.745	0.289
Below LOD		4σ
Au	<LOD=	0

Leaded Tin Bronze

04:46 — General Metals

#1251 2.4 sec

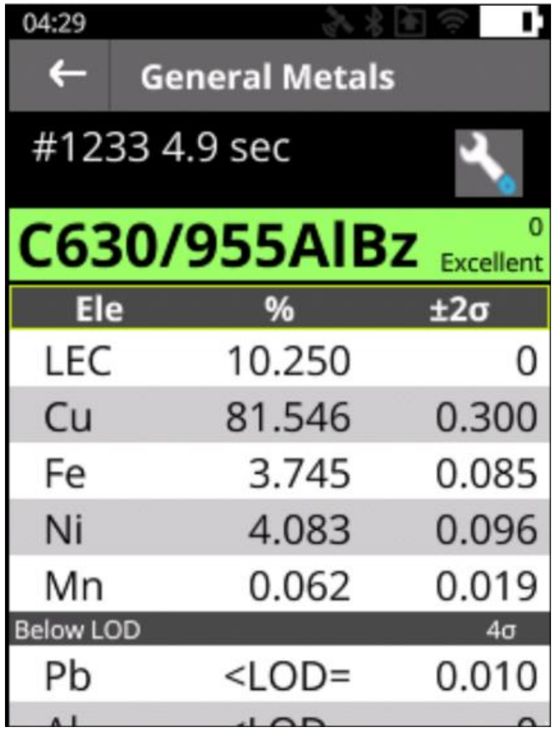
C937PbSnBz 0 Excellent

Ele	%	±2σ
Pb	9.129	0.275
Cu	80.004	0.542
Zn	0.407	0.102
Ni	0.341	0.069
Sb	0.382	0.057
Sn	9.664	0.243
Below LOD		4σ

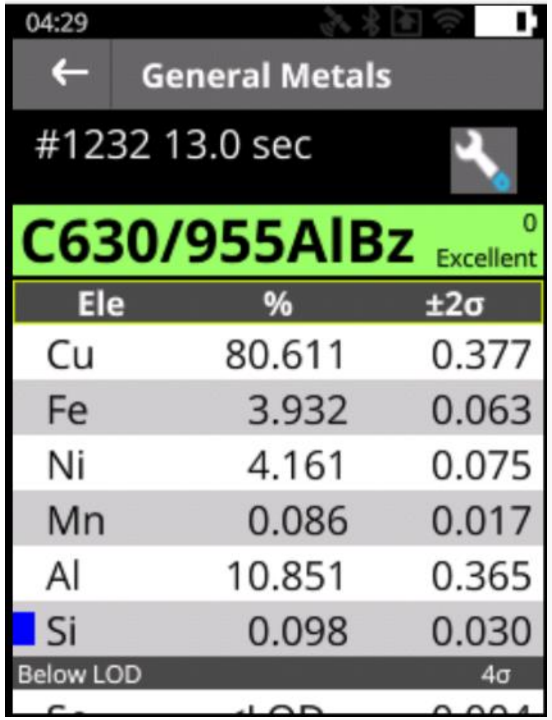
Example 2: Copper Grades Containing Light Elements

Light Element Content (LEC)

Aluminum Bronze measuring main elements only

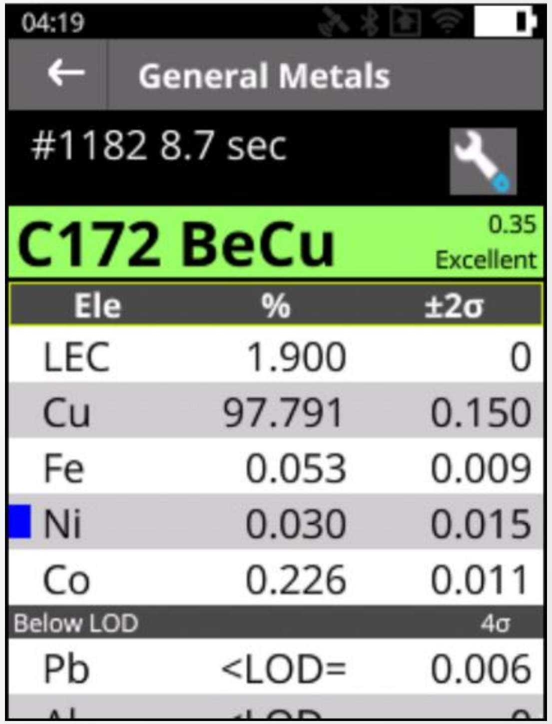


Aluminum Bronze measuring main +light elements only



Beryllium Bronze

(Be can't be measured by XRF)



Alloy grades can in some case be identified without measuring certain key elements

Pass / Fail Analysis

Example: California Proposition 65 restricts presence of lead used in plumbing to 0.2%

Red Brass Valve

Compliant Material

00:29

General Metals

#1554 5.7 sec

C230RedBs 0 Excellent

Pass ✓

Ele	%	±2σ
Pb	0.048	0.014
Cu	85.303	0.218
Zn	14.544	0.124
Fe	0.071	0.014
Below LOD		4σ
Se	<LOD=	0.012

Non-compliant Material

00:30

General Metals

#1553 5.9 sec

C230RedBs 0 Excellent

Fail ✗

Ele	%	±2σ
Pb	0.360	0.013
Cu	84.354	0.198
Zn	15.179	0.113
Fe	0.093	0.014
Below LOD		4σ
Se	<LOD=	0.011

HH-XRF sreening tool for RoHS, US-CPSIA, packaging directive, etc.

Applications for Copper Alloy Analysis

Metal Scrap Recycling

- Manual scrap sorting:
  - Rough sorting by families
  - Fine sorting by grades
  - Measurement of lead, which may lower value of scrap

Raw Material & in-process Quality Control

- Incoming materials inspection in metal fabrication
- Quality control of semi-finished & finished products

Positive Material Identification

- Pre-commissioning and retroactive and Inspection of critical materials in offshore oils and gas or marine industries

Compliance measurements

- Material compliance verification vs. regulation such as RoHS or California Proposition 65

Benefits

- On-site / at line real time measurement
- Accurate Quantitative Analysis
- No / Little sample preparation needed
- Usable by non-experts

Faster decision making with high level of confidence

Product Demonstration >>

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Questions?

For more information:
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Thank you