

New Developments in Portable XRF Instrumentation

Light Element Analysis with a Helium Purge

Aerospace Testing Expo 2005 North America

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NITON Analyzers

Outline

- The role of portable XRF analyzers in modern industry
- Evolution of portable XRF analyzers
- A Contemporary, hand-held XRF analyzer
- Applications
 - *Prohibited Materials*
 - *QC and Inspection of Alloy materials*
- New Developments – He-purged, portable XRF

Portable XRF analyzer in industry

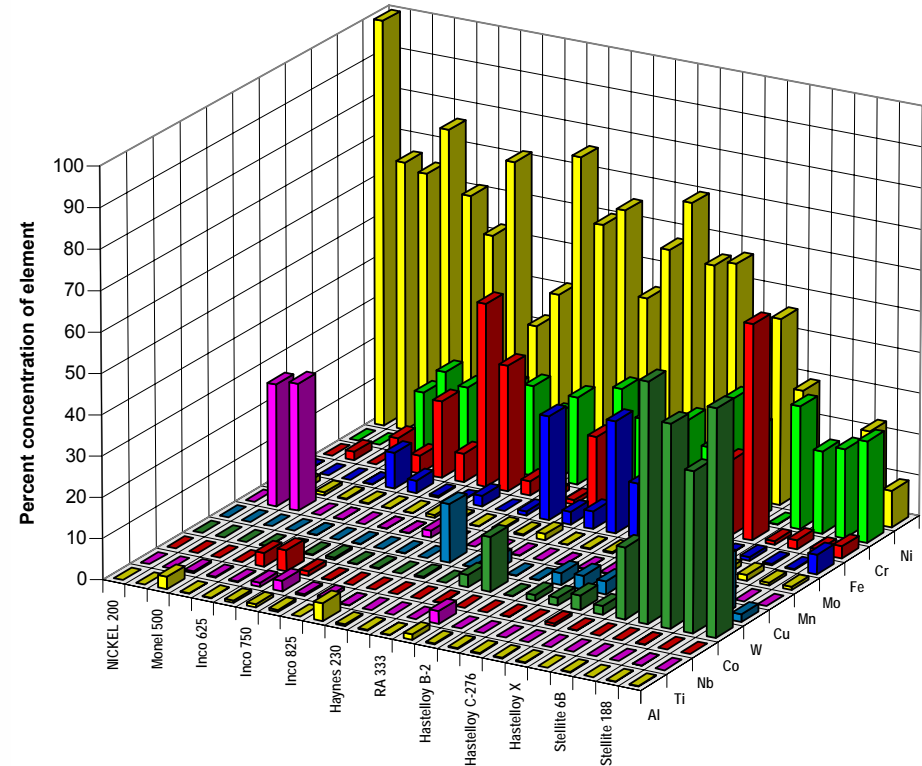
- Features of XRF Method that make it suitable for industrial and portable, field applications:
 - Wide dynamic concentration range
 - Analyzes multiple elements simultaneously
 - Fast, immediate results
 - **Truly nondestructive** to analyzed material
 - Easy to automate
 - Easy to miniaturize
 - Rugged

XRF Alloy Analysis

- Advantages
 - Fast
 - Nondestructive
 - Qualitative and quantitative
 - Multiple elements analyzed simultaneously
 - Little or no sample prep
 - Many different sample types, sizes and shapes
 - *solids, powders, liquids, turnings, etc.*
 - Robust calibration: detection limit to 100%
- Limitations
 - Limited capability for light elements (below atomic number 19)

Portable XRF analyzer in industry

We are facing a seemingly impossible task of analyzing with sufficient accuracy and precision to be able to distinguish an alloy from plethora of others



Evolution of Portable XRF Analyzer

How did we get here

- Röntgen's discovery of X-rays in 1895 starts the story
- Coolidge invents hot cathode x-ray tube, 1913
- **First reliable G-M counters, 1928**
- First commercial WDXRF spectrometer, 1948
- First transistor, 1948
- **First commercially available radioisotope source, 1953**
- **First "chip", 1958**

... all these lead to....

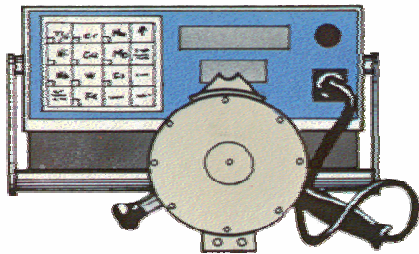
Evolution of Portable XRF Analyzer

- The First Generation FPXRF, early-to-mid 1960s, characterized by calibration graphs



Evolution of Portable XRF Analyzer

- The first microprocessor, Intel 4004, in 1970 and improvements in gas-filled proportional detector technology lead in 1978 to...
- The Second Generation of FPXRF analyzers that could hold in memory externally created calibration curve



**TN 9266 Alloy
Analyzer**



Evolution of Portable XRF Analyzer

- Better microprocessors, and availability of electronic memory allows for design of the first analyzers with onboard interactive program for calibration and data storage capabilities, and so...
- The third generation of FPXRF analyzers is brought to market in 1984



TN 9277
Metallurgist



X-MET 880 with
Proportional Counter

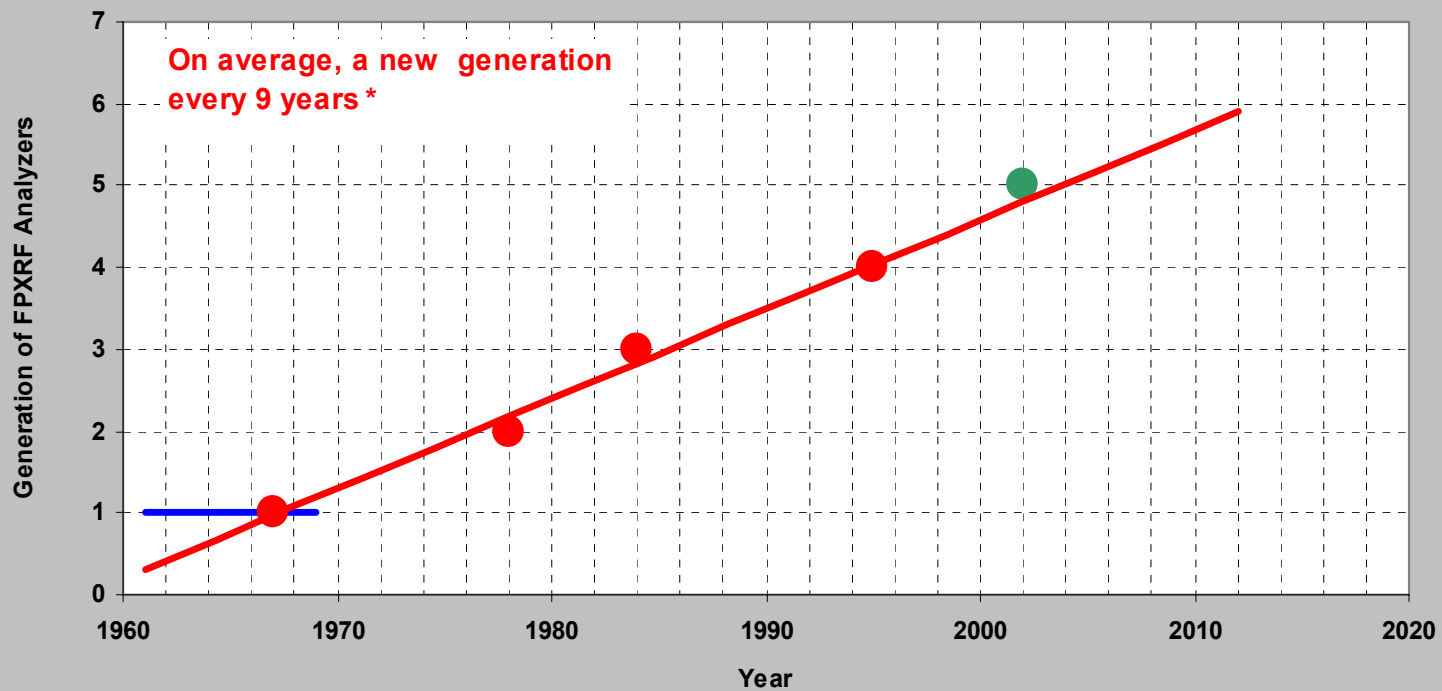
Evolution of Portable XRF Analyzer

- Further progress in electronics, detectors and battery technologies lead to yet another, some PC-based
- Fourth generation FPXRF analyzer in 1995



Evolution of Portable XRF Analyzer

Progress in Development of Portable XRF Analyzers



** NITON averages a new generation every 4 years*

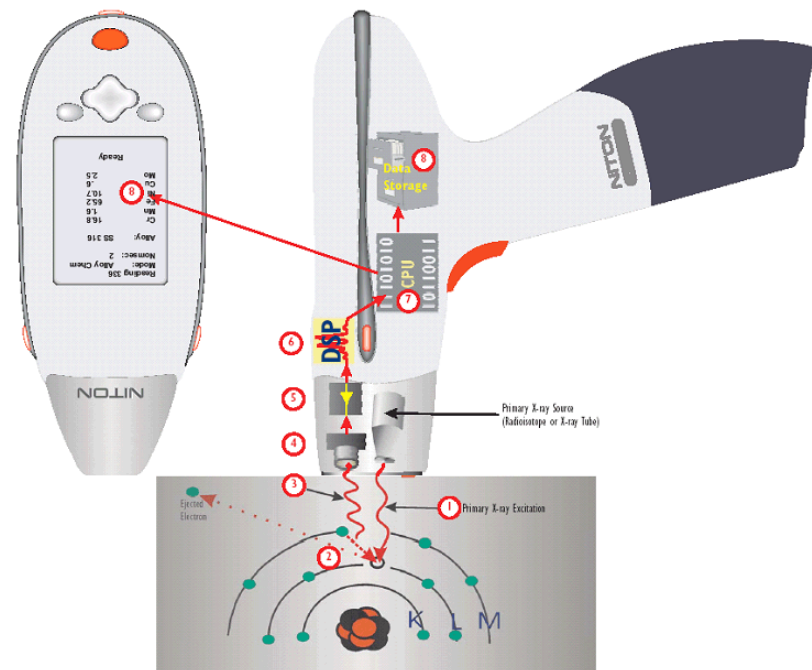
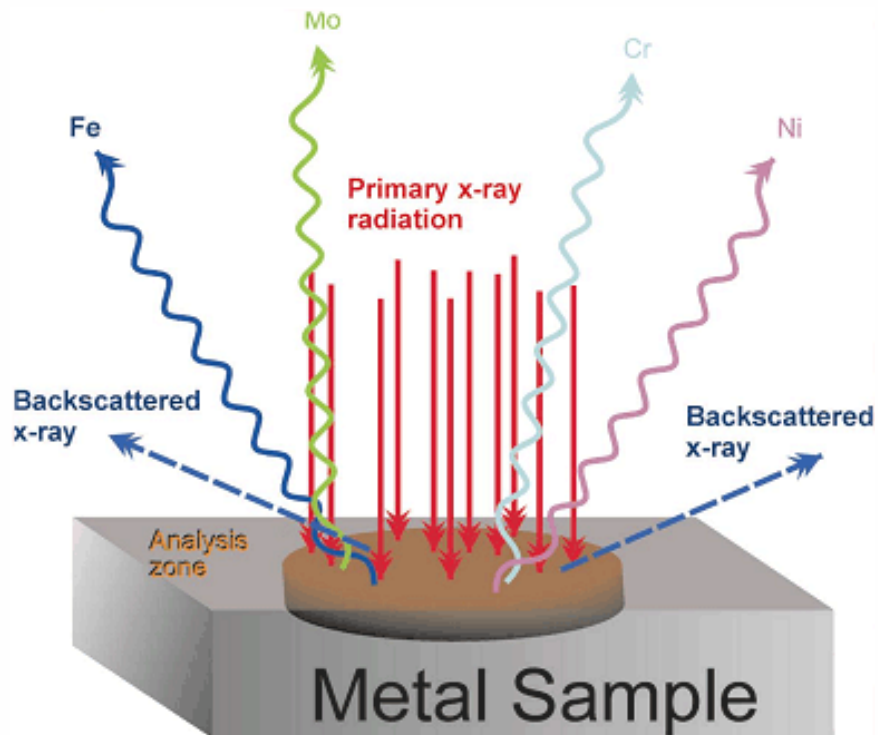
Contemporary hand-held XRF Analyzer

● **The Fifth Generation, 2002**



The NITON XLt analyzer

Energy Dispersive X-Ray Fluorescence



Performance, Analytical Range

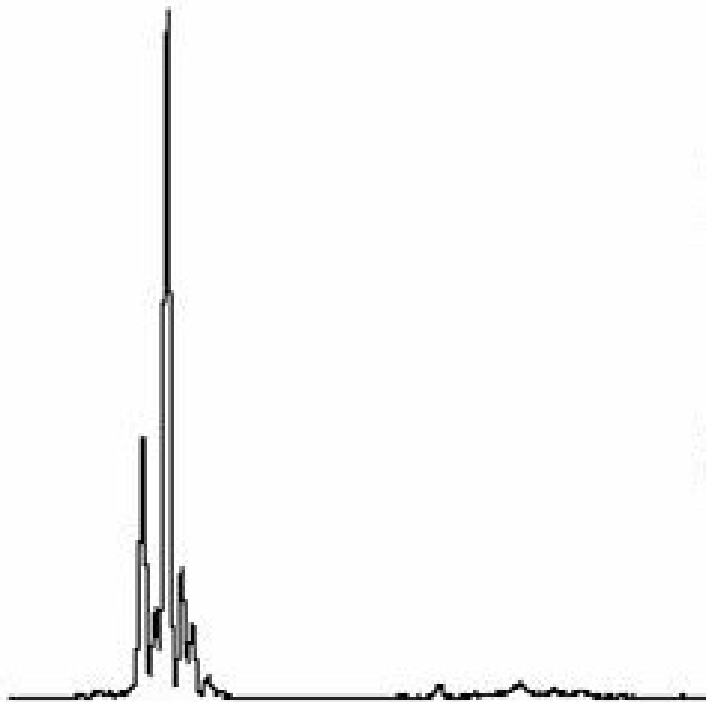
- *Standard Set of Elements Analyzed in Alloys*

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm								

- Analytical capability of XLt is not limited to the elements in green; the full analytical range extends from Ca to U

Counts into Results

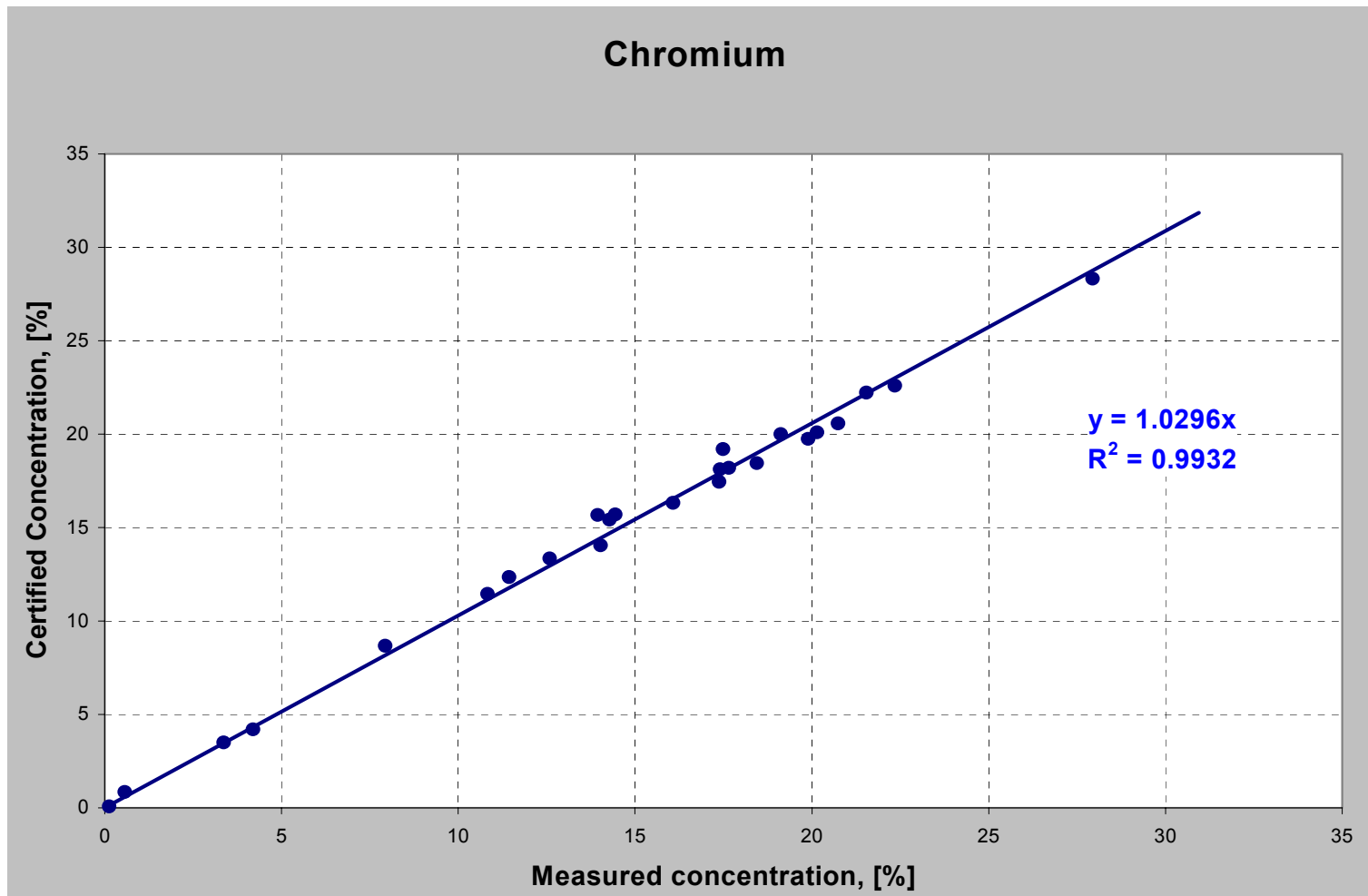
Spectra



Analytical Results

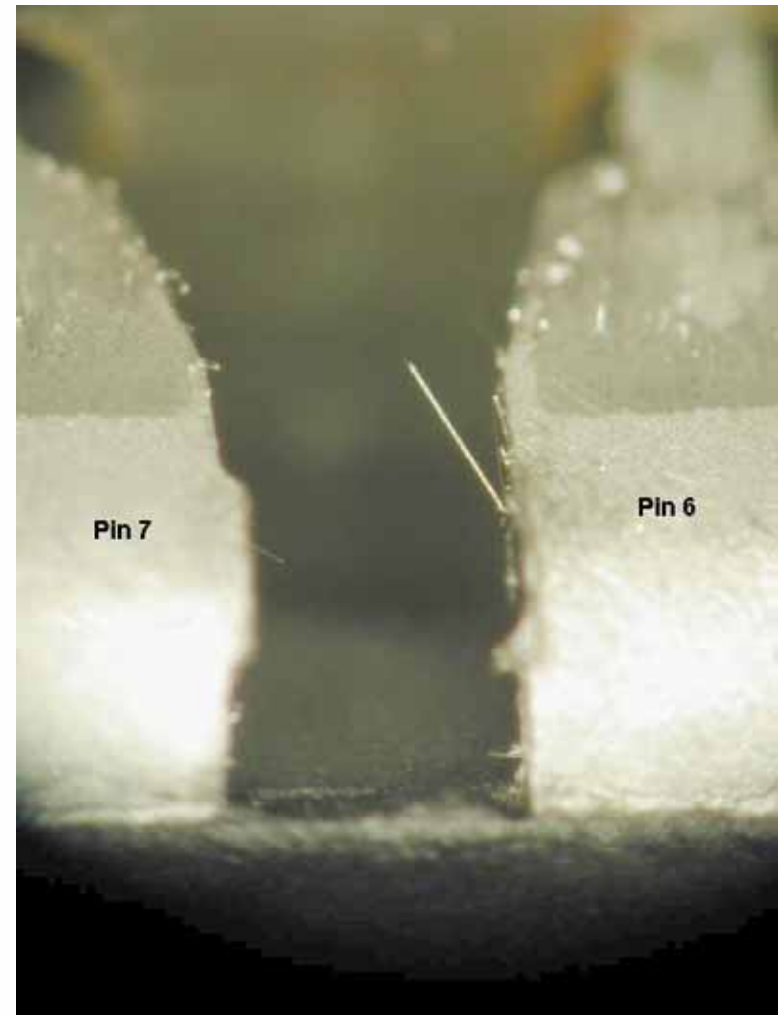
```
Reading 70
NomSec 9.3
Alloy Cu/Zn Moc
SS304 0.2
Mo 0.29 0.05
Cu 0.50 0.18
Ni 8.48 0.42
Fe 70.48 0.93
Mn 1.98 0.25
Cr 17.36 0.41
```

Performance, Analytical Accuracy



Application: Prohibited Materials (Sn, Zn, Cd “Whiskers”)

- Pure tin solder may grow metal filaments or “whiskers”
 - *Extremely thin*
 - typically 1 to 2 μ
 - Grow as straight, kinked or spiraled single crystals
 - Can reach length of 9mm (3/8") & carry 10mA current
- Northrop Grumman includes portable XRF screening in the QC protocols



Whiskers

What do they do?

- Cause sudden failures & intermittent problems
 - *ability to short closely spaced circuits*
- Crucial applications cannot tolerate whiskers
 - *aerospace, military weapons systems, medical, etc.*
- Growth rate varies tremendously – cause still not fully understood
- Problems have resulted because manufacturer failed to test for proper material composition
 - *Relied on its vendor to deliver proper components*
 - *Material mix-ups*
 - *All involved should test; cannot rely on vendors*

L= SE1

EHT= 10.0 KV

WD= 34 mm

MAG= X 112.

PHOTO= 15

200 μ m |-----|

ZINC WHISKER, 4/1/03



Prohibited Materials

What is Being Done?

- Testing for high purity Sn coatings
 - *On fasteners and terminal lugs*
 - If Pb < LOD, then 'high purity' and is 'not acceptable'
 - Sn must be alloyed (~3% or more) to be acceptable for space flight
 - *The same for Zn and/or Cd*
 - Cd and Zn have lesser tendency to whisker, but pose the problem of sublimation in a vacuum – condensing on and degrading precision optics & sensors
- All critical areas must be tested
 - *Incoming solders*
 - *Circuit board terminals*
 - *Fasteners*
 - *Must avoid using pure tin (alloyed at or < 3%)*

Application: Alloy Verification & QC

- **Material verification in aerospace is CRITICAL**
- **Certification inadequate for most audited Quality Systems**



Typical Components



- Body Panels
- Bearings
- Fasteners
- Turbine Blades
- Rocket Heads
- Engine Components
- Electronic Circuitry
- Solders
- Wear Metals
- Coatings

Typical Alloys used in Aerospace

- **Hastelloys, Monel, Waspaloy**
- **Wrought Aluminium: 2024, 7075, 7050**
- **Titanium: 6-4, 6-6-2, 6-2-4-2**
- **Stainless Steel: 300 and 400 Series**
- **Low Alloy Steels**
- **Refractory Containing Materials
PWA 693, N-115, N-155**



XRF analysis range

- Conventional portable XRF limited to the following elements:
 - V, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, W, Se, Pb, Bi, Zr, Nb, Mo, Ag, Sn, Sb, Ta, Hf, Re, Au, Pt, Ru, Pd, In, Cd, ...
 - Covers high alloy materials including Ni alloys
 - Partial capabilities for Ti and Al alloys
 - *Only heavy element concentrations measured*
 - *Partial applicability to aerospace industry due to limitations*
- More capabilities needed...
 - THE SIXTH GENERATION

The Sixth Generation – XLt 898He

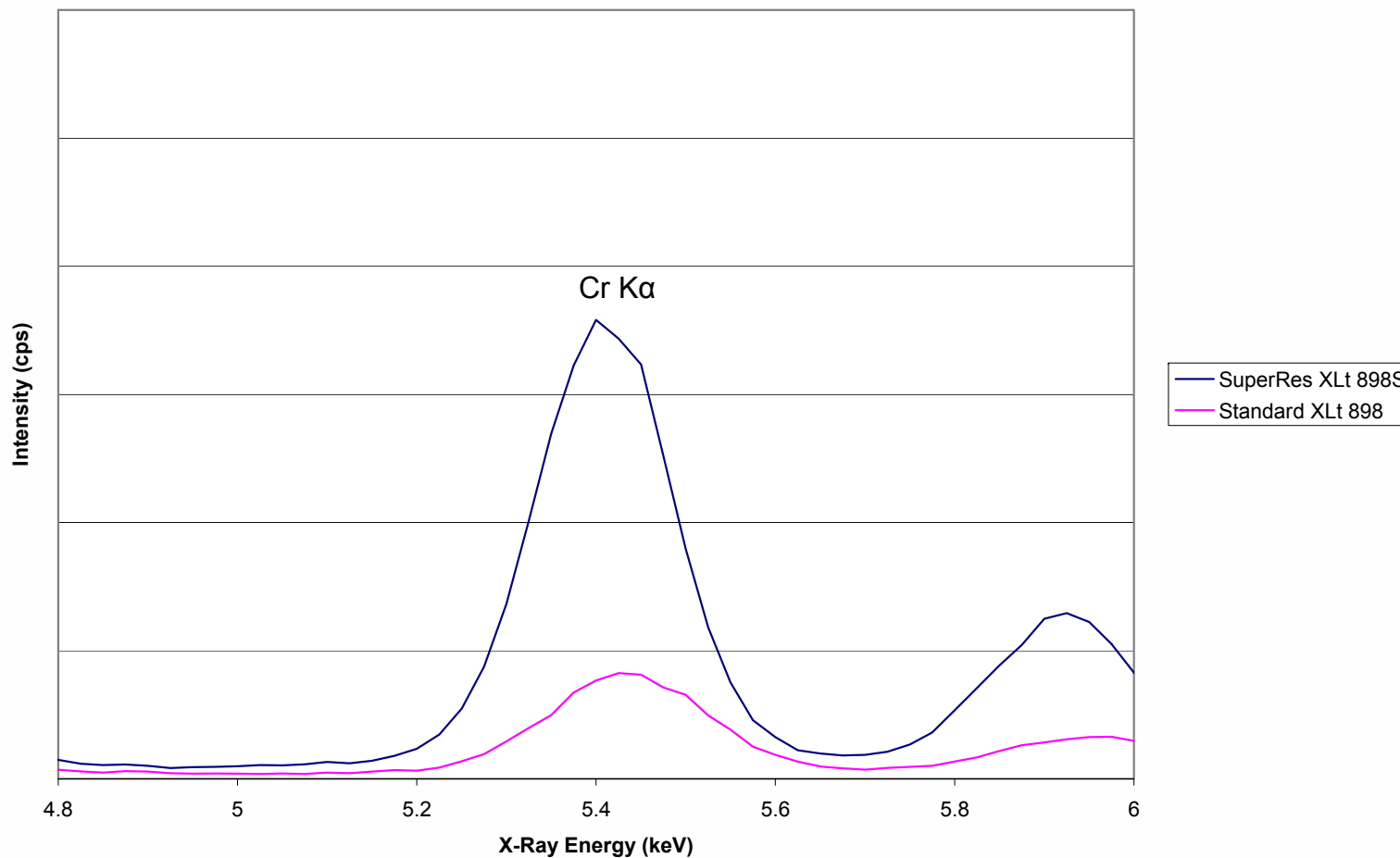
- “S” super detector
 - *Si PIN, Peltier cooling*
 - *Resolution <190 eV at Mn line*
 - *Higher count rates, very low baseline*
 - *Very good signal to noise ratio*
 - *Improved LODs*

The sixth generation of portable XRF is entering the laboratory tramp level analysis

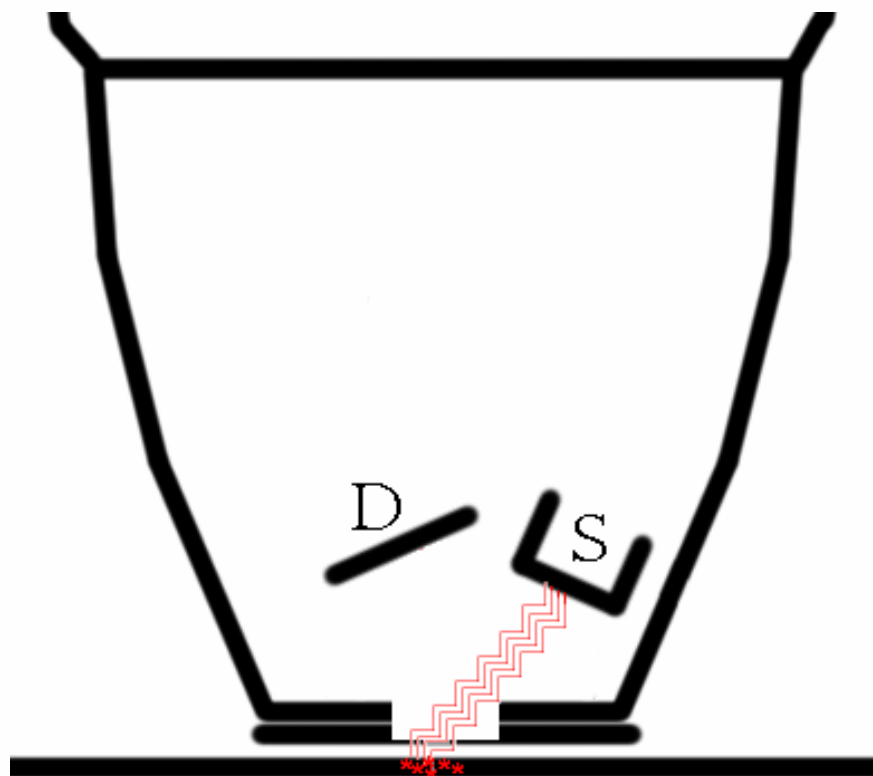
- He-purged front end:
 - *Addition of Al, Mg, Si, and P analytical capabilities*
 - *Expands analytical range to full analysis of Al and Ti alloys, Al in Ni alloys, P in Cu alloys, Si in steels...*

'S' Detector Count Rate comparison

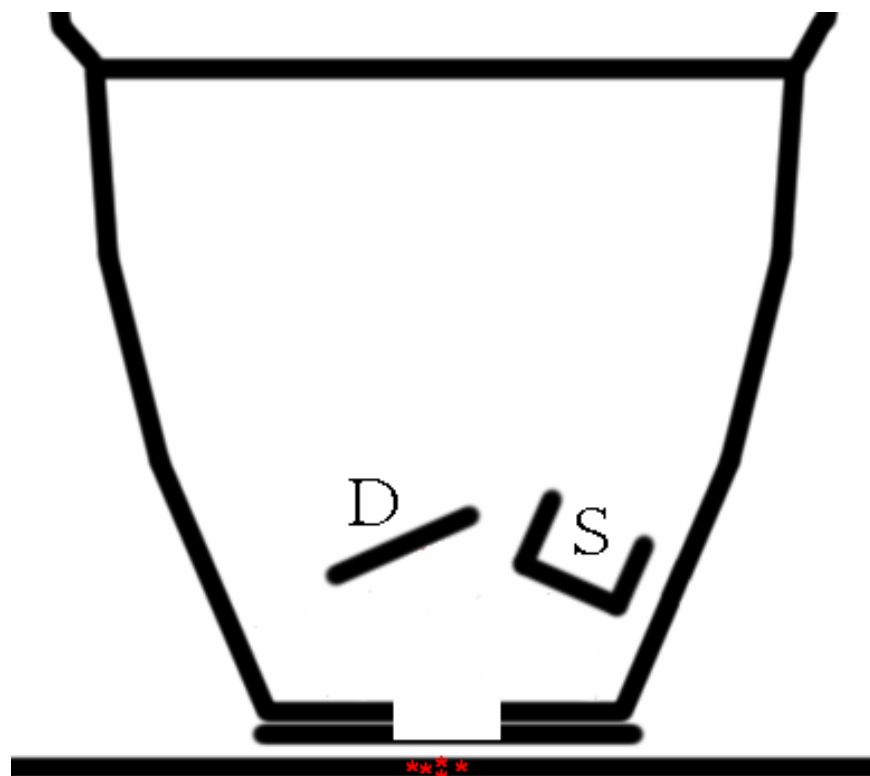
Spectral Overlay - Cr region



He purge principle

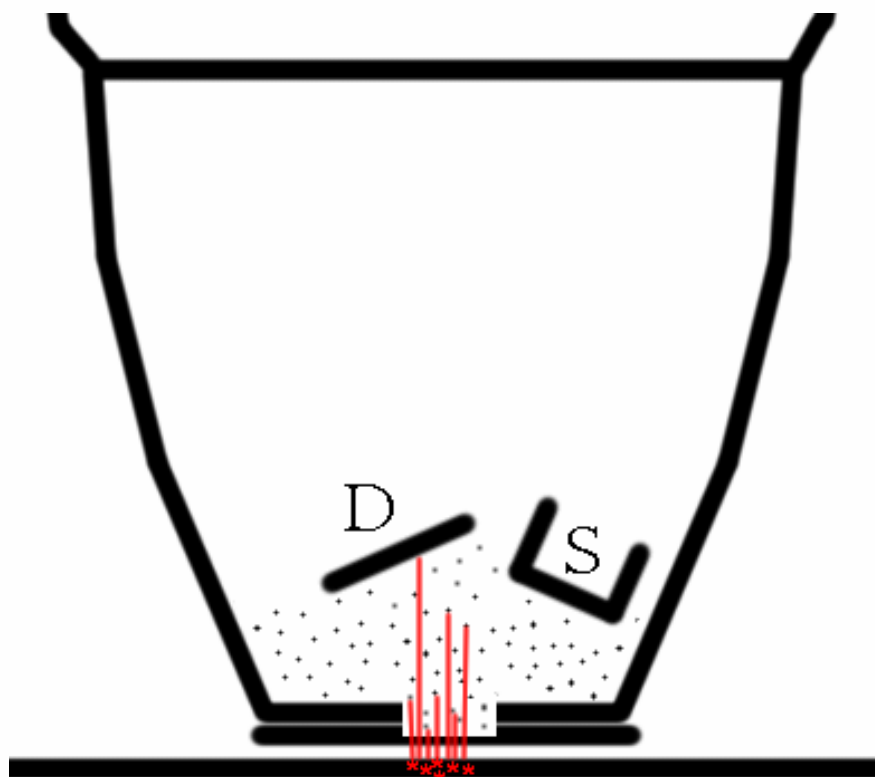


1. Source Irradiates Sample

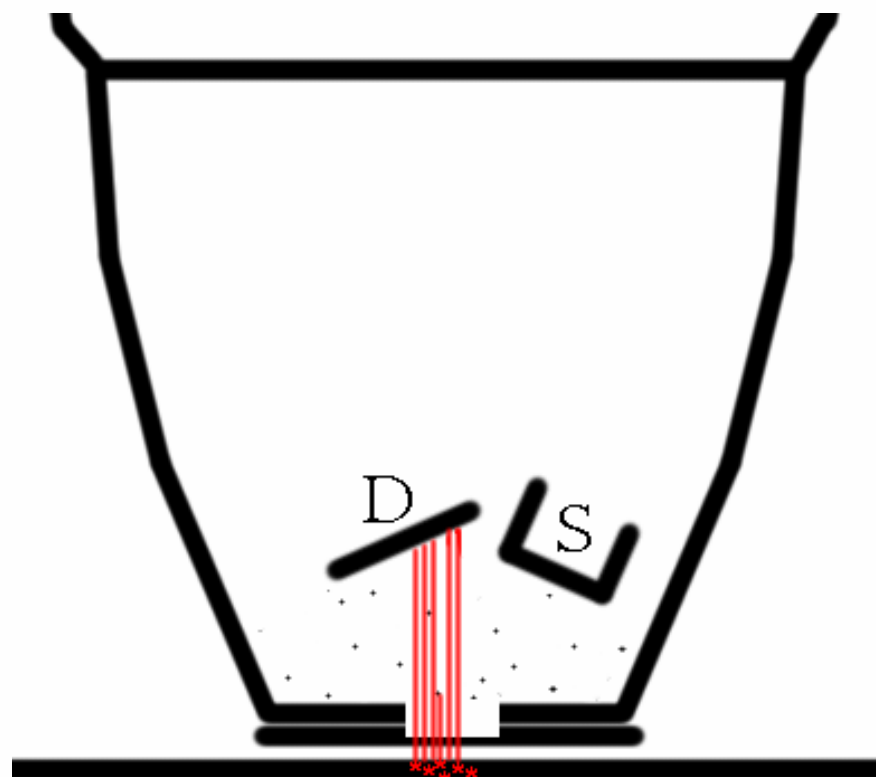


2. Excited Sample Fluoresces

He purge principle



3. Air Attenuates Fluorescence

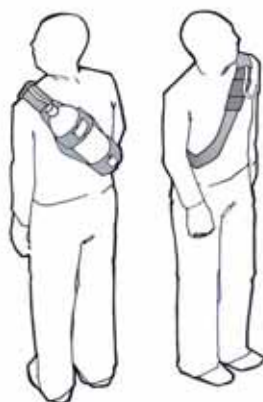


4. Little Attenuation with He

Portable Use



58L / 500 psig
He tanks

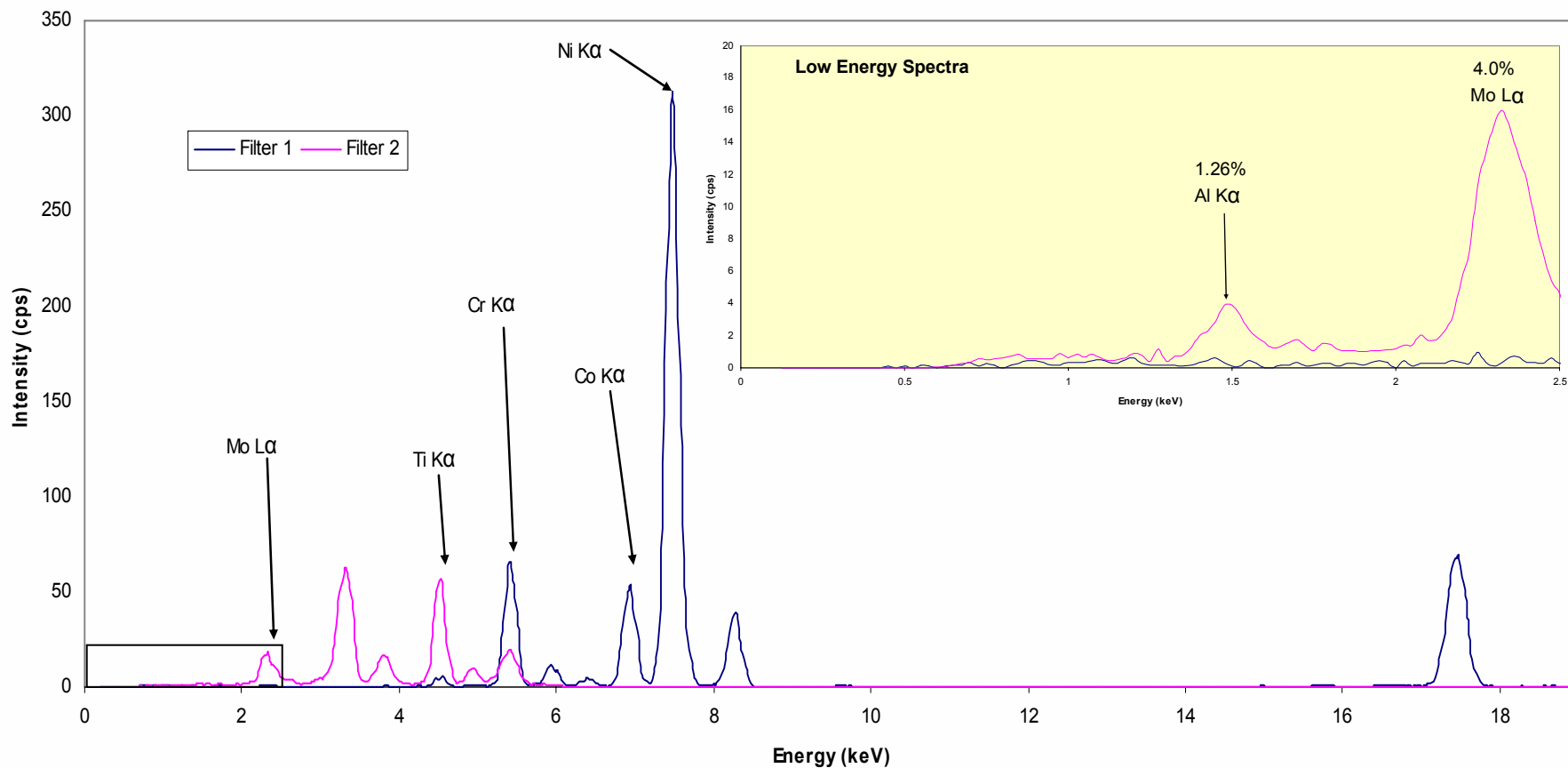


Stationary Benchtop Use



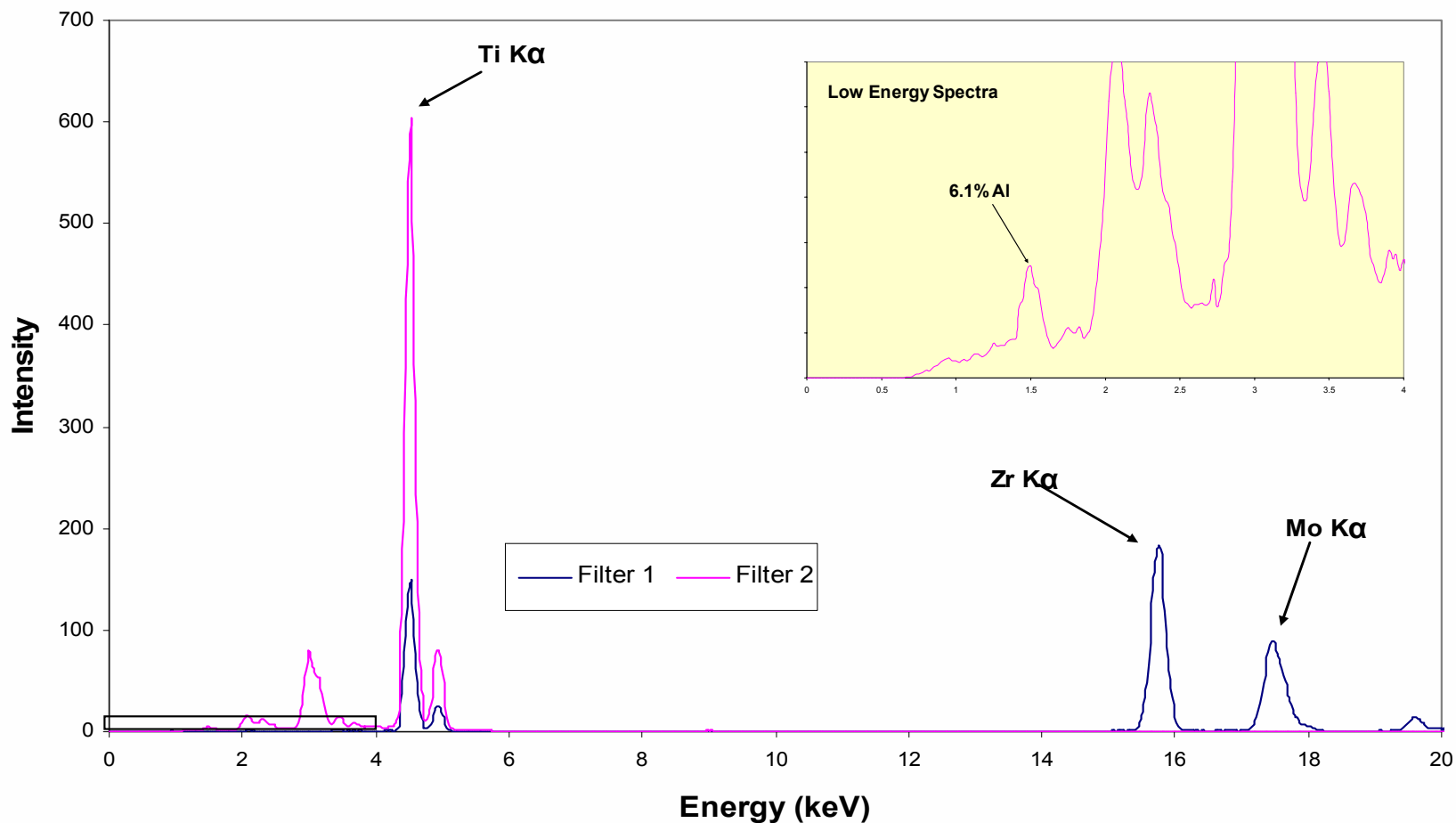
XLt 898He, Waspaloy Spectra

Spectra of Waspaloy Analysis



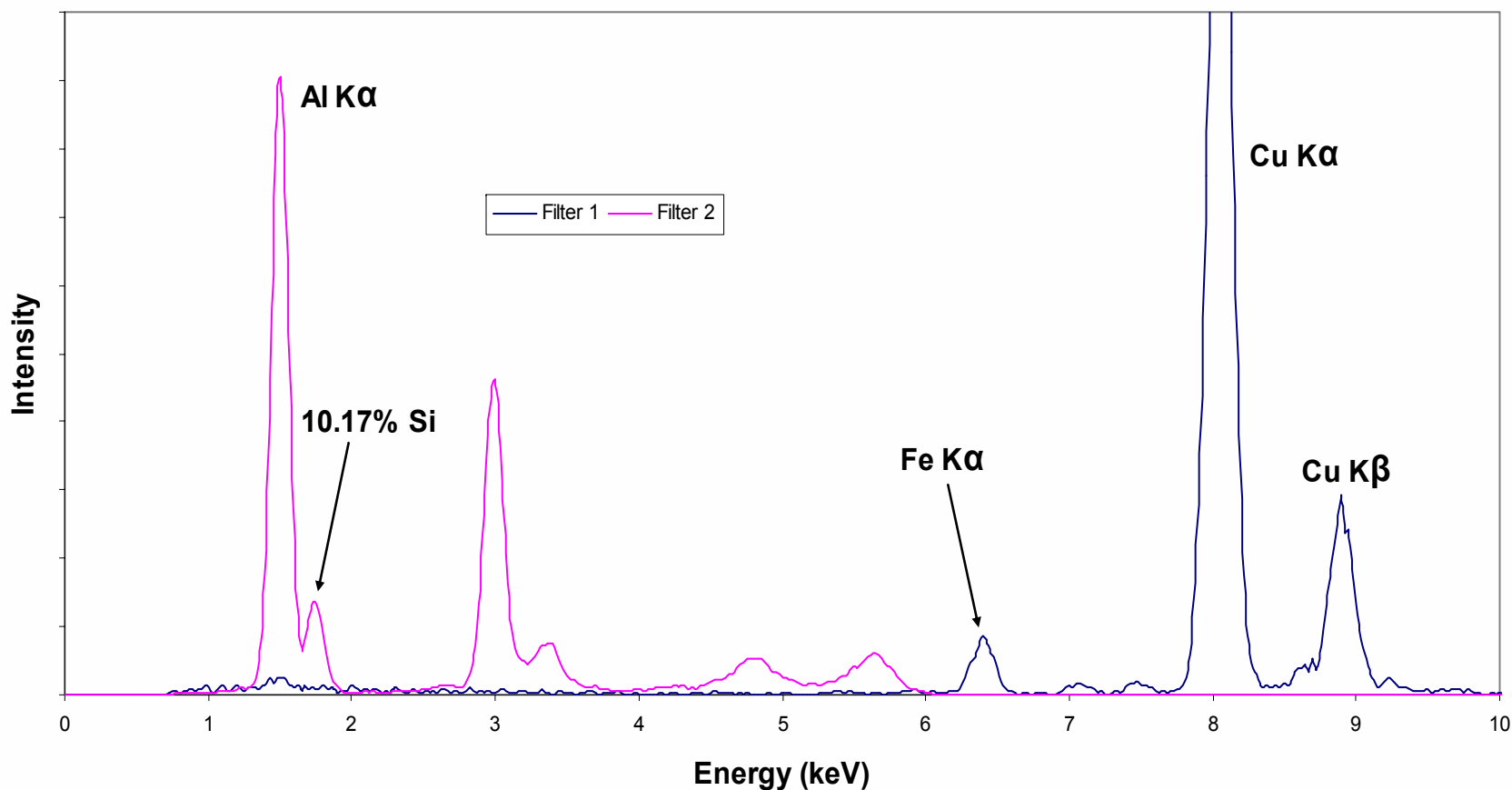
XLt 898He, Ti 6-2-4-2 Spectra

Spectra of Ti 6-2-4-2 Analysis



XLt 898He, AA4145 Spectra

Spectra of AA4145 Analysis



Analytical Performance

- Analysis Sensitivities, LODs:

Element	MATRIX				
	Al	Mg	Cu	Zn	Fe
Al	-	0.75	0.75	0.75	0.3
Si	0.4	-	0.12	-	0.2
Mg	1.6	-	-	-	-
P	-	-	0.04	-	-
Fe	0.01	0.01			
Cu	0.01	0.01			
Mn	0.02	0.01			
Cr	0.02				
Ni	0.01				
Zn	0.01				

*Two-minute
testing times*

XLt 898He Applicability

- **Applicability:**

- *Aerospace manufacturing*

- Alternative testing methods impractical, nondestructive testing wanted
 - Aluminums, Titaniums, Al coatings...

- *Aerospace maintenance and refurb*

- Material ID and QC testing

- *Specialty Manufacturers*

- Military suppliers, defense contractors, Al in high temps

- *Manufacturing*

- Al & Ti products

- **Alternative:**

- *OES*

- Better LODs, but
 - Destructive method

XLt 898He, Analysis Example

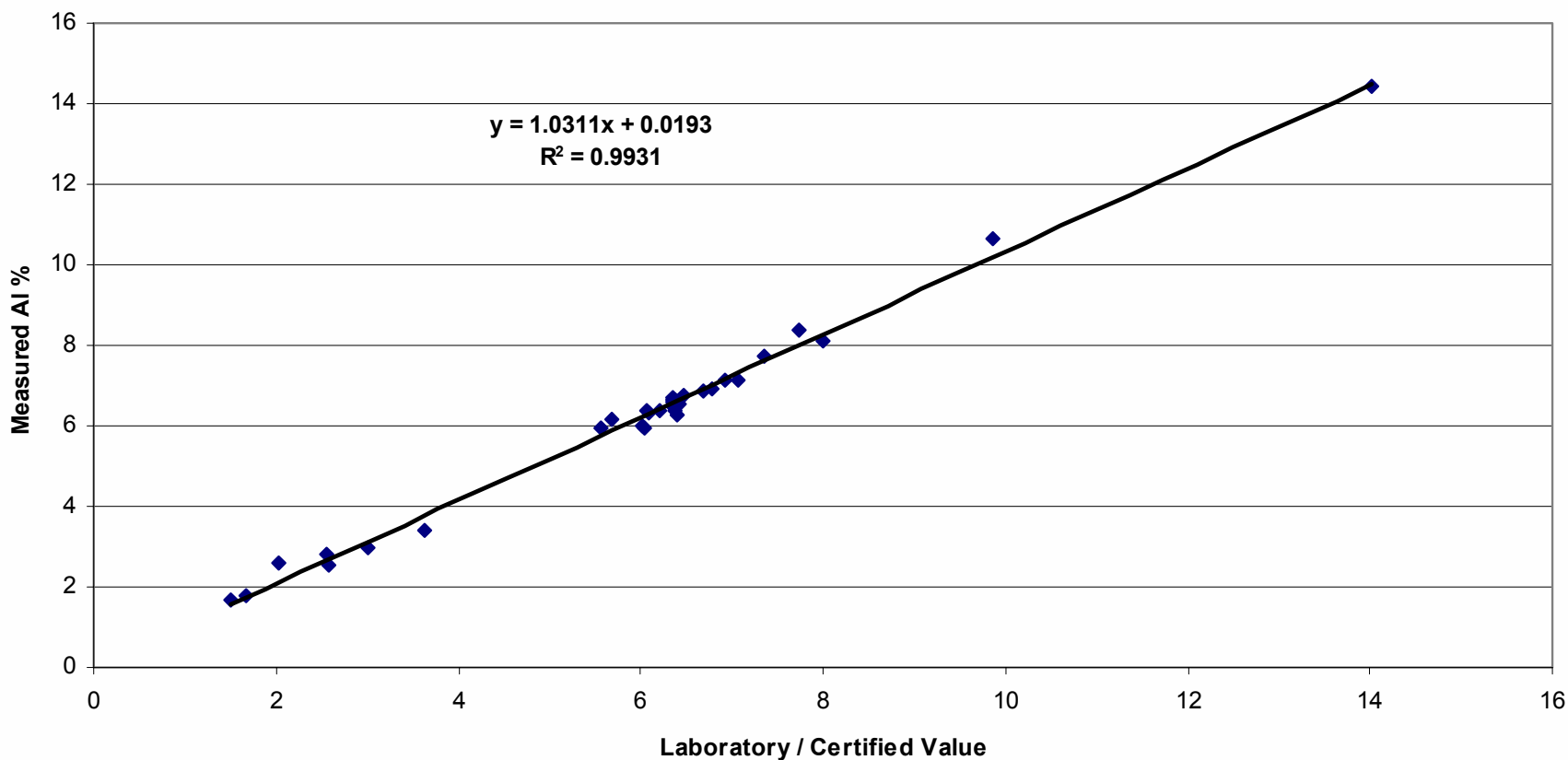
Wrought Al 4145

Rdg	Sn	Bi	Pb	Zn	Cu	Ni	Fe	Mn	Cr	Ti	Si	Al	Mg
1	0.03	0.02	0.02	0.04	3.99	0.02	0.53	0.07	0.05	0.07	10.25	84.23	0.64
2	0.01	0.03	0.02	0.05	4.01	0.02	0.51	0.05	0.05	0.05	10.68	84.49	0
3	0.03	0.03	0.02	0.05	3.96	0.04	0.52	0.04	0.06	0.1	10.28	84.7	0.14
4	0.03	0.02	0.02	0.04	3.99	0.03	0.48	0.05	0.04	0.03	10.61	84.56	0
5	0.02	0.02	0.02	0.05	3.97	0.04	0.53	0.06	0.02	0.04	10.77	84.22	0.16
6	0.03	0.02	0.02	0.05	4.04	0.03	0.53	0.04	0.03	0.06	10.75	84.35	0
7	0.02	0.02	0.02	0.05	3.8	0.03	0.48	0.05	0.04	0.08	10.28	83.96	1.11
8	0.04	0.02	0.02	0.06	3.99	0.03	0.5	0.04	0.03	0.05	10.73	84.39	0
9	0.02	0.02	0.02	0.05	3.94	0.03	0.51	0.06	0.02	0.05	10.69	84.55	0
10	0.02	0.02	0.02	0.05	3.84	0.04	0.48	0.05	0.05	0.12	10.44	84.19	0.62
11	0.03	0.03	0.02	0.05	3.95	0.03	0.5	0.05	0.03	0.06	10.83	84.36	0
AVE	0.025	0.023	0.020	0.049	3.953	0.031	0.506	0.051	0.038	0.065	10.574	84.364	<LOD
CERT	0.035	0.03	0.029	0.05	4.21	0.034	0.54	0.052	0.051	0.061	10.17	BAL	0.044

80-second testing times

XLt 898He, Performance Curve

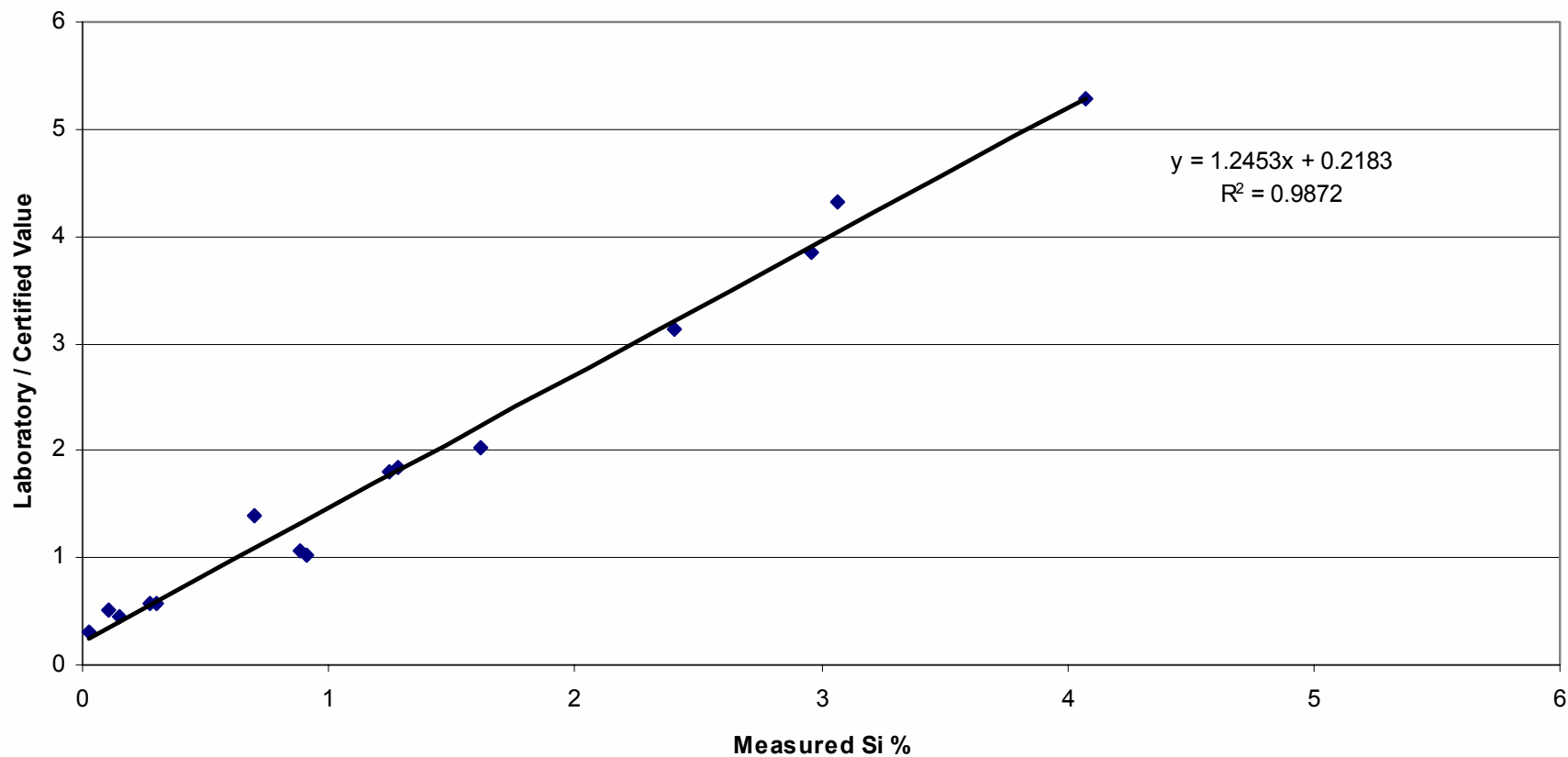
Aluminum in Titanium Alloys



100 second testing times

XLt 898He, Performance Curve

Si Correlation Curve, Multiple Matrices



100 second testing times

Conclusions

- Portable XRF had been adapted to new applications
 - *Screening for prohibited materials in electronics*
- Newest technology expands the range of alloy analysis capabilities
 - *Now its possible to certify alloy grades non-destructively by light element content*
 - *Testing can be done on-site: at the vendor, at the customer site – take it on trips*
- Development of portable analytical technology continues
 - *Where will the seventh generation take us?*