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Portable EDXRF – How it has changed the Metals Recycling Industry

The University of Western Ontario
XRF Short Course (2010)

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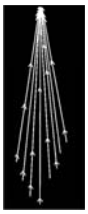
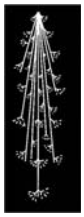
Past Methods for Sortation

- Visual/hand Sortation - Problems
  - Product form with material change
  - Incorrect stampings, color codes, tags, stickers, etc.
  - Inaccurate process
- Chemical tests (acids)
  - Example: Molybdenum Spot Test – Can indicate the presence of Mo to separate SS 316 from SS 304 (no molybdenum), but does not alone indicate 316. In the absence of other knowledge the steel could be 317, 2205, 904L, etc.
    - Requires storage of hazardous chemicals/reagents
    - OSHA restrictions
    - Liabilities
- Magnet Test
  - Can assist in determining series of stainless steel, but will not be usable for determining specific grade. For example, 400 series stainless steels are magnetic while 200 and 300 series are not.

Past Methods for Sortation - Continued

- Spark Tests

Absence/presence of alloy determined by length of spark, color of sparks, spark volume, forks (left) or bursts (right), or repeating or ending forks or bursts. Manganese steel example below has a large spark volume traveling over 6' and yellow-orange sparks with no forks or bursts.


Handheld XRF Analyzers


Spectro
xSORT


Bruker
Tracer
TRACERturbo^{SD}


Oxford
X-MET 5000
X-MET 5100


Innov-X
Delta


Thermo Scientific
Niton XL$_3$
GOLDD

NOTES:
Innov-X Woburn, MA (USA)
Thermo Scientific NITON Analyzers – Billerica, MA (USA)
Spectro (Germany)
Oxford Instruments (England) purchased Metorex (Finland)
Bruker (Germany) purchased Keymaster (Kennewick, WA - USA)

Handheld XRF Analyzer Alloys Tested

- Some low alloy steels (not C steel grade)
- Nickel and nickel-cobalt alloys
- Stainless steel alloys
- Tool steels
- Cobalt alloys
- Titanium alloys
- Copper alloys
- Zinc alloys
- Aluminum alloys
- Magnesium alloys
- Precious metals
- Solder alloys
- Electronic alloys
- Many other alloy groups: Ta, Hf, Zr, W, Mo, Nb, etc.

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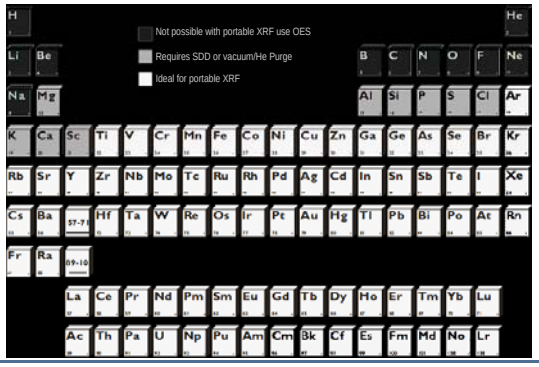
Handheld XRF Total Element Range



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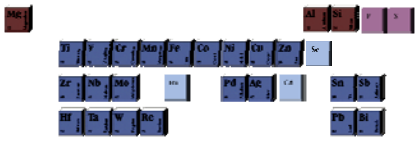
HHXRF Selected Alloying Element Channels

25-30 elements analyzed in alloys
250-500 alloys in multiple grade



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Calibration Methods

- Empirical Calibration
  - Designed to characterize samples that represent your intended use
  - Historically the only method available
  - Limited chemistry and limited alloy families (~250 of 70,000)
    - Very accurate over limited range - but cannot be made robust
  - Good for well defined set of alloys, e.g., petrochem
- FP or Fundamental Parameters
  - Currently the method of choice – can be made very accurate and robust
  - Unlimited chemistry and alloy families with “standardless” calibration
  - FP, when robust and accurate, is ideal for recycle use

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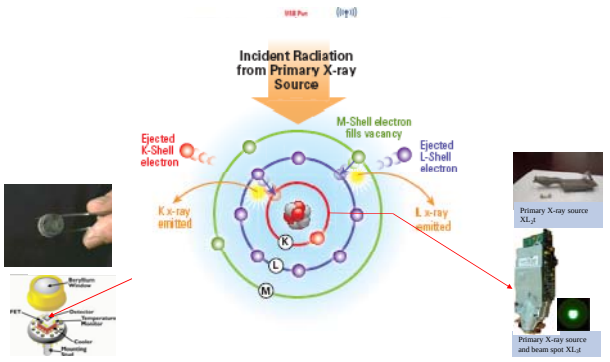
Handheld XRF Process and Analyzer Operation



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Handheld XRF Excitation Sources

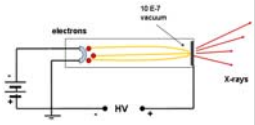
Radioisotopes

- Rugged/reliable (no electronic or moving parts)
- Proven in field use for 40 years
- Isotope (Am-241) never needs replacement
- More regulatory licensing issues, not as easy to transport or travel
- Lighter, more rugged, faster for routine sorting
- Long use battery (18-20 hours between charge)

Different shapes of isotope sources

Tubes

- Simplified regulatory issues; registration only, travel easier
- Higher performance for close alloys or tramp elements (allows automatic optimization of parameters)
- Tube may need replacement during life of analyzer
- 6-10 hours between charge



End window transmission anode tube

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Alloy Sorting with Handheld XRF
Challenges and Solutions

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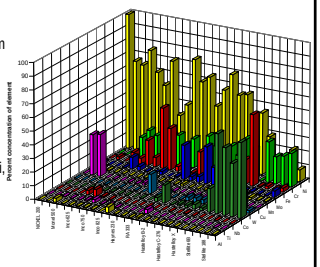
Challenge: Dealing with 70,000 Alloy Grades!

- 70% LAS (low alloy steels)
  - OES or HHXRF with SDD
    - Empirical calibration or FP with results from 0.001%
- 30% high alloys
  - Primarily HHXRF
    - Results from 0.001% to 100%
    - Ideal for high alloy (HAS, SS, TS, Ni/Co, Ti, Cu, Al, Mg, etc.)
    - Point and shoot ease of use
    - XRF moving from lab to field
    - Most recycle spectrometers are now XRF



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Dealing with Range of Forms, Shapes and Sizes

- We are facing a seemingly impossible task
  - •Correcting the results for an awesome variety of samples forms, sizes and shapes
- All latest handheld XRF calibrations automatically normalize for size, shape, curvature and distance (up to ~6 mm)
  - •Wires
  - •Turnings
  - •Powders
  - •Small fasteners
  - •Drill bits
  - •Mesh
  - •Etc.

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Dealing with Harsh Environmental Conditions

- We are facing a third seemingly impossible task
  - • Correcting for an intimidating set of environmental and sampling conditions: heat, cold, rain, hot samples, high noise, highly magnetic scrap
- Be sure it is sealed and hardened!
- PDA will not cut it …
  - • Designed for home or office use
  - • Obsolescence issues (HP no longer producing)
  - •Not environmentally sealed
  - • Not visible in sun with polarized sunglasses
  - • Slower by factor of 10
  - • Need to learn Windows™ CE
  - • Windows CE complexity, virus susceptibility, etc
  - •Easy to remove and disappear

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Best Practices

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Alloy Sample Preparation

- Grinding required
  - Coatings
  - Platings
  - Residual paint
  - Corrosion, scale, oxide layer
  - Metallic dust on surface
  - Shot-blasting (residual from pellets on surface)
  - Sand-blasting (only of concern with He Purge …reads silicon in sand)

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Cautionary Items

- Mixed alloys; turnings/powders/sweepings, etc
  - Use scan technique
  - Use averaging feature
  - May need bulk mode for sweepings
- Read-through (thin samples)
  - Results will be OK, but be aware of radiation safety concerns
- Small and undersize samples
  - Results will be OK, but be aware of radiation safety concerns

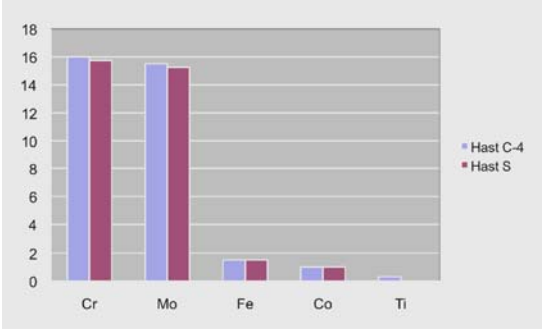
Two or More Similar Results

- Alloys with very close specifications may both be displayed as a close match
  - *Degree of similarity indicated by same (or very close) match number*
    - Clean off any corrosion, surface coatings
    - If sample is undersize (does not cover aperture) try to obtain larger specimen
      - *e.g., instead of single wire strand, measure on spool*
    - A longer reading (10 - 20s) may provide the precision necessary to separate in some cases`

Trade Name	Ti Min	Ti Max	Cr Min	Cr Max	Fe Min	Fe max	Co Min	Co Max	Mo Min	Mo Max
Hast C4	0.3	0.7	14	18	0	3	0	2	14	17
Hast S	-	-	14.5	17	0	3	0	2	14	16.5

Example of two very similar alloys with mostly overlapping specs (except the small amount of Ti difference)

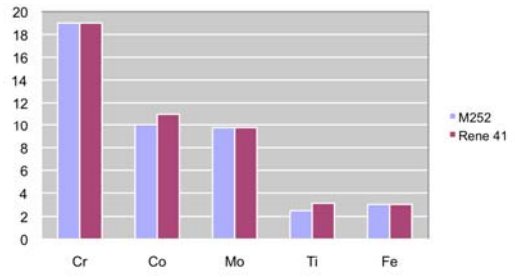
Here are Nominal Values



Examples of Close Specifications: Superalloys

Trade Name	Ti Min	Ti Max	Cr Min	Cr Max	Fe Min	Fe max	Co Min	Co Max	Mo Min	Mo Max
Rene 41	3	3.3	18	20	0	5	10	12	9	10.5
M252	2.25	2.75	18	20	0	5	9	11	9	10.5

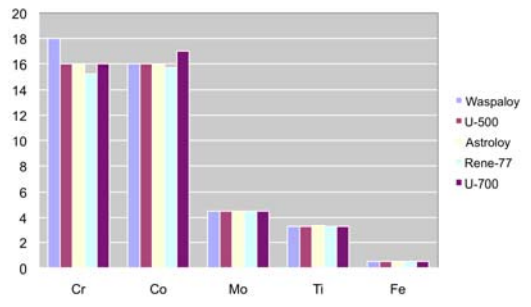
Nominal Values are Close; Separation is not routine



Examples of Close Specifications: Superalloys

Trade Name	Ti Min	Ti Max	Cr Min	Cr Max	Fe Min	Fe max	Co Min	Co Max	Mo Min	Mo Max
Waspaloy	**2.5**	**3.25**	**18**	**21**	**0**	**2**	**12**	**15**	**3.5**	**5**
U-500	**2.5**	**3.25**	**15**	**20**	**0**	**4**	**13**	**20**	**3**	**5**
Astroloy M	**3.35**	**3.65**	**14**	**16**	**0**	**0.5**	**16**	**18**	**4.5**	**5.5**
Rene 77	**3**	**3.7**	**14**	**15.25**	**0**	**0.5**	**14.25**	**15.75**	**3.9**	**4.5**
U-700	**2.75**	**3.75**	**14**	**16**	**0**	**2**	**17**	**20**	**4.5**	**5.5**

Many Overlaps Occur Within UNS Range Specs



Solutions: Overlapping Specs/Multiple Displays

- Measure longer for better chemistry (10-20s)
- Delete close alloys that are not needed
  - 301, 304, 321; delete 301, 321 if not interesting for your business
  - 17-4 Vs 15-5, sort as one alloy (17-4/15-5)
- Be aware of different names for same alloy
  - L605 (HS-25)

Solutions for Overlapping Specs : Grade ID Mode

- Adjust grade library specifications
  - Use “as produced” specs
    - May be possible to separate if overlapping UNS spec range made tighter
- Example grade library entry (301) 17/7 Vs (304) 18/8

SS 301			
Cr Lo	**16.00**	**Cr Hi**	**18.00**
Mo Lo	**0.00**	**Mo Hi**	**0.00 → 0.80**
Ni Lo	**6.00**	**Ni Hi**	**8.00 → 7.80**
Mn Lo	**0.00**	**Mn Hi**	**2.00**

Solutions for Overlapping Specs

Lab may be needed for elements XRF cannot do

- Send samples to lab; acquire SDD HHXRF or Spark OES Analyzer
  - 304, 303
    - Austenitic SS’s with overlapping specs except S (~0.3%)
    - Previous to SDD was not possible to separate on portable XRF
  - 410/416
    - Ferritic S.S.’s with overlapping specs except S (~0.3%)
  - 304/304L
  - 316/316L
    - Austenitic SS’s with ~0.03 carbon difference
    - not possible to separate on portable XRF

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What to look for from Suppliers

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Speed! (with good performance)

Why is Speed So Sought After?

Recycle application: potential extra income….
based on 500 incremental samples per day

~500 more sorted samples at ~2 kg per sample x ~$2 per kilo =

$1,000/day incremental income with latest technology compared to current installed technology

Latest technology can return an incremental $1K/day

Only a few months of highly productive use may pay for newest technology!

Speed (with Highest Performance)

- Isotopes are fast and rugged with good performance
- Miniature X-ray tubes and SDD's for vastly improved performance
  - Si PIN detector systems with X-ray tubes are least expensive and as good as needed for most routine sorting
    - No light elements without vacuum or He purge
  - SDD are fastest, highest performance and most capable
    - Without vacuum or He purge can test Mg (12) –S (15)
    - Mg most difficult: sensitivty about 1% in air
    - Mg to 0.3% with vacuum or He purge
  - SDD with 50 kV tube and excitation parameter optimization is fastest of all and best performance
    - Provides light elements, high sensitivity tramp element detection, and best close (twin) alloy separations; essentially lab quality performance

The Expectations of Today's Recycler

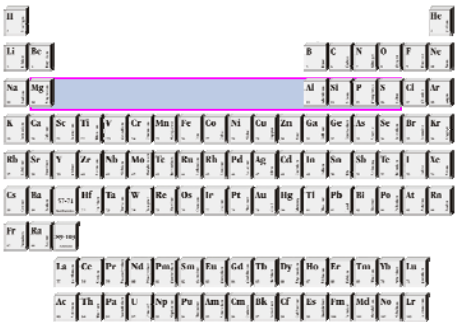
- Minimum requirements
  - Accurate robust chemistries for many thousands of alloys
  - Fast, high confidence ID's for hundreds of alloys
  - Environmentally sealed and hardened for harsh conditions
  - Point and shoot ease of use
  - Good training and support
  - Single piece, light, ergonomic, balanced, handheld unit under 4lbs
  - High power, lightweight, Li ion batteries that last for 8+ hours

Do I need to Test Difficult Alloys or Tramp elements?

- Ability to perform difficult high alloy separations for nearly twin alloys
  - 301, 303, 304, 321 (Cr/Ni - S – Ti)
  - 17-4, 15-5 (Cr/Ni)
  - U-500, U-700 (Cr/Co)
  - Waspaloy, Rene 77 (Cr/Co)
  - M-252, Rene-41 (V)
  - Monel R400 Vs Monel K500 (Ti)*
  - Alloy C-4 Vs Alloy S (Ti)
- Si PIN detector sensitivity for tramp elements (e.g., Cu, Sn, Pb)
  - Si PIN tramp element detection level: 0.05 - 0.1%
- SDD detector sensitivity for same tramp elements
  - Tramp element detection level: 0.001 - 0.05%

Do I need Light Elements?

SDD extends element range to Mg, Al, Si, P, S



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Will I Be Looking for These Alloy Groups?

Alloy Group	Potential Light Elements
Aluminum	Mg, Si
Titanium	Al
Copper	Al, Si, P
Steels	Al, Si, S
Zinc	Al
Magnesium	Mg

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Examples: Prevent Mix and/or Errors in Chemistry

- Ti BT5 (~5% Al in Ti - will mix with CP Ti)
- TI 6-4 (~6% Al - poor Ti chemistry, misses Al)
- Al 319, 380, 384 (Si ~6% - will mix with 6063 or 2024 Si 0.0)
- Al A356 (~5% Si – will mix with 6063)
- Al 4145 (~ 4% Cu, 9.3 - 10.7 Si - will mix with 2024 ~4% Cu)
- 5052 (Mg ~2.5% - may mix with 5086 Mg ~4%)
- CDA 642 (~7% Al ~2% Si – will mix with Elec Cu)
- CDA 99210 (~0.5% Si, ~0.8%P – misses Si, P)
- SS Nitronic 60 (~4% Si - poor Fe value, misses Si)
- SS 17-7 (~1% Al – will mix with 301)

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Dual Use can be Good Investment

SDD provides heavy and light element analysis in one analyzer*

* May eliminate need for OES and use of two analyzers and technologies

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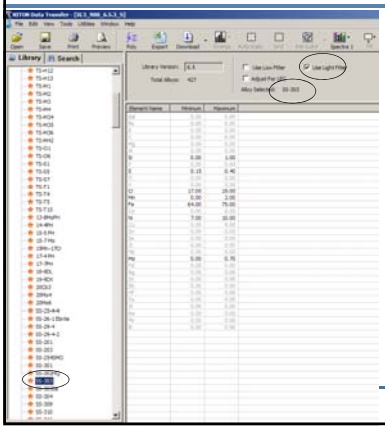
Smart Alloy Grade Library with Edit Capabilities



A computer program may be used to upload alloy libraries to the instrument or to download libraries from the analyzer…
or, latest analyzers have "on-board" edit capability

Abilities
- smart library
  - corrects for LEC
  - selects alloys for low source *(Ti, V, Cr)*
  - selects alloys for light source *(Mg, Al, Si, P, S)*
- rename alloys
- view chemical composition
- modify chemical composition
- add new alloys
- delete alloys
- create custom libraries
- print libraries

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Can I do "In Field" Software Upgrades?

- With most modern analyzers it is possible to upgrade via e-mail or Internet
- With improved software, your analyzer may perform better than new!

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Summary: Before you Buy!

Key things to consider about overall use, performance and alloy application:
- Life of source: isotope Vs x-ray tube
  - Routine alloys or difficult separations
- Speed of testing (productivity/profits)
- Light element/tramp element capability (SDD detector)
- Robustness of analyzer (sealed, hardened)
- Robustness of calibration and alloy grade library
  - FP or Empirical
  - If FP, is three consecutive element problem solved?
    - 15-3-3-3, Beta C, AlNiCo's, etc. (hundreds of alloys)
- Auto optimization of all test parameters, including tube current (on the fly)
- Ability to separate nearly twin (multiple close) alloys
- Software upgrades (cost)
- Support, expertise and quality of service
- Comparability of data (same factory calibrations)
- Bottom line: test it in the yard on your toughest samples!

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And Now…..

- Questions???

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