The Impact of Reference Material Issues on Metal and Ore Chemical Analysis Laboratories

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Introduction

Metals analysis laboratories rely heavily upon the use of various types of reference materials in the testing process. This presentation will explore laboratory issues related to availability of reference materials, pedigree of reference materials, and specifically development/use of in-house reference materials.

Reference Material Availability for Metals Analysis Laboratories

Solution CRMs are widely available from numerous sources. Most are accredited to ISO Guide 34 Compliance.

Solid CRMs such as widely used by metals analysis laboratories have limited availability. Many solid CRMs sold to and/or in use by metals laboratories were not developed by companies accredited for ISO Guide 34 Compliance.

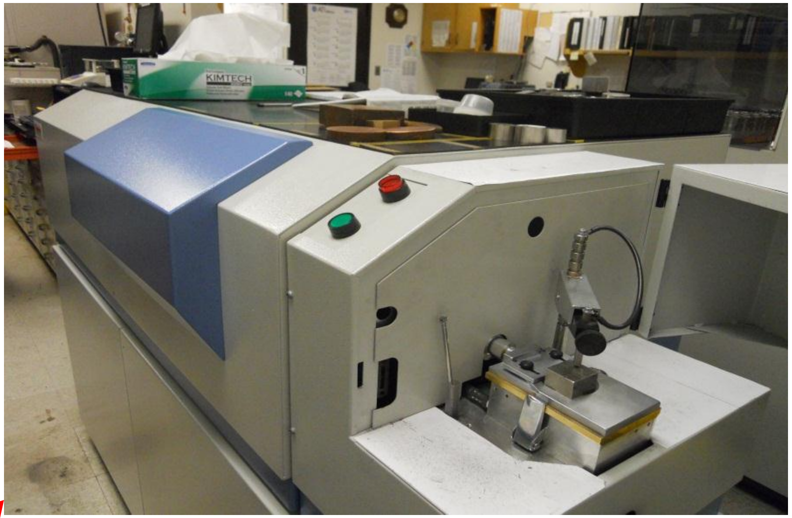
Who Uses Metal/Ore Reference Materials?

- Commodity base metal and alloy producer/user production and quality assurance laboratories
- Laboratories supporting the mining industry
- Service laboratories who support these industries
- Many of these laboratories have one or more accreditations. For materials testing laboratories, these may be ISO/IEC 17025 and/or Nadcap.

Typical Reference Materials Usage in the Metals Analysis Laboratory

- Instrument Calibration (most equipment is calibrated with solution or solid RMs)
- Instrument Drift Correction/Standardization (materials may not necessarily be RMs)
- Alloy Type Standardization (used for re-calibration of the sensitivity of the calibration model)
- Validation (validate a solid sampling method based on solid CRM calibration, validate a solution analysis method (including dissolution method), i.e. ICP-AES, ICP-MS, AA, etc.)

Metals Analysis Labs Routinely Rely Heavily on Solid Sampling Techniques



O, N, H, C, S Analyzers

Spark Atomic Emission Spectrometers

X-Ray Fluorescence Spectrometers

These techniques are absolutely essential to rapid and cost-effective process control/QA tests for many companies.

Other Techniques Employing Solid Sampling

A variety of other solid sampling methods are also used to analyze metals and alloys

- Laser Ablation-ICP-Mass Spec
- Spark- ICP-Mass Spec
- Glow Discharge Mass Spec
- Glow Discharge-Atomic Emission
- Solid Sampling Graphite Furnace Atomic Absorption

Solid Reference Material Availability

- *Availability of Solid Form* **Certified** *Reference Materials for Metals Laboratories is limited.*
- *With some exceptions Aluminum/Irons/Steels/Copper CRMs are widely available internationally.*
- *As Alloy systems become more complex/exotic the number of available reference materials (particularly* ***CRMs****) drops significantly.*

Rough Estimate of International Solid RMs by Commodity (Base Metal or Alloy)

Aluminum~1530

Iron and Steel ~1000

Copper ~750

Nickel ~240

Titanium ~60

Cobalt ~30

Nb, W, Ta, Pb, Mg, Zr, etc ~0 each

Estimate courtesy of Analytical Reference Materials International

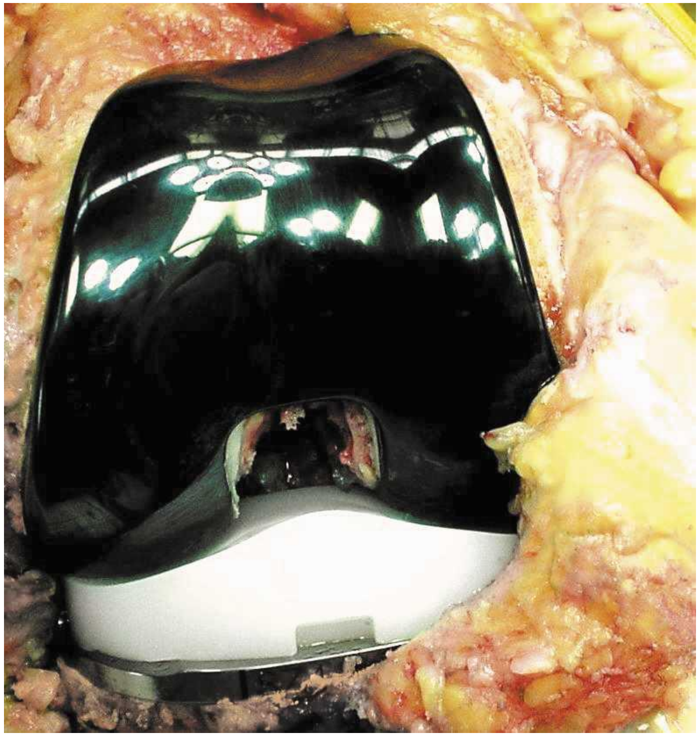
Let's Consider One Application of Metals To Which Everyone In This Room Can Relate. Think About The Variety of Reference Materials Used in Testing Just The Chemical Composition of the Metal Constituents.

http://www.atimetals.com/SiteCollectionDocuments/Interactive%20Demos/ATI%20Aerospace/index.aspx

Headline: The Washington Post 3/11/2014:

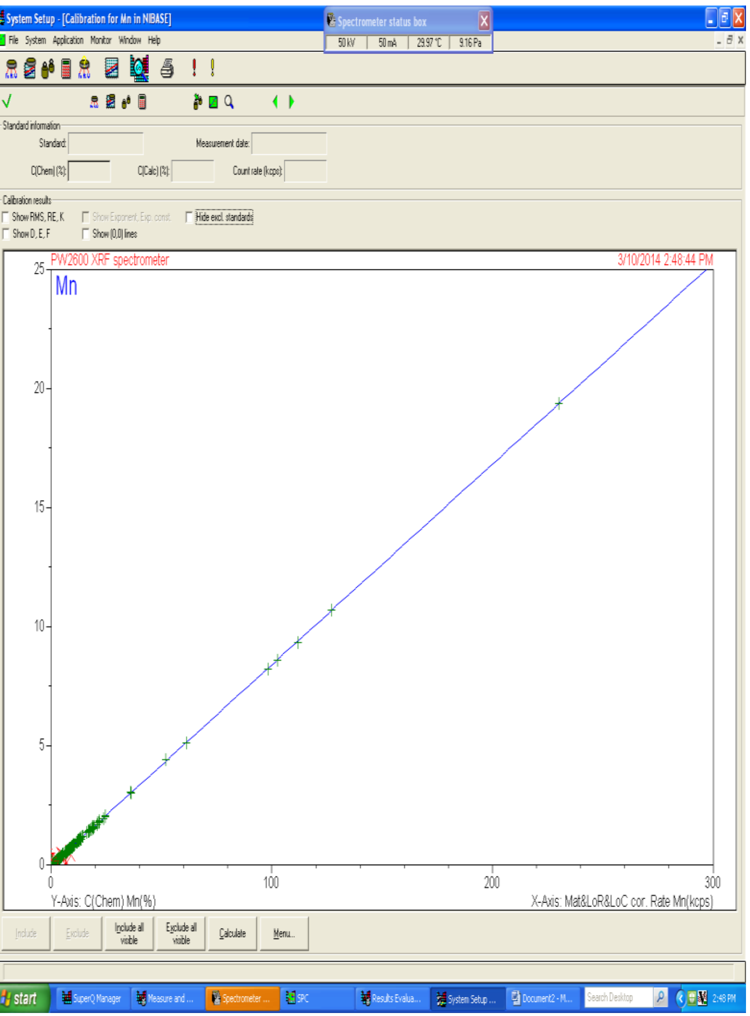
Study: 2% of Americans Have an Artificial Knee or Hip

6-4 Ti Alloy Hip Joints
(Zimmer)



Zr-2.5 Nb Alloy Femoral Knee Component (*in vivo*)
(Smith & Nephew)

Certified Reference Materials As the Sole Source of Calibration Materials for A Metals Lab



Fact: Commercial Solid CRM producers typically procure and certify off the shelf materials.

Implications:

- CRM sets may not have enough variation in elemental contents to facilitate calibration of range necessary. May need variation to calculate empirical inter-elemental interference corrections.
- CRMs may not be certified for all elements necessary for calibration.
- These CRMs are unlikely to contain elements “tweaked” as a result of a customer requirement.
- Production materials may not have measurable levels of elements necessary for calibration (i.e. trace elements).
- It is not commercially feasible for CRM producers to make CRMs for low volume alloys or proprietary materials.
- CRM producers may not be able to procure proprietary materials, yet RMs for proprietary materials are necessary.

Real Life Scenarios Where CRM Availability is an Issue

- 6Al-4V Titanium Alloy - Widely used in various applications including aerospace. Certified aluminum in few available CRMs typically ~6.3%.
- Hydrogen in Aluminum Alloys - Typical specification maximum <<1 mg/kg hydrogen. There are no available CRMs to calibrate/validate for this level of hydrogen.
- 6Al-7Nb Titanium Alloy - Biomedical implant material. Reference material availability issues.
- Trace elements in nickel, cobalt, and titanium alloys.
- Evaluation of digestion techniques

Commercially Available 6-4 Ti Solid RMs for Aluminum Calibration

RM ID	Al	
NIST 654B	6.36 %	
ARMI 175D	{6.38 %}	Provisional Certificate
ARMI 176C	{5.97 %}	Provisional Certificate
Brammer BS T-5A	6.33 %	
BCR 089	5.97 %	
MBH 101X Ti 3	6.14 %	
CT 6Al4V	6.39 %	

Range required to support typical production operation - **5.5 % to 7.0 % Al**

Hydrogen in Aluminum Alloys

- Typical Aerospace Specifications have Hydrogen Maximums of 0.10-0.15 mg/kg (PPM).
- No commercially available Hydrogen in Aluminum CRMs for calibration of inert gas fusion hydrogen analyzers.
- Hydrogen in Steel RMs typically contain > 6 mg/kg (PPM) hydrogen. Steel RMs typically have to be analyzed with different operating parameters and are a poor choice for validating analyses of < 0.5 mg/kg (PPM).

Aluminum alloys with hydrogen content above specification maximum could be subject to <u>embrittlement</u> potentially leading to <u>material failure</u>.

6Al-7Nb Titanium Alloy

- Biomedical implant alloy used for femoral components of hip prostheses.
- Only one commercial CRM for this alloy available.
- Contains niobium at 7%. Few niobium bearing RMs available for calibration of niobium.
- Critical end use!

Trace Element Reference Materials for Nickel, Cobalt, and Titanium Alloys

Nickel Alloys- Few RMs, most in chip form.

TRACE ELEMENT CONTROL

Element	Max Limit Percent	Max Limit ppm
Lead	0.0005	5
Bismuth	0.00005	0.5
Selenium	0.0003	3
Tellurium	0.00005	0.5
Thallium	0.0005	5

Certain materials may require additional 0.0050 % maximum specification for Sb, As, Cd, Ga, Ge, Au, In, Hg, K, Ag, Na, Th, Sn, U, Zn

Excerpts from SAE AMS2280 Rev B. <u>Trace Element Control Nickel Alloy Castings</u>, Sept. 2006. Available from SAE International.

Trace elements above spec limits can lead to ductility issues and <u>creep failures in service.</u>

Titanium Alloys - Few trace element RMs currently available.

Cobalt Alloys - No trace element RMs currently available.

Validation of Sample Preparation Methods

- Complex Alloys Are Typically Difficult to Dissolve due to inherent corrosion resistance of many alloys.

- ASTM MNL 25: A Manual for the Chemical Analysis of Metals by Thomas Dulski devotes an entire chapter to acid dissolution of various metals.

- Numerous References in MNL 25 to Loss of Volatile Elements During Conventional or Microwave Acid Digestion. This underscores the need for varied alloy reference materials to help validate prep methods.

What Is A Lab to Do When a Necessary Solid CRM is Unavailable?

- *Rely upon purchased RMs not necessarily developed using a ISO Guide 34 Compliant Process.*
- *Develop In-House Reference Materials Specific to the Laboratory's Need (**<u>including calibration!</u>**)*

Facts:

- *Many metals analysis laboratories must use non-Guide 34 Compliant RMs to get the job done.*
- *Most metals analysis laboratories do not produce and sell CRMs as part of their core business function.*
- *Becoming Guide 34 Compliant, Accredited is not economically feasible for most producers of in-house RMs.*
- *Use of in-house RMs can be a "rub" between laboratories and accreditors.*

- *Committee E01 is sensitive to the issues surrounding reference materials, testing needs, analytical quality requirements, and accreditation.*
- *For this reason Committee E01 is working on ASTM Standards to assist metals laboratories in validating methods of analysis and developing reference materials.*

- *ASTM E2857 Standard Guide For Validating Analytical Methods.*
- *ASTM E826 Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry*
- *ASTM WK30856 Standard Guide for Production, Testing and Value Assignment of In-House Reference Materials for Metals, Ores, and other Related Materials*

General Attributes of ASTM WK30856 Standard Guide for Production, Testing and Value Assignment of In-House Reference Materials for Metals, Ores, and other Related Materials

- *1) Guidance for uses of metal/ore in-house RMs*
- *2) Metal/Ore Specific Technical Guidance for Producing In-house RMs*

  (note: this sort of info not in ISO Guide 34)
- *3) Specific Guidance Relating to Value Assignment*
- *4) Guidance on Documentation Requirements*

When all is said and done…

- *The use of high quality reference materials, including in-house reference materials helps labs achieve world class results. PTP- the **P**roof is in **T**he **P**udding!*

II YOUR RESULTS

PTP			Chemical Cross Test Summary Inco 600- Kit 8-2									
			ANALYTICAL RESULTS				LAB STATISTICS					
LAB	ELEMENT	METHOD	No. 1	No. 2	No. 3	No. 4	Std Dev	k	Max	Min	Mean	h
158	Al	9	0.22	0.23	0.22	0.23	0.0058	1.34	0.23	0.22	0.23	-0.05
158	B	7	0.0063	0.0062	0.0063	0.0064	0.0001	0.52	0.0064	0.0062	0.0063	0.74
158	C	1	0.109	0.110	0.108	0.110	0.0010	0.60	0.110	0.108	0.109	0.40
158	Co	9	0.27	0.27	0.27	0.27	0.0000	0.00	0.27	0.27	0.27	0.08
158	Cr	9	16.37	16.37	16.35	16.36	0.0096	0.22	16.37	16.35	16.36	0.64
158	Cu	9	0.18	0.18	0.18	0.18	0.0000	0.00	0.18	0.18	0.18	0.39
158	Fe	9	8.88	8.89	8.87	8.88	0.0082	0.23	8.89	8.87	8.88	-0.26
158	Mn	9	0.229	0.229	0.228	0.229	0.0005	0.26	0.229	0.228	0.229	0.30
158	Mo	9	0.300	0.298	0.300	0.299	0.0010	0.27	0.300	0.298	0.299	0.01
158	Nb	9	0.073	0.072	0.072	0.073	0.0006	0.52	0.073	0.072	0.073	0.23
158	Ni	9	73.11	73.14	73.05	73.03	0.0512	0.35	73.14	73.03	73.08	1.21
158	P	9	0.007	0.007	0.007	0.007	0.0000	0.00	0.007	0.007	0.007	-0.21
158	S	1	0.0003	0.0003	0.0004	0.0002	0.0001	1.04	0.0004	0.0002	0.0003	-0.60
158	Si	9	0.30	0.30	0.30	0.31	0.0050	0.73	0.31	0.30	0.30	-0.40
158	Ta	9	0.014	0.010	0.011	0.009	0.0022	1.22	0.014	0.009	0.011	0.54
158	Ti	9	0.35	0.35	0.35	0.36	0.0050	1.19	0.36	0.35	0.35	0.15
158	V	9	0.018	0.017	0.017	0.018	0.0006	1.16	0.018	0.017	0.018	-0.49
158	W	9	0.024	0.026	0.024	0.025	0.0010	0.54	0.026	0.024	0.025	0.20

Data Coding		
	Class1	
	Class2	
	Class3	

k and h Statistic Coding			
Excellent		Substandard	
Good		Outlier	

Conclusions

- *There will always be a need for high quality RMs for metals analysis laboratories. These will likely include those originating from non-CRM producers.*
- *Laboratories, RM Producers, and Laboratory Accreditation Bodies must work together to insure that high quality RMs are available and used by laboratories testing metals.*