

NIST Role in the U.S. Measurement System for Industrial Commodities

Summary of Presentation

- **NIST Mission**
- **Program Coordinator**
- **Standard Reference Materials® Process**
- **Capacity for CRM Production**
- **NIST Quality System**
- **Traceability – Fact & Fiction**
- **Degrees of Equivalence of CRMs**
- **Calibration, Validation, Control**
- **Where do we go from here?**

NIST Mission

Advance measurement science –

- Develop new measurement technology

- Develop tools to validate measurement processes

Advance measurement standards –

- Participate in standards development committees

- Collaboration with industry labs and industry customers

- Collaborate with private sector reference materials producers

Promote equitable standards –

- Represent U.S. on international committees

- Support U.S. DoC International Trade Admin.

- Understand and inform accreditation and legislative processes

Program Coordinator for Industrial Commodities

- **Representation on Standards Committees**
- **Liaison with Metals Producers and Mining Companies**
- **Liaison with Commercial CRM Producers**
- **Liaison with Industry Consumers (“Primes”)**
- **Developing test methods**
- **Prioritizing SRM needs and Developing SRMs**
- **Technical customer support for SRMs**
- **Monitor other National Metrology Institutes**
- **Monitor regulations and consult with regulating bodies**

Industrial Commodities

Ferrous Metals	Nonferrous Metals	Cement
Minerals	Mining Byproducts	Ores
Glass	Ceramics	Paint
Lubricants	Organometallic Compounds	

SRM Categories of Interest Today

101 Ferrous Metals	FY13 Sales
<i>145 SRMs in stock, 8 out of stock</i>	3508
102 Nonferrous Metals	
<i>126 SRMs in stock, 3 out of stock</i>	790
111 Geological Materials and Ores	
<i>47 SRMs and RMs in stock, 2 out of stock</i>	2264
112 Ceramics and Glasses	
<i>23 SRMs and RMs in stock, 2 out of stock</i>	589

Support of Metals and Mining SRMs

- Provide technical support for standards and methods
 - Membership in ASTM E01 & F40 and IEC TC111
 - Co-author standards
 - Support validation programs
- Help industry identify and prioritize needs for CRMs and RMs
 - Meet with CRM producers at ASTM meetings and their own venues
 - Solicit written input to the NIST process
- Focus on key material compositions by industry sector
 - Provide a small number of top quality SRMs
 - Provide technical support to broaden the utility of all CRMs
 - Educate users of CRMs and their clients
- Support private sector CRM businesses; don't replace them
 - NIST couldn't replace them, if we tried

SRM Development Process

1. Determine need for a CRM and a plan of action.
 - a. **Get supporting evidence from stakeholders**
 - **Technical issues and Economic impact**
2. Submit proposal to management
3. Obtain and process material
4. Technical & Statistical Plans
- 5. Enlist collaborators**
6. Accomplish measurements
7. Statistical & Technical evaluation
8. Completion and Approval phase
9. Pricing and Catalog processes

Mean time to process completion: ~ 4 years

Capacity of CRM Producers Worldwide

How many experts are running alloy CRM development projects worldwide?

We don't know, but we estimate between 10 and 20.

How many new alloy CRMs are issued each year worldwide?

Perhaps 20 to 30.

How many renewal/reissue/upgraded CRMs are issued each year worldwide?

Perhaps 50.

How long does it take to issue a new or renewal alloy CRM?

Between 1.5 and 5 years.

The Framework of the Quality System for NIST's measurement services: calibrations, reference materials, and special tests

- NIST is the National metrology institute (NMI) for the United States
- NIST is authorized (15 US code 271) with the following functions:
 - The custody, maintenance, and development of the national standards of measurement
 - The provision of means and methods for making measurements consistent with those standards
 - The comparison of standards used in scientific investigations, engineering, manufacturing, commerce, and educational institutions



The Quality System for NIST's measurement services

- Formally established in 2003, based on the criteria of requirements found in ISO/IEC 17025 and ISO guide 34
- The scope includes NIST's Standard Reference Materials®
 - Hardness, Optical properties, Biological materials, Food, Fuel, Inorganic Solutions, Organic solutions, Sediments, Soils, Ores, Water, Ceramics, Polymers, Cement, Metals, and Alloys
- The scope also includes NIST's calibration services
 - Dimensional, Electrical, Ionizing Radiation, Mechanical, Optical Radiation, Thermodynamic, Time and Frequency capabilities



The Quality System for NIST's measurement services

In October 1999, the directors of the NMIs of 38 Member States of the Metre Convention signed a Mutual Recognition Arrangement (MRA) for national measurement standards and for calibration and measurement certificates issued by national metrology institutes.

The CIPM MRA has now been signed by the representatives of 93 institutes – from 52 Member States, 37 Associates of the CGPM, and 4 international organizations – and covers a further 151 institutes designated by the signatory bodies.

Reconnaissance mutuelle
des étalons nationaux de mesure
et des certificats d'étalonnage et de mesurage
émis par les laboratoires nationaux de métrologie

Paris, le 14 octobre 1999



Mutual recognition
of national measurement standards
and of calibration and measurement certificates
issued by national metrology institutes

Paris, 14 October 1999

Comité international des poids et mesures

Bureau
international
des poids
et mesures

Organisation
Intergouvernementale
de la Convention
du Mètre

Technical basis and Confidence in Measurements: CIPM MRA

International comparisons of measurements,
known as key comparisons;
supplementary international comparisons of measurements;
quality systems;
and demonstrations of competence by NMIs.

Outcome

statements of the calibration and measurement capabilities (CMCs) of each NMI
in a database publicly available on the Web.

<http://kcdb.bipm.org>



Mutual Recognition Arrangement

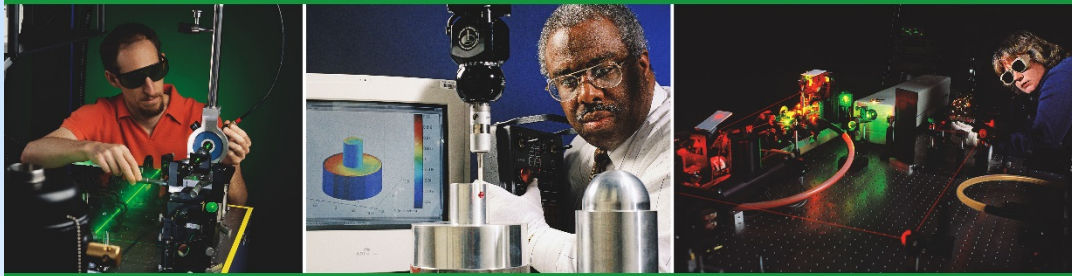
- **to establish the *degree of equivalence* of national measurement standards maintained by NMIs;**
- **to provide for the *mutual recognition* of calibration and measurement certificates issued by NMIs;**
 - **thereby to provide governments and other parties with a *secure technical foundation for wider agreements related to international trade, commerce and regulatory affairs.***
- **Intended to enable the recognition and acceptance of measurement capabilities and their results across borders**

Motivators for the Quality Management System at NIST



- Commitment to demonstrate quality via the CIPM MRA (maintains international acceptance of our measurement capabilities)
- Transparency to our customers and stakeholders (demonstration of competence, enabling customer satisfaction)
- Opportunities for process improvements

NIST QUALITY SYSTEM FOR MEASUREMENT SERVICES



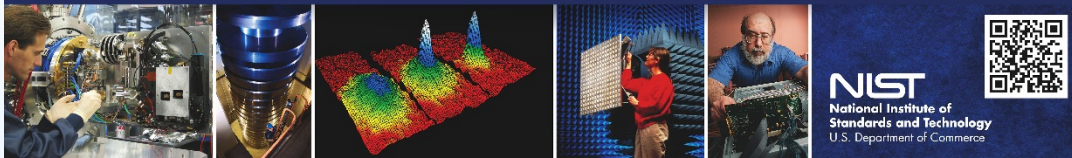
Established in 2003, the Quality System for Measurement Services controls the way we provide Calibrations, Special Tests, and Reference Materials across 17 technical divisions.

NIST's Quality System for Measurement Services is

- ▶ recognized worldwide as compliant with the International Organization for Standardization and the International Electrotechnical Commission (ISO/IEC) 17025 standard and ISO Guide 34
- ▶ assessed in each measurement capability area on a continual schedule
- ▶ accepted internationally, with measurements performed at NIST acknowledged by CIPM MRA, thus benefitting our customers' measurement capabilities and thereby effectively reducing potential barriers to trade.

Through NIST's continuous improvement in development and delivery of services, our customers have access to some of the lowest measurement uncertainties available and a dependable way to establish traceability to the International System of Units.

In 2013, over 55,000 calibrations and reference materials were delivered to NIST customers



Measurement Quality



Traceability

Method
Validation

Uncertainty
Assessment

Definition of Metrological Traceability

NIST adopts for its own use and recommends for use by others the definition of traceability provided in the most recent version of the *International Vocabulary of Basic and General Terms in Metrology (ISO VIM)*:

2.41 metrological traceability: property of a measurement result whereby the result can be related to a stated reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty

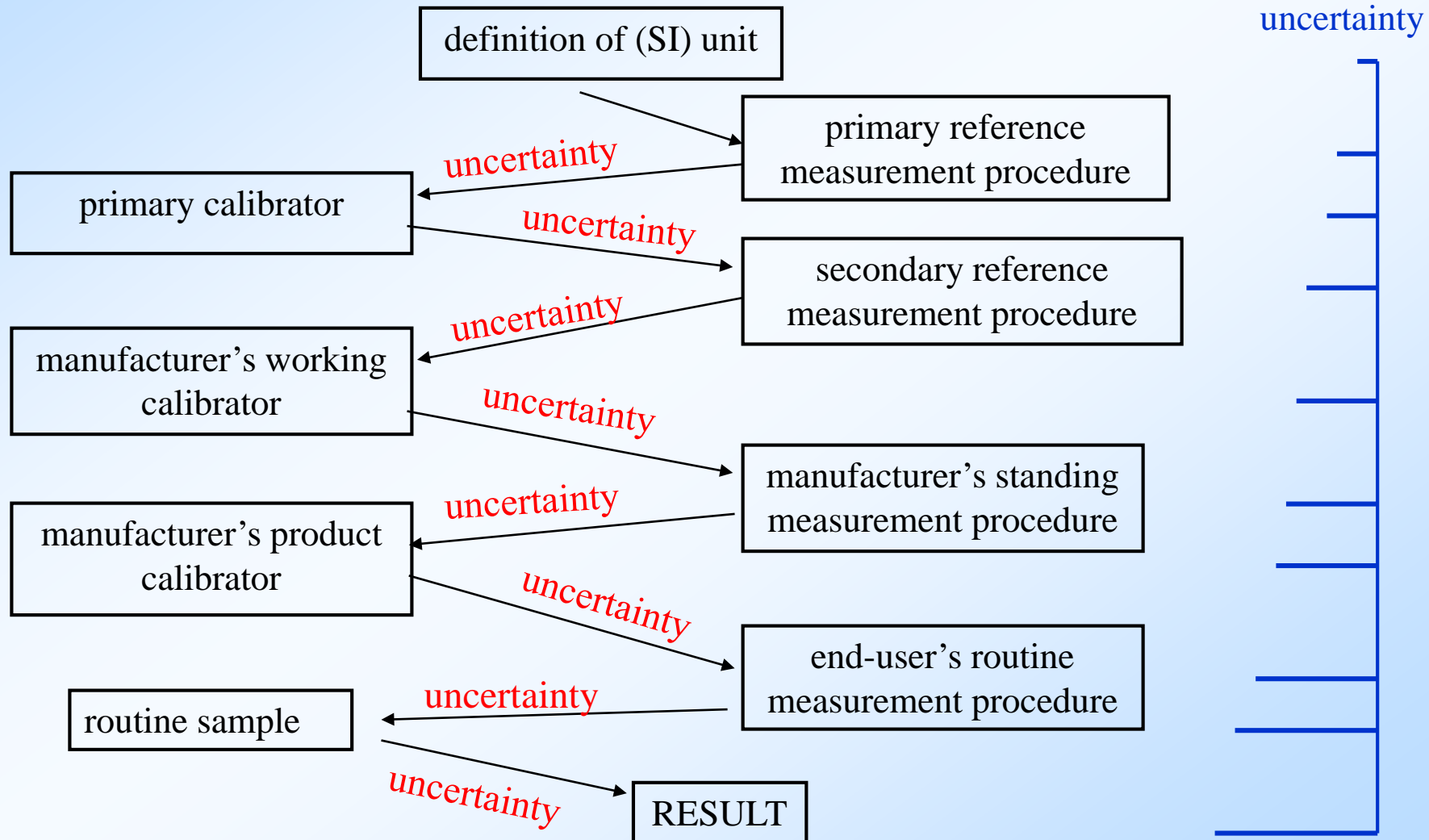
The Fine Print

1. ‘**reference**’ can be a definition of a measurement unit through its practical realization, or a measurement procedure including the measurement unit for a **non-ordinal quantity**, or a measurement standard.
2. Metrological traceability requires an established calibration hierarchy.
3. Specification of the stated reference **must include the time** at which this reference was used, along with any other relevant metrological information about the reference, such as when the first calibration in the calibration hierarchy was performed.
4. For measurements with more than one input quantity in the measurement model, **each of the input quantities should itself be metrologically traceable** and the calibration hierarchy involved may form a branched structure or a network. The **effort** involved in establishing metrological traceability for each input quantity should be **commensurate with its relative contribution** to the measurement result.
5. Metrological traceability **by itself does not ensure** adequate measurement uncertainty or **absence of mistakes**.
6. A **comparison between two measurement standards** may be viewed as a calibration if the comparison is used to check and, if necessary, correct the quantity value and measurement uncertainty attributed to one of the measurement standards.
7. The ILAC considers the elements for confirming metrological traceability to be an unbroken metrological traceability chain to an international measurement standard or a national measurement standard, a documented measurement uncertainty, a documented measurement procedure, accredited technical competence, metrological traceability to the SI, and calibration intervals (see ILAC P-10:2002).
8. The abbreviated term “traceability” is sometimes used for ‘metrological traceability’ as well as for other concepts, such as ‘sample traceability’ or ‘document traceability’ or ‘instrument traceability’, where the history (‘trace’) of an item is meant. Therefore, the **full term is preferred**.

Definition of Metrological Traceability (cont.)

- Four key elements
 - results of a measurement or value of a standard
 - related to stated references
 - national or international standards, intrinsic or derived standards, consensus standards, etc.
 - ultimate reference should be to the primary standards for the realization of the SI units
 - an unbroken chain of calibrations
 - each contributing uncertainties
 - based on sound scientific evidence, at stated points in time, etc.

Metrological Traceability Chains



Support for a Claim of Traceability

- A clearly defined particular quantity that has been measured
- A complete description of the measurement system or working standard used to perform the measurement
- A stated measurement result or value, with a documented uncertainty
- A complete specification of the stated reference at the time the measurement system or working standard was compared to it
- An internal measurement assurance program for establishing the status of the
 - measurement system or working standard at all times pertinent to the claim of traceability
 - stated reference at the time that the measurement system or working standard was compared to it.

Responsibilities for Claims Involving NIST Measurements and Standards

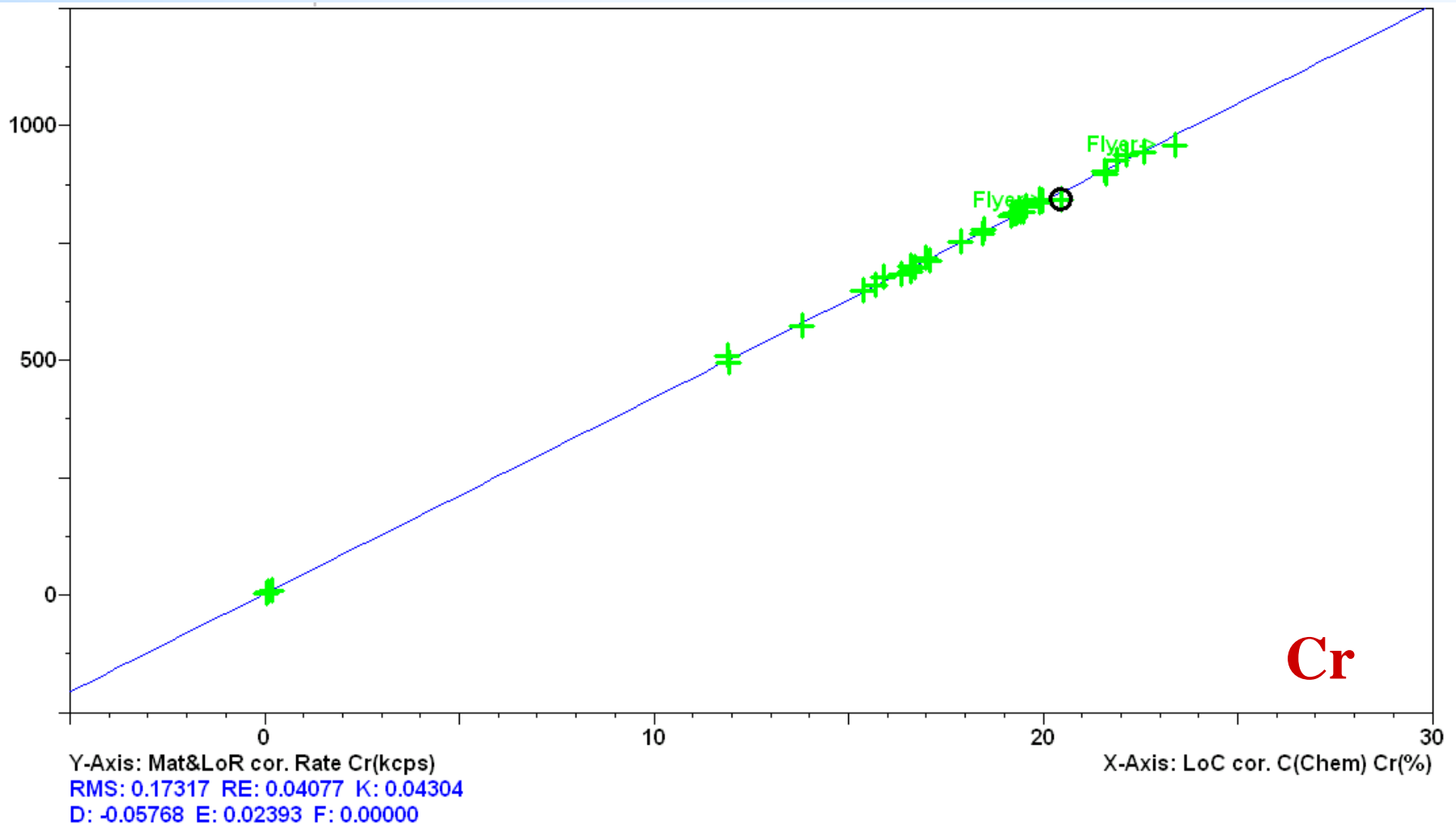
- *Service providers* must furnish details on how their claim of traceability to NIST is achieved.
- *Service users* must assess the validity of such claims and the adequacy of the supporting information for their specific purpose.

CRMs as Calibrants

- Trustworthy values, but large relative uncertainties.
- Provide traceability to the SI, but only if CRM uncertainty is in uncertainty budget.
 - Easy to understand if calibrants made from one CRM solution.
 - Difficult if a set of CRMs is used, e.g. disk alloys.
- Primary Substance RMs provide direct traceability to the mole, if both assay and stoichiometry are assured.
 - Experts assign 0.1 % relative uncertainty to assays.
 - Applies to creation of solutions both liquid and borate glass.
 - NMI and commercial solutions take advantage of this.

CRMs as Calibrants

A set of CRMs/RMs from a variety of sources used to calibrate WDXRF for a variety of steel alloys:



Estimating Degrees of Equivalence of CRMs

Concepts:

If CRMs from over 50 years are equivalent to recent CRMs, then ISO Guide 34 requirements on users must be relaxed because we've known what we're doing all along.

Provide process and tools for anyone to demonstrate equivalence within a set of CRMs.

NIST project design:

Use WDXRF on a large set of ferrous alloys to compare SRMs certified over the past half century.

Publish comparisons and 'how-to' for commercial CRM producers and laboratories.

How Much Validation?

Where there is **long practice of the successful use** of a particular analytical technique (such as ICPOES or acid digestion methods) across a range of analytes and matrices, **validation checks justifiably take the form of relatively light precautionary tests.**

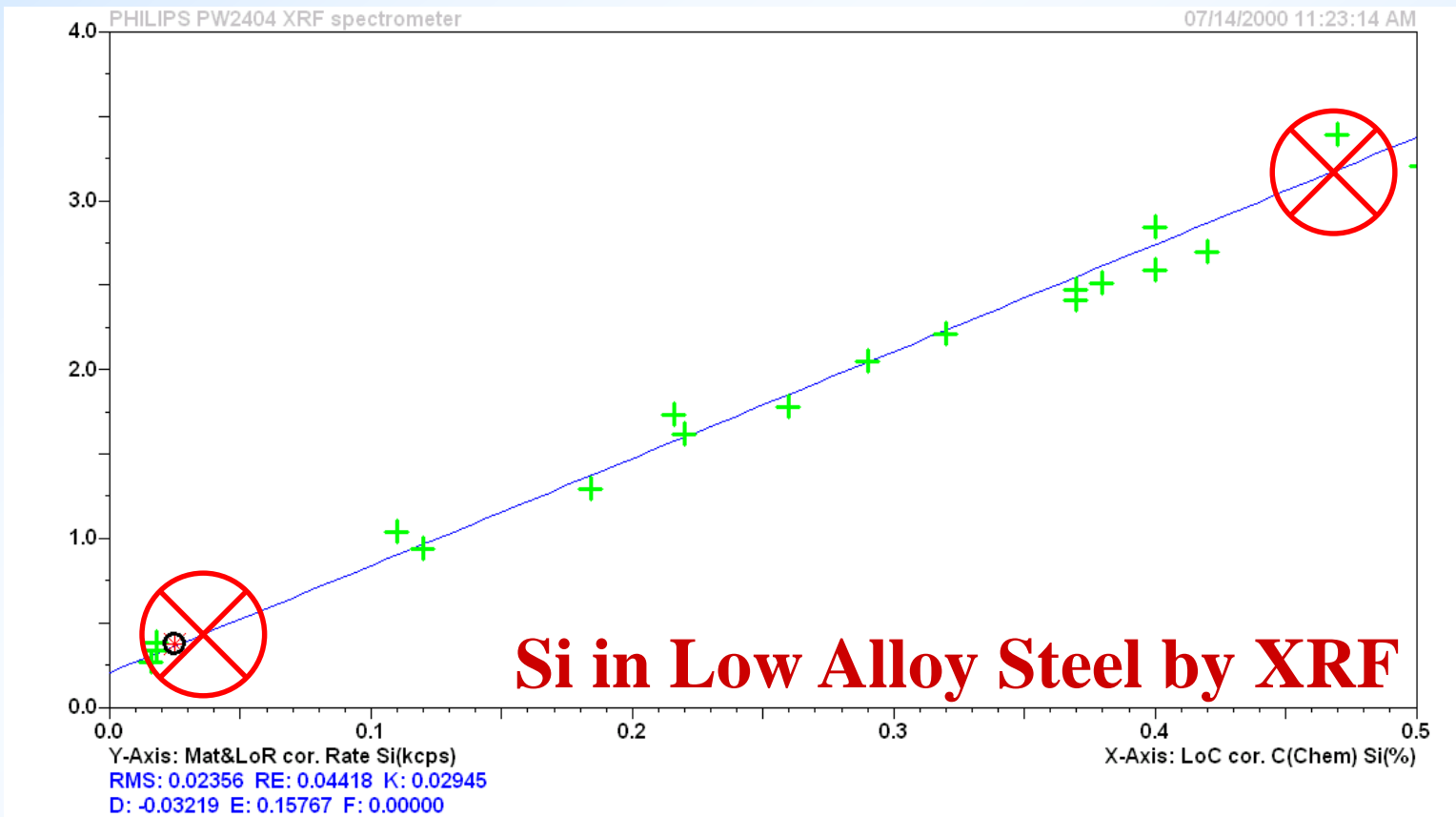
Conversely, **where experience is slight**, the validation study must **provide strong evidence** that the assumptions made are appropriate in the particular cases under study. It will generally be necessary to study the full range of circumstances in detail.

It follows that the extent of validation studies required in a given instance will depend, in part, on the accumulated experience of the analytical technique used.

Processes Under Statistical Control

After initial validation, what evidence is necessary to demonstrate that a method remains valid?

A group of experts from all parties could prepare a list of answers to this question.



Where CRMs are not available...

Use may be made of any material sufficiently well characterized for the purpose, bearing in mind that...significant bias on any material remains a cause for investigation.

Examples of reference materials include:

- materials characterized by a reference material producer, but whose values have no uncertainty statement or are otherwise qualified;
- materials characterized by a manufacturer of the material;
- materials characterized in the laboratory for use as reference materials;
- materials subjected to a restricted round-robin exercise; or
- materials distributed in a proficiency test.

The traceability of these materials may be questionable, but it is far better to use them than to conduct no assessment for bias at all. The materials can be used in much the same way as CRMs, *though with no stated uncertainty any significance test relies wholly on the observable precision of results.*

- Paraphrased from IUPAC document with emphasis added

PTP Samples as RMs

Proficiency test assigned values are generally chosen to provide a minimally biased estimate, so **a test for significant bias against such a material is a sensible practice.**

What must you know?

Assigned value \pm uncertainty with definition.

How to sample from the provided quantity.

How long the material is stable.

Note: 1) **The uncertainty estimation process need not be exhaustive.**
2) **Traceability of values is unknown.**

NIST can help by providing procedures to calculate values and uncertainties and to estimate minimum samples quantities.

Contact Information

John R. Sieber

National Institute of Standards and Technology

100 Bureau Drive, Stop 8391

Gaithersburg, MD 20899

301-975-3920

john.sieber@nist.gov

Sally S. Bruce

National Institute of Standards and Technology

100 Bureau Drive, Stop 2100

Gaithersburg, MD 20899

301-975-2323

sally.bruce@nist.gov

Robert L. Watters, Jr.

National Institute of Standards and Technology

100 Bureau Drive, Stop 2300

Gaithersburg, MD 20899

301-975-4122

robert.watters@nist.gov

Discussion Issues and Planning

1. How, when, and where can we work together?
 - a. What “primes” meetings should CRM producers attend and why?
 - b. Can more “primes” participate in E01?
2. Does everyone trust E01 to get it right?
3. Which other National Metrology Institutes supply useful CRMs?
4. How can we collaborate to get more involvement in development of CRMs and test methods?
5. How can we educate everyone in the supply chain: producers, customers, assessors, CRM producers, and labs?
6. What guidance and technical assistance do private CRM producers need to improve CRMs?
7. Are there issues with traceability statements in COAs?
8. Which government agencies impose requirements for traceability and validation, and can we contact them?
9. Does lab self-linking to SI cause issues?
10. Are in-house RMs indispensable, why or why not?
11. Are there issues with in-house RMs that can be improved by E01 and/or NIST?
12. Should section 4.1.3 on Type III calibrations of Guide 32 be changed?
13. Are current accreditation processes fostering continual improvement, why or why not?
14. What are the key areas of testing that are not sufficiently well covered by documentary standards?
15. What are the key areas of testing that are not sufficiently well covered by proficiency testing?

Types of Calibrations: ISO Guide 32

Calibration in analytical chemistry and use of certified reference materials

- Type I
 - Defined on the basis of the laws governing the physical and chemical parameters involved, using measurements taken during the analysis, e.g. gravimetric, titrimetric, etc.
- Type II
 - Compares the content of the sample to a set of calibration samples of known content, using a **detection system for which the response (ideally linear) is recognized** in the relevant working area (without necessarily being calculable by theory), e.g. calibrated ICP-OES using spectrometric solutions.
- Type III
 - Compares the sample to a **set of calibration samples**, using a **detection system which is sensitive** not only to the content of elements to be analyzed, but also **to differences of matrix** (of any type whatsoever).
“ to make up a set of **CRMs** suitable for each type of sample previously identified,”

Degrees of Equivalence of NIST SRMs

Two ways NIST establishes equivalence with other NMIs:

1. Participate in CCQM Key Comparison for a similar material
 - CCQM K33 Cr, Ni, Mn, Mo in low alloy steel (2004)
 - CCQM K42 Constituents of an aluminum alloy (2005)
 - CCQM K88 Lead in Lead-Free Solder (2012)
2. Use CRMs from other sources in our calibrations or as quality assurance materials (validation).

Comparisons among and within NMIs, are used to establish that NMI-developed CRMs intended for the same purpose are fit for purpose.