X61 - Standards and Reference Materials for Microanalysis

Baltimore, MD – Sunday August 5th, 2018

Edited by FIGMAS
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Pre-meeting congress X61 - Standards and Reference Materials for Microanalysis

Contents

Program detail ................................................................................................................................................. 3
Welcome message .............................................................................................................................................. 5

Standard-based and Standard-less Best Practices
Nicholas W. M. Ritchie, National Institute of Standards and Technology ...................................................... 6
Philippe T. Pinard, Oxford Instruments ........................................................................................................... 8
Stephen M. Seddio, Thermo Fisher Scientific ................................................................................................. 10

Standard Maintenance and Availability
Cathy Johnson, Mager Scientific ..................................................................................................................... 12
Timothy R. Rose, Smithsonian Institution - National Museum for Natural History ..................................... 14
Eugene E. Rodek, SPI supplies ...................................................................................................................... 16

Sourcing and Creating Future Standard Materials
Stephen Wilson, U.S. Geological Survey ......................................................................................................... 18
William O. Nachlas, Syracuse University ...................................................................................................... 20

And More! (Posters)
Julien M. Allaz, Owen K. Neill, and Anette von der Handt, FIGMAS ............................................................ 22
John Fournelle, University of Wisconsin, Madison ......................................................................................... 24
Edward P. Vicenzi, Smithsonian Institution - National Museum for Natural History ................................. 26
Donald Windover, National Institute of Standards and Technology ............................................................. 28

Creating & Reviewing Standard and Reference Materials in the Web-Database ................................. 30
1 BSE image - Zoned Mantle Pyroxene (Courtesy Arizona State Univ.)
2 Quantitative WDS Map - Martian Meteorite (Courtesy Univ. of New Mexico)
3 xCLent CL Ultra-low Concentration of Ti in Quartz (Geothermometry)
4 Monazite Age Map (Geochronology)
5 High Spatial Resolution 7 kV WDS C Map of Submicron Carbides in Steel
6 SXES Chemical State Map of Boron - FeB vs. FeB with a Peak Shift of ~ 1 eV
7 High Resolution Imaging at Very Low kV (2kV, 200,000X)

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Program detail

8:30 - 9:00  
*Breakfast, welcome message, and introduction*

9:00 - 9:30  
**Nicholas W. M. Ritchie, Dale E. Newbury, and Michael Mengason:** “*Complex Standards with NIST DTSA-II*”

9:30 - 10:00  
**Philippe T. Pinard, Alan Protheroe, James Holland, Simon Burgess, and Peter Statham:** “*The Role of Standards for Standardless Quantitative X-ray Microanalysis with Energy Dispersive Spectrometers*”

10:00 - 10:30  
**Stephen M. Seddio:** “*How to Not Do Poor Standards-based EDS Quantitative X-ray Microanalysis: A WDS Perspective*”

10:30 - 11:00  
*Discussion & coffee break*

11:00 - 11:30  
**Cathy Johnson** and Dalia Yablon: “*Examining the Effect of Sample Preparation on Analysis Data*”

11:30 - 12:00  
**Timothy R. Rose:** “*Return to the Collections: a Preliminary Search for New Reference Materials*”

12:00 - 12:30  
*Discussion*

12:30 - 13:00  
*Lunch*

13:00 - 13:30  
**Eugene E. Rodek:** “*The Use of Commercial MicroAnalysis Standards for WDS/EDS Techniques*”

13:30 - 14:00  
**Stephen Wilson:** “*USGS Microanalytical Reference Materials (MRMs) Development*”

14:00 - 14:30  

14:30 - 15:00  
*Discussion*

15:00 - 16:30  
*Posters and additional contributions*

**Julien M. Allaz, Owen K. Neill, Anette von der Handt:** “*Focused Interest Group on Microanalytical Standards (FIGMAS): Assessing the Quality, Availability and Need for Standards in the Microanalytical Community*”

**John Fournelle:** “*Something Old, Something New: A Look at some EPMA Reference Materials*”

**Edward P. Vicenzi,** Thomas Lam: “*Preliminary Trace Element Analysis of Vitreous Standards by SEM-based Micro-X-ray Fluorescence Spectrometry*”

**Donald Windover:** “*The Process and Protocols of Making New Standard Reference Materials at NIST*”

16:30 - 17:00  
*Final discussion and wrap up*
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The International Association of Geoanalysts has developed the G-Probe Proficiency Testing Scheme, to help microbeam labs (e.g., LA-ICP-MS and EPMA) that routinely analyse geological materials to assess their performance. Participation also provides an opportunity to contribute to the development of a range of new certified microbeam reference materials.

- G-Probe is an essential part of a microbeam laboratory’s quality assurance programme
- Accreditation agencies require routine participation in such programmes
- Increasingly, customers expect evidence of the quality of measurement results that PT schemes provide

For more details, please see Steve Wilson at this meeting (swilson@usgs.gov), www.geoanalyst.org or register your interest with Jenny Cook (IAG Secretary – jmc@bgs.ac.uk)

Mineral reference materials available through IAGeo Limited (lageo.com) in collaboration with Harvard University. They include zircon 91500 (illustrated) and some reference minerals specifically targeted at light element determinations by microanalytical techniques.
Welcome to the Pre-Meeting Congress X61!

On behalf of the Focused Interest Group on Microanalytical Standard (FIGMAS) committee, we warmly welcome you to the first pre-meeting congress on standards and reference materials. Every microanalyst, whether it is from the world of electron microscopy (e.g., EDS, WDS, µ-XRF), mass spectrometry (e.g., laser-ablation, SIMS) or another microanalytical technique, is in need of the best standards and reference materials available. However, questions regularly arise on the quality and availability of such materials. As you probably know – and if you don’t, you are at the right place – microanalytical reference materials must meet certain criteria if they are to be used to produce accurate data. Appropriate materials should sustain high vacuum levels, show resistance to beam damage (for EDS/WDS work), and be easily prepared. The material should be homogeneous at the micron-scale with an accurate and reproducible reference composition, ideally certified using multiple analytical techniques (e.g., wet chemistry, mass spectrometry, X-ray analysis at micron scale).

Throughout this pre-meeting congress, we will have the opportunity to discuss the production, verification, maintenance, and practical use of microanalytical standards in detail. With the help of several invited speakers, we will examine best practices for standard-based analysis, and also the effectiveness and underlying theory of standard-less analysis procedures. Next, we will discuss the availability of standards in our community, avenues for obtaining new standard materials, and the preparation and maintenance of standards in analytical labs. The meeting will finish by focusing on the standard materials of tomorrow, how to obtain or synthesize new materials, how to evaluate new materials for homogeneity and accurate reference compositions, as well how to distribute them to the wider community. There should be ample time throughout this PMC to discuss all of these topics, and we hope you will also take time to visit the few additional posters presenting other aspects of existing standard materials. Please visit with our sponsors, to whom we are extremely grateful for their participation.

Thank you all for attending this meeting. We wish you a not-so-standard, yet pleasant journey!

The 2017-2018 FIGMAS committee
Julien M. Allaz, leader
Anette von der Handt, leader-elect
Owen K. Neill, secretary-treasurer

1. ETH Zürich, Zürich (Switzerland)
2. University of Minnesota, Minneapolis (MN, USA)
3. University of Michigan, Ann Arbor (MI, USA)
Complex Standards with NIST DTSA-II

Nicholas W. M. Ritchie¹, Dale E. Newbury¹, Michael Mengason¹

¹ National Institute of Standards and Technology, Materials Measurement Science Division, Gaithersburg, MD 20899, USA

Standards which are similar in composition to the unknown can reduce the uncertainty in the matrix correction algorithm by minimizing errors due to inaccurate models and input parameters. It is often claimed that reducing the magnitude of the matrix correction (a correction factor closer to unity) will produce more accurate measurements. While generally good advice, this is not strictly true. Really, the improvement in accuracy behind complex standards does not depend upon the magnitude of the matrix correction but upon correlated uncertainties in the standard and unknown terms in the matrix correction that diminishes the sensitivity due to poor models and poorly known parameters [1]. It is possible to have small correction that results from a balancing in magnitude of factors that does not result in a reduction in uncertainty.

The correlations can compensate for both factors that are explicitly considered in the model and factors which are beyond the model. Examples of factors that are beyond the model are chemical and solid-state effects. An example of recent interest is the nickel silicide system measured using the Ni L-lines [2]. The four phases they studied (Ni₅Si₂, Ni₂Si, Ni₃Si and NiSi) vary from 83.9 wt% Ni to 67.6 wt% Ni. In this system they demonstrate that the assumptions that 1) the material mass absorption coefficient can be computed as a linear sum of the elemental mass absorption coefficient and 2) the fluorescence yield is independent of composition fail. These effects could be considered as beyond the standard model of matrix correction as implemented in the traditional ZAF and φ(ρz)-models. While it is, in theory, possible to develop more sophisticated models that take chemistry into account when computing material mass absorption coefficients, it is far simpler to use a standard with similar chemistry.

The use of similar standards is well established in the WDS community. However, it is less well established in the EDS community. In part, this may be due to the complexity of using standards in which the characteristic peaks are not necessarily well separated due to the poorer resolution of the detector. When two or more peaks in the standard interfere, it is necessary to deconvolve all the peaks to extract the intensity associated with any one of them. While this deconvolution can be performed with modeled line shapes, it is most accurately done with spectra collected from pure element or simple compounds that more accurately reflect the natural shape of the characteristic line family. This means that in addition to the standard and unknown spectra, it is often necessary to introduce a third class of spectra into the quantification process called “peak shape reference spectra”. Peak shape reference spectra serve to transfer intensity information measured from the standard to the unknown. Consider a simple measurement of a single characteristic line family in which the standard has $I_{std}$ intensity and the unknown has $I_{unk}$. We wish to know $k = I_{unk} / I_{std}$ but because of interferences it is not possible to fit the standard spectrum directly to the unknown. Instead a third spectrum with intensity $I_{ref}$ is fit to both the standard and the unknown producing two measurements $k_{unk} = I_{unk} / I_{ref}$ and $k_{std} = I_{std} / I_{ref}$. The desired k-ratio between the unknown and standard equals $k = (I_{unk} / I_{ref}) / (I_{std} / I_{ref}) = k_{unk} / k_{std}$. It is worth noting that in contrast to WDS, the natural quantity in EDS measurements is the k-ratio not the peak intensity. The k-ratio comes directly from fitting one spectrum to another. Determining the intensity involves extra effort.
The need for references can be confusing and does make using complex standards more challenging than simple standards. However, NIST DTSA-II has tools to help make using complex standards almost as efficient as using simple standards. The basic quantification process in DTSA-II proceeds by first specifying standards. The standards are analyzed by the software to determine what references are required and then the software requests the necessary reference spectra. If these spectra are not available, the analyst may have to return the instrument to collect them. This whole process can be tedious. A recent version of NIST DTSA-II introduced a mechanism to simplify the process by permanently associating the reference spectra with the complex standard spectrum in a file called a “standard bundle [3].” A standard bundle can be constructed once and reused many times. It shortcuts the quantification process by automatically populating the reference table. It is easy to keep multiple standard bundles for each element each associated with a different standard material.

We will discuss quantification using complex standards in EDS and demonstrate how NIST DTSA-II facilitates the process.

References:

Figure 1. Barium titanate can be used as standard for both Ti and Ba despite the interference between the Ba L-lines and the Ti K-lines by using pure Ti and barium carbonate as references. This process is simplified in NIST DTSA-II through “standard bundles” which in this case would combine the barium titanate standard with the Ti and barium carbonate reference spectra.
The Role of Standards for Standardless Quantitative X-ray Microanalysis with Energy Dispersive Spectrometers

Philippe T. Pinard¹, Alan Protheroe¹, James Holland¹, Simon Burgess¹, Peter Statham¹

¹ Oxford Instruments NanoAnalysis, High Wycombe, United Kingdom

In its simplest form, quantitative X-ray microanalysis is the conversion of X-ray intensities, generated by an electron beam and detected by a wavelength dispersive or energy dispersive (ED) spectrometer, to an elemental composition. Since the pioneering work of Castaing, different approaches have been developed to achieve this conversion by essentially combining empirical and theoretical methods. For example, k-ratios relative to standards and calibration curves are empirical methods to address the inaccuracy in fundamental physical parameters that prevents the direct calculation of X-ray intensities. Monte Carlo simulations and φ(ρz) models are theoretical methods to model and predict X-ray generation and absorption. The combination of these empirical and theoretical methods to quantify unknown samples has enabled electron probe microanalysis to address a wide range of problems.

In this regard, standardless quantification is like standard-based quantification but incorporates different empirical and theoretical methods. As selected methods can vary between approaches [1], this may explain why standardless quantification is often described as an inaccurate, unverifiable “black box” [2]. One should not however assume that all “standardless” approaches are the same and that standard-based quantification is without caveats. At its best, standardless quantification can overcome empirical difficulties related to the availability, maintainability and consistency of standards as well as reduce the analysis time. This presentation describes one approach to standardless quantification for ED spectrometers and how standards have been critical in its development and validation [3,4].

Development of our standardless approach began with the acquisition of X-ray intensities from a series of standards, consisting of pure elements and simple binaries (e.g. SiO₂, FeS₂). The take-off angle of the ED detector, thickness of carbon coating on standard block, homogeneity of standards, etc. were carefully measured prior to the measurements. Instead of measuring the beam current, a calibration standard was periodically measured, Co for the acquisitions at 20 kV and Si for those at 5 kV. By operating with good current stability and measuring intensities relative to the single calibration standard, this empirical solution eliminated the need to have a Faraday cup in the microscope. The X-ray intensities from the standards were stored in a database as ratios to the Co K or Si K X-ray intensity. To use these ratios for different ED detectors, the specific detector efficiency as a function of X-ray energy was required for each type of detector. A theoretical model for the detector efficiency was constructed based on experimental measurements at the Bessy II synchrotron, intimate knowledge of the manufacturing processes and detector parameters, and ratios of X-ray intensities measured on different standards [3,5]. In summary, standards were used to produce a universal “factory” standards database and a specific detector efficiency curve for each type of detector.

To perform unnormalized, standardless quantification of unknown samples, the end user first acquires a spectrum on a pure element standard. This is equivalent to measuring the beam current and can be repeated if the beam current fluctuates. After this “beam calibration”, the user acquires spectra on unknown samples. As in standard-based quantification, k-ratios are calculated for each identified element. The only
difference is that the X-ray intensity for the standard (denominator of the k-ratio) is calculated using the factory database and detector efficiencies. For an unknown sample containing Fe and a beam calibration performed on Mn at 20 kV, the standard X-ray intensity of Fe K ($I_{u}^{Fe}$) is equal to

$$I_{u}^{Fe} = I_{u}^{Mn} \left( \frac{I_{f}^{Fe}}{I_{f}^{Co}} \right) \left( \frac{e_{u}^{Fe}}{e_{u}^{Mn}} \right) \left( \frac{e_{f}^{Mn}}{e_{f}^{Co}} \right)$$

where the subscript and respectively indicate an intensity (I) or detector efficiency (ε) corresponding to the user or factory configuration. Note that all intensities in the equation are measured intensities from standards. The composition is then iteratively computed using the k-ratios and the XPP $\phi(\rho z)$ model as the matrix correction procedure. When the beam energy, take-off angle or specimen tilt differs between the user and factory configuration, an additional theoretical correction is applied based on the ratio of matrix corrections calculated for the respective setups.

This standardless quantification approach has previously been validated [3,4] and this test has been repeated with a new generation of silicon drift detector using 53 standards at 20 kV. Figure 1 compares the measured and expected weight fractions and analytical totals. As before, quantification with a relative error below 5% was achieved. Further validation is underway to further evaluate the standardless quantification using standards containing more than 4 elements.

Although the development and production of homogeneous, consistent, specialized standards can be used to improve empirical standard-based quantification, a more comprehensive approach is to develop standards to advance theoretical methods (physical parameters, matrix correction models, etc.) with the objective to continually improve standardless quantification and make accurate analysis more practical and applicable to an increasingly wider range of materials.

References:

Figure 1. Comparison between measured and expected (a) weight fractions and (b) analytical totals. ED spectra were acquired from the MAC6260 standard block with an UltimMax 100 ED detector on a Zeiss Leo 1450VP microscope at 20 kV, an input count rate around 50kcps, a live time of 20 s, PT5, 10 eV/channel. A beam calibration was performed on Co for every five acquisitions.
How to Not Do Poor Standards-based EDS Quantitative X-ray Microanalysis: A WDS Perspective

Stephen M. Seddio

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WDS (wavelength-dispersive X-ray spectroscopy), particularly EPMA (electron probe microanalysis), has long been the stalwart method of achieving accurate and precise quantitative X-ray microanalysis. Over the past decade, EDS (energy-dispersive X-ray spectroscopy) has been increasingly used for quantitative X-ray microanalysis, yielding results that may rival the accuracy and precision achieved by WDS-EPMA [1]. As a result, many analysts that had once relegated EDS as strictly a qualitative tool to help identify areas of a sample of interest for WDS quantitative analysis have now included EDS as part of their standards-based quantitative methodology. However, these analysts may not have received the same level of training regarding EDS quantitative methods as they have for WDS. There are many abstracts and papers that detail the proper way to do EDS and WDS quantitative analysis (e.g., [2]). Here, I highlight incorrect practices of EDS standards-based quantitative analysis common to WDS experts using my experience as a cautionary tale.

Most quantitative X-ray microanalysis errors are the result of poor sample preparation or poor analytical planning. However, most experience WDS users have been well educated and attempt to avoid these pitfalls. Instead errors in EDS quantitative analysis common the WDS user tend to stem from an incomplete understanding of the peak deconvolution capabilities of EDS software. The following is a common example. In order to test the standards-based quantification ability of a new EDS system, an analyst acquires a count-rich EDS spectrum from a standard sample of a multi-element oxide (e.g., a monazite [REEPO₄] standard sample, Fig. 1). They then declare the standard composition to the software. Next, they declare that standard files should be made using peak shapes and intensities from the acquired spectrum for all elements present in the standard composition. Lastly, expecting a trivially excellent analysis, they quantify the concentration of all elements in the standard composition using the same spectrum used for standardization (or another similar spectrum acquired from the standard sample. However, excellent results may not achieved using this methodology (Table 1, Acquired Intensities; Acquired Peak Shapes). The analytical total is only 48.3 wt%. The problem with this analysis is that the peak shapes for quantification, which are used for peak deconvolution, were taken from a spectrum with many X-ray interferences, particularly, the L-lines of La, Ce, Pr, and Nd. The proper approach to standards-based EDS quantitative analysis while still using intensities from a spectrum with confounded peaks would be to use peaks shapes taken from spectra containing the elements of interest but without any elements that yield interfering X-rays. For example, the Ce K peak shape could be taken from an EDS spectrum acquired from a sample of Ce metal, Ce₂O₃, CePO₄, etc. An alternative, albeit a less rigorous approach, is to use the default peak shapes in the analytical software and use the peak intensities from the acquired spectrum. The “Acquired Intensities; Default Peak Shapes” result in Table 1 gives the elemental concentrations determined using the default peak shapes in Pathfinder and the peak intensities from the acquired monazite spectrum (Fig. 1). This composition is an excellent match to the published composition, which is the expected result.

References:
Figure 1. EDS spectrum acquired from monazite standard sample used for standardization and quantification in Table 1.

Table 1. Standards-based quantitative analysis (wt%) of monazite

<table>
<thead>
<tr>
<th>Element &amp; X-rays</th>
<th>Published</th>
<th>Standardless</th>
<th>Acquired Intensities; Acquired Peak Shapes</th>
<th>Acquired Intensities; Default Peak Shapes</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>25.9</td>
<td>29.5</td>
<td>26.7</td>
<td>26.1</td>
</tr>
<tr>
<td>Si K*</td>
<td>n.r.</td>
<td>0.2</td>
<td>0.02</td>
<td>0.22</td>
</tr>
<tr>
<td>P K</td>
<td>12.1</td>
<td>13.1</td>
<td>11.3</td>
<td>12.1</td>
</tr>
<tr>
<td>Ca K</td>
<td>0.4</td>
<td>0.5</td>
<td>0</td>
<td>0.42</td>
</tr>
<tr>
<td>La L</td>
<td>12.9</td>
<td>11.2</td>
<td>0.79</td>
<td>12.9</td>
</tr>
<tr>
<td>Ce L</td>
<td>30.8</td>
<td>29.6</td>
<td>0</td>
<td>30.8</td>
</tr>
<tr>
<td>Pr L</td>
<td>4.2</td>
<td>3.3</td>
<td>0.02</td>
<td>4.2</td>
</tr>
<tr>
<td>Nd L</td>
<td>8.7</td>
<td>8.6</td>
<td>9.5</td>
<td>8.7</td>
</tr>
<tr>
<td>Pb M*</td>
<td>n.r.</td>
<td>0.6</td>
<td>0</td>
<td>0.61</td>
</tr>
<tr>
<td>Th M</td>
<td>3.8</td>
<td>3.6</td>
<td>0</td>
<td>3.8</td>
</tr>
<tr>
<td>SUM</td>
<td>98.8</td>
<td>100.0</td>
<td>48.3</td>
<td>99.9</td>
</tr>
</tbody>
</table>

All values are wt%. Data was acquired and processed with the Thermo Scientific Pathfinder X-ray microanalysis system using a windowless Thermo Scientific UltraDry EDS detector. “Published” refers to the composition for monazite standard sample reported by Structure Probe, Inc. “n.r.” means “not reported.” “Acquired Intensities; Acquired Peak Shapes” refers to quantifications done using peak shapes and intensities from the spectrum from the monazite standard sample. “Acquired Intensities; Default Peak Shapes” refers to quantifications done using the default peak shapes stored in the analytical software and intensities from the spectrum from the monazite standard sample. Si and Pb were quantified using standardless analysis because there were not included in the published composition but have peaks in the spectrum acquired from the monazite standard sample.
Examining the Effect of Sample Preparation on Analysis Data

Cathy Johnson¹, Dalia Yablon²

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Sample preparation is a critical process having direct impact on sample quality, but often times it is disregarded when reviewing the accuracy of the final analytical data. Developments in materials research and instrumentation have also provided for improvements and advances in preparation methodology via experimental practice, as well as technological advances. Microanalytical techniques including, but not limited to EPMA, EBSD, WDS, EDS, and AFM all rely on well prepared surfaces, free of defects and possessing near flatness. Preparation methods such as ultramicrotomy, mechanical or electro polishing, ion milling and FIB milling are the most common preparation methods utilized for these analysis techniques. Each method has its own limitations, and can generate a set of unique artifacts affecting the actual analysis.

Mechanical or electro polishing have been the traditional methods to prepare samples for EPMA, and vibratory polishing has been a favored finishing technique for EBSD. Mechanical polishing can often produce significant damage artifacts such as smearing and deformation of the existing microstructure, particularly in soft or hard/soft multiphase composites. To minimize these effects, the analyst must consider factors such as mounting resin and polishing media [1]. Surface flaws can be further reduced by utilizing an additional finishing step such as vibratory polishing or ion milling prior to the analysis. Vibratory polishing (Figure 1), results in significant surface improvement to better resolve Kikuchi patterns and analysis data for EBSD. Comparison of surface roughness or height measurement of conventionally polished steel samples - RMS roughness 7.16 nm (Figure 2) and vibratory polished - RMS roughness 3.7 nm (Figure 3), results in significant improvement of the final surface finish. For this reason, this polishing method should also be considered for other surface analysis techniques, including EPMA.

Coating is also a critical preparation step to eliminate charging effects and produce higher signal to noise ratio. Coating minimizes high energy and heating effects that can result in sample damage. Both coating material and process vacuum affect the particle size and thereby the coating integrity. An iridium coated mica standard has been shown to yield improved quantitative data that is quite comparable to SEM data acquired for carbon coated mica [2]. For materials that possess insulating properties such as mica, this alternative coating can be particularly beneficial.

Each step of the preparation process requires careful consideration. Dynamic process parameters should be controlled and monitored. With the advent of integrated software, preparation is programmable to result in consistent and reproducible preparation methods. Process automation allows sample preparation to be optimized, preparation artifacts to be reduced and the operational variation generated by different users is virtually eliminated. This presentation will include examples of preparation artifacts for various preparation methods, and an overview of parameters that affect the quality of the final preparation.

References:
Figure 1. Vibratory Polisher

Figure 2. AFM topography image 50 um x 50 um regular polished steel

Figure 3. AFM topography image 50 um x 50 um, vibratory polished steel
Return to the Collections: A Preliminary Search for New Reference Materials

Timothy R. Rose

1. Department of Mineral Sciences, Smithsonian Institution, Washington, D.C., USA

The microanalysis community always has the need for more quality reference materials covering wider ranges of compositions. We propose following a procedure similar to that used by Jarosewich et al. [1] when the original set of Smithsonian Microbeam Standards (SMS) were established from materials in the collections of the Department of Mineral Sciences at the Smithsonian Institution. This procedure has four steps: 1) identification of candidate materials; 2) a check for impurities; 3) a check of homogeneity and 4) round-robin analysis of materials that pass steps 2 and 3 to establish a consensus composition.

In the fall of 2017, a group of us were granted access to the mineral and rock and ore collections in the Department of Mineral Sciences at the Smithsonian Institution, the sources of the original Smithsonian Microbeam Standards. The goal was to identify samples to harvest as potential new reference materials. Members of the group were: Anette von der Handt (University of Minnesota); John Fournelle (University of Wisconsin); Emma Bullock (Carnegie Science); and Cathleen Brown and Tim Rose (Smithsonian). Criteria for candidate specimens were geologic setting, large crystals or chunks, lots of the material and gemminess. Seventeen mineral specimens and 9 synthetics were identified. One focus of this initial foray into the collections was to identify potential garnet specimens. Eleven of the seventeen minerals are garnet including these species: almandine, spessartine, pyrope, uvarovite and grossular. Small chips will be removed from all of the candidate garnets, mounted as polished sections and examined for impurities by analytical SEM at the Smithsonian. A subset of these will hopefully pass the impurity test and will then be prepared for analysis of entire cross-sections of the crystal or chunk. Volunteer laboratories may be enlisted in order to get this accomplished in a timely fashion.

Some of the original SMS (Johnstown hypersthene, USNM 746, and Springwater olivine, USNM 2566) were harvested from the meteorite collection. This potential source of material was overlooked by the group. Recently, while perusing the collection with a meteoriticist colleague interested in replacing the now retired hypersthene, a vial of prepared grains of enstatite from the Mt. Egerton meteorite were found (figure 1). The hand writing on the vial is from Gene Jarosewich and it says “HCl washed.” These grains may have been prepared for a study of minor and trace elements in meteorites [2]. An existing thin section was examined for impurities and analyzed. The enstatite contains very minor inclusions but has very strong cleavage leading to many fractures and pits on the thin section. Preliminary analysis of more than one hundred points suggests it is quite uniform in composition. However, cathodoluminescence imaging reveals a mottled appearance (figure 2). Permission has been granted to distribute some of the prepared grains for further evaluation.

In the course of this preliminary work, a number of questions arise for the community. Some of these are:

1. Because these will be most likely characterized by electron beam instruments, do we care about minor amounts of impurities (e.g. inclusions)?
2. What is acceptable compositional heterogeneity?
3. What are the reference material needs of the community? What minerals?
4. Do we try to select new materials in quantities so that small wafers (as opposed to tiny grains) can be distributed for analytical methods such as LA-ICP-MS and SIMS?
References:

Figure 1. Mount Egerton meteorite prepared grains.

Figure 2. Cathodoluminescent image of Mt Egerton enstatite.
The need for well characterized standards for the EPMA, WDS and EDS communities has seen a steady development since the use of these techniques. Today’s standards meet a wide range of user needs and multi-standard blocks can be built from a variety of sources. As the demand for these standards grows, commercial industries must search for acceptable materials that can provide a homogeneous matrix and serve an increasing customer base with identical compositions. Finding naturally occurring mineral resources that allow for large areas to be homogeneous in composition is challenging. At the same time, the production of synthetic material and glasses also present unique issues. A general review of the variety of commercially available standards will be reviewed. The status of interlaboratory testing and a public reference library as well as the potential need for low level homogeneous materials will be discussed.
USGS Microanalytical Reference Materials (MRMs) Development

Stephen Wilson

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As the use of microanalysis in geochemical studies continues to expand the need for reliable matrix matched reference materials increases. In support of internal studies the USGS reference materials project devotes considerable resources to the development of microanalytical reference materials (MRMs) which assist investigators in quantifying trace and major elements in a variety of matrices. Discussions will focus on two categories of USGS MRMs and the lessons learned in their development. The original USGS focus was on the development of homogeneous glasses using natural geologic materials. Due to oven heating limitations (1350°C) materials were selected for glass preparation that contained ≤55% SiO₂. Melting/mixing/cooling protocols were developed in early studies using USGS basalt materials BCR-2, BHVO-2 and BIR-1. Preparation of all glass materials is accomplished by melting powdered material at 1350°C in a 1 L heavy walled platinum bowl for several hours, mixing the contents by hand using a platinum stir rod, heating for an additional two hours and then rapidly quenching the melt in deionized water. Glass materials produced in this manner (table 1) are remarkably similar in chemical composition to the starting material and have element homogeneity appropriate for EPMA and LA-ICP-MS analysis. In addition to the use of domestic geologic materials the USGS has also collaborated with international organizations to developed glass materials using their material which further expands the range of sample types. To meet the need for instrument calibration the USGS has developed a series of synthetic basalts (Synbasalts) using a combination of a manufactured glass and reagent grade chemicals. The starting glass powder (GSE-1) was designed by the USGS and prepared by Corning Glass Works in 1969. The glass was powdered and used to monitor spectrochemical mobile laboratories in use at the time. GSE-1 is the starting material of choice because it contained 500 ppm of 46 trace elements [1][2] and was available in sufficient quantities to produce both GSE-1G (400 ppm) and serial dilutions of GSD-1G (40 ppm) and GSC-1G (4 ppm). Because the original GSE-1 material contained ≥62% SiO₂ the matrix was modified to match a BCR-2 composition through the addition of Al₂O₃, Fe₂O₃, MgO, CaO, TiO₂, and Na₂H₂PO₄. The GS series of materials was prepared as described above producing approximately 600 kg of each glass standard.

The second area of MRM development was designed to support those low temperature studies that required the presence standard trace elements and potentially volatile elements such as Hg, Te, Tl, As, Se, and Os. To meet this complex need the USGS developed a coprecipitation process which can customize the sample matrix contain trace elements that mimics natural abundances. In this process a target matrix composition is identified and soluble cation and anion solutions are prepared. Trace element aliquots are obtained from commercially available 1000 or 10,000 ppm spectroscopic solutions and mixed in a third container. In the preparation step the cation (ex. Ca(NO₃)₂) and anion (ex. Na₂CO₃) solutions are combined along with all the individual trace element aliquots. The resulting precipitate (ex. CaCO₃) is rapidly stirred until the contents are visually homogeneous. After settling overnight the solid phase is collected and repetitively wash/centrifuged until the supernatant conductivity is ≤200µS (micro Siemens). The solid material is then micronized, dried at 110C, briefly ground in an agate shatter box and then pressed into pellets at 10,000 psi. A list of materials prepared in this manner is presented in table 1.

Due to difference in physical properties (compression) of the produced materials two pellet preparation
options are utilized depending on the integrity of the pressed pellet. Materials that compress uniformly and maintain their shape during pellet extraction from the 13 mm die (ex. MASS-1) are distributed as individual pellets. Materials that tend to delaminate during pellet extraction are pressed into plastic rings (13 mm ID, 19 mm OD). The rings may be fitted with a paper backing to increase pellet stability.

MRM materials prepared in this manner undergo a preliminary homogeneity assessment at the USGS using both EPMA and LA-ICP-MS. Randomly selected fragments or pellets of each new material are analyzed at multiple locations to identify any systematic heterogeneity in the material. If the material is considered homogeneous, aliquots of glass (<2mm, ground) or powder are submitted to multiple laboratories for traditional total element analysis using a variety of methods. MRMs produced by the USGS are commonly used in the microanalytical proficiency testing program known as G-probe. This program organized by the International Association of Geoanalysts (IAG) and coordinated through the USGS distributes samples to participants to evaluate laboratory accuracy. In addition to providing laboratory performance information results are compiled by the USGS and used in the certification process for MRMs.

References:

Table 1. USGS MRM reference materials

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<th>Matrix</th>
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Some Experimental Methods for Synthesizing Standards and Reference Materials for Microbeam Analysis

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In the almost 70 years since the first electron microprobe measurements were presented [1], a major effort in developing its capabilities has focused on the procurement of suitable standards – materials of known chemical composition used for calibrating the instrument for analysis of unknowns. Pure metals and simple, stochiometric oxides were some of the first materials used as standards, but as microprobe capabilities advanced and their prevalence increased, there became a need for a centralized collection for use in all labs to enable comparison of results. This was accomplished with the Smithsonian Microbeam Standards, a collection of natural minerals and glasses from a variety of global localities for their clarity and perceived purity [2]. The centralized effort to characterize them with an absolute method and distribute them freely has created a benchmark for determining the composition of Earth materials.

With petrological advances in understanding the complex record preserved in trace-level components of minerals (e.g., [3]), there has been growing interest in quantifying part per million-level concentrations from micrometer-scale regions of materials. Attempts to measure trace elements by applying analytical routines typical for major and minor element analysis have been met with varied success, mostly because systematic errors in analytical procedures are magnified at trace levels, which can significantly affect the quality of results. While the available standards are fully adequate for calibration, their composition at the trace level is often unknown or heterogeneous, rendering them unsuitable for use as trace element reference materials (RMs).

This motivates the effort to acquire new materials to be used as trace element RMs. Development of new RMs entails either (a) finding a natural locality exposing an adequate supply of a particular natural material (crystal, glass, metal) containing a uniform distribution of the analyte of interest at concentrations similar to those expected for the unknown, or (b) synthesizing a suitable material in a laboratory experiment (e.g. Fig 1). These approaches should be used in complement because each has associated tradeoffs regarding the amount of material, the degree of compositional uniformity, and the closeness of compositions to those expected for unknowns. In addition to emphasizing the importance of identifying natural RMs, the purpose of this presentation is to discuss the abilities and limitations of some experimental methods for fabricating crystals, glasses, and metals, and evaluate their suitability as trace element RMs using a variety of in-situ analytical methods (EPMA, SIMS, LA-ICP-MS, CL).

Standards and RMs are used for specific purposes in trace element analytical procedures. In EPMA measurements, standards are used to calibrate X-ray intensity (cps/nA) for a particular element and matrix. Calibrations should be performed on materials that contain a high concentration of the analyte of interest (e.g., SiO₂ for Si a calibration, TiO₂ for a Ti calibration, etc.). Trace element RMs differ in that they contain the analyte at trace concentrations in a matrix identical to the sample, and the concentration and spatial distribution of the analyte must be determined by an independent method. Thus, a good trace element RM has a uniform distribution of the analyte at a concentration similar to those expected for the unknown. However, given the slow crystal growth rates in many natural environments, the sensitivity of trace element solubility to small changes in pressure-temperature-composition (P-T-X), and the sluggish diffusivity of...
most cations of petrologic interest, many natural materials are heterogenous at the micrometer scale. By using experiments to control \( P-T-X \) of the sample environment, it is possible to produce materials with a high degree of compositional uniformity.

There are numerous experimental methods for synthesizing crystals, glasses, and metals that could be used to produce trace element RMs. Some of these methods include wet-chemical procedures at room \( P-T \), flux-crystallization in a benchtop furnace, and synthesis at high \( P-T \) conditions in experimental devices. We present results of synthesis experiments that were performed at elevated \( P-T \) in a piston-cylinder device [4]. Piston-cylinder experiments can be performed under a wide range of \( P-T \) conditions (Fig 1a), and variations in assembly components can be used to control the chemical environment (e.g. oxygen fugacity, component activity, etc.). We have used various piston-cylinder experimental methods to synthesize crystal, glass, and metal RMs with prescribed trace element concentrations. Typical silicate RM syntheses produce ~100 mg of material (Fig 1b). Synthesized crystals have uniform trace element concentrations within individual crystals and amongst representative samplings of each experiment regardless of crystal size. For example, RM crystals of quartz synthesized at 1.0 GPa and 900 °C ranging in size from 0.02 to 1 mm (Fig 1c,d) have uniform Ti and Al concentrations within large crystals (Fig 1e), small crystals (Fig 1f) and amongst a large sample of the population (Fig 1g). We present applications of this method for producing a variety of materials and characterize them with multiple quantitative methods to determine their suitability as trace element RMs. By describing some experimental capabilities for high \( P-T \) materials synthesis and potential applications for producing standards and RMs, this presentation aims to initiate discussion on community needs and potential applications for experimental methods in the development of calibration materials for microanalysis.

References:
[5] The authors acknowledge National Science Foundation grants EAR1551343 and EAR1625835.

**Figure 1.** Overview of experimental capabilities for synthesis of trace element RMs and proof-of-concept showing consistent Ti and Al concentrations throughout a population of quartz crystals.
Reference materials and standards (RMS) play a crucial role in quantitative microbeam analysis, as they are the basis for instrumental calibration, data quality assurance (e.g., secondary standards) and interlaboratory comparison. Good standards that have been evaluated and certified for their homogeneity and reference composition are rare and only available from a handful of recognized providers. Whereas some crucial RMS have or will soon become unavailable, some researchers continue to develop and test new RMS [1,2,3], and some of these materials are becoming more widely disseminated. Unfortunately, time and money constraints make RMS development difficult [4], which often leaves the analysts with a set of “second choice” reference materials instead of certified standards. Such reference materials can be of questionable quality and origin, as they may suffer from homogeneity or impurity issues (natural samples), contamination (synthetic materials), unknown provenance, or incomplete or inaccurate reference compositions. Furthermore, some RMS can have different batches and/or reference compositions (e.g., following a revision; [1,5]) that can lead to confusion and the potential risk for mixing old and new values. Efforts still have to be made to keep a record, evaluate, and guarantee the quantity of RMS for the next century.

Accuracy and interlaboratory comparison in EPMA requires good characterization of one’s own RMS collection, knowledge of compositional variations between batches of materials of the same name [6], and adhering to proper standard maintenance protocols [7]. This is specifically relevant, as some initially “good” RMS fall later into the categories of “bad” and “ugly” for various reasons [7]. Metals that would otherwise be homogeneous and highly pure can easily oxidize, or well-characterized glasses can be altered by electron beam damage. Some RMS may have subpopulations that deviate from the published composition, and need to be evaluated carefully to identify such outliers. To make a “bad” RMS “good” (or at least better), individual labs may need to use a slightly different reference composition for what is nominally the same material in order to improve analytical accuracy. In other cases, a modification of the analytical protocol might permit the use of an otherwise sub-optimal RMS, e.g., defocusing the electron beam to minimize the effect of submicron inclusions [8], averaging over multiple grains to minimize bias due to intergrain heterogeneity [9], using intensity corrections to account for beam damage effects [10], or accounting for peak shifts or shape changes between materials [11].

Generating this level of documentation for a wide range of materials is often beyond the scope of what a single lab or RMS provider can perform. Valuable RMS information does exist in many cases, but is scattered over individual publications, conference abstracts, and personal anecdotes, and can be inconsistent or, worse, erroneous. Furthermore, recent hardware and software innovations will necessitate further characterization of reference materials for more variables. Hardware innovations include brighter electron sources (Schottky emitters), new WDS monochromator materials, modern SDD-EDS, and a new
generation of soft X-ray spectrometers (SXES, iZPS) for measuring soft or non-traditional X-ray lines. Software innovations are establishing new benchmarks in terms of improved precision, accuracy and efficiency. Accordingly, currently available and new RMS will have to be investigated for additional parameters such as nano-scale inclusions or inhomogeneities, minor and trace impurities, as well as oxidation and chemical bonding states.

There is a continued and increasing need for communication within the microbeam community in order to consolidate existing information about available standards and reference materials, and to curate analytical and maintenance protocols. The joint Microanalysis Society (MAS) and Microscopy Society of America (MSA) Focused Interest Group on Microanalytical Standards (FIGMAS [12]: https://figmas.org) was founded in 2015 to address the aforementioned issues, with the overall goal of improving access of the microanalytical community to RMS information. Some information is already available via a web-based database that collects published and unpublished RMS data as well as relevant metadata and sourcing options for available reference materials. This database is growing and the entries will be peer-reviewed by FIGMAS members. Ideally, this effort will be international, and will be complimented by round robin evaluations of both new and existing RMS to demonstrate instrumental performance, verify or establish the homogeneity and accuracy of new and existing reference materials, and further establish analytical protocols for reference material utilization, development, and characterization. This can then provide a fresh avenue to disseminate information, establish guidelines for critical evaluation of one’s own standards and help make informed decisions for future acquisitions of standard materials.

References:

Note: abstract presented in May 2017 at the annual EMAS conference in Konstanz, Germany.
Something Old, Something New: A Look at some EPMA Reference Materials

John Fournelle

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The microanalytical community owes a large debt to Gene Jarosewich and his co-workers (Joe Nelen, Julie Norberg) at the Department of Minerals Sciences at the Smithsonian Institution National Museum of Natural History for their work in developing 31 mineral and glass microbeam standards in the 1968-78 period [1]. With the development of FE SEMs and SDD EDX (not available back ~3 decades ago), researchers at the Smithsonian have re-evaluated the original NMNH standards [2][3]. Additional evaluations have been made of differences between web-purchased material vs NMNH material of nominally the same material. Fournelle [4] found that, unlike the official NMNH 111312/44 San Carlos olivine, which is Fo90.1, “San Carlos olivine” available from gem dealers spans Fo89.2 to Fo91.4. Evaluating 23 of the 200-300 micron NMNH San Carlos grains (71 measurements), he found there was a bit wider range of heterogeneity compared with the original publication, making it incumbent not to just count on one grain but to average, optimally, 5-10 grains. With assistance of NMNH, he mounted multiple grains of the 4 NMNH pyroxene standards, and found a range of compositions present in each sample [5] (Fig. 1). Thus, if one used only one grain for a standard, there could be a finite probability that the actual grain composition could differ from the published (bulk) wet chemical one (itself an average of presumably >1000s of grains). Figure 2 shows the range of possible MgO values for one unknown orthopyroxene, from one K-ratio, processed with different standards – with almost 2 wt% differences in MgO (and also SiO2) using common standards – an example of the issue stated above.

Well known to many are the NMNH “Kakanui” standards developed by Jarosewich and co-workers, from megacrysts in Oligocene tuff in the South Island of New Zealand. Further, in the late 1980s, researchers at Otago University similarly evaluated minerals from the Kakanui outcrop as EPMA standards, such as kaersutite KK2 [6] [7]. If the source Kakanui reference material occurs as megacrysts, what about larger standards? In early 2017, Fournelle visited the Kakanui type location and collected several samples, a key one being a large welded tuff (hyloclastite) (Fig. 3), with one hornblende/kaersutite megacryst are being studied at UW (Fig. 4; Table 1), to evaluate the potential for larger size standards – observing that some do have small inclusions (easily identified and avoided). Recently Pankhurst et al. [8] characterized an olivine standard by mapping out the spatial compositional domains, allowing a ‘not perfectly homogeneous’ but large reference grain to be used for accurate EPMA.

Additional potential standards being investigated at UW include: (1) ~An49 plagioclase megacrysts from Hogarth Range, NSW, Australia: gem quality labradorite (~15mm, homogeneous crystals with individuals of An48-50) weathered out of Tertiary basalt; (2) “FeO wustite” (actually Fe0.92O): mm-size, industrial-origin (Sigma Aldrich), with easy-to-avoid inclusions. We have also been investigating NIST K539, a glass synthesized as a substitute for K412; it appears to be homogeneous, with a slightly different composition than K412.

There is an excellent, free (online: google it) resource every serious EPMA lab should have and read at least once: USGS Open File Report 85-718, The Reston EPMA lab critically evaluated its standards, demonstrating the degree of questioning we should all have about the standards which we rely so heavily upon, particularly natural minerals and glasses.
References:

**Figure 1.** Histograms of compositions of 54 individual grains (average of 5 spot analyses on each) of Smithsonian NMNH Kakanui Augite (164905). Red arrow is nominal composition from the published wet chemical analysis.

**Figure 2.** Using a single K-ratio from an opx crystal, a wide range of MgO values result, dependent upon which of 9 “good” EPMA standards are used.

**Figure 3.** Block of breccia tuff from Kakanui, North Head KNH (~15 inches long).

**Figure 4.** Large fragments of hornblende megacryst from the above block. KNH 2017. In 1” mount.

**Table 1.** 767 analyses of 20 grains of KNH 2017 Kakanui hornblende (30-40 pts/grain). Comparison with other published Kakanui hornblende analyses.

No small ~melt inclusions have been found so far, as have been observed in some the NMNH grains.
Preliminary Trace Element Analysis of Vitreous Standards by SEM-based Micro-X-ray Fluorescence Spectrometry

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Large facilities and particle accelerators have long offered spatially resolved trace element microanalysis via synchrotron-based x-ray fluorescence spectrometry (S-µXRF) and particle induced x-ray emission. Laboratory-based trace element studies at the microscale have been historically performed by secondary ion mass spectrometry (SIMS), laser ablation ICP mass spectrometry (LA-ICP-MS), and electron probe microanalysis using wavelength dispersive x-ray spectrometry (EPMA-WDS). While high sensitivity methods, both SIMS and LA-ICP-MS are locally destructive. Even minimal mass loss is decidedly non-optimal for the analysis of ultra-precious objects such as heritage materials, or cosmochemical specimens. EPMA offers the advantage of localizing the analysis using an electron image, yet the serial nature of WDS imposes limitations for a group of trace elements, particularly if the target material is electron beam sensitive. The quality of an alternative nondestructive approach, where an XRF microbeam and solid state x-ray detector is available within a scanning electron microscope (SEM) is explored here using a set of well-established trace element-bearing vitreous standards.

A Bruker XTrace with a Rh source and a 15 micrometer (at Mo Kα) polycapillary x-ray optic has been mounted in an Hitachi S3700N SEM. X-rays were detected with an XFlash 4010 SDD and analyzed using Esprit v2 software and a standardless fundamental parameters (FP) methodology for quantification of XRF spectra. An unfiltered Rh source was operated at 50 kV and 600 μA. Because the XRF analyses were collected under high vacuum conditions, x-rays with energies > 1 keV were analyzed. An oxygen K line peak is observable, but not used in the analysis. XRF mass sums for anhydrous glasses totaled of 98-120 % with most > 100 %. Because FP analysis produced an overcorrection for some major elements, the data presented here have been normalized. Silicate glasses analyzed include NIST SRM 610, SRM 612, and SRM 93a [1]. Other silicate glasses that contain minor elements, or less well-characterized trace elements include VG-568 (Yellowstone rhyolite), Corning 95IRX, as well as archaeological references Corning A, B, C, and D glasses.

Our results indicate that SEM-based µXRF shows significant promise for the analysis of a number of trace elements at concentrations down to 10s of parts per million [Tables 1-3; Fig. 1]. The deviation of the FP results from the expected values for NIST SRM glasses can be divided into three general groups: 1) 0-30% (Ca, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y), 30-60% (Ti, V, Cr, Se, In, Sb, Nb, Ba, Pb, and Th), and >60% (La, Sm, Ho, Tm, Hf, Mo, Sn, and U). Zr results suffer from a detector artifact and are not representative of the technique. Surprisingly, trace Cl was measurable in the presence of the Rh L source radiation [Fig. 2] even in the absence of a source filter. Peak interferences are evaluated manually by inspection of the graphical deconvolution results [Fig. 3]. Accuracy of SEM-based µXRF data will most assuredly improve further when standards-supported FP analysis becomes available and is integrated into the current software analysis package.

References:
Table 1. Trace element results for NIST SRM 610.

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* Detector artifact

Table 2. Trace element results for NIST SRM 612.

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<td>36.9</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>36.1</td>
</tr>
<tr>
<td>As</td>
<td>36</td>
<td>35.7</td>
</tr>
<tr>
<td>Se</td>
<td>12</td>
<td>16.3</td>
</tr>
<tr>
<td>Rb</td>
<td>32</td>
<td>31.4</td>
</tr>
<tr>
<td>Sr</td>
<td>82</td>
<td>78.4</td>
</tr>
<tr>
<td>Y</td>
<td>36</td>
<td>38.3</td>
</tr>
</tbody>
</table>

Table 3. Trace element results for NIST SRM 93a.

<table>
<thead>
<tr>
<th>Element</th>
<th>NIST certified value N=3 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>720</td>
</tr>
<tr>
<td>Ca</td>
<td>61</td>
</tr>
<tr>
<td>Ti</td>
<td>69</td>
</tr>
<tr>
<td>Fe</td>
<td>206</td>
</tr>
<tr>
<td>Sr</td>
<td>23</td>
</tr>
</tbody>
</table>

Figure 1. Fitted Micro-XRF spectrum for NIST SRM 612 showing peaks for 19 trace elements from 4.5–15 keV.

Figure 2. Graphical deconvolution showing detection of trace Cl in the presence of Rh L x-ray source peaks in NIST SRM 93a.

Figure 3. Deconvolution of overlapping x-ray lines from in NIST SRM 610, including: Th L\(_{α}/Bi L_{α}/Pb L_{β}\), Rb K\(_{α}/U L_{α}\), and Y K\(_{β}/Rb K_{β}/ Pb L_{α}/Bi L_{α}\).
The National Institute of Standards and Technology (NIST) is the National Measurement Institute (for the United States) which provides users with Reference Materials (RMs) and Certified Reference Materials with metrological traceability to the International System of Units (SI-traceability) [1]. Most industry and academic instrument owners are familiar with our reference products, sold as Standard Reference Materials (SRMs), and often request for more available SRM products. Here, we show the international requirements for developing new international RMs and NIST SRMs, and bring them from an idea to a marketable product, with specific discussion on the NIST 610 series glass composition SRMs.

The first and most difficult aspect for development of a new SRM, is the SI-traceability requirement. We would like to link measured quantities (measurands) back to the definition of an SI unit, such as mass fraction (mg/kg) found in, for example, NIST SRM 610 [2]. However, this requires us to have a primary measurement method linking the mass of elements to the mass of the matrix under study. This also requires validation of sample homogeneity (i.e., no compositional heterogeneity) and extended stability over time. One primary measurement method is direct mass determination of elemental composition during the glass processing and repeated reprocessing of glass feedstock to provide adequate sample mixing. This was the primary method used in the production of the NIST SRM 610 series feedstocks. However, knowing the feedstock input composition may not reflect the final product, if precipitates form during production, or trace materials are removed from the melt into the glass processing apparatus. Due to these concerns, and others, there has been concerted efforts made to further the uncertainty analysis and further traceability with the 610 series [3].

Developing SRMs incorporating measurement methods other than feedstock material mass determination used in the 610 series, such as Mass Spectrometry (MS) and Electron Probe Micro Analysis (EPMA), requires addressing the SI-traceability of these methods, which is difficult, since these methods intrinsically require calibration reference materials. However, these methods could be incorporated as non-traceable information values, and/or be used as a formal method for heterogeneity validation during processing. To be marketed as an internationally recognized CRM through ISO and BIPM definitions, a new NIST SRM must follow a formal internationally documented protocol, requiring all aspects of material production, processing, and measurements [4]. NIST must also follow an internationally recognized competence protocol for testing and calibration laboratories which requires documentation of institute resources (personal, facilities, instruments, products, services, etc.), processes (all aspects of CRM development, as seen in [4]), and management actions (records retention, corrective actions, audits, etc.) [5]. This creates an underlying level of documentary standards which must exist below each SRM development project.

For our new glass SRM example, each, of the following bulleted steps must be documented and explored in detail. We provide a brief comment on each step, in brackets, stating any known issues or the Organizational Unit of NIST who performs this service:
ISO 17034: steps for development of new CRM [comments on glass SRM]

- material selection [glass matrix composition and trace elements]
- verification of the identity of the material [manufacture using known mass inputs]
- maintaining suitable environments for all aspects of production [difficult, if any step of the processing is not performed at NIST]
- material processing [requires glass production experts on NIST staff]
- choice of measurement procedures [mass of material, or other methods]
- validation of measurement procedures [easy, if mass, difficult with other methods]
- verification and calibration of measuring equipment [easy, if mass, difficult with other methods]
- specification of acceptance criteria for, and assessment of, homogeneity, including sampling [MS, EPMA, or other methods]
- specification of acceptance criteria for, and assessment and monitoring of stability, including sampling [very challenging, as this requires the glass to be tracked over a period of years]
- designing and organizing appropriate characterization, including sampling [NIST Statistical Engineering Division (SED)]
- assessing commutability [NIST SED]
- assigning property values [NIST SED]
- establishing uncertainty budgets and estimating uncertainties of certified value(s) [challenging]
- defining acceptance criteria for measurand levels and their uncertainties [NIST SED]
- establishing metrological traceability of measurement result(s) and certified value(s) [challenging]
- issuing RM documents [NIST Office of Reference Materials (ORM)]
- ensuring adequate storage facilities and conditions [NIST ORM]
- ensuring appropriate labelling and packaging of the reference materials [NIST ORM]
- ensuring appropriate transport arrangements [NIST ORM]
- ensuring post-production stability monitoring [requires periodic evaluation]
- ensuring an adequate post-distribution service for RM users [NIST ORM]

The two most challenging ones are underlined. However, steps as innocuous as “validation of measurement procedures” may take years of research, if a method is sufficiently novel or current data analysis techniques are suspect. The very detailed, formal, and documented way in which new SRM projects must be pursued, makes for a high energy barrier. We only develop new SRMs when there is a sufficiently high measurement impact to justify the cost in time and labor. As we are part of the Department of Commerce, are priority is for SRMs which will have a significant impact on commerce in the U.S. Other SRMs are developed where reduced uncertainty in measurement methods will facilitate industry growth, ensure safety, and protect the environment. Development of new SRMs providing calibration for a trace analysis determination method (e.g., μ-XRF, MS, EPMA, etc.) needs to include a compelling case from one of these institutional priorities.

References:

Julien M. Allaz¹, Anette von der Handt¹, Owen K. Neill¹

¹ FIGMAS committee 2017-2018

A web-based database is being developed to reference most commonly used standards and reference materials in the microanalytical community. This effort cannot be completed without the input of the people that use these materials, i.e. **YOU**, our dear microanalytical fellows. We welcome your help in contributing data to this database as well as reviewing existing entries submitted by others. The following instructions present you how to access this database and to submit any valuable information that might be hiding in your lab documentation, your garage, or in your head.

**STEP 1:** Open your favorite internet browser and go to [https://figmas.org](https://figmas.org). Click on the link “Login / Register” in the menu and enter your username and password; on a small screen, you may need to click the menu button to access this menu. Any FIGMAS members should have an account and providing you have paid your membership to FIGMAS, you should be able to log in.

If you have lost your login information, or if this is the first time you connect, click on the “Reset account” and enter your username and your email. If you have not changed it, your initial username consists of the first three letters of your first name followed by the first three letters of your last name. For instance, Raimond Castaing’s account would have been RaiCas; small or capital letter does NOT matter for the username, but it DOES for the password!

If you don’t know this information or if you believe you do not have an account yet, contact Julien at julien.allaz@erdw.ethz.ch and indicate your full name and affiliation so that we can verify who you are.

**STEP 2:** Once logged in, you will be redirected to the member page. Open the menu “Standards...” and click on “Add or modify S-RM” (= Standards and Reference Materials). You will have three options:

1. Look at the entire S-RM listing;
2. Search for an existing S-RM;
3. Create a brand-new S-RM entry
CASE 1: Submitting a review for an existing S-RM entry

We kindly invite you to first have a look at which S-RM’s are defined and double-check if the S-RM before choosing the third and last option. If an S-RM entry already exists, it is better to submit a review of this S-RM rather than creating a new standard.

The “Searching in S-RM database” option is probably your best way to do it. It is a versatile search tool that allows you to search for an entry based on the material name, the element present (or not present) in it or the minimum / maximum range of a specific element, etc. Let’s assume you have valuable information about the famous Kakanui Hornblende. You might want to first search for the keyword “hornblende”, or even just “hornb”. And Shazam… There sure is already an entry for this material! To submit a review on a sample found in the search result, press on the button on the far right of the listing to be redirected to the modification page (step 3).
CASE 2: Creating a NEW entry for an S-RM that does not yet exists

If your search does not yield any satisfactory results, you will have to create a brand-new entry. Click on the link “Create a new S-RM” visible in the page “Add or modify S-RM” to be redirected to step 3.

STEP 3: In either case, updating or creating an S-RM, the process will consist of four major points reachable by clicking on the corresponding green tab:
1. **Info**: General information on the standard;
2. **Analysis**: Certified / reference chemical analysis;
3. **Quality**: Option to tag a specific element as “homogeneous”, “certified”, etc. (in preparation);
4. **APFU**: Calculating the atom per formula unit. This step is skipped if the composition is defined by stoichiometry to a fixed mineral formula;
5. **Provider**: Information on the provider for this standard.

Your mission, if you accept it, will be to complete as much information as you can in each of these categories, as detailed below. Any FIGMAS member can submit a review. However, the data will only be visible on the public page after a peer-reviewed period. Currently, only the FIGMAS committee member can validate a review entry, but we might elect official reviewers in a near future that will also be granted the power to validate your valuable information in the “main” database.

**STEP 3-1**: The general information consists of metadata relevant to this standard or any other similar material, such as a series of natural mineral samples from an identical location (e.g., different collections of Kakanui Hornblende or San Carlos Olivine) or a different batch of an identical synthetic material (e.g., pure alloys, synthetic oxide or phosphate prepared using the same technique). Even if there are multiple batches of Kakanui Hornblende, such information should remain the same. For instance, the name of the standard, the origin of this sample, the element that is commonly used for this standard, and the mineralogical information. Any relevant (scientific) study on this standard should be listed in order to trace it. If you have information that does not fit in any of the field presented here, write it down in the “comment” field.

<table>
<thead>
<tr>
<th>General information - NEW S-RM</th>
</tr>
</thead>
<tbody>
<tr>
<td>This form should include generalities on a group of standaidentities or strong similarities (e.g., same material but different material, re-sampling of an exhausted standard material, etc.), will be able to distinguish specific &quot;batches&quot; or &quot;sources&quot; more detailed information for this specific S-RM.</td>
</tr>
</tbody>
</table>

| Collection ✧ | No collection |
| Universal ID ✧ | |
| ✡ Name ✡ | |
| ✡ Std elements ✡ | |
| ✡ Class ✡ | Element |

<table>
<thead>
<tr>
<th>Additional information</th>
</tr>
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<tbody>
<tr>
<td>Sub-class ✧</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>Synthetic?</td>
</tr>
<tr>
<td>Formula ✧</td>
</tr>
<tr>
<td>Comment ✧</td>
</tr>
</tbody>
</table>
**STEP 3-2:** The analysis section can contain multiple analysis entries. There could be different sources of certification, and/or different batches of the same sample that have slightly different composition. The analysis information can be entered as elemental (or oxide) weight-%, or as a list of atomic proportion for synthetic materials for which perfect stoichiometric is a valid assumption. You should include as much information as you have regarding the type of analysis and the instrument/method used.

When entering data as element or oxide weight-%, you must include a FIRST line containing the list of elements or oxides separated with a single space, and a SECOND line including the list of elements or oxides weight-% also separated with a space. List of elements or oxides are case sensitive, and you should write “SiO2” and not “sio2”. If the material is an oxide, and the data are entered as an element (or oxide) weight-%, the complementary oxide (or element) weight-% will be calculated automatically based on the oxidation state of each element (respectively oxide).

When data are entered as atomic proportion, the element weight-% (and oxide, if applicable) with be computed automatically.

**STEP 3-3: (in preparation)** In this step, you will have the opportunity to tag a specific element for its homogeneity, certified value, or problematic value, etc. The ability to add comments to a specific element is also being considered.

**STEP 3-4:** Minerals or alloys are often defined by their atomic proportion. This 3rd step will permit the users to recalculate the atomic proportion to be displayed in the standard information. Currently, this APFU calculation page allows calculating the atomic proportion based on an assumed total of oxygen atoms or total cations (or atoms). As the oxygen is usually not measured, the oxygen content is automatically recalculated based on stoichiometry. If you have a certified oxygen content, you should return to the analysis section AFTER running the APFU calculation and change the oxygen weight-% to the certified value. In addition, the H₂O or CO₂ content of hydrated or carbonated material (e.g., amphibole, mica, or carbonate) can be automatically calculated. For this recalculation, a perfect stoichiometry will be assumed based on the number of OH- or CO₂-groups you specify.

**STEP 3-5:** Finally, you can specify if the material can be purchased or freely obtained from an entity or commercially. If so, you should include as much information as needed to help other users to acquire this material.
**Additional comments:** it is possible some entry will become incorrect or duplicated over time. The FIGMAS committee is currently the sole entity allowed to actually validate or delete an entry and will do its best to improve the quality of the data available online in a timely manner. If, however, you find that an entry should be deleted, we kindly ask you to contact one of the committee members who will act accordingly.

There are additional functionalities to the database that are currently being developed, including:

(a) The ability to tag a specific element composition as being “certified” by an independent and trustable entity, “homogeneous” at the micron scale or a larger scale, “dubious”, etc. (step 3-3, in prep.).

(b) The ability to add comment to a specific element in an analysis (step 3-3, in prep.).

(c) The ability to upload an image to a standard, notably an EDS scan, a photo showing an example of the standard, a BSE or other image showing inclusions/homogeneity issue, etc.

(d) A review platform with a series of elected “reviewers” that will have enhanced capabilities, such as validating a review and entering the data in the main database visible on the public page or deleting an entry.

(e) And more!

As usual, we welcome any comments you may have on the database or its functionality. Note that due to complexity in coding this website, and the high risk of generating duplicates, there is NO option for a “batch” upload of S-RM. Each standard information must be entered manually, one after the other.

We also invite you to participate to the FIGMAS forum at [https://figmas.org/forum](https://figmas.org/forum) and post questions or general comments you may have.

*Many thanks for your participation and may the best standards and reference materials be with you!*

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Anette von der Handt – avdhandt@umn.edu
Owen K. Neill – okneill@umich.edu