MOLYBDENUM CONCENTRATES – COMBINING DEVELOPMENT OF AN XRF BORATE FUSION METHOD WITH CERTIFICATION OF STANDARD REFERENCE MATERIALS

John R. Sieber[1] and Donald I. Lincoln[2]

[1]*National Institute of Standards and Technology, Analytical Chemistry Division 100 Bureau Drive, Gaithersburg, MD 20899, USA*
[2]*Highland Valley Copper, P.O. Box 1500, Logan Lake, B.C. CANADA VOK 1W0*

ABSTRACT

A new borate fusion approach for molybdenum concentrates has been developed by NIST for use in the value assignments of two new Standard Reference Materials (SRMs®). The new borate fusion method is based on an old, industry method that was revised to incorporate modern practices used successfully by NIST for geological materials and their derivative products. The industry method is still used for determination of Mo and is based on fusion with $Na_2B_4O_7$ and addition of Nb as an internal standard. The revised method uses fusion with mixed $Li_2B_4O_7$ and $LiBO_2$ flux and retains the Nb internal standard. Updated by NIST, the new method provides quantitative results for Fe, Cu, Mo, and Pb, validated in part by analyses of two older certified reference materials. Cooperating industry laboratories performed analyses using three different classical methods and a flame atomic absorption spectrometry method for Mo, plus inductively coupled plasma optical emission spectrometry (ICPOES) and flame atomic absorption spectrometry (FAAS) methods for minor constituents Fe, Cu, and Pb, and trace constituents. The entire set of results, including NIST XRF and industry methods, will be used to certify SRM 333a Molybdenum Sulfide Concentrate and SRM 423 Molybdenum Oxide Concentrate.

INTRODUCTION

Reference materials for Mo concentrates are important for validation of test methods widely used by the copper and molybdenum mining industry. Molybdenum is commonly obtained during the processing of copper ore deposits. The most abundant Mo minerals are molybdenite (MoS_2) and wulfenite ($PbMoO_4$). While the pure minerals can be found as attractive specimens, the production of Mo is from ores comprised mostly of chalcopyrite and bornite. Copper and molybdenum sulfides are liberated from ore by wet grinding, then floated using a hydrophobic xanthate reagent. Differential flotation with NaHS suppresses Cu with the Mo floating. Bulk MoS_2 is roasted to MoO_3, and both forms are sold commercially. Steel manufacturers utilize approximately 75 % of produced Mo concentrates to harden steel by alloying it with Mo. Another significant commercial use of Mo compounds is in lubricating oils and greases.

In 1973 (Cali, 1977), NIST issued Standard Reference Material (SRM®) 333 Molybdenum Concentrate[1] to support molybdenum mining and refining industries. SRM 333 was a low quality sulfide concentrate because the Fe and Cu mass fractions were 1 %, and the material was not de-oiled and dried prior to packaging. SRM 333 was certified for mass fractions of Cu, Mo,

---

[1] In 1973, a provisional certificate was issued. In 1977, a full certificate was issued for SRM 333.

and Re. The only other known certified reference material (CRM) for molybdenum concentrates is CRM 5-88 from the Central Geological Laboratory of Mongolia[2] (Erdenebayar, 1986). This material was certified in 1986 and expired in 2006, but the certification was extended prior to that date (Erdenebayar, 2003). CRM 5-88 is also a low grade MoS_2 concentrate containing high Fe and Cu. It is certified for Mo and Cu with non-certified values for Fe, Pb and several other elements.

In 2007, a group of mining companies and commercial laboratories approached NIST with a proposal to develop two new SRMs, one for MoS_2 and one for MoO_3. The companies participate in an annual proficiency test program to verify their competence in elemental analysis of Mo concentrates. In all, twenty nine companies participated in the 2008 program. In the past few years, these laboratories have nearly exhausted their supplies of SRM 333. Some laboratories also determine Pb from the lead molybdate in ores and Fe from chalcopyrite, bornite, and $FeCl_3$ used as a reagent in the processing of ore. The companies were able to provide two high quality concentrates for candidate materials and a large set of analytical results from classical and instrumental test methods. The results came from five different methods for Mo, including two gravimetric methods based on precipitation of $PbMoO_4$ (Scott, 1917), or precipitation by complexation of Mo by benzoin α-oxime (Yagoda and Fales, 1936), a volumetric method based on reduction of all Mo to Mo^{+2} followed by $KMnO_4$ titration to Mo^{+3} (Scott, 1917), a sodium tetraborate fusion/XRF method, and a flame atomic absorption spectrometry (FAAS) method. Some participants of the program determined the minor elements Fe, Cu, Re, and Pb, plus a number of trace elements using FAAS or inductively coupled plasma optical emission spectrometry (ICPOES).

The SRM development project was begun in 2008. To successfully certify an SRM, NIST is required by its procedures (May, *et al.*, 2000) and its quality system to obtain quantitative results from at least two independent test methods with at least one test method performed at NIST by qualified analysts. X-ray fluorescence spectrometry (XRF) with borate fusion was chosen for determinations of Mo, and if possible, Fe, Cu, Re, and Pb. Other test methods available at NIST would have required more labor, high dilution factors, or very small specimens. NIST has applied XRF and borate fusion to numerous materials including cement, alloys, geological materials (Sieber, 2002; Sieber *et al.*, 2002; Sieber *et al.*, 2005), soils (Mackey, 2009), and more, but never to Mo concentrates. There is an old industry method (Court, 2009) for the determination of Mo after borate fusion. If that method could be implemented and validated at NIST, certification of one or more values could be possible.

The existing borate fusion and XRF method used by industry is based on fusion of 1 g of Mo concentrate with 18 g $Na_2B_4O_7$ at 1250 ºC after ignition of the concentrate at 525 ºC. The fusion procedure includes addition of BaO_2 as an oxidizer and addition of Nb_2O_5 as an internal standard for Mo determination. Barium also serves as a heavy absorber to reduce the differences in matrix effects among the various compositions of specimens and calibrants. The industry

---

[2] Certain materials, commercial equipment, and commercial laboratories were named in this paper for the purpose of adequately specifying the experimental conditions and the sources of analytical results. Such descriptions do not constitute endorsement by the National Institute of Standards and Technology, nor do they imply that the materials, equipment and services are necessarily the best for the purpose.

method is not used for determinations of other key elements such as Fe, Cu, Re, or Pb, probably because the dilution factor of 20 is too high. NIST XRF experts rely on borate fusion using mixtures of $Li_2B_4O_7$ and $LiBO_2$, always done at much lower temperatures to minimize volatilization of flux and other constituents. It was expected that Nb would serve as an acceptable internal standard for Fe, Cu, Re, and Pb because all are minor constituents (≤ 2 % each) in the candidate reference materials and in the known certified reference materials. The redesigned XRF method was validated in part by analyzing two old CRMs and in part using the data from the proficiency program because there were difficulties with the results for the two, very old, CRMs of sulfide concentrates. The two concentrate materials for the proficiency test program were evaluated to demonstrate that they were sufficiently homogeneous for the dual purposes of a proficiency program and development as NIST SRMs. NIST and industry results were used certify SRM 333a Molybdenum Sulfide Concentrate and SRM 423 Molybdenum Oxide concentrate. Certificates of analysis for these SRMs will be published by NIST after review and approval under the NIST Quality System for reference materials and measurement services.

MATERIALS

Both Mo concentrates provided by mining companies were prepared from high grade concentrates, dried, de-oiled, and packaged in foil-lined, heat-sealed plastic pouches (60 g per pouch). Samples for homogeneity testing and for the proficiency program were selected by stratified random sampling of pouches of each concentrate material. NIST performed homogeneity testing using XRF measurements of pressed briquettes prepared from 8.0 g samples, two per package from each of 16 packages. This approach was designed to follow the guidelines in ISO Guide 35 (ISO, 2006). It compares within-package variance to among-package variance using the F-test and control chart limits (Wheeler, *et al.*, 1976). Results are summarized in Table 1a for the sulfide concentrate, designated as candidate SRM 333a and Table 1b for the oxide concentrate designated as candidate SRM 423. Table 1 includes the F values, P-values, relative standard deviations (%RSD), and standard errors of X-ray counting (%CSE). In all cases, the overall %RSD is acceptable, and the data passes the F-test. Referee and specification analyses for Mo in concentrates must be performed with relative uncertainties < 1 %. Therefore, the materials selected for proficiency samples and SRMs must exhibit heterogeneity levels $\ll 1$ %. For the remaining elements, the requirements are less stringent such that %RSD < 2 is acceptable. The measured mass for each material was estimated from the attenuation length (Gullickson, 2009) of the highest energy measured X rays, Mo K-$L_{2,3}$ (17.44 keV), and the density of each pure compound. For MoS_2, the measured mass was estimated to be approximately 1.2 g. For MoO_3, the estimated measured mass was approximately 1.4 g. These quantities are acceptable to industry laboratories that routinely analyze specimens ≥ 1 g.

NEW BORATE FUSION PROCEDURE

Each specimen was prepared for fusion by weighing 1.0 g of MoO_3 or 0.9 g of MoS_2 into a 95 % Pt-5 % Au alloy crucible, followed by 1.5 g of $LiNO_3$ (high purity, Alfa AESAR, Ward Hill, MA), 0.100 g of Nb_2O_5 (high purity, Alfa AESAR), and 7.5 g of flux (66:34 $Li_2B_4O_7$:$LiBO_2$ high purity Spex Certiprep, Edison, NJ) for MoO_3 or 7.0 g of flux for MoS_2 specimens. The ingredients were stirred thoroughly using a small quartz rod.

Table 1. Summary of Homogeneity Test Results for SRM Candidate Materials.

a. Candidate SRM 333a Molybdenum Sulfide Concentrate

Element	F[a]	Passed	P-value	%RSD	%CSE
Fe	1.28	Yes	0.32	0.38	0.32
Cu	0.90	Yes	0.45	0.80	0.79
Mo	1.35	Yes	0.28	0.15	0.087
Re	2.16	Yes	0.069	0.61	0.38
Pb	0.86	Yes	0.62	1.1	0.40

b. Candidate SRM 423 Molybdenum Oxide Concentrate

Element	F[a]	Passed	P-value	%RSD	%CSE
Fe	0.84	Yes	0.63	0.23	0.23
Cu	1.18	Yes	0.37	0.29	0.75
Mo	0.65	Yes	0.80	0.11	0.082
Re	0.81	Yes	0.65	1.0	0.37
Pb	0.79	Yes	0.68	0.36	0.36

[a] Critical F value, $F_{crit} = 2.35$.

Borate fusion was carried out with a Perl'X3 induction-heated machine, (PANalytical, Almelo, The Netherlands). Platinum ware included a 100 g crucible of approximately 30 mL capacity and a 100 g casting dish designed to produce a 30 mm diameter bead. The fusion program consisted of nine steps enumerated here. Steps 5 and 6 are manual; the rest are automated.

Fusion program:
1) Heat to 200 °C for 2 min.
2) Heat to 600 °C for 6 min.
3) Fuse at 975 °C for 5 min with mixing by rocking the crucible.
4) Cool to room temperature.
5) Manually rotate crucible 90° in ceramic sleeve.
6) Manually add several drops of a 25 % LiI (aq) non-wetting agent.
7) Fuse at 975 °C for 5 min with mixing by rocking.
8) Cast into Pt-Au dish with slow cooling for 40 s followed by forced-air cooling from below the dish for 50 s.

The first step at 200 °C removes remaining moisture. The second step at 600 °C ignites and oxidizes the specimen in the presence of $LiNO_3$. The fusion program is stopped between the fusion steps for manual rotation of the crucible because the machine does not rotate the crucible during mixing, which is achieved by simple rocking. After the crucible is reheated, the molten mixture laps more of the inside of the crucible for more complete incorporation of all ingredients. While the crucible is cool, the LiI non-wetting solution is added. Doing this late in the program allows the use of a smaller quantity of iodine.

QUANTITATIVE XRF APPROACH

The calibration for this method used synthetic calibration standards to bracket the fused samples and measured count rates from Nb K-L$_{2,3}$ as the internal standard for all elements. This approach has been used successfully in many instances. It serves to control matrix effects, and it is characterized by uncertainty sources that are easily estimated and of low magnitude. The primary reference materials used to prepare the synthetic calibrants were the high-purity compounds MoO_3 (Alfa AESAR, Ward Hill, MA) and $KReO_4$ (high purity, Alfa AESAR, Ward Hill, MA), and NIST single-element spectrometric solutions: SRM 3114 Copper, SRM 3128 Lead, and SRM 3126a Iron. The solutions and the $KReO_4$ were fused as single element beads, which were crushed and used as ingredients in the synthetic calibrants. The MoO_3 was used directly after heat treatment to ensure stoichiometry. High-purity Li_2SO_4 (hemihydrate) was used in half the calibrants to bracket the S count rates from specimens of fused MoS_2.

Equation 1 is the general calibration algorithm for the internal standard approach, in this case added Nb. For the elements determined in Mo concentrates, Eq. 1 has no term for line overlap correction because, X-ray lines are available for which there are no spectral overlaps.

$$C_i = D_i + E_i \cdot R_i / R_{Nb} \qquad (1)$$

where C_i = the mass fraction of the analyte,
D_i = the intercept,
E_i = the slope of the linear model,
R_i = the measured count rate for the analyte,
R_Nb = the measured count rate for Nb internal standard.

The spectrometer was a PANalytical model PW2404 equipped with a Rh end-window tube. Measurement conditions and estimates of the limits of quantification, L_Q, are in Table 2. The same measurement conditions were applied to homogeneity testing already discussed.

Table 2. Measurement Conditions

Elem.	Line	Crystal	Collimator	Detector	kV, mA	Time (s)	L_Q (mg/kg)
S	K-L$_{2,3}$	Ge(111)C	100 µm	Ar Flow	30, 125	2	
Fe	K-L$_{2,3}$	LiF(200)	100 µm	Ar Flow	60, 63	4	**10**
Cu	K-L$_{2,3}$	LiF(200)	100 µm	Both	60, 63	8, 4	**100**
Re	L$_2$-M$_4$	LiF(200)	100 µm	Xe sealed	60, 63	84, 72	**100**
Nb	K-L$_{2,3}$	LiF(220)	100 µm	Xe sealed	60, 63	6	
Mo	K-L$_{2,3}$	LiF(220)	100 µm	Xe sealed	60, 63	2	
Pb	L$_2$-M$_4$	LiF(200)	100 µm	Xe sealed	60, 63	24, 16	**40**

Note: A 750 µm Al primary beam filter was used for Nb and Mo.

XRF RESULTS AND VALIDATION

Certified Reference Materials

Quantitative results from the NIST borate fusion/XRF procedure are given in Table 3 for candidate SRM 333a MoS_2 and in Table 4 for candidate SRM 423 MoO_3. All individual results from measurements of duplicate specimens (A and B) from each of six pouches are shown. The entire uncertainty budget is provided in each table with the components of uncertainty described in Table 5. Results for samples of SRM 333 (one each from four bottles) and CRM 5-88 (from a single bottle) are given in Table 6 and Table 7, respectively.

Results for Mo in the CRMs show a high bias of approximately 5 % relative to the certified values. Results for Cu are low for SRM 333, but accurate for CRM 5-88. Results for Re in both CRMs were 40 % to 50 % greater than the certified values. Results for Fe and Pb can only be

Table 3. Quantitative Results for SRM 333a from NIST Borate Fusion/XRF Method
(Results on as-received basis)

Sample	Fe (%)	Cu (%)	Mo (%)	Re (%)	Pb (%)
098-S-A	1.000	0.0529	55.26	0.0337	0.00892
098-S-B	1.007	0.0515	55.31	0.0390	0.00913
199-S-A	1.005	0.0542	55.61	0.0361	0.00889
199-S-B	1.001	0.0525	55.21	0.0377	0.00892
261-S-A	0.992	0.0497	55.63	0.0401	0.00849
261-S-B	1.005	0.0503	55.63	0.0399	0.00848
464-S-A	0.982	0.0536	54.43	0.0335	0.00721
469-S-B	1.030	0.0534	56.88	0.0435	0.00875
533-S-A	1.007	0.0519	55.28	0.0398	0.00911
533-S-B	0.998	0.0537	55.22	0.0369	0.00872
2008-1-A	1.003	0.0523	55.69	0.0353	0.00883
2008-1-B	1.004	0.0518	55.20	0.0368	0.00835
Average	1.003	0.0523	55.45	0.0377	0.00865
s	0.011	0.0014	0.57	0.0029	0.00051
n	12	12	12	12	12
u_f	0.021	0.0036	0.30	0.0047	0.00039
p	4	3	4	4	4
u_m	0.021	0.0036	0.30	0.0047	0.00039
u_s	0.0012	0.00009	0.055	0.00004	0.00001
u_b	0.00015	0.00001	0.0083	0.00001	0.000001
u_c	0.016	0.0030	0.28	0.0037	0.00033
$U_{k=2}$	0.033	0.0060	0.57	0.0074	0.00067

Table 4. Quantitative Results for SRM 423 from NIST Borate Fusion/XRF Method
(Results on as-received basis)

Sample	Fe (%)	Cu (%)	Mo (%)	Re (%)	Pb (%)
045-OX-A	1.702	0.0650	59.13	0.0063	0.04492
045-OX-B	1.697	0.0625	58.72	0.0071	0.04500
066-OX-A	1.703	0.0609	59.29	0.0049	0.04536
066-OX-B	1.689	0.0603	58.92	0.0068	0.04515
2008-2-A	1.690	0.0850	58.84	0.0077	0.04411
2008-2-B	1.704	0.0654	59.32	0.0052	0.04455
208-OX-A	1.700	0.0753	59.09	0.0061	0.04433
208-OX-B	1.697	0.0609	58.97	0.0075	0.04516
317-OX-A	1.716	0.0650	59.24	0.0069	0.04472
317-OX-B	1.689	0.0627	59.09	0.0026	0.04386
494-OX-A	1.648	0.0664	57.60	0.0073	0.04289
494-OX-B	1.699	0.0634	59.24	0.0067	0.04450
Average	1.695	0.0661	58.95	0.0063	0.0445
s	0.016	0.0071	0.47	0.0014	0.00069
n	12	12	12	12	12
u_f	0.035	0.0046	0.32	0.0046	0.0023
p	4	4	4	4	4
u_m	0.035	0.0046	0.32	0.0046	0.0023
u_s	0.0019	0.00012	0.059	0.00001	0.00004
u_b	0.00028	0.00001	0.0097	0.000001	0.00001
u_c	0.028	0.0041	0.28	0.0035	0.0018
$U_{k=2}$	0.055	0.0081	0.56	0.0070	0.0036

compared to the information values for CRM 5-88, and are much lower than the information values. For the two most important elements, Cu and Mo, this performance is acceptable, but not as good as is typical for methods based on the borate fusion/XRF method with custom synthetic calibrants. The most plausible explanation for the apparently poor accuracy is that the two CRMs have changed since they were developed. As was mentioned above, both SRM 333 and CRM 5-88 are more than 14 years old. Both materials are low quality MoS_2 concentrates that originally contained oils and moisture. Over years of use, these volatile constituents have been lost, causing the Mo mass fractions to increase. This assertion is based on years of observations at one industry laboratory. A test for volatile constituents was done at NIST by washing a quantity of SRM 333 with acetone. After three washes, the original mass was recovered, indicating the absence of volatile compounds. This evidence explains the high bias seen for Mo results in Tables 6 and 7. The potential for low results for Cu can be explained by the high mass fraction of S in MoS_2 concentrates. Sulfur must be oxidized during the borate fusion or it can be lost from the crucible. If insufficient oxidizer is present, the environment inside the crucible may become reducing causing small quantities of Cu to go into the surface of the Pt-Au alloy. This phenomenon has been observed in experiments at NIST when high mass fractions of halogens are present in materials prior to fusion. The fact that approximately one half of the S is lost from MoS_2 during fusion also supports this hypothesis. The following discussion comparing the NIST XRF results to industry results from different test methods will show that Cu is retained quantitatively during fusion of MoO_3 concentrate. Additional tests are warranted to improve the reliability of Cu retention during fusion of MoS_2 concentrates. Insufficient information is available to suggest hypotheses regarding the observed performance for Fe, Re and Pb.

Table 5. Components of Uncertainty of NIST Borate Fusion/XRF Method for Molybdenum Concentrates

Component	Basis	Type	DF
Variability of Sample Preparation and Measurement, s	Standard deviation of the mean of calculated mass fractions for n specimens.	A	n - 1
Variability of Calibrant Preparation and Measurement, u_f	Root-Mean-Square (RMS) deviation of calculated values from chemical values for fit of calibration model (linear equation).	A	p - 1
Uncertainty due to Calibration Model, u_m	Asserted to be no greater than u_f, the RMS deviation of the calibration model.	B	∞
Assay of Primary Material, u_s	$u_s = U/k$, where U = expanded uncertainty for each spectrometric solution SRM with expansion factor k given on the certificate. For the two pure compounds, the standard uncertainty of the assay was assumed to be 0.1 % absolute with a uniform distribution.	B	∞
Uncertainty of Balance Calibration, u_b,	0.2 mg across range of masses. Tested using NIST-traceable weights set. Estimate expressed as a relative uncertainty and converted to original sample basis. A uniform distribution was assumed.	B	∞
Combined uncertainty, u_c	Calculated from $u_c = \sqrt{\frac{s^2}{n} + \frac{u_f^2}{p} + \frac{u_m^2}{3} + \frac{u_s^2}{3} + \frac{2u_b^2}{3}}$	-	-
Expanded uncertainty, U	Defined as $U_{k=2}$ with expansion factor k = 2 for an approximate 95 % level of confidence	-	-

Industry Proficiency Program

The results from the new borate fusion XRF method can be compared to results from an industry proficiency program in which the two concentrates were analyzed by over 25 expert laboratories. For each element of interest in each concentrate, there exists a population of results obtained using two to four test methods. The NIST XRF results were shown with high probability to be indistinguishable from the rest of the members of the populations of industry test results.

Statistical tools in a spreadsheet application developed by Duewer (Duewer, 2008) were used to create Figures 1 through 5 that present the industry results and NIST XRF results. In all five figures, NIST XRF results are highlighted in a yellow box. The black horizontal line is the consensus value for the population of results in the figure. The consensus values are the mean values of the population. The red horizontal lines mark an uncertainty interval for the consensus value, which is an expanded uncertainty at the 95 % level of confidence calculated as $U = ku_c$, where k is an expansion factor chosen from the Student's t table on the basis of the number of degrees of freedom and u_c is a combined uncertainty calculated, at the level of one standard deviation, by combining a pooled, within method variance with a between method variance following the ISO and NIST Guides (JCGM, 2008). The blue horizontal lines mark a 95 % confidence interval for the population of values calculated as $t \times s$, where t = Student's t, and s = the standard deviation the results.

Table 6. Quantitative Results for SRM 333 from NIST Borate Fusion/XRF Method

(Results on as-received basis)

Sample	Fe (%)	Cu (%)	Mo (%)	Re (%)	Pb (%)
1	1.1547	0.969	58.15	0.1224	0.00746
2	1.1416	0.981	58.04	0.1186	0.00786
3	1.1482	0.972	57.89	0.1282	0.00744
4	1.1623	1.016	58.54	0.1312	0.00798
Mean	1.1517	0.984	58.16	0.1251	0.00768
s	0.0088	0.022	0.28	0.0057	0.00028
n	4	4	4	4	4
u_f	0.013	0.0095	0.56	0.0012	0.00007
p	4	4	4	4	4
u_m	0.013	0.0095	0.56	0.0012	0.00007
u_s	0.0013	0.0018	0.058	0.00013	0.00001
u_b	0.00017	0.00015	0.0087	0.00002	0.000001
u_c	0.011	0.013	0.45	0.0030	0.00015
$U_{k=2}$	0.022	0.026	0.90	0.0060	0.00030
Certified		1.038	55.3	0.087	
Uncertainty[a]		0.02	0.2	0.002	

[a] The uncertainty given on the certificate is believed to be a combined uncertainty and was multiplied by 2 to express it here at an approximate 95 % level of confidence.

Table 7. Quantitative Results for CRM 5-88 from NIST Borate Fusion/XRF Method

(Results on as-received basis)

Sample	Fe (%)	Cu (%)	Mo (%)	Re (%)	Pb (%)
1	1.4172	1.308	53.77	0.0736	0.00737
2	1.4103	1.309	54.01	0.0693	0.00653
3	1.4164	1.345	54.57	0.0763	0.00617
4	1.4169	1.330	54.16	0.0782	0.00765
Mean	1.415	1.323	54.13	0.0743	0.00693
s	0.0033	0.018	0.34	0.0039	0.00070
n	4	4	4	4	4
u_f	0.014	0.0128	0.52	0.0007	0.00007
p	4	4	4	4	4
u_m	0.014	0.013	0.52	0.0007	0.00007
u_s	0.0016	0.0024	0.054	0.00007	0.00001
u_b	0.00022	0.00020	0.0082	0.00001	0.000001
u_c	0.011	0.013	0.44	0.0020	0.00035
$U_{k=2}$	0.021	0.027	0.87	0.0040	0.00070
Certified	(2.4)	1.35	51.6	0.05	(0.019)
U		0.03	0.2	0.006	

The populations of results for Mo are shown in Fig. 1a for the sulfide concentrate and Fig. 1b for the oxide concentrate. The graphs show the Mo results grouped by test methods which are, from left to right, benzoin α-oxime gravimetric method (nine results), industry $Na_2B_4O_7$ fusion method (five results), $PbMoO_4$ gravimetric method (five results), $KMnO_4$ titration method (11 results), and FAAS (one result). The FAAS result at the right was discarded because a dilution factor of 20 000 was used to get the concentration of Mo into the measurement range of the spectrophotometer, and in the process, an apparent bias was introduced causing the value to be an obvious outlier from the rest of the population. In both Fig. 1a and Fig. 1b, the NIST XRF results obtained using Li borate fusion (highlighted in yellow) are clearly within the 95 % confidence limits (blue horizontal lines) for the entire population of 30 values. The only issue of concern is the notably poor repeatability of the NIST XRF results. Compare the vertical bars on each data point, which represent 2*s* or two times the repeatability standard deviation of each set of results. Experiences of other researchers suggest that it may be possible to improve the repeatability for Mo measurements by decreasing the mass fraction of Mo in the beads by either using a lower specimen mass or increasing the mass of flux (Anzelmo, 2009).

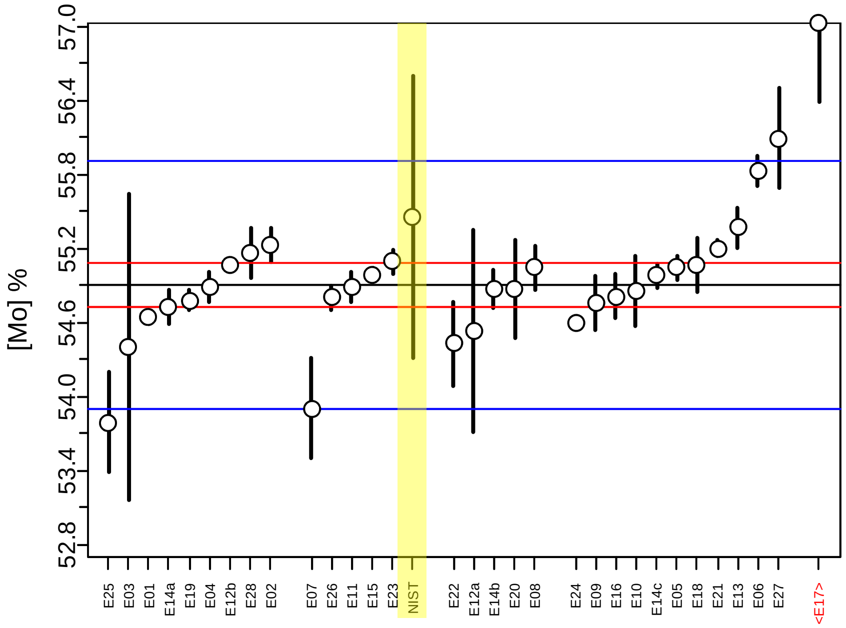

Figure 1a. Proficiency test results for Mo in candidate SRM 333a MoS_2 with results grouped by test method (l to r) oxime precipitation, XRF, $KMnO_4$ titration, $PbMoO_4$ precipitation, AAS. NIST XRF highlighted. The lab at the far right was excluded for a technical flaw in the AAS test method.

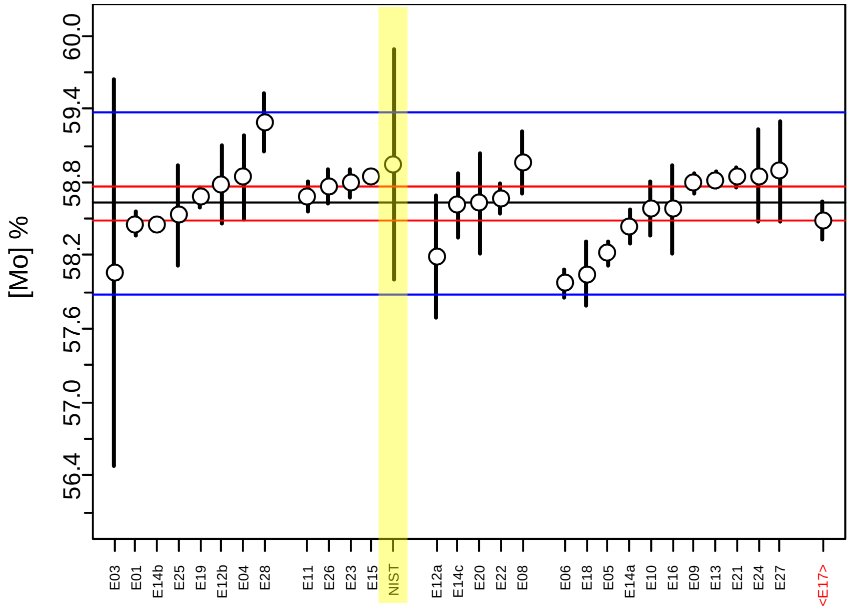

Figure 1b. Proficiency test results for Mo in candidate SRM 423 MoO_3 with results grouped by test method. The lab at the far right was excluded for a technical flaw in the AAS test method.

Similar results and comparisons were obtained for Cu in Figure 2, Pb in Figure 3, and Fe in Figure 4. In these three figures, the results are arranged in order of magnitude, not by test method. All industry results were obtained using either FAAS or ICPOES. In all cases, the NIST XRF results in the yellow box are clearly within the populations with 95 % confidence, and most times are near the consensus values of the data. For Cu in the sulfide concentrate (Fig. 2a), the NIST XRF result is near the lower end of the range of values. This result is consistent with the result for SRM 333 and supports the hypothesis of reduced S in the material causing small losses of Cu to the Pt crucible during fusion.

Results for Re are shown in Figure 5. This figure shows three or four results for each material and the unweighted mean of those results. The limited amount of data and the relatively high scatter of values prevent any conclusions except that these methods are not in good agreement at these low mass fractions of Re. One clear reason is the high estimate of the limit of quantification for Re for the NIST XRF method (Table 2) in comparison to the mass fractions in the candidate materials. It is caused in part by the low sensitivity of the line that was measured because no other Re line is available. The NIST XRF method with sample preparation by fusion with Li borate flux method cannot be used for Re without improvements. At this time, the element Re appears to be of low significance to the mining industry.

VALUE ASSIGNMENTS FOR NEW SRMS

Both the homogeneity of the materials and the collected quantitative results from multiple test methods satisfy the requirements of NIST for certification of SRM 333a Molybdenum Sulfide Concentrate and SRM 423 Molybdenum Oxide Concentrate (May, *et al.*, 2000). After final review and approval, NIST will publish certificates for these SRMs. In addition, there are values for elements not discussed in this paper that will be included in the certificates. The certificate of analysis is the sole authoritative source of values for SRM issued by NIST.

CONCLUSIONS

In this work, it has been shown that borate fusion with lithium borates and Nb internal standard can be used as the basis of a test method for quantitative determinations of Fe, Cu, Mo, and Pb in molybdenum concentrates, both MoS_2 and MoO_3. A critical evaluation of the results indicates that it may advisable to attempt to improve the repeatability of the method because the results from classical test methods for Mo are more precise. The results obtained at NIST and industry labs will be used to assign certified, reference and information values for two new SRMs.

ACKNOWLEDGEMENTS

This work would not have been possible without the investments of the participating laboratories of the proficiency test program. Unfortunately, fewer than half gave permission to credit them for their efforts.

The authors are grateful for the assistance of K. Heaton of Highland Valley Copper with the records of the proficiency program.

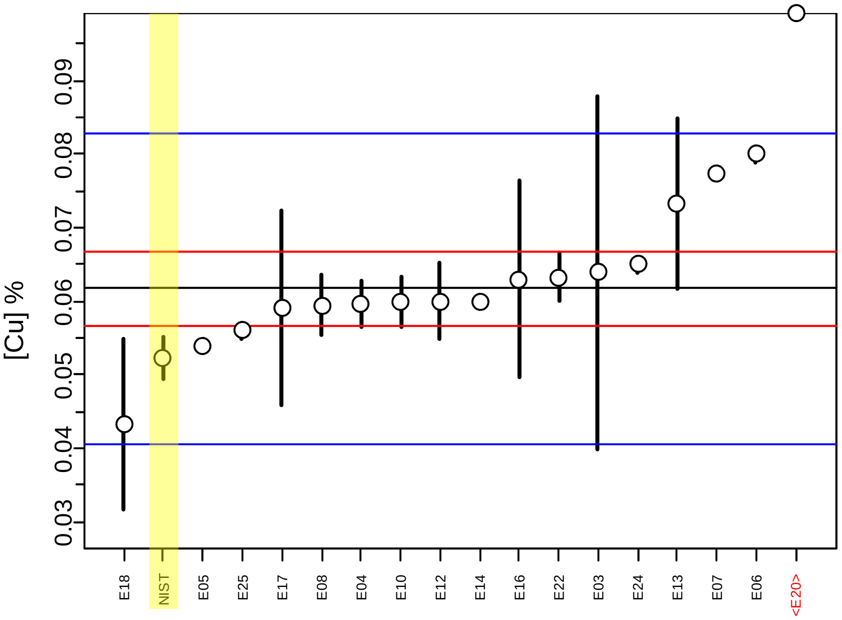

Figure 2a. Proficiency test results for Cu in candidate SRM 333a from ICP-OES and AAS methods. NIST XRF highlighted. Results are arranged in order of magnitude, not by test method. The result marked in red on the horizontal axis is off scale and was excluded as an obvious outlier.

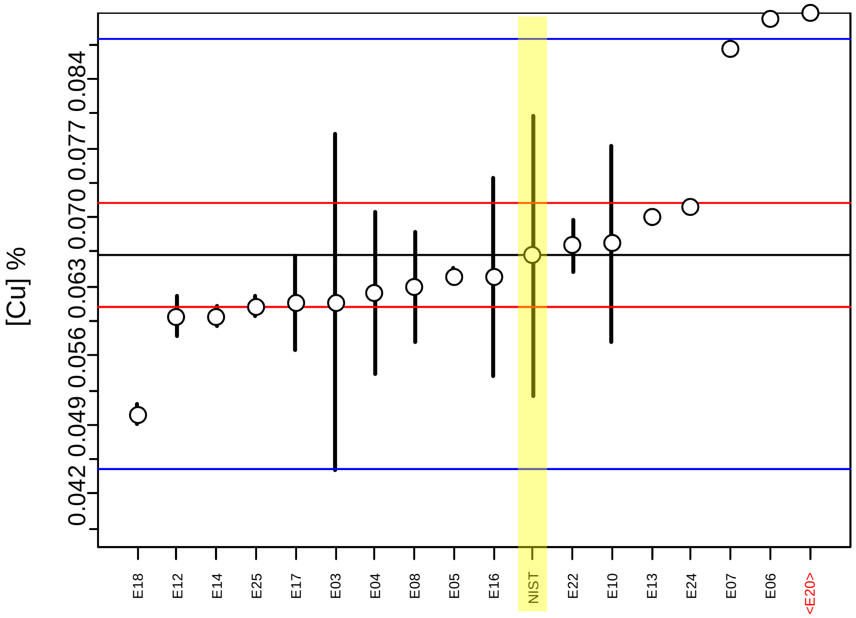

Figure 2b. Proficiency test results for Cu in candidate SRM 423 from ICP-OES and AAS methods. Results are arranged in order of magnitude, not by test method. The result marked in red on the horizontal axis is off scale and has been excluded as an obvious outlier.

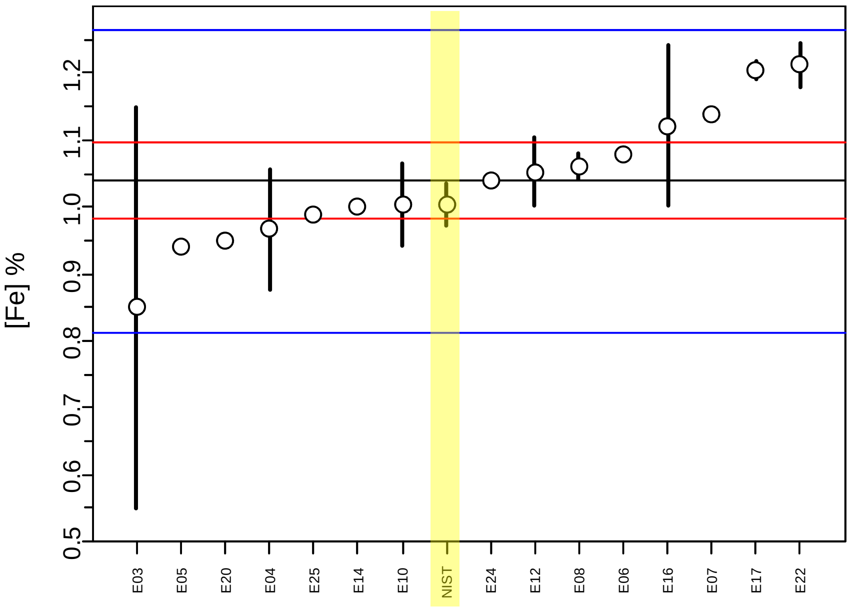

Figure 3a. Proficiency test results for Fe in candidate SRM 333a from ICP-OES and AAS methods. Results are arranged in order of magnitude, not by test method.

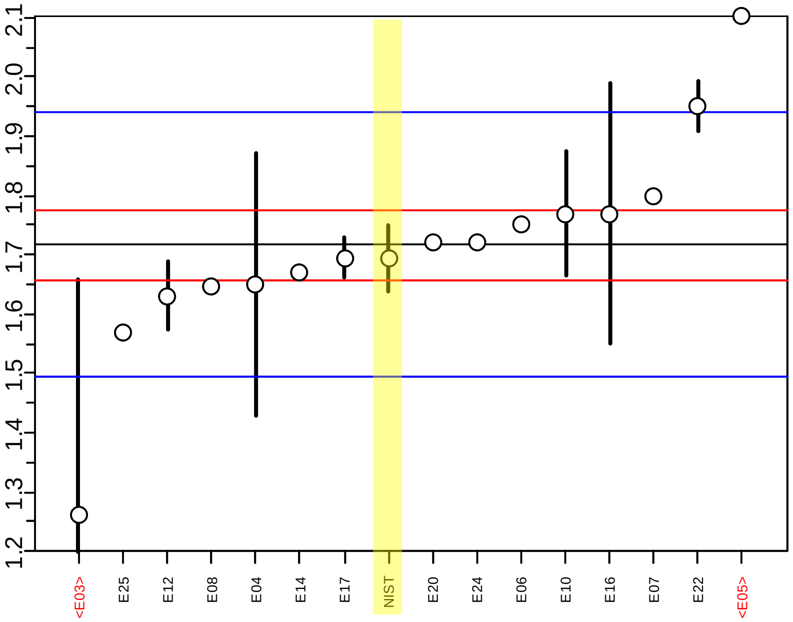

Figure 3b. Proficiency test results for Fe in candidate SRM 423 from ICP-OES and AAS methods. Results are arranged in order of magnitude, not by test method. Results marked in red on the horizontal axis have been excluded as obvious outliers.

[Fe] %

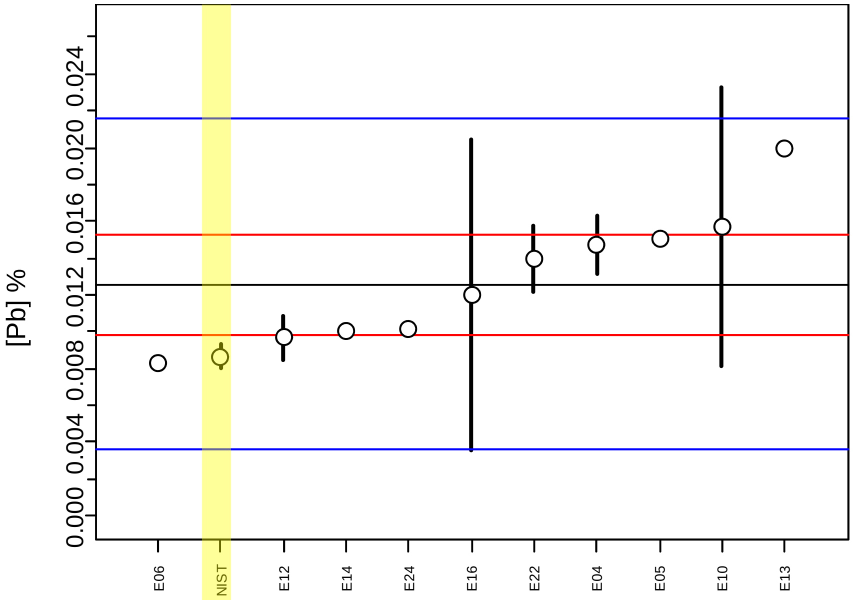

Figure 4a. Proficiency test results for Pb in candidate SRM 333a from ICP-OES and AAS methods. Results are arranged in order of magnitude, not by test method.

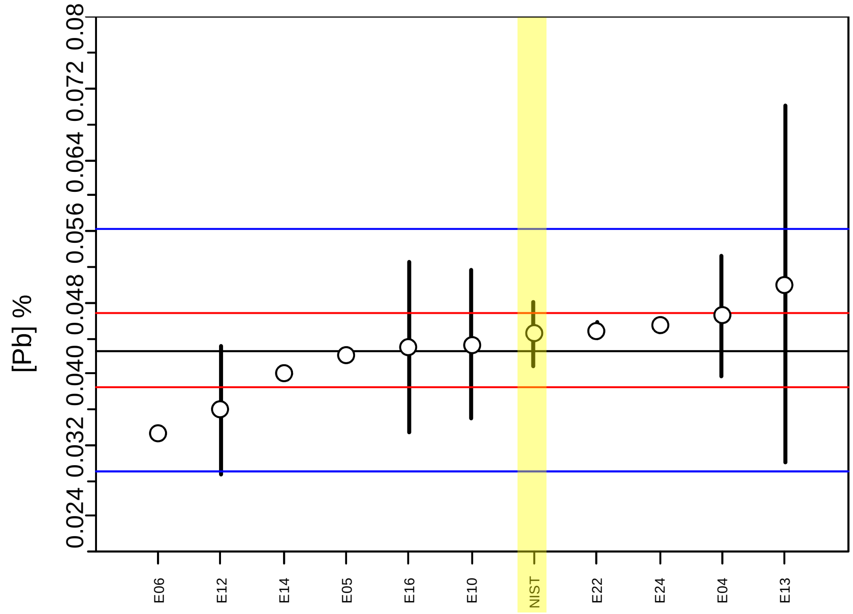

Figure 4b. Proficiency test results for Pb in candidate SRM 423 from ICP-OES and AAS methods. Results are arranged in order of magnitude, not by test method.

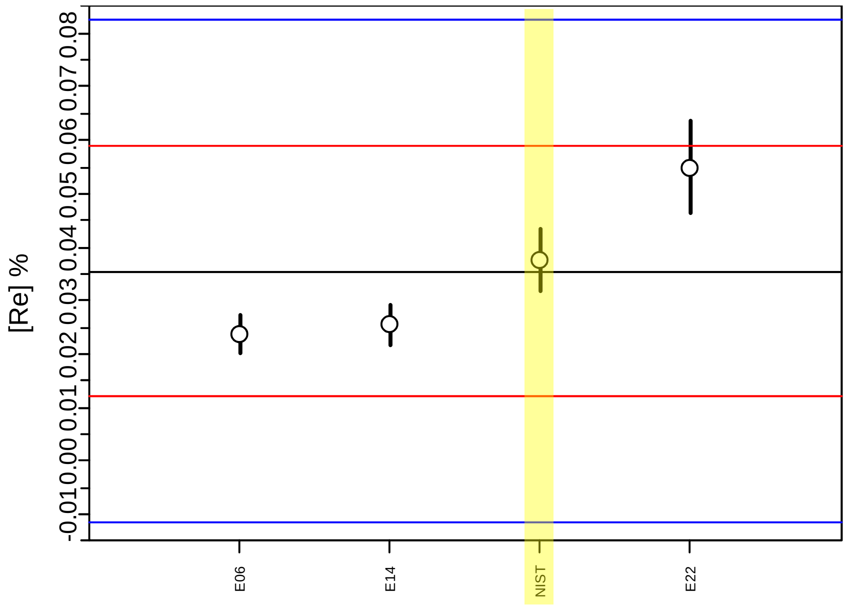

Figure 5a. Proficiency test results for Re in candidate SRM 333a from ICP-OES and AAS methods. Results are arranged in order of magnitude, not by test method.

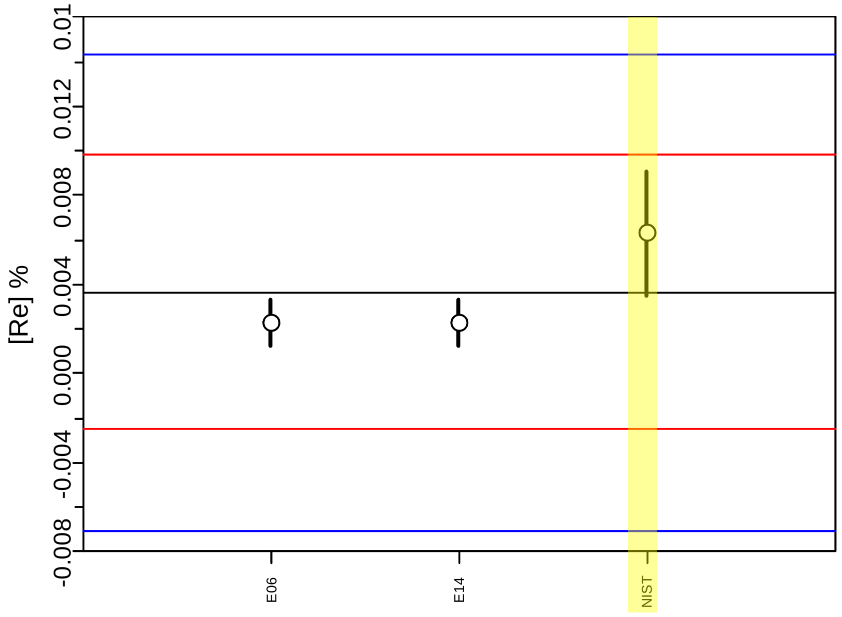

Figure 5b. Proficiency test results for Re in candidate SRM 423 from ICP-OES and AAS methods. Results are arranged in order of magnitude, not by test method.

REFERENCES

Anzelmo, J.A. (2009), personal communication, Colorado Springs, Colorado.

Cali, J. P. (1977). Certificate of Analysis for SRM 333 Molybdenum Concentrate, (Gaithersburg, Maryland): National Institute of Standards and Technology, available at http*://ts.nist.gov/MeasurementServices/ReferenceMaterials/archived_certificates/333.pdf*

Court, D. (2009), Information on the sodium tetraborate method courtesy of Alex Stewart Assayers Ltd.

Duewer, D.L. (2008). *A comparison of location estimators for interlaboratory data contaminated with value and uncertainty outliers*, Accred. Qual. Assur., **13**, 193-216.

Erdenebayar, Ts. (1986). Certificate of Analysis, USZ 5-88 Molybdenum Concentrate “Мов”, Ulaanbaatar, Mongolia: Central Geological Laboratory of Mongolia.

Erdenebayar, Ts. (2003). *Resolution of the National Centre Council for Standardization and Metrology, No. 61, “Re: Extension of validity period of Reference Material Certificates”*, Ulaanbaatar, Mongolia: Central Geological Laboratory of Mongolia.

Gullickson, E. (2009). *X-Ray Interactions With Matter*, available at http://henke.lbl.gov/optical_constants/, Berkeley, California: Lawrence Berkeley Laboratories. See also Henke, B.L., Gullikson, E.M., and J.C. Davis (1993). *X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92*, Atomic Data and Nuclear Data Tables, **54** (2), 181-342.

ISO Guide 35:2006, Reference materials -- General and statistical principles for certification, (2006). Geneva, Switzerland: International Organization for Standardization.

JCGM 100:2008; *Guide to the Expression of Uncertainty in Measurement*, Sèvres Cedex, France: international bureau of Weights and Measures, Joint Committee for Guides in Metrology; available at www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf/. See also Taylor, B.N., Kuyatt, C.E. (1994); *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; Gaithersburg, Maryland: National Institute of Standards and Technology; available at http://physics.nist.gov/Pubs/.

Mackey, E. (2009), Certificates of Analysis for SRM 2709a San Joaquin Soil, SRM 2710a Montana Soil Highly Elevated Traces and SRM 2711a Montana Soil Moderately Elevated Traces; (Gaithersburg, Maryland): National Institute of Standards and Technology, available at https://www-s.nist.gov/srmors/tables/view_table.cfm?table=111-7.htm

May, W.E.; Parris, R.M.; Beck II, C.M.; Fassett, J.D.; Greenberg, R.R.; Guenther, F.R.; Kramer, G.W.; Wise, S.A.; Gills, T.E.; Colbert, J.C.; Gettings, R.J.; MacDonald, B.S. (2000). *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Spec. Pub. 260-136, (Gaithersburg, Maryland): National Institute of Standards and Technology, available at http://ts.nist.gov/MeasurementServices/ReferenceMaterials/upload/SP260-136.PDF.

Scott, W.W. (ed.) (1917). *Standard Methods of Chemical Analysis*, 2nd ed., (Van Nostrand, New York).

Sieber, J. (2002). *Matrix-Independent XRF Methods for Certification of Standard Reference Materials*, Adv. X-Ray Anal., Vol. 45, 493-504.

Sieber, J., Broton, D., Fales, C., Leigh, S., MacDonald, B., Marlow, A., Nettles, S., and Yen, J. (2002). *Standard reference materials for cements*, Cem. Con. Res., **32**, 1899-1906.

Sieber, J.R., Yu, L.L., Marlow, A.F., and Butler, T.A. (2005), *Uncertainty and traceability in alloy analysis by borate fusion and XRF*, X-Ray Spectrom., **34**, 153-159.

Wheeler, J., Hoersch, H., and McGlinchey, E. (eds.) (1976). ASTM Special Technical Publication D, "*ASTM Manual on Presentation of Data and Control Chart Analysis*", Philadelphia, Pennsylvania: American Society for Testing and Materials.

Yagoda, H., and Fales, H.A. (1936), *The Separation and Determination of Tungsten and Molybdenum,* J. Am. Chem. Soc., **58** (8), pp 1494–1501.