

Uncertainty and traceability in alloy analysis by borate fusion and XRF

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Owing to the increasing demand for compliance with quality system standards, analytical laboratories may need to demonstrate the traceability of their results to the International System of Units (SI) or to the values of a certified reference material. To do that, they need to demonstrate the components of uncertainty in their analytical work. At NIST, the goal is to demonstrate traceability to SI units to ensure that results are accepted on a worldwide basis. For XRF spectrometry with borate fusion, traceability to SI is achieved through calibration with spectrometric solution standards or high-purity compounds. The method is capable of achieving relative expanded uncertainty estimates (95% confidence level) of 1% or lower. In this paper, the capability is demonstrated for low alloy-steel and an Al–Ti–Nb–W aerospace alloy. XRF results are compared with certified values and with results from atomic emission methods through a simple bias test. NIST uses the borate fusion/XRF method as part of the value assignment process for Standard Reference Materials®. Copyright © 2004 John Wiley & Sons, Ltd.

INTRODUCTION

The National Institute of Standards and Technology (NIST) follows the Guide to the Expression of Uncertainty in Measurement (ISO GUM)¹ through its own Technical Note 1297² based on the ISO GUM and NIST policy. All reported measurement results must have an expression of uncertainty, preferably a confidence interval based on a combined uncertainty representing statistically derived estimates of uncertainty (Type A) and estimates from other sources (Type B) that together characterize all components of the measurement process. One reason for reporting estimates of uncertainty is the obvious need to provide a measure of how well the value is believed to be known. Another important reason is to provide a means for documenting the traceability of the measurement to an accepted reference. Traceability is a property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.³ As a national metrology institute, NIST must establish traceability of its measurement results and certified values to primary reference materials for the amount of substance. In the International System of Units (SI), the amount of substance is the mole.

What are the consequences for XRF analysis at NIST of the above requirements? If XRF is to be used for value assignment of reference materials, methods must be described in relatively simple mathematical terms and must be calibrated using reference materials having a relatively short chain of traceability to SI. One can immediately

see how a typical XRF method using many calibration standards and matrix coefficients is problematic because it uses a variety of reference materials with no clear links of traceability to SI. Alternative methods based completely on fundamental parameters are difficult to use under these circumstances because the fundamental parameters lack well-defined estimates of uncertainty. In both cases, the overall uncertainty budget is complex and likely to result in higher uncertainties than can be tolerated for certification of new reference materials.

The borate fusion/x-ray fluorescence (XRF) spectrometry method employed by the NIST Analytical Chemistry Division for certification analyses has been described in papers showing its use with cement and zeolite.^{4,5} The method is related to the method of 'Reconstitution' published by Staats and Noack.⁶ The NIST version relies on a small set of synthetic calibration standards to accomplish the calibration in a single step instead of the multiple step approach of Staats and Noack. The key to both approaches is to ensure that calibration standards are so similar in composition to the unknowns that matrix corrections are unnecessary. By design, the NIST method limits the error due to matrix effects to less than 0.1% relative for every element. It is important to make it clear that this analytical approach is different from many XRF methods in that it does not require the quantification of all elements in the specimens. The analyst must account for all elements that have a significant matrix effect on the analytes. Calibration standards must include these additional elements and measurements must be made to ensure that the count rates of the additional elements closely bracket the count rates from the unknowns. However, it is not necessary to complete the quantification of the interfering elements.

This paper describes analyses undertaken for two projects. The first project was an international, pilot comparison exercise for the Consultative Committee for Amount

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of Substance (CCQM) of the International Bureau of Weights and Measures (BIPM). The second project was development of a certified reference material [NIST Standard Reference Material® (SRM)] intended for microanalysis of aerospace alloys. The CCQM project involved analyses of the elements Cr, Mn, Ni and Mo in low-alloy steel provided by the National Metrology Institute of Japan. NIST results are compared to results obtained by four expert laboratories from the US steel industry. Also provided are results for SRM 361 used as a control. The sponsoring laboratories will publish a full report on the CCQM pilot comparison at a later date. The NIST SRM project involved analyses of small pieces (2 mm cubes) of an Al–Ti–Nb–W alloy soon to be available as SRM 2061 for microanalysis and SRM 2062 for bulk analysis. The borate fusion XRF method and an inductively coupled plasma optical emission spectrometry (ICP-OES) method calibrated using matrix-matched standards with an internal standard were used to obtain two independent determinations of the four elements. A synthetic control was created from NIST SRMs to validate the XRF results.

Sample preparation and calibration details for XRF and ICP-OES performed at NIST will be summarized briefly. These topics have been covered in detail in the literature.^{4,5,7–9} The goals of this paper are to describe the uncertainty budgets for XRF determinations and to test for bias in the control results or results from other test methods and laboratories. Uncertainty budgets will be discussed to show the importance of various components of uncertainty. Once uncertainty is documented, traceability links are documented.

EXPERIMENTAL AND RESULTS

Sample preparation

Borate fusion glass bead preparation for XRF analysis

Prior to fusion, each metal sample was weighed into a 95% Pt, 5% Au crucible, with cover. Reactions were carried out on a hot-plate set to a surface temperature of ~110 °C. Low-alloy steel was reacted with high-purity concentrated HNO₃. The aerospace alloy was treated with ~3 ml of concentrated HNO₃ followed by ~1 ml of concentrated HF. Once the metal had completely reacted, the cover was removed and the liquid volume was reduced on the hot-plate. The crucible was cooled and 6.0 g of flux, a 50:50 mixture by mass of Li₂B₄O₇ and LiBO₂, were added.

It should be noted that the alloys were received as chips and small pieces. This portion of the preparation procedure is not designed to dissolve the metal chips. It is designed to put the constituents into higher oxidation states so that the specimen can be fused without problems. Reaction products that do not dissolve in acidic solution will be dissolved by borate fusion provided everything is oxidized.

The Pt crucible and casting dish are weighed empty before sample preparation begins and with glass in them after fusion. In that way, the total quantity of glass is weighed and used to calculate an accurate dilution factor that accounts for loss on ignition by the flux and all changes due to sample preparation. All masses are corrected for buoyancy with the density of the pre-fused flux used as the density of all fused beads.

Fusion of synthetic calibration standards mimicked the fusion of samples as closely as possible. A key step in the preparation of synthetic calibration standards for low-alloy steel was the use of NIST high-purity Fe metal primary reference material NP-Fe-2 to simulate the specimens. NIST primary reference materials are well-characterized, high-purity metals and compounds retained at NIST and used to prepare spectrometric solution standards and other SRMs. The appropriate mass of NP-Fe-2 was subjected to the same acid reaction procedure as the unknowns. Once the Fe had reacted, the flux and other ingredients were added and the mixture was dried and fused.

Other elements needed for synthetic calibration standards were obtained from commercial sources in high-purity form with assay values between 99.8% and 99.999% as the metal or oxide. The stoichiometry of the oxide compounds was assured by heat-treating them as recommended in the literature.^{10–13} For purposes of estimating uncertainty, the assay values were assumed to have a standard uncertainty of 0.1%. These compounds were used to prepare glass working solutions by dilution of the primary materials by borate fusion. This avoided weighing minute quantities of powder or solution.

A PANalytical/SOLED PerI'×3 automated bead preparation machine was used to fuse and cast samples as 30 mm diameter beads. The fusion program consisted of a drying step of 9 min at 200 °C, a melting/oxidation step of 3 min at 850 °C and a fusion step of 975 °C for 6 min. After fusion, the melt was cooled in the crucible, three drops of LiI non-wetting agent (0.25 g g⁻¹ LiI solution) were added and the glass was melted and cast. The resulting bead was cast in one of two platinum dishes, which were shown to produce identical beads prior to the start of the work. All beads have a flat, smooth surface; therefore, no additional preparations were required prior to measurement.

*Acid sample preparation for ICP-OES analysis*⁹

Six samples of aerospace alloy with masses between 0.035 g and 0.063 g were transferred to pre-weighed low-density polyethylene (LDPE) bottles and the bottles were reweighed. The sample mass is the difference between the two weights of the same bottle. To each bottle, 5 ml of deionized water, 5 ml of HCl and 0.4 ml of HF were added. The samples were allowed to react overnight in the loosely capped bottles. The solution in each bottle was examined for light scattering, using a diode laser, to ensure complete digestion of the alloy sample. After an additional 0.8 ml of HF had been added to each bottle, the solution was diluted to 50 g. Depending on the mass of the Al–Ti–Nb–W alloy sample, an aliquot of 2.5 g–4.0 g of the digest containing an estimated 2.7 mg of the alloy from each bottle was transferred to a 60 ml LDPE bottle. A 2 g amount of 107 mg kg⁻¹ Mn solution was added as an internal standard before the solution was diluted to 50 g for measurements by ICP-OES.

Measurements

X-ray spectrometric measurements

A PANalytical PW2404 XRF spectrometer was used to measure the borate beads. For low-alloy steel, the K–L_{2,3}(K α _{1,2})

characteristic x-ray lines of Si, P, Ti, V, Cr, Mn, Fe, Ni, Cu and Mo were measured. Si, P, Ti, V, Fe, and Cu were analyzed to account for all constituents of the steel that could influence the measured count rates of the analytes Cr, Mn, Ni, and Mo. For the aerospace alloy, the K–L_{2,3} characteristic x-ray lines of Al, Ti and Nb and the L₃–M_{4,5}(L α _{1,2}) line of W were measured. In addition to the elements of interest, the L₃–M_{4,5} line of I was measured for use in a line overlap correction because the I L₂–M₄(L β ₁) line directly overlaps Ti K–L_{2,3}. The Rh K–L Compton scatter tube line was used as an internal reference to compensate for the effects of differences in bead thickness resulting from differences in mass or shape. All measurements were made in vacuum (2 Pa–4 Pa) with the generator operated at 3.6 kW with various voltage (kV) and current (mA) settings. Counting times were chosen to obtain relative counting statistical uncertainties ranging from 0.05% to 0.25% depending on the count rate for each element and the number of measurements of the background. A single sample holder of 29 mm inner diameter carried all beads into the spectrometer and held them in the measurement position. The mask between the sample and the collimator was set to view a 27 mm circular area of the bead. For the final quantitative analyses of each alloy, the beads were measured in a batch composed of all synthetic standards, unknown samples and control samples arranged in random order. The time required for the measurements was less than 6 h. No corrections were needed for spectrometer drift because the drift has been demonstrated to be <0.05% over a 12 h period.

Preliminary XRF analyses

Nominal composition estimates were obtained using a standardless fundamental parameters method on several fused specimens of the low-alloy steel and several disks of the aerospace alloy. The composition estimates were used only to design the synthetic calibration standards for each application. Estimates of this nature are sufficiently accurate to obtain the required levels of interfering elements. As explained in the Introduction, interfering elements must be present to render their matrix effects negligible. However, once it has been established that the count rates from interfering elements in the synthetic standards closely bracket the count rates of those elements in the unknowns, the conditions for calibration have been met.

ICP-OES measurements

The samples were analyzed using a Perkin-Elmer Optima 3300 DV ICP-OES instrument. The analytes Al, Ti, Nb and W and the internal standard Mn were measured side-on with respect to the plasma at 394.401, 337.279, 269.706, 239.708 and 260.568 nm, respectively. The absence of cross spectral interferences at each analytical line was verified by measuring five single-element standards containing Al, Ti, Nb, W and Mn. A six-point calibration curve was constructed for each analyte element using matrix-matched calibration standards. The linearity of the calibration curve was verified and the analyte mass fraction in the sample was quantified against the curve.

Low-alloy steel

The objective of the quantitative calibration was to bracket the unknown sample beads with four synthetic standards. The primary calibration reference materials were NIST Single Element Solutions: SRM 3112a for Cr, SRM 3132 for Mn and SRM 3136 for Ni. Molybdenum trioxide (Alfa Aesar) was used for Mo because the NIST SRM solution contains Cl from HCl, which has a deleterious effect on Pt and would complicate the preparation of all fused specimens. Other high-purity compounds and metals plus NIST SRM solutions were used to match standards to samples for Si, P, Ti, V and Cu.

Results of quantitative analysis

Table 1 contains the quantitative results for the four elements of interest in the CCQM low-alloy steel plus a complete uncertainty budget. The calibrations were used to determine the mass fractions of constituents in the fused specimens. Reported values are given on the basis of the original material calculated by multiplying by the ratio of total borate glass formed by fusion (~6.7 g) to the mass of each specimen (~0.500 g).

There are two significant components of Type A uncertainty in Table 1. A standard uncertainty describing the precision of sample preparation and measurement was estimated using the standard deviation of the mean (u_m). Variability of calibrant preparation and measurement was estimated from the fit of a mathematical model (straight line) to the calibration data. The standard uncertainty of the calibration fit (u_f) was calculated from the root mean square (r.m.s.) deviation of the calculated values from the chemical values and the degrees of freedom in the calibration fit. The degrees of freedom in each calibration fit equal the number of calibration standards minus the number of calculated

Table 1. Quantitative results for CCQM low-alloy steel from the NIST borate fusion/XRF method: all values in mass fraction (%)

Sample ^a	Cr	Mn	Ni	Mo
A	0.48804	0.45613	1.9717	0.9444
B	0.48759	0.45486	1.9637	0.9380
C	0.48951	0.45638	1.9660	0.9405
D	0.48624	0.45528	1.9689	0.9479
Average	0.4878	0.4557	1.968	0.9427
u_m	0.00067	0.00036	0.0018	0.0022
u_f	0.00063	0.00011	0.010	0.00091
Type A	0.00092	0.00037	0.010	0.0024
u_s	0.0015	0.0014	0.0044	0.00094
u_b	0.00020	0.00018	0.00079	0.00038
Type B	0.0015	0.0014	0.0045	0.0010
u_c	0.0017	0.0014	0.011	0.0026
U	0.0035	0.0029	0.022	0.0051

^a u_m = standard uncertainty of the mean, $n = 4$; u_f = standard uncertainty of the calibration fit; u_s = standard uncertainty of primary standard; u_b = standard uncertainty of balance calibration; u_c = combined uncertainty; U = expanded uncertainty, $k = 2$, 95% confidence level.

parameters, typically four standards and two parameters, slope and intercept of the line. The values listed as Type A in Table 1 are equal to the root sum of squared standard uncertainty values.

There are two significant components of Type B uncertainty in Table 1. The first is based on the standard uncertainty (u_s) of each assay given for the SRM single-element solutions and high-purity MoO₃ used to create the calibration standards. The assay value for MoO₃ was assumed to have a relative uncertainty of 0.1%.^{10–13} The second Type B uncertainty component was the standard uncertainty of the calibration of the analytical balance (u_b). The balance calibration was tested using a calibrated weight set. The balance and calibrated weights agreed to within 0.2 mg across the range of masses encountered in this work.

The combined uncertainty (u_c) is the root sum of squares of the Type A and Type B uncertainty estimates. The expanded uncertainty ($U = ku_c$ with $k = 2$) approximates the 95% confidence level.² All four combined uncertainty estimates are less than 0.6% relative to the mass fraction of the element. Interestingly, there is no single component of uncertainty that controls the combined uncertainty estimate for all four elements. For Cu and Mn, the largest single uncertainty component is the uncertainty of the certified mass fraction of the SRM solution standard. For Ni, the largest uncertainty component is due to the fit of a straight-line equation to the calibration data. For Mo, the single largest component of uncertainty is the repeatability of preparation and measurement of the fused samples.

Figure 1 illustrates how the NIST borate fusion/XRF method compares with results provided by expert industry

laboratories. At approximately the 95% confidence level, all industry results agree with the NIST results for the CCQM material except the Mo result from Laboratory 4. Industry results were obtained using inductively coupled plasma and direct-current plasma atomic emission spectrometry with all spectrometers calibrated using commercial spectrometric solution standards having direct traceability to NIST SRM solution standards.

SRM 361 control

Control of the quantitative calibrations was demonstrated by analyzing four samples of SRM 361, an alloy similar in composition to the CCQM low-alloy steel. The results are given in Table 2, which shows the mass fractions of the four analytes expressed on the basis of the original SRM. Table 2 also contains a test for bias at the 95% confidence level based on the procedure found in NIST Special Publication 829.¹³ No bias was detected in any of the results compared with the certified values.

Aerospace alloy

The aerospace alloy is a quaternary composition designed specifically to be homogeneous on the micro scale. Certification of this alloy as SRM 2061 (microanalysis form) and SRM 2062 (disk form) is nearing completion with analyses by XRF and ICP-OES to certify the composition. The alloy was prepared using pure Al, Ti, Nb and W to a target composition of ~53% Ti, 31% Al, 11% Nb and 5% W. The composition is unusual owing to the high levels of Nb and W added to ensure homogeneity of the Al and Ti. Each specimen submitted for analysis was a single 2 mm × 2 mm

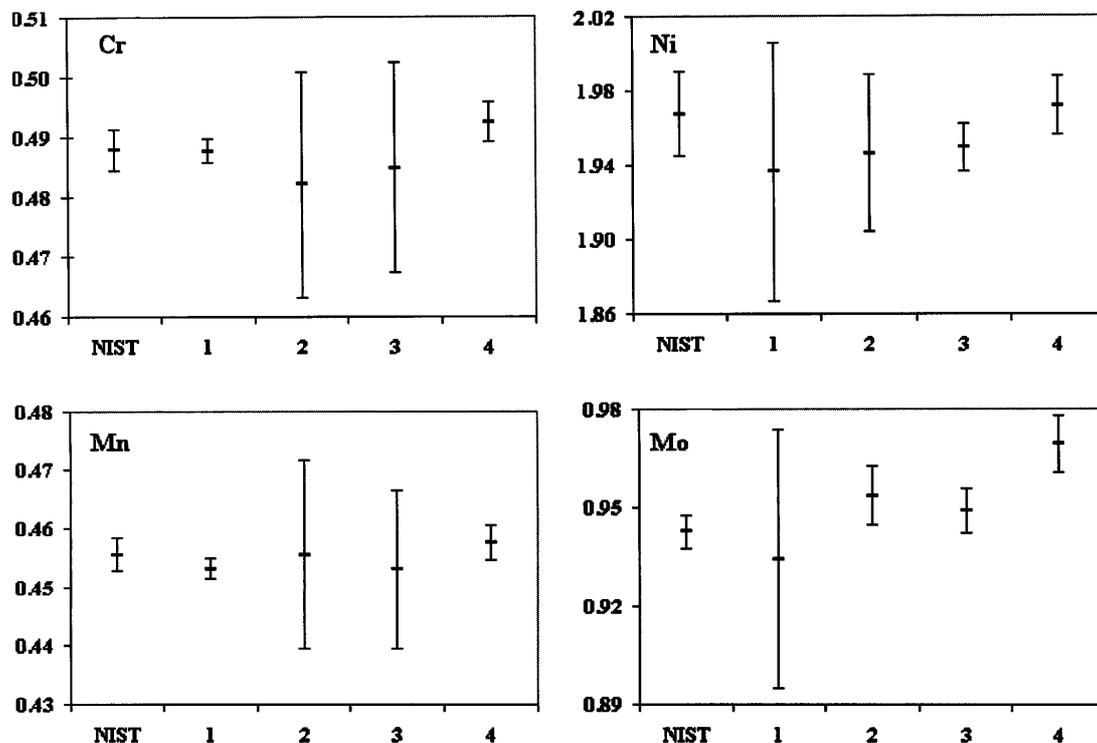


Figure 1. Comparisons of results for CCQM low-alloy steel analyzed using optical emission spectrometry at US Laboratories (1–4) and using XRF at NIST. All values are mass fraction (%). Error bars are expanded uncertainty estimates from each analysis expressed at approximately the 95% confidence level.

Table 2. Comparison of certified values for SRM 361 with results from the NIST borate fusion/XRF method: all values in mass fraction (%)

Parameter ^a	Cr	Mn	Ni	Mo
Certified	0.694	0.66	2.00	0.19
u_c	0.005	0.01	0.01	0.01
Found	0.6950	0.6698	1.9935	0.18783
s	0.0080	0.0077	0.0039	0.00032
n	4	4	4	4
Bias test ^b				
Δ	0.0010	0.0098	0.0065	0.0022
Δ_c	0.023	0.032	0.026	0.021
Detected	No	No	No	No

^a u_c = combined uncertainty listed on SRM certificate; s = standard deviation of measured results; Δ = difference between found and certified values; Δ_c = critical level for bias detection.

^b Bias test includes uncertainty of certified value.

piece weighing 30 mg–70 mg. Under typical circumstances, larger specimens would be used to avoid the high relative uncertainty associated with weighing these low masses. No treatments such as etching were done prior to weighing.

High-purity Al₂O₃ (Alfa Aesar), TiO₂ (Aldrich), WO₃ (JMC Puratronic) and Nb foil (J-M Aesar) were used to prepare the calibration standards. Each of these materials was fused to make a working glass solution. In this case, the synthetic standards were not prepared by acid reaction of the major component. The Rh K–L Compton scatter line from the x-ray tube was used as an internal reference to compensate for the effects of differences in bead thickness on the Nb count rate because the beads are not infinitely thick for Nb K–L x-rays.

Results of quantitative analysis

Table 3 contains the quantitative XRF results for the aerospace alloy. The same information is reported for this material as for the low-alloy steel, except that the sum is reported for each sample. As mentioned above, the aerospace alloy was also analyzed using ICP-OES. Table 4 shows the borate fusion/XRF results in comparison with the ICP-OES results and includes the results of a bias test¹⁴ based on the expanded uncertainty estimates from both methods. No bias was detected for any of the four elements at the 95% confidence level.

It is reasonable to expect the sum of the mass fractions of the analytes to be >99% because the aerospace alloy was prepared from pure metals. A survey analysis using a standardless fundamental parameters method on a disk of the alloy showed that it contains ~0.2% Fe by mass and 0.07% Si by mass. An average sum of 99.07% for the XRF results is slightly lower than expected, but it does not represent a significant bias with respect to the ICP-OES results. There is a high probability that the true value for each analyte is somewhere between the XRF and ICP-OES values and that the purity of the alloy is less than 99.8%.

Table 3. Quantitative results for the Al–Ti–Nb–W alloy from the NIST borate fusion/XRF method: all values in mass fraction (%)

Sample ^a	Al	Ti	Nb	W	Sum
2a	30.32	53.47	10.654	4.344	98.78
3b	30.21	53.22	10.609	4.277	98.32
4b	30.42	53.54	10.714	4.368	99.04
6a	30.20	53.84	10.734	4.354	99.13
7a	30.52	54.31	10.844	4.439	100.11
10b	30.33	53.68	10.687	4.311	99.02
Average	30.33	53.68	10.71	4.349	99.07
u_m	0.050	0.15	0.033	0.022	
u_f	0.085	0.025	0.039	0.020	
Type A	0.099	0.15	0.051	0.030	
u_s	0.12	0.21	0.043	0.017	
u_b	0.16	0.29	0.058	0.023	
Type B	0.20	0.36	0.072	0.029	
u_c	0.23	0.39	0.088	0.042	
U	0.45	0.78	0.18	0.083	

^a u_m = standard uncertainty of the mean, $n = 6$; u_f = standard uncertainty of the calibration fit; u_s = standard uncertainty of primary standard; u_b = standard uncertainty of balance calibration; u_c = combined uncertainty; U = expanded uncertainty, $k = 2$, 95% confidence level.

Table 4. Comparison of NIST XRF and ICP-OES results for the Al–Ti–Nb–W alloy: & all values in mass fraction (%)

Parameter ^a	Al	Ti	Nb	W
ICP-OES	30.28	54.15	10.84	4.421
U	0.21	0.36	0.10	0.029
MI-XRF	30.33	53.68	10.71	4.349
U	0.45	0.78	0.18	0.083
Bias test				
Δ	0.05	0.47	0.13	0.072
Δ_c	0.56	0.96	0.23	0.098
Detected	No	No	No	No

^a U = expanded uncertainty, 95% confidence level; Δ = difference between results; Δ_c = critical level for bias detection.

Control sample

Control of the quantitative calibrations was demonstrated by analyzing a synthetic sample prepared from SRM 175 Commercial Ti, SRM 277 Tungsten Concentrate, SRM C1257 High-Purity Aluminum and the Nb foil used to prepare calibration standards. The synthetic control was designed to simulate a sample of the alloy. The appropriate quantities of the SRMs and Nb foil were weighed into a Pt crucible, treated by acid oxidation and fused to make a borate bead. The control checks for errors in the weighing steps, acid oxidation performed on the alloy samples and borate fusion of the oxidized samples. It is important to test the acid oxidation because the synthetic calibration standards were not subjected to acid oxidation. Table 5 contains the XRF results with recovery values calculated on the basis of the

Table 5. Recovery of original ingredients from XRF analysis of the synthetic control sample for the Al–Ti–Nb–W alloy: all values in mass fraction (%), except Recovery

	Al	Ti	Nb	W
Ingredient	SRM C1257	SRM 175	Nb foil	SRM 277
Found in bead	0.20797	0.35886	0.07303	0.03347
Original sample basis ^a	99.82	99.08	99.76	52.96
Certified mass fraction	99.99	99.7	99.8	53.4
Recovery (%)	99.83	99.38	99.96	99.17
Calibration range:				
Min.	0.16596	0.28358	0.05725	0.02265
Max.	0.21203	0.36914	0.07581	0.02989

^a Calculated from the mass fraction found in the bead using the masses of the original ingredients and the total glass created for each bead.

original SRMs and the Nb foil. The recovery values range from 99.17% for W in SRM 277 to 99.96% for Nb in the foil. These values are consistent with the uncertainties in the certified values for the ingredients and with the uncertainties of sample preparation and calibration for the analytical method.

DISCUSSION

Uncertainty

The uncertainty budgets in Tables 1 and 3 demonstrate how simple the estimation of uncertainty can be when using XRF with gravimetric specimen preparation. Four estimates of uncertainty cover all significant components of error in the procedures. The standard deviation of the mean (u_m) of the results for unknown specimens covers weighing of alloy chips, acid digestion, borate fusion and x-ray measurements. This estimate is of Type A because it is a statistical calculation. The standard uncertainty of the calibration fit (u_f) is defined as the r.m.s. deviation between known and calculated mass fractions in the calibration standards divided by the square root of the degrees of freedom, and it includes the uncertainty associated with weighing aliquots of primary reference materials, acid digestion (in some cases), borate fusion and measuring in the x-ray spectrometer. This is also a statistically derived uncertainty estimate, i.e. Type A. It should be pointed out that the calibration fit also accounts for some of the uncertainty remaining from the assumption that the bracketing standards are correctly designed to control matrix effects completely. The uncorrected matrix effects may contribute to scatter among the calibration standards and to a slight curvature of the relationship between mass fraction and count rate.

The other two estimates of uncertainty in these error budgets are of Type B because they rely on information from other sources. One is the uncertainty of weighing (u_b), defined as the uncertainty of the balance calibration tested using a weights set. The other is the uncertainty of the assay of the primary material (u_s) and is taken as the

uncertainty of the SRM solution standard in the cases of Cr, Mn and Ni in low-alloy steel. Where pure compounds or pure metals with assay values of >99.9% were used, the relative uncertainty of the assay is estimated to be 0.1%. The compounds and metals may be more pure and with lower uncertainty, but a conservative estimate of 0.1% is sufficient at this time. This statement is not made lightly. The compounds and metals used for calibration of the borate fusion/XRF method are carefully prepared prior to weighing. For the most part, heat treatments recommended in the literature^{10–13} are employed to ensure stoichiometry and reduce contamination due to H₂O and adsorbed gases. The uncertainty estimate of 0.1% relative is good enough for two reasons. The other components of uncertainty in this method are generally of similar or greater magnitude and the requirements for uncertainty of the final results are easily met without the expense of determining impurities at the mg kg⁻¹ level. The uncertainty required for the final results is in the range 0.1%–1%, even when the results will be used for certification of a reference material. Discussions of the basic requirements for the application of primary pure compounds in inorganic bulk analysis can be found elsewhere.^{13,15}

The uncertainty of the balance calibration was demonstrated by a check of the balance using a calibrated weights set. This estimate is somewhat imperfect because there may be different numbers of weighings for standards or specimens and there is a correction made for buoyancy based on the literature value for the density of each compound. For the aerospace alloy, Table 3 indicates that the uncertainty of weighing is relatively high because the amounts of specimens were only 30 mg–40 mg. In that case, the relative uncertainty of weighing is in the range 0.5%–1.0%. For the low-alloy steel, it is roughly 0.05% because the specimens weighed 500 mg.

Observant readers will note that this paper does not explicitly present several parameters that are typically of concern in a borate fusion method, viz. loss on ignition (LOI) of the flux and possible gain on fusion or loss on fusion of the samples. These phenomena are accounted for through careful weighing of the ingredients and the platinum ware. For pre-fused lithium borate flux used in this work, the LOI is typically <0.1% by mass and uniform both throughout a batch and from batch to batch. Sample loss or gain of mass on fusion is accounted for in the total mass of glass created by fusion. All platinum ware is weighed before and after sample preparation. In that way, all changes to the sample and the flux are quantified and the associated uncertainty is part of the weighing component.

Traceability

Claims of traceability to the mole can be made when the calibration is based on high-purity, stoichiometric compounds and careful gravimetric preparation of mixtures, and the analytical method can be described in relatively simple mathematical terms. In the case of the method described in this paper, the calibration is a straight line⁴ with line overlap corrections calibrated separately. The calibration standards for Cr, Mn and Ni in low-alloy steel were NIST SRM spectrometric solution standards prepared directly from NIST

primary reference materials. The calibration standards for Mo in steel and the elements in the Al–Ti–Nb–W alloy were high-purity compounds subjected to well-documented treatments to ensure stoichiometry and having conservative estimates of uncertainty.

If the borate fusion procedure is considered to be a source of uncertainty, the analyst can convince the customer that borate fusion is an excellent mixing technique for powders or solutions by using typical means of method validation. Borate fusion exhibits excellent repeatability even when it includes acid digestion. The borate fusion/XRF approach yields relative combined uncertainty estimates consistently below 1% when the sample mass is high enough to prevent the uncertainty of weighing from becoming significant. Finally, all results were confirmed by independent analyses.

CONCLUSIONS

In these examples, uncertainty budgets were presented and explained, along with links of traceability to SI. The borate fusion/XRF approach results in accurate determinations. The results presented in this paper are indicative of the power of this approach for quantitative analysis of alloys. No biases were detected for the low-alloy steel and quaternary aerospace alloy. Three different checks were conducted. Borate fusion XRF results were compared with certified values, with ICP-OES results, and with a synthetic control sample prepared from certified reference materials. The keys to this excellent performance are the bracketing calibration standards described in previous papers^{4,5} and the use of either high-purity compounds or spectrometric solution standards as primary reference materials.

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Certain commercial equipment and commercial laboratories are 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 equipment and services are necessarily the best for the purpose.

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