Trace impurity analysis in uranium oxide via hybrid quantification techniques—gravimetric standard addition and isotope dilution mass spectrometry

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Abstract

Measurement methods for the analysis of trace impurities in uranium materials, essential in nuclear fuel production and nuclear forensics, are continuously improving. Analytical methods were developed with the goal of lowering uncertainties of next generation certified uranium oxide reference materials for trace impurity concentrations. Through addition of a traceable standard directly into the sample, gravimetric standard addition and isotope dilution followed by analysis on an inductively coupled plasma mass spectrometer can achieve lower uncertainties. Results for 28 impurities in CRM 124-1 and 124-6 from NBL Program Office were used for validation of accuracy and comparisons of uncertainties.

Keywords

Trace impurities, uranium, gravimetric, standard addition, isotope dilution, IDMS

Introduction

The processes of the nuclear fuel cycle, from mining to fuel fabrication, can introduce impurities to uranium intermediates and the final product. The ability to quantify impurities in uranium materials is important for both reactor fuel production and the nuclear forensics community. When producing uranium fuel for nuclear reactors, there are certain specifications for impurities that should be monitored during the conversion—from ore mining through to sintering into a fuel pellet [1-6]. Coincidently, the impurities from the conversion process can provide the forensics community information about the production and source [7-10]. In order to validate methods for accuracy and precision, it is ideal for a reference material of the same uranium form to serve as a quality control; unfortunately, these reference materials are in short supply or non-existent [11].

The United States Department of Homeland Security has supported the production and characterization of a set of uranium oxide reference materials for 28 impurities. Oak Ridge National Laboratory (ORNL) and other domestic and international laboratories have worked to characterize the trace element content. The current work does not report any data from these new reference materials, but details the accuracy and precision for a novel method using gravimetric standard addition and isotope dilution mass spectrometry for impurity quantification in CRM 124-1 and CRM 124-6 from NBL Program Office (NBLPO) [12-13].

Comprehensive impurity analyses in uranium are being conducted on a routine basis among nuclear laboratories worldwide. These methods typically employ matrix-matched external calibrations coupled with measurement by inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and/or inductively coupled plasma optical emission spectrometry (ICP-OES) [14-17]. For these methods, the uncertainty and precision of the measurement are adversely affected by matrix interferences, analysis-to-analysis instrumental drift and the lack of matrix specific certified reference materials, which prevent detailed compensations for these factors [18-20]. The use of the standard addition technique eliminates the requirement of matrix matched solutions for trace impurity analysis making it more convient for complex samples. Furthermore, performing standard addition gravimetrically

allows for better accuracy and precision while reducing time when compared to the volumetric technique.

Isotope dilution mass spectrometry (IDMS) is a "definitive method" providing higher accuracy due to direct traceability to a certified reference material (CRM) [21]. IDMS can be used to reduce matrix and preparation effects otherwise introduced by external calibration techniques, allowing for more precise measurements to be made. Depending on the analyte and the analyte's concentration, IDMS can provide the most accurate and precise content measurements available to analytical laboratories today. Using this technique, certified enriched isotopes are added directly into the sample matrix for the elements analyzed. All additions and dilutions are performed gravimetrically to minimize analytical uncertainties [22].

Although matrix-matched external calibration may be a more practical method when several elements are to be analyzed, gravimetric standard addition and/or IDMS presents an improvement in accuracy and precision for complex matrices. In this work, gravimetric standard addition and IDMS provided the primary characterization for provision of values for a reference material. In total, 28 impurities in uranium oxide were analyzed[1]; IDMS was applied to 17 of these, while gravimetric standard addition was applied to the remaining 11 elements where the analyte was monoisotopic or it was not feasible to obtain the enriched spikes necessary for IDMS.

Experimental

Equipment

Reverse IMDS measurements for enriched spike calibration were performed on a Neptune (Thermo Instruments, Bremen, Germany) double-focusing multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS), equipped with nine Faraday collectors

[1] The actual scope of the analysis was 28 elements, 17 by IDMS and 11 by gravimetric standard addition; however, 11 of those elements are not certified values in the CRM 124 series from NBLPO but are included for informational purposes.

88 and one secondary electron multiplier. Both low (R = 300) and medium (R = 4,000)
89 resolution modes of the instrument were used for the analyses. The samples were aspirated
90 using a 100 µl minute^{-1} self-aspirating nebulizer with a standard cyclonic double passing
91 introduction system (SIS, Elemental Scientific Inc., Omaha, NE). All data for the samples
92 were collected in the static mode. Amplifier resistors were changed between 10^{-11} and 10^{-}
93 ^{13}, as required for the analysis.

94 Elemental quantification was performed using an Element 2 (Thermo Instruments,
95 Bremen, Germany) double-focusing high resolution inductively coupled plasma mass
96 spectrometer (HR-ICP-MS), equipped with single orthogonal secondary electron
97 multiplier. The samples were aspirated using a 100 µl minute^{-1} self-aspirating nebulizer
98 with an Apex micro (SIS, Elemental Scientific Inc., Omaha, NE).

99 All samples and enriched stable isotopes were dissolved using a CEM Discover SP-D
100 microwave in 35 mL Pyrex digestion vessels lined with Teflon liners. Each digestion vessel
101 contained a small stir bar and was sealed with a disposable Teflon-lined cap.

102 Materials

103 High-purity nitric acid and hydrofluoric acid (Optima Grade, Fisher Scientific) were used
104 for sample dilutions together with >18 MΩ cm water (GenPure Pro, ThermoScientific).
105 Labware used for the project included low-density polyethylene (LDPE) bottles, pipette
106 tips (Eppendorf), sample vials (PFA, Savillex Corporation), and microwave vessels, Teflon
107 liners and caps. All labware was pre-cleaned by soaking for ≥72 hours at 60 ºC in 10%
108 HNO_3 prepared with trace-metals grade nitric acid (Fisher Scientific), followed by ≥72
109 hours at 60 ºC in 18 MΩ cm water, rinsed and then dried in a laminar flow hood inside an
110 ISO Class 5 cleanroom. Certified reference materials, CRM 124 series, were purchased
111 from NBLPO and used as quality control (QC) samples for the reference material
112 characterization project. Enriched stable isotopes for IDMS were either purchased from the

National Isotope Development Center[2] (NIDC) or from Inorganic Ventures, Inc. Single element standard solutions were purchased from the National Institute of Standards and Technology (NIST) with the exception of Zr and V which were purchased from Inorganic Ventures, Inc. Information for the purchased spikes and standards can be found in supplemental information Tables 1, 2 and 3.

Sample and blank dissolution

Microwave digestion was employed to ensure total dissolution of the uranium oxide materials. A single analysis sample consisted of approximately 200 mg of oxide which was weighed into a PFA vial. A 4 mL aliquot of concentrated HNO_3 was added to the vial and heated on a hot plate for ~2 hours at 125 ºC, followed by an addition of 20 µL concentrated HF (CRM 124-1) or 5 µL concentrated HF (CRM 124-6). The largely dissolved sample was quantitaively transferred and rinsed into a microwave digestion vessel resulting in an approximate solution volume of 7 mL. The sample was digested in a CEM Discover microwave by ramping the temperature to 190 degrees C for 5 minutes and holding that temperature for 10 minutes at 200 psi and 300W with stirring. In some cases, the microwave digestion was performed more than once until no refractory particles were visible. After digestion, the solution was quantitativly transferred to a tared LDPE bottle and diluted to a final solution U concentration of ~5 mg/mL in 8 M HNO_3-0.02M HF; this was the master solution.

Gravimetric standard addition

The experimental design of standard addition calls for three solutions to be mixed in varying proportions: the unknown (*X*), a solution of known concentration for each analyte (*S*), and a diluent (*D*) as shown in Fig. 1. As opposed to standard addition by volume, gravimetric standard addition employs the use of a balance for all additions and dilutions

[2] The NIDC manages isotope production funded by the Isotope Development and Production for Research and Applications within the Office of Nuclear Physics of the United States Department of Energy Office of Science.

allowing for a more precise determination of the quantities of solutions. The analytes measured by gravimetric standard addition were divided into four groups, shown in Table 1, based on the optimal resolution mode for the HR-ICP-MS and minimization of isobaric interferences. To create the known solution, *S*, NIST spectrometry SRMs were gravimetrically combined for each group and then diluted with 2% HNO_3 to create a 'standard addition cocktail' of known concentration, C_S. The cocktail was prepared based on estimated values of impurities in the unknown, so that the signal for each analyte increased by approximately 25% with incremental additions of the known solution.

All additions were weighed to create the measurement solutions, starting with a 2 g aliquot of the unknown (m_X) to which incremental 0.5 g additions (m_S) of the known solution were added, followed by diluent (m_D), 2% HNO_3, to achieve a final mass of 5 g. A total of four measurement solutions were created ($m_S = 0$ in the first solution). The concentration of analyte in a method blank was calculated the same as samples. Blank values were subtracted from the sample when the analyte concentration in the blank was statistically greater than zero. The measurement solution introduced to ICP-MS was ~100 ppm U for CRM 124-1 and ~200 ppm U for CRM 124-6. It should be noted that the same batch of 2% HNO_3 used for the dilutions of the known standards was used as the diluent to maintain an identical matrix in each sample.

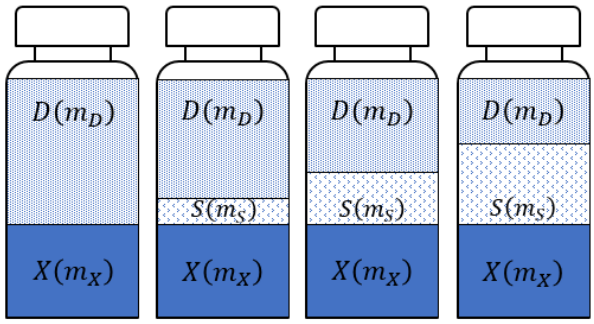

Fig. 1 Standard addition experimental design: measurement solutions consisting of sample *X*, increasing additions of standard *S*, and diluent *D* to bring the final solution to a constant mass. Mass fractions for the additions are represented as m_X, m_S and m_D, respectively

Table 1 Groups and resolution modes of the gravimetric standard addition analysis

Group	Elements	Resolution Mode
1	Nb, Ta, Y	Low
2	Ce	Low
3	Al, Ca, V, P	Medium
4	Co, B, Mn	Medium

The treatment of data from gravimetric standard addition analyses is based on formulation developed in earlier works [23, 24]. Eq. (1) represents the analysis variables arranged in a linear form, $y = mx + b$. The left side of the equation (y) is plotted versus the portion in parenthesis on the right side of the equation (x). R is the corrected instrument response for the analyte and C_X is the concentration of analyte in the unknown. Here, k represents the sensitivity of the system and is equivalent to the slope, m, if the plot of Eq. (1) yields a straight line.

$$\left(\frac{m_X + m_S + m_D}{m_X}\right)R = k\left(\frac{m_S}{m_X}\right) + kC_X \#(1)$$

The concentration of the analyte, C_X, can be calculated according to Eq. (2), where b is the intercept and m is the slope given by linear regression. Further information on the regression calculation can be found in supplemental information.

$$C_X = \frac{b}{m}C_S \#(2)$$

Isotope dilution mass spectrometry

Isotope dilution mass spectrometry method

In IDMS, an isotopically enriched spike (of known concentration and isotopic abundance) of the analyte element is added into the unknown and then a measured ratio, R_m, of the major isotope in the sample, i, to the major isotope in the spike, k, is used to calculate concentration of the unknown, C_x, using Eq. (3);

$$C_x = \frac{m_s A_x a_{ks}(R_s - R_m)}{W_x A_s a_{kx}(R_m - R_x)} \#(3)$$

where m_s is the elemental mass in the spike, W_x is the weight of the sample solution, a_{ks} is the atom abundance of k in the spike, a_{kx} is the atom abundance of k in the sample and A_x and A_s are the molar mass of the sample and the spike, respectively. C_x can only be determined if the isotope abundance of the analyte in the sample is known. The CRM 124 series was doped with elements of natural abundance. The isotope ratios are defined in Eq. (4) where a is atomic abundance and the subscripts are x for the sample, s for the spike and m for the mixture.

$$R_x = \frac{a_x(i)}{a_x(k)}, R_s = \frac{a_s(i)}{a_s(k)}, R_m = \frac{a_m(i)}{a_m(k)} \#(4)$$

The IDMS analytes were divided into five groups (Table 2) to reduce the possiblity of concomitant impurities and interferences. Aliquots of the master solution were weighed into a PFA vial and spiked with known enriched isotopes and allowed to equilibrate on a hotplate for >24 hours at 90 ºC. The unknown was spiked so as to achieve an R_m approximately equal to 1. Uranium was removed via extraction chromatography with a stacked Eichrom UTEVA-Prefilter column as shown in Fig. 2. The column chemistry was very similar to the method outlined in ASTM C1647-13, substituting pre-packed 2 mL columns and adjusting the loading and elution volumes [25]. The eluted portion was submitted for HR-ICP-MS analysis and the R_m from Table 2 was measured for each analyte.

Table 2 Groups and quantifying ratios for isotope dilution mass spectrometry

Group 1		Group 2		Group 3		Group 4		Group 5	
Metal	R_m	Metal	R_m	Metal	R_m	Metal	R_m	Metal	R_m
Er	$^{167}Er/^{164}Er$	Hf	$^{178}Hf/^{179}Hf$	Mo	$^{95}Mo/^{97}Mo$	Ti	$^{48}Ti/^{47}Ti$	Fe	$^{56}Fe/^{57}Fe$
Dy	$^{163}Dy/^{160}Dy$	Nd	$^{146}Nd/^{143}Nd$	Pb	$^{208}Pb/^{204}Pb$	Zr	$^{90}Zr/^{91}Zr$	Cr	$^{52}Cr/^{53}Cr$
				Li	$^{7}Li/^{6}Li$	Ni	$^{60}Ni/^{61}Ni$	W	$^{182}W/^{183}W$
				Mg	$^{24}Mg/^{25}Mg$	Cu	$^{63}Cu/^{65}Cu$		
				Si	$^{28}Si/^{30}Si$				

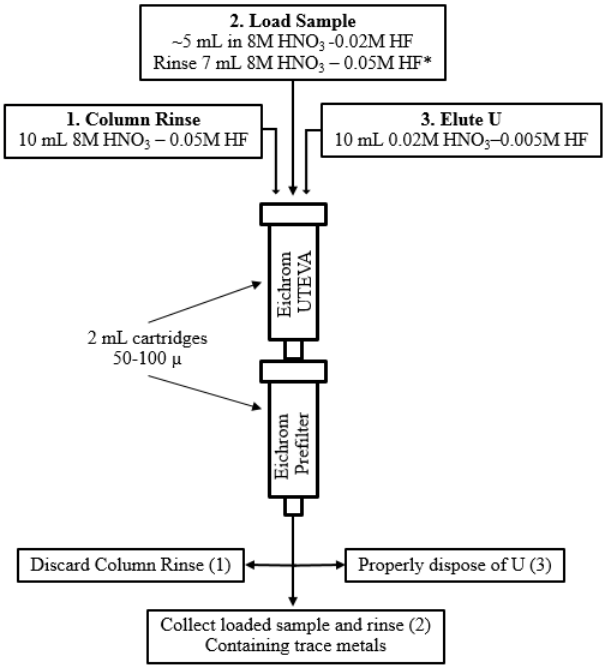

Fig. 2 Column chemistry of uranium extraction for IDMS samples. *The addition of HF is only needed for the elution of Zr and Hf. In this study, if these metals were not to be eluted, only 8 M HNO_3 was used

Traceability of enriched spikes

As mentioned in the materials section, enriched spikes were purchased from two suppliers. Six enriched isotopes (^{61}Ni, ^{204}Pb, ^{25}Mg, ^{65}Cu, ^{57}Fe, ^{6}Li) were purchased as solutions from Inorganic Ventures, Inc and used as received. The certificates of analysis included the certified isotopic abundance and a concentration that was certified directly versus a NIST standard reference material (SRM).

The enriched isotopes from NIDC (^{53}Cr, ^{164}Er, ^{97}Mo, ^{143}Nd, ^{47}Ti, ^{183}W, ^{91}Zr, ^{179}Hf, ^{160}Dy, ^{30}Si) were purchased as solids, digested and diluted to approximately 1 mg/mL. Traceable calibration of the enriched solutions was achieved by performing reverse-IDMS (three repeated measurements) using NIST spectrometry SRMs that are certified for elemental concentration. The reverse-IDMS technique yields a traceable concentration value by adding the spike solution to a well known standard and performing the necessary isotopic

measurements for IDMS. Any subsequent dilutions of the spike solutions were made gravimetrically with 8 M HNO_3, which was the matrix needed for loading the column.

Sample Analysis

Purified elemental groups were analyzed by HR-ICP-MS. Elements quantified by standard addition were analyzed with 3 runs and 50 passes with a mass window of 125% and 30 peaks per samples. The intergration time was 0.0200 ms for a total segment duration of 0.760 ms. The interferences were monitored with a mass window of 125% and 10 peaks per sample. The intergration time was 0.0100 ms. Elements quantified by IDMS were analyzed with 3 runs and 25 passes with a mass window of 5% and 200 peaks per sample. The intergration time was 0.0200 ms for a total segment duration of 0.200 ms. The interferences were monitored with a mass window of 20% and 25 peaks per sample with an intergration time of 0.0050 ms.

The standard addition sequence consisted of a washout blank → instrument blank→ sample 1 → sample 2→ sample 3→ sample 4→ washout blank → instrument blank, this was repeated for each sample. A 60 second probe wash with 5% HNO_3 was placed between samples but no data was collected. The samples were bracketed by controls at the beginning and end of analysis. Sample count rates were corrected for blanks and inteferences. The list of interferences can be found in Table 3. Single element standards were analyzed at the begining and end of the sequence run. The analyte intensity was diluted to yield approximately 5 x 10^6 cps. The correction factors were averaged and applied to the appropriate isotope. Correction factors ratios of 9 x 10^{-8} or less were not applied.

Table 3 A list of possible interferences that were monitored and corrected for each element analyzed

Element	Interferences (monitor and corrected)
Mo	MnAr, CoAr, FeAr, NiAr, Os^{++},Pt^{++}, Ir^{++}
Pb	OsO, PtO, IrO, DyAr, ErAr, YbAr
W	ErO, NdAr, HoO, SmO, Dy, CeAr
Mg	LiO

Nb	Re^{++}, Os^{++}, W^{++}, ZrH, MoH
Ta	WH, DyOH, HfH, HoO
Y	Hf^{++}, SrH, TiAr
Zr	Ta^{++}, W^{++}
Ca	Sr^{++}
V	Ru^{++}, Pd^{++}, Rh^{++}
Ti	Mo^{++}, Zr^{++}, Nb^{++}

The IDMS sequence was bracketed with instrument blanks and every 6 samples/controls were bracketed by a natural isotopic abundance standard to correct for mass fractions. A 30 second probe wash with 5% HNO_3 was placed before each sample or control. Sample count rates were corrected for blanks, inteferences and mass fractionation. The list of interferences can be found in Table 3. Single element standards were analyzed at the beginning and end of the sequence run. The analyte intensity was diluted to yield approximately 5 x 10^6 cps. The samples were diluted to maintain a count rate of 5 x 10^6 cps, thus keeping the detector in counting mode. The correction factors were averaged and applied to the appropriate isotope. Correction factor ratios of 9 x 10^{-8} or less were not applied.

Results and discussion

Gravimetric standard addition

The analytical method was validated for accuracy and precision using two materials of the CRM 124 reference material set, CRM 124-1 and CRM 124-6. Of the 11 analytes measured by gravimetric standard addition, six of them have certified values in these reference materials. The experimental results for CRM 124-1 and CRM 124-6 are shown in Tables 4 and 5, respectively. All analytes were measured within the stated uncertainty of the CRM except for aluminum in CRM 124-6, however aluminum was measured within the stated uncertainty of the re-evaluated value. CRM 124-6 does not report certified values for B and Ca and therefore no statement can be made about accuracy at that level. The majority of the elements had a smaller associated uncertainty than the CRM from the certificate of analysis. Uncertainties varied with each analyte, that analyte's concentration and the blank

levels. In general, the relative uncertainty for single measurements was 1-12% for CRM 124-1 and CRM 124-6. Boron was difficult to analyze at low levels, exhibiting less reproducibility due to high blank levels; a relative uncertainty of 35% and 96% were reported for CRM 124-1 and CRM 124-6, respectively.

Table 4 Gravimetric standard addition method for CRM 124-1 compared to certificate of analysis values and re-evaluated values [12,13]

Analyte	n	Experimental, µg/g U ± u_c	Certified, µg/g U ± u_c	Re-evaluated, µg/g U ± u_c
Al	4	208 ± 11	205 ± 37	217 ± 37
B	4	3.7 ± 1.3	5.1 ± 1.0	5.5 ± 1.0
Ca	4	208 ± 26	200 ± 36	207 ± 36
Co	4	25.3 ± 1.4	25.0 ± 6.1	23.3 ± 6.1
Mn	4	51.5 ± 1.9	51.0 ± 7.6	50.2 ± 7.6
V	4	50.2 ± 8.5	50.0 ± 7.2	49.9 ± 7.2

Table 5 Gravimetric standard addition method for CRM 124-6 compared to certificate of analysis values and re-evaluated values [12,13]

Analyte	n	Experimental, µg/g U ± u_c	Certified, µg/g U ± u_c	Re-evaluated, µg/g U ± u_c
Al	2	5.62 ± 0.71	10 ± 1.4	7.6 ± 1.4
B	2	0.99 ± 0.95	0.2[a]	N/A[b]
Ca	2	10.42 ± 0.94	5.8[a]	N/A[b]
Co	2	0.572 ± 0.010	0.60 ± 0.09	0.54 ±0.09
Mn	2	1.421 ± 0.013	1.70 ± 0.49	1.71 ± 0.49
V	2	0.998 ± 0.085	1.00 ± 0.13	1.06 ±0.13

[a]Values are not certified [12], [b]Values were not re-evaluated

Uncertainty contributions from gravimetric standard addition

The expanded uncertainty for each single replicate measurement was reported with a coverage factor (k) of 2 with the following contributions:

- Standard deviation of the slope and intercept calculated from linear regression, least-squares method;
- All weights from the original solid and subsequent dilutions as well as from dilutions of the certified solutions;

- Standard uncertainty of certified element solutions reported on the certificate of analysis (COA);
- Standard deviation of replicate blank measurements when the blank was subtracted.

The uncertainty, u_c, reported in Tables 4 and 5 are the standard deviation for n replicates multiplied by a coverage factor of 2 to provide a simplified estimate of 95% overall measurement uncertainty.

Fig. 3 exhibits the typical major contributors to the uncertainty budget for a single measurement. As shown, the deviations from linear regression (slope, *m*, and intercept, *b*) resulted in >90% contribution to the uncertainty, as was typical for each analyte in this analysis. To decrease this contribution and tighten precision and accuracy, more data points could be used to plot the standard addition line. Also, considering Eq. (1), while noting that masses have a small associated error, it can be assumed that deviations from the best fit line were a result of *R* which could be attributed to instrumental drift; improvements could be made with an internal standard introduced during instrumental analysis.

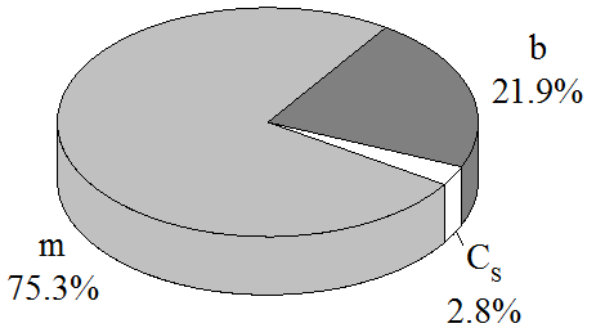

Fig. 3 Graph of major contributors to the uncertainty budget as given in GUM Workbench for a single measurement of calcium in CRM 124-1 by the gravimetric standard addition method

Isotope dilution mass spectrometry

Again, method validation was performed with CRM 124-1 and CRM 124-6 which are certified for 11 of the metals measured by IDMS. The experimental results for CRM 124-1 and CRM 124-6 are shown in Tables 6 and 7, respectively. All elements were reported within the standard uncertainty of the CRM, except for zirconium and tungsten in CRM

124-1 which fell in the 95%-99% level of confidence of the certified value. When Zr and W experimental values are compared to the re-evaluated values, there is a slight improvement, however there still appears to be a bias. A recent study by Boulyga et al. found similar results with Zr and W at higher concentrations in CRM 124-1 [26]. Previous authors have suggested this could be a dissolution problem for W, however, the precision in this W data set between replicates suggests this is not likely to be the source of the bias for this analysis as dissolution problems are more random. The cause for the bias is still under investigation.

Isotopic equilibration is necessary for accuracy in IDMS methodology, and if this is not achieved, systematic errors can result [22]. Isotopic equilibration can be achieved by complete sample dissolution synchronously with the enriched isotope spike as well as oxidation/reduction reactions. However, these could not be justified due to the cost of adding the enriched spikes at these levels and addition of contamination due to the number of spikes that would be added and/or the composition of the oxidative/reductive species. In the current method, the liquid mixture was heated to 90 ºC in 8 M HNO_3 for ~24 hours for equilibration. Isotopic fractionation biases were assessed by analysis of the suitable CRM analyzed in parallel the sample. In any case, any fractionation that might have occurred was negligible in comparison to other contributions of uncertainty.

IDMS achieved a smaller relative uncertainty for single measurements than gravimetric standard addition, typically 0.1-3% for CRM 124-1 and 1-15% for CRM 124-6. The standard deviation of replicate measurements was typically 1-8% for CRM 124-1, but more sporadic for CRM 124-6 due to lower analyte concentrations. The high uncertainty for silicon can be attributed to the use of HF for sample dilution which produces volatile SiF_4. For this same reason, silicon was not reported for CRM 124-6.

Table 6 IDMS method results for CRM 124-1 compared to certificate of analysis values and re-evaluated values [12,13]

Analyte	n	Experimental, µg/g U ± u_c	Certified, µg/g U ± u_c	Re-evaluated, µg/g U ± u_c
Cr	4	108.1 ± 1.8	102 ± 14	107 ± 14
Cu	4	50.5 ± 0.8	50.0 ± 9.4	46.3 ± 9.4

Fe	3	208.9 ± 5.1	210 ± 24	196 ± 24
Mg	4	105 ± 18	101 ± 13	104 ± 13
Mo	4	98.6 ± 2.3	100.0 ± 5.5	100.5 ± 5.5
Ni	4	208.2 ± 4.2	202 ± 17	208 ± 17
Pb	4	50.8 ± 0.7	51 ± 15	46 ± 15
Si	4	206 ± 68	202 ± 58	221 ± 58
Ti	4	47.5 ± 1.1	50 ± 14	44 ± 14
W	4	164.7 ± 9.4	200 ± 22	195 ± 22
Zr	4	282.8 ± 2.2	200 ± 61	228 ± 61

Table 7 IDMS method results for CRM 124-6 compared to certificate of analysis values and re-evaluated values [12,13]

Analyte	n	Experimental, µg/g U ± u_c	Certified, µg/g U ± u_c	Re-evaluated, µg/g U ± u_c
Cr	2	4.39 ± 0.66	4.3[a]	N/A[b]
Cu	2	1.25 ± 0.34	1.40 ± 0.44	1.45 ± 0.44
Fe	2	10.8 ± 2.7	15[a]	N/A[b]
Mg	2	2.58 ± 0.81	3.00 ± 0.55	2.69 ± 0.55
Mo	2	2.237 ± 0.003	2.00 ± 0.66	2.24 ± 0.66
Ni	2	6.58 ± 0.22	7.0 ± 1.0	6.6 ± 1.0
Pb	2	1.26 ± 0.01	1.80 ± 0.45	1.30 ± 0.45
Ti	2	1.068 ± 0.018	1.30 ± 0.28	1.15 ± 0.28
W	2	4.3 ± 0.03	5.0 ± 1.0	4.8 ± 1.0
Zr	2	7.3 ± 0.06	5.0 ± 1.7	6.7 ± 1.7

[a]Values are not certified [12].

Uncertainty contributions from isotope dilution mass spectrometry

The expanded uncertainty was reported with a coverage factor (k) of 2 with the following contributions:

- All weights from the original oxide and subsequent dilutions as well as from dilutions of the enriched spike solutions;
- Elemental concentrations of enriched isotope spikes (measured with three replicates by reverse IDMS);
- Uncertainty in atom percent of the enriched spike provided on the COA;
- The measured ratio, R_m, as determined by instrumental analysis with contributions from counting statistics and corrections for interferences;

- Standard deviation of replicate blank measurements when the blank was subtracted.

The uncertainty, u_c, reported in Tables 6 and 7 are the standard deviation for n replicates multiplied by a coverage factor of 2 to provide a simplified estimate of 95% overall measurement uncertainty.

The uncertainty contributions depended heavily on analysis of replicate blanks; two situations are shown for chromium in Fig. 4. The uncertainty budget has shown that better precision and accuracy could be achieved if blank subtraction was negligible, however, when this is not possible a larger number of blanks could be analyzed for a blank value with a tighter standard deviation. Apart from the blanks, the major contributors were the R_m measured by ICP-MS as well as the uncertainty in atomic abundance in the enriched spikes supplied on the COA.

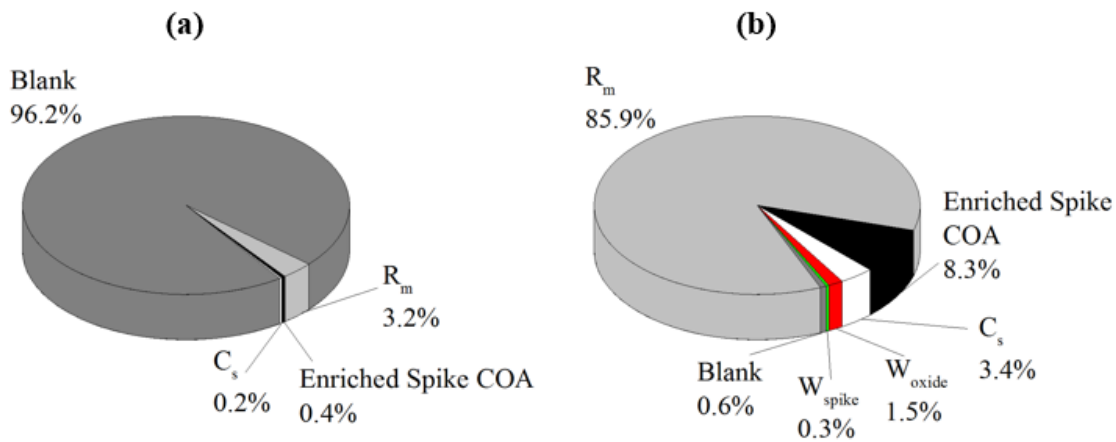

Fig. 4 An example of uncertainty budgets calculated in GUM Workbench for chromium in CRM 124-1 analyzed by the IDMS method. (4a) A measurement in which the standard deviation of replicate blank measurements was large and contributed to the majority of uncertainty (4b) In the case that the standard deviation of replicate blank measurements was small, other sources of uncertainty played a bigger role

Zeta scores

A zeta (ζ) score (calculated as in Eq. (5)) is essentially a quantitative comparison of experimental results $x_{measured}$ with a standard uncertainty $u^2(x_{measured})$ to a certified reference value $x_{certified}$ with a standard uncertainty $u^2(c_{ertified})$ [27]. If $|\zeta| < 2$, then the result is in good

agreement with the certified value at 95% confidence, if |ζ| < 3 the same can be said at 99% confidence. A zeta score greater than 3 signals that action should be taken to assess the problem.

$$\zeta = \frac{x_{measured} - x_{certified}}{\sqrt{u^2(x_{measured}) + u^2(x_{certified})}} \#(5)$$

Figures 5 and 6 show the calculated zeta scores for CRM 124-1 and CRM 124-6. The reproducibility and accuracy of measurements were generally better at higher concentrations of analytes. CRM 124-1 and CRM 124-6 have rather large uncertainties; thus, it should be recognized this has the effect of reducing |ζ|. The single way to alleviate this problem would be comparison to a CRM with smaller uncertainties, which is in part why development of these methods was conducted.

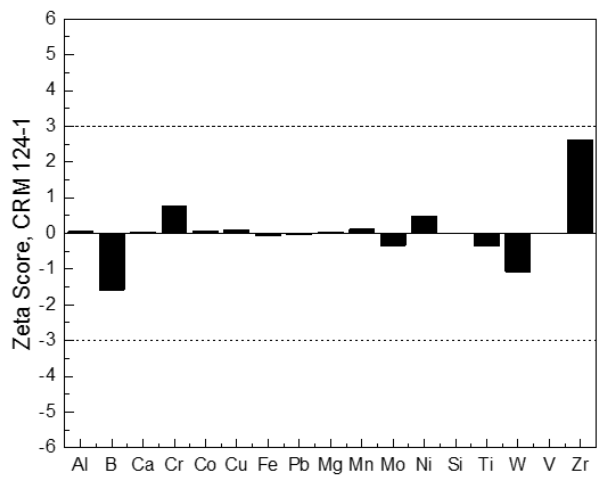

Fig. 5 Zeta scores for 17 analytes evaluated by gravimetric standard addition method and IDMS for CRM 124-1.

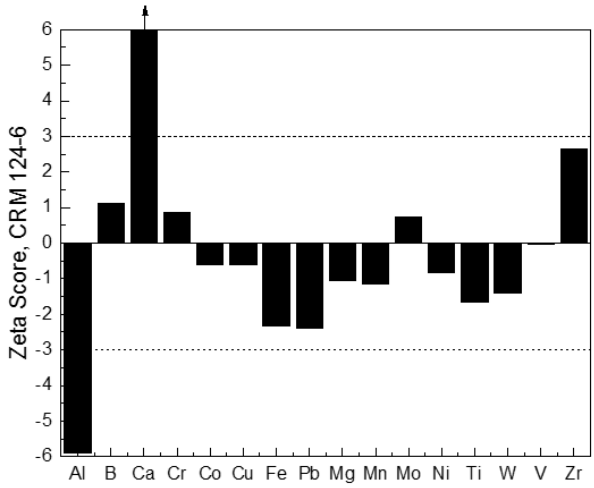

Fig. 6 Zeta scores for 16 analytes evaluated by gravimetric standard addition method and IDMS for CRM 124-6.

Conclusions

This work has highlighted efforts to characterize a potential set of uranium oxide reference materials for impurities. Gravimetric standard addition and IDMS present techniques for tightening precision through an unbroken chain of comparisons to an SRM; the result being smaller or similar uncertainties when compared to CRM 124-1 and CRM 124-6. When compared to CRM 124-1, the results showed improvements of an order of magnitude reduction of uncertainty for elements Cr, Cu, Fe, Pb and Ti. Elements such as Mo, Ni, W, Al, Ca, Co and Mn showed moderate reduction in uncertainties while Mg, Si, B and V had uncertainties that showed no improvement from the certificate. The uncertainties for the CRM 124 series certificate were a result of compiled data from several laboratories—which will usually lead to higher uncertainties due to between-lab reproducibility; thus the preceding statement is made just as a comparison. As expected a lower uncertainty resulted when analyte concentrations increased due to smaller contribution of blank subtraction and improvements in counting statistics. This technique is also useful when samples are complex and a suitable material cannot be found to create a matrix-matched calibration curve. Several potential improvements have been discovered in the analysis of the data including lowering uncertainty contributions from blanks, instrumental analysis and

linearity in standard addition. Future work is to study combining the elements that have been divided into groups into one single analysis for each method giving rise to a more efficient analysis for several elements. Other future work includes refining the method and possibly expanding the techniques to include other impurities.

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Notes

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