LA-UR-12-22149
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Intended for: Report

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Uncertainty Measurement for Trace Element Analysis of Uranium and Plutonium Samples by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

David Gallimore

Introduction

The measurement uncertainty estimation associated with trace element analysis of impurities in U and Pu was evaluated using the Guide to the Expression of Uncertainty Measurement (GUM).[1] In this evaluation the uncertainty sources were identified and standard uncertainties for the components were categorized as either Type A or B. The combined standard uncertainty was calculated and a coverage factor k = 2 was applied to obtain the expanded uncertainty, U.

The ICP-AES and ICP-MS methods[2] used were developed for the multi-element analysis of U and Pu samples. A typical analytical run consists of standards, process blanks, samples, matrix spiked samples, post digestion spiked samples and independent calibration verification standards. The uncertainty estimation was performed on U and Pu samples that have been analyzed previously as part of the U and Pu Sample Exchange Programs.[3,4] Control chart results and data from the U and Pu metal exchange programs were combined with the GUM into a concentration dependent estimate of the expanded uncertainty. Comparison of trace element uncertainties obtained using this model was compared to those obtained for trace element results as part of the Exchange programs. This process was completed for all trace elements that were determined to be above the detection limit for the U and Pu samples.

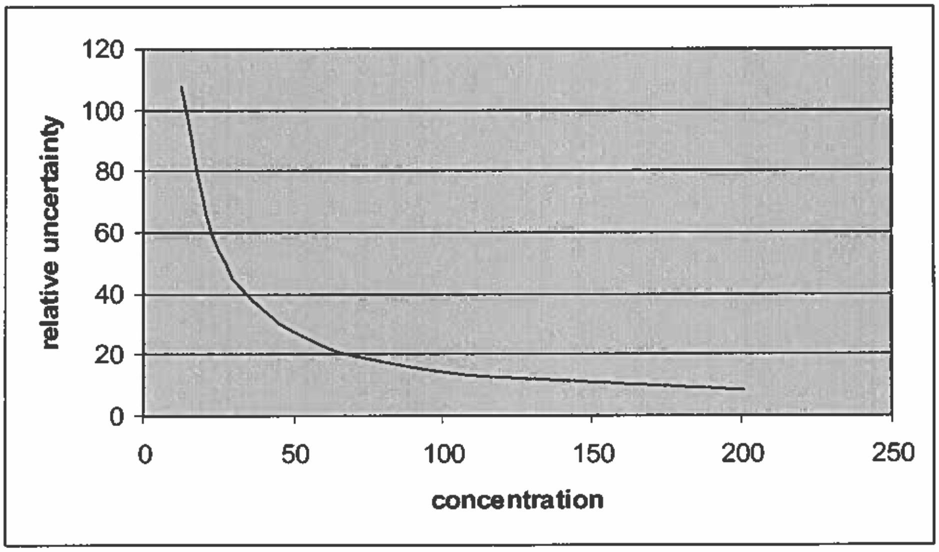
The uncertainty model

For both ICP-AES and ICP-MS the relationship between uncertainty and concentration can be expressed using the following expression where $u(x)$ is the uncertainty at concentration x and s_0 and s_1 are constants.

$$u^2 = s_o{}^2 + (s_1 x)^2$$

This model is given in Appendix E.4 of the EURACHEM / CITAC Guide.[5] At low concentrations (near the detection limit) s_0 is dominant and can be interpreted as the standard deviation of the blank. At higher concentrations s_1 is dominant and is considered the near constant relative standard deviation observed in the upper part of the linear dynamic range of the calibration. This is expressed graphically in Figure 1 and is typical for any element measured by ICP-AES or ICP-MS where the relative uncertainty approaches 100% at the detection limit and a constant value at higher concentrations. The GUM model developed for this study combined with data from control charts spanning a year timeframe were used to estimate the combined standard uncertainty. The GUM model was especially useful in identifying the major contributors to the combined standard uncertainty when the concentration was within the higher concentration range of Figure 1.

Figure 1 Relative uncertainty as a function of concentration



A typical analysis of U or Pu metal consists of accurately weighing ~0.25 grams of metal, transfer to a dissolution vessel and addition of mineral acids (HCl, HNO_3, HF) dependent on the matrix. The sample is taken to volume using deionized water and aliquots are taken for ICP-AES and ICP-MS analysis. The aliquot used for ICP-AES analysis is further diluted using HNO_3 + HF to adjust the molarity and added to a column containing ion exchange resin that binds the U or Pu and allows the trace elements to be collected in the eluant. The sample volume is adjusted and analysis performed using ICP-AES instrumentation. Internal standards are added to the ICP-MS aliquot and the sample diluted to a matrix concentration of 250 ug/mL to minimize matrix effects. For both the ICP-AES and ICP-MS analysis calibration blanks and multi-element standards are prepared by serial dilution from standard stock solutions, matching acid content to the samples. A process blank, control samples and independent calibration verification standards are included in each analytical batch. Results are reported on the basis of the solid sample by multiplying by the dilution factor. The GUM model equations and the definitions for the variables are shown in Table 1 for ICP-MS analysis. During an analysis batch independent calibration verification (ICV) standards are periodically analyzed to ensure that the instrument response has not drifted significantly. A term representing the uncertainty due to this allowed drift is included in Equation 5 in Table 1. The analytical procedure specifies a value of ± 20% before recalibration is required. Data from control charts indicate this value is typically much less than 20%. The value for each element from the control charts were used as the input for the contribution from drift. The other variable quantities along with their uncertainty were also input into the GUM workbench[6] which then calculated the uncertainty contribution for each component and the expanded uncertainty for the measurement. The expanded uncertainty (*U*) was obtained by multiplying the combined uncertainty $u_c(x)$ by a coverage factor of 2 to obtain *U*, so that the reported result $x \pm U$ is estimated to have a level of confidence of ca. 95%. This procedure was repeated for each trace element and the uncertainty results from this model were then compared to that observed as part of the U and Pu metal exchange programs.

Table 1 GUM model equations and definitions for ICP-MS analysis of U or Pu metal

Concentration calculations

C_solid = C_soln * DF (1)

DF = V_init / M_splwt * V_dilA / V_aliq * V_final / V_aliqofdilA (2)

conc_low = C_stock1 * V_stock1 / V_cal1 (3)

conc_high = C_stock2 * V_stock2 / V_cal2 (4)

C_soln = ((cps_spl - b) / m) + \delta_drift (5)

Definitions

C_solid = concentration in solid, ug/g
C_soln = concentration in solution, ug/mL
DF = dilution factor
V_init = initial volume of sample, mL
M_splwt = weight of sample, g
V_dilA= first dilution volume, mL
V_aliq = volume of aliquot taken from first dilution, mL
V_final = final volume of analytical sample, mL
V_aliqofdilA = volume of aliquot taken from dilution A, mL
conc_low = concentration of low standard, ug/mL
C_stock 1= concentration of stock standard #1, ug/mL
V_stock1 = volume of stock standard #1, ug/mL
V_cal1 = final volume of low calibration standard, mL

conc_high = concentration of high standard, ug/mL
C_stock2 = concentration of stock standard #2, ug/mL
V_stock2 = volume of stock standard #2, ug/mL
V_cal 2 = final volume of high calibration standard, mL
cps_spl = counts per second, sample signal
b = intercept of linear calibration curve
m = slope of linear calibration curve
\delta_drift = allowed instrument drift

Results and Discussion

Examples of the output from the GUM workbench for the determination trace Ni in U and Cr in Pu by ICP-MS are shown in Tables 2 and 3 respectively. The relative expanded uncertainty is in the range expected when the concentration is not at the low end of the calibration range. This corresponds to the concentration range that is not noise limited, i.e. the portion of the curve (Fig. 1) that has a slope approaching zero. The contribution to the uncertainty for Ni in U is dominated by the signal, allowed drift and one of the volume measurements. This is useful information and can be used to focus on the components that contribute the most to the uncertainty of the measurement if improvement in U is sought. For example, the 5 mL volume dilution for Ni in U (Table 2, V_{dilA}) accounts for 13%, signal intensity (cps_{spl}) is ~15% and instrument drift (δ_{drift}) is ~59% of the contribution to the uncertainty. A potential modification to the procedure to reduce the uncertainty associated with the 5 mL volume would be to perform the measurement by weight instead of by volume. From Table 3 the major contributors to the measurement of Cr in Pu are a dilution and the sample signal, V_{dilA}, cps_{spl} respectively. In this case instrumental drift is less significant. This demonstrates that for each analyte the major contributors can be different and must be evaluated individually. It is likely that drift is more significant for Ni due to the fact that the ICP-MS instrument vacuum interface cones are composed of Ni giving rise to a higher and more variable background signal. Table 4 compares the Ni and Cr concentration determined using the GUM model with the value that was obtained using the normal calculation using the instrument software and an Excel spreadsheet. The agreement in concentration indicates that the GUM model is generating values that are consistent with the normal mode of calculating analytical results. This process was repeated for each trace element that was determined in the U and Pu samples using a combination of ICP-MS and ICP-AES instrumentation and is presented in Tables 5, 6, 7 and 8.

As previously discussed the uncertainty is a function of the analyte concentration and increases to a relative standard deviation (%RSD) of 100% at the detection limit. As the concentration of the analyte increases the uncertainty approaches the asymptote of Figure 1 and is reflected in Tables 5, 6, 7 and 8. In general, the GUM model in this study indicates that at low concentration the major contributor to the combined uncertainty is the analyte signal. At higher concentrations the uncertainty is dominated by the allowed instrumental drift in the instruments.

Table 2

Concentration of Ni in U (LIMS sample #200183632; submitters sample ID: LANL-UEX-JUN09) determined by ICP-MS

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C_{soln}	0.0113 ug / mL	$3.78\cdot10^{-4}$ ug / mL				
DF	3541.1 mL / g	47.7 mL / g				
V_{init}	3.00 mL	$5.14\cdot10^{-3}$ mL	normal	13	0.069 ug / g	0.2 %
M_{splwt}	0.2824 g	$3.54\cdot10^{-4}$ g	normal	-140	-0.050 ug / g	0.1 %
V_{dilA}	5.00 mL	0.0650 mL	normal	8.0	0.52 ug / g	13.0 %
V_{aliq}	0.300 mL	$3.80\cdot10^{-4}$ mL	normal	-130	-0.051 ug / g	0.1 %
V_{final}	10.0 mL	0.0220 mL	normal	4.0	0.088 ug / g	0.4 %
$V_{aliqofdilA}$	0.500 mL	$6.50\cdot10^{-4}$ mL	normal	-80	-0.052 ug / g	0.1 %
$conc_{low}$	0.0200 ug / mL	$8.84\cdot10^{-5}$ ng / mL				
C_{stock1}	10.001 ug / mL	$8.02\cdot10^{-3}$ ug / mL	normal	3.1	0.025 ug / g	0.0 %
V_{stock1}	0.0200 mL	$7.50\cdot10^{-5}$ mL	normal	1500	0.11 ug / g	0.6 %
V_{cal1}	10.0 mL	0.0220 mL	normal	-3.1	-0.067 ug / g	0.2 %
$conc_{high}$	0.100 ug / mL	$3.08\cdot10^{-5}$ ng / mL				
C_{stock2}	10.001 ug / mL	$8.02\cdot10^{-3}$ ug / mL	normal	0.94	$7.6\cdot10^{-3}$ ug / g	0.0 %
V_{stock2}	0.100 mL	$2.00\cdot10^{-4}$ mL	normal	94	0.019 ug / g	0.0 %
V_{cal2}	10.0 mL	0.0220 mL	normal	-0.94	-0.021 ug / g	0.0 %
cps_{spl}	61100 counts / sec	769 counts / sec	normal	$720\cdot10^{-6}$	0.56 ug / g	14.9 %
δ_{drift}	0.0 ug / mL	$1.06\cdot10^{-4}$ ug / mL	rectangular	3500	1.1 ug / g	58.6 %

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
C_{solid}	40.0 ug / g	2.9 ug / g	2.00	95% (normal)

Table 3
Concentration of Cr in Pu (LIMS sample #200184708; submitters sample ID: LANL-NMIP-Pu1) determined by ICP-MS

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C_{soln}	0.0122 ug/mL	$2.86\cdot10^{-4}$ ug /mL				
DF	3641.7 mL / g	49.1 mL / g				
V_{init}	3.00 mL	$5.14\cdot10^{-3}$ mL	normal	15	0.076 ug / g	0.4 %
M_{splwt}	0.2746 g	$3.54\cdot10^{-4}$ g	normal	-160	-0.057 ug / g	0.2 %
V_{dilA}	5.00 mL	0.0650 mL	normal	8.9	0.58 ug / g	23 %
V_{aliq}	0.300 mL	$3.80\cdot10^{-4}$ mL	normal	-150	-0.056 ug / g	0.2 %
V_{final}	10.00 mL	0.0220 mL	normal	4.4	0.098 ug / g	0.7 %
$V_{aliqofdilA}$	0.500 mL	$6.50\cdot10^{-4}$ mL	normal	-89	-0.058 ug / g	0.2 %
$conc_{low}$	0.0200 ug / mL	$8.84\cdot10^{-5}$ ng / mL				
C_{stock1}	10.001 ug / mL	$8.02\cdot10^{-3}$ ug / mL	normal	3.1	0.025 ug / g	0.0 %
V_{stock1}	0.0200 mL	$7.50\cdot10^{-5}$ mL	normal	1600	0.12 ug / g	1.0 %
V_{cal1}	10.0000 mL	0.0220 mL	normal	-3.1	-0.069 ug / g	0.3 %
$conc_{high}$	0.100 ug / mL	$3.08\cdot10^{-4}$ ng / mL				
C_{stock2}	10.001 ug / mL	$8.02\cdot10^{-3}$ ug / mL	normal	1.2	0.010 ug / g	0.0 %
V_{stock2}	0.100 mL	$2.00\cdot10^{-4}$ mL	normal	120	0.025 ug / g	0.0 %
V_{cal2}	10.00 mL	0.0220 mL	normal	-1.2	-0.027 ug / g	0.0 %
cps_{spl}	$2.6500\cdot10^{5}$ counts / sec	4450 counts / sec	normal	$180\cdot10^{-6}$	0.79 ug / g	43 %
δ_{drift}	0 ug / mL	$4.21\cdot10^{-5}$ ug / mL	rectangular	3600	0.15 ug / g	1.6 %

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
C_{solid}	44.5 ug / g	2.4 ug / g	2.00	95% (normal)

Table 4

GUM model concentration compared to standard calculation

Concentration and Uncertainty Estimated by this Study				
Element	Sample ID	GUM calculated concentration, ug/g	GUM uncertainty k=2, ug/g	Result using standard method of calculation, ug/g
Cr	200184708	45	2.4	44
Ni	200183632	40	2.9	44

Table 5

Pu Metal Analysis by ICP-MS

Element	Detection Limit, ug/g	Sample 200184708, LANL-NMIP-Pu1		Sample 200184709, LANL-NMIP-Pu2	
		Conc., ug/g	U, ± ug/g (k=2)	Conc., ug/g	U, ± ug/g (k=2)
Cd	0.2	0.22	0.20	0.25	0.20
Cr	0.6	45	2.4	44	2.3
Mn	0.5	8.7	2.0	8.6	2.0
Mo	0.3	2.4	0.22	2.7	0.25
Pb	0.4	7.6	1.7	7.7	1.7
Sn	0.2	1.8	0.27	1.9	0.27
Ta	0.3	7.0	1.3	6.3	1.2
Th	0.4	< 0.4	—	< 0.4	—
Ti	0.9	3.3	0.30	3.4	0.31
W	0.4	2.9	0.30	1.7	0.20
Zr	0.1	0.34	0.07	0.29	0.06
Np	0.1	130	10	131	10

Table 6

Pu Metal Analysis by ICP-AES

Element	Detection Limit, ug/g	Sample 200184708, LANL-NMIP-Pu1		Sample 200184709, LANL-NMIP-Pu2	
		Conc., ug/g	U, ± ug/g (k=2)	Conc., ug/g	U, ± ug/g (k=2)
Al	17	37	7.0	38	7.0
Be	1	< 1	—	< 1	—
B	2	2.4	0.48	2.2	0.44
Ca	10	< 10	—	< 10	—
Cu	8	9.3	1.7	10	1.8
Fe	1	171	14	169	14
Mg	2	< 2	—	< 2	—
Ni	5	75	9.8	74	9.6
Si	20	30	6.9	30	6.9
Zn	5	<5	—	<5	—

Table 7 U Analysis by ICP-MS

Element	Detection Limit, ug/g	Sample 200183632, LANL-UEX-JUN09, cut 1		Sample 200183632, LANL-UEXJUN09, cut 2	
		Conc., ug/g	U, ± ug/g (k=2)	Conc., ug/g	U, ± ug/g (k=2)
Al	3	13	1.3	13	1.3
Be	0.4	< 0.4	—	< 0.4	—
B	2	5.0	1.6	5.8	1.9
Cu	0.6	12	1.6	12	1.6
Fe	50	88	13	91	14
Mg	1	< 1	—	1.2	1.2
Ni	7	40	2.9	42	3.0
Zn	3	< 3	—	< 3	—
Zr	0.1	4.7	0.61	5.1	0.66
Cd	0.2	0.20	0.20	0.30	0.27
Cr	0.6	18	2.5	18	2.5
Co	0.2	1.0	0.30	1.1	0.33
Pb	0.4	0.40	0.24	0.49	0.29
Mn	0.5	6.4	1.7	6.4	1.7
Mo	0.3	39	3.9	40	4.0
Ta	0.3	0.44	0.22	0.55	0.28
Sn	0.2	0.33	0.17	0.42	0.21
Ti	0.9	1.5	0.75	1.6	0.80
W	0.4	27	1.9	28	1.9
Th	0.4	< 0.4	—	< 0.4	—

Table 8

U Analysis by ICP-AES

Element	Detection Limit, ug/g	Sample 200183632, LANL-UEX-JUN09, cut 1		Sample 200183632, LANL-UEXJUN09, cut 2	
		Conc., ug/g	U, ± ug/g (k=2)	Conc., ug/g	U, ± ug/g (k=2)
Al	17	< 18	—	< 17	—
Be	1	< 1	—	< 1	—
B	2	5.2	0.78	4.6	0.69
Ca	10	< 10	—	< 10	—
Cu	8	14	2.5	14	2.5
Fe	1	118	16	120	17
Mg	2	< 2	—	< 2	—
Ni	5	49	8.1	48	8.0
Si	20	228	34.2	214	32.1
Zn	5	< 6	—	< 5	—
Zr	2	< 2	—	< 2	—
Cd	7	< 7	—	< 7	—
Cr	10	19	4.2	21	4.6
Co	5	<6	—	< 5	—
Pb	22	< 23	—	< 22	—
Mn	0.7	7.0	1.1	7.1	1.1
Mo	12	34	10	38	11
Ta	5	< 6	—	< 5	—
Sn	51	< 54	—	< 51	—
Ti	2	< 2	—	< 2	—
W	22	32	16	28	14

Conclusions

The model utilizing a combination of GUM with control chart (QC) data has been previously demonstrated and is advantageous when a large number of analytes are reported.[8,9] The use of U and Pu metal exchange and QC data in combination with GUM is an improvement over the two point relationship of equation 5 since it includes multiple concentrations spanning the dynamic range of measurement collected over many years. This approach is more in agreement with the EURACHEM method, in which at least ten concentration levels are used to determine the uncertainty-concentration relationship.[6] Using this model, uncertainty was calculated for 41 trace element determinations in U and 22 in Pu metal samples using a combination of ICP-MS and ICP-AES. Comparison of concentration results obtained using the model are in agreement with those using calculations normally performed to obtain trace element results which validates the model equation. In this study the major contributions to the uncertainty budget was found to be concentration dependent and is consistent with the relationship between uncertainty and concentration in ICP analysis. The GUM model calculates the uncertainty for each component for a measurand and indicates which components contribute the most to the combined uncertainty. With this model a knowledgeable decision can be made regarding which components will produce the most improvement in uncertainty if the analytical procedure is modified. If feasible, the next phase of this exercise will be the improvement in the combined uncertainty by modifying the analytical procedures.

References

1. ISO (1993) Guide to the expression of uncertainty in measurement, ISO, Geneva
2. ANC-102, R.1.3, Inductively Coupled Plasma – Mass Spectrometry using the VG Elemental Plasma Quad, Los Alamos National Laboratory, Actinide Analytical Chemistry Group
3. ANC-189, R.4, Operating the TJA Inductively Coupled Plasma – Atomic Emission Spectrometer, Los Alamos National Laboratory, Actinide Analytical Chemistry Group
4. K. Duff, UK/US Uranium Metal Exchange Program Progress Summary Report 2009, AWE Report 131/10
5. L. Tandon, et. al., Los Alamos National Laboratory Controlled Publication, Plutonium Metal Exchange Data Metals 465, D, E and F, LA-CP-10-00184, October 2009
6. EURACHEM / CITAC (2000) Guide CG4, Quantifying Uncertainty in Analytical Measurement, 2nd edition, http://www.eurachem.ul.pt/
7. GUM Workbench Pro, Version 2.4.1.346, 1996-2009, Metrodata GmbH
8. V. Barwick, S. Ellison, B. Fairman, Analytica Chimica Acta, 394 (1999) 281-291
9. T. Ruth, Accred Qual Assur (2004) 9:349-354