Quantifying multiple trace elements in uranium ore concentrates: an interlaboratory comparison

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Abstract An intercomparison was organized, with six laboratories tasked to quantify sixty-nine impurities in two uranium materials. The main technique employed for analysis was inductively coupled plasma mass spectrometry in combination with matrix-matched external calibration. The results presented highlight the current state-of-the-practice; lessons learned include previously unaccounted polyatomic interferences, issues related to sample dissolution, blank correction and calibration, and the challenge of estimating measurement uncertainties. The exercise yielded consensus values for the two analysed materials, suitable for use as laboratory standards to partially fill a gap in the availability of uranium reference materials characterized for impurities.

Keywords Impurity analysis · Inductively coupled plasma mass spectrometry · Interlaboratory comparison · Reference material · Uranium ore concentrate

Introduction

Analysis of trace elements (impurities) in uranium-bearing materials, from uranium ore to nuclear fuel, is performed in a variety of fields and for different purposes. The presence of certain elements affects the chemical, physical, and nuclear properties of materials involved in the nuclear fuel cycle; therefore industrial standards specify limits for a range of impurities [1, 2]. The information on trace elements is also utilized for attributing materials or for understanding variations through the uranium processing [3–8]. The International Atomic Energy Agency (IAEA) uses information on trace elements in uranium-bearing materials, such as uranium ore concentrate (UOC) and intermediate conversion products, to support verification of States' declarations in terms of correctness and completeness. The information on impurity concentrations is used in several ways, in particular to judge material conformity to the nuclear-grade material specifications, to evaluate facility design information, to assess material origin and to detect possible substitution of material [9–12].

Impurities in uranium materials have been analysed over the past decades using an array of different analytical techniques and procedures [13] including atomic absorption spectrometry [14], atomic emission spectrometry [15–17], X-ray fluorescence spectrometry [3], ion chromatography [4], variations of inductively coupled plasma mass spectrometry (ICP-MS) including combination with

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laser ablation [18], quadrupole ICP-MS with or without collision/reaction cell [3, 19–21], time-of-flight ICP-MS [22], sector-field ICP-MS [6, 23, 24], and liquid chromatography ICP-MS [25]. The different analytical procedures exhibit specific merits and drawbacks hence they demonstrate diverse analytical performance and applicability.

To evaluate laboratory performance in the analysis of impurities in uranium materials, and to obtain a batch of well characterized material to serve as a laboratory standard for the analysis of impurities in uranium, in 1983–1984 the IAEA conducted two interlaboratory comparisons [26, 27], which involved the same U₃O₈ powder material.[1] The 19 participating laboratories applied different analysis techniques, predominantly variations of absorption and emission spectroscopy. As a result of the exercise, the U₃O₈ powder was certified as a reference material (RM), with concentrations of 19 impurity elements characterized [28].

Recently, CETAMA organized a similar performance testing, which involved 17 laboratories from the nuclear industry and the nuclear safeguards community [29]. The laboratories performed impurity measurements using predominately ICP-MS and, to some extent, ICP atomic emission spectrometry (ICP-AES). The comparison was carried out on one solution of uranyl nitrate, with only 12 elements requested for analysis, having concentration range of about three orders of magnitude. Generally, ICP-MS results showed better performance than ICP-AES. To the authors' knowledge this was the only exercise on the subject performed within the past decade or more.

The interlaboratory comparison discussed herein was organized by the IAEA during 2011–2012. Six laboratories participated in the exercise: Canadian Nuclear Safety Commission Laboratory, Institute for Transuranium Elements (ITU) of the European Commission Joint Research Centre (EC JRC), the IAEA Safeguards Analytical Laboratory (SAL), and three laboratories of the US Department of Energy: Los Alamos National Laboratory, Lawrence Livermore National Laboratory, and Oak Ridge National Laboratory.

The laboratories were tasked to analyse trace elements in two powder materials of composition typical for UOC, which is a considerably more challenging matrix compared

to a solution. The samples were to be chemically treated by the laboratories, including the sample dissolution as is employed in the analysis of real-world samples. Determination of 69 trace elements was requested, with the concentration range spanning seven orders of magnitude. This interlaboratory comparison also served the purpose of identifying the current state-of-the-practice as well as establishing consensus values for the two materials.

Experimental

Scope of the interlaboratory comparison

The goal of this exercise was to identify analytical capabilities of the participating laboratories and to assess the performance of the different analytical procedures in place to determine between-laboratory differences and their potential causes, to identify chemical elements that are problematic and/or difficult to analyse with established analytical techniques, to review the associated measurement uncertainties as reported by the laboratories, and, finally, to assign consensus values to the two materials for their future use for quality control (QC) in analysis of impurities in uranium materials.

The participating laboratories were requested to perform determination of concentrations (relative to uranium) for the following 69 chemical elements: Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, V, W, Y, Yb, Zn, Zr. The concentrations of these elements in the two materials selected for the exercise spanned more than seven orders of magnitude, ranging from below 1 ng/gU to higher than 1 mg/gU.[2]

A total of five randomly selected aliquots of each material were sent to each participating laboratory, with a request to perform three replicate analyses per aliquot. Each replicate analysis included all steps of sample preparation and measurement, including sample dissolution and instrument calibration. Hence, a total of $3 \times 5 = 15$ data points per element and material were to be reported by each laboratory. In addition, for each result the laboratories were asked to report the associated measurement uncertainty (at 95 % level of confidence) and the critical level L_c (detection decision at 99 % level of confidence, according to the widely accepted terminology introduced by Currie [30, 31]. Laboratories were requested to treat the materials in the same manner as they treat the majority of the

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[1] The preparation of the U₃O₈ material was arranged by the Laboratoire Central d'Analyse et de Controle in Grenoble. A large uranium metal billet of industrial origin was molten together with a small uranium ingot carrying the trace elements. It was then converted to U₃O₈ by ignition under a stream of oxygen. The resulting U₃O₈ itself was milled, ground, and sieved in order to obtain a 100 mesh grain size powder. The whole batch was then homogenized, and the homogeneity was verified by six laboratories. In 1982 the French Government donated a batch of the resulting material to the IAEA.

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[2] Concentrations of Br and Cl impurities, not measured by any of the participating laboratories, remain undetermined.

samples routinely analyzed for impurities. A standardised template for the reporting of the measurement results was distributed to the participants, who were also requested to fill out a questionnaire aimed at gathering description of the analytical procedures and techniques employed.

The major limitation of this interlaboratory comparison was that the two materials used were not certified for the impurity concentrations; a few exceptions apply (see below). Hence, evaluating the accuracy of the reported data had its limitations; nonetheless between-lab differences were assessed. Furthermore, evaluating the reported measurement uncertainties as a statement of overall uncertainty against the 'true value' was not made; nonetheless an evaluation with respect to within-lab dispersion was performed to assess potential underestimation of the reported uncertainties.

The six laboratories participating in the exercise were assigned random codes, Lab 1 through Lab 6. Samples were distributed to the laboratories in autumn of 2011, with the deadline for reporting the final results to the IAEA set in February 2012. The pooled analysis results, their evaluation and findings were presented to the participants and discussed in May 2012.[3]

Description of the two materials

Two isotopically natural uranium materials were selected for the interlaboratory comparison: an ammonium diuranate powder (ADU = $(NH_4)_2U_2O_7$, sample # 9064) and a triuranium octoxide (uranyl uranate) powder (U_3O_8, sample # 9449). The two materials were chosen based on several criteria, including availability of a sufficient amount of the material and its acceptable homogeneity. In addition, the U_3O_8 material was known to have a comparably low total amount of impurities allowing the limits of detection of the laboratories' analytical procedures to be investigated, and the ADU material was known to have several impurities with comparatively high concentrations of 1 mg/gU or more.

Sample # 9064 was prepared at SAL from an ADU material obtained by the IAEA in 1994 from the Rössing uranium mine (Namibia). Uranium isotopic composition in this material was certified in 1995 by the EC JRC Institute for Reference Materials and Measurements (IRMM) as SMS 7267 [32][4] and later measured at SAL using the method of modified total evaporation multi-collector

thermal ionisation mass spectrometry (MTE MC-TIMS).[5] However this ADU was not certified for any impurities. A homogeneity study with respect to impurity distribution was performed at SAL in 2010 using ICP-MS, by analyzing eleven randomly selected aliquots of approximately 0.5 g each. For the current exercise, aliquots of 1.5–2.0 g were weighed into individual bottles and distributed to the participating laboratories. Polyethylene bottles were used deliberately, as it had earlier been demonstrated by dedicated experiments that storage and transportation of powder samples in glass bottles may result in a sample contamination with such common elements as Na and Si.

Sample # 9449 was prepared from the U_3O_8 material certified for impurities through the two IAEA interlaboratory comparisons conducted in 1980s [28]; however the original powder was later modified to increase the Fe concentration. A homogeneity study with respect to impurity distribution was performed at SAL in 2010 by analyzing eleven randomly selected aliquots of approximately 0.5 g each. Uranium isotopic composition in this material was also measured by SAL.[6] For the current exercise, aliquots of 1.5–2.0 g were weighed into individual polyethylene bottles and distributed to the participating laboratories.

Results and discussion

Summary of the questionnaires

The six participating laboratories were requested to return a completed questionnaire in order to provide details about their analytical procedure. A summary of the collected information is presented in Table 1.

Measurement techniques

The main technique employed by the laboratories was ICP-MS (mostly single-collector high-resolution sector-field instruments) in combination with matrix-matched external calibration. The majority of the participating laboratories developed their analytical procedures based on ASTM C1287-10 document [20], which represents a standard test method for the ICP-MS determination of 67 elements in nuclear grade uranium compounds without matrix

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[3] Technical Meeting on Analysis of Elemental Impurities in Uranium Samples. IAEA, Vienna, 30 May–1 June 2012.

[4] The certified atom (molar) ratios with respective expanded uncertainties ($k = 2$) are: $^{234}U/^{238}U = 0.00005472(76)$, $^{235}U/^{238}U = 0.0072568(36)$. Certified atom ratio $^{236}U/^{238}U$ is $< 2 \times 10^{-8}$.

[5] Recent measurements at SAL using MTE MC-TIMS yielded the following atom (molar) ratios, traceable to CRM IRMM-184, with respective expanded uncertainties ($k = 2$): $^{234}U/^{238}U = 0.00005471(21)$, $^{235}U/^{238}U = 0.0072544(29)$, and $^{236}U/^{238}U < 5 \times 10^{-9}$.

[6] Recent measurements at SAL using MTE MC-TIMS yielded atom (molar) ratios traceable to CRM IRMM-184, with respective expanded uncertainties ($k = 2$): $^{234}U/^{238}U = 0.00005449(23)$, $^{235}U/^{238}U = 0.0072561(30)$, and $^{236}U/^{238}U < 1 \times 10^{-8}$.

Table 1 Summary of the questionnaires on the analytical procedures used by the participating laboratories. Some details are generalized in order to protect anonymity of the laboratories

Laboratory code	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6
Analytical instrument used	Four laboratories used ThermoFisher Scientific Element 1, or Element 2, or XR sector-field ICP-MS; two laboratories used quadrupole ICP-MS (with reaction system/collision cell); one laboratory, in addition, employed XRF for selected elements					
Internal ICP-MS marker(s)	Bi, In, ^{6}Li, Sc	^{6}Li, In	^{115}In, ^{6}Li, ^{233}U added, but only ^{115}In used	Rh	In	normalized to ^{235}U
Mass resolution	For sector-field ICP-MS, in most cases a combination of high resolution (R in the range of tens of thousands), medium resolution (R being a few hundred) was used; in one case medium resolution was applied to all isotopes. In case of quadrupole ICP-MS, standard resolution was used					
Calibration strategy	Matrix matched and non-matrix matched external calibration	Matrix-matched external standards (100 ppm of U)	Matrix-matched external standards (100 ppm of U)	Matrix-matched external standards (100 ppm of U)	Non-matrix matched	Matrix-matched external standards (~100 ppm of U)
U matrix-matching	NBL 145B	NBS 960 NBL 112A	NBL 112A	In-house	None	NBL 112A
Calibration standards	Inorganic Ventures NIST traceable custom mixes and single element standards	ICP-MS standards from Alfa Aesar	Mono-element standards from High Purity Standards (Charleston, SC)	PerkinElmer multi-element standard 2–5	E.g., SPEX CertiPrep reference materials, Metuchen, NJ, USA	Claritas PPT Grade Multi-Element Solutions, SPEX CertiPrep
Standards preparation	Gravimetric	Gravimetric	Gravimetric	Volumetric	Volumetric	Gravimetric
Number of calibration points	7	5	5	2	6	7
Calibration range	4 orders of magnitude	4 orders of magnitude	2 orders of magnitude	3 to 4 orders of magnitude	3 orders of magnitude	3 orders of magnitude
Calibration curve	Linear fit through calibration blank	Linear fit	Linear fit excluding zero point	Linear fit	Linear fit	Linear fit
Interference correction	Isobaric and molecular	No details provided	Isobaric, oxides, others	Applied to several elements	Mathematical correction for In; kinetic energy discrimination mode (collision cell)	Isobaric, oxides, double-charged, peak-tailing
QC standards measured	CANMET CUP-2, NBL 124/1	CANMET CUP-2, NBL 124 series	CANMET CUP-2, NBL 124/1, NBL 124/3	Inorganic Ventures iv-ICP-MS-71 A-D	Water NIST 1643a, contaminated soil NIST 2710a	CETAMA *Morille* & *Chanterelle*, NBL 124 series
QC charts	Accuracy and precision of QC sample results	Results of QC samples	Several parameters and results	Recovery of QC elements	Results of QC samples	Results of QC samples
Sample dissolution	Conc. HNO$_3$, 0.09 M HF Seastar high purity, microwave 200 °C for 40 min	8 M HNO$_3$ overnight at 140 °C	8 M HNO$_3$, 0.16 M HF, overnight at 50 °C; orange-red precipitate in # 9449	HCl, HNO$_3$ suprapure or in-house subboiled, heating overnight	HCl, HNO$_3$, microwave oven at 200 °C for 15 min, centrifuged	HNO$_3$, microwave, heating
Dissolution quality	Most laboratories perform a visual inspection of the dissolved aliquots; one laboratory noted that they added HF to dissolve residue in material # 9449; three laboratories noted that they also dissolve QC samples: one laboratory uses NIST SRM 2710a (highly contaminated Montana soil) for this purpose					

Table 1 continued

Laboratory code	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6
Determination of uranium concentration	Davies & Grey titration	Isotope dilution mass spectrometry	Davies & Grey titration	Modified Davies & Grey titration or isotope dilution (TIMS)	ICP-MS analyses in High Matrix Introduction mode using internal standard	Internal normalization to ^{235}U
Pre-cleaning	VWR metal free tubes	All materials pre-cleaned in 8 M HNO$_3$, distilled water, most materials also pre-cleaned in 6 M HCl	Vials, bottles, pipette tips acid-washed using 6 M HCl, 8 M HNO$_3$, 18.2 MΩ DI H$_2$O in sequence. Labware dried in laminar flow hoods, bagged until used	All flasks, pipettes, etc. pre-cleaned in ethanol, 10 % HNO$_3$, ultrapure H$_2$O; dried under laminar flow	Gamma sterilized plastic tubes from Fisher	Metal-free vials from VWR, pre-cleaned pipette tips, pre-cleaned teflon vials
Uncertainty calculation	Two standard deviation (SD) of internal precision of the analysis	Two SD internal uncertainty, propagation of several sources of uncertainty	Expanded uncertainties using GUM methodology	Expanded uncertainties using GUM methodology	SD of the mean	Expanded uncertainties using GUM methodology

separation. However, the analysts chose different options for sample dissolution and for the calibration of the ICP-MS instrument.

The calibration was performed using commercially available multi- and mono-element standards mixed with uranium matrix at concentration of about 10^{-4} g/gU of solution. Typically, 5–7 calibration points were used covering a range of 3–4 orders of magnitude of the analyte concentration; a linear fit was made. Lab 4 used a 2-point calibration based on the international norms [20, 33, 34], which require using a blank and one or two (matrix matched) standard solutions for the daily calibration.

Li, Sc, In, Bi, Rh, and/or ^{233}U were added to samples as internal standards or, alternatively, ion intensities of impurities were normalized to isotope ^{235}U after uranium isotopic composition was determined (see Table 1).

The measurement results were reported as relative concentrations of impurities normalized to the concentration of uranium in μg/gU. The uranium concentration was typically determined by Davies & Gray (D&G) titration and/or isotope dilution mass spectrometry (IDMS). In one case all intensities measured in samples and in matrix-matched standards with known uranium concentration were normalized to the ^{235}U signal during ICP-MS measurement—an approach that does not require a determination of the uranium concentration in the samples.

Sample preparation

The general recommendations for dissolution of uranium materials can be found in ASTM C1347-08 [35] that is applicable to the test methods used for analysis of such materials for uranium elemental concentration, isotopic composition, and for impurities. According to the ASTM guidelines, the analyst may select appropriate dissolution procedures (e.g. heating with a steam bath or hot plate, or combination of acids and a high pressure microwave), reagents and labware to ensure safety and to avoid contamination of samples.

In this work the sample dissolutions were performed using nitric acid and heating, in some cases with a microwave oven, and/or supported by adding HCl or HF. The laboratories made an effort to perform measurements within one day after the sample dissolution, however holding times of as much as two to four weeks occurred in some cases.

Quality control

Uranium RM with certified or recommended values for impurity concentrations were utilized as QC materials, including NBL CRM 124, various CETAMA materials, and CANMET CUP-2. Results were monitored using QC charts.

Summary of the reported analytical results

The analytical results as reported by the laboratories were pooled, evaluated and plotted for visual inspection for each element and material separately.

For those impurity elements where an appropriate number of data points are available well above the critical level, it can be concluded that, overall, the between-laboratory relative differences are comparatively small. The between-laboratory relative standard deviation is usually within 30 % and for a large number of cases it does not exceed 15 %. However, several issues were identified within this interlaboratory comparison: potentially incomplete sample dissolution, unaccounted interferences, inaccurate blank correction, inaccurate calibrations, and significantly underestimated measurement uncertainties.

Effect of sample dissolution

It is known that the use of nitric acid alone might yield incomplete digestion of solid matrices [35]. Thus, significant differences in the reported results for Zr and Hf in material # 9449 were observed for those laboratories which used different acids for dissolution; see Fig. 1. One laboratory noted that a residue was observed after chemical dissolution of this material. The highest Zr and Hf
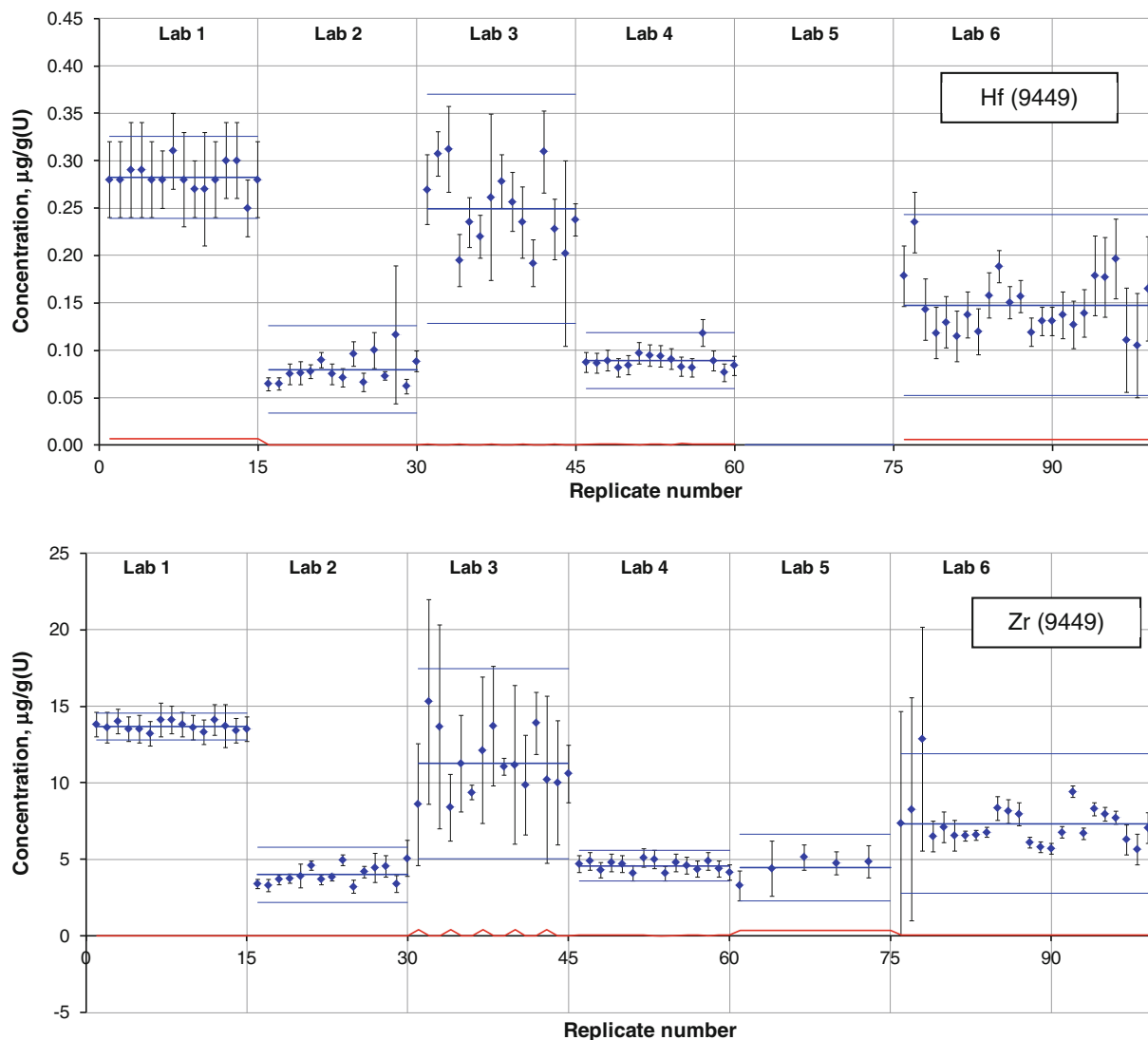
Fig. 1 Pooled results for elements Hf (*upper plot*) and Zr (*lower plot*) for material # 9449. *Blue dots* with uncertainty *bars* are the reported results; *red lines* are the respective L_c values; *blue lines* show average (*thick line*) and average ±3 standard deviations (*thin lines*) values for each laboratory. *Lab 1* and *Lab 3* employed the help of hydrofluoric acid in the sample digestion. These two laboratories reported the highest Hf and Zr concentrations, and Hf results correlate with Zr results. The pattern observed for Zr of *Lab 6* results hint on incomplete dissolution as well. (Color figure online)

concentrations were reported by those laboratories that employed HF, which likely indicates on incomplete sample dissolution or a precipitation if HF is not added. No correlation with other tetravalent elements including Ti, W, Mn, Sn, Ge, Re, Pb, or Mo is observed. On the other hand, the use of hydrofluoric acid may also generate insoluble fluorides of some elements, e.g. thorium fluoride [36], which complicates the analysis. As such there is a trade-off when using HF for sample dissolution. It highlights one of the challenges inherent to this type of analysis. The use of aqua regia resulted in better recoveries for some elements

(e.g. tungsten); however the presence of HCl introduced additional interferences in the ICP-MS analysis.

Effect of interferences

Some laboratories reported results that exhibited a positive bias for concentrations of elements Ag, La, or Sc. It was confirmed that these biases resulted from unaccounted interferences of ZrO^+, UAr^{2+}, and Zr^{2+} ions (Fig. 2). Other interferences relevant to the ICP-MS analytical procedures were accounted for by the laboratories to some
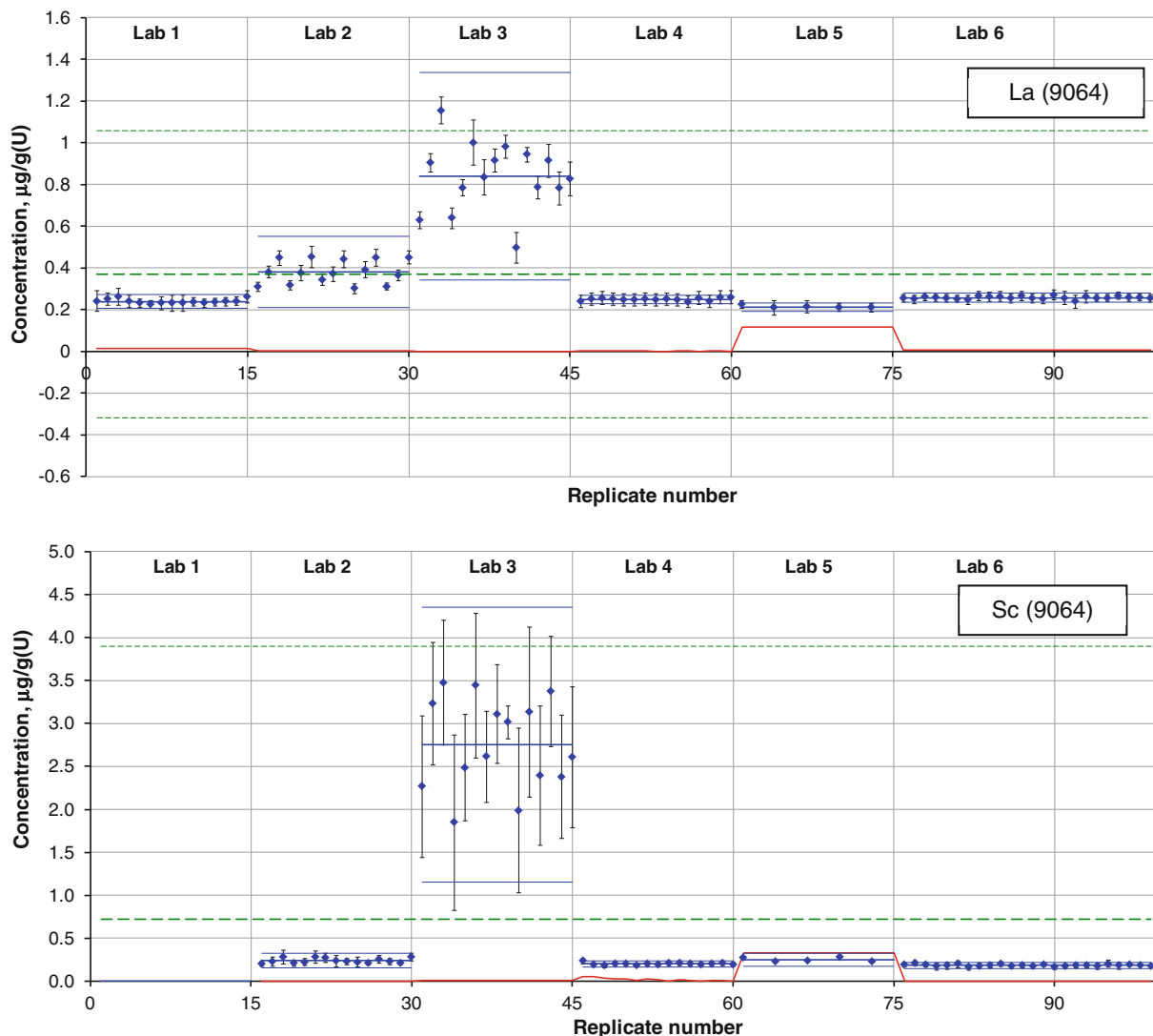
Fig. 2 Pooled results for elements La (*upper plot*) and Sc (*lower plot*) for material # 9064. *Blue dots* with uncertainty *bars* are the reported results; *red lines* are respective L_c values; *blue lines* show average (*thick line*) and average ±3 standard deviations (*thin lines*) values for each laboratory; *dotted green line* shows average value for all laboratories. The results reported by a few laboratories were biased

or associated with larger uncertainties due to inaccurate correction of interferences that affected these analytes (*Lab 2, Lab 3* for La; *Lab 3* for Sc). *Lab 1* did not report Sc concentrations as this element was used for calibration as an internal standard in the analytical procedure. (Color figure online)

Table 2 Some recognized ICP-MS interferences in impurity analysis of uranium materials using discussed analytical procedures

Affected isotopes	Interfering elements					
	Mo	Ta	Sr	Ba	Zr	Other
^{42}Ca, ^{44}Ca			×			
^{45}Sc	×				×	
^{46}Ti	×				×	^{46}Ca
^{47}Ti	×				×	
^{60}Ni						^{44}Ca^{16}O
^{69}Ga				×		
^{72}Ge						^{40}Ar^{32}S, ^{35}Cl^{37}Cl, ^{56}Fe^{16}O
^{89}Y			×			
^{93}Nb	×					
^{99}Ru	×					
^{103}Rh						CuAr
^{105}Pd	×		×			CuAr, ^{89}Y^{16}O
^{107}Ag					×	
^{109}Ag	×				×	
^{111}Cd	×				×	
^{126}Te, ^{128}Te	×					UO^{2+} peak-tailing
Sn						U^{2+} peak-tailing
^{133}Cs						UO$_2$$^{2+}$ peak-tailing
REE						light REE oxides on heavy REE
^{139}La				×		UAr
^{140}Ce	×					
^{141}Pr	×					
^{146}Nd	×					
^{147}Sm	×					
^{151}Eu				×		
^{157}Gd				×		
^{165}Ho			×			
^{172}Yb	×					
^{178}Hf	×					
^{181}Ta						REE oxides
^{191}Ir		×		×		
^{195}Pt		×				
^{197}Au		×				
^{232}Th						U peak-tailing

Concentration of elements Mo, Ta, Sr, Ba, and Zr in uranium-bearing materials may be particularly high, and they are prone to produce (oxide) interferences

degree or another; they are summarized in Table 2. These interferences are mostly double-charged species and/or oxides species, in addition to some recognized species produced by the uranium matrix (e.g., UAr^{2+}). As a matrix-matched approach is used by the laboratories, interferences stemming from uranium species are to be expected. Since the formation of interferences is influenced by the elemental composition of the impurities in the

Fig. 3 Pooled results for elements S (material # 9064), Si (material # ▶ 9449), and P (material # 9449). *Blue dots* with uncertainty *bars* are the reported results; *red lines* are respective L_c values; *blue lines* show average (*thick line*) and average ± 3 standard deviations (*thin lines*) values for each laboratory. One laboratory employed XRF for analysis of sulphur; all other results for the three elements were produced using ICP-MS. (Color figure online)

uranium material, many more interferences may need to be accounted for.

Blanks and cross-contamination

A disproportionally large number of positive outliers (deviating by as much as 4 standard deviations) are found in the results for concentrations of Ba, Ca, Mg, Na, K, Pb, and Zn. Concentrations of these elements in the analyzed sample solutions as well in the process blank solutions can be potentially subject to significant non-controlled changes during sample preparation and analysis because of a high risk of sample contamination with ubiquitous elements present in the laboratory environment. Positive biases in selected Rb and B data were also observed, potentially due to blank issues.

Calibration

Trends or biases in reported results are apparent for selected elements or laboratories. These were likely caused by calibration issues, e.g., significant day-to-day variations or negative bias due to issues related to the matrix-matching or to the determination of the uranium content.

Measurement uncertainty

The participating laboratories made an effort to identify and propagate uncertainty sources, in some cases applying the GUM methodology [37]. Nonetheless, in a large number of cases the reported uncertainties appear to be significantly underestimated with respect to the observed within-lab dispersion. Considering that the between-lab dispersion is usually larger than the within-lab dispersion, the reported uncertainties are potentially underestimated in even more cases. The laboratories tend to assess the measurement repeatability using internal precision which is prone to result in significant underestimations. Other significant sources of uncertainty, including calibration, interferences, and blank corrections were either not included or appear to be underestimated.

Challenging elements

Several laboratories did not report data for phosphorus, sulphur, and silicon, because these elements are difficult to
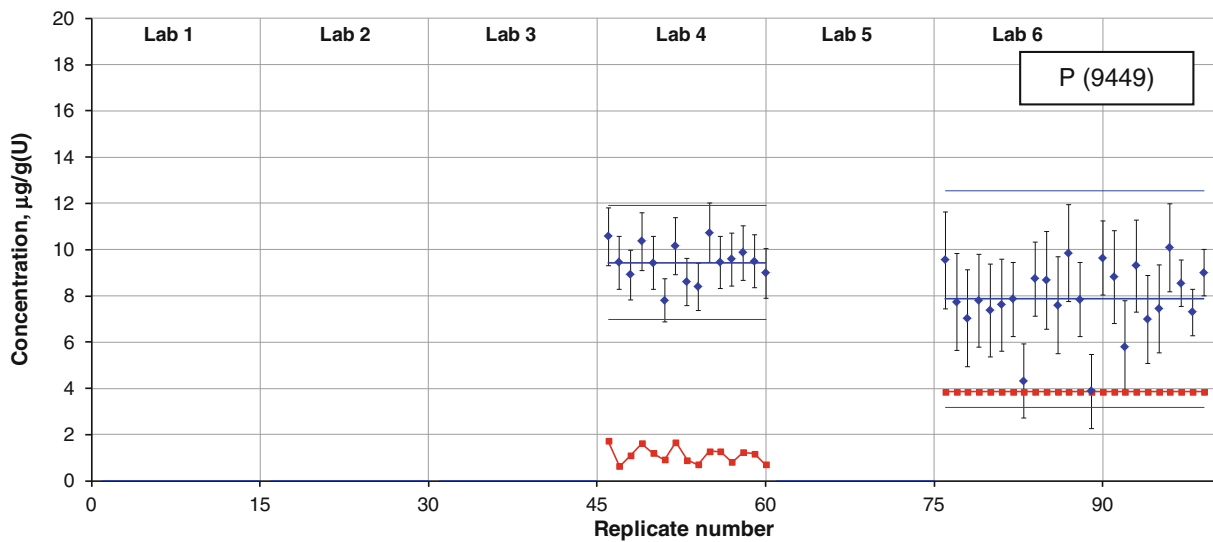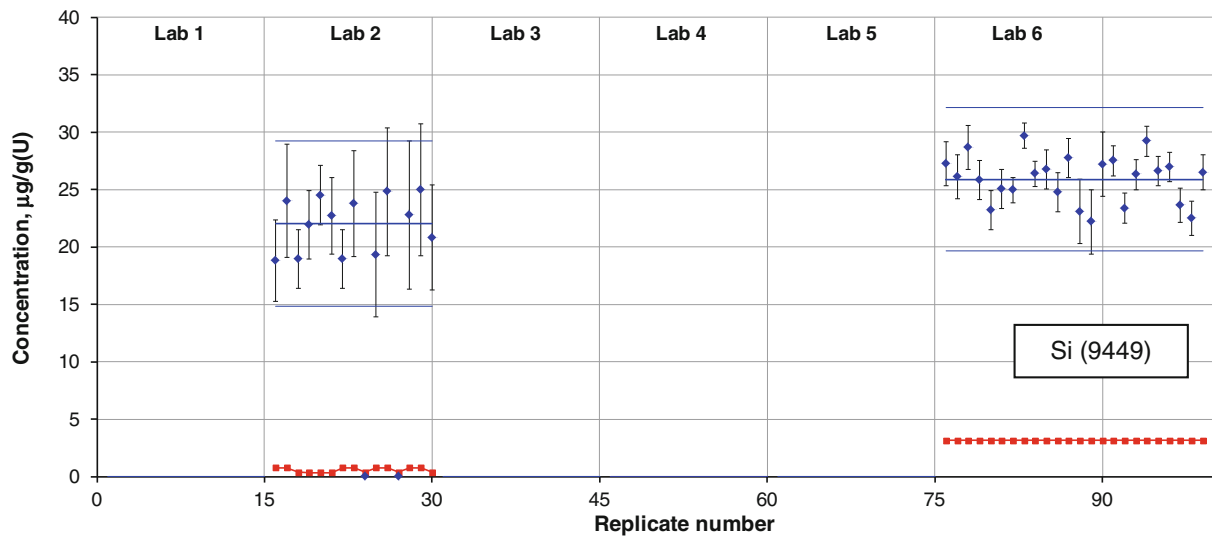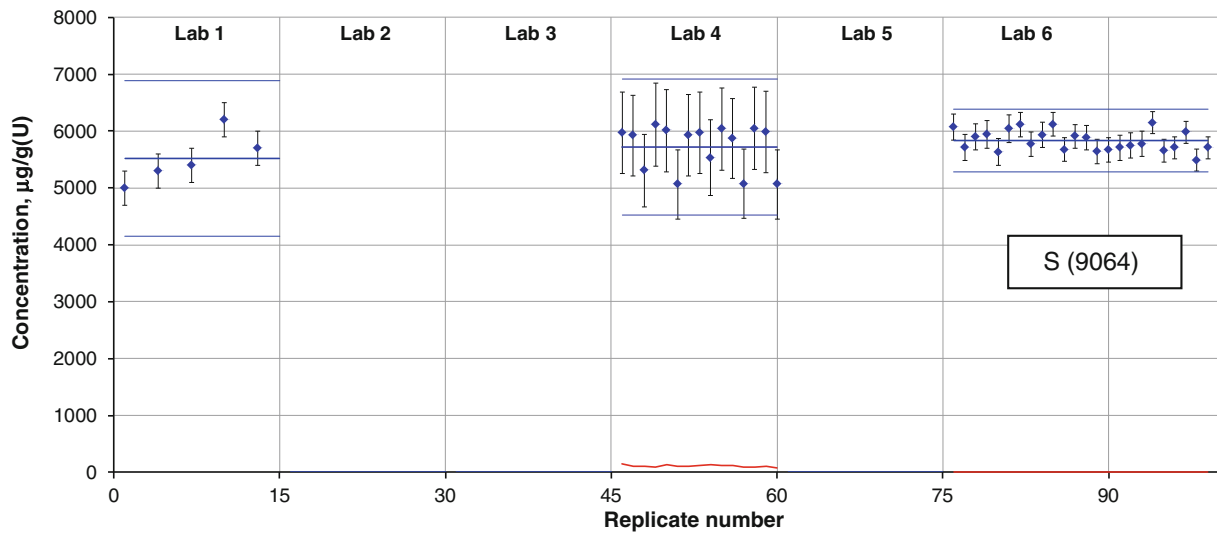
quantify by ICP-MS. However, P, S, and Si results were reported by selected laboratories which used sector-field ICP-MS instruments. On Fig. 3, these sector-field ICP-MS results are compared to the X-ray fluorescence (XRF) results for sulphur submitted by one laboratory; these results are judged to be in a reasonable agreement.

None of the participants reported results for Cl and Br as these elements are a challenge for quantification by ICP-MS. Several laboratories did not report data for Au and In. Indium is frequently used as internal marker for the ICP-MS signal normalization, and in such cases it cannot be quantified.

Detection decision

The values for the detection decision threshold (critical level, L_c) reported by the participants for the lanthanides are below 1×10^{-9} g/gU, while such elements as Ca, Fe, K, Li, Mg, Na, Ni, P, S, and Si have comparatively high L_c—on the order of 10^{-4} g/gU. As illustrated on Fig. 4, this mirrors low versus high instrumental and chemical blanks, as expected for the respective elements. Reported L_c values appear to be overestimated in a few cases.

The effect of data 'censoring' by apparently overestimated L_c values is demonstrated in Fig. 5, which presents relative concentrations of 14 rare earth elements (REE) normalized to the sum of lanthanides. Although the concentrations of six REE were reported by Lab 5 as 'below L_c' (Fig. 5a), the comparison of 'uncensored' data obtained from Lab 5 (Fig. 5b) with the results reported by Labs 1, 4 and 6 (Fig. 5c) demonstrates a very good agreement of

relative REE concentrations determined by different laboratories. In practice, the use of the 'censored' data presented on Fig. 5a would reduce the ability of data evaluators to attribute samples by analyzing REE patterns. We conclude therefore, that a proper estimation of detection decision is essential to avoid a loss of useful information about investigated samples.

Assigning consensus values to the materials

One of the goals of this interlaboratory comparison was to assign a consensus value with associated measurement uncertainty for the concentration of each impurity element of interest (in units of microgram per gram of uranium) in the two materials. The materials can then be used, for example, as laboratory standards for QC purposes. It is noted that they shall not be used as calibration standards, since the consensus values were not established by a rigorous certification campaign. Although the laboratories employed traceable standards for the analysis calibration, traceability of the consensus values to the SI is not claimed here, because of potentially unrecognized interferences or matrix-effects.

After initial submission of the analysis data, some laboratories later revised selected results, in order to address preliminary findings of the exercise. This included revisions to blank subtractions, interference corrections, and rejection of selected results demonstrated to suffer from calibration or other issues. These revised data were used in the calculation of the consensus values.
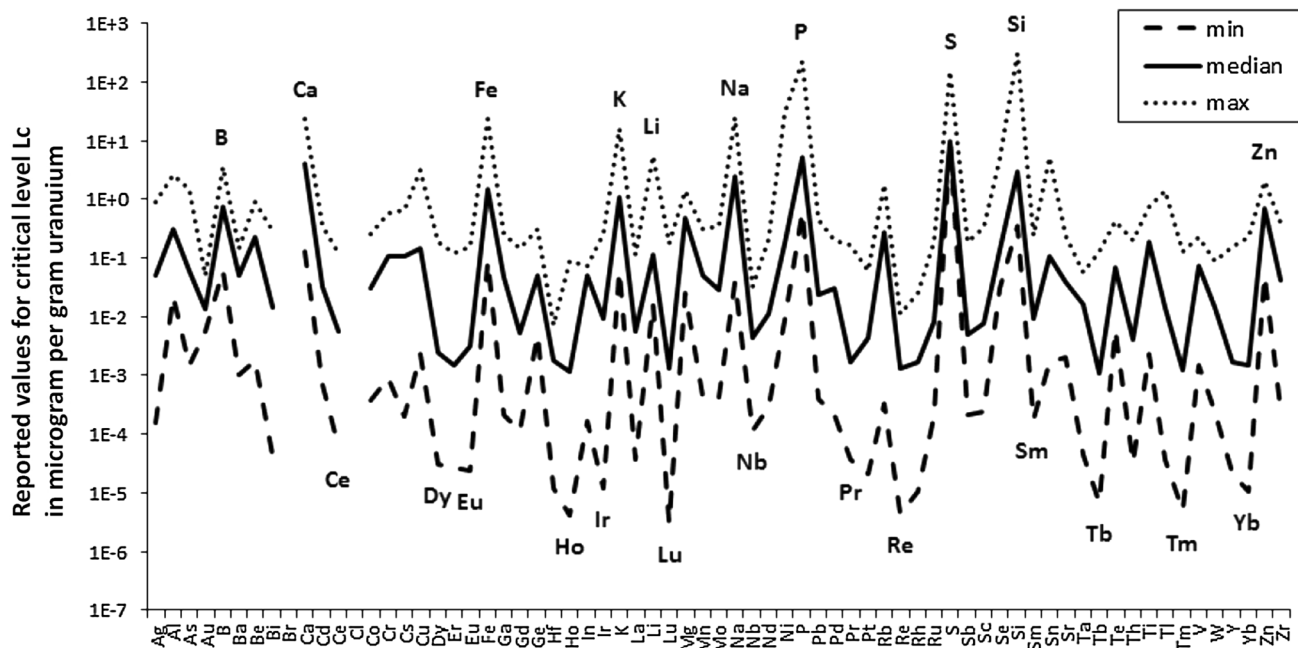
Fig. 4 Minimum, median, and maximum of the reported L_c values for the measured elements, combined for six laboratories and the two analysed materials
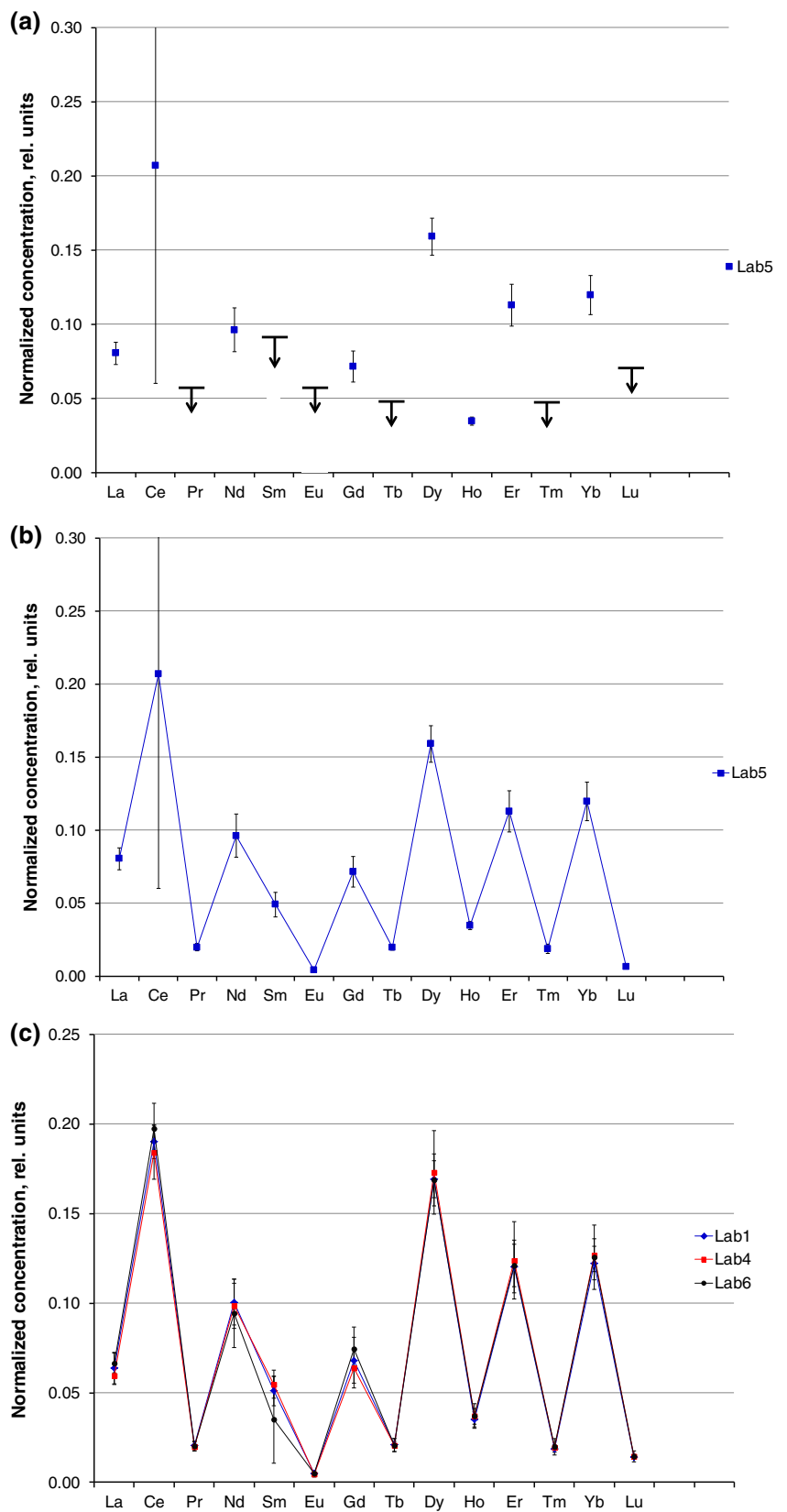
The methodology used to assign consensus values is based on ISO Guide [38] and was used earlier in the re-certification of NBL CRM 124 [39]. The methodology considers four cases:

1. No consensus value is assigned if only $n = 2$ laboratories or less have reported data, which is indicated with 'n/a' for 'not applicable'. In both materials, this applies to elements Br, Cl ($n = 0$) and Au, In ($n = 2$). It also applies to S in material #9449 ($n = 2$; all data points are below the respective L_c values). As elements P and Si ($n = 2$, both materials) are of particular interest in most applications of the impurity data, no consensus values are assigned, but the range is stated (minimum result to maximum result) for informational purpose only.

2. No consensus value is assigned to Hf and Zr in material #9449 ($n > 4$) due to potential issues with incomplete sample dissolution as discussed above. The range is stated (minimum result to maximum result) for informational purpose only.

3. An upper limit is assigned as consensus value for an element concentration in a given material if at least $n = 3$ laboratories reported data with the majority of the data points below or close to the corresponding L_c values. The upper limit is calculated as 95 % percentile (no uncertainty assigned). The 95 % percentile is calculated using all reported measurement values by all the laboratories. In case where a reported measurement value is below the corresponding L_c, the measurement value is ignored, and the L_c value is used instead. A selected number of data points were rejected for the calculation of the consensus values as these data points are likely affected by signal spikes (typically more than three times higher than the within-lab standard deviation) mostly due to issues with contamination (high blank result) and/or significantly larger uncertainty. The data points that were rejected amount to less than 0.5 % of the entire data set.

4. A consensus value is assigned to an element concentration in a material if at least $n = 3$ laboratories have reported data and the majority are above the corresponding L_c. The consensus value is calculated as the mean of laboratory means. Data points below L_c are ignored, however the number of data point thus ignored was small. An expanded uncertainty $U(95.5\%)$ using respective coverage factor k is assigned using GUM methodology [33] by incorporating and estimating all recognized sources of uncertainty. These include:

   - Between-laboratory variation: standard deviation of laboratory means;
   - Uranium concentration determination: IDMS, D&G, or normalization to ^{235}U signal is used, hence conservative $U(k = 2) = 1$ % rel. is assigned;

   - Weighing and dilutions: usually gravimetrical preparation, conservative $U(k = 2) = 1$ % rel. is assigned;
   - Uncertainties of certified values of mono- or multi-element calibration standards employed to establish metrological traceability: typically $U(k = 2)$ of the certified value is smaller than 0.5 %, hence a conservative $U(k = 2) = 0.5$ % rel. is assigned;
   - Regression of calibration curve, uranium matrix effect, internal maker normalization: these uncertainty components are difficult to estimate but an inappropriate matrix-matching was observed to produce as much as 20 % bias, hence $U(k = 2) = 20$ % rel. is assigned;
   - Detector non-linearity including dead-time correction: assumed to be not more than $U(k = 2) = 2$ % rel.;
   - Purity of uranium material used for matrix-matching: no uncertainty is estimated for this component, as different materials were used by the laboratories and hence it is difficult to assess; it is assumed that this component of uncertainty will be reflected to some extent in the between-laboratory variation;
   - Blank correction, including process blank and memory effects: results for several elements including Mg, Ba, Ca, Na, K, Pb, and Zn show a significant number of signal spikes indicating memory effects, cross-contamination, and/or increased blanks; $U(k = 2) = 10$ % rel. is assigned to these elements;
   - Interference correction including isobars, oxides, double-charged ions, hydrides, and peak-tailing: difficult to estimate as it depends on the ratio of analyte to interfering element and on the formation of interferences as a function of the plasma settings, mass resolution applied, etc. At a minimum, elements Sc, Ag, Sn, and La were identified, for which significant interference corrections had to be performed. An $U(k = 2) = 10$ % rel. is assigned to these elements;
   - Sample inhomogeneity: no significant degree of inhomogeneity at the 0.5 g minimum sample size was observed, based on triplicate measurements of each element on five independent dissolutions of each material performed by each laboratory; hence the uncertainty component is assumed to be negligible, and not included.

Other sources of uncertainty are assumed to be insignificant. A revision of the uncertainty calculation will be performed in the future if other significant sources of uncertainty are identified or if the estimation of those listed above need to be improved. A revision of the consensus values will be performed in the future if additional data become available.

The consensus values established using the approach described above are listed in Tables 3 and 4 for materials

Table 3 Consensus values for material # 9064 (IRMM SMS 7267) stated as elemental concentration of impurity in microgram per gram of uranium

Element	Consensus value or *interval*, μg/gU	U	k	Relative U (%)	Number of labs	Between-lab SD
Ag	**<0.88**				5	0.024
Al	**56**	**17**	2.13	29.9	6	13
As	**0.93**	**0.23**	2.06	24.9	5	0.14
Au	n/a				2	0.0018
B	**<29**				4	10
Ba	**1.20**	**0.31**	2.03	26.2	6	0.18
Be	**<0.92**				6	0.088
Bi	**4.0**	**1.3**	2.25	32.4	4	0.83
Br	n/a				–	
Ca	**186**	**95**	2.32	51.0	6	86
Cd	**5.2**	**1.7**	2.16	32.0	6	1.4
Ce	**0.71**	**0.17**	2.04	23.9	5	0.094
Cl	n/a				–	
Co	**0.130**	**0.028**	2.01	21.7	5	0.011
Cr	**1.09**	**0.38**	2.20	34.9	6	0.33
Cs	**<0.38**				5	0.26
Cu	**1.13**	**0.28**	2.06	25.0	5	0.17
Dy	**0.61**	**0.16**	2.07	26.5	6	0.12
Er	**0.44**	**0.11**	2.07	26.2	6	0.082
Eu	**0.0182**	**0.0040**	2.01	21.8	5	0.0016
Fe	**1,470**	**340**	2.03	23.1	6	190
Ga	**<0.25**				6	0.041
Gd	**0.263**	**0.067**	2.06	25.7	6	0.047
Ge	**<0.35**				6	0.18
Hf	**0.083**	**0.020**	2.04	23.8	5	0.011
Ho	**0.132**	**0.034**	2.06	25.8	6	0.024
In	n/a				2	0.0052
Ir	**<0.25**				6	0.0053
K	**134**	**40**	2.07	29.6	6	29
La	**0.264**	**0.080**	2.08	30.1	6	0.059
Li	**<3.3**				4	0.11
Lu	**0.056**	**0.013**	2.02	22.8	5	0.0061
Mg	**12.6**	**3.8**	2.08	30.3	6	2.8
Mn	**6.8**	**1.6**	2.04	24.4	6	1.1
Mo	**225**	**55**	2.04	24.5	6	36
Na	**148**	**45**	2.08	30.2	6	33
Nb	**3.77**	**0.87**	2.04	23.1	4	0.39
Nd	**0.356**	**0.088**	2.05	24.6	6	0.057
Ni	**0.41**	**0.10**	2.07	24.8	4	0.052
P	*38–56*				2	2.3
Pb	**0.90**	**0.24**	2.05	27.0	5	0.14
Pd	**0.20**	**0.14**	2.87	73.3	4	0.092
Pr	**0.080**	**0.017**	2.00	20.7	5	0.0040
Pt	**<0.018**				5	0.0024
Rb	**<1.1**				3	0.22
Re	**0.0143**	**0.0032**	2.02	22.1	5	0.0013
Rh	**<0.0050**				4	0.00087

Table 3 continued

Element	Consensus value or *interval*, µg/gU	U	k	Relative U (%)	Number of labs	Between-lab SD
Ru	**<0.029**				6	0.0056
S	**5,700**	**1,200**	2.00	20.5	3	160
Sb	**0.030**	**0.044**	4.53	146	3	0.016
Sc	**0.208**	**0.060**	2.13	29.1	3	0.027
Se	**2.51**	**0.81**	2.20	32.1	5	0.59
Si	*68–510*				2	250
Sm	**0.190**	**0.054**	2.12	28.2	5	0.037
Sn	**1.01**	**0.39**	2.23	38.6	5	0.30
Sr	**15.6**	**3.9**	2.05	25.2	6	2.7
Ta	**<0.12**				4	0.046
Tb	**0.079**	**0.017**	2.01	22.0	5	0.0074
Te	**<0.40**				3	0.096
Th	**40.8**	**9.9**	2.04	24.3	6	6.3
Ti	**2.7**	**1.2**	2.32	45.1	6	1.1
Tl	**0.060**	**0.013**	2.01	21.7	4	0.0044
Tm	**0.074**	**0.017**	2.03	23.0	5	0.0084
V	**0.89**	**0.22**	2.05	24.9	6	0.15
W	**40.6**	**9.3**	2.03	23.0	5	4.6
Y	**2.51**	**0.60**	2.04	24.1	6	0.38
Yb	**0.45**	**0.12**	2.07	26.1	6	0.083
Zn	**6.5**	**1.7**	2.04	26.5	5	0.94
Zr	**45.0**	**9.2**	2.00	20.5	5	1.4

Bold indicates certified or consensus values

Italics indicates value or interval for information only

'*U*' denotes the expanded uncertainty (at 95.5 % confidence level), '*k*' is the respective coverage factor, '*relative U*' is the expanded relative uncertainty in percent, 'n/a' stands for 'not assigned'. The number of laboratories which results were included in the calculation is indicated. 'Between-lab SD' is the standard deviation of the laboratory means. For elements P and Si, the range of reported results is stated *for information* only

9064 and # 9449, respectively. Typical (relative) expanded uncertainties (at 95.5 %) for material # 9064 are in the range of 10–50 %. For material # 9449 the range is significantly larger, from 20 to 80 %, mirroring the fact that the concentrations of many elements in this sample are significantly lower compared to sample # 9064 with several impurities approaching the corresponding critical levels. For material # 9449, certification of the concentrations of eight elements (Al, Co, Cr, Cu, Fe, Mn, Mo, and Ni) was performed in 1985 [28] using data from two interlaboratory comparisons [26, 27]. These certified values are listed in Table 4 as well. The consensus values established in this paper agree with the certified values from 1985. The only exception is the Fe impurity; this was expected since the original certified material was later modified by increasing the concentration of iron (by an amount not known to the authors). Relative differences of the participants' results to the consensus values often not exceed 15 % for those elements where the concentrations are well above the detection decision.

Available uranium RMs for determination of impurities

It is a good practice to utilize RM for the purpose of validation and monitoring of the performance of the analytical procedure from sample preparation to data reporting. A survey of RM suitable for this purpose in the quantification of impurities in uranium materials is presented in Table 5. Several of these RMs were indeed used by the participating laboratories; refer to Table 1.

In general, the available uranium-matrix RM do not cover the complete range of elements that are of interest in the analysis of uranium-bearing samples. In addition, the chemical composition of the available uranium matrix RM does not always correspond to the composition of real-world samples. Analysis of materials with high amounts of elements such as Mg, Na, Zr, and Mo (e.g. low-quality UOC) might require different procedures for sample treatment and analysis, and specific approaches for correction of interferences. Laboratories are encouraged to share their experience on the use of RMs for QC purposes

Table 4 Consensus values for material # 9449 stated as elemental concentration of impurity in microgram per gram of uranium, compared to the data from [28]

Element	Current work						SR-54 (1985)	
	Consensus value or *interval*, µg/gU	U	k	Relative U (%)	Number of labs	Between-lab SD	Certified or *information* value, µg/gU	Certified or *information* interval
Ag	**<0.88**				5	0.034	*0.42*	–
Al	**68**	**16**	2.04	24.2	6	10	**71.3**	54.8–82.0
As	**0.95**	**0.20**	2.00	20.8	5	0.052		
Au	n/a				2	0.0026		
B	**<22**				3	8.9	*0.53*	*0.47–0.59*
Ba	**0.161**	**0.096**	2.52	59.4	5	0.075		
Be	**<0.92**				5	0.030		
Bi	**<0.30**				4	0.078		
Br	n/a				–			
Ca	**31**	**18**	2.37	56.3	6	16		
Cd	**0.062**	**0.062**	3.31	100	4	0.035	*0.10*	*0.06–0.11*
Ce	**0.014**	**0.011**	2.87	76.5	4	0.0071		
Cl	n/a				–			
Co	**4.38**	**0.95**	2.01	21.8	6	0.42	**4.2**	4.0–4.3
Cr	**3.4**	**1.1**	2.14	31.0	6	0.86	**3.6**	3.1–4.3
Cs	**<0.19**				5	0.014		
Cu	**4.5**	**1.0**	2.02	22.6	6	0.53	**5.0**	4.2–6.7
Dy	**0.00230**	**0.00047**	2.00	20.3	3	0.000022		
Er	**0.0033**	**0.0022**	2.87	66.6	4	0.0014		
Eu	**<0.0034**				6	0.0010		
Fe	**1,310**	**520**	2.25	39.9	6	470	64.7[a]	46.0–77.5[a]
Ga	**0.093**	**0.021**	2.02	22.7	5	0.010		
Gd	**<0.010**				6	0.0010		
Ge	**<0.31**				6	0.060		
Hf	*0.062–0.31*				5	0.092		
Ho	**0.00073**	**0.00033**	2.52	45.8	4	0.00022		
In	n/a				2	0.0013		
Ir	**<0.044**				6	0.0049		
K	**<16**				6	2.3	*1.7*	–
La	**<0.15**				6	0.051		
Li	**< 1.4**				4	0.11		
Lu	**0.00072**	**0.00016**	2.04	22.8	3	0.000058		
Mg	**2.3**	**1.2**	2.43	52.7	5	0.95	*0.99*	*0.81–1.1*
Mn	**15.3**	**3.4**	2.02	22.3	6	1.7	**15.6**	14.3–16.9
Mo	**9.9**	**2.2**	2.01	22.2	6	1.0	**13.0**	9.5–17.5
Na	**5.4**	**7.1**	4.53	132	3	2.5	*2.8*	–
Nb	**<0.082**				4	0.037		
Nd	**<0.030**				6	0.0072		
Ni	**10.7**	**2.8**	2.07	26.5	6	2.1	**11.4**	8.4–13.9
P	*3.9–11*				2	1.1		
Pb	**1.3**	**1.2**	2.52	92.5	6	1.1	*1.03*	*0.32–2.15*
Pd	**<0.16**				6	0.0067		
Pr	**<0.17**				6	0.00072		
Pt	**<0.024**				5	0.0032		
Rb	**<0.62**				5	0.022		
Re	**<0.010**				5	0.0009		

Table 4 continued

Element	Current work						SR-54 (1985)	
	Consensus value or *interval*, µg/gU	*U*	*k*	Relative *U* (%)	Number of labs	Between-lab SD	Certified or *information* value, µg/gU	Certified or *information* interval
Rh	**<0.025**				4	0.0010		
Ru	**<0.020**				6	0.0033		
S	n/a				2	29		
Sb	**0.028**	**0.020**	2.87	70.5	4	0.013		
Sc	**<0.020**				4	0.010		
Se	**<3.4**				5	0.13		
Si	*19–30*				2	2.7	*34.3*	*18.0–53.5*
Sm	**<0.013**				6	0.0010		
Sn	**0.29**	**0.16**	2.65	55.3	4	0.10		
Sr	**0.059**	**0.020**	2.28	33.7	4	0.013		
Ta	**<0.12**				4	0.061		
Tb	**<0.0032**				5	0.0012		
Te	**<0.33**				3	0.070		
Th	**0.265**	**0.058**	2.02	21.8	4	0.020		
Ti	**0.64**	**0.29**	2.43	46.1	5	0.23	*0.98*	–
Tl	**<0.018**				5	0.0081		
Tm	**0.00039**	**0.00010**	2.11	25.3	3	0.000044		
V	**0.063**	**0.039**	2.87	63.0	4	0.024	*3.7*	–
W	**0.230**	**0.065**	2.15	28.1	4	0.038		
Y	**0.0190**	**0.0056**	2.15	29.7	5	0.0040		
Yb	**0.0034**	**0.0011**	2.25	32.9	4	0.00071		
Zn	**<5.7**				5	2.1	*2.4*	*0.89–3.2*
Zr	*3.2–15*				6	4.1		

Bold indicates certified or consensus values

Italics indicates value or interval for information only

'*U*' denotes the expanded uncertainty (at 95.5 % confidence level), '*k*' is the respective coverage factor, '*relative U*' is the expanded relative uncertainty in percent, 'n/a' stands for 'not assigned'. The number of laboratories which results were included in the calculation is indicated. 'Between-lab SD' is the standard deviation of the laboratory means. For elements Hf, P, Si, and Zr, the range of reported results is stated *for information* only

[a] The original material was modified by increasing the Fe concentration

with the aim to select the most suitable RMs for potential future re-certification.

REE patterns are known to be powerful provenance indicators and have been utilized in the earth science community for decades [40]; its applicability for attribution of uranium materials has been recognized [7, 41–43]. Therefore, it is desirable to certify REE concentrations in at least one RM with a matrix and element composition that is typical for UOC. At present, there appears to be no uranium matrix RM available with all lanthanides certified for elemental concentration. Potential candidates among those listed in Table 5 are CETAMA materials *Beryl* and *Feldspath*.

Conclusions

The current state-of-the-practice in elemental impurity analysis of uranium materials, as it applies to the majority

of laboratories that participated in this interlaboratory comparison, is to use an ICP-MS in combination with matrix-matched external calibration. This technique permits to make a multi-element analysis of almost all element of interest within the same measurement. For digestion (dissolution) of uranium-containing samples, the participating laboratories used hot plate and microwave, nitric acid alone as well as mixtures of nitric acid with hydrochloric acid and nitric acid with hydrofluoric acid. Adding HF was observed to affect the sample dissolution significantly for Zr and Hf. In general, no universal procedure exists for the sample dissolution, which would make possible analysis of all investigated elements with the same level of quality. As such there is a trade-off when using different approaches for sample dissolution. It highlights one of the challenges inherent to this type of analysis. The quality of results as well uncertainty budgets also critically

Table 5 Uranium reference materials with certified concentrations of impurity elements [44–47]

Matrix	Material	Certified impurities—(number)	Sum of certified impurities, µg/gU
UO$_2$	CETAMA *Viognier*	Br*, Cl, F, N, P—(5)	163
U$_3$O$_8$	NBL CRM 123/1–7**	Al, B, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, V, Zn, Zr—(18)	44–2510
	NBL CRM 124/1–7**	Ag*, Al, B, Be, Bi, Ca, Cd, Cr, Co, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ti, V, W, Zn, Zr—(24)	89–2680
	CETAMA *Agaric*	Ag, Al, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Dy, Eu, Fe, Ga, Gd, In, Li, Mg, Mn, Mo, Pb, Si, Sm, Sn, Th, Ti, V, W, Zn, Zr—(30)	<45
	CETAMA *Bolet*	Ag, Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Dy, Eu, Fe, In, Li, Mg, Mn, Mo, Ni, Pb, Si, Sm, Sn, Th, Ti, V, W, Zn, Zr—(30)	245
	CETAMA *Chanterelle*	Ag, Al, B, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Mg, Mn, Mo, Ni, Pb, Si, Sn*, Ti, V, W, Zn, Zr—(24)	642
	CETAMA *Morille*	Ag, Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Dy, Eu, Fe, Gd, In, Li, Mg, Mn, Mo, Ni, Pb, Si, Sm, Sn, Th*, Ti, V, W, Zn, Zr*—(31)	1560
UOC (not specified)	CANMET CUP-2*	As, B, Ca, Fe, K, Mo, Mg, Ni, Na, S, Si, P, Ti, V, Zr—(15)*	39400
Ammonium uranate	CETAMA *Beryl*	Fe, P, S—(3)	
	CETAMA *Feldspath*	Fe, P, S—(3)	
Magnesium uranate	CETAMA *Amethyste*	Ca, Cl, Fe, Na, S, Si—(6)	
	CETAMA *Calcedoine*	Ca, Cl, Fe, Na, P, S, Si, V, Zr—(9)	
	CETAMA *Diamant*	Ca, Cl, Fe, Na, P, S, Si—(7)	
	CETAMA *Emeraude*	As, Ca, Fe, Mo, S, Si, Zr—(7)	
	CETAMA *Hyacinthe*	Ca, Fe, Na, P, S—(5)	
Sodium uranate	CETAMA *Grenat*	C, Fe, Mo, Na, S, Si, Zr—(7)	

* Recommended values only

** Set of seven RMs; limited availability

depend on the judicial choice of RM used for calibration, and on optimization of the ICP-MS conditions, such as sample introduction, interference removal and/or correction, and calibration. The analysis of procedural blanks was deemed useful for determining the detection limits. The quality of the sample digestion and overall analysis depend on the labware cleanliness and on the carryover from the previous sample in the ICP-MS.

Uranium RMs with certified or recommended values for impurity element concentrations were utilized by all laboratories for QC purposes, and results were monitored using QC charts. However, the available RMs did not cover the complete range of the analyzed elements. It is necessary for proper QC to subject a well characterized material (preferably standard RM) to the same sample preparation procedure as the unknown samples. There is a general need to have a RM for uranium ore concentrate with well characterized and certified concentrations of impurities, especially REE.

For those impurity elements, where an appropriate number of data points were available and the concentration was well above the detection threshold, the overall between-laboratory relative standard deviations were

usually within 30 % and often not exceeding 15 %. Impurity concentrations were determined spanning seven orders or magnitude; a reliable quantification of the REE at levels of part per trillion was demonstrated. This was achieved in a multi-element analysis without separation or pre-concentration of the analytes. Within the community of analytical laboratories this is regarded as satisfactory performance. Of those 69 elements requested, elements Cl and Br are not readily analysed with the established ICP-MS techniques; elements P, S, and Si are challenging. Issues in the reported results were identified due to the sample dissolution, interference and blank corrections, and calibration. In selected cases, systematic trends are observed in replicate data points indicating potential day-to-day variations in calibration, instrument drifts, and memory effects.

Consensus values with associated measurement uncertainties for both materials were established based on the results of this interlaboratory comparison. Eight impurity elements in the U$_3$O$_8$ material (# 9449) were certified previously. The consensus values established herein for these eight elements are in agreement with the certified values. Relative differences of the participants' results to

the consensus values often did not exceed 15 % for those elements where the concentrations are well above the corresponding detection threshold.

Both materials are suitable for future use as laboratory standards; they fill gaps in the availability of uranium matrix RM characterized for impurities. It is noted that both materials shall not be used as calibration standards since the consensus values were not certified by a rigorous certification campaign. Although the participating laboratories employed traceable mono- or multi-element standards for calibration, traceability of the consensus values to the SI is not claimed because of potentially unrecognized interferences or matrix effects.

One of the advantages of using ICP-MS is the possibility to achieve comparatively low detection thresholds even when using a matrix-matched approach. This is reflected in the reported L_c values which for the lanthanide elements are as low as sub-nanogram per gram uranium. With respect to the lanthanides, low L_c values and reasonable accuracy of the element concentrations even at very low levels are indeed desirable as these results are featured in the REE patterns. However, for elements including Ca, Fe, K, Li, Mg, Na, Ni, P, S, and Si the reported L_c values are as high as several hundred microgram per gram uranium (see Fig. 4). This observation is expected (as it mirrors high instrumental and chemical blanks for the respective elements) and highlights one of the analytical challenges. It is noted that the maximum reported detection threshold values for such impurities as B, Ca, Fe, Mg, Ni, P, and Si approach the corresponding upper limits specified for nuclear-grade material [1], therefore reliable quantification of these elements may be an issue when utilising the impurity data to assess sample conformity to the nuclear-grade material requirements.

In some cases, L_c values appear to be too conservative (overestimated). In practice, overestimation of detection thresholds can lead to a loss of valuable information if measurement results are replaced with overestimated 'below L_c values' in reporting. That can particularly affect the use of REE patterns. Such loss of information should be avoided by a proper and realistic estimation of the L_c values. Therefore laboratories are encouraged to report analysis results even if the measured concentrations are below the estimated L_c values. This information can be used for assessing the current capabilities of the analytical laboratories for impurity measurements in the low concentration range. It is furthermore desirable to develop unified approaches for the calculation and expression of L_c.

With respect to measurement uncertainties, the laboratories made an effort to identify and propagate uncertainty sources, in some cases using GUM methodology. Nonetheless, in a large number of cases the reported uncertainties were significantly underestimated. The laboratories should try to identify those sources of uncertainty that were not (properly) accounted for to improve the estimation of associated measurement uncertainties in the future.

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