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# Expanded uncertainty modeling of the uranium isotope dilution standards



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## Abstract

In this paper, a statistical uranium isotope dilution mass spectrometry approach is presented to simulate the wide range of spike-sample mixed ratios of  $^{235}\text{U}/^{238}\text{U}$ , in terms of their related expanded uncertainties and uncertainty budget indexes. To obtain the lowest expanded uncertainty in uranium isotope dilution mass spectrometry (U-IDMS) technique, uranium certified materials of U-CRM 112A (spike) and U-CRM 149 (treated as unknown) are statistically employed and simulated. The simulated data is further applied to project U-IDMS samples by using the "Guide to the Expression of Uncertainty in Measurement (GUM)" software.

**Keywords:** Uranium isotope dilution, Expanded uncertainty, Thermal ionization mass spectrometry, Certified reference material

## Introduction

High accuracy and precision are required with traceable expanded uncertainties in the measurement techniques of the certified reference materials (CRMs) (Heumann 1988; Vogl and Pritzkow 2010; references therein). Isotope dilution mass spectrometry (IDMS) is one such measurement method commonly used in the quantitative analysis of uranium and trace isotopes in nuclear safe-guards and forensics as well as isotope geology (Fasset and Paulsen 1989). The calibration of isotopic reference materials and multi-element isotopic tracers were developed and applied statistically for U-Pb ID-TIMS geochronology (Mc Lean et al. 2011; references therein). This statistical estimation gave rise to accuracy increase and the availability of mixed element tracer calibrations for other IDMS experiments (Mc Lean et al. 2011). In addition to other techniques, such as titrimetry and gravimetry, for the determination of the uranium content, IDMS is applied using  $^{233}\text{U}$  as a spike (CRM 111A) (ASTM 2010). Determination of U-content was recently tested by applying uranium isotope dilution mass spectrometry (U-IDMS) with major isotopes ( $^{235}\text{U}$ ,  $^{238}\text{U}$ ) of natural uranium (NU), low and high

enriched samples (LEU, HEU) instead of  $^{233}\text{U}$  (Hasozbek et al. 2013). This IDMS technique mentioned was later granted the international standards organization (ISO) accreditation for its use in relevant laboratories (A2LA, 2012).

According to Hasozbek et al. (2013), the major contributor to the expanded uncertainty is related to the comparator used for determining the mass fractionation factor during the thermal ionization mass spectrometry (TIMS) measurements. The spike to sample ratio of the mixtures also impacts the uncertainty in the unknown samples and requires detailed observation to achieve a clear understanding of the uncertainty budgets in the U-IDMS analysis.

In this study,  $^{235}\text{U}$ – $^{238}\text{U}$  atomic fractions of the certified uranium solutions (CRM 112A and CRM 149) were carried out to simulate (i) spike + sample mixtures of the extreme compositions (e.g. 5x diluted spike solution mixed with sample solution), (ii) the conditions for optimizing the accuracy and precision in U-IDMS by using the GUM software (GUM Workbench), and (iii) the limits of the re-established U-IDMS method for the routine determinations, not only for re-issuing of CRMs, but also for geochronological applications, where applicable. In this paper, it is aimed to extend the limits of U-IDMS analysis in terms of sample to spike mol ratio and

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expanded uncertainties, where wet chemistry applications for U-IDMS can be improved.

### Methodology

In this paper, suitable and available CRMs of the New Brunswick Laboratory (NBL) are selected as end members, which are assigned as unknown sample (CRM 149) and spike (CRM 112A). Assigned unknown sample of CRM 149 contains  $U_3O_8$  in which the  $^{235}U$  isotope is enriched to 93%. The spike used in this study is a uranium metal assay standard that has an essentially “natural” U isotopic composition. Details of the U-IDMS principle by using U-CRMs of the New Brunswick Laboratory (NBL) with TIMS measurements were discussed in terms of geochemistry and analytical properties (Hasozbek et al. 2013). The main requirements of the U-IDMS are (i) well-equilibrated sample-spike mixture with accurately known proportions of the solutions and (ii) state-of-the-art TIMS measurements attentively evaluating the mass bias by using related U-comparators (quality control (QC) samples). In the following, the steps of the U-IDMS simulation approach will be given in detail.

### Spike (SP) and sample (SA) concentration estimations

In order to test comprehensive concentration range of the spike end members, more diluted spikes were calculated from the original stock of CRM 112A (Spike 1-SP1-, Table 1). Four different diluted spikes, including the original stock, were employed by using the dilution factors of 5-8-33 times (SP2, SP3, SP4) from the CRM 112A original stock (SP 1).

In terms of IDMS wet-chemistry applications, optimum conditions were considered in order to trace the weighing uncertainties as described in Hasozbek et al. (2013). Therefore, 20 ml vials are recommended to prepare the equilibrated mixtures. In these

simulations, the mass of the mixture solutions is taken not to exceed 10 g to keep the recommended 20 ml vials half-full during the equilibration process of the mixtures. In this study, eight different CRM 112A spike and CRM 149 sample mixtures with different diluted CRM 112A mixtures are tested. The details of the spike to sample proportions are given in Tables 2 and 3. The related aliquant weights of the spike solutions and sample solutions are taken by considering the vial size of 20 ml. Moreover, spike aliquant weights are preferred not to be exceeding 2 and/or 3 g in the sets of the simulations (Table 2). The weighing uncertainties of the aliquant (for 4-decimal tares), and the relative deviation (RD%) values are referred from Hasozbek et al. (2013).

### Spike and sample ratio estimations

By using the certified values of the spike and sample CRMs, spike-sample mixture ratios, atom/atom (at/at), are calculated with the assigned masses of the solutions (Tables 2 and 3). Sample to spike proportions ranging from 1:2 to 1:4 are tested to display the wide ranges of atom ratios, whether there is a relevant contribution to the uncertainty budget or not. Four mixtures with duplicates (total eight) were simulated within the certified values of the CRMs and their related spike and sample solution amounts (Table 4). To estimate  $^{235}U/^{238}U$  mixture ratios (at/at) of the blends,  $^{235}U$  and  $^{238}U$  in both end members summed separately (Table 4). The ratio variations are ranging from 1.83 to 14.17 (at/at); however, mass fractionation corrections will be included in the GUM simulations to understand the uncertainty budget indexes of the comparator (quality control sample). This will be presented in correlation to the previous results of Hasozbek et al. (2013).

**Table 1** Properties of the evaluated spike solutions from the CRM 112A (original stock) (CRM 112A-1, SP 1; CRM 112A-2, SP 2; CRM 112A-3, SP 3; CRM 112A-4, SP 4)

|                  | CRM 112 A-1 (SP1) | CRM 112A-2 (SP2) | CRM 112A-3 (SP3) | CRM 112A-4 (SP4) | CRM 149 (SA) |
|------------------|-------------------|------------------|------------------|------------------|--------------|
| C(U) (g U/g)     | 0.004402361       | 0.000880909      | 0.000542279      | 0.000130669      | 0.005144913  |
| At.Wt            | 238.028918        | 238.028918       | 238.028918       | 238.028918       | 235.19792    |
| c(U) (mol U/g)   | 1.84951E-05       | 3.70085E-06      | 2.27821E-06      | 5.48963E-07      | 2.18748E-05  |
| AF(235 U)        | 0.0072017         | 0.0072017        | 0.0072017        | 0.0072017        | 0.93257      |
| AF(238 U)        | 0.9927458         | 0.9927458        | 0.9927458        | 0.9927458        | 0.053294     |
| R(58) (at/at)    | 0.0072543         | 0.0072543        | 0.0072543        | 0.0072543        | 17.49859271  |
| C(235) (mol U/g) | 1.33196E-07       | 2.66524E-08      | 1.6407E-08       | 3.95347E-09      | 2.03998E-05  |
| C(238)(mol U/g)  | 1.83609E-05       | 3.674E-06        | 2.26168E-06      | 5.44981E-07      | 1.1658E-06   |

See Certified Reference Material (CRM) certificates issued by NBL for major and minor isotope ratios. The presumed spike solutions (SP2, SP3, SP4) were calculated by diluting (factors of 5, 8, 33 times) the known quantities of SP1 (original spike solution weight is ca. 20 g). The relative atomic mass and the atom fractional abundances of  $^{235}U$  and  $^{238}U$  in the simulated solutions remain unchanged. SP1 Spike 1-original stock-, SP2 Spike 2, SP3 Spike 3, SP4 Spike 4, SA sample-treated as unknown-; for the abbreviations, see the Table 6

**Table 2** CRM 112A Spike proportions with different diluted spike solutions (SP1, SP2, SP3, SP4)

|                                | CRM 112 A-1 (SP1) | CRM 112 A-2 (SP2) | CRM 112 A-3 (SP3) | CRM 112 A-4 (SP4) |
|--------------------------------|-------------------|-------------------|-------------------|-------------------|
| mgU/g (spike)                  | 4.402361          | 0.88090847        | 0.542278906       | 0.130669117       |
| proportions (g)                | 2.1               | 2.06              | 2.06              | 2.05              |
| Spike mg U                     | 9.2449581         | 1.814671448       | 1.117094546       | 0.267871691       |
| Spike to sample portions (ca.) | 1:4               | 1:2               | 1:3               | 1:2               |

Due to the volumetric usage of the solutions, amounts may vary. For the abbreviations, see Table 1

**Uranium content and uncertainty estimations**

The uranium content in the simulated mixtures is calculated by using the IDMS equation (Eq. 1, see Table 6 for abbreviations) given by Bièvre De and Peiser (1997).

$$C_{U\text{Sample}} = \left( \frac{R_{58\text{mix}} - R_{58\text{spike}}}{R_{58\text{Sample}} - R_{58\text{mix}}} \right) \cdot \left( \frac{M_{\text{spike}}}{M_{\text{sample}}} \right) \cdot \left( \frac{C_{238\text{spike}}}{AF_{238U\text{Sample}}} \right) \quad (1)$$

This equation is reproduced here for an assigned reference to two major isotopes (<sup>235</sup>U and <sup>238</sup>U) in both spike and sample solutions (Eq. 2, see Table 6 for abbreviations).

$$\begin{aligned} C_{238\text{spike}} &= C_{\text{spike}} * AF_{238\text{spike}} \\ C_{\text{spike}} &= C_{\text{spikeg}} * At_{\text{wtspike}} \\ C_{\text{spikeg}} &= Wt_{\text{piece}} * Wt \end{aligned} \quad (2)$$

Two minor isotopes of <sup>234</sup>U and <sup>236</sup>U are also taken into consideration; however, the contribution of the minor isotope content in the simulated certified materials is quite low.

By using this equation, uranium content of the assigned unknown simulated samples will be reported as either in moles per gram of solution or grams per gram of solution. The uranium content of the simulated unknown solution in *U<sub>mix</sub>* (g/g) can be calculated by knowing the relative atomic weight of uranium in the unknown sample. This value is either obtained or calculated from the certified isotopic composition determinations (see details in Table 4). Further details of the abovementioned IDMS equation can be found in Table 5 and Hasozbek et al. (2013).

The uncertainty estimations are simulated in the GUM software, (GUM workbench, student edition). This software provides the uncertainty in estimation of the U-content, sample concentration (*C<sub>sample</sub>*), linked to the expression of uncertainty in measurements (BIPM

2008; Bürger et al. 2010; Mathew et al. 2012; references therein). The uncertainty sources stated on the modified equation of Bièvre De and Peiser (1997) are all taken into consideration. Besides that, Hasozbek et al. (2013) reported the details of the uncertainty budget based on IDMS TIMS measurements with different CRMs (CRM 115; CRM 116, and CRM 112A). According to this study, the major uncertainty contribution of the IDMS analysis is related to the type of comparator used during TIMS analysis. Therefore, in this simulated unknown samples, the minor uncertainty contributors, such as weighing and the evaporation of the U-metals (moisture correction) which effects the main U concentration of the solution, are taken from Hasozbek et al. (2013).

Furthermore, uncertainties for uranium isotopic ratios and isotopic composition (in atomic and mass fractions) are given in NBL certificates for both sample and spike solutions used here. The relative standard deviation (RSD %) is taken as reported in Hasozbek et al. (2013) and is equal to the observed variation in the U630 (CRM 630) comparator measurements. This value (expanded uncertainty = 0.0000781095; std. dev = 0.000141119) is assigned as the multiplicate delta factor in the GUM estimations. All GUM workbench results expressed as statistical simulations of the U-content in the blends will be given in detail in the following.

**Results**

**Blend tests**

The uranium content of the treated unknown sample (CRM 149-SA1; SA2; SA3, SA4) is calculated by the equation of Bièvre De and Peiser (1997) and the results are listed in Table 5. All the mixture ratios are corrected for mass fractionation by using of U630 as

**Table 3** CRM 149 sample proportions to duplicate the sample-spike mixtures (SA1, SA2, SA3, SA4).

|                                | CRM 149 (SA1) | CRM 149 (SA2) | CRM 149 (SA3) | CRM 149 (SA4) |
|--------------------------------|---------------|---------------|---------------|---------------|
| mgU/g (sample)                 | 5.14015756    | 5.14015756    | 5.14015756    | 5.14015756    |
| proportions (g)                | 8.28          | 4.13          | 6.2           | 4.1           |
| Sample mg U                    | 42.5605046    | 21.22885072   | 31.86897687   | 21.074646     |
| Sample to spike portions (ca.) | 4:1           | 2:1           | 3:1           | 2:1           |

Due to the volumetric usage of the solutions, amounts may vary. For the abbreviations, see Table 1

**Table 4** Calculated ratios of the spike and sample mixtures with duplicates

| Spike + sample         | SP1 + SA1  | SP1 + SA1   | SP2+ SA2    | SP2 + SA2   | SP3 + SA3   | SP3 + SA3 | SP4 + SA4   | SP4+ SA4    |
|------------------------|------------|-------------|-------------|-------------|-------------|-----------|-------------|-------------|
| Spike/sample portion   | 1:4        | 1:2         | 1:2         | 1:2         | 1:3         | 1:3       | 1:2         | 1:2         |
| Mixture no.            | SP1-1      | SP1-2       | SP2-1       | SP2-2       | SP3-1       | SP3-2     | SP4-1       | SP4-2       |
| <b>235 U spike</b>     | 6.6608E-05 | 9.34141E-05 | 1.31114E-05 | 1.31414E-05 | 8.05092E-06 | 8.059E-06 | 1.93253E-06 | 1.93642E-06 |
| <b>235 U sample</b>    | 0.0397475  | 0.0262613   | 0.0198501   | 0.0198647   | 0.0297869   | 0.0298043 | 0.0198615   | 0.0198527   |
| <b>238 U spike</b>     | 0.00918    | 0.01288     | 0.00181     | 0.00181     | 0.00111     | 0.00111   | 0.00027     | 0.00027     |
| <b>238 U sample</b>    | 0.00227    | 0.00150     | 0.00113     | 0.00114     | 0.00170     | 0.00170   | 0.00114     | 0.00113     |
| <b>235 U mix sum</b>   | 0.03981    | 0.02635     | 0.01986     | 0.01988     | 0.02979     | 0.02981   | 0.01986     | 0.01985     |
| <b>238 U mix sum</b>   | 0.01145    | 0.01438     | 0.00294     | 0.00295     | 0.00281     | 0.00281   | 0.00140     | 0.00140     |
| <b>R(235U/238U)mix</b> | 3.47622    | 1.83302     | 6.75211     | 6.74569     | 10.59544    | 10.59368  | 14.17368    | 14.16706    |

All mixtures simulated with duplicates. Ratio of  $U^{235}/U^{238}$  mixture is not corrected for the mass fractionation. It will be taken into account for the extended uncertainty estimations

$$^{235}\text{U}(\text{spike/sample}) = \text{Spike/Sample Conc (g/g)} \times \text{Spike/Sample (g)} \times ^{235}\text{U Frac. sample/spike}$$

$$^{238}\text{U}(\text{spike/sample}) = \text{Spike/Sample Conc (g/g)} \times \text{Spike/Sample (g)} \times ^{238}\text{U Frac. sample/spike}$$

$$R(^{235}\text{U}/^{238}\text{U})\text{mix} = ^{235}\text{Uspike+sample}(\text{mix sum})/^{238}\text{Uspike+sample}(\text{mix sum})$$

See Certified Reference Material (CRM) certificates issued by NBL for regarded atomic fractions. All concentration values are listed in Tables 2 and 3 for the diluted spike solutions (SP1, SP2, SP3, SP4) and sample (CRM 149). For the abbreviations, see Table 1

a comparator as stated above (Table 5). The results are shown in Table 5.

**CRM 112A-1 (SP1) -CRM 149 (SA1) mixtures (SP1 + SA1)**

Duplicate mixtures (SP 1-1; SP 1-2) are considered mixed with CRM 112A (SP1-original stock-) as a spike and CRM 149 (SA1) as an unknown sample. The mixtures of this set are estimated as mixed in the proportion (spike to sample) of 1:4 and 1:2, respectively. The uranium content of the SP 1-1 yields  $2.1874 \times 10^{-5} \text{ mol U g}^{-1}$  with a slightly negative 0.004 RD%, and SP 1-2 yields  $2.1873 \times 10^{-5} \text{ mol U g}^{-1}$  with -0.006 RD% (Table 5). Similar to the reference U-content value of the CRM 149 sample (treated as unknown), Davies and Gray (D&G) titration value of the CRM 149 is also presented for comparison (Fig. 1). According to the Hasozbek et al. (2013), the relative deviation of the D&G is ca. 0.008%.

In order to compare the simulated results, relative deviations in the simulated IDMS determinations of U-

content in CRM 149 sample solution using the spike solution of CRM 112A with its diluted sub-splits are included and shown in Fig. 1.

**CRM 112A-2 (SP2) -CRM 149 (SA2) mixtures (SP2 + SA2)**

This set of mixtures is conceived as duplicates with CRM 112A-2 (SP2) spike, which is diluted as 5 times of the original stock (CRM 112A-1 (SP1)). The mixture ratios (at/at) are calculated as almost double times of the first set as described above (Table 5 and Fig. 1). CRM 149 is assigned as unknown sample and mixed with CRM 112A-S (SP2) in proportions of 1:2 (spike to sample). According to the U-content evaluations of the mixtures (SP 2-1 and SP2-2),  $2.18848 \times 10^{-5}$  and  $2.18843 \times 10^{-5} \text{ mol U g}^{-1}$  with 0.046% and 0.043 RD% are yielded (Table 5). Within the RD% of the unknown samples, the mixtures are compatible with the titrimetry result of the CRM 149 sample as seen in SP 1-1 and SP 1-2 (Fig. 1).

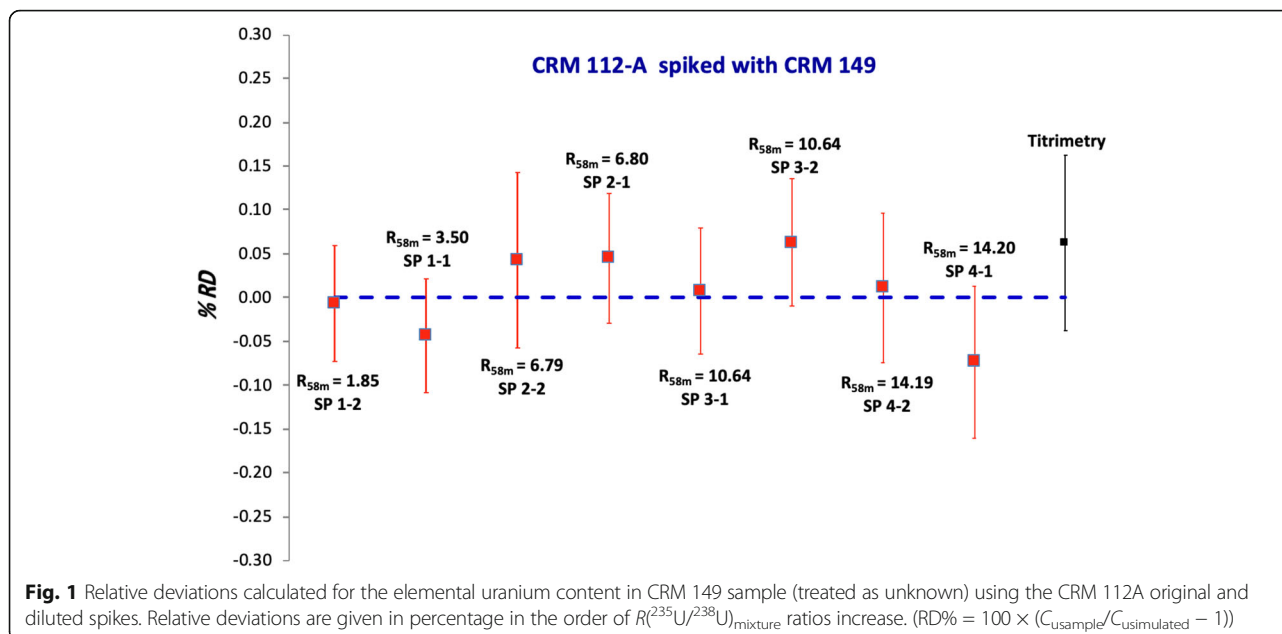
**Table 5** Estimated results of the U-content for the CRM 149 sample (treated as unknown) spiked with CRM 112A original stock (SP1) and diluted spike mixtures (SP2, SP3, SP4)

| Spike                                     | C112A-1 (SP1)   |            | C112A-2 (SP2)   |             | C112A-3 (SP3)   |            | C112A-4 (SP4)   |           |
|---|-----------------|------------|-----------------|-------------|-----------------|------------|-----------------|-----------|
|   | CRM 149-1 (SA1) |            | CRM 149-1 (SA2) |             | CRM 149-1 (SA3) |            | CRM 149-1 (SA3) |           |
| Mixture number                            | SP 1-1          | SP 1-2     | SP 2-1          | SP 2-2      | SP 3-1          | SP 3-2     | SP 4-1          | SP 4-2    |
| Corr. R5/8 mix <sup>a</sup>               | 3.5094          | 1.8525     | 6.8036          | 6.7971      | 10.6457         | 10.6463    | 14.2038         | 14.1995   |
| CU unk <sup>b</sup> mol U g <sup>-1</sup> | 2.1874E-05      | 2.1873E-05 | 2.18848E-05     | 2.18843E-05 | 2.1876E-05      | 2.1886E-05 | 2.186E-05       | 2.188E-05 |
| CU unk gU/g                               | 0.005145        | 0.005145   | 0.005147        | 0.005147    | 0.005145        | 0.005148   | 0.005141        | 0.005145  |
| RD% <sup>c</sup>                          | -0.004          | -0.006     | 0.046           | 0.043       | 0.007           | 0.063      | -0.073          | 0.011     |

<sup>a</sup>Mass fractionation corrected values used for the mixture ratios from Hasozbek et al. (2013) and Mathew and Hasozbek (2016)

<sup>b</sup>See Certified Reference Material (CRM) certificates issued by NBL

<sup>c</sup>RD% for mixture simulations for  $C_{\text{unknown}}$  is evaluated from the certified value For the abbreviations, see Table 1 and 6



#### CRM 112A-3 (SP3) -CRM 149 (SA3) mixtures (SP3 + SA3)

CRM 149 samples are simulated with eight times diluted of CRM 112A-1 spike. SP 3-1 and SP 3-2 are assigned for this set of calculations as given in Table 5 and Fig. 1. In this set of blends,  $^{235}\text{U}/^{238}\text{U}$  mixture ratios are increased almost 10 times ( $^{235}\text{U}/^{238}\text{U})_{\text{mix}} = 10.64$  at/at) from the first set ( $(^{235}\text{U}/^{238}\text{U})_{\text{mix}} = 1.85\text{--}3.51$  at/at) (Table 5, Fig. 1). SP 3-1 mixture gives the U-content determination as  $2.18746 \times 10^{-5} \text{ mol U g}^{-1}$  and  $2.18886 \times 10^{-5} \text{ mol U g}^{-1}$  for the SP 3-2 mixtures (Table 5). RD% values are slightly positive and varies between 0.007 and 0.06% (Table 5, Fig. 1).

#### CRM 112A-4 (SP4) -CRM 149 (SA4) mixtures (SP4 + SA4)

From the original stock of CRM 112A spike, 33 times diluted CRM 114A-4 (SP 3) is taken to be mixed with CRM 149 sample. This set of IDMS estimations display the highest  $^{235}\text{U}/^{238}\text{U}$  mix ratios among the other sets which yields 14.20 and 14.21 at/at, respectively (Table 5, Fig. 1). U-content of the samples spiked with CRM 112A-4 (SP 4) are calculated as follows:  $2.18588 \times 10^{-5} \text{ mol U g}^{-1}$  for SP 4-1 and  $2.18773 \times 10^{-5} \text{ mol U g}^{-1}$  for SP 4-2. RD% of this two samples are  $-0.073$  and  $0.001$  (Table 5, Fig. 1). All the simulated CRM 149 samples (treated as unknown) are also in agreement with the certified value of NBL and D&G titration result as given in Fig. 1.

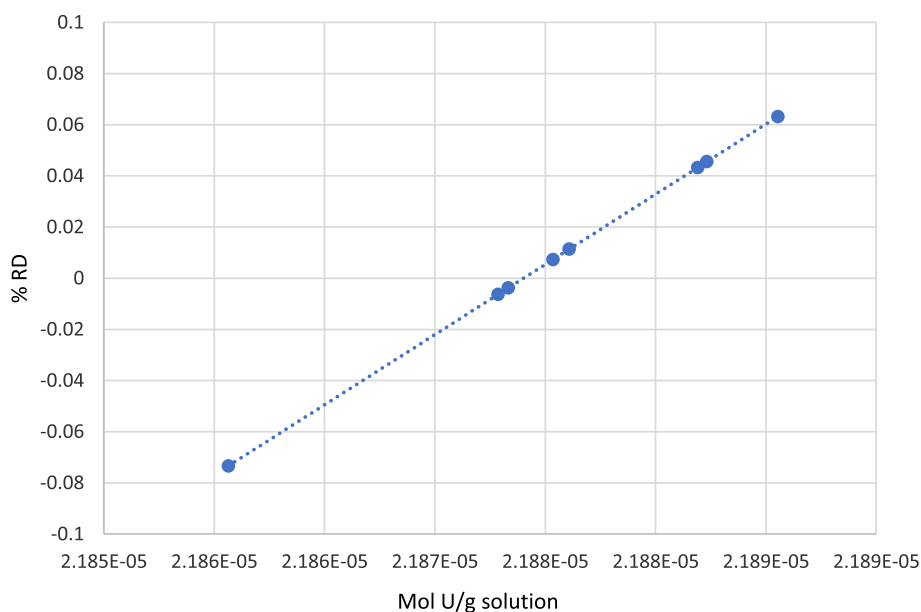
#### GUM modeling for CRM 112A and CRM 149 mixtures

There are three different sets of IDMS equations used in geochemistry and related fields. Each of the equations derived from the basic equation that defines the

preparation of isotopic blends by mixing two end members with widely different isotopic composition. The blend equation of Bièvre De and Peiser (1997) is suitably reset to be useful for the determination of the uranium contents of the treated unknown sample as described above. By selecting the certified values of the CRMs (CRM 112A; CRM 149) for simulation of the different sets of blends, it provides the traceability of the uncertainty indexes. Therefore, modeling the uncertainty of the test blends is suitable to simulate in accordance with to the guide to the expression of uncertainty in measurement (BIPM 2008; Bürger et al. 2010).

In the GUM software, it is possible to calculate the expanded uncertainty ( $k = 2$ ) by using the certified values of the end members (CRM 112A as a spike, CRM 149 as an unknown sample) including previously reported uncertainties. Moreover, the data for the mass fractionation corrections for  $R(^{235}\text{U}/^{238}\text{U})_{\text{mix}}$  (at/at) and weighing uncertainties are included in the sets of the blends, which are provided from Mathew et al. (2012) and Hasozbek et al. (2013). Due to the lower abundance of the blanks and minor isotopes such as  $^{234}\text{U}$  and  $^{236}\text{U}$ , their contributions are also considered.

Based on the simulated data of the blends, about 0.02% difference exists between two extreme values of U-content in the treated unknown sample (CRM 149) ( $2.1855 \times 10^{-5}$  to  $2.1895 \times 10^{-5} \text{ Mol U/g solution}$ ) (Fig. 2). This is a clear indication of a linear variation as a function of  $^{235}\text{U}/^{238}\text{U}$  ratios in the blends. In order to perform mathematical and/or statistical manipulations in the IDMS sets, GUM software (GUM Workbench) is used to present all sources of uncertainties (Table 6).



**Fig. 2** U-content (Mol U/g solution) in the unknown sample (CRM 149) as a function of RD% in the simulated blends

The GUM Workbench worksheet is used to calculate uncertainties for isotopic ratio estimations and relative abundances derived from the isotopic ratios. This worksheet utilizes isotopic ratios with U-238 as the denominator.

For this Workbench worksheet, the  $^{234}\text{U}/^{238}\text{U}$  minor ratio data are internally normalized to correct for mass fractionation using the major ratio value previously determined in paper Mathew et al. (2012) and Hasozbek et al. (2013) by Total Evaporation measurements.

According to the simulated GUM workbench data, major uncertainty contribution for the original spiked stock samples is observed in  $R(^{235}\text{U}/^{238}\text{U})_{\text{mix}}$  (39.1%) and  $\delta R_{58\text{comparator}}$  (88.3%) quantities. Expanded uncertainty ( $k = 2$ ) for this set of SP 1 blends vary between 0.083 and 0.066% (Table 7).

In the second set of samples, SP 2, where the  $R(^{235}\text{U}/^{238}\text{U})_{\text{mix}}$  ratios are between ca. 6.80 and 6.79 at/at, the expanded uncertainties are slightly higher (0.1–0.074). In regard to this, the uncertainty budgets display higher in both  $R(^{235}\text{U}/^{238}\text{U})_{\text{mix}}$  (55.2%) and  $\delta R_{58\text{comparator}}$  (71.6%) (Table 7). In the SP 3 blends, the uncertainty budget indexes in the simulated estimations display similar majority contribution in  $\delta R_{58\text{comparator}}$  (75.5–74.7%) quantities. The expanded uncertainties calculated from the GUM workbench are also the lowest (0.072%,  $k = 2$ ) among the set of blends (Table 7). The SP 4 set of blends present 0.087–0.085% ( $k = 2$ ) expanded uncertainty values. The major contribution of uncertainty in these blends are  $\delta R(^{235}\text{U}/^{238}\text{U})_{\text{comparator}}$  (52.4–50.9%) and  $R(^{235}\text{U}/^{238}\text{U})_{\text{sample}}$  (42.1%) (Table 7).

## Discussion

The U-IDMS method was considered a development method project for NBL by using the existing CRMs, such as CRM 112A, CRM 115, CRM 116, and CRM 149. This project was implemented as an alternative U-IDMS determination without using the  $^{233}\text{U}$  as a tracer. By applying the U-IDMS technique with major isotopes, routine TIMS measurements to identify the U-content in the unknown samples were also accredited (A2 2012). Previous results of this accredited U-IDMS method provide ca. 0.1% expanded uncertainty ( $k = 2$ ) and U-IDMS method yields acceptable accuracy and precision in comparison with certified and D&G titration values of the U-content with TIMS analysis (Hasozbek et al. 2013).

In addition to the U-IDMS data presented in Hasozbek et al. (2013), it was noted that the uncertainties in the analysis of the  $^{235}\text{U}/^{238}\text{U}$  mol ratios in the blends contribute most to the uncertainty budgets. Besides, the meticulous adjustments of the spike and sample proportion in the U-IDMS blends are not clearly tested in terms of their related uncertainty values from its original source in Hasozbek et al. (2013). This fact arises from the comparator material that is used for the quality control (QC) purposes. The atomic fractionation factor based on this comparator preference likely contributes more to the uncertainty budget, when the measured ratios are closer to the spike composition. To correct the mass fractionation factor during the TIMS analysis, the comparator ratios are also included to the calculations of the RSD%. However, it is not possible to find the

**Table 6** Quantity descriptions of the model equation for the GUM workbench. Equation is taken from Bièvre De and Peiser (1997)

| Symbols                          | Unit    | Definition  |
|----------------------------------|---------|---|
| $C_{U\text{Sample}}$             | mol U/g | Mol U/g of solution in the unknown sample (taken from the certificate value of NBL and D&G)   |
| $R_{58\text{mix}}$               | at/at   | $^{235}\text{U}/^{238}\text{U}$ ratio in the mixture (spiked sample) (calculated from the assigned masses)  |
| $R_{58\text{spike}}$             | at/at   | Certified value of $^{235}\text{U}/^{238}\text{U}$ ratio in the spike   |
| $R_{58\text{Sample}}$            | at/at   | Certified value of $^{235}\text{U}/^{238}\text{U}$ in the sample  |
| $M_{\text{spike}}$               | g       | Mass of spike (assigned proportions as described in Tables 1 and 2)   |
| $M_{\text{sample}}$              | g       | Mass of sample (assigned proportions as described in Tables 1 and 2)  |
| $C_{238\text{spike}}$            | mol/g   | $^{238}\text{U}$ in spike calculated from uranium content in U-metal and atom fraction of $^{238}\text{U}$ in the spike, the latter value is from the certificate                   |
| $AF_{238\text{USample}}$         | mol/g   | Atom fraction of $^{238}\text{U}$ in the unknown sample and calculated from the assigned masses and certificate values  |
| $\delta_{CF58\text{comparator}}$ |         | Delta value for the correction factor of the comparator $^{235}\text{U}/^{238}\text{U}$ (RSE% $7.810995 \times 10^{-5}$ , Hasozbek et al. 2013)                                     |
| $C_{\text{spike}}$               | mol/g   | Concentration of spike molU/g (taken from the certificate value and diluted estimations are given in Table 3)   |
| $AF_{238\text{spike}}$           | mol/g   | Atom fraction of $^{238}\text{U}$ in spike from the certified value   |
| $C_{\text{spikeg}}$              | mol/g   | Spike aliquant concentration (taken from the certificate value and diluted estimations are given in Table 3)  |
| $At_{\text{wtspike}}$            |         | Atomic weight of spike (CRM 112A)   |
| $Wt_{\text{solution}}$           | g       | Weight of the metal and powder solution (for the dilution and equilibration purposes, 20 ml of vials are taken into account and the mixtures do not exceed over 10 ml)              |
| Purity                           | gU/g    | Uranium content from the certificate  |
| $R_{48\text{Sample}}$            | at/at   | Certified value of $^{234}\text{U}/^{238}\text{U}$ in sample  |
| $R_{68\text{Sample}}$            | at/at   | Certified value of $^{236}\text{U}/^{238}\text{U}$ in sample  |
| $\delta_{R58\text{comparator}}$  |         | Delta factor representing the relative uncertainty on the comparator used for the mass fractionation correction (expanded uncertainty is 0.00065 ( $k = 2$ ), Hasozbek et al. 2013) |

{Calculation of concentration of target element in sample using IDMS equation based on assigned amount ratios}- $C_{U\text{Sample}} = ((R_{58\text{mix}} - R_{58\text{spike}})/(R_{58\text{Sample}} - R_{58\text{mix}})) \times (M_{\text{spike}}/M_{\text{sample}}) \times (C_{238\text{spike}}/AF_{238\text{USample}}) \times \delta_{CF58\text{comparator}}$   
 {Calculation of the concentration of the  $^{238}\text{U}$  in spike}- $C_{238\text{spike}} = C_{\text{spike}} \times AF_{238\text{spike}}$   
 {Calculation of the U concentration of the spike}- $C_{\text{spike}} = C_{\text{spikeg}}/At_{\text{wtspike}}$   
 {Calculation of the concentration of the spike solution}- $C_{\text{spikeg}} = Wt_{\text{piece}}/Wt_{\text{solution}} \times \text{Purity}$   
 {Calculation of the atom fractions of  $^{235}\text{U}$  and  $^{238}\text{U}$  in the sample}- $AF_{238\text{USample}} = 1/((R_{48\text{Sample}} + R_{58\text{Sample}} + R_{68\text{Sample}}) \times \delta_{R58\text{comparator}} + 1)$

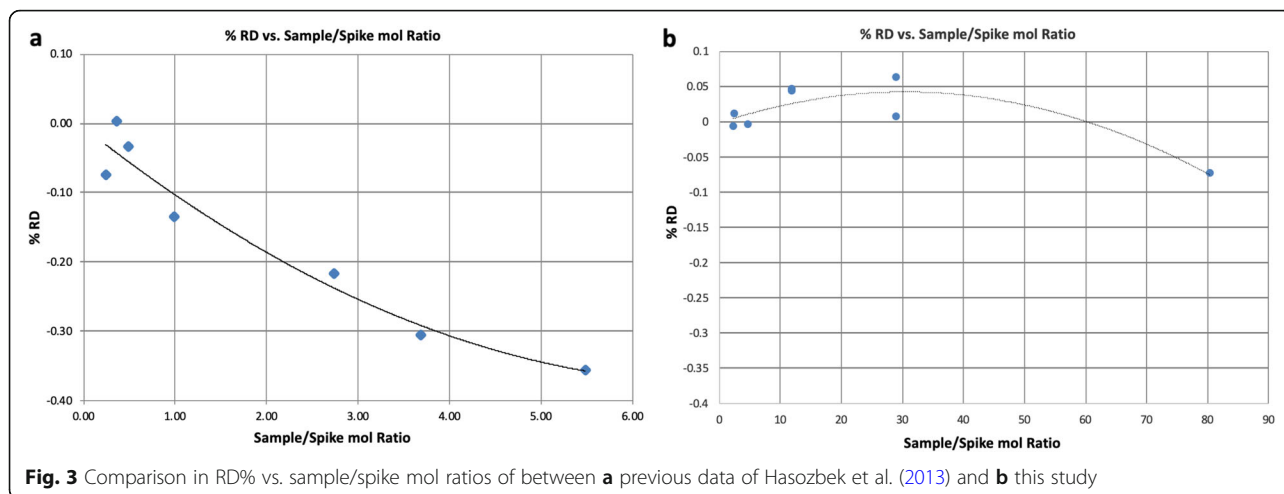
proper and/or comparator ratio which will be close to the matrix of the unknown sample.

In this study, by using the certified values of CRMs and previously published data for U-IDMS are carried out to test the limits of U-IDMS method by only using the major U-isotopes ( $^{235}\text{U}$  and  $^{238}\text{U}$ ). Therefore, end members from NBL Certified Reference Materials (CRMs) C112A (NU) and C149 (HU) were chosen as spike and sample (treated as unknown), respectively. CRM 112A is a uranium metal assay standard that has an essentially “natural” U isotopic composition. CRM

112A was selected as a spike due to its low amount of 0.72%  $^{235}\text{U}$  and higher amount of 99.2%  $^{238}\text{U}$  (Mathew et al. 2012). CRM 149 is picked as unknown sample, which is enriched  $\text{U}_3\text{O}_8$  material that contains about 93.2%  $^{235}\text{U}$ . Due to its low enrichment in  $^{238}\text{U}$ , CRM 149 and CRM 112A are considered a suitable sample and a spike, respectively. By using the CRM 112A as a spike and CRM 149 as an unknown sample, the U-content of the unknown sample is evaluated by simulating the reference values of the CRMs, GUM software and previously presented data (Mathew et al. 2012;

**Table 7** Uncertainty budget indexes of simulated CRM 112A/CRM 149 IDMS mixtures

| Quantity                         | SP 1-1 (%) | SP 1-2 (%) | SP 2-1 (%) | SP 2-2 (%) | SP 3-1 (%) | SP 3-2 (%) | SP 4-1 (%) | SP 4-2 (%) |
|----------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| $R_{58\text{mix}}$               | 39.1       | 4.2        | 16.7       | 55.2       | 8.1        | 9.1        | 3.3        | 1.6        |
| $R_{58\text{Sample}}$            | 0.7        | 0.9        | 4.4        | 2.4        | 9.9        | 9.8        | 42.1       | 42.1       |
| $\delta_{CF58\text{comparator}}$ | 4.1        | 6.5        | 7.3        | 3.9        | 6.5        | 6.3        | 3.8        | 3.9        |
| $\delta_{R58\text{comparator}}$  | 56.1       | 88.3       | 71.6       | 38.4       | 75.5       | 74.7       | 50.9       | 52.4       |
| Expanded uncertainty ( $k = 2$ ) | 0.083      | 0.066      | 0.074      | 0.1        | 0.072      | 0.072      | 0.087      | 0.085      |



Hasozbek et al. 2013). Accordingly, the equation of Bièvre De and Peiser (1997) is adapted to the GUM software including the previous data of Mathew et al. (2012) and Hasozbek et al. (2013). The assigned values from the certificates and simulated masses of the spike and sample solutions give rise to calculate the ratios of the blends and the U-content ( $-0.004$  to  $0.08$  RD%) of the unknown sample (CRM 149). These results lead to simulate the uncertainty budgets of the tests with expanded uncertainties ( $0.07$ – $0.1\%$ ,  $k = 2$ ). RD% vs. sample/spike mol ratios of the blends conclude that the U-content difference between two end members are  $2.1855 \times 10^{-5}$  to  $2.1895 \times 10^{-5}$  Mol U/g solution, which gives rise to be around  $0.02\%$  difference. However, it was reported that about  $0.4$  difference exists between the extreme values of  $2.184 \times 10^{-5}$  and  $2.192 \times 10^{-5}$  (Fig. 1) (Hasozbek et al. 2013). In comparison between RD% vs. sample/spike mol ratio of these two studies, it is noted that there is no such a systematic variation as a function of  $^{235}\text{U}/^{238}\text{U}$  blends; however, much shallower slope exists in this study, which is closer to the “0” (RD%) value (Fig. 3).

## Conclusions

U-IDMS simulated results of four sets of mixtures in different proportions and duplicates are presented in Tables 1, 2, 3, 4, 5, 6, and 7. According to these simulated results of U-IDMS, the following are concluded:

1. Simulated mixtures RD% in the U-content yield –  $0.004$  to  $0.07$ , which are acceptable for traceability of the unknown samples
2. Expanded uncertainties ( $0.06$ – $0.1\%$  ( $k = 2$ )) presented in this study are lower due to the optimized spike to sample ratios and the selection of the relevant comparator.

3. Simulated Mol U/g U-content values of the unknown sample (CRM 149) are all in agreement with the certified values of CRM 149 and D&G titration data
4. By modeling wide range of  $^{235}\text{U}/^{238}\text{U}$  ratios of the blends, it is tested that fractional contribution in the uncertainty budget can likely be decreased by the factor of  $0.1\%$ .
5. Regardless of the mass quantities of the end members (spike and sample), it is possible to test the U-content determination in a wide range of spike to sample quantities. Therefore, 1:2, 1:3, and/or 1:4 spike to sample proportions are suitable for major isotope U-IDMS analysis

Overall, certified values of NBL U-materials were simulated by using the U-IDMS technique for its applicability to a range of spike to sample amounts. Natural Uranium reference material of CRM 112A (NU) and high enriched uranium reference material of CRM 149 (HEU) solutions are all suitable candidates to replace the use of  $^{233}\text{U}$  majored tracers (CRM 111A) in geochemistry and related applications.

## Abbreviations

CRMs: Certified Reference Materials; GUM: Guide to the expression of uncertainty in measurement; U-IDMS: Uranium isotope dilution mass spectrometry; U-Pb: Uranium-lead; ID-TIMS: Isotope dilution mass spectrometry; NU: Natural uranium; LEU: Low enriched uranium; HEU: High enriched uranium; NBL: New Brunswick Laboratory; ISO: International standards organization; SP: Spike; SA: Sample; QC: Quality control; RD: Relative deviation; RSE: Relative standard deviation; at/at: Atom/atom; D&G: Davies and Gray;  $\text{U}_3\text{O}_8$ : Triuranium octoxide

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**Competing interests**

The author declares no competing interests.

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