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Isotopic dilution analysis using ICP/AES: application to uranium samples and comparison to MC ICP/MS measurements

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Abstract An ICP/AES owning a high resolving power is able to measure the isotopic shift in emission atomic lines for heavy elements such as uranium. ^{235}U and ^{238}U are therefore clearly separated and identified. Using this phenomenon, the transposition of isotopic dilution mass spectrometry method to the ICP/AES instrument allows to quantify, with accuracy and precision, the ^{235}U content of a solution. The method, named IDAES, is the first that combine isotope dilution method and ICP/AES measurements. In order to demonstrate the validity of the IDAES method, an IDMS protocol using a MC ICP/MS instrument, is also applied to determine the amount content of ^{235}U of the sample.

Keywords Isotopic dilution · ICP/AES · uranium · MC ICP/MS

Introduction

The ICP/AES technique is widely used for analysis of major, minor and trace elements in the routine laboratory [1, 2]. The ICP/MS is more dedicated to the analysis of trace and ultra-trace elements and to the determination of isotopic composition. Among ICP/MS instruments, the MC ICP/MS is a particularly powerful instrument to determine isotopic ratios, which combined to isotopic dilution methods, allows the quantification of elements or isotopes with high accuracy and precision.

Nevertheless, few people know that ICP/AES is also able to realise isotopic measurements. Indeed, atomic transitions of the same element but from different isotopes emit light at slightly different wavelengths ("isotopic shift"). Two effects can contribute to this shift in atomic emission lines: the field (or volume) effect and the mass effect [3, 4]. In the case of heavy elements, such as uranium, the field effect is the most important. The complex electronic structure of uranium leads to in several electronic states with substantial isotopic splitting [5–7]. The isotopic shift can reach tens of picometers.

Thanks to this phenomenon, a high resolution ICP/AES allows the determination of isotopic ratio such as ^{238}U/^{235}U. Moreover, combined to isotopic dilution methods, accurate and precise quantifications of uranium isotopes can be achieved. At our knowledge, this study is the first that combined isotopic dilution method and ICP/AES measurements to determine an accurate and precise quantity of ^{235}U. The method is named IDAES. It may be valuable when plutonium or lead have a significant presence in samples.

The isotopic dilution is the preferred method when high accuracy quantitation of an element or an isotope is required [8]. Isotopic dilution method is a highly accurate procedure because there are minimal sources of potential systematic error. However, a prerequisite is that the element of interest owns at least two isotopes and those are free of isobaric interferences (ICP/MS) and spectral interferences (ICP/AES). It is also assumed that the isotopic ratios of the sample and the "spike" (material contained an enriched isotope of the element of interest), taken individually, are known. A deliberate addition of spike (a perfectly known amount of enriched isotope) to the sample

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and the determination of the isotopic composition of the resulting blend allow to quantify the analyte or one of its isotopes. Once the spike and the sample mixed, quantitative sampling is no longer required since the calculation depends only on the ratio of the blend. Gravimetric procedures for sampling are inherently more precise and accurate than volumetric ones and, therefore, are used in this protocol.

The main aims of our study are to determine the amount content of ^{235}U in a sample by ICP/AES and MC ICP/MS thanks to an isotopic dilution method and to compare the accuracy of both measurements, since MC ICP/MS is the preferred choice. The sample is a highly enriched uranium solution which was prepared by dissolution of an uranium powder (U_3O_8) SRM U-930 in nitric acid. The uncertainties associated to each measurement for both techniques are also determined and compared, in order to estimate the precision.

The terms IDMS and IDAES are used in the following document to name isotopic dilution applied to MC ICP/MS and ICP/AES respectively.

Experimental

Instrumentation

All isotopic measurements are made using an ACTIVA M (HORIBA Jobin–Yvon, Longjumeau, France) ICP/AES and a Neptune Plus MC ICP/MS (ThermoFisher Scientific, Villebon-sur-Yvette, France). The operational conditions for both instruments are summarised in Table 1.

The ICP/AES Activa M (HORIBA Jobin–Yvon) is based on Czerny-Turner optical system equipped with a megapixel low noise CCD detector, leading to spectral windows up to 8 or 16 nm with simultaneous measurement of multiple lines and backgrounds. Based on dual large back-to-back gratings, the resolution is constant over the spectral range. Indeed, the resolution is equal to 10 pm with the 4343 grooves/mm holographic grating (in the range of 120–430 nm) and equal to 16 pm with 2400 grooves/mm one (in the range of 430–800 nm). The capabilities of simultaneous measurements of multiple lines in a 8 nm spectral window associated to the good resolution around 400 nm allow to use this instrument to determine ^{238}U/^{235}U ratios. As mentioned by Krachler, in the case of ICP/AES measurements of uranium only three wavelength regions (406.25, 411.60 and 424.42 nm) seem to provide sufficient isotopic splitting of uranium emission lines [9]. So the wavelengths corresponding to ^{235}U and ^{238}U are monitored in this study.

This instrument is then compared to a MC ICP/MS instrument, Neptune Plus (ThermoFisher Scientific) used routinely to determine accurate and precise uranium isotopic ratios. This MC ICP/MS has a double focusing Nier geometry with mass dispersion of 81 cm. It is equipped with 9 Faraday cups (8 moveable collectors and a central fixed) connected to 1010, 1011 or 1012 Ώ amplifiers (multiplexing amplifier array featuring a 50 V dynamic range). Table 1 provides the instrument settings, which are optimized daily for optimal sensitivity and stability, and the data acquisition parameters. The Neptune's sample introduction system, including the cone interface region, operates at ground potential. The ions are accelerated in stages up to 10 kV potential at the detectors. The ICP system is a 27 MHz generator (Seren IPS, Inc., New Jersey, USA) coupled to a standard Fassel style torch with platinum capacitive discharge guard electrode. For MC ICP/MS measurements, 5 of the 9 Faraday's cup of the Neptune are used for the isotopic measurement of uranium. The cup configuration is as follows (Table 2).

The ^{236}U ion current measured on L1 Faraday's cup is corrected for $^{235}U^{1}H^{+}$ signal thanks to the determination of the $^{238}U^{1}H^{+}$ signal on the H1 Faraday's cup.

Reagents and certified reference materials

Nitric acid of analytical grade (Suprapur Merck, Fontenay-sous-Bois, France) and high purity water (18 MΩ/cm) produced by a MilliQ (Millipore, Guyancourt, France) system are used to prepare all solutions.

The spike isotopic reference materials (primary standards), with an isotope amount content of ^{235}U or ^{238}U certified (respectively IRMM-050 and IRMM-053), employed for isotopic dilution are from the Joint Research Centre of the European Commission, IRMM (Geel, Belgium) are used as received.

The uranium isotopic reference materials with a certified isotopic composition (SRM U-005, SRM U-350, SRM U-500, SRM U-750, SRM U-930 and SRM U-970) from New Brunswick Laboratory (Argonne, Illinois, USA) are dissolved in nitric acid to form solutions of uranyl nitrate.

Those standards are used:

- For mass bias correction attached to any measurement of uranium composition by MC ICP/MS,
- For bias correction occurring in measurement of uranium composition by ICP/AES.

The characteristics of the CRMs are listed in the Table 3.

Sample

The sample is an uranyl nitrate solution which was prepared, few years ago, from the isotopicaly certified uranium oxide powder (U_3O_8, SRM U-930) dissolved in nitric acid. The concentration of ^{235}U is supposed to be lower

Table 1 Instrumental conditions of the ICP/AES and MC ICP/MS for U isotopic measurements

	ICP/AES	MC ICP/MS
Plasma parameters		
Radio frequency	40 MHz	27 MHz
Forward power	1000 W	1200 W
Argon gas flow rates		
Plasma gas (L.min^{-1})	12	15
Nebuliser gas (L.min^{-1})	0.9	0.945
Auxiliary gas (L.min^{-1})	0.15	0.70
Acquisition parameters		
Spray chamber	Quartz cyclonic	Quartz tandem spray chamber (combination of a cyclonic and a Scott-type spray chamber)
Nebuliser	Concentric nebuliser	Self-aspirating PFA concentric nebuliser
Sample uptake	1 mL.min^{-1} (peristaltic pump)	100 µL.min^{-1}
Integration time (s)	10	8.392
Number of replicates	10	30
Collection mode	Not applicable	Static

Table 2 Cup configuration used for uranium measurement by MC ICP/MS

Cup configuration				
L3 (mobile)	L2 (mobile)	L1 (mobile)	C (fixed)	H1 (mobile)
^{234}U	^{235}U	^{236}U	^{238}U	^{238}U^{1}H

than 1 g.kg^{-1}. The precise and accurate determination of the amount content of ^{235}U is required for physical follow-up and nuclear materials account.

With the amount content of the certified reference material IRMM-053 used for isotopic dilution method (~50.45 µg of ^{238}U.g^{-1} of solution), a 10-fold dilution of the sample (SRM U-930, ~1 mg of ^{235}U.g^{-1} of solution) is needed before mixing with the spike (IRMM-053).

The dilution of the sample is realised precisely by weighting. The amount content of ^{235}U determined, thanks to the isotopic dilution formula, is the one of the diluted sample. Taking into account the 10-fold dilution, the initial amount content of ^{235}U of the SRM U-930 is determined. In practice, 1.024 g of sample is diluted with nitric acid to give a solution weighting 10.5387 g (dilution factor = 10.404). The amount content of ^{235}U in the diluted sample is closed to 100 µg.g^{-1} of solution. The solution is named "diluted sample" in the whole document.

Isotopic dilution

The general formula of isotopic dilution relates the amount content of isotope of interest (I1) contained in the sample to the amount content of enriched isotope of the spike (I2), weights of spike and sample used and isotopic ratios of spike, sample and blend [10, 11]. The formula results from the mass balance equation. The complete isotopic composition of the element is not required in this Eq. (1).

$$C_{\mathrm{S}}^{\mathrm{I1}} = C_{\mathrm{Sp}}^{\mathrm{I2}} \times \frac{m_{\mathrm{Sp}}}{m_{\mathrm{S}}} \times \frac{1}{R_{\mathrm{Sp}}} \times \frac{R_{\mathrm{Sp}} - R_{\mathrm{B}}}{R_{\mathrm{B}} - R_{\mathrm{S}}} \quad (1)$$

where R_{s} = amount ratio n(I2)/n(I1) in the unknown sample, R_{Sp} = amount ratio n(I2)/n(I1) in the spike material, R_{B} = amount ratio n(I2)/n(I1) in the blend, m_{S} = weight of the unknown sample used to prepare the blend, m_{Sp} = weight of the spike solution used to prepare the blend, C_{S}^{I1} = amount content of I1 per kilogram of sample (mol.kg^{-1}), $C_{\mathrm{Sp}}^{\mathrm{I2}}$ = amount content of I2 per kilogram of spike solution (mol.kg^{-1}).

Some precautions shall be taken to ensure that isotopic ratios measured are representative of the amounts of I1 and I2 present in the blend. Indeed, it is assumed that full equilibration between the sample and the spike is achieved and both isotopes are in the same chemical form, ensuring identical behavior during the analytical procedure. This can be achieved, for example, by an oxidation or reduction step. In our study, uranium contained in samples and spikes is in the uranyl nitrate form in nitric acid media, so no treatment, other than dilution, is applied for its.

Moreover, in the general formula of isotopic dilution (Eq. 1), ratios are assumed to have been corrected for instrumental effects (such as mass bias for ICP/MS). This can be achieved by running an alternating sequence of standards and samples named "Sample Standard Bracketing" (SSB) [12, 13]. This method is applied for ICP/MS measurements but also for ICP/AES ones.

The diagram below (Fig. 1) shows the principle of the isotopic dilution applied to a highly enriched uranium sample. The abundances of ^{235}U and ^{238}U are represented for the sample (^{235}U most abundant isotope), the spike (^{238}U most abundant isotope) and the blend (similar amounts of ^{235}U and ^{238}U).

In our case, the goal of measurements (by MC ICP/MS and ICP/AES) is the quantification of ^{235}U contained in sample. The formula presented below (2), leads to this determination thanks to the amount content of ^{238}U per quantity of spike, weights of sample and spike and amount ratios of sample, spike and blend.

$$C_{\mathrm{S}}^{235_{\mathrm{U}}} = C_{\mathrm{Sp}}^{238_{\mathrm{U}}} \times \frac{m_{\mathrm{Sp}}}{m_{\mathrm{S}}} \times \frac{1}{R_{\mathrm{Sp}}} \times \frac{R_{\mathrm{Sp}} - R_{\mathrm{B}}}{R_{\mathrm{B}} - R_{\mathrm{S}}} \tag{2}$$

where Rs = amount ratio $n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$ in the unknown sample, R_{Sp} = amount ratio $n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$ in the spike material, R_{B} = amount ratio $n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$ in the blend, m_{S} = weight of the unknown sample used to prepare the blend, m_{Sp} = weight of the spike solution used to prepare the blend, $C_{\mathrm{S}}^{235_{\mathrm{U}}}$ = amount content of ^{235}U per kilogram of sample (mol.kg^{-1}), $C_{\mathrm{Sp}}^{238_{\mathrm{U}}}$ = amount content of ^{238}U per kilogram of spike solution (mol.kg^{-1}).

As indicated previously, the abundance of each isotope of the element of interest is not required with this equation. So, this formula may be used with ICP/AES measurements (for which ^{234}U and ^{236}U isotopes could not be measured) to determine amount content of ^{235}U.

Some analysts calculated an error propagation factor (EPF_{opt}) to determine a theoretical optimum for spiking samples to achieve the best precision for the ratio measurements [14]. The following formula is used (3):

$$\mathrm{EPF_{opt}} = \sqrt{\frac{\text{Main spike abundance}}{\text{Minor spike abundance}} \times \frac{\text{Minor sample abundance}}{\text{Main sample abundance}}}. \tag{3}$$

In this approach, practical aspects, such as blank influence, have not been considered. A compromise between the theoretical optimum and practical aspects is therefore recommended [15].

In our case, the highest precision is reached with a molar ratio between spike and sample around unity [16]. This criterion is driven by the intensities of ion currents or photons (measured by Faraday's cup for MC ICP/MS and diode array for ICP/AES) and uncertainty associated, by background corrections and the dynamic range of both instruments. So a reasonable rule of thumb is to mix the spike and sample on an equimolar basis ($R_B \sim 1$).

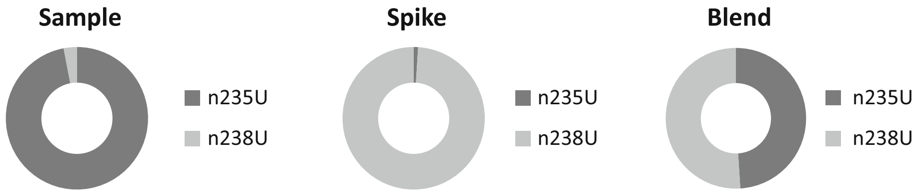
In practice and as mentioned before, a gravimetric procedure is used to prepare the blend by mixing known weights of the diluted sample and the spike. A 1.2403 g of diluted sample and 2.6127 g of spike (IRMM-053) are

Table 3 Certified amount content and certified isotopic composition with uncertainties of materials used

CRM	Certified amount content of major isotope (mol.g^{-1})	Certified isotopic composition (amount fraction %)				Amount ratio
		^{234}U	^{235}U	^{236}U	^{238}U	$n(^{238}\mathrm{U})/n(^{235}\mathrm{U})$
IRMM-050	(4.2543 ± 0.0011) × 10^{-9}	0.0361 ± 0.0005	99.9414 ± 0.0018	0.0095 ± 0.0010	0.0130 ± 0.0005	0.0001296 ± 0.0000030
IRMM-053	(2.1194 ± 0.0026) × 10^{-7}	0.005508 ± 0.000022	0.72183 ± 0.00030	0.0000150 ± 0.0000045	99.27265 ± 0.00030	137.5289 ± 0.0568
SRM U-005	–	0.00218 ± 0.0004	0.4895 ± 0.005	0.00466 ± 0.00005	99.504 ± 0.001	203.293 ± 0.204
SRM U-350	–	0.2498 ± 0.0006	35.190 ± 0.035	0.1673 ± 0.0005	64.393 ± 0.036	1.8298 ± 0.0019
SRM U-500	–	0.5181 ± 0.0008	49.696 ± 0.050	0.0755 ± 0.0003	49.711 ± 0.050	1.0003 ± 0.0010
SRM U-750	–	0.5923 ± 0.0009	75.357 ± 0.025	0.2499 ± 0.0008	23.801 ± 0.024	0.31586 ± 0.00032
SRM U-930	–	1.0812 ± 0.0020	93.336 ± 0.010	0.2027 ± 0.0006	5.380 ± 0.005	0.05764 ± 0.00006
SRM U-970	–	1.6653 ± 0.0017	97.663 ± 0.003	0.1491 ± 0.0005	0.5229 ± 0.0006	0.00535 ± 0.00001

Uncertainties are given at $k = 2$

Fig. 1 Principle of the isotopic dilution method



weighed with an accuracy of 0.3 mg on a balance. The blend obtained has a molar ratio closed to unity.

Once the blend is performed and processed, large dilutions can be made (even without the use of calibrated volumetric glassware) in order to achieved a signal-to-noise ratio for suitable measurements by MC ICP/MS or ICP/AES. This action has no effect on the isotopic ratio measured.

Bias correction

Mass bias occurs when ions of different mass are transmitted through the mass spectrometer with different efficiencies within the MC ICP/MS instrument, resulting in non-uniform response across the mass range and inaccurate isotope ratio measurements. In ICP/AES, an instrument bias is observed when certified reference materials are analysed. Unlike ICP/MS, ion transmission efficiencies could not be advanced to explain this phenomenon.

In this study, the "Sample Standard Bracketing" (SSB) method is applied for MC ICP/MS and ICP/AES measurements. For both instruments, the SSB method is used to correct instrumental bias. Indeed, among methods used to correct bias, SSB is perfectly adapted to uranium. Indeed, a wide range of uranium certified reference materials, from highly enriched to depleted, is commercially available (NIST, IRMM).

The SSB method is based on an external correction [13, 17]. An isotopic reference material measured before and after the sample is used and the relative bias between the true and the experimental value is assumed to be valid for the sample as well. Best results are obtained when standards and samples show a similar matrix composition and target element concentration. Once these conditions are met, accurate and precise isotope ratio determinations can be obtained using SSB for instrumental bias correction.

The correction factor is first determined in SRM U-500 solutions that bracket the blend. The resulting value is applied to correct the measured ratio for the blend. Moreover, blank analysis is still required because any isotopic contribution to the mixture (from reagents, contamination) will affect the isotopic abundance ratio and ultimately lead to a systematic bias. So, blank analyses are also realised before and after both SRM U-500 and blend and used to correct all intensities.

In practice, measured ratios of blends are obtained from simultaneous measurements of ions (MC ICP/MS) or photons (ICP/AES) resulting from ^{235}U and ^{238}U. Each ratio blend results from 30 replicates for MC ICP/MS and from 10 replicates for ICP/AES. The bias corrected ratios of the blend (for each instrument) are obtained from the mean of two ratio blends values obtained from using bias correction factors in the bracketing standards using the following Eq. (4) [18]:

$$R_{\mathrm{B}} = R_{\mathrm{B}}^{\mathrm{meas}} \times \left(\frac{R_{\mathrm{std}}^{\mathrm{True}}}{R_{\mathrm{Std}}^{\mathrm{meas}}} \right) \tag{4}$$

where R_{B} = bias corrected ratio of the blend, $R_{\mathrm{B}}^{\mathrm{meas}}$ = measured ratio of the blend, $R_{\mathrm{Std}}^{\mathrm{meas}}$ = measured ratio of the standard (SRM U-500) and $R_{\mathrm{Std}}^{\mathrm{True}}$ = true ratio of the standard (SRM U-500).

Uncertainty

Uncertainties associated to the SSB measurements and to the isotopic dilution method are determined thanks to the "law of propagation of uncertainty" [19, 20].

Uncertainty for SSB measurements

The uncertainty associated to the bias corrected ratio of the blend, $u_{R_{\mathrm{B}}}$, is determined from the following Eq. (5):

$$u_{R_B} = R_{\mathrm{B}} \times \sqrt{\left(\frac{u_{R_B^{meas}}}{R_B^{meas}} \right)^2 + \left(\frac{u_{R_{Std}^{meas}}}{R_{Std}^{meas}} \right)^2 + \left(\frac{u_{R_{Std}^{True}}}{R_{std}^{True}} \right)^2} \tag{5}$$

where, $u_{R_{\mathrm{B}}}$ = uncertainty associated to the bias corrected ratio of the blend, $u_{R_{\mathrm{B}}^{\mathrm{meas}}}$ = uncertainty associated to the measured blend ratio, $u_{R_{\mathrm{Std}}^{\mathrm{meas}}}$ = uncertainty associated to the measured standard ratio, $u_{R_{\mathrm{Std}}^{\mathrm{True}}}$ = uncertainty associated to the true standard ratio.

The uncertainty associated to the measured blend ratio $u_{R_{\mathrm{B}}^{\mathrm{meas}}}$ is obtained using the corrected sample standard deviation formula [20], where n = number of measurements, $R_{\mathrm{B}i}^{\mathrm{meas}}$ = the observed value for the ith measurement and $\overline{R_{\mathrm{B}}^{\mathrm{meas}}}$ = the mean value of the n measurements. A 2σ outlier test is performed at each run.

$$u_{R_{\mathrm{B}}}^{\mathrm{meas}} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left(R_{\mathrm{B}i}^{\mathrm{meas}} - \overline{R_{\mathrm{B}}^{\mathrm{meas}}} \right)^2}. \tag{6}$$

The uncertainty associated to the measured standard ratio $u_{R_{\mathrm{Std}}^{\mathrm{meas}}}$ is also calculated using the corrected sample standard deviation formula (6). The $u_{R_{\mathrm{Std}}^{\mathrm{True}}}$ is given by the certificate of the SRM U-500 material.

The results are given in the following format: $R_{\mathrm{B}} = \text{value} \pm \mathrm{U}$. The expanded uncertainties (U) are obtained by multiplying the uncertainty $u_{R_{\mathrm{B}}}$ by a coverage factor k ($U = k \cdot u_{R_{\mathrm{B}}}$) equal to 2.

Uncertainty for isotopic dilution method

The uncertainty of amount content of $^{235}\mathrm{U}$ in the sample is given by the formula (7):

$$u_{C_{\mathrm{S}}^{235\mathrm{U}}} = C_{\mathrm{S}}^{235\mathrm{U}} \times \sqrt{\left(\frac{u_{C_{\mathrm{Sp}}^{238\mathrm{U}}}}{C_{\mathrm{Sp}}^{238\mathrm{U}}}\right)^2 + \left(\frac{u_{m_{\mathrm{Sp}}}}{m_{\mathrm{Sp}}}\right)^2 + \left(\frac{u_{m_{\mathrm{S}}}}{m_{\mathrm{S}}}\right)^2 + \left(\frac{u_{R_{\mathrm{Sp}}}}{R_{\mathrm{Sp}}}\right)^2 + \left(\frac{u_{(R_{\mathrm{sp}}-R_{\mathrm{B}})}}{R_{\mathrm{Sp}}-R_{\mathrm{B}}}\right)^2 + \left(\frac{u_{(R_{\mathrm{B}}-R_{\mathrm{S}})}}{R_{\mathrm{B}}-R_{\mathrm{S}}}\right)^2}. \tag{7}$$

where $u_{C_{\mathrm{Sp}}^{238\mathrm{U}}}$ is uncertainty associated with the amount content of the spike (given by the certificate of the CRM), $u_{m_{\mathrm{Sp}}}$ and $u_{m_{\mathrm{S}}}$ are the uncertainties of s of spike and sample respectively used to prepare the blend and $u_{R_{\mathrm{Sp}}}$ is the uncertainty associated to the spike ratio (given by the certificate of the CRM).

The results are given in the following format: $C_{\mathrm{S}}^{235\mathrm{U}} = \text{value} \pm \mathrm{U}$. The expanded uncertainties (U) are obtained by multiplying the uncertainty $u_{C_{\mathrm{S}}^{235\mathrm{U}}}$ by a coverage factor k ($U = k \cdot u_{C_{\mathrm{S}}^{235\mathrm{U}}}$) equal to 2.

Results and discussion

Choice of optimum wavelengths for ICP/AES measurements

Firstly, analyses of SRM U-005, SRM U-350, SRM U-500, SRM U-750 and SRM U-970 solutions (with an uranium concentration closed to 5 mg.L^{-1}) are realised to determine the wavelengths allowing stable and intense signals for $^{235}\mathrm{U}$ and $^{238}\mathrm{U}$ isotopes. As mentioned before, the three wavelength regions allowing the detection of a split in U emission lines are studied (Table 4).

Only the ones at ~424 nm are fully baseline separated (Fig. 2). So taking into account a resolution of 10 pm and the gap observed between peaks, all measurements are realised on the wavelengths at 424.412 and 424.437 nm corresponding to the $^{235}\mathrm{U}$ isotope and $^{238}\mathrm{U}$ isotope. The analysis of the uranium isotopic certified materials, from the most depleted (SRM U-005) to the highest enriched (SRM U-970), perfectly demonstrated the increase of the signal at 424.412 nm (corresponding to $^{235}\mathrm{U}$) and the decrease of the one at 424.437 nm (corresponding to $^{238}\mathrm{U}$) (Fig. 3).

In acquisition, the spectral background is subtracted from all peak intensities to obtain accurate results.

It is important to note that for the wavelength at 385.958 nm, which is widely used for uranium quantification, a slight shift of 5 pm to lower wavelengths is observed between SRM U-005 and SRM U-970 (Fig. 4). In this region the isotopic shift is not sufficient to induce a baseline separated split in U emission lines. So analysts must be aware that for measurement of enriched uranium samples, a false quantification of uranium may occur. Considering a resolution of 10 pm and a shift of 5 pm between the highly enriched and the depleted uranium materials, the quantification of an highly enriched sample could be reduced by 50 % (at a given concentration, Apex of SRM U-005 corresponds to the half-maximum of the SRM U-970).

Spike and assay standard mix

In order to verify the integrity of the spike (IRMM-053) and the accuracy and precision of the IDMS procedure using the MC ICP/MS, a blend is prepared using a primary assay standard (IRMM-050) and the IRMM-053. This IRMM-050 standard is provided in the form of a nitrate solution with a perfectly known amount content of $^{235}\mathrm{U}$ and an accurate and precise isotopic composition. The certified amount content of $^{235}\mathrm{U}$ of this material is 50 times lower than the amount content of $^{238}\mathrm{U}$ of the IRMM-053. So, although a dilution of standard is often

Table 4 Wavelengths measured for $^{235}\mathrm{U}$ and $^{238}\mathrm{U}$ and gap between both adjacent peaks

Wavelengths used (nm)		Gap between peaks (pm)
$^{235}\mathrm{U}$	$^{238}\mathrm{U}$	
406.241	406.253	12
411.593	411.608	15
424.412	424.437	25

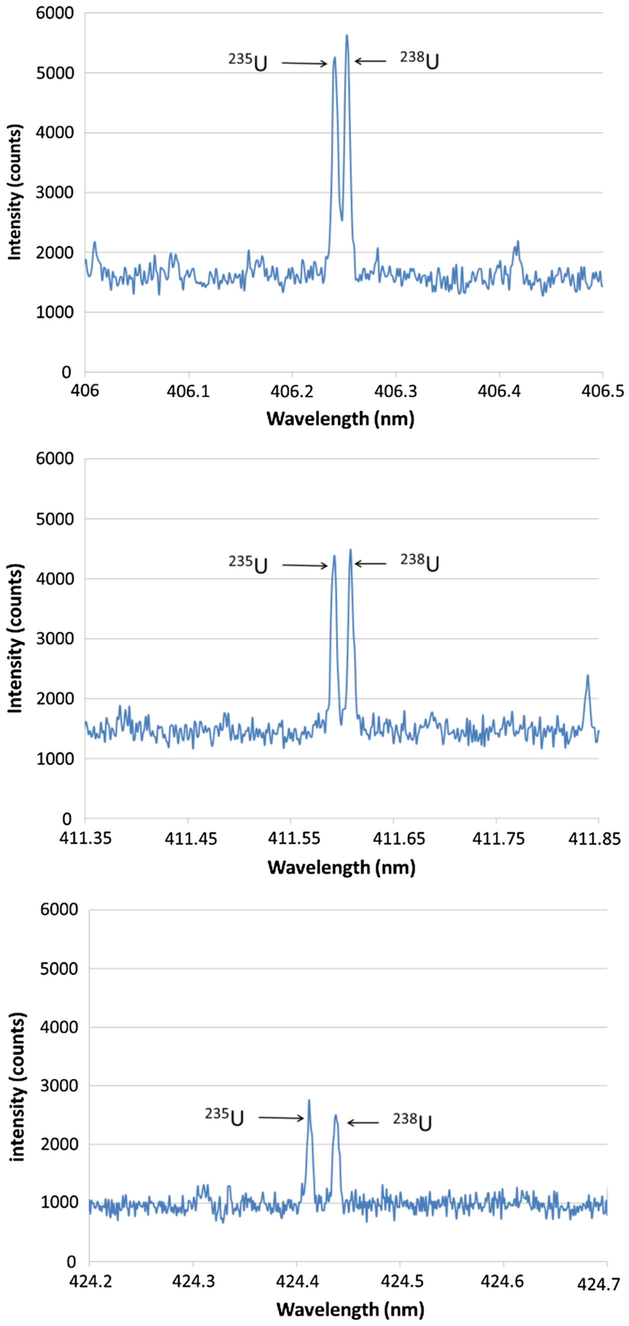


Fig. 2 Simultaneous acquisition of ^{235}U and ^{238}U signals in the three wavelength regions for SRM U-500 (5 mg.L^{-1})

not recommended, the spike IRMM-053 is diluted before mixing with the IRMM-050, in order to achieve a molar ratio closed to unity and to weigh significantly amount of solution (more than 500 mg) to minimize uncertainties. The dilution of IRMM-053 is realised twice, leading to two diluted spike named “IRMM-053 D1” and “IRMM-053 D2”.

The weights of IRMM-053 used, those of the final solutions and the amount contents of ^{238}U calculated in both diluted solutions are indicated in the following table (Table 5). The uncertainties mentioned in the table take into account the amount content of ^{238}U of IRMM-053, the weight of IRMM-053 used and the one of the final solution. They are given with a confidence level of 95 % ($k = 2$).

Two blends, named “blend 1” and “blend 2”, are prepared. Blend 1 is composed of known weights of IRMM-053 D1 and of assay standard (IRMM-050). Blend 2 is prepared from known weights of IRMM-053 D2 and of IRMM-050. Each blend is analysed with the SSB method by MC ICP/MS to determine the R_B with accuracy and precision.

Thanks to the determined R_B and the isotopic dilution formula, the amount content of ^{235}U of the IRMM-050 could be obtained. The result confirms the integrity of the spike and the accuracy and the precision of measurements thanks to the isotopic dilution method and the MC ICP/MS instrument.

The weights of spike and assay standard and the corrected molar ratio for each blend (R_B) are mentioned in the table below (Table 6). It also indicates the amount contents of ^{235}U in IRMM-050 determined thanks to the two distinct blends with the corresponding uncertainties given with a confidence level of 95 % ($k = 2$). The differences between the fair value and the measured ones are calculated.

The amount contents of ^{235}U in IRMM-050 determined by IDMS from two distinct blends, perfectly match with the fair value of IRMM-050 indicated in the Table 6 ((4.2543 ± 0.0011) 10^{-9} mol.g^{-1}). The differences between values are lower than 0.2 %. The integrity of the spike is confirmed and the accuracy and precision of the MC ICP/MS measurements are in conformance with our requirements (RSD < 1 %).

The spike IRMM-053 is used to determine the amount content of ^{235}U of SRM U-930 solution by IDAES and IDMS from the mix of spike and diluted sample (diluted SRM U-930 sample).

Spike and diluted sample

In order to compare the accuracy and the precision of the amount content determined by IDAES to IDMS, the blend composed from diluted sample (diluted SRM U-930 solution) and spike (IRMM-053) is analysed by ICP/AES and MC ICP/MS. The blend is named “Blend 3”.

In practice, the blend 3 is composed of 2.6127 g of IRMM-053 and 1.2403 g of diluted sample (diluted NBS-930 solution). An adjustment of the volume of the blend 3 is realised by addition of diluted nitric acid ($[HNO_3] = 1$ M), to adapt the concentration of uranium to the sensitivity of each instrument. As previously, this action has no effect on the ratio R_B.

Therefore, for ICP/AES measurements, the optimum uranium concentration of the blend 3 is equal to 5 mg.L^{-1}

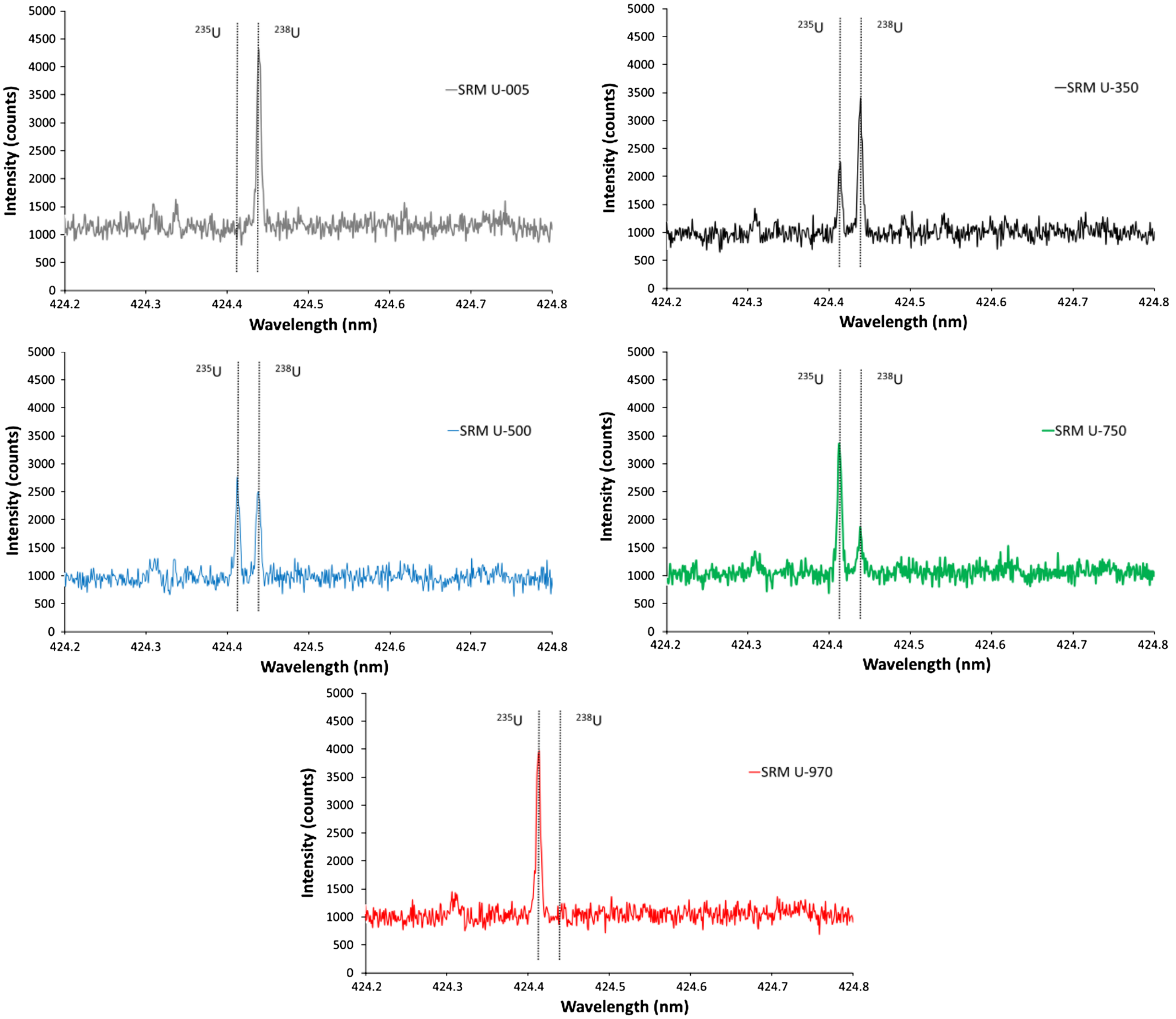


Fig. 3 Spectra obtained in the 424 nm region from depleted (SRM U-005) to highly enriched uranium (SRM U-970) CRM at about 5 mg.L^{-1}

to ensure an intense and stable signal for both isotopes. Moreover, the uranium concentration of SRM U-500, used as standard in the SSB protocol, is also adjusted to 5 mg.L^{-1} in order to perfectly match the one of the blend.

For MC ICP/MS measurements, the uranium concentration of the blend 3 is adjusted to 200 µg.L^{-1} to ensure an intense and stable ions counting by Faraday's cup. As previously, the concentrations and the matrix of the standard SRM U-500 and of the blend have to be matched in order to perfectly correct mass bias and give an accurate and precise ratio R_B.

The use of the SSB protocol allows to determine R_B of the blend 3 by ICP/AES and MC ICP/MS measurements. As is highlighted in Table 7, the ratios R_B determined for the same blend 3 by ICP/AES and by MC ICP/MS are only distinct by the third digit after the decimal point. The accuracy of measurements of the isotopic ratio ^{238}U/^{235}U by ICP/AES is demonstrated.

Nevertheless, the uncertainty associated to the R_B of the blend 3 (given with a coverage factor $k = 2$) measured by ICP/AES is twenty times more larger than the one measured by MC ICP/MS.

Once R_B determined, the isotopic dilution formula is applied to obtain the amount content of ^{235}U of the diluted sample for both method IDAES and IDMS. Considering the weights of sample and of nitric acid used to prepare the diluted sample, the amount content of ^{235}U of the SRM U-930 is determined. The results and uncertainties associated (given with a coverage factor $k = 2$) are indicated in the following table (Table 8).

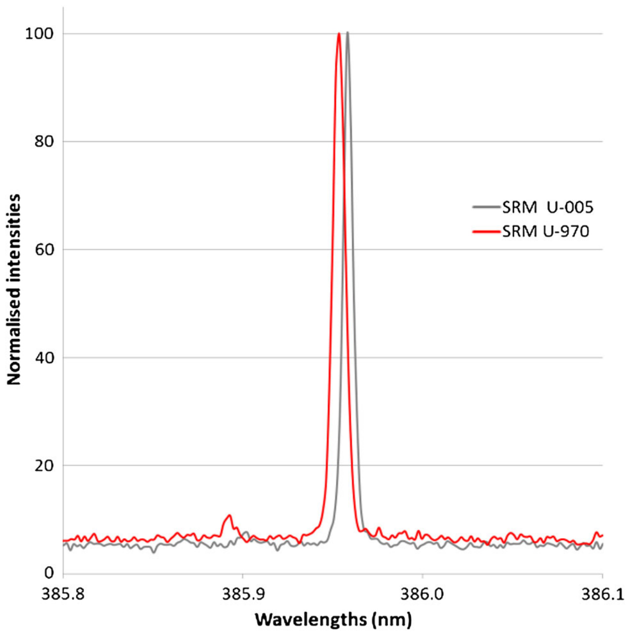


Fig. 4 Wavelength shift observed between SRM U-005 and SRM U-970 for uranium measurement at 385.958 nm

Using the molar mass of ^{235}U (235.0439 mol.g^{-1}) and the amount content of ^{235}U in SRM U-930 in mol.g^{-1}, the amount content of ^{235}U could be expressed in g.g^{-1}. The amount content of ^{235}U is equal to 0.753 ± 0.024 g.g^{-1} and matches with the expected one.

Comparison of IDAES and IDMS

The accuracy of both methods (IDAES and IDMS) is demonstrated. The difference between the amount contents of ^{235}U determined by each method in the diluted sample is less than 0.1 %. This result is particularly notable since measurements are realised using two different physical measurements methods.

However, measurements realised by MC ICP/MS and ICP/AES did not led to the same level of precision. Indeed, the uncertainties associated to the amount content of ^{235}U of the blend determined by IDAES and IDMS are different. Considering the uncertainty budget for IDAES and IDMS methods (Fig. 5), the precision of signal measurements (by ICP/MS or ICP/AES) clearly affects the blend ratio measurement (R_B) and the uncertainty associated to the amount content of ^{235}U of the diluted sample. This point is particularly critical for measurements by ICP/AES. Nevertheless, the precision of the IDAES method remains highly satisfactory since the RSD (Relative Standard Deviation) is about 3 %.

Table 7 ^{238}U/^{235}U ratio of blend 3 determined by ICP/AES and MC ICP/MS

Instrument	R_B
ICP/AES	1.4945 ± 0.0460
MC ICP/MS	1.4955 ± 0.0022

Conclusion

ICP-AES technique combined to isotopic dilution method (leading to IDAES) is fully appropriate for the determination of ^{235}U and/or ^{238}U concentrations, in terms of accuracy (trueness of the results) and precision. Indeed, results obtained thanks to this technique are quite similar to those given by MC ICP/MS (IDMS method) which is the preferred choice. This result is particularly remarkable because the physical principles of measurements of both instruments are different.

Provided that the uranium concentration is sufficient, IDAES or IDMS could be applied to determine highly accurate amount content of ^{235}U or ^{238}U of a sample. The choice between the two methods is governed by the level of precision required. The highest precision of the IDMS method compared to the IDAES one is the result of the high precision of measurement of the MC ICP/MS.

Table 5 Spikes prepared from the CRM IRMM-053

Spike name	Weight of IRMM-053 used (g)	Weight of final solution (g)	Amount content of ^{238}U calculated (mol.g^{-1})
IRMM-053 D1	1.1732 ± 0.0003	101.2034 ± 0.0003	(2.4569 ± 0.0016) × 10^{-9}
IRMM-053 D2	1.1704 ± 0.0003	100.2529 ± 0.0003	(2.4743 ± 0.0016) × 10^{-9}

Table 6 Amount contents of ^{235}U determined in assay standard (IRMM-050)

Blend name	m_{spike}	$m_{assay\ standard}$ (IRMM-050)	R_B	Amount content of ^{235}U in IRMM-050 (mol.g^{-1})	Difference between fair and measured value (%)
Blend 1	2.0640 ± 0.0003	1.1634 ± 0.0003	1.0160 ± 0.0032	(4.2592 ± 0.0151) × 10^{-9}	0.12
Blend 2	2.0628 ± 0.0003	1.1593 ± 0.0003	1.0266 ± 0.0032	(4.2572 ± 0.0149) × 10^{-9}	0.07

Table 8 Amount contents of ^{235}U in diluted and undiluted SRM U-930 solution by IDAES and IDMS

Method	Amount content of ^{235}U in diluted sample (mol.g^{-1})	Amount content of ^{235}U in SRM U-930 sample (mol.g^{-1})
IDAES	$(3.081 \pm 0.099) \times 10^{-7}$	$(3.205 \pm 0.103) \times 10^{-6}$
IDMS	$(3.079 \pm 0.007) \times 10^{-7}$	$(3.203 \pm 0.007) \times 10^{-6}$

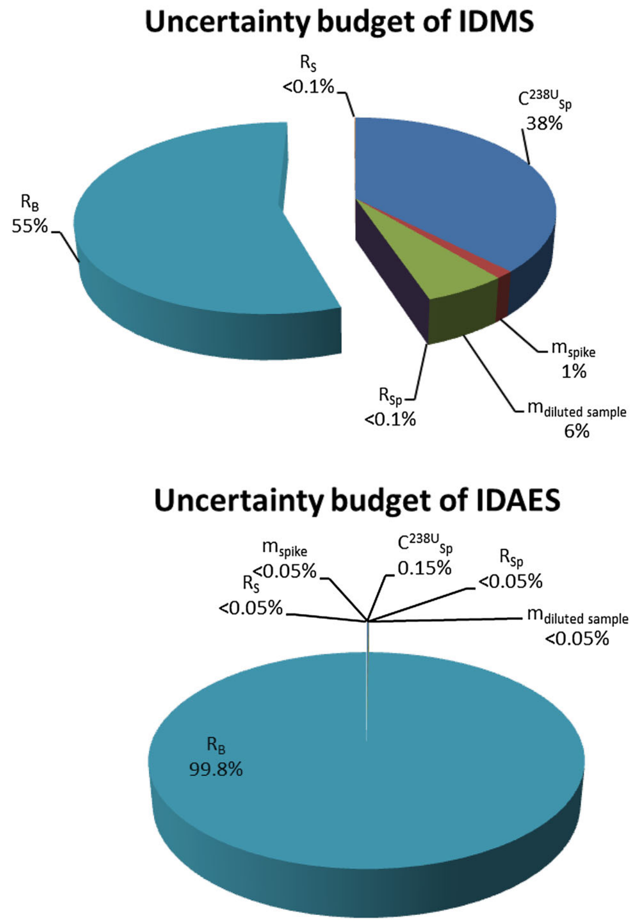


Fig. 5 Uncertainty budget for IDMS (*up*) and IDAES (*down*)

Nevertheless, this instrument is ten times more expensive than the ICP/AES one.

A great advantage of IDAES is that in the case of uranium concentrated samples, the clogged up of the ICP/AES instrument is limited to the torch and the carryover effect is easily removable unlike ICP/MS. The method is usable for physical follow-up and nuclear materials account. Moreover, the IDAES method may be useful for uranium measurements when significant amounts of lead or plutonium are supposed to be present. Indeed in ICP/MS, lead oxide and plutonium isotopes create isobaric interferences.

Studies will be conducted to improve the precision of ICP/AES measurements in order to decrease the uncertainty of the blend ratio (the major contributor of the whole uncertainty). Improvements will try to minimise sources of instabilities (such as nebulisation) and to enhance ions counting (uranium concentration, amount of spike added, number of replicates, integration time).

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