

Isotope measurements in uranium using a quadrupole inductively coupled plasma mass spectrometer (ICPMS)

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A series of measurements were carried out to establish the reliability associated with isotope ratio ($^{235}/^{238}$) measurements on uranium samples using a quadrupole inductively coupled plasma mass spectrometer (ICPMS). Figures of merit related to the isotopic measurements were determined using non certified as well as certified materials provided by the New Brunswick Laboratory (NBL). The experimental results showed that repeatability is around 0.5% while reproducibility was calculated as 0.27%. Mass discrimination was determined as 0.03% per mass unit and the system linearity check over five orders of isotope ratios yielded a mass discrimination factor (K factor) of 1.0002 ± 0.0081 (0.81%, 2s). The mean error of measurement obtained from six different certified reference materials was 0.77%.

Introduction

It is well known that uranium is found in nature as a blend of three isotopes whose mass and abundance (atomic percentage) are 234 (0.0055%), 235 (0.7200%) and 238 (99.27%),¹ respectively. This element has also another eleven artificial isotopes from which those of mass 233 and 236 are the most important ones. The former is produced by the neutron irradiation of ^{232}Th , as a fissionable isotope and has being used as a spike in isotope dilution mass spectrometry (IDMS). The latter is produced in reactor burn up.²

The discovery that among the naturally occurring isotopes, just that of mass 235 undergoes a nuclear chain reaction determined the necessity to get artificially enriched uranium to feed nuclear reactors. Thus, a reliable determination of the uranium isotopic composition started to be one of the most important analytical measurements of the nuclear fuel cycle.³

The determination of isotope composition has been applied not only for the characterization of feed or burn-up of reactor materials, but also for the quantification of secondary fission products, for safeguard purposes, inventory of sensitive materials and for detecting traces of nuclides inside or outside nuclear facilities.⁴

Among the techniques currently used to determine uranium isotopes, gas source mass spectrometry (GSMS) is recognized as the most precise and accurate one.⁵ Nevertheless, it has some drawbacks like low sample throughput, the intense memory effect in the ion source and the lack of commercial reference materials for the whole range of isotopic compositions.

Thermo ionization mass spectrometry (TIMS), on the other hand, although has proved to be a highly precise

and accurate destructive technique has also some limitations: the need of extensive sample preparation, of skilled operation, low sample throughput, inability to analyze refractory materials and a high cost.⁶

These factors allowed the advent of a new technique, namely inductively coupled plasma mass spectrometry (ICPMS). Its advantages are a much simpler sample preparation, a higher sample throughput, ability to analyze refractory elements and lower cost.⁷

Although several new designs and updates have come to the market since the commercial introduction of the ICPMS in 1983, the aim of this work is to assess the reliability of the simplest ICPMS version, the quadrupole based instrument, to perform uranium isotope ratio measurements.

In this way, typical values of repeatability and reproducibility were determined through the use of non certified materials whereas the mass discrimination effect, linearity and errors of measurement over five orders of magnitude were evaluated with the use of certified isotope reference materials.

Finally, the fact that typical values for precision and error of measurement provided by the most traditional techniques, TIMS and GSMS, are known to be around 0.05% and 0.005%, respectively,⁸ prompted the decision to determine these figures for a quadrupole ICPMS.

Experimental

Instrument

The instrument used was a PlasmaQuad PQII Plus manufactured by VG Elemental (Winsford, Cheshire, UK). Its vacuum system has two magnetic bearings turbomolecular pumps Turbovac 340M and two double

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stage mechanical pumps D 25 manufactured by Leybold-Heraeus (Koln, Germany) which allowed an ultimate pressure of $1.0 \cdot 10^{-5}$ Pa within the spectrometer chamber.

It is also equipped with a peristaltic pump MiniPlus 2 from Medical Electronic Company (Middletown, WI, USA), mass flow controller model FC 260 from Tylan (Rancho Dominguez, CA, USA), double pass water cooled quartz spray chamber, De Galan cross flow nebulizer, quartz torch of Fassel type, Channeltron continuous dynode electron multiplier from Galileo Electro Optics Corporation (Stunbridge, MA, USA) and a 2.0 kW, 27.1 MHz solid state radio frequency generator from RF Power Products (Marlton, NJ, USA).

Solutions

The 18 M Ω deionized water used in this study was supplied by an ultrapurifier Elgastat Maxim model from Elgast Scientific (Bucks, England). Nitric acid Suprapur 65% and single element standards of Be, Mg, Co, In, La, Pb, Bi and U at a concentration of 1.000 $\mu\text{g/ml}$ were provided by Merck (Darmstadt, Germany).

The isotopic certified reference material (CRM) in the form of uranium dioxide (UO_2) was provided by the New Brunswick Laboratory (Chicago, IL, USA).

Non certified material in the form of uranium trioxide (U_3O_8) was provided by our own laboratory. The solutions were prepared by dissolving the uranium oxides in nitric acid and diluting to a final concentration of uranium of 100 ng/ml, 2% nitric acid.

Measurements

The instrument was calibrated using a multielement solution containing Be, Mg, Co, In, La, Pb, Bi and U at a concentration of 10 ng/ml, 2% nitric acid to assure that the peaks were centered at its correct position. The sensitivity for each element in the calibration solution was also verified. Typical values were $1.0 \cdot 10^5$ counts per second. Finally short-term and long-term stability tests were carried out to see whether the system was able to give stable ion count rates.

The complete optimization of the instrument was described elsewhere⁹ and its operating parameters are summarized at Table 1.

In order to carry out isotopic measurements, the measurement parameters were selected conveniently, as shown in Table 2.

An adequate choice of solution processing times is highly recommended to avoid cross contamination as well as undesired ion count rate variations. The selected values are shown in Table 3.

Table 1. Instrumental parameters

Source	
Cooling gas	Argon
Forward RF power, W	1.350
Reflected RF power, W	2
Cooling gas flow rate, l/min	14.0
Auxiliary gas flow rate, l/min	1.0
Nebulizer flow rate, l/min	0.96
Sample uptake, ml/min	0.80
Interface	
Plasma sample depth, mm	10
Sampling cone diameter, mm	Ni, 1.0 mm
Skimmer cone diameter, mm	Ni, 0.7 mm
Nebulizer pressure, p.s.i.	20
Spray chamber temperature, °C	4.2

Table 2. Measurement parameters

Scan mode	Peak jumping
Dwell time per scan, s	1.35
Dwell time per peak, ms	
^{235}U	100
^{238}U	10.24
Number of points per mass peak	5
Number of repeats	10
DAC steps	10

Table 3. Solution processing times

Uptaking time, s	120
Acquisition time, s	60
Washing time, s	120

Results and discussion

Vocabulary and estimation of uncertainty

The technical vocabulary used followed the recommendations of international organizations as BIPM¹⁰ and ISO.¹¹ The estimation of the expanded uncertainty for all the experimental data was done according to ISO-GUM¹² and Eurachem/Citac Guide.¹³ A coverage factor (k) of 2 was used throughout this work.

Dead time correction

This effect is related to the fact that after the arrival of an ion, for a short period of time, the detector becomes unable, to detect the arrival of any more ions. Thus a certain number of ions will not be measured. Also the higher the countrates, the greater the number of ions lost.¹⁴ The correction is done by:

$$I_{\text{true}} = I_{\text{obs}} / (1 - DT \cdot I_{\text{obs}}) \quad (1)$$

where I_{true} is the true count rate in counts per second, I_{obs} is the observed count rate in counts per second, DT is the dead time in seconds.

The value for the dead time was determined according to the procedure suggested elsewhere.¹⁵ Three solutions of the NBL CRM U005, at concentrations of

10, 50 and 100 ng/ml, 2% nitric were prepared. Isotope measurements were then carried out varying the dead time from 10 to 100 ns for each solution. Experimental data were plotted and the obtained three straight lines crossed each other at the value of 19.5 ± 2.1 ns. This is considered to be ideal to isotope ratio measurements because it is independent of sample concentration.

Repeatability

The evaluation of the repeatability or internal precision¹¹ was carried out using a non-certified material whose isotopic ratio was around 0.2440. It was seen that an analysis consisting of 10 runs, 60 seconds each provided a typical relative internal standard deviation (RISD%) of 0.50% though it can vary between 0.10 and 1.0%. This value expresses the dispersion of results in just one operational condition.¹⁶

Reproducibility

The evaluation of the external precision or reproducibility¹¹ consisted in repeating the analysis described above in 18 different days so as to assess not only the influence of different operational instrument conditions but also the inevitable different environmental conditions.¹⁶ The calculated relative external standard deviation (RESD%) was 0.27%.

Table 4 presents the isotopic ratios while Fig. 1 shows the isotopic and the average ratio. The uncertainty bars represent twice the value of the standard deviation (2s).

Table 4. Observed isotopic ratios for a non certified material

Analysis	Observed ratio	S.D.	RSD, %
1	0.24382	0.00072	0.30
2	0.24704	0.00096	0.39
3	0.24659	0.00056	0.23
4	0.24104	0.00015	0.06
5	0.24359	0.00112	0.46
6	0.24309	0.00184	0.76
7	0.24502	0.00108	0.44
8	0.24706	0.00174	0.70
9	0.24714	0.00088	0.36
10	0.24277	0.00194	0.80
11	0.24319	0.00274	1.13
12	0.24233	0.00104	0.43
13	0.24741	0.00080	0.32
14	0.24874	0.00140	0.56
15	0.24757	0.00066	0.27
16	0.24007	0.00084	0.35
17	0.24131	0.00112	0.46
18	0.23882	0.00054	0.23
Mean:	0.24426		
S.D.	0.00293		

Mass discrimination correction

In an ICPMS this effect is related to the preferential transmission of heavier ions mainly due to space charge interactions occurring after the skimmer cone region. Differently of what happens in TIMS, it is a time independent phenomenon as the sample is continuously introduced into the analyzer¹⁷

The determination of the mass discrimination correction factor was made running the NBL CRM U500, where the isotope ratio is almost equivalent to one: $^{235}\text{U}/^{238}\text{U} = 0.99970 \pm 0.00142$.

Although there are several correlation models between the true and the observed ratio, the simplest one was used, known as the linear function:¹⁷

$$K_{\text{Discr}} = \frac{R_{\text{cert}}}{R_{\text{med}}} = 1 + \alpha \cdot n \quad (2)$$

where K_{Discr} is the mass discrimination factor, R_{cert} is the certified isotopic ratio for the NBL U 500, R_{obs} is the observed isotopic ratio for the NBL U 500, α is the error per mass unit, n is the mass difference ($238 - 235 = 3$).

Ten isotopic measurements provided the data presented at Table 5. The average value was 1.0006 ± 0.0076 (0.76%, 2s), which allowed the calculation of the average mass bias per mass unit. The result according to equation 1 is 0.03%. Hence, this figure was used to correct every observed isotope ratio.

The distribution of observed isotopic ratio measurements around the certified value of the CRM U500 is presented at Fig. 2. In this figure, the uncertainty bars on each point represent twice the value of the standard deviation (2s).

Table 5. Observed isotopic ratios for CRM U 500

Analysis	Observed ratio	S.D.
1	1.01330	0.00488
2	0.98764	0.00681
3	1.00810	0.00568
4	0.98991	0.00602
5	1.00190	0.00463
6	0.99242	0.00755
7	1.00060	0.00368
8	1.01280	0.00794
9	1.01170	0.00588
10	0.98788	0.00572
Average:	1.00063	
S.D.	0.01055	

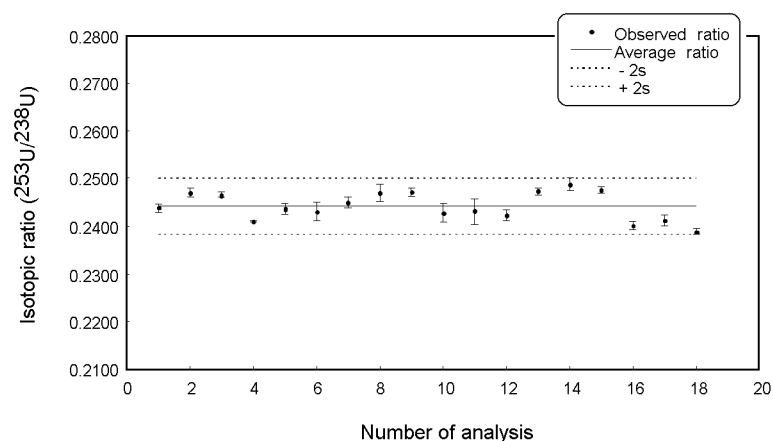


Fig. 1. Observed isotopic ratios for a non-certified material

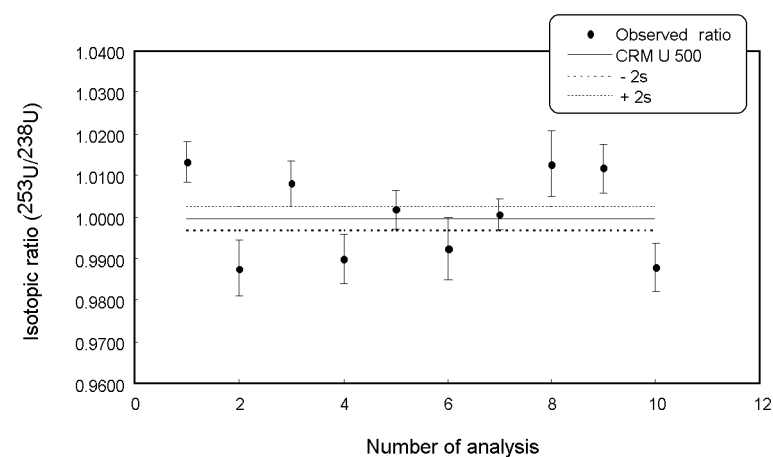


Fig. 2. Observed isotopic ratios for CRM U 500

Table 6. Certified, observed and K factor values

CRM	Certified	Uncertainty	Corrected	Uncertainty	K	Uncertainty
U 005A	0.005090	0.000003	0.00510	0.00002	0.9989	0.0040
U 015	0.015565	0.000015	0.01572	0.00015	0.9903	0.0075
U 030A	0.031366	0.000016	0.03106	0.00015	1.0098	0.0050
U 200	0.25126	0.000260	0.25264	0.00122	0.9945	0.0049
U 500	0.99970	0.00142	1.00070	0.00313	0.9990	0.0034
U 970	186.772	0.214	185.16	1.45	1.0087	0.0085

Table 7. Error of measurement for corrected isotopic ratios

CRM	Certified	Uncertainty	Corrected	Uncertainty	Error, %	Uncertainty
U 005A	0.005090	0.000003	0.00510	0.00002	0.11	0.78
U 015	0.015565	0.000015	0.01572	0.00015	0.98	1.06
U 030A	0.031366	0.000016	0.03106	0.00015	-0.97	1.88
U 200	0.25126	0.000260	0.25264	0.00122	0.55	1.50
U 500	0.99970	0.00142	1.00070	0.00313	0.10	1.98
U 970	186.772	0.214	185.16	1.45	-0.86	2.20

Linearity

The verification of the linearity is a very important step because it can demonstrate to which extent the system is able to measure isotopes independently of concentrations.¹⁸

The experiment was carried out by measuring the set of NBL CRM standards presented in Table 6. In these materials, the isotopic compositions varies from $5.1 \cdot 10^{-2}$ to $1.87 \cdot 10^2$.

The observed isotopic ratios were now corrected by the mass discrimination factor. Then the resulting figures were divided by the value of the respective certified isotopic ratio to produce the K values.

The straight line obtained over five orders of isotopic ratios, as shown in Fig. 3, indicates the degree of the system linearity ($K = 1.0008 \pm 0.0082$) proving that isotopic ratios can be measured independently of the isotope concentration ranges.

The error of measurements

The error of the measurements is defined as the percentile difference between the certified and the corrected isotopic ratios. It is a simple figure to assess the ability of a mass spectrometer to produce accurate measurement results:¹⁹

$$E_{\text{Meas}} = (R_{\text{Cert}} - R_{\text{Corr}}) / R_{\text{Cert}} \cdot 100 \quad (3)$$

where E_{Meas} is the error of measurement, R_{Cert} is the certified isotopic ratio, R_{Corr} is the corrected isotopic ratio.

The mean error of measurement comprising all the six reference materials analyzed is given by:¹⁹

$$E_{\text{Mean}} = [\sum E_{\text{Meas}}^2 / (N-1)]^{1/2} \quad (4)$$

where E_{mean} is the mean error of measurement, E_{Meas} is the error of measurement for each certified material, N is the number of certified materials measured.

The errors of measurement can be seen in Table 7 as well as in Fig. 4. The mean error of measurement calculated according to Eq. (4) was 0.77%.

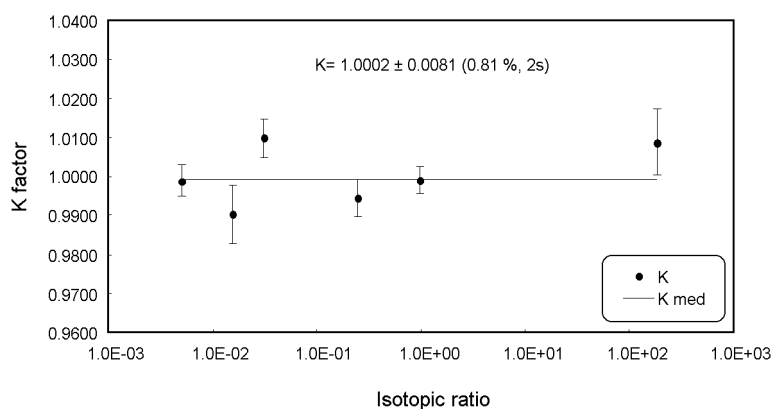


Fig. 3. System linearity

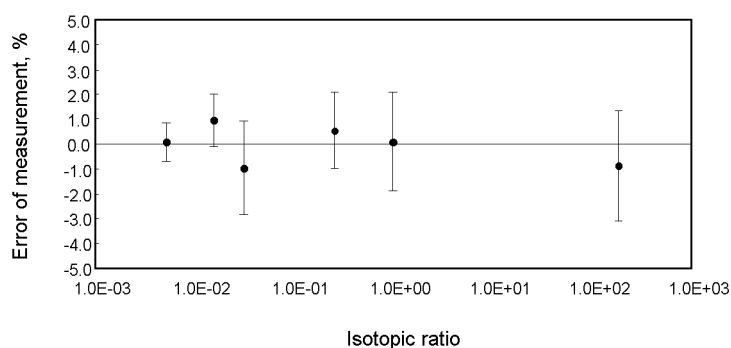


Fig. 4. Error of measurement over 5 isotopic ranges

Conclusions

A quadrupole ICPMS can easily provide (235/238) uranium isotopic ratio measurements with repeatability and reproducibility values of 0.50 and 0.27%, respectively. The system is linear over five orders of magnitude with a K factor of 1.0002 ± 0.0081 (0.81%, 2s) and mean error of measurement of 0.77%.

This study also confirmed that a quadrupole ICPMS does provide fast isotopic ratio measurements with great simplicity, though with just limited levels of precision and error of measurement. Hence the technique is clearly unable to reach the reliability provided by either TIMS or GSMS.

Although usually high precision and low error of measurement are the features of good analytical procedures, it should not be forgotten that a suitable analytical procedure is the one that can meet some requirements. Therefore, in spite of its limited performance, a quadrupole ICPMS can carry out several measurement tasks within the nuclear industry with some good advantages.

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