Uranium isotopic analyses by using a sector field inductively coupled plasma mass spectrometer

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A sector field mass spectrometer using an inductively coupled plasma as an ion source was used in order to determine the uranium isotopic ratios in reference materials supplied by the National Institute of Standards and Technology (NIST) (NBS 950, 010, 030, 200, 500, 750, and 970). The accuracy obtained for the major isotopes was better than 0.2%.

Introduction

The measurement of uranium isotope ratios is of great interest in a wide variety of areas mainly in the nuclear and geological fields.[1-3] In the nuclear fuel cycle, different samples such as ores, concentrates, fuels as well as biological and environmental matrices have to be analyzed routinely. Thermal ionization mass spectrometry (TIMS) plays a key role in the isotopic analysis as it is capable of measuring high accurate and precise isotopic ratios.[2,4] However, this technique is relatively time consuming and requires extensive sample preparation. In the beginning of the eighties, the mass spectrometry based on inductively coupled plasma ions source (ICP-MS) emerged as a new powerful analytical tool for elemental and isotopic analyses.[5,6] It offered some advantages over TIMS, like, for instance, higher sample throughput, measurement of element concentrations simultaneously with it's isotopic ratio, low cost and the possibility of measuring a wide range of element simultaneously. However, the new equipment was somehow limited to the capability to obtain isotopic ratios with high precision. This has been attributed to the coupling of a scanning mass analyzer to a noisy ICP ion source, the sample introduction system and the ion extraction method.

Some years later, 1989, a new generation of ICP mass spectrometers based on a double focusing sector field analyzer and capable to reach spectrum resolution up to 10,000 became available. This new configuration allowed high ion transmission and better precision in isotopic analysis.

Uranium isotopic ratios obtained by ICPMS is still scarce in the literature[1,7,8], if compared to TIMS data. Some of these data[8] were obtained with multi-collector instruments providing more precise and accurate results.

In this work a double focusing sector field mass spectrometer (Finnigan MAT Element, Bremen Germany) was used to measure uranium isotopic ratios ($^{234}U/^{238}U$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$) in several reference materials supplied by NIST. The accuracy, precision and long term stability will be evaluated.

Experimental

Instrumentation

Uranium isotopic ratios were obtained by using a high-resolution inductively coupled plasma mass spectrometer (Finnigan MAT Element, Bremen, Germany). The low resolution mode (nominal $m/\Delta M = 300$) was used as no isobaric interferences is observed in the measured masses. A Meinhard concentric nebulizer (J. E. Meinhard Associates Inc., USA) in free aspiration mode with a Scott-type spray chamber maintained at 4–5 °C using a closed water circuit refrigeration system (Typ 0001, Van der Heijden, Germany) was used. The standard conditions are summarized in Table 1.

Sample, reagents and materials

NBS 950, 010, 030, 200, 500, 750, and 970 Reference Materials from NIST, (former National Bureau of Standards) were used in this work. The solutions were prepared from the powder and solubilized in a PTFE beaker with a nitric acid solution at room temperature during 8–10 hours. All the solutions used were prepared in 2% nitric acid (Merck, SupraPur) solution. Deionized water obtained from Academic Milli-Q system (Millipore Milli-Q) was used throughout.

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Table 1. Standard instrumental conditions and uranium isotopes measurement parameters

Radio frequency (rf power), W	1330
Argon flow rates, l/min*	
Outer	15
Intermediate	1.3
Internal	1.1
Sample uptake, l/min*	0.8
Sample cone and skimmer	Nickel
Mass window,%	5
Number of samples	300
Number of scans (runs x passes)	200 (10×20)
Segment duration, s	0.0100
Total measurement time, min	1
Deadtime, ns	20
Detection mode	Counting
Scan type	Electrostatic scanning

* Gas flow and sample uptake optimized daily.

Results and discussion

Blank and sample concentration

In order to verify the uranium blank intensity, a 2% nitric acid solution was run just before each set of samples as a blank. As the uranium memory effect was low whatever isotope concerned no blank correction was necessary.

The influence of the counting rate in the precision was already discussed by VANHAECKE.[3] Sample concentration was defined to obtain signal intensities between 10^3 to $2 \cdot 10^6$ cps as the isotope abundances are different in these reference materials.

Introduction system

Introduction system is a critical source of signal instability.[12] The peristaltic pumping aided systems were rejected because showed pulsed nebulization although give high counting rates. Meinhard free aspiration introduction system was then chosen as it gives good counting rates and low signal fluctuation at the working conditions.

Instrument optimization

Before starting the data acquisition, the main instrument parameters had to be optimized in order to give the highest counting rate. Mass calibration was checked daily; focus, x- and y-deflection, and shape lenses and sample gas flow rate were optimized. Sample gas flow is a critical parameter[9] as it defines the particle size distribution of the nebulized solution and, this way, the signal intensity and stability.

Dead time and mass discrimination factor

The determination of uranium isotopic ratio has to be done observing some prior care. As the abundances of its isotopes can vary depending on the sample source, the signal of each isotope can also vary from low thousands to over millions of counts. The detector dead time has to be calculated as high counts can produce non-linear responses above a certain value depending on the detector condition. A 20 ns dead time was then obtained (Fig. 1) for the detector using the procedure proposed by RUSS III.[13] This value is in accordance with those found in the literature.[14-16]

Mass discrimination was evaluated in order to know the experimental mass bias for the $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ ratios in the reference materials used in this work. Correction for this bias is necessary as the mass difference between light and heavy isotopes produces different ion transmission. In this way, mass discrimination has to be used to correct (external correction) results from unknown sample.

As the value can vary somewhat from day to day, mass discrimination has to be obtained just before a set of sample analyses.

Mass discrimination (md) was calculated using the following equations

$$f_{md} = R_{certified}/R_{measured} \qquad (1)$$

$$md = (f_{md} - 1)/\Delta m \qquad (2)$$

where f_{md} is the mass discrimination factor, $R_{certified}$ and $R_{measured}$, are certified and measured ratios, respectively, and Δm is the mass difference.

In Table 2 mass discrimination average values obtained for the $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ ratios are showed. Mass discrimination is expected not to vary even when analyzing samples with different isotope ratios ($^{234}U/^{238}U$, $^{235}U/^{238}U$). However, when the abundance of an isotope is very low, as in the NBS 950, 010, and 030, the mass discrimination value can be affected due the low counting statistics of one or both isotopes.

Table 2. Mass discrimination obtained from different uranium isotopic ratio

$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$
−0.0024	−0.0019	−0.0056

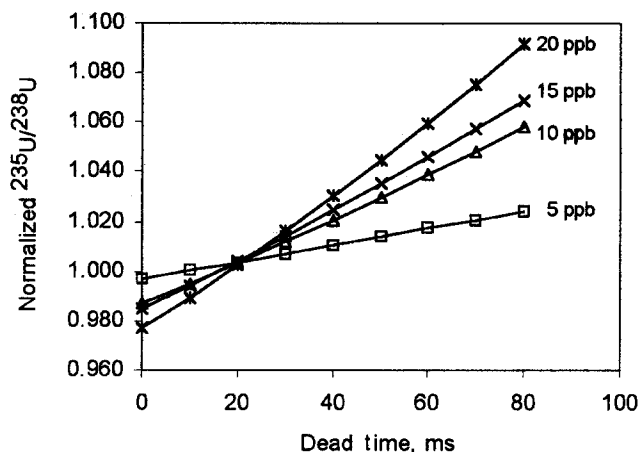*Fig. 1.* Graphical representation of dead time calculation

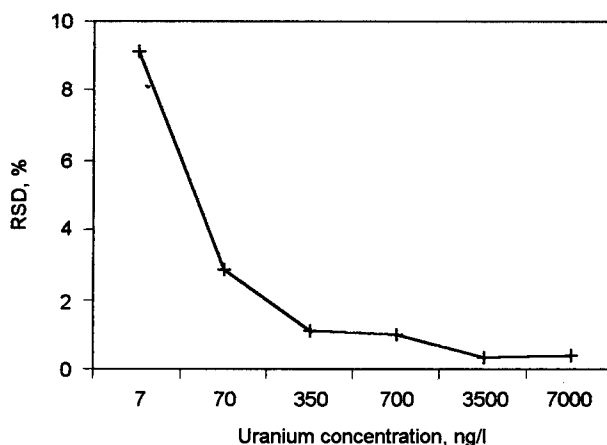*Fig. 2.* Uranium concentration effect on $^{235}U/^{238}U$ ratio precision, RSD

Table 3. Relative standard deviation for $^{235}U/^{238}U$ obtained using different sample time (in ms)

Sample time, ms	RSD, %
1	0.26
2	0.26
3	0.17
5	0.20

Sample time

Low abundance isotopes produce low countings and a poor and, sometimes, deformed peak shape. The ^{234}U and ^{236}U uranium isotopes are usually present at very low abundances so the sample time has to be adjusted in order to obtain high statistical countings. The $^{235}U/^{238}U$ ratio was obtained measuring with 1, 2, 3, and 5 ms (10^{-3} s) and the results are shown in the Table 3. Using 1 and 2 ms, the RSD (0.26%) are higher than when using 3 or 5 ms (RSD = 0.16 and 0.20%, respectively). Using 3 and 5 ms the obtained RSD are 0.17 and 0.20%,

respectively. Although the little difference in the RSD when using 3 and 5 ms, one can save almost 50% in the time consumed when using 3 ms. That makes difference when many samples have to be analyzed.

Uranium concentration

The precision of the isotopic determination is dependent of the counting rate. For very low abundance isotopes in low concentration solutions will be a very challenge in determining their isotopic ratio. The high ion transmission of the Element was tested in different uranium concentration. NBS500 solutions ranging from 7 to 7000 ng/l were prepared and analyzed only the $^{235}U/^{238}U$ ratio. The results are shown in Fig. 2. For very low concentrations, i.e., 7 and 70 ng/l high RSD (~9 and 3% RSD) were obtained. As the concentration increase, the RSD decrease to below 0.5% showing the influence of the isotope concentration.

Table 4. $^{235}U/^{238}U$ ratios (n = 10) obtained for NBS 500 Reference Material using the Finnigan MAT Element HR-ICPMS

Date	$^{235}U/^{238}U$	RSD, %
06/05	0.9964	0.16
07/05	0.9937	0.07
11/05	1.0013	0.13
12/05	0.9965	0.06
13/05	0.9915	0.08
14/05	0.9910	0.04
17/05	0.9907	0.06
19/05	1.0020	0.19
25/05	0.9937	0.09
26/05	1.0013	0.10
Average:	0.9959	
RSD, %:	0.45	
Certified value:	0.9997	

Uranium isotope ratios

The $^{235}U/^{238}U$ ratio in the NBS 500 reference material was obtained along ten days in order to verify the instrumental stability and the results are shown in the Table 3. The average value obtained along these days is 0.9959 with a relative standard deviation, RSD, of 0.45%. This result is highly in agreement with the certified value of 0.9997 obtained by TIMS. The RSD obtained in each day is around 0.1%.

In order to verify the applicability of this procedure in determining other uranium isotopes ratios, solutions of a set of NBS reference materials (NBS 950, 010, 030, 200, 500, 750, and 970) were prepared and analyzed. The $^{234}U/^{238}$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ ratios were measured and the results are presented in Table 4.

The values were obtained from 0.0071 to 187.1 for $^{235}U/^{238}U$ showing good agreement with the certified values. This means that the technique can be used to analyze samples with uranium isotope abundance as different as in the NBS 010 (from ^{234}U, 0.00541 at%, to ^{235}U, 98,984 at%). Although the ^{234}U and ^{236}U isotopes are less abundant than the ^{235}U and ^{238}U, they were measured in all reference materials even when present in low concentration near the detection limit (~1 ng/l).

Conclusions

In the case of nuclear applications, ICPMS results are precise enough to fulfill all the requirements as shown in this work. The results presented in this study show that the determination of the $^{234}U/^{238}$, $^{235}U/^{238}U$, and $^{236}U/^{238}U$ ratios using the HR-ICPMS can be done similarly to those of analyzed materials. Very good precision values were obtained using the standard conditions and short time analysis. As no special chemical treatment is necessary, more samples can be analyzed (high sample throughput) in the same time consumed by TIMS with needed data quality. Instrument optimization, dead time correction and mass discrimination have to be known and well adjusted in order to obtain accurate and precise results.

Table 5. Obtained uranium isotope ratios for NBS 950, 010, 030, 200, 500, 750 and 970 Reference Materials by using the Finnigan MAT Element HR-ICPMS

Material	$^{234}U/^{238}U$	RSD, %	$^{235}U/^{238}U$	RSD, %	$^{236}U/^{238}U$	RSD, %
NBS 950						
Obtained	5.7E-5	1.2	0.0071	1.2	3.7E-6	8.9
Certified	–	–	0.0073*	–	–	–
NBS 010						
Obtained	5.6E-5	1.5	0.0108	0.5	7.8E-5	0.5
Certified	5.5E-5	–	0.010140	–	6.90E-5	–
NBS 030						
Obtained	2.1E-4	1.8	0.0307	0.4	2.2E-4	1.5
Certified	2.0E-4	–	0.03143	–	2.1E-4	–
NBS 200						
Obtained	0.00158	1.6	0.2525	0.1	0.00269	0.8
Certified	0.00156	–	0.25126	–	0.00266	–
NBS 500						
Obtained	0.01037	0.9	0.9965	0.1	0.00155	0.3
Certified	0.01042	–	0.9997	–	0.00152	–
NBS 750						
Obtained	0.0249	0.1	3.127	0.1	0.0106	0.2
Certified	0.0249	–	3.166	–	0.0105	–
NBS 970						
Obtained	3.139	0.2	187.1	0.5	0.2869	0.6
Certified	3.185	–	186.78	–	0.2851	–

* Calculated from the natural isotope abundances.

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