High Accuracy Measurement of Uranium Enrichment $n(^{235}U)/n(^{238}U)$ ratios by Gas Source and Multi-Collector ICP Mass Spectrometry

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Abstract:
The measurement of $n(^{235}U)/n(^{238}U)$ ratios is one of the most critical measurements made in the nuclear cycle as this determines the amount of fissionable ^{235}U in a nuclear material. The classical technique to measure this ratio is the gas source mass spectrometry (GSMS) on UF_6, using a multi-inlet system, and comparing ratios measured on the sample with ratios measured on certified isotope reference materials, preferably with enrichments bracketing that of the sample.
This method can reach relative combined uncertainties lower than 0.05% (k=2) and is also convenient because it allows the UF_6 product from enrichment plants to be measured directly.
The disadvantages of the method lie in the time taken for a measurement, the fact that the mass spectrometer can only be used for measuring UF_6 and the cost of such instruments.
Modern multi collector inductively coupled mass spectrometers (MC-ICPMS) have several characteristics similar to the UF_6 gas mass spectrometers. In particular, a high reproducibility can be achieved. They have the considerable advantage of being multi purpose and therefore more cost effective but the absolute response, as measured by the mass discrimination is not always straightforward to control.
An experimental programme was devised to compare the data provided by both techniques on a set of real uranium samples. In this work, just the measurement results of three samples are presented.
The purpose of the programme is to assess to what extent the MC-ICPMS can be used for the highest quality (i.e. smallest combined uncertainty) measurements of the $n(^{235}U)/n(^{238}U)$ ratio in uranium materials.

Keywords: uranium enrichment measurement, metrology, gas source mass spectrometry, multiple collector inductively coupled plasma mass spectrometry.

1. Introduction

The measurement of uranium isotope ratios is required to characterise uranium materials at all stages of the nuclear fuel cycle. The enrichment, as defined by the ^{235}U abundance, is one of the most important characteristics. Accurate measurements of the $n(^{235}U)/n(^{238}U)$ ratio are needed in practice [1].

The most established techniques used in this field are gas source mass spectrometry (GSMS) and thermal ionisation mass-spectrometry (TIMS). Both provide precise measurement results but require expensive instrumentation and skilled operation.

The former is the technique of choice when the sample is in the form of uranium hexafluoride (UF_6), as in the uranium enrichment facilities. Considerable amount of sample is needed and therefore the method is applied where the sample size is adequate and where the highest quality $n(^{235}U)/n(^{238}U)$ isotope ratios are required.

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The latter technique is preferred when the sample size is smaller and particularly when the minor isotope ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ are needed. An optimised approach employed at IRMM is to measure the $n(^{235}U)/n(^{238}U)$ ratio by GSMS and the minor isotope ratios $n(^{234}U)/n(^{238}U)$, $n(^{236}U)/n(^{238}U)$ by TIMS [2].

Inductively coupled plasma mass spectrometry equipped with multiple Faraday collectors (MC-ICPMS) is a measurement technique that can compete with the traditional ones. Its high quality measurement capability, high sample throughput, simpler sample preparation requirements and the feasibility of analysing a range of chemical elements besides uranium makes it an attractive alternative in the field of uranium isotope measurements [3,4].

This paper presents the initial results of a programme devised to assess to what extent the MC-ICPMS could provide the high accuracy measurement results of ^{235}U enrichment provided by GSMS technique. Of particular interest is the question of how far the technique of bracketing the sample with isotope reference materials, as used in the GSMS, can be effectively applied to measurements in MC IC-PMS.

2. Experimental

2.1. Instrumentation

An electron impact, magnetic sector mass spectrometer manufactured by Finnigan MAT (Bremen, Germany), equipped with two Faraday collectors to determine the ratios of uranium isotopes $n(^{235}U)/n(^{238}U)$ directly in UF_6 samples was used in this work. The sub-systems of this instrument are presented in Table 1 and its most important features are described in Table 2.

Sample introduction	UF_6 into two gas inlet tanks
Ion source	Electron impact
Analyser	Permanent magnet of 6.350G, 90° curvature and 22,5 cm of radius
Detector	Double fixed Faraday cups
Vacuum system	Mechanical, diffusion and cryopumps pumps

Table 1 Sub-systems of the gas source mass spectrometer Finnigan MAT model 511

Mass range	2 to 511 a.m.u.
Resolving power ($\Delta m/m$)	358
Sample pump down time	68 s
Sensitivity	$9.6\ 10^{-10}$ A
Sample consumption	2.84 mg $UF_6\ h^{-1}$

Table 2 Features of the gas-source mass spectrometer Finnigan MAT model 511

A magnetic sector, multi-collector inductively coupled plasma mass spectrometer manufactured by NU Plasma (Nu Instruments, Wrexham, Wales) was used in this work. The sub-systems are presented in table 3 and its most important features are described in table 4.

Sample introduction	Liquid sample in the form of $UO_2(NO_3)_2$
Ion source	Inductively coupled plasma, 27 Mhz, 2 KW generator
Analyser	ESA 300mm radius, magnet with 250 mm radius
Detector	12 Faradays cups, 3 ion counters
Vacuum system	Mechanical, turbo-molecular and ion pumps

Table 3 Sub-systems of the inductively coupled plasma mass spectrometer Nu Plasma

4. Results and discussion

The experimental results for the three samples are presented in table 7. They results were normalised to the values provided by GSMS instrument. The uncertainties were estimated according to the ISO-BIPM Guide [7].

Sample	Isotope amount ratio (mol/mol)
2078	1.00018 (50)
2079	1.00025 (50)
2082	1.00006 (50)

Table 7 Normalised measurement results provided by MC-ICPMS. Uncertainties in brackets apply to the last 2 digits and are expanded uncertainties, k=2.

Measurements made on ratios of $n(^{235}U)/n(^{238}U)$ around 1:50 on the MC-ICPMS instrument show similar relative reproducibilities to those achieved on the gas source mass spectrometer (<0.03%, k=2). Use of a single certified isotope reference material also allowed the $n(^{235}U)/n(^{238}U)$ ratio to be measured on the MC-ICPMS to total relative uncertainties (k=2) of < 0.1%. Use of two IRMs bracketing the isotope ratio value as applied in the gas source mass spectrometer has the potential of lowering the measured uncertainty using MC-ICPMS. In order for this method to be successful, the reproducibilities of the ratio measurements must be as low as possible. This condition appears to be fulfilled by the MC-ICPMS.

A full measurement programme as routinely done on the gas source mass spectrometer is difficult to translate onto the MC-ICPMS because of the long rinsing steps required when changing between samples. However, we see a number of possibilities to reduce the rinse times, for instance by lowering sample concentrations and by rationalising of the measurement programme to reduce the number of repeat measurements without significantly increasing the combined standard uncertainty of the measured values.

Results are often quoted for techniques such as MC-ICPMS with uncertainties based solely on reproducibilities. However this is only one source of uncertainties involved in the final result. In particular small biases, difficult to observe when the reproducibility of measurement is poor, can easily be the major contributors to the final uncertainty. Use of bracketed, well-defined IRMs is a design that in principle should avoid most of the systematic effects conceivable. To introduce this technique into measurements using a MC-ICPMS will, however, need compromises in setting up the measurement procedures.

The work being carried out here will use exactly the same IRMs and samples already measured by gas source mass spectrometry. This gives us then a unique chance to compare the two methods and allow us to make conclusions as to how far the MC-ICPMS technique can be expected to substitute for the much more limited gas source mass spectrometry.

References/bibliographies

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Mass range	6 to 260 a.m.u.
Resolving power ($\Delta m/m$)	350
Sensitivity	$1.6\ 10^{-10}$ A for 1 µgU/g
Abundance sensitivity	3 p.p.m.

Table 4 Features of the inductively coupled plasma mass spectrometer Nu Plasma

2.1.1. Materials and solutions

Three uranium samples (depleted, natural and enriched relative to ^{235}U) were selected to provide the initial comparison data. They were in the form of UF_6 and could be directly measured by the Finnigan MAT 511 spectrometer.

To prepare the samples for the MC-ICPMS instrument, UF_6 aliquots were collected from metal ampoules, transferred to Teflon ampoules, hydrolysed by the addition of deionised water and dried overnight over a hot plate. Then nitric acid was added to convert the sample to uranyl nitrate. Finally the concentration was adjusted to the value of 1.0 µgU/g in 2% HNO_3. The nitric acid employed was Suprapur 65% (Merck, Darmstad, Germany) diluted with 18 MΩ deionised water.

The Isotope Reference Materials used to correct the mass discrimination effect are described in table 5 for the GSMS instrument and table 6 for MC-ICPMS. They are provided by the Institute for Reference Materials and Measurement (Geel, Belgium).

Isotope Reference Material	Certified Isotope Amount Ratio ($n^{235}U/n^{238}U$)
IRMM 021	0.0044036 (21)
IRMM 2079	0.0071505 (24)
IRMM 071	0.0072623 (17)
IRMM 185	0.0200552 (60)
IRMM 295	0.0307712 (51)
IRMM 2411	0.0406210 (83)

Table 5 Isotope reference material used the GSMS instrument.

Isotope Reference Material	Certified Isotope Amount Ratio ($n^{235}U/n^{238}U$)
IRMM 184	0.0200552 (60)

Table 6 Isotope reference material used to calibrate the MC-ICPMS instrument

3. Measurement procedures

3.1. GSMS procedure

The isotope amount ratios, $n(^{235}U)/n(^{238}U)$, of the samples were calculated using the double standard method [5].

The principle of this method lies on the bracketing of the sample, making use of two isotope reference materials (IRM), one having a certified value slightly lower (IRM 1) and the other slightly higher (IRM 2) than the value of the sample.

Currents at masses 330 and 333 from the $^{330}UF_5^+$ and $^{333}UF_5^+$ ions are measured on fixed Faraday cups. Usually ten internal ratios are taken to provide the first measurement value for the sample.

After the sample is pumped off, the IRM 1 is admitted into the ion source and the isotope ratio is measured using the same procedure. A series of alternating measurements between sample and IRM 1 constitutes the first measurement block. This block provides a correcting factor, an average ratio between the measured isotope ratio of the sample and the certified isotope ratio of IRM 1. The same measurement block is repeated twice.

An identical procedure is applied to IRM 2 generating a second correcting factor.

The corrected value for the sample takes in consideration the certified isotope ratios of IRM 1 and 2, the measured isotope ratio of the sample and both correcting factors. The relation between them is described by equation 1.

$$R_c = (\alpha_b - \alpha_a) / ((1 / R_1) * (1 - \alpha_a) + (1/ R_2) * (\alpha_b - 1)) \qquad (1)$$

Where.

R_c = Corrected isotope amount ratio for the sample
R_1 = Certified isotope amount ratio for IRM 1
R_2 = Certified isotope amount ratio for IRM 2
α_a = Correction factor relative to IRM 1
α_b = Correction factor relative to IRM 2

3.2. MC- ICPMS procedure

A different measurement procedure was applied for the initial set of measurements on the MC-ICPMS. After the instrument's basic calibration routine, the following sequences of solutions were introduced into the spectrometer: blank, IRMM-184, blank, sample, blank and IRMM-184.

The blank values were subtracted from the sample and IRMM-184 measurements and were also used to monitor the rinsing procedure between samples. The measurements are described in detail elsewhere [6].

At this early stage of the programme, just the conventional procedure of correcting the mass discrimination in MC-ICPMS instruments was applied. Later, the double standard method, as described in item 3.1, will be adapted to this technique.

The mass discrimination factor (K) was measured on IRMM-184 as below:

$$K = R_{irm} / R_{obs} \qquad (2)$$

Where,

R_{irm} = Certified isotope amount ratio of IRMM 184
R_{obs} = Observed isotope amount ratio for IRMM 184
K = Correcting factor

Then this factor was used to correct the isotope amount ratio of the sample, as described in equation 3.

$$R_c = K \,.\, R_{obs} \qquad (3)$$

Where,

R_c = Corrected isotope amount ratio for the sample
K = Correcting factor
R_{obs} = Observed isotope amount ratio for the sample

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