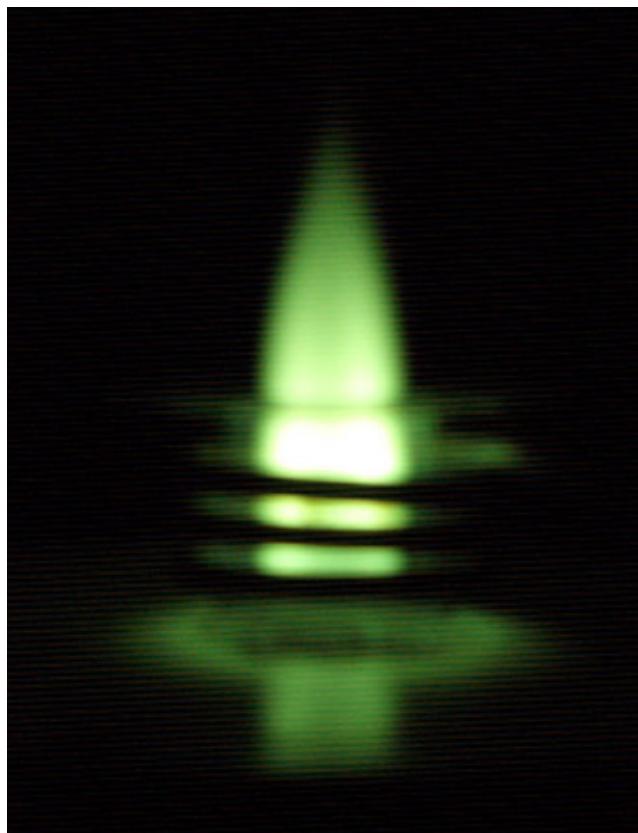


# A Feasibility Study on the Use of Isotope Dilution as a Tool for Quantifying Uranium Isotopic Concentrations by Quadrupole ICP-MS

Geoscience Skills and Facilities Directorate  
Internal Report IR/05/102





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Picture of an analytical ICP viewed through green welder's glass. *Courtesy of wikipedia.org*

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# A Feasibility Study on the Use of Isotope Dilution as a Tool for Quantifying Uranium Isotopic Concentrations by Quadrupole ICP-MS

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## Foreword

This report is the published product of a study by the British Geological Survey (BGS) under the Analytical Geochemistry Laboratories' continuing programme of development of capability but also forms part of one of the author's (KB) research study programme within the Department of Chemistry, Loughborough University.

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# Contents

<b>Foreword.....</b>	<b>i</b>
<b>Acknowledgements.....</b>	<b>i</b>
<b>Contents.....</b>	<b>ii</b>
<b>Summary.....</b>	<b>iv</b>
<b>1 Introduction.....</b>	<b>1</b>
1.1 Background .....	1
1.2 Internal standardisation techniques.....	3
<b>2 Experimental.....</b>	<b>5</b>
2.1 Optimisation of the ICP-QMS instrument for the determination of uranium isotopes $^{238}\text{U}$ , $^{235}\text{U}$ and $^{233}\text{U}$ .....	5
2.1.1 ICP source and ion lens tuning parameters .....	5
2.1.2 ICP quadrupole dwell time.....	5
2.1.3 ICP detector including dead-time correction .....	6
2.2 TEST SAMPLES.....	7
2.3 Chemical sample preparation .....	7
2.3.1 Reagents .....	7
2.3.2 Solid sample digestion .....	7
2.3.3 Sample uranium pre-concentration and separation.....	8
2.3.4 Analysis.....	8
2.3.5 Data processing .....	8
2.4 Determination of the $^{233}\text{U}$ spike concentration and $^{238}\text{U}/^{235}\text{U}$ isotopic ratio .....	9
2.4.1 Reverse isotope dilution.....	9
2.4.2 Optimum spiking concentration for samples .....	9
2.4.3 Precision of routine analysis compared to theoretical calculations.....	11
2.5 Determination of uranium isotopes $^{238}\text{U}$ , $^{235}\text{U}$ and $^{233}\text{U}$ in Certified Reference materials USING FULL IDMS quantification .....	11
<b>3 Results/Discussion .....</b>	<b>12</b>
3.1 Enhancement/suppression of $10 \mu\text{g l}^{-1}$ U signal due to major element matrix effects .	12
3.2 Comparison of $^{233}\text{U}$ with In, Bi or Re as traditional internal element standards .....	14
3.3 Determination of uranium isotopes $^{238}\text{U}$ , $^{235}\text{U}$ and $^{233}\text{U}$ in certified reference materials using full IDMS quantification .....	16
3.4 Practical and health & safety considerations .....	17
<b>4 Conclusions .....</b>	<b>18</b>
<b>References .....</b>	<b>20</b>

## Figures

Figure 1 Theoretical concentration of $^{233}\text{U}$ required to achieve % RSD <1, based on the routine sensitivity of instrument .....	10
Figure 2 Enhancement/suppression effects of major elements on a $10 \mu\text{g l}^{-1}$ $^{238}\text{U}$ signal .....	12
Figure 3 Variation of $10 \mu\text{g l}^{-1}$ internal standard signal with Mg concentration.....	13
Figure 4 Precision and accuracy using $10 \mu\text{g l}^{-1}$ internal standards and $^{233}\text{U}$ spike to correct uranium, based on routine instrument sensitivity.....	15

## Tables

Table 1 ICP-QMS conditions optimised for $^{238}\text{U}^+$ sensitivity.....	5
Table 2 Changes in $^{238}\text{U}/^{235}\text{U}$ isotope ratio with concentration and dead time .....	6
Table 3 Reference materials chosen for testing .....	7
Table 4 Theoretical RSD assuming a count rate of 50 Mcps/ppm.....	10
Table 5 Experimental protocol .....	11
Table 6 RSD achieved experimentally using various internal standards and the $^{233}\text{U}$ spike to correct $^{234}\text{U}$ , $^{235}\text{U}$ and $^{238}\text{U}$ .....	14
Table 7 Results and associated recoveries in % for CRMs using $^{233}\text{U}$ as an internal standard ....	16
Table 8 Results and associated recoveries in % for CRMs using full IDMS.....	16
Table 9 Long term results for uranium determination for SDO-1 (n=65) and JR-2 (n= 87) .....	17

## Summary

The determination of uranium elemental concentrations and isotope ratios has been a major task for the BGS inductively coupled plasma mass spectrometry (ICP-MS) laboratory over the last five years. UK government departments and the nuclear industry have ongoing environmental monitoring programmes which require high quality data. The need for a greater understanding of chemical pathways, sinks and sources has been a driver for BGS to continue to improve analytical performance but with a minimal increase in costs. This study seeks to identify whether isotope dilution could provide a significant increase in analytical performance with minimal cost implications.

This report reviews the fundamental concepts of isotope dilution and its advantages over related techniques such as internal standardisation. It considers the potential benefits of quadrupole ICP-MS (ICP-QMS) over other techniques where high productivity is an issue, such as for environmental monitoring. The optimisation of the ICP-MS acquisition parameters including peak dwell times, detector dead-times, spike concentrations and operating conditions are examined.

Isotope dilution (ID) relies heavily on the accurate calibration of the  $^{233}\text{U}$  spike and the process of reverse isotope dilution is used and discussed as part of this study. A series of experiments was conducted to ascertain the degree of chemical preparation required for accurate isotope dilution determination. These included comparing the effectiveness of using the  $^{233}\text{U}$  spike with internal standardisation by a proxy element, to overcome ICP-MS matrix effects and changes in sensitivity. Finally, the proposed methodology was tested using a range of natural rock reference materials with known uranium concentrations covering various common igneous and meta-sedimentary types.

This project established that the use of  $^{233}\text{U}$ , a by-product of nuclear fuel processing, provided superior precision when used as an internal standard for measurements of other uranium isotope concentrations, compared to indium, rhenium or bismuth.

The data suggest that the within sample precision is better when full ID quantification is performed, regardless of the matrix, than when using the spike as an internal standard. The IDMS technique could potentially eliminate the current column separation procedure, which would achieve significant savings in staff time and consumables. A small systematic bias has been observed in the data. It is thought that one of the most likely factors is the assumption made about the density of the  $^{233}\text{U}$  spike solution, which would affect the IDMS calculations but have no influence when  $^{233}\text{U}$  is used as an internal standard.

It will not always be appropriate to use this method for the determination of uranium isotope concentrations and a decision tree needs to be devised to determine the appropriate method to be used for each potential application.

The investigation has proved the value and potential of this methodology for isotope concentration analysis by quadrupole ICP-MS. Once a robust, fit for purpose methodology can be applied routinely, the possibility of the use of IDMS for other stable isotopes should be considered.

# 1 Introduction

## 1.1 BACKGROUND

In recent years BGS has recognised the need to move into new areas of research and geoscience applications away from the traditional areas of geology. These new areas frequently require a sophisticated understanding of geochemistry and therefore an improved analytical geochemical capability. A rapidly growing area of research is the study of sources, pathways and sinks of contaminants, which is providing an improved understanding of the mobility, toxicity and bioavailability of trace elements. Forensic geology and cryptogeology (i.e. using geochemistry as an aid to geological mapping and interpretation) are also becoming more commonplace. Such projects are heavily reliant on a high degree of resolution between chemical data; therefore, the quality of analytical measurements in terms of accuracy and precision are vital for the correct interpretation of data.

Although, nuclear power generation has been in decline worldwide, this may well reverse as climate change becomes a more pressing issue and the option of a new phase of nuclear power generation is being discussed at the highest political and scientific levels. The downside to this is the need for ensuring safe disposal of long-lived radioactive wastes from both civil and military sources. This would suggest that the development of improved and cost effective analytical techniques for uranium and other radio-nuclides or their stable analogues is a priority if BGS wishes to maintain its expertise and remain a leader in this field.

BGS has been studying low-level radioactivity in the environment for many years. In the early 1980s joint development of the ICP-MS technique by BGS and the University of Surrey was funded by the EU Uranium Exploration programme. Major research into the disposal options for nuclear waste for NIREX involved a large number of BGS staff during the late 1980s. More recently, projects as diverse as DFID funded work in Jordan, activity dispersion in marine sediments off the NW English and SW Scottish coasts for MAFF/DEFRA and dispersion of depleted uranium derived from munitions in the former Yugoslavia and Iraq for the MoD have been undertaken.

Research is required to develop a better understanding of the chemical interactions of contaminants between the environment and humans. To aid this process, an improvement in the quality of analytical measurements that underpin this research is required, i.e. better accuracy, precision and detection limits, especially as chronic exposure to extremely low concentrations of some contaminants can be potentially hazardous to human health. Mass spectrometry generically, has been one of the analytical techniques at the forefront of measurements of radio-nuclides and their analogues.

In recent years, ICP-QMS instrumentation has improved significantly in both sensitivity and precision, and a greater understanding of the processes influencing analytical measurements has improved accuracy. Instruments are now available that are capable of sensitivities several orders of magnitude greater than those available 20 years ago, thus reducing detection limits. With such improvements, ICP-QMS is now capable of analysing samples that were previously only analysed by thermal ionisation mass spectrometry (TIMS). These improvements in ICP-QMS also mean that there is now scope for the development of cost effective ID techniques and methodologies for specific applications.

The principles of the ID technique and associated methodologies have been well documented for more than 30 years. Isotope dilution has proved to be useful in many areas of research, notably geological, environmental and health sciences as well as the nuclear industry. However, it has been used infrequently because of the labour involved in the spiking process and the complex chemical separations required for mass spectrometry techniques. There were also relatively few

elements that could be efficiently ionised by the early techniques and sample throughput was slow. ICP-MS alleviated the need for such complex chemistry, but early quadrupole instruments did not have the sensitivity needed to measure the less abundant isotopes with the required precision.

Initially, ID methods were developed for TIMS and more recently magnetic sector/multicollector inductively coupled mass spectrometry (MS/MC-ICP-MS). These instruments produce high precision isotope ratio measurements coupled with high sensitivity allowing spiking with small masses of rare enriched isotopes. Isotope dilution requires more labour and expense than externally calibrated analysis, but it gives more precise and accurate data and is used where the ultimate precision and accuracy is required. The primary application of such extremely accurate and precise determinations has been the characterisation of Certified Reference Materials (CRMs). This is because ID is a technique based on the mass/number of atoms and is directly traceable back to the fundamental SI quantity, the mole.

Isotope dilution measurements by MS/MC ICP-MS and TIMS are time consuming and expensive. Sample throughput in terms of sample preparation and analyte measurement are usually low, sometimes fewer than 10 samples a day. Analysis of the highest accuracy and precision is also an iterative process and can take several weeks (Sargent *et al*, 2002). The improvements made to ICP-QMS instrumentation in recent years means that, although it is still less accurate and precise compared to MS/MC ICP-MS and TIMS, the technique is capable of producing good quality ID analysis with the advantage of significantly higher sample throughput (up to 100 samples per day). Therefore, it is more cost effective and ideally suited to environmental monitoring and mapping projects where the best precision and accuracy is not required.

Isotope dilution by ICP-QMS can be applied to a number of elements, including uranium and thorium; a full list can be found in Date and Jarvis (1989). As early as 1982, ID was being used to evaluate the proportion of lead derived from anti-knock agents in petrol in the blood of residents exposed to petrol fumes. This was achieved by measuring the  $^{206}\text{Pb} : ^{207}\text{Pb}$  ratio (Facchetti *et al*, 1982). By 1985 multielement analysis of saline and non-saline natural waters was being determined by ID (McLaren *et al*, 1985), but before the 1990s most ID analysis was traditionally carried out using TIMS. During the 1990s MS/MC ICP-MS challenged this technique and isotope ratio measurements by ICP-MS during this period were mainly carried out using magnetic sector ICP-MS, as the precision and accuracy of quadrupole instruments was not good enough.

By the beginning of this decade, ICP-QMS was becoming a more viable technique for ID as the improvement in sensitivity was now at least a magnitude better than for the first instruments developed in the 1980s. A paper published in 2002 compared different ICP-MS instruments for the analysis of uranium in environmental samples (Boulga *et al*, 2002) and there have been evaluations of internal standard calibration techniques including ID by Salin *et al* (2004). A more recent paper on the progress in precise and accurate isotope ratio measurements by various spectrometric techniques, including ICP-QMS and MC ICP-MS, has been published by Becker (2005). With the evolution of even more sensitive quadrupole instruments there have been an ever increasing number of publications on the evaluation and applications of ID by ICP-QMS.

The BGS ICP-QMS laboratory carries out several thousand uranium elemental determinations and several hundred uranium isotope analyses per year. The uranium isotope determinations require matrix separation and pre-concentration procedures to provide optimum results.

The primary aim of the current study was to use a  $^{233}\text{U}$  isotope spike for improved determination of uranium elemental and isotopic concentrations in environmental test materials.

The specific objectives of the current study were to:

- Assess the current internal standards used for the determination of uranium concentrations
- Assess the behaviour of these internal standards compared to a  $^{233}\text{U}$  spike in different matrices
- Improve internal elemental standardisation for the determination of uranium concentrations
- Explore the use of full isotope dilution quantification when measuring uranium concentrations
- Use ID to correct for any loss of uranium during the dissolution or separation phases of sample preparation
- Use ID to improve the accuracy and precision of concentration measurements
- Assess the need for matrix separation if IDMS can produce the required accuracy and precision

## 1.2 INTERNAL STANDARDISATION TECHNIQUES

An internal standard is any element(s) added at a known concentration to a sample. Internal elemental standardisation has several analytical purposes in mass spectrometry:

1. To monitor and correct for short and long term variations in instrumental response, colloquially known as 'drift'.
2. To calibrate the instrumental response for a second analyte (element, isotope or compound).
3. To correct changes in instrumental response with respect to mass/concentration due to unspecified sample matrix effects.

The effectiveness of an internal element standard relies on its behaviour being similar to that of the analyte it is used to correct (IUPAC, 1997). The relative change in signal and sensitivity between an internal standard and unknown analyte should, ideally, be constant. In practice this is rarely the case in ICP-QMS, as there may be significant differences in relative elemental or isotope response throughout an analytical run and a single element used as an internal standard cannot truly reflect the behaviour of all the other elements. This difference in relative response is systematically related to mass, ionisation energy, matrix and plasma effects (Date and Jarvis, 1989). Quantitative ICP-MS multi-element analysis is therefore a compromise, as there are a limited number of suitable internal standards available.

The use of an isotopic spike of the element of interest as an internal standard can have several advantages over any other element:

1. Physical and chemical interferences would have an identical effect on all isotopes of the same element
2. Adding the spike at the earliest possible stage of sample preparation will compensate for any partial loss during the procedure.

Isotope dilution is a special case of internal standardisation. The isotopic spike concentration is first accurately determined and is then added gravimetrically, rather than volumetrically. Isotope dilution uses the known mass/absolute number of atoms in the isotopic spike to calculate the mass/absolute number of atoms in the unknown sample.

The method of isotope dilution measures the change in the ratio of signal intensities for two isotopes of the element of interest after the addition of a known quantity of a spike of one of

these isotopes. From the measurement of this ratio the concentration of the element in the sample can be calculated. This method can be applied to any element where there are at least two stable isotopes. It is advantageous for the spike to be added at the earliest possible stage of preparation; for solids this would be at dissolution. After equilibrium of the spike and sample any partial losses during preparation will not affect the accuracy of the results. Theoretical modelling of the addition of spikes to a sample show that the spike should be added in approximately equal or greater than the expected concentrations to achieve optimum precision and this should be considered when preparing the spike (McLaren *et al*, 1985).

## 2 Experimental.

### 2.1 OPTIMISATION OF THE ICP-QMS INSTRUMENT FOR THE DETERMINATION OF URANIUM ISOTOPES $^{238}\text{U}$ , $^{235}\text{U}$ AND $^{233}\text{U}$

The isotope ratio measurements were made on a VG PQ ExCell ICP-QMS instrument (THERMO ELECTRON Corp, Hemel Hempstead, Herts. HP2 7GE.)

#### 2.1.1 ICP source and ion lens tuning parameters

The precision of uranium isotope ratios as determined by ICP-QMS is primarily limited by the counting statistics for the minor isotopes and instrument stability. For optimal precision, the  $^{238}\text{U}^+$  response was tuned to a maximum sensitivity of approximately 100M counts per second (cps) for a 1mg l<sup>-1</sup> uranium standard. This ensured the signal stayed within the linear limitations of the detector system. The typical instrument gas flows and ion lenses settings are given in Table 1.

**Table 1** ICP-QMS conditions optimised for  $^{238}\text{U}^+$  sensitivity

(a) Lens settings

Extraction	LI	L2	L3	D1	Focus	Pole bias
-717	2.7	-72.7	-115	-24.1	24.1	-4.7

(b) Torch settings

Forward power (W)	Reflected power (W)	Horizontal	Vertical	Depth
1350	2	-90	41	386

(c) Vacuum and nebuliser pressures

Analyser (mBar)	Expansion (mBar)	Nebuliser (Bar)
5.1	1.7	2.5

#### 2.1.2 ICP quadrupole dwell time

The mass spectrometer sits at a particular mass for a period of time acquiring data before passing on to the next isotope – this is known as the dwell time. There are a number of competing factors limiting the choice of dwell time for each isotope: (i) relative abundance of the isotope, i.e. it is better to dwell for longer on a minor isotope than a major one to acquire a larger number of counts thus improving the counting statistics; (ii) time for the quadrupole to jump to a new mass position and settle; and (iii) noise sources in the plasma. The choice of conditions has been reviewed in detail by Begley and Sharp (1997). They concluded that to minimise factor (iii) the settle time should be as short as possible until data were limited by factors (i) and (ii). Experimentation proved this to be the case and a dwell time of 2.5 ms was chosen for all isotopes.

### 2.1.3 ICP detector including dead-time correction

The PQ ExCell instrument is fitted with a dual mode detector allowing simultaneous collection of analogue (AN) and pulse counting (PC) signals. For the isotope ratio measurements, only the pulse counting mode was used to avoid problems of cross-calibration. The pulse counting mode is linear to 2 M cps providing the accelerating voltages on the detector are set correctly to avoid problems such a ‘fatigue’ at high count rates and the dead-time correction of the detector is accurately applied.

To establish the correct dead-time for uranium (Moser *et al*, 2003), a series of uranium solutions with concentrations close to the linear limit of the detector were analysed using different dead-time correction values. The measured  $^{238}\text{U}/^{235}\text{U}$  ratios were compared, and the optimal dead-time value derived using the assumption that at the correct value the isotope ratio will be constant, despite changes in concentration (Begley and Sharp, 1997). These results are given in Table 2 and a dead-time of 38 ns was chosen. It is known that dead-time for a detector will change over its lifetime (Held and Taylor, 1999) and the dead-time was checked prior to isotope ratio measurements.

**Table 2** Changes in  $^{238}\text{U}/^{235}\text{U}$  isotope ratio with concentration and dead time

Dead time (ns)	2 ppb U	10 ppb U	20 ppb U	40 ppb U
0	294	288	285	276
35	296	293	294	291
50	301	295	299	299
70	297	303	301	309

Note: This uranium solution does not have a natural isotopic composition.

## 2.2 TEST SAMPLES

Eight geological reference materials were chosen to cover a sufficiently wide range of geological matrices and uranium concentrations. These are detailed in Table 3 below.

**Table 3** Reference materials chosen for testing

Reference Material	Material Type	Expected Uranium Concentration (mg kg <sup>-1</sup> )
BGS450	Phonolite	5.63
SDO-1	Devonian Ohio Shale	48.8
JR-2	Rhyolite	10.5
SCo-1	Cody Shale	3.0
BCR-1	Basalt	1.75
WS-E	Dolerite	0.65
AGV-1	Andesite	1.92

## 2.3 CHEMICAL SAMPLE PREPARATION

### 2.3.1 Reagents

All reagents used were of at least ARISTAR® grade purity. Doubly de-ionised water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ ) obtained from a Milli-Q (MQ) water system was used throughout.

Calibration solution  $10 \text{ }\mu\text{g ml}^{-1}$  diluted by volume, with 1% nitric acid, from “Multi-Element Solution 2”, Claritas PPT™, Spex CertiPrep Inc., Metuchen, N.J., USA.

For the matrix effect experiments,  $10,000 \text{ mg l}^{-1}$  Single Element Major Standards (Aldrich Chemical Company Inc. Milwaukee WI53233 USA.) were diluted with 1% nitric acid for the required concentration and mixed as appropriate.

For all procedures,  $10 \text{ mg l}^{-1}$  In, Re and Bi internal Standards Claritas PPT™ (Spex CertiPrep Inc., Metuchen, N.J., USA) and the  $^{233}\text{U}$  spike of unknown origin (originally obtained more than 10 years ago by BGS radiochemical staff for alpha spectrometric analysis) were also diluted with 1% nitric acid.

### 2.3.2 Solid sample digestion

For the digestion, 0.2 g of sample was weighed into a PTFE tube and 2 ml concentrated HF added to tubes. The samples were left at room temperature at least overnight. Then 1.6 ml concentrated  $\text{HNO}_3$  and 0.8 ml concentrated  $\text{HClO}_4$  acid were added and the contents of the PTFE tube taken to dryness in a programmable hot block over 12 hours (BPL Status Model Step 1, serial number 492/048). This consists of a 180-place aluminium block connected to a WEST 2050 programmer-controller designed to control the rate of heating and the temperature attained and held in pre-defined steps. The residual digested sample was re-dissolved in 10 ml of 10% v/v  $\text{HNO}_3$  and stored in high density polyethylene (HDPE) bottles prior to use.

Quality control samples were added throughout the dissolution run, including blanks and samples prepared in duplicate. All relative samples were spiked, gravimetrically, immediately after weighing, before any reagent was added.

Before analysis dissolved samples were treated variously depending on experimental requirements; these treatments included pre-concentration and separation of the uranium from the dissolution matrix and/or dilution (see Table 5, Section 2.5).

### 2.3.3 Sample uranium pre-concentration and separation

#### 2.3.3.1 REAGENTS AND EQUIPMENT

10% v/v nitric acid ( $\text{HNO}_3$ ) in 18 MΩ quality water – Aristar® grade

0.025 M ammonium oxalate – AnalaR® grade in 0.1% v/v  $\text{HNO}_3$

0.1% v/v nitric acid ( $\text{HNO}_3$ ) in 18 MΩ quality water – Aristar® grade

Pre-packed Tru-Spec Ion Exchange Columns containing 2 ml of resin, Eichrom Europe, Paris, France.

#### 2.3.3.2 METHOD

- 1) Drain storage acid to waste.
- 2) Add 4 ml of 0.025M ammonium oxalate in 0.1% nitric acid and drain to waste. *Blanking phase.*
- 3) Add 4 ml of 0.1% nitric acid and drain to waste. *Washing phase.*
- 4) Add 2 ml of 10% nitric acid and drain to waste. *Column conditioning phase.*
- 5) Add 2 ml or more of sample in 10% nitric acid and drain to waste. *Sample loading phase.*
- 6) Add 2 ml of 10% nitric acid and drain to waste. *Sample wash-in phase.*
- 7) Add 4 ml of 0.1% nitric acid and drain to waste. *Major element wash-out phase.*
- 8) Add 8 ml of 0.025M ammonium oxalate in 0.1% nitric acid and collect in appropriate container until needed for analysis. *Uranium collection phase.*
- 9) Add 4 ml of 0.025M ammonium oxalate in 0.1% nitric acid and drain to waste. *Blanking phase.*
- 10) Add 4 ml of 0.1% nitric acid and drain to waste. *Washing phase.*
- 11) Add 2 ml of 0.1% nitric acid and immediately cap column top and bottom. *Wet Storage.*

#### 2.3.4 Analysis

Except for the matrix tests, all analysis was carried out using a matrix of 1% nitric acid. Samples that had been separated contained a maximum 0.012 M ammonium oxalate. All internal standards and spikes were added gravimetrically. Samples were analysed on the PQ Excell ICP-QMS instrument using a CETAC 500 auto sampler (CETAC Technologies, South Shields, Tyne and Wear) with a sample washout solution of 2% nitric acid.

#### 2.3.5 Data Processing

All data were processed off-line and were corrected for blank response, instrumental drift and mass bias effects. It is necessary to compensate for any mass bias in the instrumentation because the interface (cones) between the ICP source and mass spectrometer, and electro-optics of ICP-QMS instruments do not transmit ions of different mass equally. Although the mass bias affects are less obvious with increasing mass, there is still a measurable deleterious effect with a heavy ion such as uranium. The mass bias was estimated and corrected using a solution of known  $^{238}\text{U}/^{235}\text{U}$  ratio.

For the ID calculations the following simultaneous equation was used.

$$C_x = C_s \times (M_x/M_s) \times (W_s/W_x) \times (((A_s - R*B_s)) / ((R * B_x) - A_x))$$

Where:

$C_x$  = concentration of analyte in the sample

$C_s$  = concentration of analyte in the spike solution

$A_s$  = abundance (atomic fraction) of reference isotope in spike

$B_s$  = abundance (atomic fraction) of spike isotope in spike

$A_x$  = abundance (atomic fraction) of reference isotope in original sample

$B_x$  = abundance (atomic fraction) of spike isotope in original sample

$W_s$  = mass of spike taken

$W_x$  = mass of samples taken

$M_s$  = relative atomic mass of spike

$M_x$  = relative atomic mass of sample

$R$  = ratio of reference isotope/spike isotope

All the parameters of this equation can be calculated or are known except  $R$ , the  $^{238}\text{U}/^{235}\text{U}$  ratio, which was measured and corrected as described above.

## 2.4 DETERMINATION OF THE $^{233}\text{U}$ SPIKE CONCENTRATION AND $^{238}\text{U}/^{235}\text{U}$ ISOTOPIC RATIO

Before any ID measurements could be made, the concentration of the  $^{233}\text{U}$  spike had to be accurately determined by a process known as reverse isotope dilution. In this procedure a solution with a known  $^{238}\text{U}$  concentration is used to determine the unknown concentration in the  $^{233}\text{U}$  spike.

### 2.4.1 Reverse isotope dilution

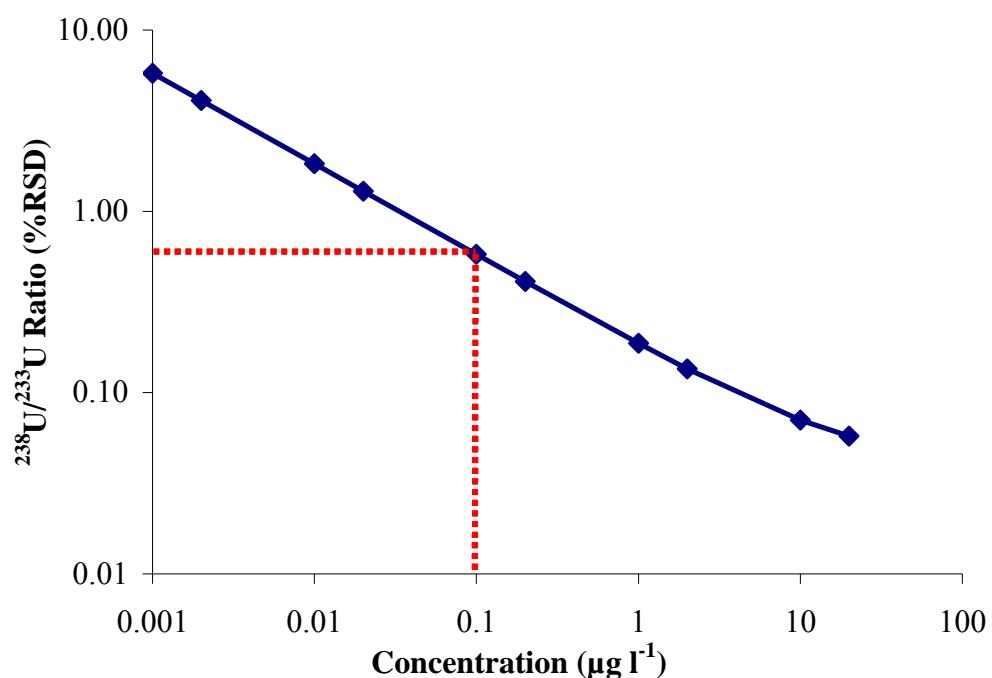
Measurement was made of the  $^{238}\text{U}/^{233}\text{U}$  ratio of the spike, the  $^{238}\text{U}/^{233}\text{U}$  ratio of a standard with a known uranium concentration and a mixture of the two in a predetermined ratio to give an approximately equal signal for both  $^{233}\text{U}$  and  $^{238}\text{U}$ . A simultaneous equation (see above) was then used to determine the exact concentration of the  $^{233}\text{U}$  spike.

### 2.4.2 Optimum spiking concentration for samples

A series of measurements of concentration and isotopic ratios of the above test solutions were then made and processed using Poisson based counting statistics to determine the concentration of spike needed to achieve the required precision, in this case, 1% RSD or better. From the theoretical data in Table 4 and Figure 1 a concentration of  $0.1 \mu\text{g l}^{-1}$  was chosen for the addition of  $^{233}\text{U}$  spike.

**Table 4** Theoretical RSD assuming a count rate of 50 Mcps/ppm

Concentration (ppb)	Count rate (cps)	RSD ratio
20	1000000	0.06
10	500000	0.07
2	100000	0.14
1	50000	0.19
0.2	10000	0.41
0.1	5000	0.58
0.02	1000	1.29
0.01	500	1.83
0.002	100	4.08
0.001	50	5.77

**Figure 1** Theoretical concentration of  $^{233}\text{U}$  required to achieve % RSD <1, based on the routine sensitivity of instrument.

### 2.4.3 Precision of routine analysis compared to theoretical calculations

For routine analysis, the overall total uncertainty of ICP-QMS measurements is approximately 10%. This uncertainty is dominated by the natural limitations of the technique such as nebulisation, quadrupole settle time and background effects, such as drift and matrix. When determining uranium isotopes, counting statistics become an important factor due to the large difference in isotopic abundance between  $^{238}\text{U}$  and the other isotopes  $^{235}\text{U}$  and  $^{234}\text{U}$ . For the  $^{238}\text{U}$  signal to remain in the pulse counting mode of the detector, the signal needs to be under 2M cps and this results in a low signal for the other isotopes. Counting statistics for these less abundant isotopes then dominates the accuracy and precision of any measurements.

The RSD of a typical uranium ICP-QMS analysis using 15 x 30 second acquisitions is typically of the order of 2%. Therefore, to justify using a  $^{233}\text{U}$  spike, the accuracy and precision would need to be significantly better than 2%.

## 2.5 DETERMINATION OF URANIUM ISOTOPES $^{238}\text{U}$ , $^{235}\text{U}$ AND $^{233}\text{U}$ IN CERTIFIED REFERENCE MATERIALS USING FULL IDMS QUANTIFICATION

The study then tested the use of a  $^{233}\text{U}$  spike for full ID quantification and as an internal standard, using various Certified Reference Materials (CRMs). The dissolution, separation/pre-concentration and analysis procedures are described in section 2.3. The spike was either added before dissolution or after separation, just prior to analysis, to assess the flexibility and robustness of the technique and any error associated with different points of spiking. The experimental protocol for these determinations is given in Table 5. Control samples that had been processed by the usual routine procedure for uranium isotope determination were also analysed.

**Table 5** Experimental protocol

	Dissolution	Separation from matrix/pre-concentration	Analysis
Test 1	$^{233}\text{U}$ spike	Yes	As prepared
Test 2	$^{233}\text{U}$ spike	None	As prepared
Test 3	No spike	None	$^{233}\text{U}$ spike
Control	No spike	Yes	As prepared

Test solutions were diluted to give a  $^{238}\text{U}$  response of approximately 1 Mcps/ppm. A chemical uranium standard was run every five samples to monitor instrument mass bias. Solution uptake into the ICP was via the auto-sampler in the following manner: 2 minutes uptake and stabilisation; 15 integrations each of 30 seconds duration; and a 2 minute wash between solutions.

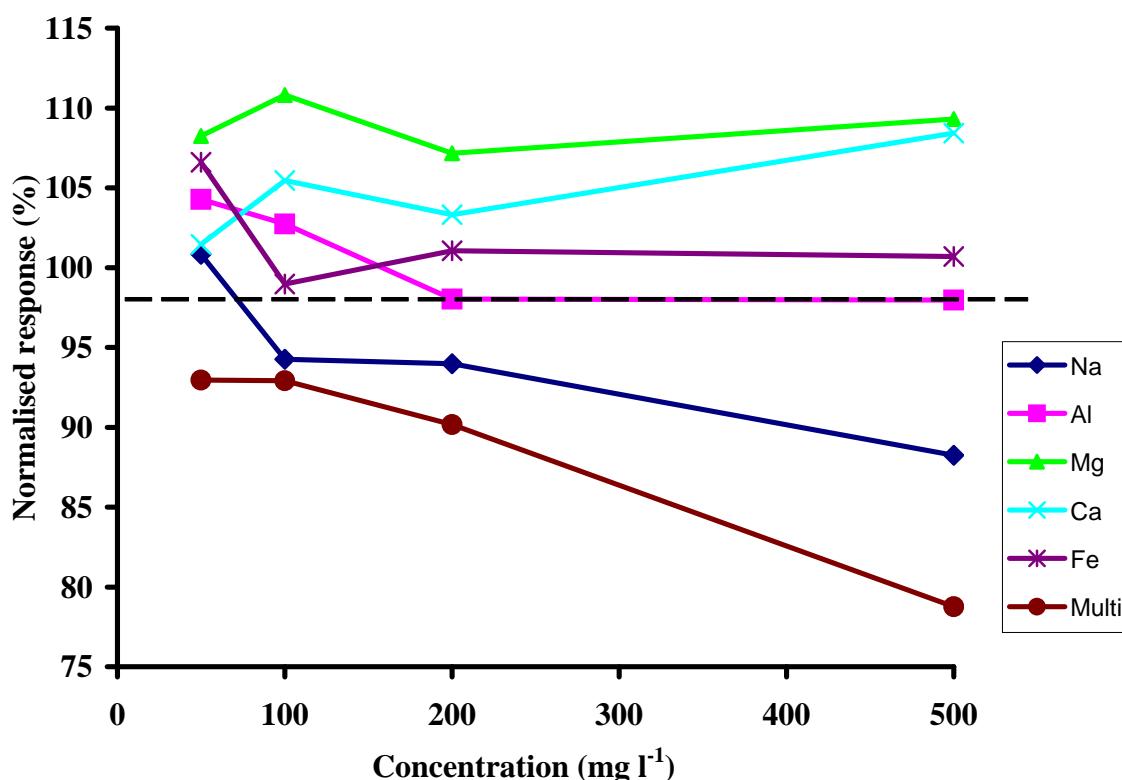
### 3 Results/Discussion

During the routine analysis of environmental samples, the use of conventional internal standards, such as indium (In), bismuth (Bi) and rhenium (Re), to correct for matrix effects was not as effective for the correction of  $^{238}\text{U}$  as for other elements. General investigation into these matrix effects suggested that: (i) high levels of Na and Ca had an antagonistic effect on signal suppression and enhancement; and (ii) suppression and enhancements of the signal were not simply dependant on mass or ionisation energy.

It was decided to repeat these experiments, concentrating particularly on the effects of the matrix on the behaviour of uranium and various internal standards, to gain a better understanding of these effects before moving on to the IDMS technique itself.

#### 3.1 ENHANCEMENT/SUPPRESSION OF $10 \mu\text{g l}^{-1}$ U SIGNAL DUE TO MAJOR ELEMENT MATRIX EFFECTS

Major element solutions were prepared with a range of concentrations from  $100 \text{ mg l}^{-1}$  to  $500 \text{ mg l}^{-1}$ , as might typically be found in rock, soil or sediment digests, and spiked with  $10 \mu\text{g l}^{-1}$  uranium to assess how the different matrices affect the signal of the major uranium isotope  $^{238}\text{U}$  normally used for elemental concentration determinations. All data were normalised to a simple 1% nitric acid matrix response.



**Figure 2** Enhancement/suppression effects of major elements on a  $10 \mu\text{g l}^{-1}$   $^{238}\text{U}$  signal

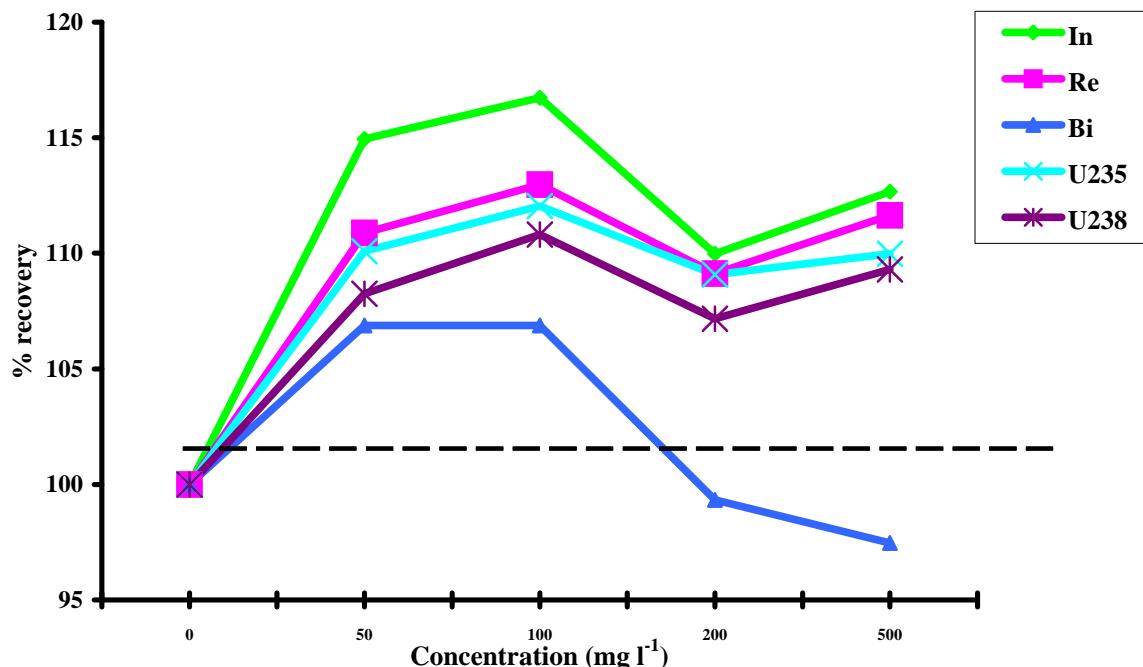
As can be seen from Figure 2, different major element matrices had varying affects on the uranium signal. In the majority of cases the suppression or enhancement effect increases with concentration, but not always, and the reproducibility of these effects was poor. It was interesting to observe that when a multi-element solution containing major elements that both enhanced and

suppressed the signal was analysed, the overall effect was one of suppression - the effects did not cancel each other out.

When dealing with matrix effects arising from high concentrations of various elements it is difficult to separate effects due to: (i) changes in nebulisation efficiency, expected to affect all elements equally; (ii) changes in ionisation efficiency/oxide formation etc in the plasma, which will affect elements differentially; (iii) changes in ion transport efficiency due to cone blockage, a dynamic process with material being rapidly laid down during nebulisation of a high total dissolved solids (TDS) solution with refractory elements and slow removal during nebulisation of "blank" acid solutions. This study confirmed earlier assessments from work at BGS and elsewhere that matrix effects are extremely difficult to quantify, this highlights the importance of using an appropriate internal standard to correct for these effects.

The same major element solutions were then spiked with  $10 \mu\text{g l}^{-1}$  uranium standard and various internal standards at the same concentration to assess whether they were all behaving in the same way and which internal standard was the most appropriate to correct uranium.

The graph for the Mg matrix is shown in Figure 3. Although there were different enhancement/suppression effects depending on the matrix, this was typically how the internal standard signals were grouped compared with the uranium signal.



**Figure 3** Variation of  $10 \mu\text{g l}^{-1}$  internal standard signal with Mg concentration

For routine uranium analysis, based on previous experience, indium has been the usual choice of internal standard. It is clear from Figure 3 that, although indium is following a similar pattern to the uranium, Re would be a more appropriate choice and this was the case for all matrices. On investigation the reason for this may well be because Re and U have very similar oxide bond strengths. The choice of internal standard has usually been dictated by considerations such as ionisation potential and atomic mass, but there may now have to be some reassessment and further work done to look at oxide formation and bond strengths when selecting an internal standard. As predicted, the uranium isotopes all behave in a similar way.

### 3.2 COMPARISON OF $^{233}\text{U}$ WITH In, Bi OR Re AS TRADITIONAL INTERNAL ELEMENT STANDARDS

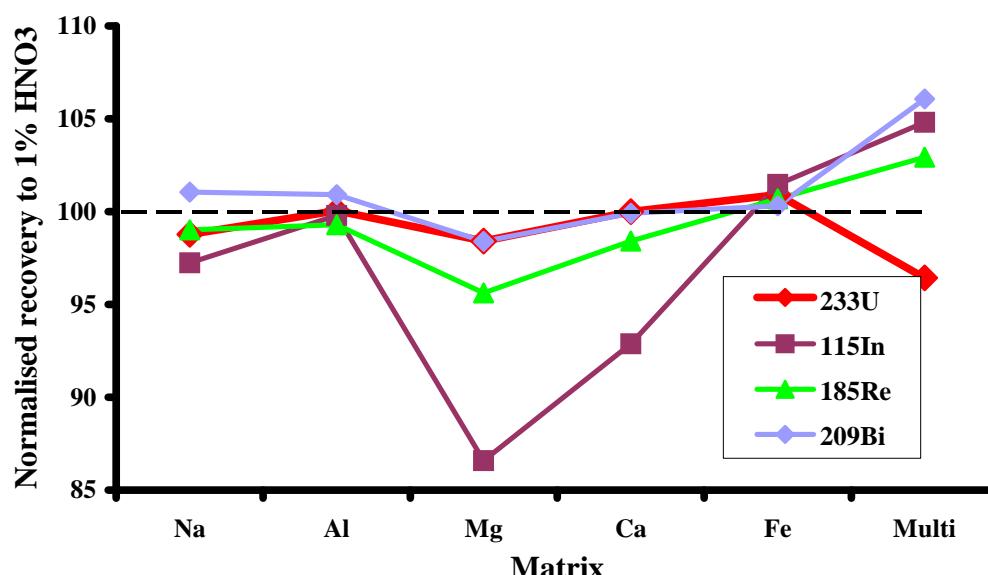
Having calibrated the concentration of the  $^{233}\text{U}$  spike, a series of 50 mg l<sup>-1</sup> major element solutions were spiked with  $^{233}\text{U}$  and internal elemental standards In, Bi and Re, as well as the target isotopes  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$ . These were then analysed using the same acquisition parameters used for the theoretical calculations in section 2.4. The accuracy and precision were calculated and compared with what might be expected from counting statistics. All spikes were added gravimetrically and the weights recorded to limit inherent errors due to pipetting solutions by volume. A mean for all solutions was used to calculate the overall precision.

**Table 6** RSD achieved experimentally using various internal standards and the  $^{233}\text{U}$  spike to correct  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$

		Internal Standard			
Isotope		Indium	Rhenium	Bismuth	$^{233}\text{U}$
$^{234}\text{U}$	Mean (cps)	72	72	73	72
	%RSD	<b>8.0</b>	<b>5.1</b>	<b>5.2</b>	<b>4.7</b>
$^{235}\text{U}$	Mean (cps)	2179	2169	2210	2189
	%RSD	<b>5.7</b>	<b>2.2</b>	<b>2.3</b>	<b>1.8</b>
$^{238}\text{U}$	Mean (cps)	283643	282285	287654	284956
	%RSD	<b>5.8</b>	<b>2.2</b>	<b>2.2</b>	<b>1.4</b>

The RSD achieved experimentally using major element solutions spiked with various internal standards clearly show that the uranium spike produces better precision than In, Bi or Re (Table 6). The theoretical target precision of 1% RSD or better on the  $^{238}\text{U}$  concentration measurements using a  $^{233}\text{U}$  spike was based purely on the count rate for various concentrations of uranium and was not achieved in practice; however, it was approached with an RSD of 1.4%. Other parameters such as drift and matrix affects were contributing to the overall precision of measurement, but the improvement was significant and consistently less than the 2% RSD normally achieved for routine analysis. It was decided that no significant improvement would be achieved by increasing the concentration of uranium spike because of the contribution of other sources to the overall precision.

A balance needs to be struck between using the minimum amount of  $^{233}\text{U}$  spike (as it a radioactive isotope and therefore its use, disposal and cost need to be taken into account) and achieving a signal of such a magnitude to minimise inaccuracies due to counting statistics.



**Figure 4** Precision and accuracy using  $10 \mu\text{g l}^{-1}$  Internal Standards and  $^{233}\text{U}$  spike to correct uranium, based on routine instrument sensitivity

It is clear from Figure 4 that the  $^{233}\text{U}$  spike is the most appropriate internal standard, not surprisingly, but consideration of other elemental internal standards was enlightening. Indium, which has used routinely to correct uranium, performed poorly in comparison to Bi and Re. Rhenium and Bi behaved in a very similar way and these results also suggest that more work is required into the choice of internal standards.

Figure 4 shows that different matrices have varying enhancement or suppression effects and the choice of an appropriate internal standard for analysis may not be straightforward. As predicted theoretically, precision and accuracy can be improved by using a  $^{233}\text{U}$  spike for the determination of other uranium isotopes concentrations.

### 3.3 DETERMINATION OF URANIUM ISOTOPES $^{238}\text{U}$ , $^{235}\text{U}$ AND $^{233}\text{U}$ IN CERTIFIED REFERENCE MATERIALS USING FULL IDMS QUANTIFICATION

Tables 7 and 8 show the data obtained from the three tests described in Section 2.5 and Table 5. These results were obtained from the same solutions; in Table 7 they were calculated using the uranium spike as an internal standard, whereas in Table 8 they were calculated using a full IDMS calculation.

**Table 7** Results and associated recoveries in % for CRMs using  $^{233}\text{U}$  as an internal standard

CRM	Ref. Value mg/kg	Test 1 No Matrix	Test 2 Matrix	Test 3 Matrix	Control No matrix	Mean recovery and range	Range in recoveries %
BGS450	5.63	98	89	97	98	89-96-98	9
SDO-1	48.8	93	-	93	93	93	-
JR-2	10.5	106	95	97	116	95-104-116	21
SCo-1	3.0	102	96	98	95	95-99-102	7
BCR-1	1.75	102	95	99	100	95-99-102	7
WS-E	0.65	104	92	94	104	92-99-104	12
AGV-1	1.92	105	97	100	105	97-102-105	8
Mean recovery and range	-	93-102-106	89-94-97	93-97-100	93-102-116		

**Table 8** Results and associated recoveries in % for CRMs using full IDMS

CRM	Ref. Value mg/kg	Test 1 No Matrix	Test 2 Matrix	Test 3 Matrix	Mean recovery and range	Range in recoveries %
BGS450	5.63	90	86	91	86-89-91	5
SDO-1	48.8	86	93	87	86-89-93	7
JR-2	10.5	98	94	91	91-94-98	7
SCo-1	3.0	95	93	92	92-93-95	3
BCR-1	1.75	94	93	95	93-94-95	2
WS-E	0.65	96	91	91	91-93-96	5
AGV-1	1.92	97	96	97	96-97-97	1
Mean recovery and range	-	86-94-98	86-93-96	87-92-97		

For both sets of data, there is no significant difference in the mean recovery for each of the different tests within each table. However, the recoveries obtained using full IDMS (Table 8) have a small but consistent negative bias, whereas the use of  $^{233}\text{U}$  as an internal standard provided 100% recovery, within experimental error.

Looking at the data for the individual CRMs, it can be seen that although there is a negative bias for the IDMS data, the range of results for any single CRM is much smaller using full IDMS than if  $^{233}\text{U}$  is treated as an internal standard, with the exception of SDO-1. This indicates that the use of IDMS improves the precision of uranium concentration analysis for any individual CRM. It would not have been possible to observe this bias in the accuracy of uranium analysis previously during routine multi-element analysis, where the precision is of the order of 10%. This potential bias will be investigated in further more detailed studies.

The long term results for the determination of uranium in SDO-1 and JR-2 are given in Table 9 for comparison. These data were obtained using indium as the internal standard and demonstrate that the overall precision of the routine method is approximately 10% with a bias of up to 10%.

**Table 9** Long term results for uranium determination for SDO-1 (n=65) and JR-2 (n= 87)

Reference material	Reference Value mg/kg	Mean mg/kg	Recovery %	SD %	RSD %
SDO-1	48.8	47.8	98	4.2	8.9
JR-2	10.5	11.6	110	1.1	9.8

### 3.4 PRACTICAL AND HEALTH & SAFETY CONSIDERATIONS

Practically, it was easy to spike samples at any of the various stages of preparation, although this was time consuming. The data processing, although more complicated than normal calibration/quantification, was straightforward and less arduous than the usual workup. Overall, the additional time spent spiking the samples gravimetrically was more than compensated for by the reduction in time required for data processing.

There are always health and safety issues to be considered when using radioactive material. This methodology makes use of a relatively stable radioactive spike so only minimal health and safety procedures are required. Because of its low activity, the spike can be used on an open bench with the normal laboratory personal protection equipment such as safety spectacles, laboratory coat and gloves. Spills should be diluted and mopped up with wipes but no special disposal of these wipes is required. All waste does need to be collected and disposed of using the BGS radioactivity guidelines and via the BGS Radiological Protection Officer. The spike solution should be clearly marked as radioactive and locked in an appropriate cupboard.

## 4 Conclusions

Current practice in the BGS laboratories is to use indium and rhenium as internal standards to correct for matrix suppression (or enhancement) in ICP-MS. However, it is difficult to provide adequate correction when determining uranium because there is not a suitable element available at the heavy end of the mass spectrum. This project established that the use of  $^{233}\text{U}$ , a by-product of nuclear fuel processing, provided superior precision when used as an internal standard for measurements of other uranium isotope concentrations, compared to indium, rhenium or bismuth.

A comparison of performance of  $^{233}\text{U}$  as an internal standard against full IDMS calculations was then made. These experiments showed:

- Recovery, i.e. the measured concentration as a proportion of expected concentration, did not appear to be dependent on the concentration of uranium in the original reference material.
- All recoveries were within a very similar range and were not dependent on the type of reference material, i.e. soil, igneous or sedimentary rock, etc.
- The separation and pre-concentration procedure did not appear to affect recovery.
- Recoveries were independent on the point at which the spike was added in the process, i.e. prior to dissolution or at the analysis stage.
- There is a slight negative bias in the IDMS results. The cause is unknown and requires further investigation.
- The within sample precision appears to be better with full IDMS compared to use of  $^{233}\text{U}$  purely as an internal standard.

Thus, the data indicate that the within sample precision is better when full ID quantification is performed, regardless of the matrix, than when using the spike as an internal standard. More work is required to determine if this improvement is significant and justifies the use of a radioactive spike for applications requiring an enhanced analytical performance. There are advantages and disadvantages when using this technique. Adding the spike to every sample gravimetrically can be time consuming and needs to be done accurately. The data processing was also time consuming initially but, when a template is used to handle the data manipulation, it is considerably quicker and has fewer steps than for routine analysis.

The IDMS technique could potentially eliminate the column separation procedure, although this may still be necessary where concentrations of uranium are low in the samples. Where suitable concentrations are available, eliminating this separation stage would achieve significant savings in staff time and consumables. The data suggest the point at which the spike is added makes no discernable difference to the result but, in theory, the spike should go through the whole of the procedure to achieve the most accurate result.

A negative bias was observed in the IDMS data which requires further investigation. There are several factors that could be influencing the data:

- Formation of uranium oxide in the ICP
- Interference from thorium hydride on  $^{233}\text{U}$
- Solution density
- Instrument set up, e.g. settle time, safe resting mass
- Dry weight calculations may need to be applied

- Original bias in CRM data
- Calibration of the original spike using reverse ID

Several of these have been considered and tested; no single factor is thought to be responsible for the overall error. However, it is thought that one of the most likely factors is the assumption made about the density of the  $^{233}\text{U}$  spike solution, which would affect the IDMS calculations but has no influence when  $^{233}\text{U}$  is used as an internal standard. Until this issue is resolved, it will be difficult to identify other significant factors contributing to the overall bias.

A CRM with a certified value for uranium determined by ID-TIMS is to be purchased and assessed by ID ICP-MS before any further studies are designed. Once this has been done, full statistical analysis of the data and the quantification of uncertainties within the procedure will be undertaken.

Potentially this procedure is cost effective, as the spike is relatively inexpensive to buy, and the small amount of radioactive material involved can be disposed under the present BGS arrangements without entailing any further expense. Savings can be made on eliminating the column separation and data processing time. It will not always be appropriate to use this method for the determination of uranium isotope concentrations and a decision tree needs to be devised to determine the appropriate method to be used for each potential application.

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Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

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