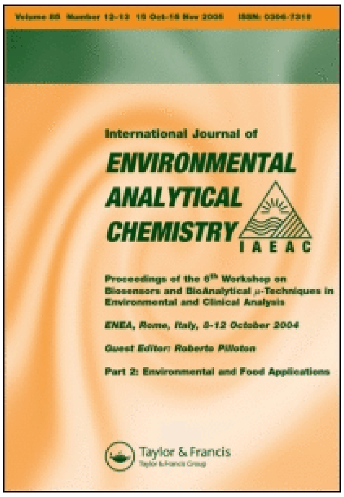

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Accurate measurement of uranium isotope ratios in soil samples using thermal ionization mass spectrometry equipped with a warp energy filter

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To cite this Article Sahoo, Sarata Kumar , Nakamura, Yuji , Shiraishi, Kunio and Masuda, Akimasa(2004) 'Accurate measurement of uranium isotope ratios in soil samples using thermal ionization mass spectrometry equipped with a warp energy filter', International Journal of Environmental Analytical Chemistry, 84: 12, 919 — 926
To link to this Article: DOI: 10.1080/03067310410001729015
URL: http://dx.doi.org/10.1080/03067310410001729015

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 12, pp. 919–926, 15 October 2004

ACCURATE MEASUREMENT OF URANIUM ISOTOPE RATIOS IN SOIL SAMPLES USING THERMAL IONIZATION MASS SPECTROMETRY EQUIPPED WITH A WARP ENERGY FILTER

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(Received 17 February 2004; In final form 20 April 2004)

A chemical and mass-spectrometric procedure for uranium isotopic analysis using a thermal ionisation mass spectrometer equipped with a Wide Aperture Retardation Potential energy filter has been developed and applied to uranium isotopic measurements for various soil samples. Soil samples were digested using a microwave digestor. Uranium was isolated from soil samples by the chemical separation procedure based on the use of anion-exchange resin and UTEVA extraction chromatography column. The isotope ratios were measured for two certified reference materials by using a VG Sector 54-30 thermal ionisation mass spectrometer in dynamic mode with Faraday cup and Daly ion counting system. Replicates of standard reference materials showed excellent analytical agreement with established values supporting the reliability and accuracy of the method. Precision of the $^{235}U/^{238}U$ ratio was achieved by a correction factor of 0.22% amu as a function of ion-beam intensity with sample loads of around 250 ng of U. The resulting reproducibility for standards and soil samples was better than 0.2% at two standard deviations (SD). Uranium isotopic compositions have been determined in several reference soil samples such as Buffalo river sediment, NIST 2704, river sediment SRM 4350b and ocean sediment NIST-4357 and a Chernobyl soil sample. There was a significant deviation from the natural uranium in comparison with Chernobyl soil samples.

Keywords: Uranium; Isotope ratios; Soil; WARP filter; TIMS

INTRODUCTION

Precise measurement of the relative abundances of naturally occurring radionuclides, such as the isotopes of uranium, in natural series of radioactive decay originating with ^{238}U has been used to study a wide variety of problems in geology, hydrology and environmental science [1]. Uranium is becoming an increasingly important

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ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310410001729015

component in nuclear waste owing to its release into the environment during nuclear accidents (e.g. Windscale in 1957, Three Mile Island in 1978 and Chernobyl in 1986). Soils and sediments were suitable materials to preserve any remains of the anthropogenically altered uranium. Analysis of historical deposits of uranium using soil samples is potentially difficult as the amount of deposited uranium can be significantly less than the inherent content of natural uranium (~0.5~3.0 ppm) [2].

Uranium consists of three natural isotopes, viz. ^{234}U, ^{235}U and ^{238}U with relative isotopic abundances of 0.0054%, 0.720% and 99.275%, respectively [3]. Both ^{238}U and ^{235}U isotopes are of primordial origin. The ^{238}U isotope, upon radioactive decay, produces long-lived daughter products, ^{234}U and ^{230}Th. ^{234}U is present in secular equilibrium with ^{238}U [4]. However, a radioactive disequilibrium state between ^{238}U and ^{234}U has been observed by many workers in both sea water and freshwater [5]. Anthropogenic uranium also contains an ultra-trace quantity of ^{236}U, which is produced by neutron capture of ^{235}U in nuclear industrial processes. Therefore, ^{236}U can be used as a 'fingerprint' for the presence of uranium in the environment that originates from a nuclear reactor. In this regard, it has substantial advantages over anthropogenic ^{238}U and ^{235}U; both isotopes are quickly diluted by the natural background in soils and sediment, making them unsuitable markers for the spent uranium released into the environment [6]. Thus, uranium isotope ratios may have small variations depending on the geological origin of the sample, due to natural isotopic fractionation, nuclear reactions or anthropogenic contamination.

Earlier methods used to determine ^{234}U/^{238}U were based on either alpha spectrometry [7,8] or mass spectrometric studies [9–11]. However, alpha spectrometric determination lacks the sensitivity or precision to detect minute level of contamination. A low level of ^{236}U, likely to be encountered in soil samples, is difficult to detect by alpha spectrometry measurement. Since the α-particle energy of ^{236}U is very close to that of ^{235}U, alpha spectrometry is not a practical method of analyis. In addition, the concentration of ^{236}U in environmental samples is below the detection limit for alpha spectrometry, therefore an alternative technique such as mass spectrometry would be preferable. In recent years, there has been a rapid progress in high-precision uranium isotopic measurements, to measure the ^{234}U/^{238}U ratio, using multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) [12] and a thermal ionisation mass spectrometer equipped with a Wide Aperture Retardation Potential (WARP) energy filter or RPQ lens system [13,14]. Multi-collector thermal ionization mass spectrometer (TIMS) techniques, in which the high abundance ^{238}U isotope is collected using a Faraday collector and the low-intensity isotopes (^{234}U and ^{236}U) are collected in ion multiplier channels equipped with ion counting systems, allow static data collection without the loss of data collection time when jumping between masses. By contrast, TIMS measurements yield data with a much better precision than conventional alpha counting methods. In addition, less sample and less time are needed for analysis.

The aim of this paper is to report a chemical procedure for isolation of uranium based on extraction chromatography and precise determination of uranium isotopic composition (^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U) in uranium ores, different reference soil samples and a soil sample affected by the Chernobyl nuclear accident (30-km exclusion zone) using TIMS equipped with a WARP filter to detect minute levels of enriched or depleted uranium contamination.

EXPERIMENTAL

Instrumentation

The isotopic analyses of uranium were performed on a single focusing VG Sector 54–30 TIMS at the National Institute of Radiological Sciences. The instrument is equipped with nine new bucket-type Faraday collectors and a Daly ion-counting system detector positioned behind the axial Faraday and WARP energy filter. Signals from the Daly detector are received by an EG&G Ortec 9302 amplifier/discriminator and EG&G Ortec 996 ion counter/timer.

Reagents and Standards

High-purity water was obtained with a Millipore Milli-Q water purification system. High-purity HCl, HNO_3, HF and $HClO_4$ were purchased from Tamapure chemical industries (Kawasaki, Japan). The strong anion-exchange resin Dowex 1X-8 (200–400 mesh, Cl^- form) was purchased from Bio-Rad Labs (Richmond, CA). This was soaked in 6 M HNO_3 and subsequently washed with distilled water. Commercial extraction chromatographic resin, UTEVA, was purchased from Eichrom Industries (Darien, IL); this consisted of a neutral organophosphorus diamyl amylphosphonate extractant adsorbed onto an inert polyacrylamide support. It was conditioned with 7 M HNO_3.

Sample Description

Two NBL standards, NBL U005a and NBL U010, were used to check the accuracy of the calibration and optimisation of procedures. Two uranium ores and three soil samples were chosen for this study: sediment reference materials such as Buffalo river sediment, NIST 2704, river sediment SRM 4350b and ocean sediment NIST-4357 and a Chernobyl soil sample from Ukraine 30-km exclusion zone affected by the Chernobyl accident. Sediment sample and soil samples were dried at $80 \pm 5°C$. After homogenisation, 500-mg soil samples were digested with HNO_3, HF and $HClO_4$ in a closed pressure decomposition vessel (PTFE vessel). A microwave unit (MLS 1200 Mega, Italy) was used to heat the samples [15]. Microwave digestion was performed using 650 W of power for 20 min. After cooling, the digested samples were evaporated to dryness on a hot plate. For further treatment, the sample residues were dissolved in 7 M HNO_3.

Chemical Separation

We used a combination of anion-exchange and extraction chromatography with a little modification of the earlier methods [16,17]. The first column was prepared by using precleaned anion exchange resins (Dowex 1X-8, 200–400 mesh, Cl^- form) and packed into 2 cm i.d. Pyrex columns up to a height of 6 cm and a second column (1.0×0.5 cm internal diameter) containing Eichrom UTEVA resin. Both columns were conditioned by passing 15 mL of 7 M HNO_3. The dissolved sample was transferred to an anion-exchange column, and the eluent was subsequently passed onto the

UTEVA column. Both columns were washed with 10 mL of 7 M HNO_3 followed by 20 mL of 3 M HNO_3.

Uranium was eluted from UTEVA column using 5 mL of 0.02 M HCl. Concentration of eluent was adjusted to 9 M HCl. The resulting solution was loaded onto an anion exchange column preconditioned with 9 M HCl and washed with 10 mL of 9 M HCl. Finally, U was eluted with 10 mL of 0.02 M HCl, and the eluent was evaporated to dryness in a Teflon beaker. Some organic residues were noticed in uranium fraction collected from UTEVA column. It is undesirable to load such fractions on the Re filaments, as the presence of trace organic residues on the filaments severely affects the ionization efficiency of uranium and contaminates the source of TIMS. Therefore, a second anion-exchange column was necessary for the re-purification of uranium. We used about 5 µg of isotopic standard for chemical separation studies. Recovery of uranium from the samples is about 80–90%.

Mass Spectrometry

A triple filament assembly was used for the thermal ionization of uranium isotopes. The filament material was a five-pass zone refined rhenium ribbon (H. Cross, 99.999%) 0.003 cm in thickness and 0.07 cm in width. Triple Re filaments were prepared by degassing for 1 h with a 4 Å current under a vacuum better than 5×10^{-6} Torr. The isolated U fraction was loaded onto a separable outer side filament and heated with a 0.9 Å current to leave a dry residue.

The centre filament was heated to produce a ^{187}Re ion current of 0.2 V, and then the side filaments were heated to produce an ion current of 0.03 V for ^{238}U. Uranium with masses of 234, 235, 236 and 238 was measured dynamically using both a Daly-ion counting system and Faraday cup collectors with mass peak jumps as shown in Table I. $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios were determined by static data collection on the Daly-ion counting and Faraday cup collectors. All ratios were taken as the grand mean of seven blocks of 10 measurements over a period of 80 min. The vacuum during data acquisition was better than 1×10^{-8} Torr in the flight tube as well as in the ion source.

Accuracy and precision of $^{235}U/^{238}U$ measurement depends on the linearity of the detection system and mass fractionation of the isotopes during the run. The ion-counting-multiplier system was broadly linear when used in the peak-jump measurement of $^{235}U/^{238}U$ over a range of ion-beam intensities generated during analytical runs (1.5×10^{-13} to 3.0×10^{-13} Å of ^{238}U). There is a conventional approach to measure Faraday/Daly gain at low intensity, by switching an ion beam between detectors, before increasing the ion beam for measurement. Mass 235 is measured in the Daly detector, and the $^{235}U/^{238}U$ ratio is used for calibrating the Faraday–Daly gain. The gain calibration is done for every individual block, and the intensity of ^{235}U is taken

TABLE I Collector arrangement and mass jump sequences used in uranium measurement

Collector	*Axial Daly*	*Faraday H1*	*Faraday H2*	*Faraday H3*	*Faraday H4*
Zeros	232.5	233.5	234.5	235.5	236.5
Sequence 1	234.0	235.0	236.0	–	238.0
Sequence 2	235.0	236.0	–	238.0	–
Sequence 3	236.0	–	238.0	–	–

into consideration for mass fractionation. F/D gain varies in the range of 0.998–1.002 during several measurements of the NBL 010 standard. Lighter isotopes are known to ionize more readily than the heavier isotopes. For higher amounts of ionized uranium, fractionation for a given interval will be reduced.

RESULTS AND DISCUSSION

The reproducibility and accuracy of the method were verified by analyses of two certified reference materials such as NBL U010 and NBL U005a. NBL CRM U010 comprises ^{234}U, ^{235}U, ^{236}U and ^{238}U with certified isotope abundances (in atom percent) of 0.00541, 1.0037, 0.00681 and 98.984, respectively. The isotope ratio of ^{235}U/^{238}U has been certified to be 0.01014 for NBL CRM U010. The results of our measurement for isotope ratios such as ^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U compared with the certified values are given in Table II using the WARP energy filter. The results were found to be in good analytical agreement. Under optimal conditions, five replicate analysis of NBL U005a yielded an average value of ^{235}U/^{238}U as 0.005089(46) against a certified value of 0.00509. Thus, the measurements of the isotopic ratio in the reference materials demonstrate that isotopic fractionation, if it occurs in the system, is less than the uncertainty in the measurement.

In the case of triple filament assembly, a hot centre filament is ionized, and the sample on the side filament evaporates. Because the sample is not directly ionized, it has been observed that fractionation is much slower than for a single filament [18]. Using the dynamic method, a period of 2.5 h is required to measure 20 blocks, each of which is a mean of 10 individual isotope ratios. There is no significant variation in ^{235}U/^{238}U ratios with time, and there is less fractionation as shown in Fig. 1. From the various loads of ^{235}U/^{238}U isotope ratio measurement, we calculated a correction factor of 0.22% per amu, which was then applied to other ratios such as ^{234}U/^{238}U and ^{236}U/^{238}U.

The measured isotope ratios, ^{234}U/^{238}U, ^{235}U/^{238}U and ^{236}U/^{238}U, of two uranium ore samples are given in Table III. The ^{235}U/^{238}U is comparable to the well-known 'normal terrestrial' ratio of about 0.00725. The original ratio was established in the r-process of nucleosynthesis in a stellar, presolar environment and has then decreased due to α-decay since that time, leading to the present terrestrial value. The instrument detection limit for the ratio ^{236}U/^{238}U was calculated as three times the standard uncertainty of the background rate divided by the typical ^{238}U intensity ($^{238}\mathrm{U} \cong 2 \times 10^{-11}$ A).

TABLE II Isotopic composition of uranium NBL U010 reference sample measured by NIRS TIMS

No	*$^{234}U/^{238}U$*		*$^{235}U/^{238}U$*		*$^{236}U/^{238}U$*	
	Observed	*Certified*	*Observed*	*Certified*	*Observed*	*Certified*
1	0.0000545	0.0000546	0.0101408	0.010140	0.0000694	0.0000687
2	0.0000547		0.0101428		0.0000695	
3	0.0000547		0.0101467		0.0000695	
4	0.0000546		0.0101407		0.0000691	
5	0.0000545		0.0101414		0.0000689	
Mean	0.0000546	0.0000546	0.0101424	0.010140	0.0000692	0.0000687
SD (2σ)	0.0000002		0.000005		0.0000005	

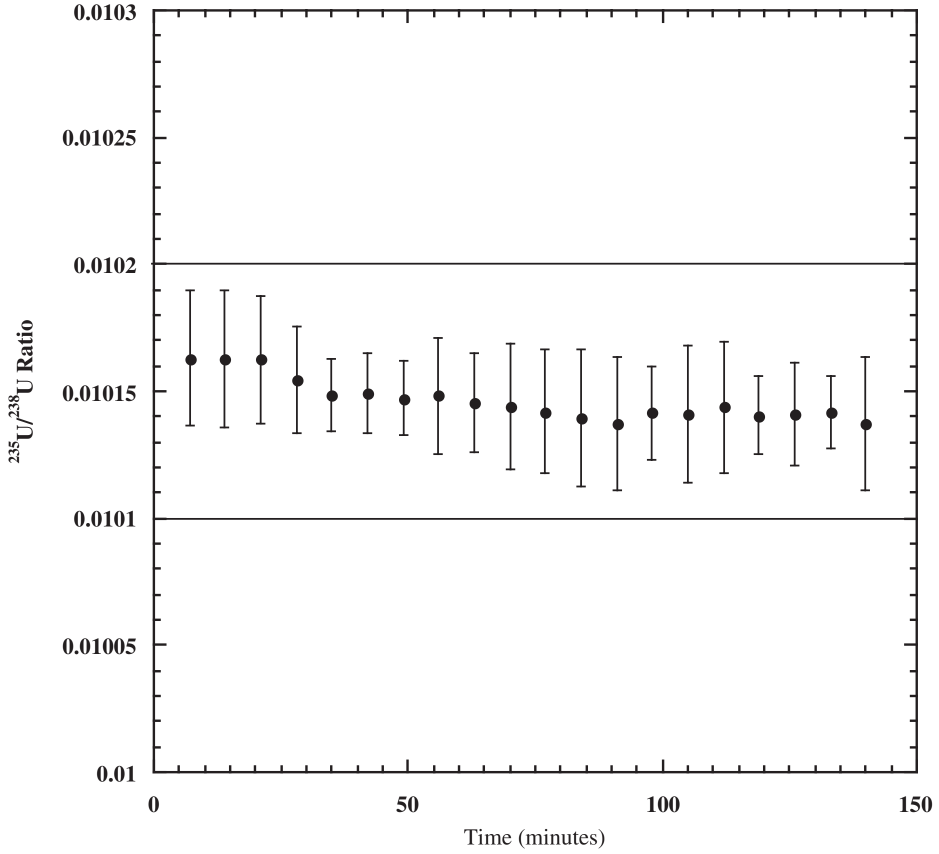

FIGURE 1 Measurement of $^{235}U/^{238}U$ ratio with time.

TABLE III Isotope ratios of uranium measured from two uranium ore

Sample name	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$
Faraday Mine (Canada, Bancroff)	0.0000544 (51)	0.0072560 (32)	1.59136 (67) × 10^{-8}
Mistamisk (Canada, Labrador)	0.0000544 (46)	0.0072553 (39)	8.145183 (59) × 10^{-9}

Analytical uncertainties are expressed as $2\sigma_m$.

This yields a value for the detection limit of 1.2×10^{-10}. Some ^{236}U has been found in exceptional natural samples, e.g. the Oklo reactor.

A representative duplicate set of samples from standard and soil samples from Chernobyl exclusion zone is listed in Table IV to help detect the presence and potential source of anthropogenic uranium. However, samples collected from the Chernobyl exclusion zone do show a spread in the uranium isotope ratio well outside the 99.7% confidence limit. Enrichment of ^{234}U as well as ^{235}U is noticeable in the case of the Chernobyl sample and shows evidence of radioactive disequilibrium between ^{234}U and ^{238}U. These results show the isotopic heterogeneity in the soil samples,

TABLE IV Isotope ratios of uranium measured from soil samples

Sample name	$^{234}U/^{238}U$	$^{235}U/^{238}U$	$^{236}U/^{238}U$
NIST 2704 (Buffalo river sediment)	0.0000554 (51)	0.0072591 (32)	n.d.
SRM4350b (river sediment)	0.0000582 (76)	0.0072599 (45)	n.d.
NIST 4357 (ocean sediment)	0.0000554 (67)	0.0072542 (42)	2.14×10^{-9} (76)
GBW 07312 (Chinese standard)	0.0000548 (49)	0.00726274 (36)	2.11×10^{-9} (68)
Chernobyl soil	0.000090 (46)	0.008194 (39)	0.0000325 (45)

Analytical uncertainties are expressed as $2\sigma_m$.

which can be attributed to the distribution of isotopically enriched material. Duplicate runs of each sample confirmed that such deviations from natural ratios were readily reproducible at statistical levels predicted by standard measurements.

CONCLUSIONS

We have developed a procedure to measure $^{234}U/^{238}U$, $^{235}U/^{238}U$ and $^{236}U/^{238}U$ to better than 0.2% at two SDs. This method is applicable to a wide range of environmental and geological problems which are limited by the sample size or where a higher precision is required. However, while measuring the $^{236}U/^{238}U$ ratio, the possibility of distinguishing between different samples is limited by the instrument detection limit. Therefore, the natural abundance of ^{236}U may still be lower than that detected by the present instrument. This method can be used more precisely to determine the $^{235}U/^{238}U$ ratio in soil samples from Ukraine, Russia, Serbia or Iraq affected by nuclear accidents or where penetrators have been used during conflict to determine the enrichment or depletion in the sample and put a limit on the variability of this ratio.

Acknowledgements

One of us (SKS) is highly grateful to the President of NIRS in funding for upgrading TIMS as well as equipping it with the WARP energy filter. We are much obliged to Professor H. Hidaka (Hiroshima University), Dr. Y. Muramatsu (NIRS) and Professor I.P. Los (Kiev) for providing the natural samples. This work was supported in part by a Grant-in-Aid for Scientific Research (15256001) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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