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Uranium Determination in Geological Materials by Isotope Dilution Mass Spectrometry with ^{233}U as Isotope Tracer

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Experimental details regarding the determination of uranium in rocks and minerals by mass spectrometric isotope dilution technique with ^{233}U as tracer is discussed. The values obtained are compared with other techniques and also with isotope dilution technique where ^{235}U enriched spike is employed. The importance of sampling in the accurate determination of uranium in rock sample, where it is heterogeneously distributed, is pointed out.

Es werden experimentelle Einzelheiten über die U-Bestimmung in Gesteinen und Mineralien beschrieben, die unter Anwendung der massenspektrometrischen Isotopenverdünnungsanalyse mit ^{233}U als Tracer ermittelt wurden. Die erhaltenen Analysenwerte werden mit anderen Methoden verglichen, wobei auch die Isotopenverdünnungsanalyse mit angereichertem ^{235}U eingesetzt wurde. Die Bedeutung der Probennahme und ihre Auswirkung auf die Genauigkeit der Uranium-Gehalte in Gesteinsproben wird erläutert.

Keywords

accuracy; errors; isotope dilution; isotope ratio; mass spectroscopy; reliability; sampling; uranium 233

1. Introduction

For the accurate and precise determination of uranium at low concentration in geological materials, the only method that offers high sensitivity and free from matrix effects is stable isotope dilution analysis by thermal ionization mass spectrometry. Generally for the geological samples ^{235}U enriched spike is employed for isotope dilution. However, for complex chemical matrices or media such as highly radioactive solutions, ^{233}U enriched spike is used due to their absence in reactor grade uranium eliminating the need for separate determination of the isotopic composition of the sample [1]. In the geological materials the isotopic ratio $^{235}U/^{238}U$ has been found to be constant [2] and is assumed so. Therefore, while using ^{233}U as enriched spike for isotope dilution analysis, no analysis of the isotopic composition of the sample is carried out. However, with the use of ^{233}U as tracer, the isotopic ratios $^{235}U/^{233}U$ and $^{238}U/^{233}U$ may be used for the isotope dilution analysis calculations. Further, the use of highly enriched ^{233}U spike makes the isotope dilution equation simple and in the calculation of the precision based on the propagation of errors, the relative standard deviation depends on a single ratio.

In the present publication the experimental details involved in the determination of uranium in rocks and minerals using ^{233}U as tracer is described. The precision and accuracy of the values obtained on the samples are discussed in the light of the values obtained by isotope dilution analysis using ^{235}U as tracer and by other analytical methods.

2. Experimental procedures

2.1. *Preparation and calibration of tracer solution*

The tracer solution was prepared from the isotopic standard supplied by CEA Fontenay, France, and was calibrated by mass spectrometric isotope dilution using NBS uranium isotopic standard NBS U950a. The concentration of the solution was $9.93 \cdot 10^{-5}$ g of uranium/g of solution. Aliquots of weighed amounts of tracer solutions were transferred to glass ampoules and sealed for future use.

2.2. *Dissolution of rock samples and chemical separation*

Depending on the concentration of uranium in the rock sample known quantity of tracer was added to obtain $^{238}U/^{233}U$ ratio near unity. The sample as dissolved in a teflon pressure bomb following the method of *Patchett* and *Tatsumoto* [3] in order to bring in to solution resistant minerals like zircon, apatite, etc., where uranium is

generally concentrated. The reagents for the digestion were 40% hydrofluoric acid, concentrated nitric acid and 72% perchloric acid. The dissolution was complete in 30 hours.

The uranium was separated by two stage ion exchange method. In the first stage uranium was separated from thorium [4] using Dowex 1X-8 resin (200–400 mesh) in chloride form and then separated from iron, alkaline earth metals and other elements on the same resin after Fe(III) is reduced to Fe(II) with iodic acid [5].

2.3. *Mass spectrometric procedure*

The isotopic measurements were done with a Varian TH 5 solid source single focussing mass spectrometer equipped with Faraday cup and electron multiplier. The spectrometer is coupled to a microcomputer for data acquisition and processing [6].

Samples were loaded in the nitrate form on one of the filaments in a double filament assembly using an automatic loading unit [7], while the other filament is used for ionizing the atoms emitted from the sample filament. Five to ten microgram amounts of sample were loaded on the filament.

The ion current was measured with Faraday detector and the data are processed by the microcomputer system which lists the isotope ratios and the relative standard deviation.

3. Results and discussion

On Tab. 1 are shown the values of uranium obtained for different samples of rocks and minerals using ^{233}U as tracer solution. The precision of the individual isotopic analysis is of the order of 0·5% and the external precision for different sets of independent analysis for same sample is of the order of 1%. The sample S_{18} gave higher variation probably due to slight heterogeneous distribution of uranium in the mineral.

On Tab. 2 are compared the uranium values obtained with those reported by other investigators using different techniques. It can be seen that for the rocks GMI-50,11 the variation in the values obtained is of the order of 14%, whereas, for the rock sample GMI-87,17 the variation is of the order of 6%. These variations are more than the analytical precision of the techniques employed. In the granitic samples analysed, *Stuckless* et al. [8] have shown, based on fission track studies, that uranium is generally concentrated in accessory minerals like zircon, apatite, monazite, biotite and magnetite and thus the uranium concentration in the rock sample is dependent on the distribution of these accessory minerals. A study of sampling errors caused by mineral distribution in rocks in the determination of uranium, carried out by *Ingamels* et al. [9], has shown that errors can be of the order of 100% or more. Hence sampling is an important factor to be considered during the analysis of uranium in geological samples, especially in granites.

Tab. 2. Comparative values of U (ppm) in geological samples

Sample	Present work	Values by other investigators	
		Mass spect. isotope dil. ^{233}U tracer	Other techniques
GMI-87,17	57·49	59[a], 58·48[a], 56·21[a], 56·69[a]	56·43[a], 56·5[b]
GMI-50,11	1378	1581[a], 1459[a]	1380[b]
S_{12}	134		140[c]
S_{17}	363·5		370[c]
S_{18}	756·5		770[c]

a) Isotope dilution alpha spectrometry[a]
b) Neutron activation analysis[a]
c) Values certified by International Atomic Energy Agency.

The present study provides a method for isotope dilution analysis of uranium with ^{233}U tracer, which is simple precise and accurate.

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4. References

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Tab. 1. Determination of uranium in geological samples

Sample number	Sample type	Mass of the sample [g]	Mass of the tracer [g]	(^{234}U+^{238}U)mixt.	Conc. U [ppm]
GMI-87,17	Granite, Wyoming USA	0·18029 0·19783	0·14297 0·19358	1·398 1·731	57·59 57·39
GMI-50,11	Granite, Wyoming USA	0·02020 0·02725	0·28977 0·43846	1·064 1·477	1368 1387
S_{12}	Pitchblende Albala Spain	0·07045 0·09173	0·47924 0·25211	1·863 2·171	139 129
S_{17}	Phosphate matrix uranium mineral	0·04494 0·02733	0·27365 0·24779	1·706 2·521	362 365
S_{18}	Phosphate matrix uranium mineral	0·04121 0·03649	0·29536 0·25196	0·960 0·927	757 756

Concentration of tracer = $9{\cdot}93 \cdot 10^{-5} \pm 2 \cdot 10^{-7}$ g of U/g of solution ($^{234}U/^{233}U$)tracer = $1{\cdot}15 \cdot 10^{-3} \pm 2 \cdot 10^{-5}$

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