

TRACE URANIUM ANALYSIS BY ISOTOPE DILUTION ALPHA AND MASS SPECTROMETRY AND COMPARISON WITH OTHER TECHNIQUES

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In this paper uranium determination by isotope dilution mass (MSID) and alpha spectrometry (ASID) using ^{233}U as an isotope diluent is discussed. In addition, a new form of MSID employing two tracers (^{235}U and ^{233}U) is developed, where two independent uranium values are obtained for single dilution. The precision and accuracy of each technique are evaluated by comparison with other techniques like X-ray fluorescence and instrumental neutron activation analysis. The techniques, employed here for geological samples, can easily be adapted for environmental materials.

1. Introduction

The high toxicity as well as the effect of radiation (mainly alpha particles) makes uranium an element that poses a serious hazard to health by accumulating in tissues, bones, liver and kidney [1]. Uranium in trace concentration is present in natural materials like rocks, minerals, soil, water, etc., and with the increasing exploration and exploitation the environmental monitoring of it is becoming more and more important.

Of all the techniques employed in the determination of uranium, namely fluorometry [2,3], radiometric [4], mass spectrometric [5] and neutron activation [6], mass spectrometric isotope dilution (MSID) alone has the advantage of high precision, sensitivity and freedom of matrix effects. However, the high cost and low output restricts it from being employed for routine analyses. On the other hand, application of the isotope dilution principle to alpha spectrometry (ASID) employing the natural alpha radiation of uranium isotopes results in a precise, accurate and relatively cheaper technique for the uranium analyses [7,8], but with low output due to long counting times needed for samples of low concentrations. In spite of the disadvantages, MSID and ASID could serve as monitors to judge other analytical techniques due to their high sensitivity, precision and accuracy.

In the present paper experimental details of MSID and ASID employed in the determination of uranium in geological samples are discussed. For these two techniques a tracer enriched in ^{233}U was employed, while a new form of MSID was developed with the addition of two tracers enriched in ^{233}U and ^{235}U [9]. In the latter variation of MSID two independent values for uranium are obtained in single dilution. The results of each technique are evaluated and their possible use for environmental samples discussed.

2. Principle of the technique

The basic principle of isotope dilution involves the addition of a known quantity of tracer with an isotope composition different from that of the sample. The concentration of the element can be calculated using standard equations [10,11] employing the isotope or alpha activity ratios measured in the sample, tracer and mixture. For the MSID with two tracers, the tracer solutions are added separately and in the equations correction factors are applied for the presence of ^{238}U in the tracers.

3. Experimental

The tracer solutions were prepared from isotope standards enriched in ^{233}U and ^{235}U supplied by CEA Fontenay-aux-Roses, France and the National Bureau of Standards (NBS), USA respectively. The solutions were calibrated by mass spectrometric isotope dilution technique using the uranium isotope standard (NBS U-950^a) with isotopic abundance of natural uranium.

Depending on the concentration of uranium, known amounts of tracers were added to the previously weighed sample. The procedures employed in the dissolution of the sample, separation and purification of uranium have already been discussed in our earlier publications [9,12]. For the mass spectrometric isotope analyses sample solutions in the form of nitrate were deposited on one of the side filaments of a double filament assembly in a Varian TH-5 mass spectrometer, with automated data acquisition and processing units.

For the alpha spectrometric measurements the uranium fraction was electrodeposited in a stainless steel disc and an Ortec dual spectrometer 576 was used for the analyses. With an energy resolution of 23 keV

(FWHM) at 5.486 MeV (^{241}Am) the activity ratios of alphas were measured in terms of the integrated area of the ^{238}U peak (4.195 MeV) and the sum of the peaks of ^{233}U and ^{234}U (~ 4.82 MeV). Long counting times of the order of 80000 s were needed because of the low activity of the samples.

4. Results and discussion

Uranium analyses in three mineral samples provided by the International Atomic Energy Agency and two granite samples from Wyoming, USA, were carried out by MSID and ASID techniques employing ^{233}U as tracer (table 1). Generally, for MSID analyses of geological samples, the tracer employed is enriched in ^{235}U , whereas ^{233}U is used in the analyses of nuclear fuel solutions. However, the application of ^{233}U tracer for geological samples makes the isotope dilution equation simpler, as $^{233}\text{U}/^{238}\text{U}$ in the sample is zero. From table 1 it can be observed that the precision of individual analyses, which depends mainly on isotope and activity ratio measurements, is of the order of 0.5% for MSID and 2% for ASID. The total precision obtained for most of the samples is found to be 1% for MSID and about 5% for ASID. The uranium values determined by both techniques agree well for all the samples except for S_{12} ,

where a large variation was observed between the two uranium values measured by MSID and ASID. This large variation can be attributed to the heterogeneous distribution of uranium in the samples, as various workers, using different techniques, also observed a similar variation [13]. The accuracies of the MSID and ASID techniques are evaluated by comparing the uranium values for the same samples measured by other workers using similar and different techniques (table 1). It can be seen that the agreement is good for most samples and for some samples like GM1(50, 11) there is a large variation resulting from the nonuniform distribution of radioactive minerals like zircon, apatite, monazite, etc., where uranium is mainly concentrated.

The two-tracer isotope dilution technique was developed to evaluate the distribution of uranium and in table 2 are shown the uranium values obtained in mineral samples. The samples have a concentration range from 2 to 4000 ppm and for each dilution two independent uranium values ($C_{\text{S}^{233}}$ and $C_{\text{S}^{235}}$) are obtained. These two values are in agreement, demonstrating the accuracy of the chemical procedures as well as the negligible effect of the mass fractionation in the isotope dilution analysis [14,15]. In the case of feldspar and zircon the triplicate analyses show a large spread in the values, which may be the result of the inhomogeneous distribution of uranium in these samples. Thus the technique is

Table 1
Uranium analysis of geological samples by MSID and ASID using ^{233}U as isotope tracer, and comparison with other techniques

Sample	Sample type	Uranium values [ppm]				
		Present work ($C_s \pm \sigma_{\text{in}}$) ^{a)}		Other investigators (C_s)		
		^{233}U tracer		^{235}U tracer	^{236}U tracer	Other techniques
		MSID	ASID	MSID	ASID	
GM1(87, 17)	Granite, Wyoming, USA	56.1 ± 0.2	51.7 ± 0.4	56.21 [16]	56.4 [16]	56.5 ^{b)}
		56.8 ± 0.2	57.7 ± 0.3			
		56.6 ± 0.2	56.4 ± 0.3	59 [5]		
S_{12}	Pitchblende, Albala, Spain	144.5 ± 0.5	113 ± 3	–	–	119 ^{c)}
		137.6 ± 0.4	123 ± 3			
S_{17}	Phosphate, matrix uranium mineral	360 ± 2	351 ± 2	–	–	370 ^{c)}
		364 ± 2	416 ± 2			
S_{18}	Phosphate, matrix uranium mineral	761 ± 4	797 ± 7	–	–	770 ^{c)}
		755 ± 4	797 ± 8			
		753 ± 3	795 ± 9			
GM1(50, 11)	Granite, Wyoming, USA	1364 ± 8	1558 ± 40	1459 [16]	1378 [16]	–
		1383 ± 6	1518 ± 30	1581 [5]	–	–
		1453 ± 5	1558 ± 30			

a) σ_{in} = internal standard deviation.

b) M.B.A. Vasconcellos, private communication (1987).

c) Values certified by IAEA.

Table 2
Uranium analyses of mineral samples by MSID with addition of two tracers (^{233}U and ^{235}U), and comparison with other techniques

Sample	Uranium values [ppm]		Other techniques	
	Present work MSID tracers ($^{233}\text{U} + ^{235}\text{U}$)		XFR ^{b)}	INAA ^{c)}
	^{233}U tracer	^{235}U tracer		
	$C_{\text{S}}^{233} \pm \sigma_{\text{in}}^{\text{a)}$	$C_{\text{S}}^{235} \pm \sigma_{\text{in}}^{\text{a)}$		
Feldspar	3.23 ± 0.02	3.170 ± 0.010	5	2.21
	2.46 ± 0.01	2.498 ± 0.020		
	2.32 ± 0.01	2.360 ± 0.008		
Phosphorite	102.4 ± 0.3	103.7 ± 0.4	107	101
	103.2 ± 0.3	103.5 ± 0.5		
	102.6 ± 0.3	103.1 ± 0.8		
Zircon	244.8 ± 0.7	246 ± 1	210	257
	231.0 ± 1.0	230 ± 1		
	254.2 ± 0.8	251 ± 1		
Monazite	1929 ± 6	1952 ± 10	1740	1780
	1885 ± 6	1891 ± 7		
	1862 ± 10	1865 ± 10		
Caldasite	3848 ± 30	3836 ± 25	4000	3850
	3857 ± 10	3878 ± 20		
	3860 ± 20	3850 ± 20		

^{a)} σ_{in} = internal standard deviation.

^{b)} V.L.R. Salvador, private communication (X-ray fluorescence analysis) (1987).

^{c)} M.B.A. Vasconcellos, private communication (instrumental neutron activation analysis) (1987).

capable of identifying the nature of the distribution of uranium within the sample. On the average, the total precision of the technique is of the order of 1%. To check the accuracy of the technique the uranium values are compared (table 2) with those obtained by other techniques like X-ray fluorescence and neutron activation and the values are in agreement.

The study has shown that MSID and ASID using ^{233}U as a tracer and MSID with two tracers are techniques that yield high precision and accuracy for complex matrices like rocks and minerals and as such they can be easily adapted for other types of environmental materials like soil, water, etc. MSID cannot be used as a routine technique due to its high cost and low output. In the case of ASID the cost is relatively low but counting times are higher for samples with low concentrations of uranium. By processing large quantities of samples and preconcentrating uranium, the counting times can be reduced and thus the number of samples analysed in a given time may be increased. In the isotope dilution technique a knowledge of the percentage of chemical recovery of the element being studied is not necessary and hence such a processing will not affect the precision and accuracy of the technique. This is very useful for liquid samples. The ASID technique has an added advantage in that the alpha spectrometry provides information about other alpha emitting nuclides in the samples.

5. Conclusion

Mass spectrometric and alpha spectrometric isotope dilution techniques using a ^{233}U tracer yield precise and accurate values for uranium in geological samples. The MSID technique with two tracers yields two independent uranium values in a single dilution and is thus capable of verifying the uranium distribution in a sample. These techniques, generally employed for geological materials, can easily be adapted for other environmental materials. MSID can be used to monitor the precision and accuracy of other techniques whereas ASID can be employed for routine analyses.

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