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ISOTOPE DILUTION ALPHA SPECTROMETRY WITH SPIKE ENRICHED IN ^{233}U FOR THE DETERMINATION OF URANIUM IN GEOLOGICAL SAMPLES

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Isotope dilution alpha spectrometric /IDAS/ method has been developed for the determination of uranium in geological materials. The spike employed was uranium enriched in the isotope 233. The results of the analysis for rock and ore samples show that the precision and accuracy of the method are comparable to other analytical techniques and the method can be employed for routine analysis.

INTRODUCTION

Interest in accurate and precise methods for the determination of uranium and thorium in natural materials, especially geological samples, is ever increasing due to their application in the field of U-Th-Pb systematics, which can add valuable data to the investigation of proposed repositories for high level radioactive waste[1].

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Added to that these determinations are important in uranium exploration as well as for environmental monitoring. Of all the methods employed in the determination of the concentration of uranium, mass spectrometric isotope dilution /MSID/ offers the greatest advantage in term of precision and accuracy[2]. However, the method is expensive and cannot be employed for routine analysis. Stuckless et al.[3] have shown that alpha spectrometry, combined with isotope dilution, offers adequate accuracy and that the technique can measure the long lived isotopes in the decay chain /^{238}U, ^{234}U, ^{230}Th/ which is useful in distinguishing radioelement disequilibria[4]. The isotope spike employed by Stuckless et al.[3] was uranium enriched in the isotope 236, which is expensive and difficult to obtain. Hence in the present work an attempt is made to use the more commonly available spike enriched in ^{233}U.

The details of the experimental procedures adopted in the dissolution, isotope dilution, chemical separation, electrodeposition, alpha activity measurement and the calculation of the results are presented in this work. The precision and accuracy of the method are evaluated by comparison of results obtained by other methods for the same samples.

EXPERIMENTAL

In Figure 1 are shown the various experimental steps involved in the determination of uranium by isotope dilution alpha spectrometry. The spike used is prepared from ^{233}U supplied by CEA Fontanay, France and is calibrated by mass-spectrometric isotope-dilution method and the concentration is found to be $4.80\times10^{-8}\pm2\times10^{-10}$

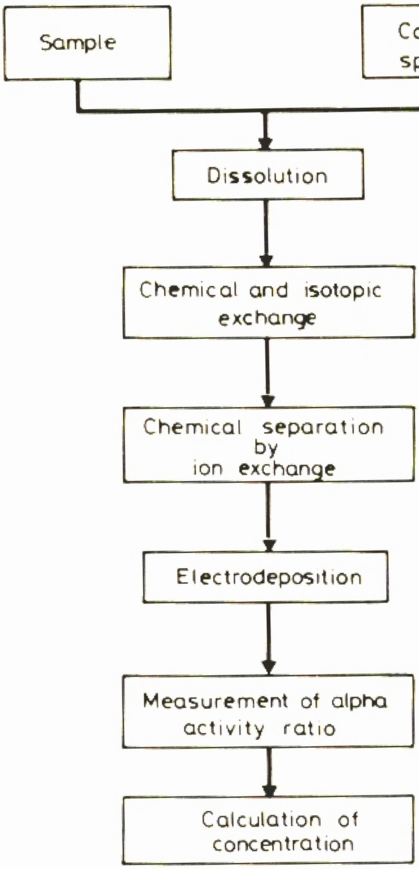

Fig. 1. Schematic diagram of the experimental steps involved in the determination of uranium by IDAS

g U/g sol. Weighed amounts of sample and spike are subjected to dissolution and chemical separation procedure[5] and the separated uranium fraction is electrodeposited in a stainless steel disc and the experimental conditions employed for the electrodeposition are given in Table 1.

TABLE 1

Experimental conditions employed in the electrodeposition of uranium

Electrolyte	NH_4Cl
Volume and concentration of electrolyte	5 ml, 3N
Current density	0.8 A cm^{-3}
pH of solution /sample and electrolyte/	1.0
Distance between the electrodes	0.5 cm
Time of electrodeposition	90 min

MEASUREMENT

The alpha measurements are carried out with an ORTEC dual alpha spectrometer model 576 coupled to a multichannel analyzer and data processing equipment. The energy resolution of 23 keV /FWHM/ at 5.486 MeV /^{241}Am/ was obtained under routine conditions. As the alpha energies of ^{233}U and ^{234}U peaks overlap the ratio of the activities of alpha is measured in terms of the integrated area of the alpha peak of ^{238}U /4.195 MeV/ and the sum of the peaks of ^{233}U and ^{234}U /∿4.82 MeV/. The equation employed in the calculation of the concentration of uranium is:

$$C_s = C_{sp} \cdot \frac{m_{sp}}{m_s} \cdot \frac{M_s \, [/FA_3/_{sp}\lambda_3 + /FA_4/_{sp}\lambda_4]}{M_{sp}[/FA_8/_s\lambda_8]} \cdot \frac{1-R_M R_{sp}}{R_M - R_s} \qquad /1/$$

where:

C_s, C_{sp} = concentration of U in the sample and the spike solution, respectively (g U/g sol.);

m_s, m_{sp} = masses of sample and spike, respectively /g/;

M_s, M_{sp} = atomic masses of U in the sample and the spike, respectively /g/;

$\lambda_3, \lambda_4, \lambda_8$ = alpha decay constants of ^{233}U, ^{234}U and ^{238}U, respectively;
$/FA_8/_s$ = atomic fraction of ^{238}U in sample;
$/FA_3/_{sp}$, $/FA_4/_{sp}$ = atomic fraction of ^{233}U and ^{234}U in the spike solution, respectively;
R_{sp} = alpha activity ratio of $^{238}U/(^{233}U+^{234}U)$ in spike;
R_s, R_M = alpha activity ratio of $(^{233}U+^{234}U)/^{238}U$ in the sample and mixture, respectively.

The samples were counted for 80,000 sec due to the low activity of ^{238}U and the uranium values obtained were corrected for reagent and other blanks.

RESULTS AND DISCUSSION

The analytical data for the determination of uranium in two granite and two pitchblende samples are shown in Table 2. In order to reduce uncertainty in the factor $/R_M-R_s/$ in Eq. /1/, a change in the activity ratio of R_M in the spiked samples by at least ten times the initial values of the unspiked sample would be necessary[6] and as can be seen from Table 2 such values are obtained in the analysis. The concentration of uranium in the sample shows an internal precision about 2% and a total precision is about 5% for all the samples, except for S_{17} for which it is about 10%. In order to evaluate the accuracy of the method, the results are compared with the values obtained for the same samples by isotope dilution mass spectrometry with ^{233}U /Ref. 5/ and ^{235}U /Ref. 7/ spike, isotope dilution alpha spectrometry with ^{236}U spike[4] and other techniques /Table 3/. The results obtained in the present study seem to agree well with those by the different techniques. A large

TABLE 2

Determination of uranium in geological samples by the IDAS technique with ^{233}U spike

Sample	Mass /g/		Activity ratio $(^{233}U + {}^{234}U)/^{238}U$ in mixture $(R_{3+4/8})_M \pm S_{in}$	Concentration of uranium in sample $C_A \pm S_{in}$ /ppm/	Mean concentration of uranium in sample $C_A^{*} \pm \sigma$ /ppm/
	Spike m_{sp}	Sample m_s			
GM1 /87,17/	0.57980	1.51410	11.08 ± 0.06	54.0 ± 0.4	55 ± 3
	0.71858	1.50113	12.24 ± 0.01	60.0 ± 0.3	
	0.70526	1.50388	12.34 ± 0.01	58.7 ± 0.3	
S_{12}	0.51741	0.59188	11.8 ± 0.3	115 ± 3	118 ± 7
	0.58409	0.58770	12.2 ± 0.2	125 ± 3	
S_{17}	0.56174	0.26974	9.46 ± 0.02	353 ± 2	383 ± 39
	0.67957	0.28600	9.17 ± 0.01	418 ± 2	
S_{18}	0.65291	0.13619	9.59 ± 0.04	799 ± 7	759 ± 5
	0.55509	0.12505	9.00 ± 0.04	799 ± 8	
	0.66474	0.13099	10.10 ± 0.08	797 ± 9	
GM1 /50,11/	0.63666	0.06088	10.56 ± 0.06	1560 ± 40	1544 ± 27
	0.68285	0.06827	10.38 ± 0.03	1520 ± 30	
	0.67876	0.06920	9.98 ± 0.04	1560 ± 30	

C_A^{*} = values corrected for reagent blank.

. Alpha activity ratio of $^{238}U/(^{233}U + {}^{234}U)$ in spike = $4.11 \times 10^{-8} \pm 1 \times 10^{-10}$

. Alpha activity ratio of $(^{233}U + {}^{234}U)/^{238}U$ in sample = 1

TABLE 3

Comparison of uranium values by IDAS with different techniques

Sample	Present work IDAS ^{233}U spike	Values found in the literature IDAS ^{236}U spike	IDMS ^{233}U spike	IDMS ^{235}U spike	Other techniques
GM1 /87,17/	55 ± 3	56.4[4]	57.49[5]	59[7]; 56.21[4]	56.5[11]
S_{12}	118 ± 7	-	134[5]	-	119[a]
S_{17}	383 ± 39	-	363.5[5]	-	370[a]
S_{18}	795 ± 5	-	756.5[5]	-	770[a]
GM1 /50,11/	1544 ± 27	1378[4]	1378[5]	1581[7];1459[4]	-

- Values certified by International Atomic Energy Agency[a].

variation in the uranium value observed for sample GM 1 /50,11/ is due to the heterogeneous distribution of uranium in the sample and this has an important implication in sampling methods[4,5,8]. The precision and accuracy obtained in the present work is of the same order as obtained by Stuckless et al.[3] using spike enriched in ^{236}U demonstrating that spike enriched in ^{233}U can also be applied for routine uranium determination in geological and other samples. The method is simple and relatively less expensive compared to MSID. The precision and accuracy of the method can be improved by different deposition techniques[9] and correction procedures for the contribution of tail in the alpha spectrum[10].

CONCLUSION

Uranium enriched in ^{233}U can be employed as a spike in accurate and precise determination of uranium by isotope-dilution alpha spectrometry. The sample spike has the advantage of serving as an isotope diluent in the uranium determination by isotope-dilution mass spectrometry. The accuracy and precision of the method are comparable to other techniques like delayed neutron, X-ray fluorescence, neutron activation, etc.

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