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## ABSTRACT

Interest in the development of analytical techniques for the accurate determination of trace levels of uranium in natural samples is due to the importance of this element in many geochemical, geophysical and environmental studies. Mass spectrometric isotope dilution and alpha spectrometric isotope dilution techniques were developed in our laboratory for the accurate determination of uranium in rock and mineral samples. The experimental details involved in the determination of uranium by these methods are described and the results obtained for rock and mineral samples, with a concentration of uranium in the range of 2 to 2000 ppm, are discussed in relation to their precision and accuracy. The uranium concentration in some samples were also measured, in other laboratories, by non-destructive techniques like X-ray fluorescence and neutron acti-

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(*) Paper present at "V Encontro Nacional de Química Analítica" - Salvador - Brazil, Sept. 4-6, 1989.

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vation. A general comparison of the techniques is made based on the factors like, precision, accuracy, limit of detection, time and cost of analysis. Finally, problems arising from non-homogeneous distribution of uranium are discussed and suggestions to overcome these problems are offered.

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## RESUMO

O interesse no desenvolvimento de técnicas analíticas para a determinação precisa de urânio, em nível de traços, em amostra natural é devido à importância deste elemento em muitos estudos da geoquímica, geofísica e ambiental. Desenvolveu-se, em nosso laboratório, as técnicas de diluição isotópica por espectrometria de massa e por espectrometria alfa para a determinação precisa de urânio em amostras de rocha e mineral. Os detalhes experimentais envolvidos na determinação de urânio por esses métodos são descritos e os resultados obtidos nas amostras de rocha e mineral, com concentração de urânio na faixa de 2 a 2000 ppm, são discutidos em relação as suas precisões e exatidões. A concentração de urânio em algumas dessas amostras foram também medi-

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(*) Trabalho apresentado no "V Encontro Nacional de Química Analítica" - Salvador - Brasil, de 4 a 6 de setembro de 1989.

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das, em outros laboratórios, por técnicas não destrutivas como a fluorescência de raios-X e ativação de neutrons. Apresenta-se uma comparação geral das técnicas, considerando fatores como precisão, exatidão, limite de detecção, tempo e custo de análise. Finalmente, discute-se os problemas da distribuição heterogenea de urânio nas amostras apresentando sugestões para contornar esse efeito.

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## 1. INTRODUCTION

The importance of the accurate determination of trace amounts of chemical elements and their isotopes in physical, chemical and biological systems has resulted in the development of analytical methods capable of providing high precision, accuracy, sensitivity, large range of detection, and freedon from matrix effects. Mass spectrometric isotope dilution (IDMS) is one such technique and has an added advantage of providing the values for isotope abundances. The isotope dilution technique is based on the variation in the isotopic composition of an element due to the addition of a known concentration of a tracer solution and from this variation the elemental concentration is calculated. The isotopic composition of the tracer should be relatively different from that of the sample. The principle of isotope dilution can also be extended to alpha spectrometry (IDAS), excepting that in the IDMS, isotope ratios are measured, whereas in the IDAS ratio of the activities of alpha particles are made use of (Ramaniah et al, 1980). The present study describes the determination of uranium in geological samples by these two techniques. A tracer enriched in $^{233}$U was employed for both MSID and ASID. A new form of MSID was developed with the addition of two tracers in $^{233}$U and $^{235}$U (Shihomatsu et al, 1988). This technique provides two independent uranium values for a single dilution, which helps in distinguishing between sampling and analytical errors. A general comparison with other techniques, like XRF and neutron activation, is made.

## 2. EXPERIMENTAL PROCEDURE

The figure 1 shows schematically experimental steps involved in the determination of uranium by MSID and ASID.

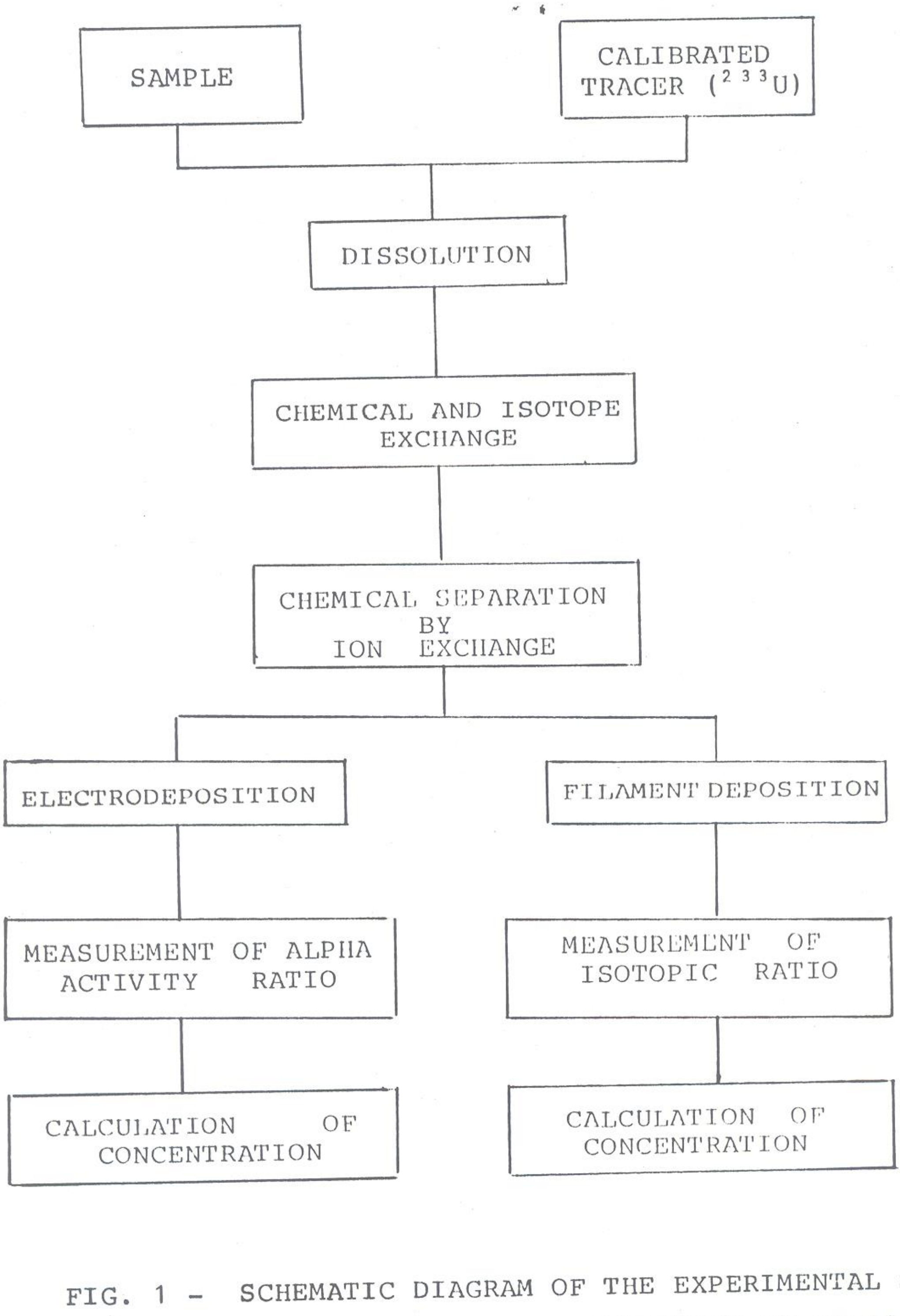

FIG. 1 - SCHEMATIC DIAGRAM OF THE EXPERIMENTAL STEPS INVOLVED IN THE DETERMINATION OF URANIUM BY MSID AND ASID

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## 2.1 Preparation and Calibration of Tracers Solutions

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

## 2.2 Dissolution

The procedure adopted is based on the work of Patchett and Tatsumoto (1980). The mixture containing the sample and the tracer was dissolved in a pressure vessel made up of teflon becker and cap, which was kept inside a stainless steel outer cover. The acid digestion was carried out using a mixture of 40% HF, conc. $HNO_3$ and 72% $HC\ell O_4$.

## 2.3 Chemical Separation

The uranium was separated by two stage ion exchange method. In the first stage uranium was separated from thorium (Krtil et al, 1975) 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 (Boase et al, 1961).

## 2.4 Mass Spectrometric Procedure

Varian MAT TH5 solid source thermoionic mass spectrometer, coupled to a microcomputer for data acquisition and processing, was employed for the isotope abundance measument. The nitrate solutions were deposited on one of the side filaments of a double filament assembly and the $^{233}U/^{238}U$ and $^{235}U/^{238}U$ ratios were measured.

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## 2.5 Alpha Spectrometer Procedure

An ORTEC model 576 surface barrier detector coupled to a 4096 channel analyser was employed for the alpha spectrometric measurements. The solutions in the form of nitrates were electrodeposited (Veselsky, 1974) on a stainless steel disc (see table 1) and the activity ratio of $^{233}U + ^{234}U/^{238}U$ was measured.

## 3. RESULTS

Uranium analyses in rock and mineral samples by IDMS and IDAS are presented in Table 2 and 3. The values obtained are compared with the measurements carried out on the same samples by other investigators using similar and different techniques (X-ray fluorescence and neutron activation analysis). From the comparison following results are obtained:

a) The precision of individual analysis is 0.5% for IDMS and 2% for IDAS, whereas the total precision obtained is 1% for IDMS and about 5% for IDAS.

b) The uranium values obtained by both the techniques agree well for most of the samples and the discrepency for the samples $S_{12}$ and GM 1 (50,11) is due to the sampling problems. The uranium values measured also agree with those obtained by other workers.

c) The two independent uranium values obtained for two tracer IDMS (Table 3) agree well, demonstrating the accuracy of chemical procedures and negligible effect of mass discrimination.

d) The large spread in the values for zircon and feldspar is due to the inhomogeneous distribution of uranium in these samples.

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TABLE 1. EXPERIMENTAL CONDITIONS EMPLOYED IN THE ELECTRODEPOSITION OF URANIUM

| | |
|---|---|
| ELECTROLYTE | $NH_4Cl$ |
| VOLUME AND CONCENTRATION OF ELECTROLYTE | 5ml, 3N |
| CURRENT DENSITY | 0.8A/cm$^3$ |
| pH OF SOLUTION (SAMPLE AND ELECTROLYTE) | 1,0 |
| DISTANCE BETWEEN THE ELECTRODES | 0.5cm |
| TIME OF ELECTRODEPOSITION | 90 min. |

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## 4. DISCUSSION AND CONCLUSION

The IDMS and IDAS are two techniques capable of satisfying the need of accurate and precise methods for trace element analysis. The two tracer IDMS has the added advantage of providing two independent values, where analytical procedure can be monitored. These methods, applied here for geological samples, can be adopted to any physical, chemical or biological system.

A general comparison of the different analytical techniques based on the measurement of uranium shows that IDMS technique is one that offers high precision, accuracy and low limit of detection. But the major disadvantages are long time and high cost involved in the analysis. However, microwave dissolution techniques and fully automated mass spectrometers are able to reduce the time of analysis. Thus it is recommended that IDMS technique is used as a standard method to compare other routine method. The IDAS technique is a relatively cheaper method, but the counting times are higher for samples with low uranium concentration. This problem may be overcome by processing large amounts of sample and using more efficient detectors. The IDAS technique may be employed as a routine method.

One of the major problem of the analysis of uranium in geological samples is its heterogeneous distribution and the present study has clearly shown that two tracer IDMS is capable of distinguishing errors resulting from this effect. We are also developing multitracer IDAS to study this effect and the preliminary results are encouraging.

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TABLE 2. COMPARISON OF URANIUM VALUES BY MSID AND ASID USING $^{233}U$ TRACER WITH OTHER TECHNIQUES

| SAMPLE | THIS WORK | | VALUES OF THE LITERATURE | | |
|---|---|---|---|---|---|
| | $^{233}U$ TRACER | | MSID | ASID | OTHER |
| | MSID | ASID | $^{235}U$ TRACER | $^{236}U$ TRACER | TECHNIQUES |
| GM1(87,17) | 56.5 ± 0.4 | 55 ± 3 | 56.21[7]; 59[2] | 56.4[7] | 56.5[a] |
| $S_{12}$ | 141.4 ± 0.5 | 118 ± 7 | -- | -- | 119[b] |
| $S_{17}$ | 362 ± 2 | 383 ± 39 | -- | -- | 370[b] |
| $S_{18}$ | 756 ± 4 | 795 ± 5 | -- | -- | 770[b] |
| GM1(50,11) | 1400 ± 47 | 1544 ± 27 | 1459[7]; 1581[2] | 1378[7] | -- |

a - Vasconcellos,M.B.A. (Pers. Commun., 1987)

b - Values certified by International Atomic Energy Agency

Obs: Values are in ppm.

TABLE 3. COMPARISON OF THE AVERAGE URANIUM VALUES IN ppm OBTAINED BY TWO TRACERS MASS SPECTROMETRIC ISOTOPE DILUTION TECHNIQUE WITH OTHER TECHNIQUES

| SAMPLE | THIS WORK MSID TRACERS $^{233}U$ and $^{235}U$ | | OTHER TECHNIQUES | |
|---|---|---|---|---|
| | TRACER $^{233}U$ $C_{S^{233}}$ | TRACER $^{235}U$ $C_{S^{235}}$ | XRF[a] | INAA[b] |
| FELDSPAR | 2.7 ± 0.5 | 2.7 ± 0.4 | <5 | 2.21 |
| PHOSPHORITE | 102.7 ± 0.4 | 103.4 ± 0.3 | 107 | 101 |
| ZIRCON | 243 ± 12 | 242 ± 11 | 210 | 257 |
| MONAZITE | 1892 ± 34 | 1903 ± 44 | 1740 | 1780 |
| CALDASITE | 3856 ± 6 | 3855 ± 21 | 4000 | 3850 |

a - Salvador, V.L.R. - 1987 Pers. Comun. (X ray fluorescence analysis)

b - Vasconcellos, M.B.A. - 1987 Pers. Comun. (Instrumental Neutron Activation Analysis)

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