TWO TECHNIQUES USING MAKROFOL ® KG FOR MEASUREMENT OF URANIUM LOW CONCENTRATIONS

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ABSTRACT

The fission track registration technique using Makrofol KG as detector and the wet and dry methods were developed for the determination of microgram amounts of uranium in several samples. These methods allows the determination of uranium concentrations within the interval of 8.0 to 0.4 μg U/l (wet method) and 7.6 to 0.9 μg U/l (dry method), with a overall error ranging from 3.3% to 29.0% and 2.7% to 23% respectively. Results obtained for water, hair, urine and botanic samples are reported.

KEYWORDS

Track detector; Makrofol; uranium determination; chemical etching; track counting.

INTRODUCTION

It was developed two techniques using the solid state fission fragments track detector Makrofol KG(R) for determination of uranium concentration in order of μg U/l: the "wet" method and the "dry" method. The "wet" method was used in analysis of water and botanic samples and the "dry" method was used for measurements of uranium concentration in hair and urine samples. The experimental procedure consists in the exposure simultaneously to a neutron flux of a unknown concentration sample and a standard sample, in contact, each one, with the detector. A direct relation between track densities gives the unknown concentration. The samples were treated to ensure the transformation of all the uranium in uranyl nitrate. The resulting solution was adjusted to the pH ~1 by adding HNO_3(5%) to avoid clusters of tracks in the detector.

PROCEDURES

Solution Preparation

For this experiment several samples was prepared from an uranium standard solution whose concentration determined by the gravimetric dilution method was 10^{-4}mg U_3O_8/ml. These solutions were used in the detector calibration, in the neutron flux monitoring and in the determination of the uranium content in unknown samples.

Irradiation

The irradiations were performed at the IEA-R1, 2 MW pool type research reactor.The thermal neutron flux measured with gold foils at the irradiation position (GI) was 7.2 x 10^{12}n/cm^2.s and the cadmium ratio was 4.2. In "wet" method the sample containers were polystirene vials holding about 50ml of solution. The Makrofol(10 μm thickness foils) was used in the form of a strip(2.5 x 22.0 cm) and was zigzag fixed in a lucite support by means of cloroform. The solution with known uranium concentration(monitor and/or standard) was irradiated simultaneously with the sample in analysis. The irradiation time of 30 minutes was used for all samples, since this time was found to be convenient for samples analysis with uranium concentration of the order of microgram per liter. In "dry" method 10 μl of the sample and 5 μl of Teepol(R) detergent 0.1% were dried over the detector foil using a rotating platform beneath a infrared lamp. This procedure avoid the ring of tracks formation. For each sample was prepared a number of sandwiches(a deposition covered with a clear Makrofol - 10 μm thickness foils) and between two sandwiches there was a Makrofol 40 μm thickness foil. This have been to avoid the fission fragments influence of the deposit neighbour. The set of unknown and standard sample series were irradiated in a polypropilene container. In this case, the irradiation time used was only 8 minutes.

Chemical Etching

After the irradiation the Makrofol foils were etched in a KOH solution(1.223 g/ml) at a temperature of 60°C. Eight irradiation of 30 minutes each were performed for HNO_3(.3M) solutions to determine the etching time. The HNO_3(0.3M) solution was chosen because it was the reagent blank. Best results were obtained for 12 minutes etching time(Fig. 1). During the etching a mechanical stirrer was used in order

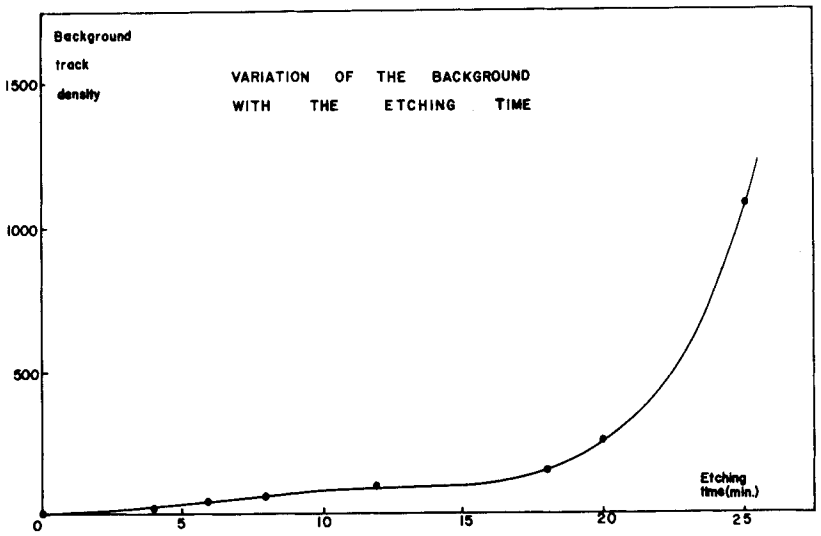

Fig. 1. Variation of the background with the etching time in KOH solution(1.223 g/ml) at 60°C, for a Makrofol foil (10 m).

to keep the solution in continuous motion. In this way, the probability of the etched products remaining on the detector surface and forming a protective layer was reduced.

Track Counting

The total number of tracks was counted in an automatic discharge chamber. Initially 1300 V were applied in order that all the holes in the Makrofol were completely opened. Then a count in a scaler was made applying 550 V in a predetermined area (2.8 cm^2). For scanning conditions a reproducibility around 0.2% was found. As the uranyl nitrate is a uniform solution, it is enough scan some areas of the Makrofol foil, in the "wet" method. For the "dry" method, on the contrary, all the detector area is scanned, because the deposit is nearly always heterogenous.

Detector Calibration

In the "wet" method the detector calibration was obtained performing 14 irradiations of uranium solutions, with concentrations ranging from 8.0 x 10^{-6}mg U/ml to 0.4 x 10^{-6}mg U/ml. The same irradiation period (30 minutes) was used for all the solutions in order to have a better radiation damage control. In Fig. 2 one can see the experimental results and the adjusted straight line. Using this calibration curve, the samples can have the concentrations determined with an overall error ranging from 3.3% to 29.0%, for concentrations within the interval considered. The higher the concentration the lower the errors. In the "dry" method, nine standard solutions

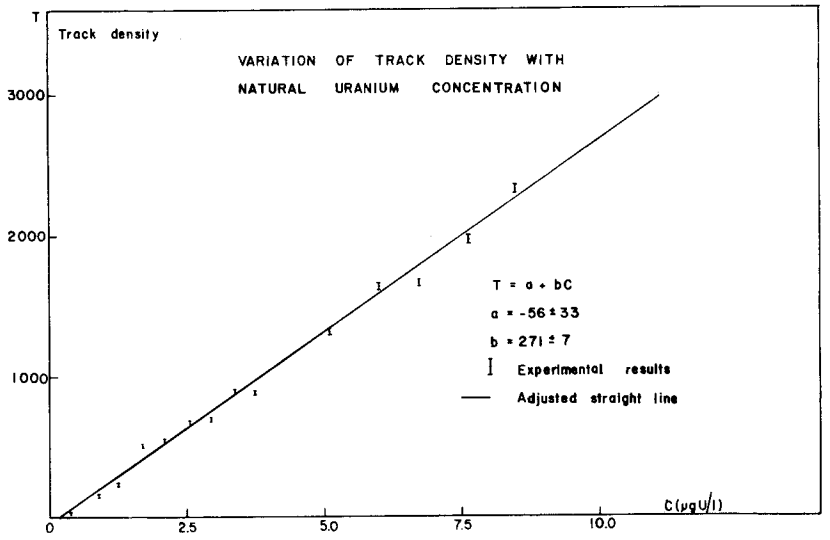

Fig. 2. Variation of track density with natural uranium concentration-wet method.

with concentration ranging from 7.6 x 10^{-6}mg U/ml to 0.9 x 10^{-6}mg U/ml, were utilized. The track density obtained was plotted against uranium concentration in Fig. 3. For concentrations within the interval considered the overall error range from 2.7% to 23%.

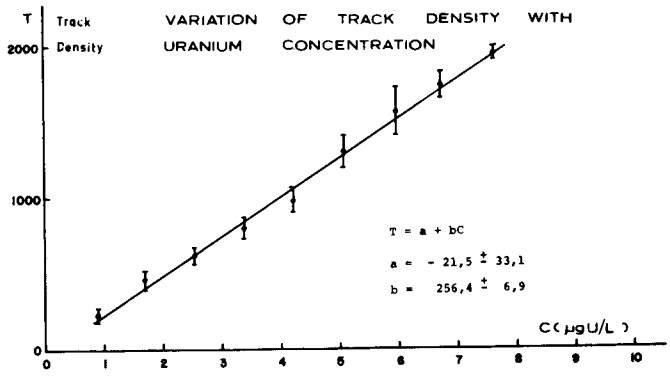

Fig. 3. Variation of track density with natural uranium concentration-dry method.

The Methods Applications

The "wet" method described was used in the determination of the uranium content in various water samples, obtained from several sources like rivers, sea, mineral waters and in eucalyptus tree, in the São Paulo state, Brasil.

River waters. The uranium concentrations of river waters are not expected to be constant. Therefore, the range determined by us is in reasonable agreement with other authors and methods(Table 1), considering the fact that the samples analysed were completely different ones. A high value of uranium (1.67 μg U/l) was obtained in Juqueri river and is presumed to be due to uranium occurrence in the collect area (Moraes, 1956).

TABLE 1. Ranges of Uranium in River Waters

Rivers	Range (μg U/l)	Method
Japan (Miyake, 1964	0.34 - 1.23	Absorption spectrophometric
U.S.A. (Bertine, 1970)	0.01 - 1.22	Fission tracks in Lexan
Brasil	0.29 - 1.67	This work

Mineral waters. The variation in the uranium concentration obtained in mineral waters was 0.45 to 2.30 μg U/l. These values are within the range of 0.1 to 120 μg U/l, determined by (Scott, 1958) in ground water of the United States.

Sea water. The sea water samples were obtained near São Paulo coast, in the Ubatuba region. The average uranium content in sea water is in good agreement with the average values determined by other authors (Table 2). Thus it has been confirmed that the uranium content of normal sea water is constant, within the limits of experimental error, irrespective of location and depth.

TABLE 2 Average Uranium Concentration in Sea Water

Author	Method	µg U/l
Hashimoto (1971)	Fission track in muscovite	3.40 ± 0.12
Rona (1956)	Isotopic dilution (mass spect.)	3.39
Wilson (1960)	Pulse polarographic	
	Isotopic dilution	
	Fluorimetric	3.33 ± 0.08
This work	Fission track in Makrofol	3.27 ± 0.12

Eucalyptus tree. The results obtained with eucalyptus tree samples in Table 3, are according to Carpenter, that found a range of 1.6 to 15.2 ppm, in leaves of the white oak.

TABLE 3 Uranium in Eucalyptus Tree

Samples	Range (ppm)
eucalyptus tree leaves	1.5 to 6
eucalyptus tree stem	15 to 24

The "dry" method was used in the analysis of uranium content in hair and urine samples, obtained from several persons of the Instituto de Energia Atômica (IEA). For a comparative study also have been made analysis of sea water samples by this method. The average value measured was 3.0 ± 0.4 µg U/l, that is in good agreement with 3.27 ± 0.12 µg U/l obtained by "wet" method and with average determined by other authors, within the limit of experimental error.
Hair samples. The values found (Table 4), are in direct relation with the working areas where the uranium ores are handled in great amounts. This correspondence also was found by Atalla (1970), using the activation analysis method.

TABLE 4 Uranium in Hair Samples

Areas	Range (µg U/l)
Chemistry Engineering Area	3.8 to 9.2
Nuclear Metallurgy Area	2.4 to 4.6
Administration Area	0.14 to 0.26

Urine samples. These samples, firstly were analysed by Passarelli(1977) using fluorimetric method. The results of this author are lower than 5 µg U/l, that is the limit of method sensibility. The range determined by us was 1.4 to 4.5 µg U/l,that is also lower than 5 µg U/l, hence, according to Passarelli (1977).

CONCLUSION

The methods developed in this work are quick and inexpensives for determining uranium at concentration of micrograms per liter, in the samples studied or in any material that can be reduced to an uranyl nitrate solution.

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