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BY THE FISSION TRACK REGISTRATION TECHNIQUE**

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CENTRO DE OPERAÇÃO E UTILIZAÇÃO DO REATOR DE PESQUISAS
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DETERMINATION OF URANIUM CONCENTRATION
IN WATER SAMPLES
BY THE FISSION TRACK REGISTRATION TECHNIQUE

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The fission track registration technique using Makrofol KG as detector and the wet method was developed for the determination of microgram amounts of uranium in water samples. This method allows the determination of uranium concentrations within the interval of 8.0 to 0.4 $\mu\text{g U/l}$, the overall ranging from 3.3% to 29.0%. Results obtained for water samples from several sources in the State of São Paulo, Brasil, are reported.

Introduction

The feasibility of uranium determinations using induced fission tracks in a suitable detector was first shown by PRICE and WALKER in 1963.¹ Since then many applications² of the procedure have been reported in the literature.

In this paper we describe the determination of uranium at concentrations of micrograms per liter, using the wet method and an automatic discharge chamber.

The determination of uranium concentration in water is of considerable interest to oceanographers, geologists and nuclear scientists for various reasons, such as:

- (1) Searching for a new source of nuclear fuel in sea-water;
- (2) Development of a new technique for uranium prospection in the case of river waters;
- (3) Information for Public Health Services and Health Physicists, in the case of mineral and tap waters.

The experimental procedure consists in the exposure to a neutron flux of a uranium solution with the Makrofol detector immersed in it.

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The track density T (number of tracks/cm²) recorded by the detector is related to the uranium concentration in the solution through the equation:

$$T = K \frac{C}{M} A \sigma_f \Phi t$$

where K – track registration efficiency;
 C – concentration of the uranium solution, g/cm³;
 M – atomic weight of natural uranium, g;
 A – Avogadro's number;
 σ_f – fission cross-section, cm²;
 Φ – neutron flux, n · cm² · s⁻¹;
 t – irradiation time, s.

Having a standard sample of known uranium concentration (C_p), the uranium concentration of an unknown sample (C_x) is determined from the equation:

$$C_x = C_p \frac{T_x}{T_p}$$

where T_x and T_p are the track densities of the unknown and standard sample, respectively.

The influence of thorium, which is the other natural nuclide undergoing a fission reaction with reactor neutrons, was not taken into consideration since the thorium content of water is usually very low ($\sim 10^{-4}$ μg/l)³ compared with the uranium content. Moreover, thorium undergoes a fission reaction only with fast neutrons of energies higher than 1.2 MeV ($\sigma_f = 0.078$ b for fast neutrons).

Experimental

Solutions preparation

For this experiment several samples were prepared from a uranium standard solution whose concentration determined by the gravimetric dilution method was 10^{-4} mg U₃O₈/ml. These solutions were used in the detector calibration, in neutron flux monitoring and in the determination of the uranium content in unknown samples.

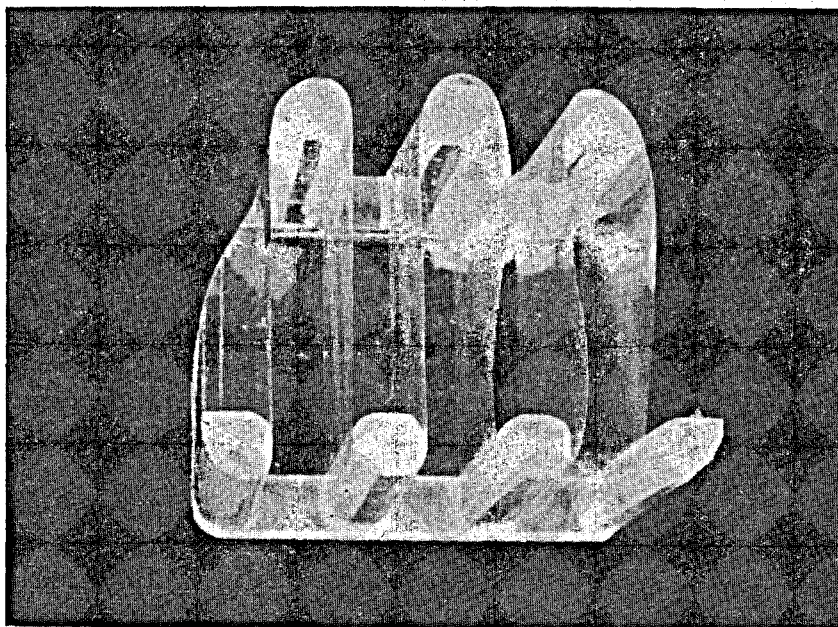


Fig. 1. The detector assembly. A Makrofol strip fix in a lucite support

Irradiation

The irradiations were performed in an IEA-R1, 2 MW pool type research reactor. The thermal neutron flux measured with gold foils at the irradiation position (GI) was $7.2 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ and the cadmium ratio was 4.2.

The sample containers were polystyrene vials holding about 50 ml of solution. The Makrofol detector was used in the form of a strip (2.5X22.0 cm) fixed to a lucite support by means of chloroform. The detector assembly is shown in Fig. 1. This assembly was made in order to have a large detector area in contact with the solution and a better geometrical control.

The neutron flux during irradiations was also monitored by the fission track registration technique. A solution with a known uranium concentration (monitor) was irradiated simultaneously with the sample to be analyzed; knowing the track density obtained from the monitor and its property of being proportional to the neutron flux, it is possible to obtain the relative neutron flux.

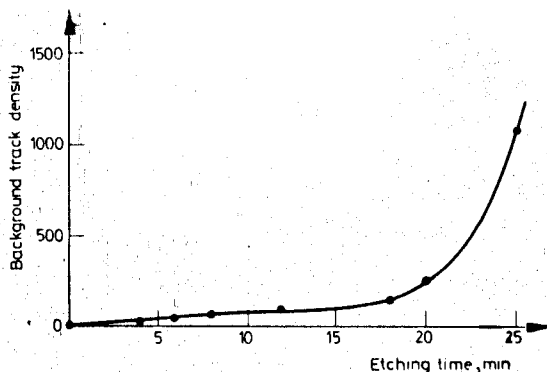


Fig. 2. Variation of the background with the etching time in KOH solution (1.223 g/l) at 60 °C, for a Makrofol foil (10 μm)

Chemical etching

After irradiation the Makrofol strips were etched in a KOH solution (1.223 g/l) at a temperature of 60 °C.

In low neutron fluxes the etching time was chosen as a function of the background due to the Makrofol defects and radiation damages were not taken into account.

In high neutron fluxes, as in the case of reactors, the radiation damage to the Makrofol is important and must be considered. The main effect of this damage is to increase the etching rate of the chemical reagent,⁴ i.e., the rate at which the surface is removed, when chemically etched, is greater in the case of radiation damaged detector.

Taking into consideration that the radiation damage is proportional to the period of exposure, it is convenient to know the relation between track density and etching time for each irradiation time if different neutron fluxes are utilized in the irradiations.

Another alternative is to fix the irradiation time for solutions in a certain range of concentrations. In this way, all detectors will be exposed to approximately the same radiation damage and so only one etching time will be needed for all measurements.

In this work an irradiation time of 30 min was used for all samples, since this time was found to be convenient for sample analyses with uranium concentrations of the order of microgram per liter.

Eight irradiations of 30 min each were performed for HNO₃ (0.3M) solutions to determine the etching time. The HNO₃ (0.3M) solution was chosen because it

was the reagent blank. Best results were obtained for an etching time of 12 min and an irradiation time of 30 min (Fig. 2).

During the etching a mechanical stirrer was used in order 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.⁵ Initially 1300 V was 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 pre-determined area (2.8 cm²). This last step was repeated 4 times and care was taken for not moving the Makrofol during count repetition. For scanning conditions a reproducibility around 0.2% was found.

The reproducibility obtained with the same etching and irradiation conditions was 3%. In all the results a confidence level of 95% was used for the calculation of the variances.

Detector calibration

In order to check the radiation damage effects in the detector when the neutron flux changes, nine irradiations were performed with known different concentrations of natural uranium solutions. The concentrations varied from $8.0 \cdot 10^{-5}$ mg U/ml to $0.8 \cdot 10^{-5}$ mg U/ml and the irradiation times varied from 2 to 30 min. All the Makrofol strips were etched for 15 min. This etching time was reported in the literature⁶ and utilized by other authors for the same etching conditions and different thermal neutrons fluences.

The track density obtained was plotted against the uranium concentration (Fig. 3). Using this calibration curve, the samples can have the concentration determined with an overall error ranging from 6% to 32%, for concentrations within the interval considered. The higher the concentration, the lower the error.

In order to reduce the errors, a second calibration curve was also obtained by performing 14 irradiations of uranium solutions, with concentrations ranging from $8.0 \cdot 10^{-6}$ mg U/ml to $0.4 \cdot 10^{-6}$ mg U/ml, which is the range usually found for waters. The same irradiation period (30 min) was used for all the solutions in order to achieve better radiation damage control.

The etching conditions were the same as employed previously. Therefore, the 12 min etching time was used (Fig. 2).

In Fig. 4 one can see the experimental results and the adjusted straight line. Using this calibration curve, the samples can have the concentrations determined

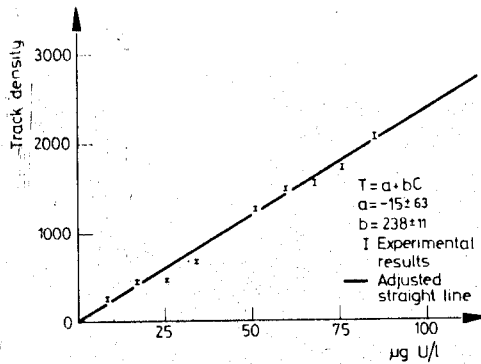


Fig. 3. Variation of track density with natural uranium concentration, for an etching time of 15 min and irradiation times ranging from 2 to 30 min

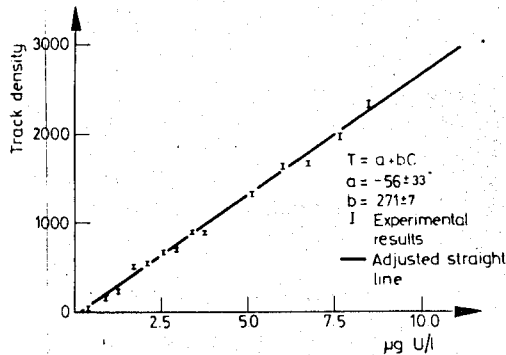


Fig. 4. Variation of track density with natural uranium concentration, for an etching time of 12 min and the same irradiation period (30 min)

with an overall error ranging from 3.3% to 29.0%, for concentrations within the interval considered.

To determine the contribution of uranium from the reagents and also from eventual laboratory and environment contamination, blank solutions were prepared, in the same laboratory, and, using the same reagents (nitric acid) applied to prepare the uranium solutions. The reagents blanks were found to contain 0.05 $\mu\text{g U/l}$.

It can be observed from the results that 9 of the 14 points in Fig. 4 have a lower overall error than the lowest overall error of the points in Fig. 3.

Considering that in Fig. 3 the track density of the blank sample was negligible and that the uranium concentration and the overall error were higher than in Fig. 4, it can be inferred that, possibly, the greater error in Fig. 3 is due to radiation damage.

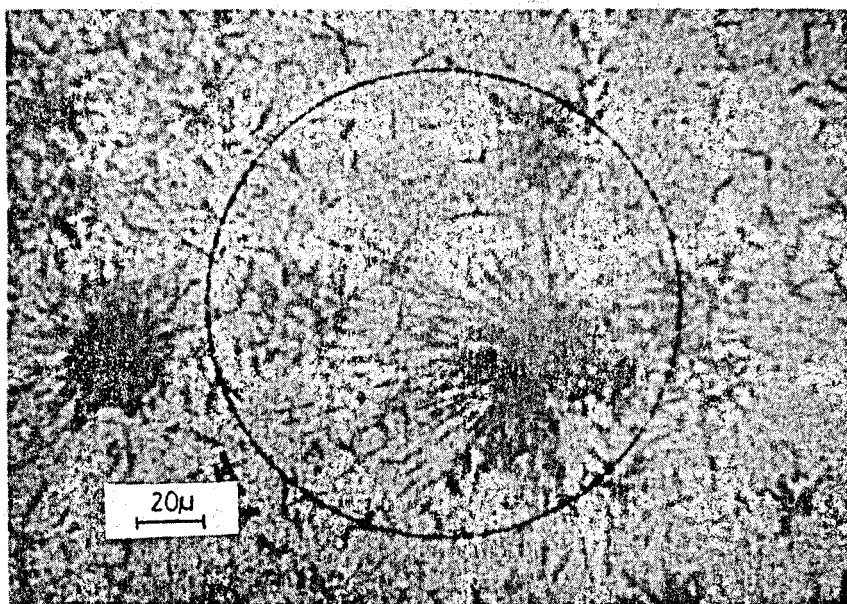


Fig. 5. Clustering of tracks in the Makrofol after chemical etching relative to water analysis with no chemical reagent

Application for waters

The method described was used in the determination of the uranium content of various water samples, obtained from several sources like rivers, sea, mineral waters and Cercado (Poços de Caldas) uranium mine water, in São Paulo State, Brasil.

The water samples were collected in glass bottles (1 l) from locations where water was always mixed well by strong currents. All the water samples were acidified immediately after collection with 20 ml of concentrated nitric acid per liter of water. The storage time ranged from 3 to 30 days. Under these conditions the loss of uranium by absorption in the container was kept at a minimum.

The samples (80 ml each) were completely evaporated and 20 ml of a HNO_3 (4M) solution was added and boiled to remove the carbon dioxide present as carbonate ion, since the greater amount of uranium may exist in water as uranyl carbonate complex anions $\text{UO}_2(\text{CO}_3)^{2-}$ or $\text{UO}_2(\text{CO}_3)_2^{4-}$.⁷ The resulting solution (uranyl nitrate) was adjusted to pH ~ 1 by adding a HNO_3 (0.3M) solution.

In order to check the dissolution of the uranium compound with HNO_3 (4M), one water sample with no chemical reagent was analyzed. The results can be seen in Fig. 5, showing a considerable clustering of tracks in the Makrofol after chem-

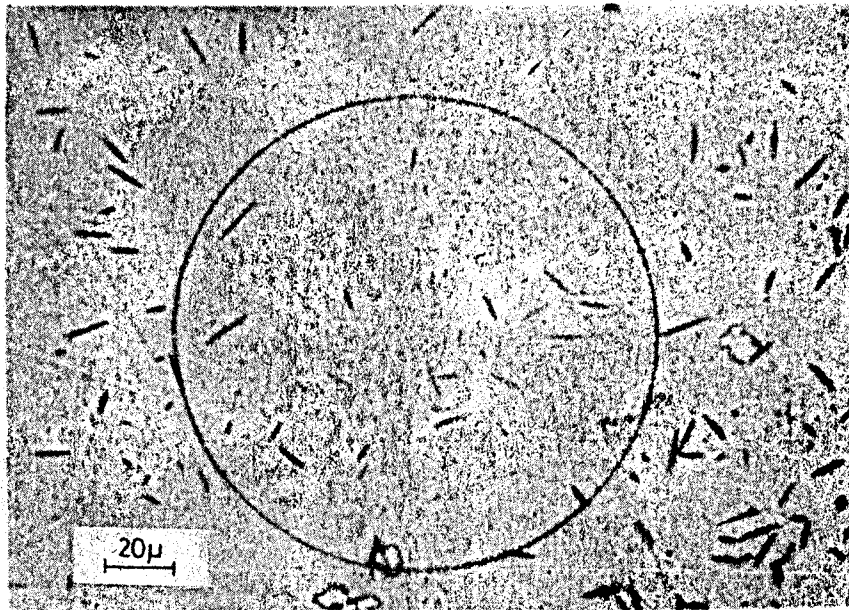


Fig. 6. Track distribution in Makrofol after chemical etching relative to water prepared in the form of uranyl nitrate

ical etching. This may be caused by the heterogeneous distribution of uranium in water. This clustering of tracks causes difficulties in track counting, particularly when an automatic discharge chamber is used.

The same water sample was prepared in the form of uranyl nitrate and it was analyzed as the previous sample. As can be seen in Fig. 6, an uniform distribution of tracks is obtained by the dissolution method used.

Results and discussion

Cercado (Poços de Caldas) uranium mine water

First calibration curve $(425 \pm 22) \mu\text{g U/l}$; second calibration curve $(400 \pm 23) \mu\text{g U/l}$.

The uranium concentration in this water was determined using both calibration curves, by extrapolation, due to the high content of uranium, which was outside the concentration interval covered by the calibration curves.

Table 1
Uranium in river waters

Sample	Location	Concentration, $\mu\text{g U/l}$
Brilhante river	Rio Brilhante	0.29 ± 0.06
Pardo river	Viradouro	0.53 ± 0.06
Grande river	Colombia	0.55 ± 0.06
Miracema river	Miracema	0.65 ± 0.06
Dourados river	Dourados	0.81 ± 0.06
Mogi Guaçu river	Pitangueiras	0.88 ± 0.06
Pomba river	Miracema	0.99 ± 0.06
Tiete river	Pederneira	1.17 ± 0.07
Juqueri river	Caieiras	1.67 ± 0.08

Table 2
Ranges of uranium in river waters

Rivers	Range, $\mu\text{g U/l}$	Method
Japan ⁷	0.34–1.23	Absorption spectrophotometry
USA ⁸	0.01–1.22	Fission tracks in Lexan
Brasil	0.29–1.61	This work

Tap water

$(0.42 \pm 0.01) \mu\text{g U/l}$

This value is within the range noted by EDGINGTON⁸ (0.11 to 640 $\mu\text{g U/l}$) for United States tap waters.

River waters

The uranium concentrations of river waters as reported in Table 1 are not expected to be constant. Therefore, the range determined by us is in reasonable agreement with the results of other authors and methods (Table 2), considering the fact that the samples analyzed were completely different.

The high value of uranium obtained in the Juqueri river is presumed to be due to uranium occurrence in the collect area.⁹

Mineral waters

The variation of the uranium concentration of mineral waters is also within the range of 0.1 to 120 $\mu\text{g U/l}$, determined by SCOTT and BARKER¹⁰ in ground waters of the United States.

Table 3
Uranium in mineral waters

Sample	Location	Concentration, $\mu\text{g U/l}$
Prata water	Market	0.45 ± 0.12
Minalba water	Market	1.17 ± 0.13
Lindóia water	Market	2.30 ± 0.14
Source P.1	Itapecirica da Serra	2.04 ± 0.13
Source P.11	Itapecirica da Serra	0.79 ± 0.12

Table 4
Uranium in sea waters

Location	Concentration, $\mu\text{g U/l}$
Flamengo beach	2.89 ± 0.15
Vermelha beach	2.89 ± 0.10
Tenorio beach	3.36 ± 0.12
Flamengo beach (depth of 10 m)	3.39 ± 0.11
Tenorio beach	3.49 ± 0.11
Vermelha beach	3.57 ± 0.12

Average 3.27 ± 0.12

Sea water

The sea water samples were obtained near the 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 5). 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.

From the comparative study made in the Table 6, some advantages can be seen in the method based on the fission track registration technique in the determination of uranium at concentrations of micrograms per liter:

(1) With only one scan per sample it is possible to obtain a precision comparable to the Fluorimetric Method.

(2) The preparation of the samples does not require a chemical separation or any other purification, but only simple dissolution in HNO_3 .

(3) Both the time and the human effort required for the analysis are less than in the other three methods. The analysis time can be further reduced by working

Table 5
Average uranium concentration in sea water

Author	Method	Concentration, $\mu\text{g U/l}$
HASHIMOTO ³	Fission track in muscovite	3.40 ± 0.12
RONA and ALII ^{1,1}	Isotopic dilution (mass spectrometry)	3.39
WILSON and ALII ^{1,2}	Pulse polarography	
	Isotope dilution	
	Fluorimetry	3.33 ± 0.08
This work	Fission track in Makrofol	3.27 ± 0.12

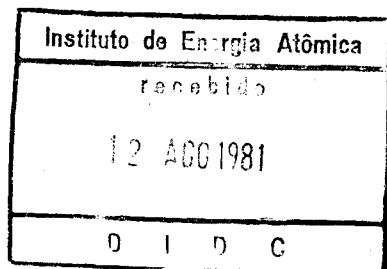
Table 6
A comparison between four methods of uranium analysis for sea water samples

Method	Pulse polarography ^{1,2}	Isotopic dilution ^{1,2}	Fluorimetry ^{1,2}	Fission track registration
Precision	0.7%	0.52%	3%	3.3%
Number of scans for any one sample	As many scans as possible in order to obtain high precision			1
Size of sample required	4000 ml	100 ml	100 ml	80 ml
Minimum time for an analysis	3 d	2 d	1.5 d	1.5 d
Effort per sample	15 man hrs	5 man hrs	6 man hrs	1 man hr
Mean value of the concentration ($\mu\text{g U/l}$) obtained	$3.41 \pm 0.17^*$	$3.31 \pm 0.17^*$	$3.25 \pm 0.23^*$	$3.27 \pm 0.36^*$
Sample preparation	Extraction of the uranium by 8-hydroxyquinoline			Uranium compound dissolution with HNO_3

*These errors are 3 times the estimated standard error of the mean value

with pure material containers and/or working in suitable places for active sample handling (e.g., fume hood with adequate shielding).*

(4) The method does not need specialized electronic equipment. If a nuclear reactor is available, the cost per sample is fairly low.



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Conclusion

The method developed in this work is rapid and inexpensive for determining uranium at concentrations of micrograms per liter in water samples or in any material that can be reduced to a uranyl nitrate solution.

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