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Abteilung Strahlenschutz und Sicherheit

Application of Fission Track Etching Process for Determination of Low-level Uranium Concentration in Liquids and Aerosols

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Application of fission track etching process for determination of low-level uranium concentration in liquids and aerosols

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Abstract

The technical aspects of applying fission track etching process for rapid determination of low-level uranium concentration in liquids and aerosols are presented and discussed. The calibration procedures for both microscopical counting of etch pits with Nomarski interference contrast equipment and spark counting are given. Some experimental results are included for illustration and comparison.

Zusammenfassung

Es werden die technischen Aspekte einer Anwendung der Spaltfragment-Ätzmethode zur Ermittlung von geringen Urankonzentrationen in Flüssigkeiten und Aerosolproben diskutiert. Es werden Kalibriermethoden für eine mikroskopische Auszählung der Kernspuren und für eine automatische Auszählung mit einem Funkenzähler beschrieben. Experimentelle Ergebnisse sollen die Möglichkeiten dieser Methode aufzeigen.

1. Introduction

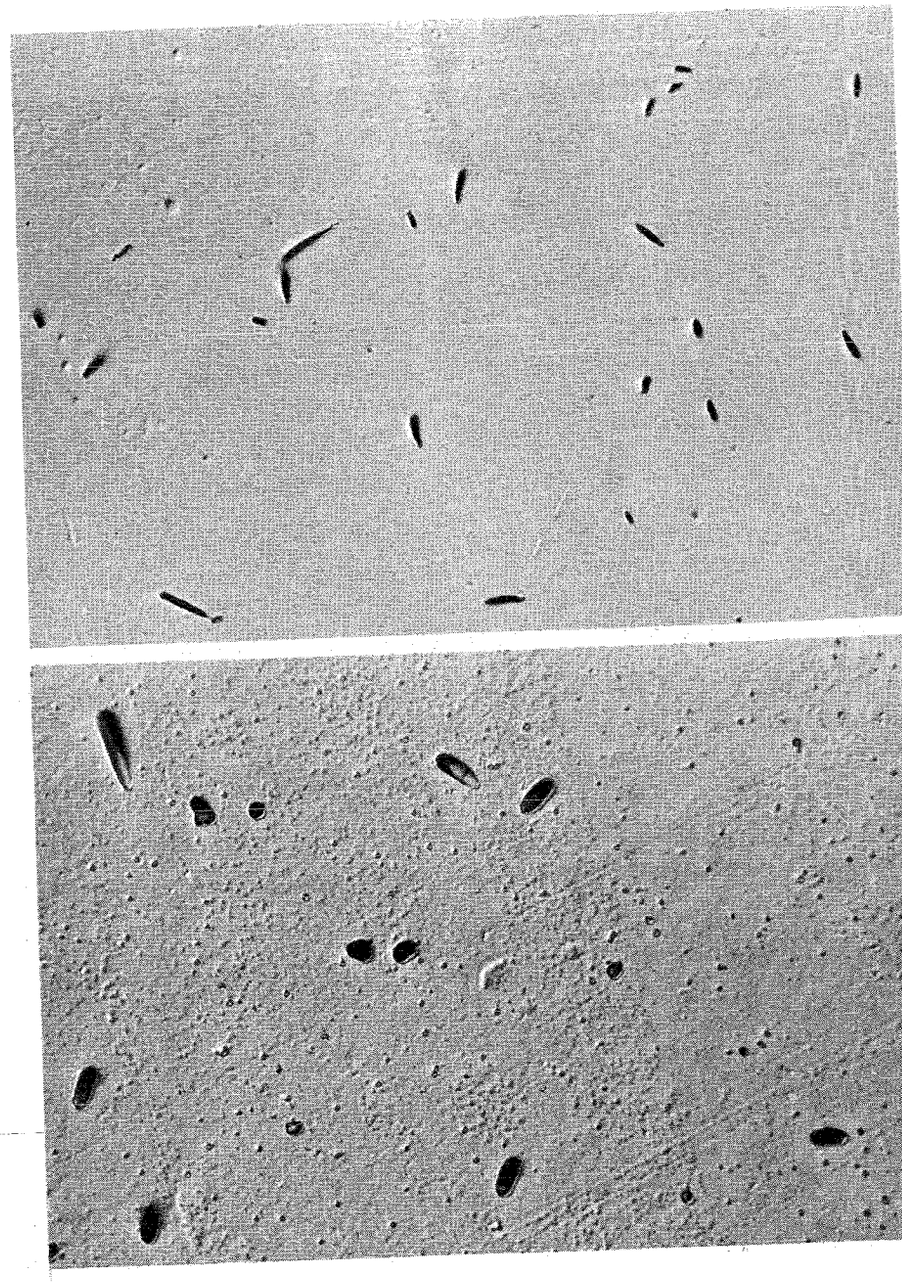
The application of fission-fragment etch-pit techniques in uranium detection has been discussed and practiced recently as a result of the improvement of the detector material and the pit-registration method (1 - 3). The feasibility of applying this technique for water and air control at nuclear power stations has been studied and proposed (4 - 7). In the following emphasis will be given to the technical aspects of applying the fission track etching method in the determination of trace amount of uranium in liquids and aerosols at nuclear reactor sites.

2. Detector and sample preparation

Of the available materials for fission track registration, plastic foils (e.g., Makrofol E by Bayer, Germany) of 3oo µm and 12 µm thickness, respectively, were chosen. This plastic material is of polycarbonate in nature and provides a very low uranium background. The diameter (ca. 2o mm) of the foil is determined by the easily handling of liquid sample with more uniform distribution of fission tracks up to o.2 ml which is pipetted onto the foil surface and evaporated in an oven maintained at 6o°C. The Eppendorf microliter pipette is preferred to avoiding contamination by uranium in pipetting liquids.

The 12 µm foil is clamped on a teflon or nylon frame consisting of two adjacent rings so that the thin foil can easily be mounted and stretched even without using any glue or gelatin material. Numbering of foils can be done by an iron stamp. The foils should be thorough cleaned with an ultrasonic cleaner and rinsed in alcohol if necessary, and then kept in a desicator prior to be used.

A small and known amount of water sample or body fluid is pipetted onto the foil surface of either kind. If the spark counting is preferred, the liquid sample is evaporated on the thin foil till complete dryness and then covered with the thick foil. On the other hand, if the microscopical counting is preferred, the liquid sample is evaporated on the thick foil and then covered with the thin foil. The former method will be referred



a)

b)

Fig. 1: Fission fragment tracks in Makrofol after neutron irradiation

to as "thick foil" or "thick foil method" in the following text. The covered foil will serve as a reference for cross-check during measurement.

The Scotch tape is not suitable for putting these two foils together due to the difficulty in removing its residue on the foils. It is thus preferred to using fine metal wire (e.g., transformer wire) to tighten two foils together.

For the aerosol sample one foil only is used. Since the total quantity of uranium in the samples is usually very small and the uranium background of the filter paper is relatively high, some authors prefer to having chemical treatment (e.g., ether extraction) in order to concentrate and separate the uranium from other material dissolved during the filter-paper digestion, and to prevent absorption of the fission fragments during penetration through the filter paper to the foil (5). In a reactor site, however, the results of measurement are often compared with that of the background. It is not necessary that chemical treatment is required as can be seen in the later part of this paper.

3. Track Counting

In the past years an interference contrast equipment based on the Nomarski principle (8) was used to improve the contrast of transparent structure in comparison to phase contrast and conventional bright-light microscopy. This technique has been proved adequate for nuclear track counting (2), in particular for the detection of fission fragments in plastic material such as Makrofol.

A photomicroscope (Carl Zeiss, Oberkochen, Germany) with a Nomarski interference contrast equipment was used during track measurement. A magnification of 12.5 x 2o or 78.5 x $1o^{-4}$ cm^2/view was normally used. A larger magnification of 12.5 x 5o or 11.2 x $1o^{-4}$ cm^2/view was also occasionally used. During the microscopical counting a detector surface of approximatly 3 cm^2 were scanned.

The needle-shaped tracks of about 1o μm length appear on both types of foil (Fig. 1). The etch pits can be adjusted darker or brighter compared to the image background. The distribution of the brightness can be changed continuously till an optium constract is achieved. The contrast can be improved by selecting the useful interference color for the corresponding image background as white, gray, yellow, brown, red, and blue. The image background and the etch pits appear in different colors and degrees of brightness. The sharp edges of etch pits can be shown in contrast to background tracks and to the roughness of the detector surface. By diminishing the contrast of the microscopical image, background tracks can be restrained. The various possibilities resulting from a combination of brightness contrast, color contrast, and object contrast demonstrate the special qualification of the interference contrast equipment to detect non-photographical tracks in Makrofols and other solid-state detectors as well.

Detection foils with low etch pits density can be counted automatically by using the jumping spark method developed by Cross and Tomasino (9). The detection foil of 12 μm thickness is situated between a high-voltage electrode and a mylar foil, the aluminumised surface of which is in contact with the detector foil and is on zero potential. The detector foil will be perforated by a condensator discharge, which is jumping from one etch pit to the other. The number of sparks is counted with a routine counting device. The spark counter normally used (see Fig. 2) for the measurement of neutron fluence with a Makrofol foil in contact with fission material is suitable for a counting range from 1 $\frac{\text{track}}{\text{cm}^2}$ to $3 \times 10^3 \frac{\text{tracks}}{\text{cm}^2}$ (see Fig.3). The reason for the upper detection limit is the large replica of the etch pits in the mylar foil which is of the order of 2oo μm in diameter (see Fig. 2c).

In contrary to the microscopical track counting method there are no plateau for the graphical curve of the counted number of tracks/cm^2 as a function of etching time. From the experimental results found for different samples of uranium, e.g., uranium foils, or uranium deposited by evaporation and electrodeposition, an etching time of 6o min

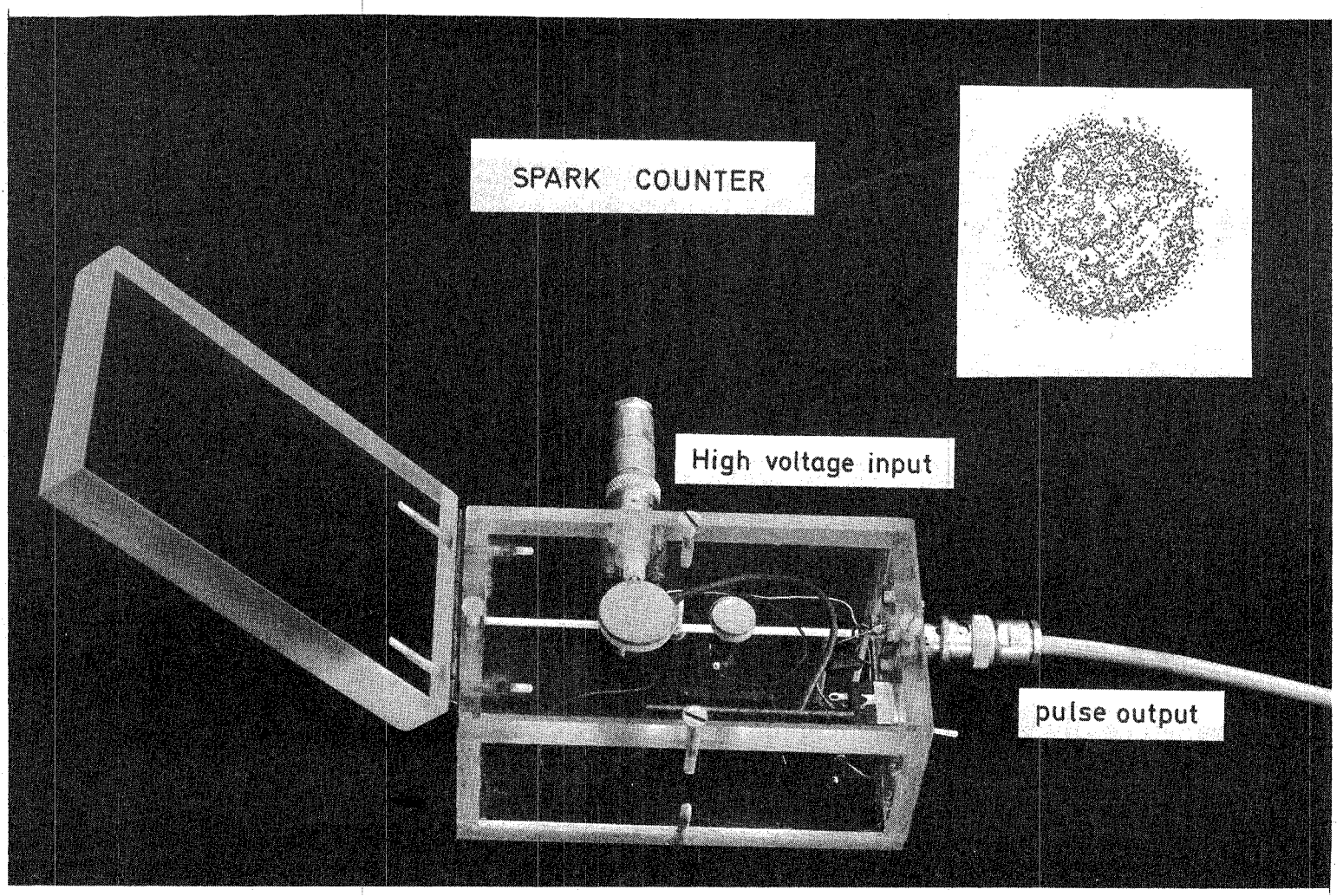


Fig. 2: Spark counter device and replica of etch pits in the mylar foil after spark counting

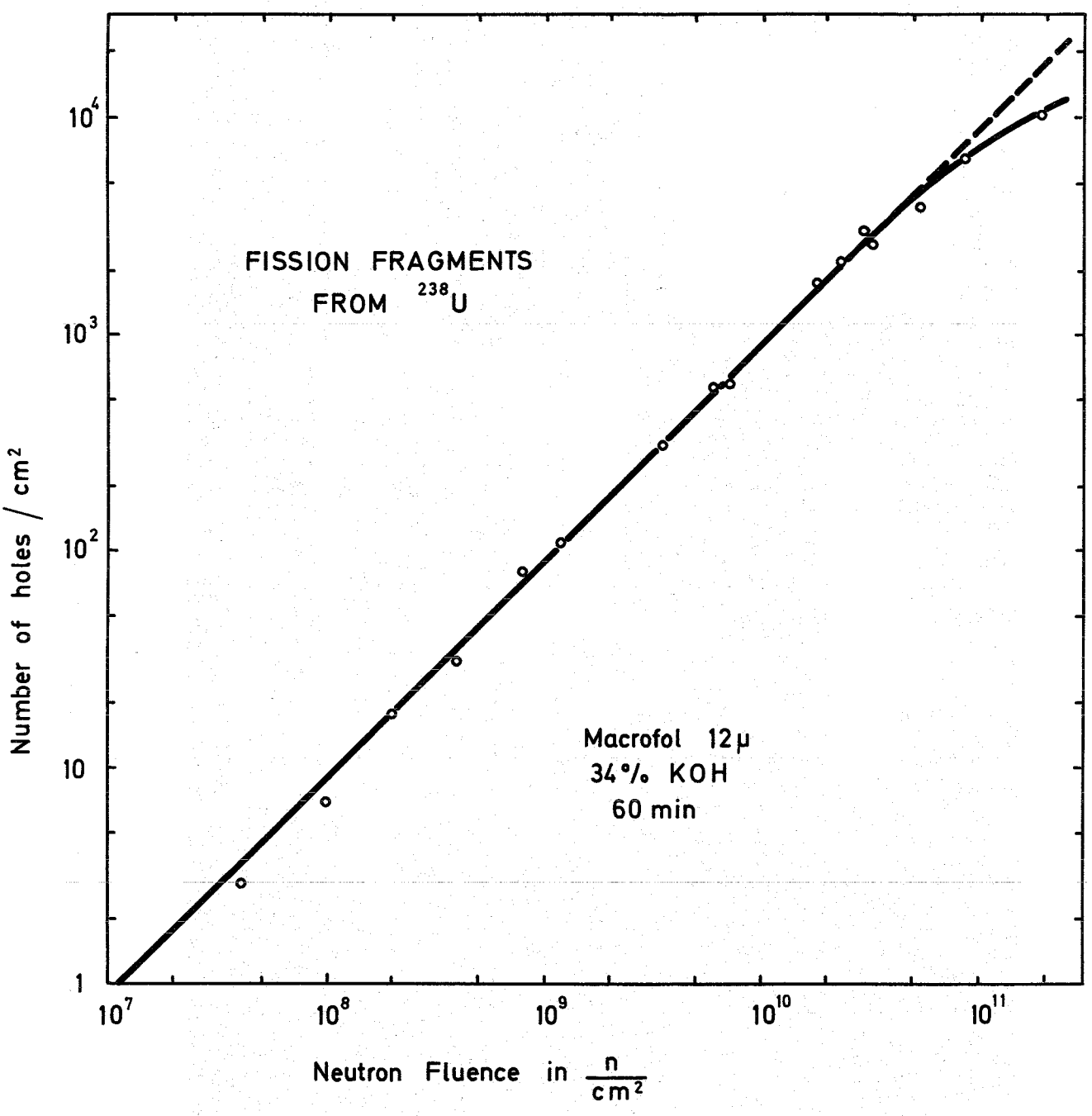


Fig. 3: Number of fission fragments in Makrofol counted with the spark counter as a function of neutron fluence from electroplated uranium

is chosen for the spark counting technique (see Fig.4). The background count rate of the spark counter is lower than 1 $\frac{track}{cm^2}$.

For spark counting, the electrode was designed to fit the thin foil clamped by two adjacent teflon ring properly. The clamped foil was used throughout the experiment including etching and sparking. In this way it is easy to handle the fragile foil. A high voltage of 6oo V was selected for the spark counter. The reproducibility of total count is fairly good and was found to have a standard deviation of ± 1o %. The electrode made of stainless steel should be cleaned with alcohol constantly.

4. Calibration

A simple calculation of the number of the tracks that will appear in the foil which bears known amount of uranium and is exposed to a known thermal neutron fluence is always possible. The calculation is shown below

$$Z = \frac{C \bar{\Phi} \sigma_f I \varepsilon V N}{A} \qquad (1)$$

where

Z = number of tracks appearing in the foil,
C = uranium concentration (g/ml),
$\bar{\Phi}$ = thermal neutron fluence (n/cm^2),
σ_f = microscopic fission cross section of ^{235}U (cm^2),
I = isotopic ratio of $^{235}U/^{238}U$,
ε = foil detecting efficiency,
V = volume of liquid (ml),
N = Avogadro's number,
A = atomic mass of uranium.

The detecting efficiency of the foil can be set equal to unity for a preliminary calculation. For a thermal neutron flux density of $2 \times 1o^{11}$ $n/cm^2/sec$ at full power (44 MW_{th}) in the thermal column of the reactor FR-2, an irradiation time of one hour is sufficient. In practice, the neutron fluence should be measured with cobalt wire

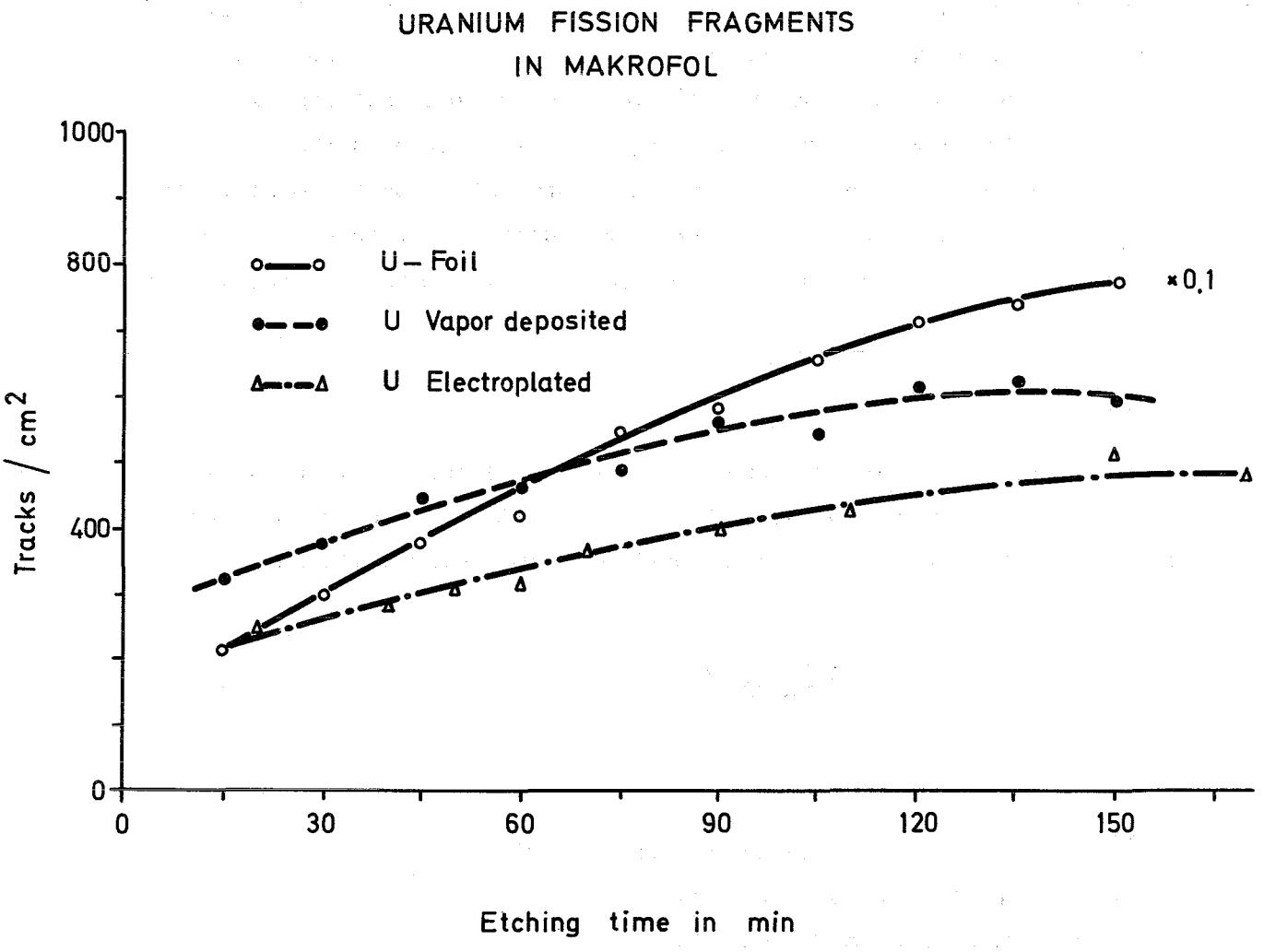


Fig. 4: Number of fission tracks counted in Makrofol with the spark counter as a function of etching time for a electroplated, vaper deposited and metalic uranium

or gold foil activation.

Several foils containing known amount of uranium taken from a standard solution (U_3O_8 dissolved in 2N HNO_3) were irradiated in the FR-2. Following irradiation the thin foils were etched in a 34 % KOH solution at a temperature of 6o°C for 6o minutes, while the thick foils were also etched under the same condition for 8o minutes. After cleaning and drying procedures, the foils are now ready for measurement.

5. Experimental results

The calibration curve for the thick foil method is shown in Fig. 5 from which one can easily calculate the detecting efficiency of Makrofol E. As compared to the detecting efficiency of thin foil mounted on a spark counter, it is comparatively high for the thick foil under this experimental condition.It was shown elsewhere, that the spark counter counts only 6o % of the visible tracks in the thin foil. The total number of counted tracks of the uranium sample, which was situated between both foils are approximatly 1oo % of the tracks found by calculation. In fact once the calibration curve is well established, it is possible to use only the result of neutron fluence measurement and one can obtain the detecting efficiency of thick foil without resorting to the entire calibration procedure for several different concentrations.

It is usually that several samples should be detected in a short period of time in radiation protection, so that several samples in a capsule are irradiated at the same position simultaneously. In this case the neutron flux distribution along the longitudinal axis should be measured. In the first irradiation of this investigation 17 samples were irradiated, and the neutron flux was found to vary from $2.2o \times 1o^{11}$ n/cm^2/sec at one and to $2.35 \times 1o^{11}$ n/cm^2/sec at the other end of the capsule as measured with cobalt wire, and gold foils situated along with 17 samples in a rotating aluminum capsule. Taking account of a longitudinal flux distribution factor one can obtain a more reliable and accurate calibration factor.

The calibation curves in Fig. 5 are based on the thick foil method. The choice between two methods is in fact a matter of preference. However, it is obvious that the thin foil method is suitable for routine work while the thick foil method is more suitable for research and investigation.

The uranium concentrations in various water samples taken from reactor sites in Germany and Taiwan, respectively, are listed in Table 1.

Table 1: Uranium Concentrations in Water Samples from Reactor Sites in Taiwan and Germany

No.	Sample	U Concentration (g/l)
1	Drinking Water, KfK	1.2×10^{-6}
2	Drinking Water, TRR	3.0×10^{-8}
3	Ground Water, TRR	4.0×10^{-8}
4	Rain Water, TPR	2.6×10^{-8}
5	Rain Water, THOR	3.2×10^{-8}
6	Well Water, TPR	3.6×10^{-8}
7	Well Water, THOR	3.8×10^{-8}
8	River Water, TRR	3.2×10^{-8}
9	Sea Water TPR	3.8×10^{-7}

where KfK stands for Karlsruhe Nuclear Research Center, TRR stands for Taiwan Research Reactor under construction, TPR stands for Taiwan Power Reactor under construction, and THOR stands for Tsing Hua Open-pool Reactor in operation.

The numerical data listed in Table 1 are based on microscopical readings by thick foil method, and a comparison with other methods is shown in Table 2.

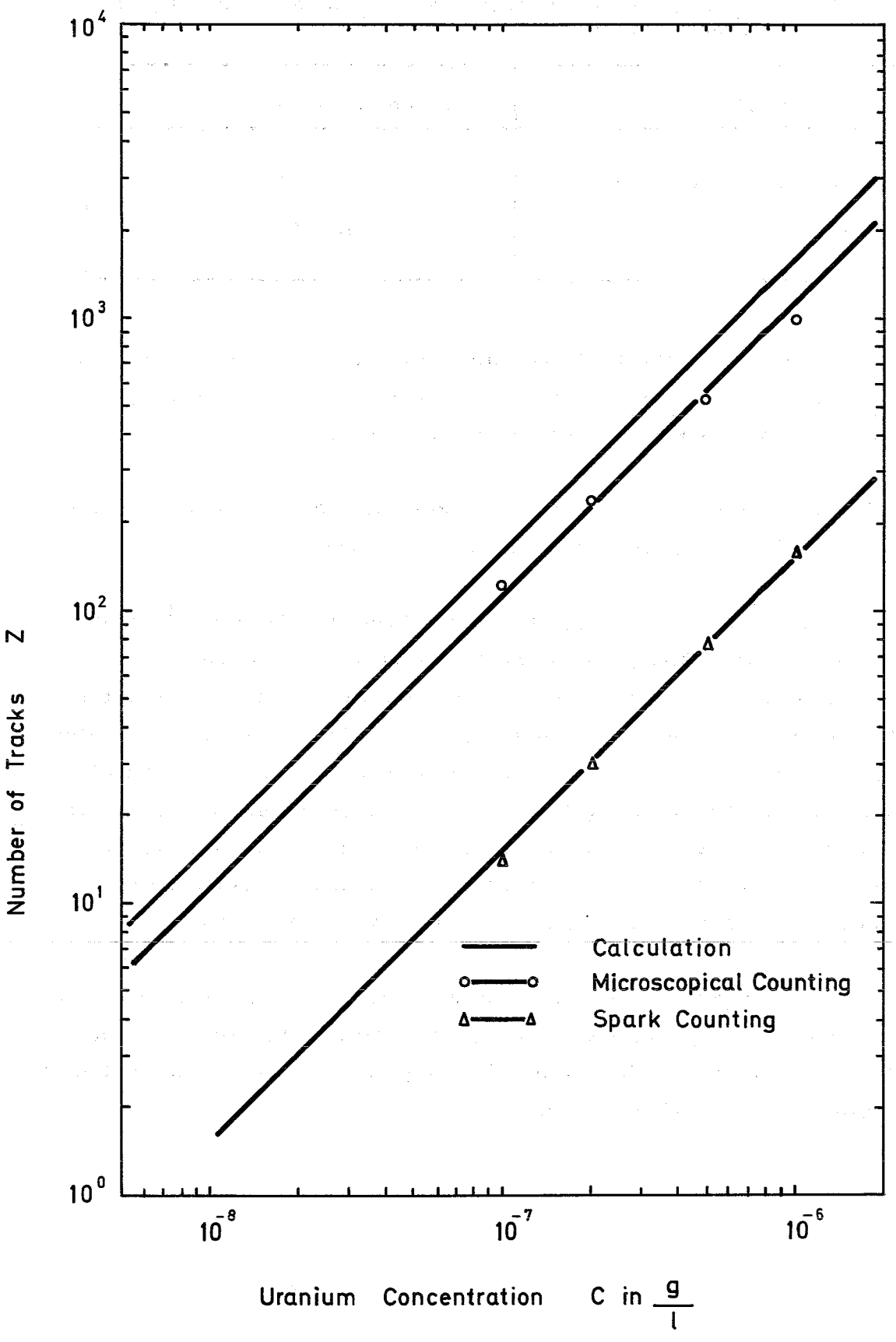


Fig. 5: Number of fission tracks in thick Makrofol foils as a function of the uranium concentration in water from a o.2 ml sample after reactor irradiation with 7 x $1o^{14}$ n/cm^2 for microscopical counting and spark counting

Table 2: Intercomparison of U Concentrations in Water Samples by Different Methods

Method	U Concentration (g/l)
Microscopic, thick foil	1.2×10^{-6}
Fluorimetric	1.6×10^{-6}

The discrepancy between microscopic reading and fluorimetric reading is probably due to the fact that the tap water from a chemistry laboratory of KfK was not sampled at the same time.

It is of interest to notice that the uranium concentration in German water sample is much higher than that in Taiwan's.

Several filters through which a known volume of different m^3 of air had passed individually in an inactive area would, in contact with a foil, undergo the same procedure as mentioned above for the determination of trace amounts of uranium in the filter from the environment. The same procedures were also applied to detect uranium or plutonium in an active area within the reactor site or in hot cells. Due to the high uranium background in the filter material, it is advisable to use spark counting instead of microscopical counting. Visual microscopic counting is, on the other hand, too inaccurate and tedious.

A first experimental run with 12 cm disc samples of glass fiber filter paper showed a high amount of background tracks. Therefore further investigations should be performed taking into account a separation of uranium from the filter paper.

6. General conclusion

The application of the fission fragment etch-pit technique in uranium detection is limited by the sensitivity of the fission detection ($\sim 10^{-9}$ g/l), which is governed by the background tracks from the fissionable material in the sample material (e.g., filter) or the detector and the sensitivity of the counting technique.

The errors involved for a rapid uranium detection are estimated as below:

(1) The volume measurement including both water sample by pipette and aerosol by air sampler, respectively may amount to $\pm$ 1 %.

(2) The neutron fluence measurement including the flux distribution along the longitudinal direction may amount to $\pm$ 10 %.

(3) The track counting by a spark counter my amount to $\pm$ 10 %. However, it is not likely to estimate for high track density and inhomogeneous distribution of tracks. For microscopical counting of an area of about 1 cm^2, the error involved is approximately about $\pm$ 10 % also.

(4) A calibration factor of $\pm$ 5 % was found for the foil calibration run.

(5) The influences of pipette contamination, inhomogeneous distribution of tracks as a result of evaporation, and self-absorption of fission fragments in aerosol filter will also contribute some errors in the results.

The over-all error estimated from a more conservative point of view is thus within $\pm$ 20 %.

From the practical point of view there are some parameters as indicated below which can simplify and optimize the application of the measuring technique.

(1) Track Counting:

Low track densities of 1 – 1000 tracks/cm^2 only are suitable for the track counting technique. This is applicable for a concentration below 10^{-6} g/l based on a 0.2 ml sample volume and an active area of 1-2 cm^2

and with a neutron fluence of 1 x $1o^{15}$ n/cm^2. For higher track densities a microscopical track counting is preferred if the track distribution is homogeneous enough and the area of the total sample detector is known. Otherwise too many microscopical fields must be scanned over the entire area of the detector foil. On the other hand a lower neutron fluence will produce a lower track density and make the spark counting possible.

(2) Neutron irradiation:

The irradiation time in the thermal column of the reactor should be varied corresponding to the uranium concentration. For low uranium content a neutron fluence of 1 x $1o^{15}$ n/cm^2 is needed, while for high uranium content, a lower neutron fluence of 1 x $1o^{12}$ n/cm^2 is sufficient. If the magnitude of the uranium content is not known, it is practical to have two samples irradiated with different neutron fluences.

(3) Calibration

After a calibration run based on a given unchanged technique of sample preparation, water preparation, detector combination, neutron irradiation, etching process, and track counting, no further similar calibration is actually needed However, the measurement of neutron fluence is necessary.

In conclusion the above methods for determination of low-level uranium concentration are proved suitable for water and aerosol control in reactor sites and the extension of its applications to urine analysis is also adequate.

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Figure captions

Fig. 1 Fission fragment tracks in Makrofol after neutron irradiation in contact with uranium

a) after 6o min etching time

b) after 12o min etching time

Fig. 2 Spark counter device and replica of etch pits in the mylar foil after spark counting.

Fig. 3 Number of fission fragments in Makrofol counted with the spark counter as a function of neutron fluence from electroplated uranium

Fig. 4 Number of fission tracks counted in Makrofol with the spark counter as a function of etching time for a electroplated, vaper deposited,and metalic uranium.

Fig. 5 Number of fission tracks in thick Makrofol foils as a function of the uranium concentration in water from a o.2 ml sample after reactor irradiation with $7 \times 1o^{14}$ n/cm^2 for microscopical counting and spark counting.