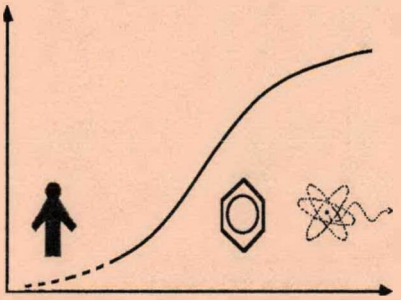
DOE/NV/10574-3

TECHNICAL PROGRESS REPORT TO THE U.S. DEPARTMENT OF ENERGY
NEVADA OPERATIONS OFFICE

Re: Contract AC-08-86-NV-10574

FISSION TRACK ANALYSIS OF PU IN SMALL SPECIMENS OF BIOLOGICAL MATERIAL



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PROGRESS REPORT

August 30, 1988

Track Measurement of Pu in Human Urine by Fission Track Analysis

1. OBJECTIVE

The objective of this research is to develop a highly specific and ultrasensitive method capable of detecting 100 aCi/liter of ^{239}Pu in human urine. The method using neutron induced fission track analysis is to be made free of interference from uranium, the only naturally occurring element with an isotope which fissions with thermal neutrons.

2. OVERVIEW OF METHOD

A simplified flow diagram for the method is shown in Figure 1. Briefly ^{239}Pu is co-precipitated quantitatively from urine with rhodozonic acid. The precipitate containing the ^{239}Pu is dissolved in HCl and is sequentially passed through two ion exchange columns and reduced in volume. The element is then deposited in a circular area on a thick polycarbonate detector and a thinner detector is placed over the circular deposit. The plastic detectors are then irradiated to a high thermal neutron fluence in a research reactor. The detectors are etched in a caustic solution for controlled times and temperatures in order to develop the fission tracks. Images of tracks are formed both on the thin and thick plastic detectors. Total tracks in the thinner detector are measured with a locally developed spark counter and in the thick plastic are measured by counting with a microscope. The results will be made quantitative by constructing a calibration curve for ^{239}Pu.

3. OVERVIEW OF PROGRESS

During the last year we have made the following significant progress:

1. The basic chemistry procedures to separate Pu from urine have been modified and improved. The major modification was adding a second ion exchange column to increase the separation factor of plutonium from uranium.
   A. The separation achieved was 10^{-8}.
   B. The yield of the co-precipitation step which has been measured in 6 samples was close to 100%.
   C. The overall yield is 90%.

2. We have shown that the addition of boron to urine as a preservative does not significantly interfere with the recovery of Pu from urine using our procedure.

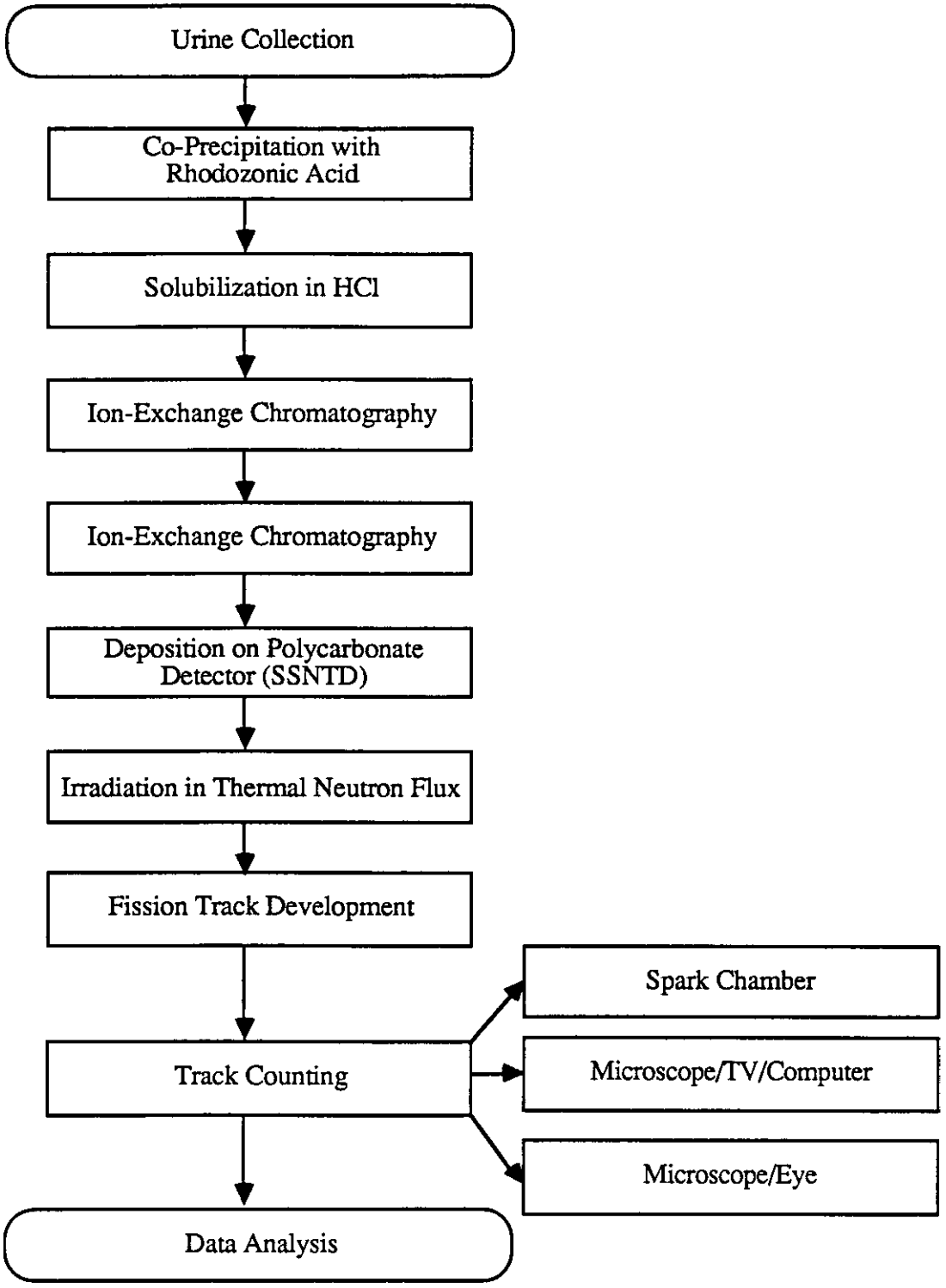


Figure 1: Simplified flow diagram for the preparation of samples, chromatographic separation of Pu from U and from bulk contaminants, and fission track development and data analysis.

3. We have evaluated the performance of a commercially available Italian spark chamber (here called the Tommasino chamber) in counting tracks induced in thin plastic detectors with fission fragments from a ^{252}Cf source. The response was linear, but the variability (coefficient of variation 10 to 20%) was too great to be due to poisson counting statistics.

4. We have evaluated the response of a second version of our locally developed spark chamber (called SLC2) to fission tracks induced with ^{252}Cf and determined both the optimum presparking voltage and readout voltage. In addition we have shown that the number of sparks counted electronically corresponds to the number of holes induced in the aluminized foil.

5. We have shown that we can obtain neutron induced fission tracks on both the thick and thin plastic detectors simultaneously.

6. We have measured the uranium content below the ppb level of high purity commercially available chemical reagents used in our process.

4. ANALYTICAL METHOD DEVELOPMENT

4.1 CO-PRECIPITATION - SEPARATION OF PU FROM URINE

Several authors have reported that Pu can be efficiently removed from urine by co-precipitation with several compounds. Co-precipitation is much faster than complete dissolution of organics by ashing with nitric acid. We used Rhodozonic acid for the precipating agent because it has been shown that the average recovery of Pu from urine volumes between 50 and 2500 ml using potassium rhodozonate followed by ion exchange and electrodeposition exceeded 91% (We 61). Later work by Poppelwell *et. al* (Po 75) showed that Pu in human urine is present primarily as the citrate and is not significantly protein bound as it is in the blood. More recent work has shown that alkaline earth precipitation (especially calcium oxylate) produces similar yields slightly above 90% (Kr 81) for this step plus ion exchange. We did not wish to add calcium to the urine, since most sources of calcium also contain traces of uranium, an interfering element in the fission activation technique.

Table 1 shows our results for the recovery of ^{238}Pu tracer from the co-precipitation with Rhodozonic acid. The procedure is briefly as follows: Urine samples obtained are acidified with HCL to pH 1. After spiking with Pu tracer, 200 mg of Rhodozonic acid was added per 100 ml of urine sample. The pH was then adjusted to ~9 by adding NaOH and

the volume was doubled with absolute alcohol. The experimental conditions were varied as described in Table 1 to investigate the influence of temperature and other factor on the yield. The yield for three experiments using optimum conditions averaged 101.6%.

4.2 ION EXCHANGE - SEPARATION OF PU FROM URANIUM AND OTHER TRACE ELEMENTS

Separation of uranium from plutonium is effected by two sequential ion exchange operations. We tested the efficiency of this double column method in separating uranium from ^{239}Pu using ^{233}U tracer. The results are shown in Table 2. The order of magnitude of the separation obtained was 10^{-8}.

It will be necessary to remove uranium from the reagents used in the chemical separation so that after the separation there will be less than 10^{-14} grams of uranium present in the eluant which contains the ^{239}Pu. To achieve this the input of uranium in regents to the analysis should not exceed ~10^{-6} grams or one microgram.

The double ion exchange step has the additional function of removing mass from the sample.

In Table 2 we show that for Pu added to two human urine samples we obtained an average 89.6% recovery through the second ion exchange step. This is consistent with the 91% yield reported by Weiss (We 61).

4.3 DEPOSITION ON THICK PLASTIC

We have previously reported a method for producing uniform depositions on plastic in a circular drop with a diameter of approximately 6 mm. The pictures of tracks in the etched drops which underwent neutron irradiation show that uranium from reagents in solution directly applied to the drop is uniformly distributed in these drops.

4.4 NEUTRON IRRADIATION-FLUENCE AND THERMALIZATION

We have chosen a reactor source with a thermal neutron flux of 8×10^{12} $_{th}n/cm^2/sec$ and a Cd ratio of about 30. This produces a highly thermalized neutron source; thermalization is important in order to minimize fission tracks from fast neutron fission of trace elements such as Thorium. The irradiation time may be varied in order to change the fluence.

This year we irradiated samples to 3×10^{16} neutrons/cm^2. We find that we can produce excellent quality tracks (clear structure, high resolution, readily distinguishable from artifacts and with minor damage) and measurable track densities in thick plastic slides. We have just irradiated two sets of samples to an increased fluence of 9×10^{16} neutrons/cm^2 in order to investigate the influence of this higher fluence upon the etching development time for thick and thin plastics.

Table 1

Determination and Recovery from Co-Precipitation of ^{238}Pu Added to Human Urine

Amount of $NaNO_2$ or NaOCl added	Addition of $NaNO_2$ in ice bath/room temp.	Overnight Stirring	% Recovery After Co-Precipitation Only
50 mg	ice bath	yes	19.5 ± 10.9%
100 mg	ice bath	yes	28.2 ± 9.1%
200 mg	ice bath	yes	27.3 ± 9.2%
200 mg x 2	ice bath	yes	40.6 ± 9.2%
0.1 ml NaOCl	ice bath	yes	28.9 ± 7.6%
200 mg	ice bath	yes	51.0 ± 9.0%
200 mg	room temp.	no	94.8 ± 6.8%
200 mg	room temp.	no	96.5 ± 4.8%
200 mg	room temp.	no	95.6 ± 4.7%
200 mg	hot plate 50 °C	no	103.9 ± 4.7%
400 mg	room temp.	no	71.2 ± 5.5%
200 mg	40°C - 50°C	no	98.3 ± 4.4%
200 mg	40°C - 50°C	no	102.7 ± 4.3%

Table 2

Recovery of ^{239}Pu (%) and ^{233}U (fraction) in Eluant after Passage through Two Sequential Ion Exchange Columns

	^{239}Pu	^{233}U
Experiment A	91.6% ± 4.7%	1.1×10^{-8}
Experiment B	87.6% ± 4.8%	1.8×10^{-8}

In addition the Nuclear Engineering Laboratory at the University of Utah operates a TRIGA Nuclear Research Reactor in support of research and educational activities associated with the University's Graduate Program in Nuclear Engineering. The TRIGA Reactor which has been licensed to operate since 1975 provides a peak thermal neutron flux of 3.0×10^{12} neutrons per square centimeter per second and a thermal neutron fluence of 1×10^{16} neutrons per square centimeter in one hour of irradiation. The TRIGA Reactor will be available for future irradiation services for this program.

4.5 ^{252}CF IRRADIATION

In the laboratory we can irradiate plastic detectors directly with fission fragments from the decay of ^{252}Cf which decays partly by spontaneous fission.

4.6 ETCHING PROCEDURE

4.6.1 THIN PLASTIC

The procedure after ^{252}Cf irradiation is to etch in 6N KOH at 70° C for 12 minutes. In order to produce suitable tracks in thin plastics we have found that the etching time for the thin plastic has to be shorter after thermal neutron irradiation in a reactor than after ^{252}Cf irradiation.

4.6.2 THICK PLASTIC

The etching procedure consists of exposing the slides to 6.25 N KOH at 70 degrees C for 10 to 30 minutes. Subsequently the slides are washed with copious amounts of deionized water.

Figure 3 shows the tracks induced after etching times of 15 minutes. We have found that etching times of 10-30 minutes are acceptable and we will conduct experiments to determine the optimal etching time after thermal neutron irradiation in thick plastics. This optimum time will depend upon the rate at which artifacts which are able to masquerade as fission tracks are enlarged.

4.7 THICK PLASTIC DETECTORS

4.7.1 TRACKS VS IRRADIATION TIME WITH ^{252}Cf

We have investigated the detection of tracks in both thick and thin plastics following irradiation with a ^{252}Cf source. Figure 2 shows the calibration curve in which tracks in thick plastic counted with a microscope are plotted against irradiation time with the ^{252}Cf source. The plot is quite linear with a correlation coefficient of 0.997.

4.7.2 BACKGROUND

We found no tracks in thick plastic exposed to 3×10^{16} $_{0}^{1}$n/cm^2 outside the area where the source was deposited on the plastic.(See Figure 3)

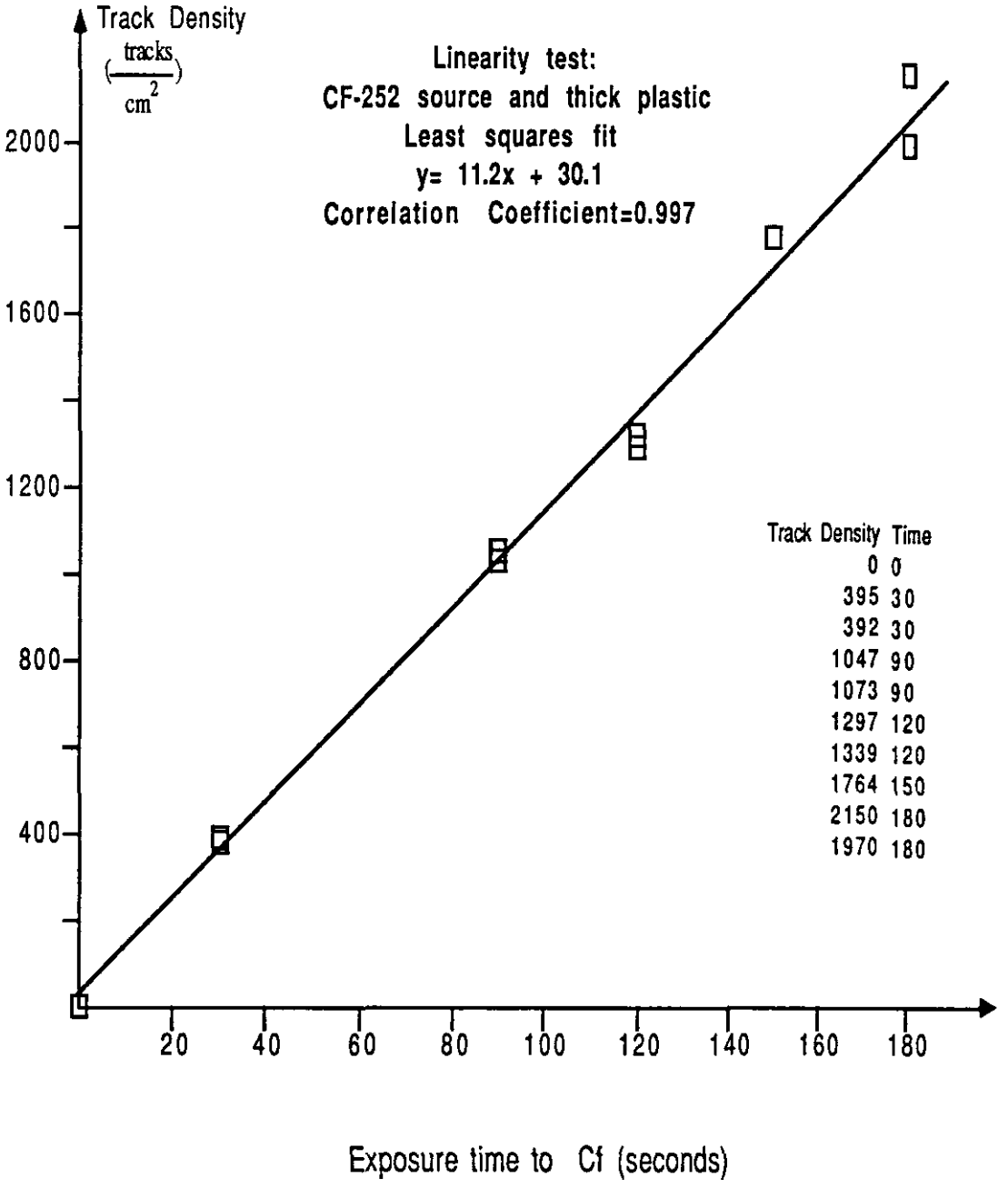
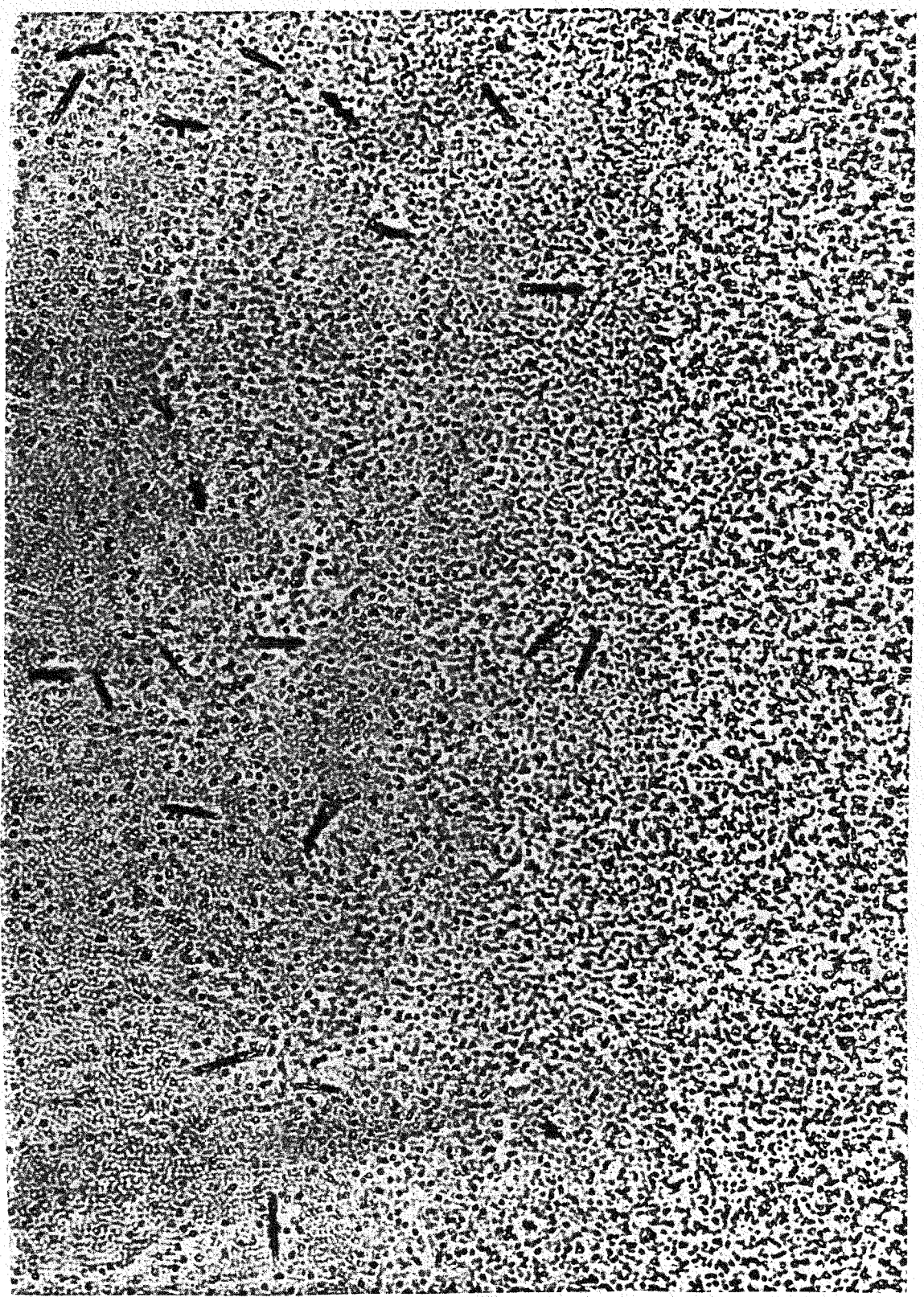


Figure 2: Track density in thick plastic Vs. irradiation time (seconds) for the ^{252}Cf source

FIGURE 3: Fission tracks from naturally occurring uranium present in HCl. Note the absence of tracks on the right of the photograph which is outside the active area.



4.8 TRACK QUANTIFICATION

Tracks are counted in a microscope at a magnification between 100 and 450x. A reticle with 100 fields is used and the number of fields required to obtain 400 tracks is measured. The random error associated with this track numbers is $\pm 5\%(1\sigma)$. Total tracks are calculated by multiplying this track density by the circular area of the deposit. This is a temporary procedure used for developmental work.

4.8.1 SPARK CHAMBER DEVELOPMENT

4.8.1.1 EVALUATION OF TOMMASINO SPARK CHAMBER

We evaluated the performance of an Italian spark chamber which we call SLC#41. The irradiated thin plastic is placed on the electrode of the chamber and aluminized mylar placed over it. The chamber is then closed so that contact can be made between the two electrodes and a pre sparking voltage applied (generally above 700 volts). As the discharge proceeds it effectively punches holes through the tracks in the thin plastic. It is then necessary to spark the chamber a second time. The voltage for the second sparking is called the operating voltage.

Figure 4 shows counts obtained as a function of operating voltage. It is clear that an operating voltage between 450 and 500 volts is acceptable for this chamber. Figure 5 shows that there is a linear relationship between track density and irradiation time with our ^{252}Cf source provided that the track density remained below 2500 tracks/cm^2. Figure 6 shows the results of an experiment designed to investigate whether the battery or an electronic voltage supply influenced the variability in results. The electronic voltage supply generally gave a lower coefficient of variation. However, the results are linear and the Tommasino chamber is acceptable for irradiation with ^{252}Cf provided a coefficient of variation on the order of 20% is acceptable.

4.8.1.2 UTAH SPARK CHAMBER

A second model of the local spark chamber which we designated SLC#2 was constructed this year . In addition we purchased and assembled a second NIM bin and scaler/counter/high voltage system to be operated with SLC#2.

4.8.1.2.1 ^{252}CF FISSION COUNTING

We determined the optimum pre sparking voltage using 20 samples of thin plastic irradiated identically with the ^{252}Cf source for two minutes each. Figure 7 shows the number of counts obtained in pre sparking as a function of the pre sparking voltage. There was little difference between 900 and 1200 volts . Based on this work a pre sparking voltage in this range is acceptable for thin film irradiated with ^{252}Cf. No significant change in counts was found during normal operational (500 volts) counting with presparking voltages from 900 to 1200 volts.

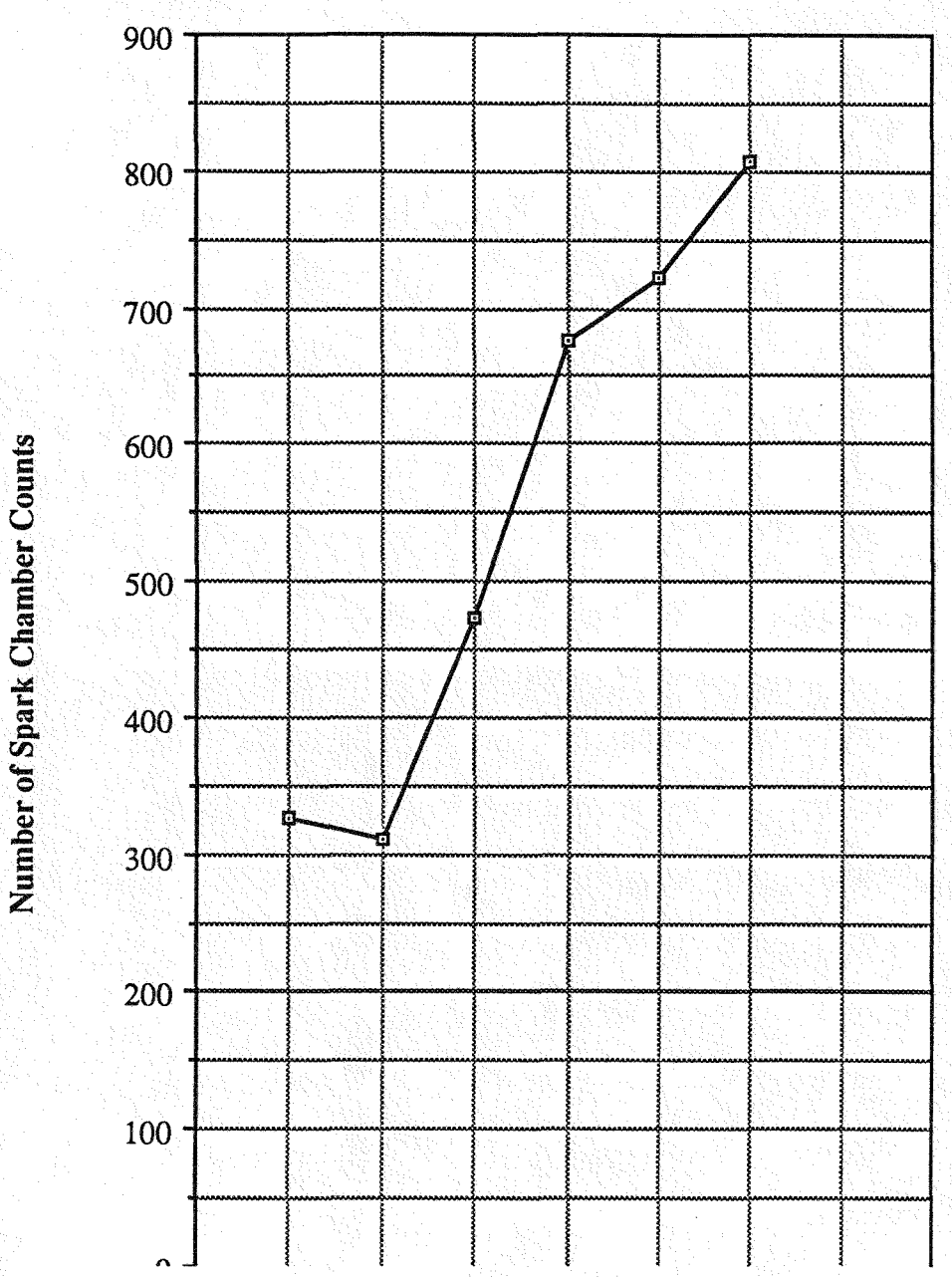


Figure 4: Counts in Tommasino spark counter VS. operating voltage (^{252}Cf irradiation)

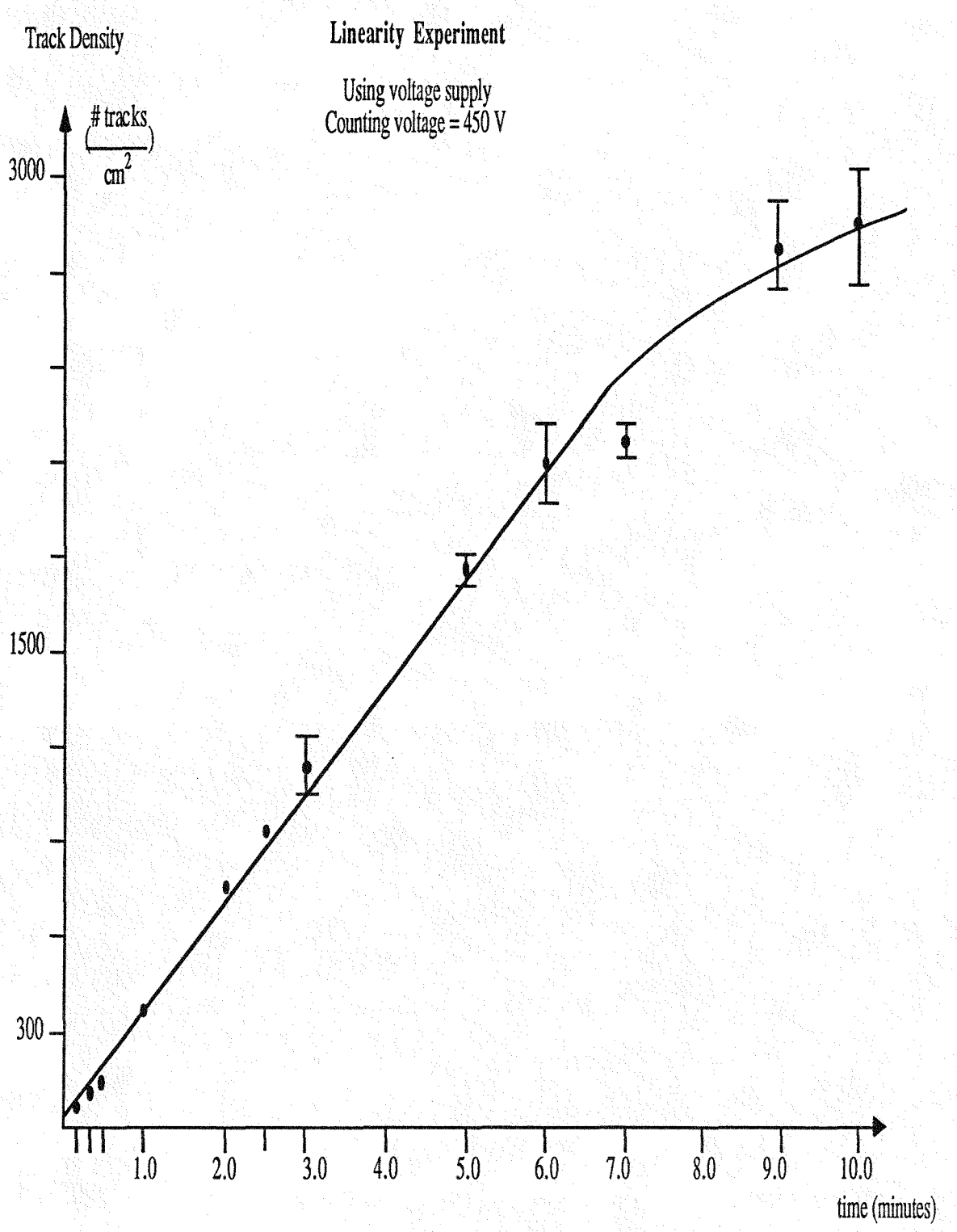


Figure 5: Fission track density vs. irradiation time with ^{252}Cf (Tommasino spark counter)

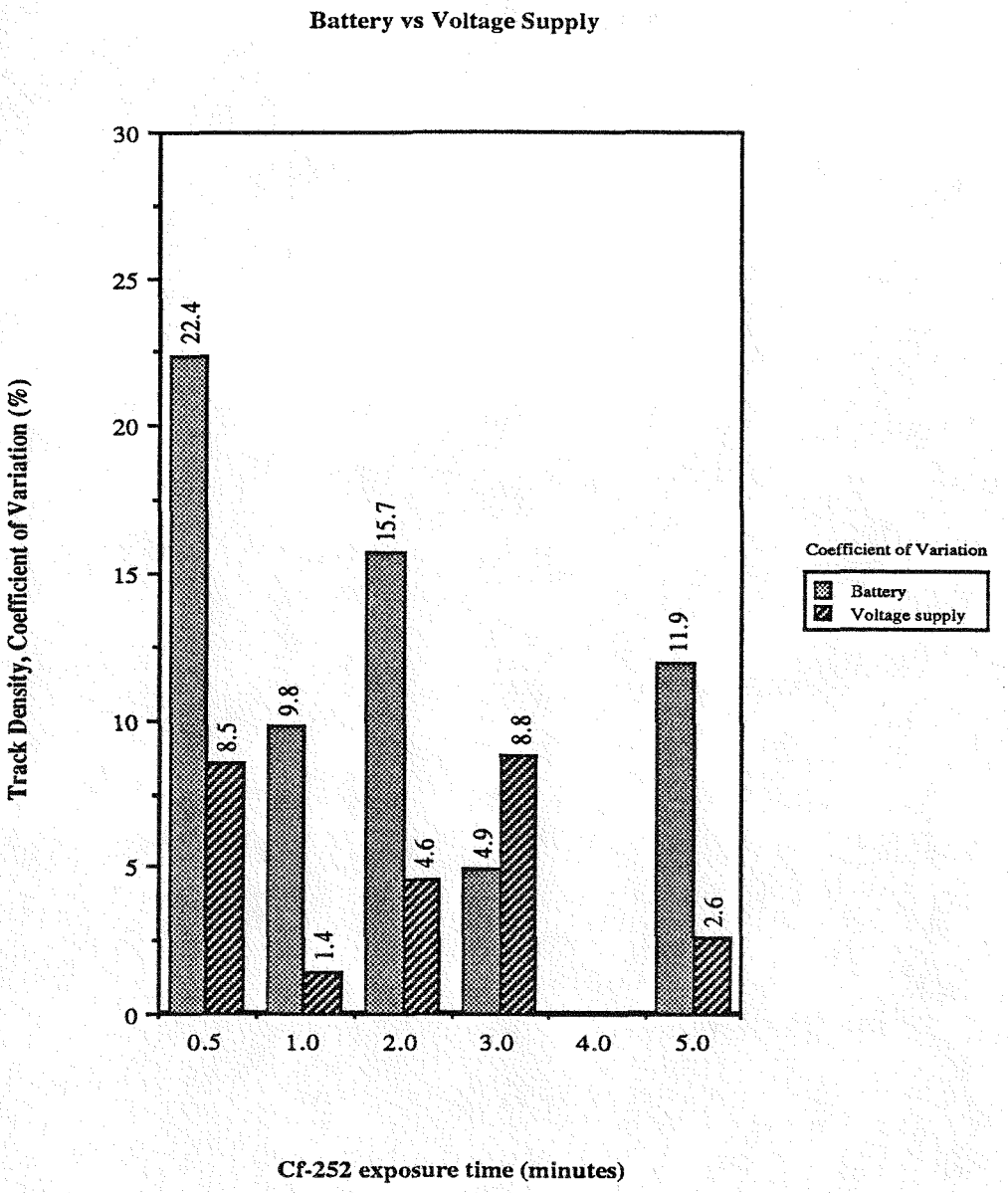


Figure 6: Coefficient of variation as a function of irradiation time (^{252}Cf) and power supply. (Tommasino Chamber)

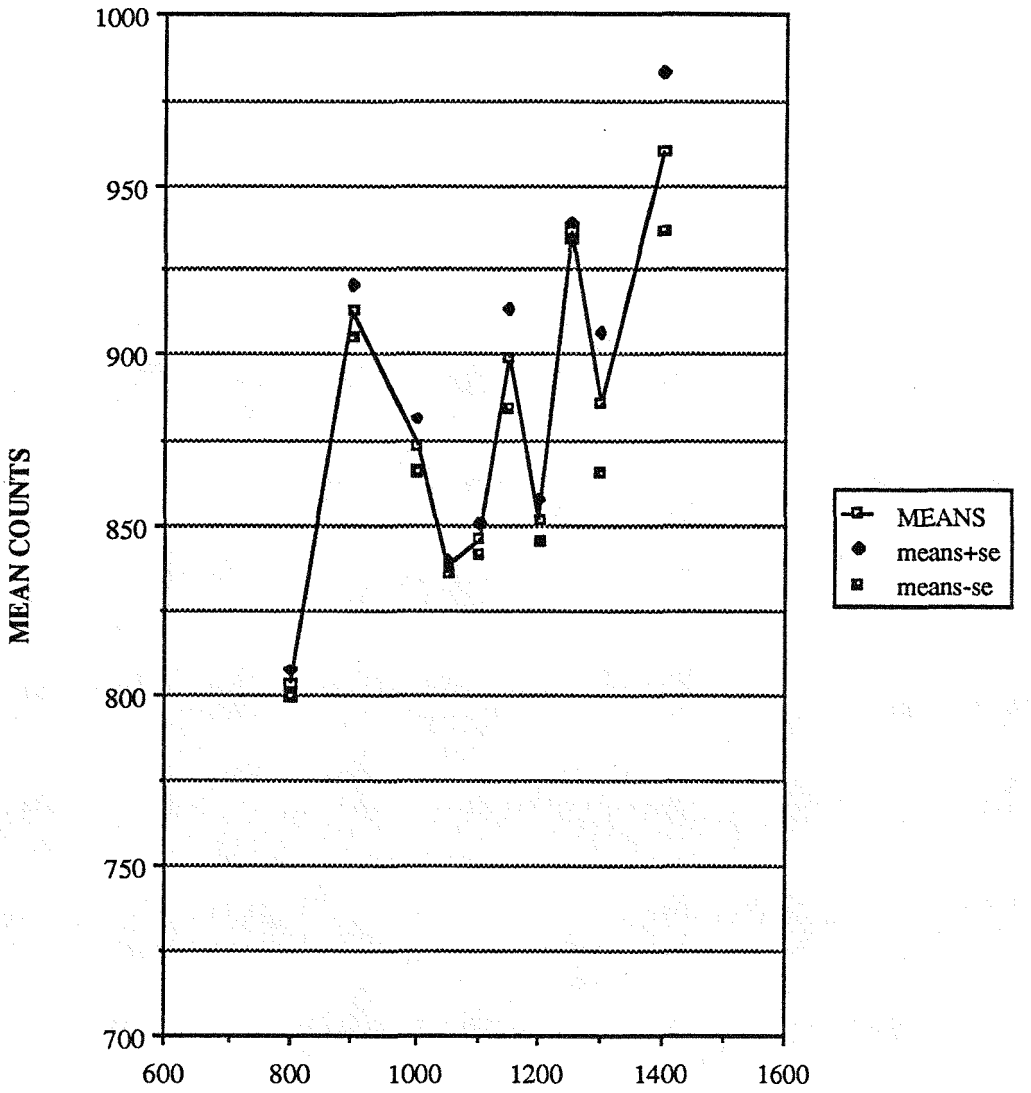


Figure 7: Mean counts during pre-sparking vs. presparking voltage

4.8.1.2.2 NEUTRON INDUCED FISSION TRACKS

We attempted to use this spark counter on samples irradiated in a reactor to a fluence of 3 x 10^{16} neutrons/cm^2. In this initial experiment we failed to determine the optimum etching time since reactor irradiation made the plastic much more sensitive to attack by the KOH than plastic not irradiated in a reactor but exposed to an equivalent number of fissions by ^{252}Cf. A second experiment is in progress to determine the optimum etching time for the thin plastic irradiated to 9 x 10^{16} neutrons/cm^2.

4.8.2 VISUAL (semi-automated) COUNTING OF TRACKS

Fortunately, tracks found in the thick plastic were of very good quality with excellent resolution, readily identifiable structure (i.e. depth and length), so that confusing tracks with artifacts is unlikely; the major problem with quantifying tracks is that they need to be counted through a microscope which is tedious and time consuming. A semi-automatic system for counting these tracks is under design. It will consist of a transmission type microscope, TV camera, monitor, and analog to digital conversion equipment interfaced to a Macintosh-II computer.

5. RESULTS FROM NEUTRON IRRADIATIONS AT 3 X 10^{16} $^1_0$n/cm^2

5.1. OBJECTIVES OF IRRADIATION

Sixty samples were irradiated at 3 x 10^{16} neutrons/cm^2 to test whether we could measure tracks in both thin and thick plastic, to provide a calibration for both uranium and plutonium if the first objective was met, and to measure uranium contamination in reagents, deionized water and human urine. This experiment was successful with the exception of the ^{239}Pu calibration and the measurement of uranium in human urine. In pursuing the first objective we found that several of the samples were over etched so that the plastic became too friable for handling without disintegration. We are in the process of conducting a second experiment using a higher neutron to gamma ratio in the reactor and a higher neutron fluence and lower etching times to investigate whether mechanical integrity can be maintained in the thin plastic at the higher fluence of 9 x 10^{16} neutrons/cm^2.

5.2. TRACK QUALITY AND DEVELOPMENT TIME

When we etched the thick plastic we found excellent tracks. Tracks from uranium present in reagent grade HCl are shown in Figure 8. In addition after we found that by minimizing the etching time for the thin plastic we could preserve the integrity of the thin plastic, we noticed that the spark counter data was much more variable than had been the case after irradiation with the ^{252}Cf source. Therefore we have identified major developmental work to be done in order to make spark counting useful at the high fluence required to obtain the sensitivity required for this work.

5.3. URANIUM TRACK DENSITY

Figure 8 shows photographs of the tracks in thick plastic at a magnification of about 100x to 400x not including camera lens magification for several reagents and water containing known uranium concentrations. We irradiated one sample of water which we had measured previously using alpha spectrometry. This sample contains 250 micrograms of natural uranium per liter and was diluted in factors of ten to concentrations 1/100,000 of that. Based on this work and theoretical calculations, we conclude that one track from natural uranium can be obtained from as little as 10^{-14} grams of uranium.

5.4 URANIUM CONTENT OF HIGH PURITY REAGENTS

Table 3 lists the uranium content of reagents measured in this experiment. HCl and HNO_3 have sufficiently low uranium content to be acceptable for use in our procedure with a DF of 10^{-8}.

5.5 URANIUM TRACKS FROM DEIONIZED WATER

Figure 9 shows tracks from our deionized water. It is interesting to note that outside of the drops the thick plastic shows no tracks, indicating that the plastic is uranium free. This deionized water contains unacceptably high concentration of uranium, about 1 μg/l. Work is underway to find a source of water with uranium content orders of magnitude smaller.

6. PLANS FOR THE NEXT YEAR

6.1 SEARCH FOR URANIUM-FREE WATER

We will assay a series of available high purity water sources such as single, double and triple distilled water to find a source for our analyses with sufficiently low uranium to be acceptable. If necessary we will distill water in quartz glassware.

6.2 VERIFICATION OF LOW BACKGROUND BLANKS

We will verify that the blanks in the urine analysis produce an acceptably low number of tracks at a fluence of 9×10^{16} $^{1}_{0}n/cm^2$.

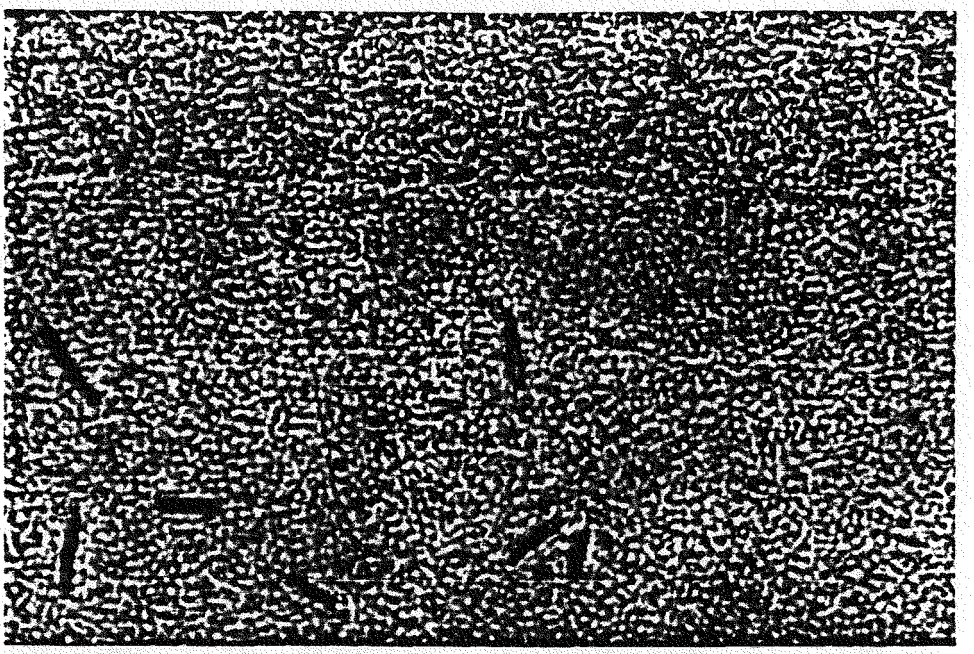
6.3 OPTIMIZE TRACK DEVELOPMENT

We will determine the optimum etching time to develop tracks in thin and thick plastic using a fluence of 9×10^{16} $^{1}_{0}n/cm^2$.

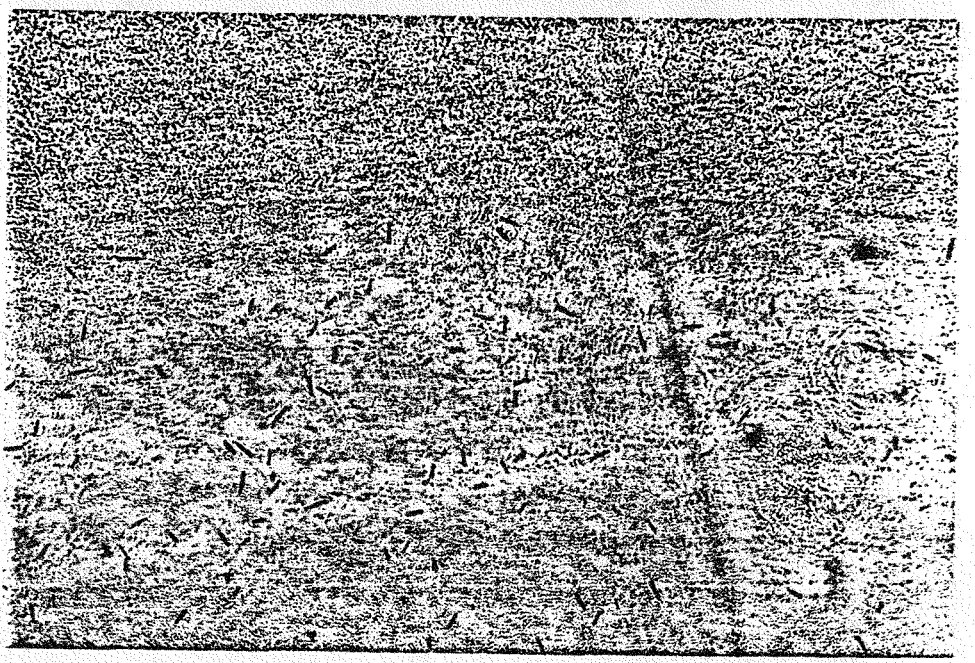
6.4 DEVELOPMENT OF SEMI-AUTOMATED VISUAL COUNTING

We will develop a semi-automated track counting system to count tracks in the thick plastic with a semi-automated system consisting of microscope, TV camera, monitor, and analog to digital converter for the Mac-II computer analysis. We will write computer programs for this procedure.

Figure 8:Tracks from uranium naturally present in reagent grade HCl at several magnifications (100x to 400x)



$HCl + Cl_2$
(Outside clean room)
400x



HCl (Outside clean room)
100x
Note lack of tracks from background U on thick plastic at the top of photograph.

$HCl + Cl_2$
(Outside clean room)
100x

*Camera magnification not included.

Figure 9: Fission tracks due to uranium in deionized water (magnification about 100x)

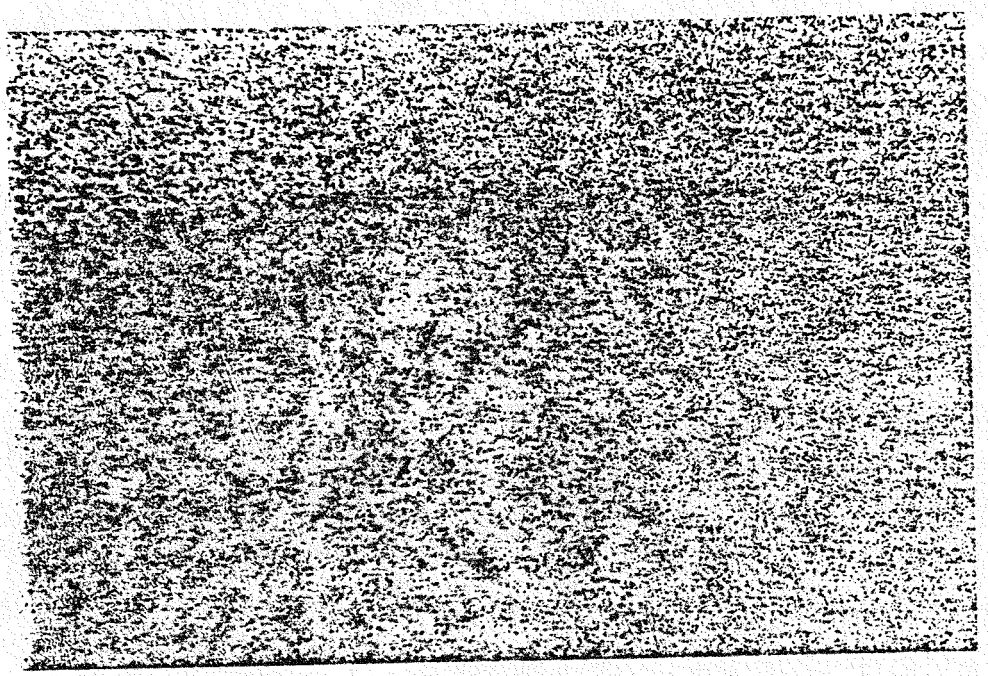


TABLE 3

NATURAL URANIUM CONTENT MEASURED BY FISSION TRACK ANALYSIS IN WATER AND REAGENTS

Reagent	µG Uranium/l
Concentrated HCl	0.051
Concentrated HNO_3	0.049
*Drinking Water with Elevated Uranium	26.00
Deionized Water	1.4
Tap Water	3.3

*Measured by Alpha Spectrometry

6.5 SPARK COUNTER DEVELOPMENT

We will continue the development of a spark counter designed to reduce the time and effort required to count the fission tracks. It will be necessary to calibrate this against the results from the semi-automated method of detection in thick plastic.

6.6 CALIBRATION FOR PU-239

We will calibrate the overall analytical procedure for Pu-239.

6.7 DETERMINATION OF OVERALL YIELD FOR PU

We will determine the overall yield of Pu-239 in the analytical procedure. It appears to be about 90%.

6.8 MEASUREMENT OF 50 URINE SAMPLES FOR PU-239

We will measure 50 urine samples from the Marshall islands for ^{239}Pu.

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