A SENSITIVE ANALYTICAL METHOD FOR THE DETERMINATION OF VERY LOW LEVEL PLUTONIUM IN HUMANS

By L. C. SCHWENDIMAN and J. W. HEALY

Hanford Laboratories Operation, Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

INTRODUCTION

THE early detection of possible plutonium deposition in individuals working with this element is of prime importance in providing radiation protection for these people within established limits. Analysis of urine samples from exposed individuals reflects the body burden of plutonium on the assumption that the excretion rate is a function of the quantity of deposited plutonium. Because of the low maximum permissible body burden of plutonium, 0·04 μc (0·6 μg)[1] and the attendant very low excretion rate, it is essential that sensitive methods be available to detect the element in urine. For an acute plutonium exposure to soluble plutonium compounds resulting in deposition of the maximum permissible body burden, only 6 disintegrations per min ($4{\cdot}2\times10^{-5}$ μg) per day will be excreted in the urine 100 days after the exposure[2]. For incipient chronic intake which eventually builds up to a maximum permissible body burden, even smaller quantities of plutonium are excreted per day because of the nearly complete immobilization of plutonium which occurs with time.

Since it is important to detect a small fraction of the permissible body burden in order to permit timely corrective action, the urine analysis for plutonium should be capable of measuring much less than 1 dis/min (disintegrations per minute) in a sample. The objective of the work reported was to develop an adequately sensitive and reproducible method for plutonium in urine.

BACKGROUND

The routine procedure used at Hanford prior to this development required evaporating the urine sample to dryness, muffling, and dissolving remaining salts. Any plutonium present was then co-precipitated with lanthanum as the fluoride. After solution of the lanthanum precipitate, thenoyltrifluoroacetone (TTA) was used to chelate the plutonium now in the +IV oxidation state. The plutonium was subsequently released from the organic phase to the aqueous phase with 8N HNO_3, and the resulting acid evaporated to near dryness. Evaporation was continued to dryness after transfer of the acid to a $1\frac{1}{2}$-in. counting dish. Low-background alpha counters were used to record the alpha particles entering the sensitive volume of the counter. The air chambers used were sensitive to noise and other minor disturbances and much maintenance and

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operator time was expended in keeping the sets in control with low backgrounds. A measurement time of up to 2 hr was needed to give a detection limit of about 0·5 dis/min per sample.

Nuclear track emulsions were considered to replace the electronic counters as the alpha-particle detector, since several of the disadvantages of the then currently used electronic detectors could be eliminated or minimized. The analysis as visualized would separate the plutonium from the sample and deposit it uniformly onto a small disk. This disk would be held against the nuclear track emulsion for a period long enough to produce a significant number of alpha tracks upon development. These would be counted by viewing the exposed area under a microscope. The quantity of plutonium present could then be calculated from the emulsion efficiency, area examined, area of deposit, and exposure time.

ELECTRODEPOSITION

It was first necessary to develop a method for depositing the plutonium contained in the urine sample uniformly onto a small area. An electrodeposition procedure was developed in which plutonium was first oxidized in a basic medium, then electrodeposited on a 7 mm diameter area in the center of a $\frac{1}{2}$ in. diameter stainless steel disk[3]. In 1–2*N* KOH and in the presence of sodium hypochlorite it was found that nearly quantitative recovery of 10^{-6} μc of plutonium was achieved. The sample preparation, lanthanum fluoride and thenoyltrifluoroacetone method for prior separation of plutonium from urine was retained. Hydrochloric acid was substituted for 8*N* HNO_3 in the extraction, when it was found that nitrate ion caused low electrodeposition yields under the conditions employed.

An electrodeposition cell was developed and multi-position equipment designed to permit simultaneous analysis of as many as twenty samples. Figure 1 shows the lucite electrodeposition cells and the twenty-sample electrodeposition apparatus developed.

In the application of the procedure, urine samples "spiked" with a known quantity of plutonium and blank samples are processed with each group of actual samples in order to provide data on the control of the process. Detailed procedures for the chemical processing of these samples cannot be presented in this report, due to space limitations, but will be made available[4].

NUCLEAR TRACK FILM DETECTION

The nuclear track emulsion chosen to record the alpha particles emitted from the 7 mm diameter area was Kodak NTA emulsion 25 μ thick on 1 × 3 in. microslides. A study was undertaken to determine optimum conditions for eradication of background latent tracks, exposure, processing, and reading the exposed slides.

As received, the emulsion contains latent track images from alpha-emitting impurities. The background tracks from these sources must be extremely few to provide maximum sensitivity. Background tracks in the emulsion were effectively eradicated before development by exposing the emulsion at room temperature to saturated vapor from 0·3% hydrogen peroxide. Dessication

for 3–4 hr restored the original sensitivity of the film. A reduction of background to less than 10% of the original track density was thus easily accomplished. Backgrounds are commonly experienced of 0·002–0·004 dis/min/cm², which is virtually negligible.

The latent image of a bona-fide track in an emulsion will be destroyed over a period of time by the same processes which are deliberately accelerated in background eradication. High humidity and warmth are particularly deleterious to retention of the latent track image. It was found that imperceptible fading of latent images occurred in 8 weeks after exposure if the exposed emulsion was held at 5° C during the period following exposure.

Optimum developing time was determined to be six minutes in D-19 developer at 68° F±2°. Developing proceeds with no agitation. Fixing requires 45 min with agitation, and washing, one hour. Slides are dried in a dust-free atmosphere.

A necessary part of the development was a device to support the ½in. diameter disks against the emulsion. A "radioautographic camera" described in Fig. 2 was constructed. All cameras used are identical and each permits the simultaneous exposure of eight disks.

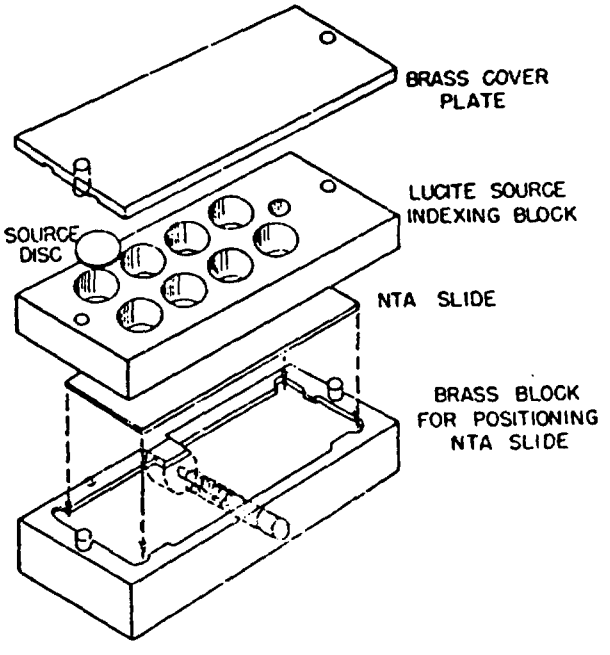

FIG. 2. Radioautographic "camera"

The eradicated NTA slide is inserted emulsion-side up into the milled recess of the brass base block. The thumb clamp draws the slide against three edge-index bosses corresponding to the edge contact points of the mechanical stage of the microscope used. This three-point indexing permits the co-ordinates of the disk centerlines to be established reproducibly with respect to the stage vernier scale, even when some variation occurs at the edges of the emulsion slides. The lucite block is placed over the slide, indexing to dowels in the base block. The ½ in. disks are placed in the holes, plated side against the emulsion,

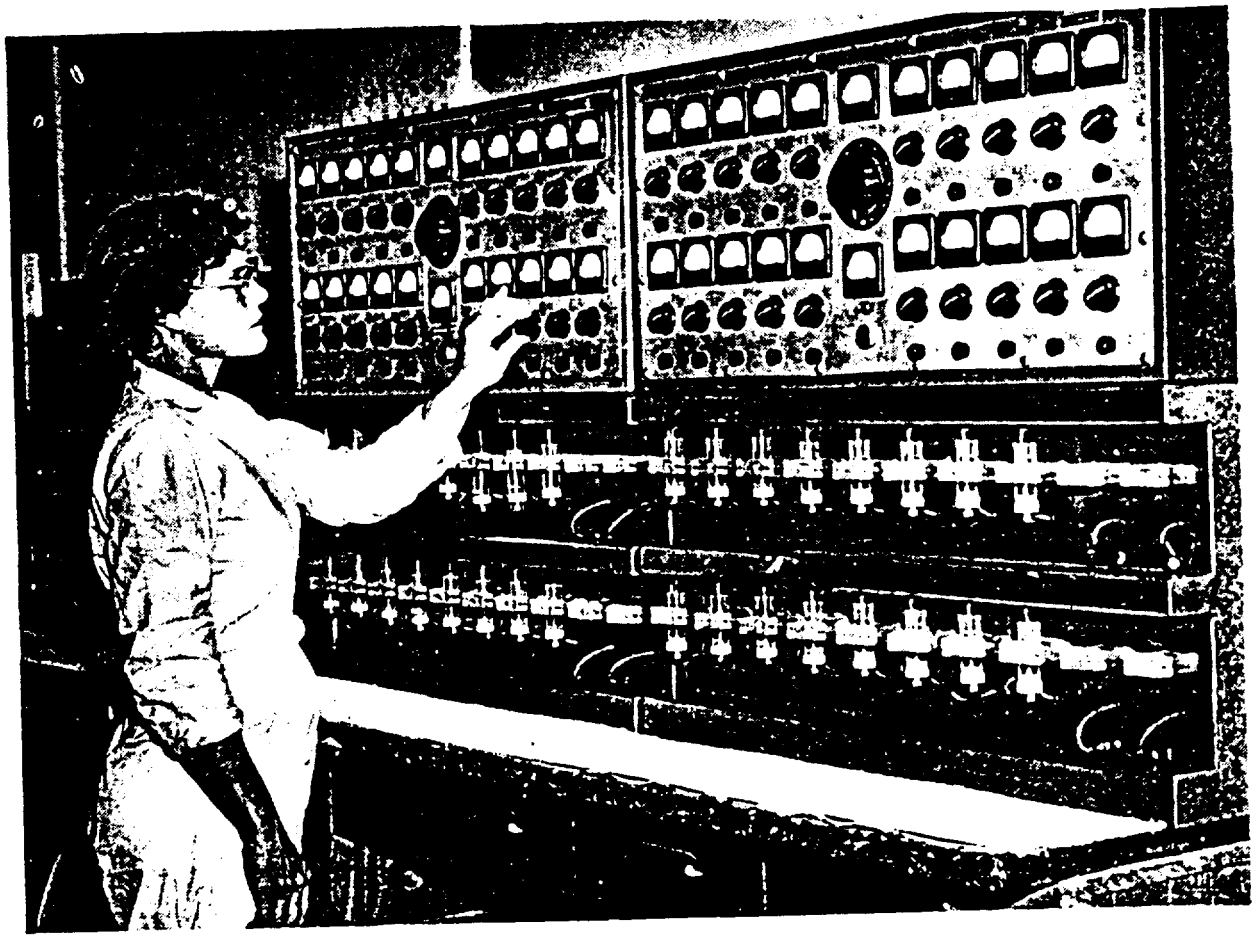

FIG. 1. Electrodeposition apparatus and lucite cells.

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and the cover place located. Printed forms are used to assist in the identification and placing of the source disks.

The NTA slides are handled with as little exposure to safelight (Wratten Series OA) as possible to keep the single grain background to a minimum.

After the disks have been exposed at 5° C to the emulsion for the exposure time, generally 168 hr. the slides are removed and processed. A microscopic count of tracks is then made in the exposed areas of the emulsion. Dark field illumination and a 43× objective and 10× eyepiece are used giving a total magnification of 430. Immersion oil is used between the condenser lens and the slide.

A scanning system of counting is employed. A rectangular reticule in the eyepiece delineates a 0·10 mm×0·2 mm area of the emulsion. From the coordinates of the area to be examined the lateral limits of the scan (4 mm long) are determined. Two stops are then positioned on the right–left traverse bar of the mechanical stage. These stops limit the motion of the stage to the length of the scan. A rachet-stop attachment to the knob for forward–back motion permits the stage to be moved in $\frac{1}{2}$ mm increments perpendicular to the lateral motion. These devices permit several traverses to be made on each exposed area with the total area scanned in the standard procedure, about 4 mm^2. The number of tracks per unit area is thus determined and a conversion to disintegrations per min made using exposure time, exposure area, and film efficiency.

The film efficiency is routinely checked by exposing a standard source of known disintegration rate for a known period of time.

RESULTS

The frequency distribution of the number of tracks found in 3·8 mm^2 of emulsion for 545 blank urine samples analyzed by this procedure is shown in Fig. 3. The frequency distribution calculated from the Poisson function is plotted adjacent to the observed frequency. Data accumulated subsequently have shown ever increasing agreement with the Poisson distribution. It is assumed for purposes of defining a detection limit that samples containing a significant quantity of plutonium will also be distributed to conform to the Poisson function. The detection limit is then defined as that quantity which, if actually present, would give a positive result above the background distribution in 99% of the samples analyzed. These data indicate that 0·033 dis/min actually present in the sample would result in a measured dis/min greater than the 99% upper limit in the background distribution 99% of the time. It should be noted that values greater than the 99% upper limit of the background distribution but lower than the 0·033 dis/min indicate positive values and should be treated as such.

Figure 4 illustrates the result of the analysis of 553 samples each "spiked" with 0·57 dis/min of plutonium as determined by repeated calibrations on a PC/2A proportional counter. These samples were analyzed concurrently with the regular bioassay urine samples. The standard deviation of the 553 results shown is 12%. If only random variations from reading the tracks were present, a standard deviation of 7% should be demonstrated. The remaining variation results from all other random errors in the process. The long-time average of

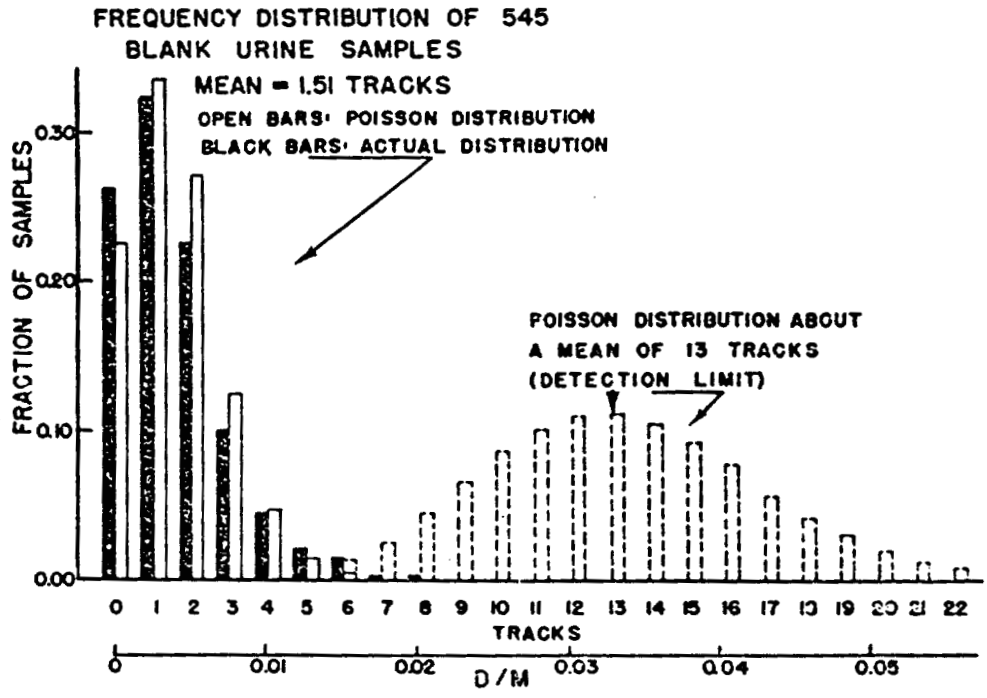

FIG. 3. Blank sample frequency distribution and the detection limit

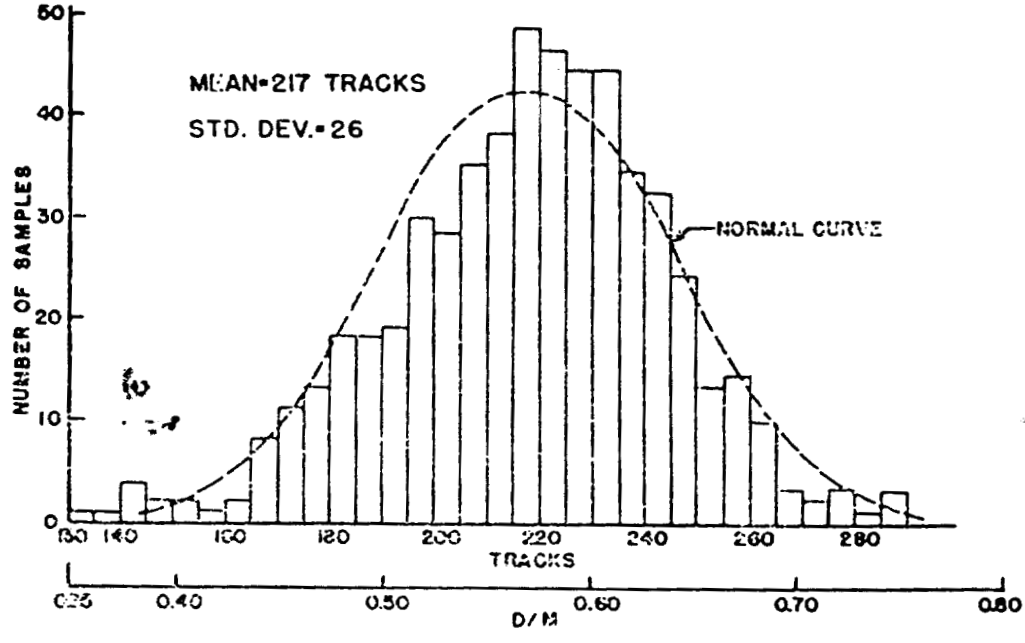

FIG. 4. Frequency distribution of 553 urine samples spiked with 0·57 dis/min plutonium

the overall process yield is 89%, assuming a 50% emulsion geometry. Emulsion geometry will, in general, be slightly less than 50%, principally because of the inability of the microscopist to record tracks perpendicular to the plane of the emulsion.

The particular advantage of this method is that there is virtually no limit to its ultimate sensitivity since by a combination of reducing source size and increasing the exposure time almost any desired sensitivity should be obtained.

Experiments have shown that electrodeposition on 1 and 2 mm diameter areas is feasible. Another advantage is the complete freedom from the somewhat unpredictable behaviour of low background electronic counters, and the attendant high initial cost and subsequent maintenance costs.

For incidents in which plutonium present in urine must be known within a very short time of the incident the method described with the standard exposure time would require too long an interval. However, in these cases the plutonium will appear in the urine in much higher concentrations because of the short delay between exposure and sample collection. For these cases the usual alpha-counting after a chemical separation is generally adequate. In a routine bio-assay program designed to discover incipient plutonium exposures and identify such individuals who may require work with less chronic exposure liability, this method has proved reliable, sensitive, and adequately precise. In this application the lag time required between sampling and recording of results is of little consequence.

REFERENCES

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