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Health and Biology

AEC Research and Development Report

DETERMINATION OF PLUTONIUM IN URINE

by

S. Marshall Sanders, Jr.

Health Physics Section

Savannah River Plant

March 1956

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ABSTRACT

A description is given of the procedure used at the Savannah River Plant for the determination of plutonium in urine. The procedure includes two bismuth phosphate coprecipitations, two lanthanum fluoride coprecipitations, a thenoyltrifluoroacetone (TTA) solvent extraction, an electrodeposition, and a radioautographic determination. An average plutonium recovery of 77 per cent with a standard deviation of ± 17 per cent was obtained from 272 samples spiked with plutonium to give 1.08 disintegrations per minute. Mention is also made of similar procedures used at other locations. The information contained in this report was presented in a talk given before the Bio-Assay and Analytical Chemistry Meeting that was held at the Fernald Plant of the National Lead Company on October 6, 1955.

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DETERMINATION OF PLUTONIUM IN URINE

INTRODUCTION AND SUMMARY

It is necessary to employ extremely rigid control over all plutonium operations because of the possibility that small amounts of plutonium accumulated in the skeletal systems of workers may, over a period of from ten to thirty years, cause pathological effects. Urinalysis gives the best indication of the effectiveness of control but is difficult due to the very small quantities of plutonium which are toxic and the extremely slow rate of excretion of plutonium from the body.

In an effort to obtain a satisfactory method of analysis for plutonium, a study of existing urinalysis procedures was made late in 1952 under the Bio-Assay Program of the Savannah River Plant. Although none of the existing procedures were ideal, the use of a combination of several procedures enabled work to begin immediately on plutonium analysis.

To avoid the evaporation of large quantities of urine, a procedure similar to one developed by L. B. Farabee at the Oak Ridge National Laboratory was adopted. This procedure included two bismuth phosphate and two lanthanum fluoride coprecipitations to separate the plutonium from the urine. Rather than use an alpha-counting technique, the latter portion of a more sensitive procedure presently used at Hanford was adopted which added a solvent extraction, an electrodeposition, and a radioautographic step, to make a total of 111 operations.

Using this procedure, laboratory technicians have been able to obtain an average recovery of 77 per cent with a standard deviation of ± 17 per cent from 272 urine samples spiked with plutonium to give 1.08 disintegrations per minute.

Additional development work on the existing procedure is now being done. It is hoped that the method will be simplified and recoveries will be improved.

DISCUSSION

BACKGROUND

Since the discovery of plutonium late in 1940 by Seaborg, McMillan, Kennedy, and Wahl of the Radiation Laboratory at Berkeley, the quantity of plutonium in the world has continuously increased. Observations of plutonium toxicity in rodents and the experiences of the radium dial industry have emphasized the necessity of employing extremely rigid control over all plutonium operations. The major health problem associated with plutonium processing is, of course, the possibility that small amounts of plutonium accumulated in the skeletal systems of workers may, over a period of from ten to thirty years, cause bone changes similar to those observed in chronic radium poisoning. The possibility is serious enough to justify the adoption of a rigid maximum permissible body burden.

At first, a tentative limit was established on an arbitrary basis. From purely physical considerations it seemed that plutonium, weight for weight, should be approximately one-fiftieth as toxic as radium. Since the tolerance amount of radium in the body is generally accepted as 0.1 μg , the body tolerance for plutonium was initially set at 5.0 μg . In July 1945, on the basis of experimental evidence, the Manhattan District lowered the plutonium tolerance limit to 1.0 μg . The level adopted at Hanford and Oak Ridge was 0.5 μg , since operating conditions made this lower level achievable without added facilities. At Hanford this tolerance was tentatively lowered in 1948 to 0.1 μg . In March 1950, the Division of Biology and Medicine of the Atomic Energy Commission adopted 0.5 μg (0.032 μc) as the official maximum permissible tolerance for plant personnel. The value of 0.04 μc (0.57 μg) was agreed upon by the Subcommittee on Permissible Internal Dose of the National Committee on Radiation Protection and the Subcommittee on Permissible Dose for Internal Radiation of the International Commission on Radiological Protection. This value was subsequently recommended by the ICRP in 1955 following the Seventh International Congress of Radiology in Copenhagen.

The only way to make certain that plant personnel do not approach this body tolerance is through frequent analysis of urinary excretions. The chemist therefore has been faced with the problem of developing a urinalysis which is sensitive to tracer quantities of plutonium. The problem is further aggravated by the fact that only an extremely small percentage of the plutonium in the body is excreted daily. This amount in the urine is in the order of 0.5 per cent the first day after assimilation, but decreases rapidly during the first year to about 0.0025 per cent⁽¹⁾. To help comprehend the magnitude of this problem, imagine that every person in the whole world was injected with 0.5 μg of plutonium and all their urine was collected for a one-year period following the injection. Assuming that there are 2.5 billion people in the world and each person excreted 3.4 per cent of the injected plutonium during the first year, the urine, which would fill an average-size dam reservoir with a capacity of about one million acre-feet, would contain plutonium weighing only as much as a number 9 rubber stopper.

To conquer this problem, in the latter part of 1943 E. R. Russell of the University of Chicago Metallurgical Laboratory was asked to develop a procedure sensitive enough to detect these minute quantities of plutonium in urine. The procedure developed by him is commonly referred to as the bismuth phosphate - lanthanum fluoride coprecipitation method⁽²⁾. In this method the urine sample is ashed with nitric acid. The plutonium is then coprecipitated with bismuth phosphate, the precipitate being dissolved in hydrochloric acid and then coprecipitated with lanthanum fluoride. The lanthanum fluoride precipitate is slurried on a stainless steel plate and is counted for alpha activity in a low-background alpha proportional counter. This procedure has been compared with other methods many times since it was first adopted in 1944 and is still used by the Canadian, Los Alamos, and Argonne groups.

Early in 1947, L. B. Farabee developed a procedure which, using this principle, provided a method of precipitating plutonium directly from urine, thereby eliminating the evaporation of large volumes of liquid⁽³⁾. The Oak Ridge National Laboratory group later discontinued the use of this procedure due to the belief that bismuth contains active impurities which interfere with their counting technique.

The bismuth phosphate procedure was replaced by an earlier one employing calcium oxalate to coprecipitate the plutonium⁽⁴⁾. This procedure includes a direct precipitation of calcium oxalate from urine, an oxidation of the oxalate to dissolve the precipitate, a precipitation of lanthanum hydroxide to separate the plutonium from the calcium, and a final coprecipitation with lanthanum fluoride. The LaF_3 precipitate is mounted on a platinum disc and counted in a standard alpha chamber. An average plutonium recovery of about 92 per cent with good precision is reported, but the sensitivity is not felt to be low enough for the present tolerances.

A procedure developed by W. H. Langham was used during 1945 at the Los Alamos Scientific Laboratory⁽⁵⁾. The procedure consists of collecting a 24-hour urine sample under very rigorous conditions to avoid contamination of the sample from traces of plutonium on the hands. The sample is evaporated almost to dryness and wet ashed by repeated treatments with concentrated HNO_3 . After all organic matter is destroyed, the sample is dissolved in weak acid and the plutonium is extracted from the solution using cupferron and chloroform. The chloroform solution is evaporated, and the residue is digested with perchloric acid. The plutonium is coprecipitated from the perchloric acid solution with a small amount of LaF_3 . The LaF_3 is transferred to a platinum plate and the plutonium alpha activity is counted in a proportional alpha counter for at least one hour. For statistical reasons alone the results are seldom better than ± 50 per cent. This method was abandoned in 1948 in favor of Russell's procedure developed at Argonne⁽²⁾.

Only the British presently use the cupferron - chloroform method. They have improved the counting procedure by the use of a zinc sulfide scintillation counting system. The samples are counted

for a period of 8 to 16 hours.

Work on a plutonium analysis was begun independently at the Hanford Engineering Works in 1946. After early attempts to use resin columns to separate the plutonium had failed, an analysis was developed on the basis of an extraction process then used by the Biology Group at the University of California for the analysis of biological samples. The process consists of first ashing and muffling a 24-hour sample of urine. The residue is then dissolved and coprecipitated with LaF_3 ; the precipitate in turn is dissolved and extracted with thenoyltrifluoroacetone (TTA). The plutonium is then leached from the solvent layer with an acid solution and is plancheted on stainless steel planchets.

With a reduction in the tolerance level established in 1948, it became apparent that the method in use at that time would require revision in order to detect with confidence much less than 0.33 d/m of plutonium. Another situation which made this change necessary was the large amount of instrument maintenance required on the low-background alpha counters. At times as many as half of the sets were "out" for extended periods. Several items to come from this revision⁽⁶⁾ were the reduction in the 60 mg of lanthanum used to 20 mg (originally 80 mg were used), the incorporation of a second LaF_3 precipitation, the substitution of an electrodeposition step for plancheting, and the addition of a radioautographic step. The radioautographing procedure consists of placing the stainless steel discs, which have been plated with plutonium, in contact with nuclear track alpha plates for one week. The plates are then processed, and the number of tracks from the alpha particles are counted with a microscope using 430X magnification.

PROCEDURE

Late in 1952 the Bio-Assay Program for the Savannah River Plant began to take form. Early plans were to adopt the Hanford procedure per se. Steps were taken so that there would be none of the characteristic Bio-Assay odors caused by prolonged boiling of large quantities of urine. A plastic exhaust system using water-jet ejectors was designed and installed in the new laboratory to carry off the odors. In addition to this, a chemical method of eliminating the evaporation step used by most installations was sought. Several methods were considered, but the direct coprecipitation of the plutonium from the urine seemed most promising. A number of precipitates were tried, including calcium oxalate and bismuth phosphate. Better recoveries were obtained during the developmental stage using bismuth phosphate, so a procedure based on Farabee's method⁽³⁾ was adopted.

The collected urine is placed in a two-liter beaker and is made about 0.2 normal in nitric acid. The beaker is placed on a hot plate and heated until the temperature of the urine reaches 65°C. The agitation of the urine is started and continued throughout the precipitation. The urine is then made 0.1 molar in phosphoric acid. From a separatory funnel, 10 ml of bismuth (III) nitrate solution

(232g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 1 liter of 10N HNO_3) is added dropwise over a period of approximately 15 minutes. Thorough stirring of the urine and precipitate is continued for 30 minutes. The precipitate is allowed to digest overnight at room temperature.

After standing overnight, all but about 25 ml of the clear supernatant liquid is aspirated. The precipitate is now dissolved in 23.5 ml of concentrated nitric acid. Ten ml of 30 per cent hydrogen peroxide is added to the beaker, and a watchglass is placed over it. The solution is heated until the reaction stops. More hydrogen peroxide may be added if needed. This operation destroys most of the organic matter. Upon cooling, two ml of 6 per cent sulfurous acid is added to reduce any Pu(VI) to Pu(IV). (The addition of sulfurous acid in addition to hydrogen peroxide is now believed to be unnecessary.) Reduction for 15 minutes is adequate.

Bismuth phosphate is again precipitated by adding 1500 ml of distilled water heated to 65°C , and adding 7.5 ml of 85 per cent phosphoric acid dropwise while agitating the solution. The precipitate and solution are then stirred for 30 minutes and allowed to digest for two hours at room temperature. The clear supernatant liquid is then aspirated, leaving not more than 25 ml over the precipitate. The precipitate is slurried in the liquid and the contents are poured into a 50-ml cone-shaped centrifuge tube. As much water from a wash bottle as is necessary is used to wash the remaining precipitate into the centrifuge tube. The precipitate is centrifuged at 2000 RPM for ten minutes and the supernatant is decanted. Four ml of concentrated hydrochloric acid is added to the two-liter beaker. A watchglass is placed over the beaker and the beaker is heated until the acid fumes wash down the remaining precipitate. The contents of the beaker are then added to the centrifuge tube. One ml of acid is then used to wash down the walls of the centrifuge tube.

These two precipitations eliminate all but a trace of the original urine. To separate the plutonium from the large quantity of salts present, the plutonium is coprecipitated with lanthanum fluoride. The volume of the liquid and precipitate in the centrifuge tube is approximately 12 ml and contains sufficient hydrochloric acid to dissolve the precipitate completely and to leave an excess acidity of from 1.0N to 2.0N. One mg of La(III) carrier is added and the solution is made 2N in hydrofluoric acid. Larger amounts of lanthanum carrier, used in other analyses, introduce more active impurities and were found to be unnecessary. With occasional stirring, the precipitate is digested for five minutes and centrifuged for ten minutes at 2000 RPM. The supernatant is then decanted.

To the precipitate, which may contain some organic matter, 0.2 ml of 60 per cent perchloric acid is added. With continuous shaking, the acid is fumed cautiously in a bunsen flame until the organic matter is completely destroyed. After cooling, 0.5 ml of concentrated hydrochloric acid is added, and the volume is increased to 5 ml with distilled water. Then 0.4 ml of 6M hydroxylamine-hydrochloride is added and 15 minutes are allowed for the reduction of Pu(VI) to Pu(III).

A second lanthanum fluoride coprecipitation occurs when the solution is made 2N in hydrofluoric acid. The precipitate, after being digested for five minutes with occasional stirring, is centrifuged for ten minutes at 2000 RPM and washed once with 1N HNO₃ - 1N H₂F₂ solution.

After the second lanthanum fluoride coprecipitation, some procedures call for slurrying the precipitate and transferring it to a planchet for counting. These procedures lack the sensitivity that is felt necessary with the present tolerance levels. To overcome this difficulty, the method used at Hanford⁽⁶⁾ to increase the sensitivity of their analysis was adapted to the procedure. Thus by combining these two analyses, the procedure used at the Savannah River Plant eliminates the evaporation of large volumes of urine but maintains the desired sensitivity.

The first step to increase the sensitivity is to extract the trace quantities of plutonium from the lanthanum by using a (TTA) solution. To prepare the sample for the solvent extraction, the precipitate is dissolved in 40 ml of a solution which is two molar in aluminum nitrate with the pH adjusted to 0.45. (Smaller amounts of this solution are now believed to be adequate.) This solution is then poured into a 125-ml Squibb separatory funnel. The centrifuge tube is rinsed with 10 ml of distilled water and the rinse is added to the funnel. The plutonium is oxidized to Pu(IV) by adding 0.25 ml of a freshly prepared 2M sodium nitrite solution, shaking the separatory funnel briefly, and allowing the mixture to stand for 15 minutes. Ten ml of the solvent solution containing 50 gm of TTA in a liter of toluene are added to the funnel. (Due to its higher vapor pressure and lower toxicity, toluene is used rather than benzene.) The funnel is shaken for 20 minutes and allowed to stand until the phases separate. The aqueous phase is then discarded and the solvent is washed by shaking for 10 minutes with first 20 ml and then 10 ml of distilled water. The washings are discarded and the plutonium is leached from the solvent by shaking for 20 minutes with 10 ml of 8N HCl, and washing with an additional 5 ml of the same acid. The acid layers are collected in a 100-ml beaker and evaporated to 1 or 2 ml without boiling.

Since the more sensitive method employs radioautographing rather than counting, it is necessary to have a uniform source of plutonium on a small area of accurately known size. Such a source is prepared by the reduction of Pu(VI) to Pu(IV) in a basic solution and the electrodeposition of Pu(IV) as Pu(OH)₄ on a stainless steel disc. To do this, the evaporated acid leach containing the plutonium is neutralized with 12N KOH. The plutonium is then oxidized to the hexavalent state by adding 2 ml of NaClO (5 per cent Cl₂). The solution is then made basic with 5 ml of 2N KOH and the volume is reduced to one-half by heating. This solution is transferred to an assembled electrodeposition cell with a stainless steel disc as the cathode and a platinum stirrer as the anode. A plating current of 350 ma is applied at a potential of 3 volts for 5 hours.

Lanthanum nitrate contains an appreciable amount of actinium and protactinium contamination. In the Hanford procedure, the daughters from the radioactive decay are removed by several successive precipitations of lanthanum with ammonium hydroxide before it is used. The experiences of the Bio-Assay group at the Savannah River Plant indicate that such purification is unnecessary, since none of the active daughters are carried through the electrodeposition step.

After electrodeposition the stainless steel discs are placed in a radioautographic camera. This is a device which positions the plated area (7 mm diameter) of the disc against the Kodak NTA emulsion. The emulsion, which is 25 microns thick, is contained on 1 x 3-inch glass plates and covered with a protective coating. After being exposed for one week, the NTA plates are developed for 10 minutes in Kodak D-19 developer, rinsed in distilled water for 1 or 2 minutes, and fixed in Kodak F-5 fixer. After the plates have been washed for an hour and air dried, the tracks in the emulsion caused by the plutonium alpha are counted. A Leitz Model XI-C microprojector, equipped with a large field of view 12.5X eyepiece and an Achromat 14/0.40 objective, is used in this operation. All tracks which lie in a 12.92 mm² area of the emulsion, are counted. A background count is made on an unexposed portion of the emulsion and subtracted from the sample count. The amount of plutonium present is calculated by comparing the number of tracks from the sample with the average number of tracks found in the analysis of a large number of urine samples spiked with a known amount of plutonium.

The use of the microprojector instead of the microscope is an innovation not used elsewhere. It was adopted because of two principal advantages. One is that a forty-fold larger field of view can be projected than can be viewed under a microscope, thus lessening the number of settings required to count a sample. The other is the ease in training new technicians where specific tracks may be pointed out and simultaneous countings made.

CONCLUSIONS


Since the adoption of this procedure for plutonium analysis at the Savannah River Plant in 1954, 244 urine samples spiked with 1.08 d/m of plutonium and 30 spiked with ten times this amount have been analyzed. The average recovery for all except two, which were deleted due to known analytical errors, was 77 per cent with a standard deviation of ± 17 per cent. A recent routine study of 27 analyses of blank urine showed that the average activity in 1500 ml was 0.016 d/m with an upper 99 per cent confidence level of 0.04 d/m.

The practice of coprecipitating plutonium directly from raw urine is viewed with some skepticism by those responsible for the development of other plutonium urinalyses where the urine is eliminated by evaporation and oxidation. The reasons for the evaporation and oxidation step are to destroy any organic compound whose varying concentration in the urine might influence the coprecipitation of plutonium, and to dissolve any insoluble basic plutonium colloid

which may have been formed due to the pH of the urine. The experience with this analysis at the Savannah River Plant and that of Farabee at Oak Ridge⁽³⁾ seems to indicate that the preliminary evaporation and oxidation is not necessary. Since the urine used for the spikes is collected in a 6-1/2-gallon container and represents the voidings of a large number of people, the possibility that a single voiding might contain interfering material still remains. This possibility is presently being investigated. The possibility seems remote, since the samples are collected for plutonium analysis over a three-to ten-day period and will not be greatly influenced by a single voiding.

Work to improve the plutonium urinalysis is continuing at the Savannah River Plant and other AEC installations. Developmental work on this type of procedure, of necessity, must progress very slowly. Each change must be tested before it can be incorporated into the procedure. Only one change at a time can be allowed where an established procedure is relied on for large quantities of routine work. If too many changes are made too quickly, the cause of an analytical failure would be extremely difficult to isolate.

One change which is anticipated in this procedure is the elimination of one or more of the bismuth phosphate and lanthanum fluoride coprecipitations. The elimination of all but one coprecipitation has been accomplished with some promising results. This procedure needs a great amount of developmental work before it can be used. The use of "Dowex" 50-8X resin to separate plutonium from urine has recently been tried at Hanford with some preliminary success. The possibility of plating plutonium on the polished end of a 1/16-inch diameter wire has been tried at Hanford, with the only difficulty being the locating of the plated area on the NTA slide. This method of plating is being considered at the Savannah River Plant as a means of reducing the quantity of urine necessary for the analysis.


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