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THE QUANTITATIVE DETERMINATION OF PLUTONIUM IN BIOLOGICAL MATERIALS

PART I. THE ANALYSIS OF URINE

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by

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The majority of the experimental work in developing and testing these procedures is due to the efforts of Mr. Ercole Botta, Dr. M.D. Taylor, Miss Cordelia Brown, Mr. David Revinson and Mr. Roman Lesko. The authors wish to express their appreciation.

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1. Introduction

In the early phases of the Project it was essential for the development of a plutonium (Pu) extraction process that analytical procedures be devised whereby tracer quantities of this element could be determined with a fair degree of accuracy. As the various processes were being investigated, it became apparent that no one analytical procedure was suitable for the various plutonium-containing solutions. Usually the final step in each method involved a co-precipitation of plutonium with lanthanum fluoride. The amount of lanthanum required to carry plutonium quantitatively from up to 50 ml of solution was sufficiently small that when spread over a one inch diameter platinum plate less than one per cent absorption of the alpha particles from tracer amounts of plutonium was observed.

Likewise, a similar experience was encountered by investigators in the Health Division when it became necessary to determine quantitatively the amounts of plutonium in various biological specimens. Little difficulty was encountered in applying the previously developed analytical procedures where relatively large amounts of plutonium were handled. Simple ashing of the organic matter, dissolving the ash and counting an aliquot of the solution after evaporation on a platinum plate was feasible. Where the residue on the plate gave rise to mass absorption of the alpha particles a simple co-precipitation of the plutonium with lanthanum fluoride reduced the absorption of the alpha particles to negligible percentages. Over 200 animal specimens, including tissues, feces, and urine, have been successfully assayed in the above manner.

Such a simple procedure is not applicable to an accurate analysis of biological materials containing minute quantities of plutonium, of the order of

10^{-5} micrograms per gram of ash. A suitable analytical method involves the preliminary separation of the plutonium from the organic material or the ashed residue.

Part I of this series of three papers deals with the development of methods for the quantitative determination of plutonium in urine. Since methods applicable to the determination of minute quantities of plutonium are usually applicable in determinations of larger amounts, the reverse not always being true, the methods discussed here will take these facts into consideration.

An accurate method for determining the plutonium in urine serves many purposes, among which are (1) estimation of the rate of urinary plutonium excretion from animals or humans after parenteral intake of a known quantity of the element and (2) a means of checking the amounts in the bodies of individuals working with, or in, areas contaminated by plutonium.

The following discussion will include a description and an evaluation of the three general analytical procedures employed on the Project for the detection of plutonium in humans. It is emphasized that these methods are not limited in application to human urines.

2. Adsorption

The efficacy of cation exchange as a means of extracting, decontaminating, and concentrating plutonium from large volumes of solution has received ample demonstration. 1,2 Because the determination of Pu from urine was a similar problem, it was felt that an analogous adsorption procedure could be applied. An extensive investigation of optimum conditions was made by E.R. Russell and co-workers.

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In this report a detailed description of much of the preliminary work is omitted, and only the most recently developed flowsheet is presented. A short discussion of the use of an anion exchanger is also included.

Very briefly, the adsorption process for determining plutonium in urine consists of passing a liter of acidified urine through an adsorption column 3 of Amberlite cation exchange resin, IR-1, and eluting the adsorbed Pu with 7 M HCl. The solution of Pu in the 7 M HCl is evaporated to near dryness to remove the bulk of the acid and then diluted with water. This aqueous solution of Pu is passed through a second column of adsorbent. This second column contains only about 1/16 by weight as much resin as is present in the first column. The adsorbed Pu is eluted with 7 M HCl and is contained in a total volume of 60 ml. This solution is evaporated and mounted directly on a large platinum disc. The deposited plutonium is determined by counting the alpha activity. The advantages claimed for the column method are:

1. No preparation of the urine is necessary. When received, the urine is acidified.
2. No carrier such as LaF_3 or $BiPO_4$, for example, is used at any time.
3. The operation may be interrupted at any stage desired.
4. One technician can run several samples simultaneously.
5. The equipment and adsorbent, when once set-up, is used repeatedly.

2.1 Theory. The chemistry involved in the extraction of plutonium by a cation exchanger is given in the project literature[3], as well as a discussion and description of the applications of column adsorption processes to analytical chemistry. The preparation and properties of ion exchangers is discussed elsewhere.[5]

Essentially, the cation exchange reactions follow the law of mass action.[4] A given reaction, then, can be made to proceed in any direction merely by altering the relative concentration of the reactants and products. In the adsorption process for extracting and subsequently eluting plutonium from urine, the principle reaction for both the adsorption and desorption steps is:

$$Pu^{+4} + 4\ HR \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} PuR_4 + 4\ H^+$$

The symbol, R, represents the non-diffusible anionic part of the cation exchanger.

The adsorption of the plutonium is made from urine 0.1 N in hydrochloric acid, while the desorption is carried out with 7 N hydrochloric acid.

2.2 Experimental: Materials and Apparatus. Amberlite resin IR-1 is employed in the first column adsorption step because of its high capacity, though IR-100 can be substituted if desired.[5] In the second column step a more insoluble resin, IR-100H, is employed because it serves to reduce the amount of solid matter associated with the plutonium.

The glass columns are set up in the usual manner.[3] Glass wool, when carefully inserted, serves as a satisfactory support for the resin bed. A straight glass stopcock is used to regulate the flow rates. A two liter leveling bottle serves as a storage tank in Step I, while a 500 ml size suffices for Step II. Satisfactory flow rates are provided by the water pressure produced by elevating the leveling bottles two feet above the resin bed.

It is assumed that column operations[3] such as backwashing, etc. are familiar to the reader.

Large platinum discs, 4.5-5 cm in diameter are employed for counting. Flaming

of the discs before counting is important in reducing self-adsorption of the alpha radiations. Experiments indicate that flaming results in about 5 per cent increase in counting efficiency.

2.3 Discussion of Procedure. The accompanying flow sheet provides all the details of the operations involved in the analysis of liter quantities of urine for plutonium. It is well to enumerate the function served by the different solutions employed.

1. The acidification of the urine prevents the precipitation of calcium salts, keeps the Pu in ionic form, and breaks up any unadsorbable complexes that plutonium may form with urinary constitutents.

2. The 0.4 HCl removes some adsorbed organic matter as well as calcium and other cations.

3. The 7 M HCl serves to elute the Pu quantitatively and in a small volume.

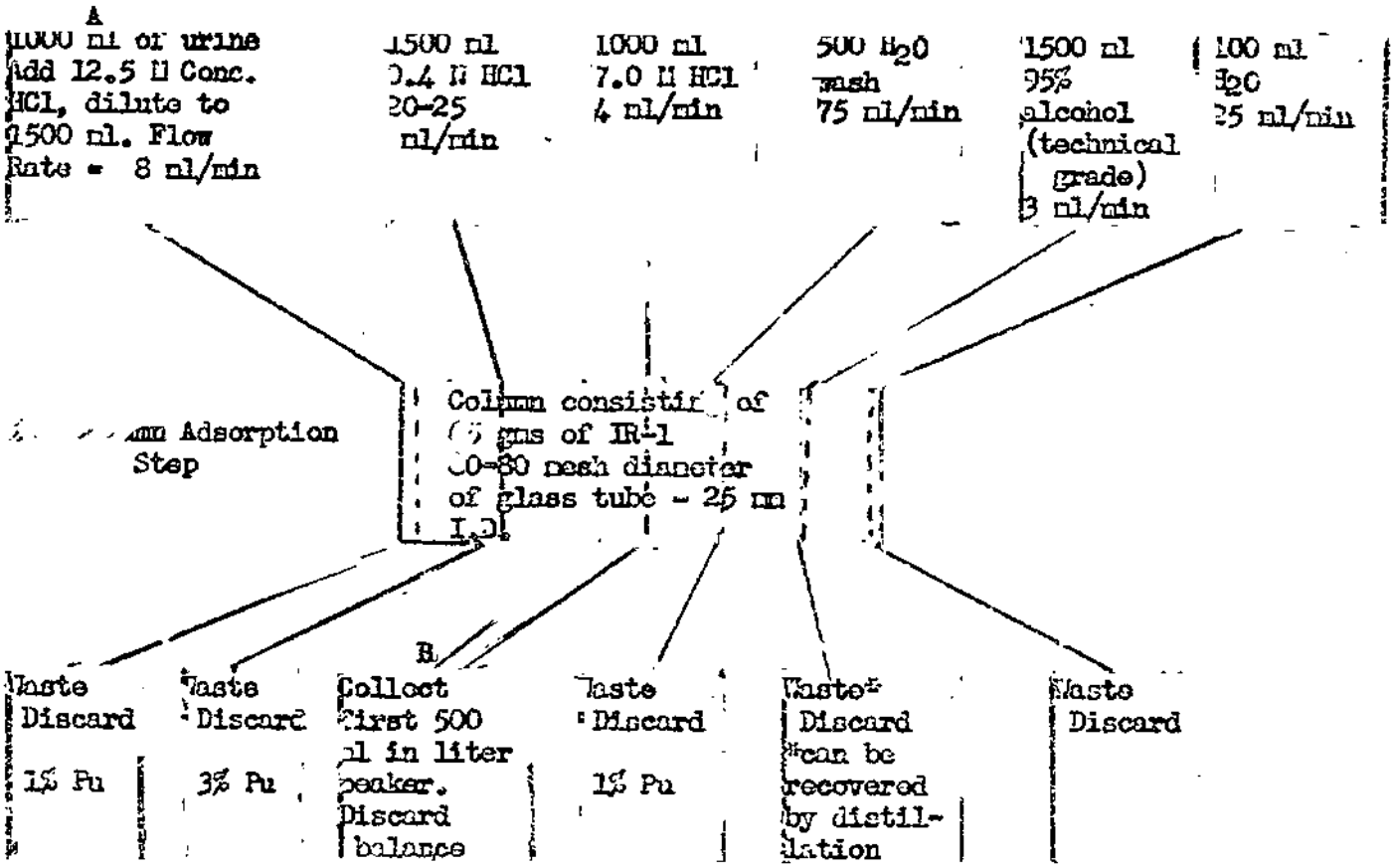
4. The 95 per cent alcohol also removes remaining organic matter. This step was introduced by Schubert[6] when it was found that the adsorption of Pu from liter quantities of urine kept decreasing, i.e. the breakthrough point was quite erratic and as much as 35 per cent of the Pu would be lost. It was presupposed that alcohol soluble organic matter coated the resin particles so that the adsorption of Pu was hindered. The alcohol wash was found to prevent the premature breakthrough of plutonium.

2.4 Results. The adsorption method as it now stands gives overall consistent recoveries averaging about 85 per cent of plutonium present in urine. Thus, four consecutive runs gave recoveries of 85, 75, 90, and 81 per cent respectively. No effect of plutonium concentration on recovery was noted.

2.5 Effect of Acids and Urinary Constituents on Plutonium Adsorption. Because the concentration of substances such as albumin and urea which normally appear in urine is quite variable, it was desirable to ascertain their effect on plutonium adsorption.

Figure I

Flow Sheet for the Determination of Plutonium in Human Urine by Column Adsorption



1. Evaporate on hot plate to moist dryness.
2. While on hot plate add sufficient 1:1 HNO_3 to cover residue and evaporate.
3. Repeat step 2.
4. Allow to cool. Add 20 ml 1:1 HNO_3 and evaporate to dryness. Allow to cool.
5. Add 10 ml 1:1 HNO_3 and evaporate to moist dryness.
6. Dilute to 400 ml with distilled water. Add 1 ml concentrated HCl.
7. Pass through second column.

Albumin

The presence of up to 2 grams of albumin per liter of urine has no observable effect.

Urea

In the range of concentrations studied, 0-4.0 grams of urea per 100 ml of urine, no effect on Pu adsorption was noted.

Acids

The equilibrium adsorption of plutonium by IR-4 from urine acidified with each of the following acids was studied: acetic, sulfuric, hydrochloric and nitric in concentrations ranging from 0.1 N to 1.0 N. The maximum adsorption was obtained when the solutions were 0.1-0.2 N in acid. Higher concentrations of acids caused a marked decrease in plutonium adsorption.

Solutions of urine having no added acid showed low adsorption. In this case, as with acetic acid, the low adsorption is probably due to the formation of complex ions with plutonium by the acetate ion and the organic salts present in urine. These complexes are broken down when the urine is acidified with a mineral acid.

Sodium chloride

Concentrations of NaCl up to 1.2 per cent do not reduce the adsorption of plutonium.

2.6 The Use of Anion Exchangers for Determining Pu in Urine[6] A minimum of 0.5 gram of the anion exchanger, IR-4, in the HCl form, to 100 ml of urine has been used to extract plutonium. Generally, about 10 grams of IR-4 (42-60 mesh) was shaken until equilibrium adsorption of plutonium was reached (minimum of 2 hours).

Following the shaking, the urine was decanted and the resin washed into a medium pore sized fritted glass funnel. The adsorbed Pu was removed by allowing 6 N HCl (~ 30 ml) to percolate through the resin contained on the fritted glass. Finally, the resin was washed with distilled water and sucked dry. The plutonium in the eluant was determined by the usual LaF_3 precipitation. Experiments have shown that material dissolved from the resin does not interfere with the LaF_3 method for the assay of plutonium.

Acetic acid in concentrations up to 0.6 M and oxalic acid in concentrations as high as 0.8 seem to have little effect on the adsorption of Pu by IR-4. Hydrochloric acid in concentrations above 0.1 M reduces the adsorption considerably.

While recoveries as high as 95 per cent have been achieved, results on the whole have been erratic. One of the chief drawbacks has been the variable results obtained with different batches of urine. For undetermined reasons different urine samples would so effect the adsorption of Pu by IR-4, that recoveries sometimes dropped as low as 40 per cent. It seems apparent that the anion exchange method is adversely affected by changes in the concentration of urinary constituents.

3. Solvent Extraction

The extraction of plutonium from aqueous solutions into organic solvents has been accomplished by the salting out of inorganic compounds of plutonium such as in the case of ether[7] and hexone[8] extractions and by the formation of organic complexes of plutonium which are more highly soluble in organic solvents. The plutonium complex of cupferron is very highly soluble in chloroform[9] and the plutonium complex of thiophenyltrifluoroacetone is very highly soluble in benzene[11].

Since all of these organic solvents are only slightly soluble in aqueous solutions, it should be possible to devise an extraction procedure to remove plutonium from urine or a solution of the ash.

The extraction of plutonium from natural urine by any of the above solvents is inhibited by the presence of fat soluble materials. Erratic results have always been obtained. As a necessary factor, then, the organic constituents of urine must be completely destroyed or a preliminary precipitation performed which would separate the plutonium from the urine. Both of these procedures are used in the methods described in this section.

3.1 Cupferron-chloroform Procedure 10. A 50 ml aliquot of an ashed urine solution is adjusted to a pH between 0.4 and 0.7 using methyl violet indicator. One ml of 20 per cent hydroxylamine hydrochloride is added. The solution is heated under a lamp for about two hours to facilitate the reduction of plutonium. The pH is readjusted using the same indicator. Twenty-five ml of 10 per cent oxalic acid are added after 0.1 gram of calcium has been stirred in. The precipitate is centrifuged out and washed once with one per cent oxalic acid. About 10 ml of fuming nitric acid are added to the precipitate and the solution taken to dryness under an infra red lamp. The residue is dissolved in 25 ml of 2 M hydrochloric acid and transferred to a 125 ml separatory funnel. Five drops of 20 per cent hydroxylamine hydrochloride and one ml. of iron are added. The acidity is adjusted so that a bright green color is obtained with methyl violet indicator. After allowing a half hour for reduction of plutonium, about one ml of a 6 per cent aqueous solution of cupferron is added. Four or five extractions using about 2 ml of chloroform for each extraction are carried out. The chloroform phases are

collected in a 40 ml centrifuge cone. The cone is placed in a hot water bath to evaporate the chloroform. One ml of concentrated nitric acid and one ml of 72 per cent perchloric acid are added to the residue and the tube placed in an oil bath at 100°C. The temperature of the oil bath is raised to about 180°C over a period of one hour. At the end of this time about one ml of a clear perchloric acid solution remains. This is diluted to 5 ml with distilled water. Two drops of 20 per cent hydroxylamine solution are added and the solution allowed to stand for one-half hour. Two hundred micrograms of lanthanum followed by one-half ml of 27 N hydrofluoric acid are added. The lanthanum fluoride precipitate is centrifuged out, transferred to a platinum plate, and counted.

It is necessary that a preliminary precipitation be made in order to apply a cupferron-chloroform extraction. Since at the pH where plutonium is most effeciently extracted, a portion of the urine ash will precipitate, carrying plutonium, and thereby cause erratic results. Other preliminary precipitations, as lanthanum fluoride, calcium phosphate, and lanthanum oxalate, have been used with a fair degree of success. The adopted method eliminates the possibility of alpha contamination which is usually present in commercial lanthanum. The method is reported to give better than 80 per cent recovery.

3.2 Thiophenyltrifluoroacetone Procedure (T.T.A.)[11]. The use of T.T.A. for forming a complex with plutonium which is very soluble in benzene was developed by K.G. Scott[12] at Berkeley. The original method proposed by Scott for extracting plutonium from solutions of biological ash has been altered slightly to be used as a routine analytical method for the determination of plutonium in human urine specimens[13]. The method is applicable to any solution

from which plutonium can be co-precipitated with lanthanum fluoride.

The residue obtained from ashing the urine is dissolved in 100 ml of 2 M nitric acid which is 0.1 N in hydroxylamine hydrochloride. The solution is divided between two 100 ml centrifuge tubes and 20 mg of lanthanum added to each. Plutonium is co-precipitated with lanthanum when 10 ml of 12 N hydrofluoric acid are added to each tube and stirred. The tubes are allowed to stand for 5 minutes and then centrifuged at 2000 R.P.M. for 5 minutes. The supernate is discarded and the precipitate washed with 10-20 ml of 1.5 N hydrofluoric acid. The tubes are centrifuged a second time and the supernate discarded.

The lanthanum fluoride precipitates are dissolved in a total of 50 ml of 2.2 M aluminum nitrate which is 0.2 M in nitric acid. The solutions are combined in one tube. The plutonium is brought to the plus four oxidation state by allowing the solution to stand 15 minutes after the addition of 0.25 ml of a 11 per cent sodium nitrate solution. The solution is then transferred to a 100 ml separatory funnel and shaken 10 minutes with 10 ml of 6 per cent solution of T.T.A. in benzene. When the phases have separated the water layer is drawn off and discarded. The benzene layer is washed twice with 10-20 ml of water. The plutonium is extracted into 10 ml of 8 M nitric acid and this solution evaporated on a platinum counting plate and the plate counted for alpha particles.

It is possible to eliminate the extraction into the nitric acid solution as a negligible amount of solids are contained in the benzene solution. With care, this solution can be evaporated on a large counting plate. The extraction step alone as described above has been shown to be approximately 90 per cent

efficient. Tests on the overall procedure at Chicago excluding the final nitric acid extraction has shown approximately 80 per cent efficiency.

"Blanks (no plutonium present) have given less than 0.2 c/m. even though

The methods which are discussed in this section are based on the principles of coprecipitation and no attempt will be made to distinguish the type of the process involved.

4.1 Lanthanum Fluoride Method: Where the concentration of plutonium in the urine specimen is relatively high, the precipitation of 1 mg of lanthanum as the fluoride from a maximum of 40 ml of solutions will serve as a convenient and rapid method for determining the plutonium present. When the urine is made 1.5 M in hydrochloric acid and 2-4 M in hydrofluoric acid after the addition of 1 mg of lanthanum, from 85 to 95 per cent of the plutonium is coprecipitated with the lanthanum. The residue containing the plutonium is spread over a 3 cm diameter platinum plate and negligible absorption of the alpha particles results. In cases where larger volumes of urine are necessary, excessive amounts of lanthanum are required or when the urine is ashed and dissolved in a small volume of acid, the coprecipitation of other ions causes a large deposit on the counting plate. Accurate counting of the alpha particles is difficult.

4.2 Calcium Oxalate Method. The use of calcium oxalate as a preliminary precipitation in the analysis of ashed urine for plutonium was discussed previously[10]. M.E. Kosbland[14] has adapted the use of this material to the analysis of large volumes of urine for plutonium. The procedure is essentially a coprecipitation of plutonium with calcium oxalate, followed by oxidation of the oxalate, a coprecipitation of the plutonium with lanthanum hydroxide and a final coprecipitation of the plutonium with lanthanum fluorids. The details are given below.

Calcium Oxalate Precipitation. In order to obtain the maximum carrying of plutonium by calcium oxalate, the temperature of the urine should be at 25°C.

before precipitation, and the urine should be fresh and clear.

To approximately 1500 ml of urine are added; (a) sufficient hydrochloric acid (about 15 ml) to reduce the pH to 1.5-2.0, (b) 5 ml of a 3 M calcium nitrate solution, making the calcium concentration in the urine about 1×10^{-2} M.

While the urine is being mixed by a mechanical stirrer, 15 ml of 0.1 oxalic acid are introduced, and two to five minutes later the pH is adjusted to 3 on a Beckman industrial model by the addition of concentrated ammonium hydroxide. The vigorous stirring is continued for another two to five minutes and then the precipitate is allowed to digest overnight at room temperature.

As much of the clear supernatant is removed by a pipette as is possible without disturbing the precipitate. The calcium oxalate is slurried in the remaining 30 to 70 ml of liquid and is transferred to a 100 ml round-bottom centrifuge tube. With the aid of a rubber policeman, the beaker is washed three times with small aliquots of distilled water and the washes added to the original slurry. The combined solution is centrifuged for 10 to 15 minutes and the supernatant completely removed by suction using a pipette.

Oxidation of the Oxalate. To the calcium oxalate precipitate are added 2 ml of concentrated perchloric acid and the tube heated slightly for several minutes in a water bath until a clear dark brown solution is obtained. Three ml of a 1 M sodium bromate are introduced and the solution is oxidized for 50 to 60 minutes in a boiling water bath. The volume of solution is maintained nearly constant by the addition of distilled water.

Lanthanum Hydroxide Precipitation. At the end of the oxidation period, the colorless solution may be clear or slightly cloudy due to the high salt concentration.

While still hot, the solution is transferred to a 15 ml pyrex centrifuge tube containing 0.6 mg of lanthanum. The 100 ml tube is washed three times with distilled water and the washes added to the 15 ml tube. When the volume has been made up to 12 ml with distilled water, 3 ml of concentrated ammonium hydroxide are added and the solution stirred for several minutes until the lanthanum hydroxide precipitate appears. If the precipitate does not come down immediately, visible flocculation will occur with additional heating and stirring. After the lanthanum hydroxide has been allowed to digest 15 to 20 minutes, the light-brown flocculent precipitate is centrifuged down, washed once with dilute ammonium hydroxide and dissolved in 0.3 ml of concentrated hydrochloric acid.

Lanthanum Fluoride Precipitation. The acid solution is diluted to 2-2.5 ml with distilled water, 0.2 ml of 6 M hydroxylamine hydrochloride is added and the solution allowed to stand 10 to 15 minutes for the reduction of plutonium. The solution is made at least 2 N in hydrofluoric acid and is digested for 5 to 10 minutes with occasional stirring. The lanthanum fluoride precipitate is centrifuged for 10 minutes, washed once with a solution 1 N in nitric acid and 1 N in hydrofluoric acid, mounted, and counted.

4.3 Bismuth Phosphate Method. In the development of an analytical procedure for the determination of plutonium in urine it was felt desirable to work out a method whereby ashing of the urine could be avoided. Though ashing large volumes of urine was considered a drawback in an analytical procedure, experience has taught that there is little time saved in the analysis of a large number of samples. As a consequence the bismuth phosphate method has been adapted to both ashed and unashed urine. Some of the preliminary data which have been collected on these methods along with the details of each procedure is discussed.

Analysis of Unashed Urine. Preliminary tests showed that less than 5 per cent of the plutonium contained in urine which is 0.5 M in nitric acid is co-precipitated with bismuth phosphate, the bismuth concentration being 1 mg per ml. When the nitric acid concentration was reduced to 0.25 M and using identical conditions, over 98 per cent of the plutonium is coprecipitated. The tests were carried out on 30-1000 ml urine specimens containing 7,500 c/m of plutonium. The optimum amount of bismuth for quantitative carrying of plutonium from urine 0.25 M in nitric acid is shown in Table I.

Table I

Effect of Bismuth Concentration on the Carrying of Plutonium from Urine

Conc. Bi^{+3}/ml	Pu Recovery
0.2 mg	2.7 %
0.2 "	3.1
0.5 "	80
0.5 "	80
0.7 "	95
0.7 "	95
0.9 "	96
0.9 "	93
1.1 "	95
1.1 "	92

The data indicate that a minimum of 0.7 mg Bi^{+3} per ml should be used. It is advantageous to use as small a quantity of bismuth as is feasible as the amount of residue contained in the final lanthanum fluoride precipitate will be too high if more than 1 mg/ml is used.

The main difficulty which was encountered when liter volumes of urine were analyzed was the large organic residue obtained when the bismuth phosphate was centrifuged down. That this organic residue might not be attributed to any

specific acid, several experiments were run using in different samples 0.25 N nitric acid, 0.25 N sulfuric acid, and 0.1 M phosphoric acid respectively. The least residue was obtained where nitric acid was used. At the suggestion of S. Thompson, settling of the bismuth phosphate precipitate followed by syphoning off the supernatant liquid was tested. This procedure proved time consuming but was quite satisfactory in eliminating most of the organic residue.

The bismuth phosphate is dissolved in 35 ml of concentrated nitric and the solution diluted to 1 liter with distilled water. The bismuth is reprecipitated by adding 1.5 ml of phosphoric acid while the solution is stirred and digested at 80°C. This step gives a clear bismuth phosphate precipitate apparently free of organic material. This precipitate is dissolved in 5 ml of 4-5 M hydrochloric acid and transferred to a 15 ml pyrex centrifuge tube. The container is washed with an additional 3 ml of acid and the washings added to the 15 ml tube.

To the bismuth solution is added 0.5 mg of lanthanum (1 mg La^{+3}/ml 0.1 M HCl) and 2 ml of hydrofluoric acid. The solution is stirred, allowed to stand five minutes and centrifuged. The lanthanum fluoride is fumed with 0.2 ml of sulfuric and 2 drops of nitric acid. After dilution with 5 ml of distilled water, the lanthanum fluoride is reprecipitated by the addition of 1 ml of hydrofluoric acid. The precipitate is mounted on a platinum plate and counted. The results of two runs using 1000 ml of urine spiked with 10^6 c/m of plutonium are shown in Table II.

Losses in a Bismuth Phosphate-Lanthanum Fluoride Procedure

Step	Run 1 Loss	Run 1 Recovery	Run 2 Loss	Run 2 Recovery
Total supernate after two $BiPO_4$ precipitations	5.7%		5.9%	
Supernate after 1st LaF_3	9.7%		2.9%	
Supernate after 2nd LaF_3	2.2%		1.7%	
Plutonium Recovered in final LaF_3		87.7%		93.2%
Material Balance		105 %		104 %

When tests were made on large volumes of urine containing less than 5 c/m of plutonium, erratic results were obtained. Investigation of the method was discontinued in favor of the use of the ashed urine.

Analysis of Ashed Urine. The urine, up to 1500 ml may be ashed by any convenient method which leaves a soluble residue. This is usually done by evaporating the specimen to dryness after the addition of 100 ml of nitric acid. The residue which should never be heated strongly at dryness is taken up in 20-25 ml nitric acid and again evaporated to dryness. This procedure is repeated until a clear white residue is obtained. The residue is saturated with 2 ml of nitric acid, allowed to stand 15-20 minutes and then 35 ml of water added. A small insoluble suspension is usually present and this is transferred to a 50 ml centrifuge tube along with the liquid from the ashing vessel. The suspension is centrifuged down and the liquid transferred to a 90 ml pyrex centrifuge tube. The ashing

container is washed with 3 ml of 5 M nitric acid and the washings transferred to the 50 ml centrifuge tube. The acid is thoroughly mixed with the insoluble residue to leach any plutonium possibly adsorbed. The liquid is centrifuged and combined with that in the 90 ml centrifuge tube.

The solution is diluted to 80 ml and 2 ml of a saturated sulfur dioxide solution added. The solution is allowed to stand 20 minutes for the reduction of plutonium and is then heated to 75-80°C on a water bath. During the heating the solution is agitated constantly with a mechanical stirrer. One ml of a bismuth solution, containing 0.1 gram Bi^{+3}/ml 10 M nitric acid, is added dropwise. This is followed by the addition of 1 ml of concentrated phosphoric acid which is added slowly over a period of 3-5 minutes. The mixture is stirred and digested at the elevated temperature for 1 hour. After this period the stirring is discontinued and the bismuth phosphate allowed to settle. The bulk of the supernatant liquid is drawn off and discarded. Centrifugation may be used if desired. The precipitate and the remaining 1-2 ml of solution are transferred with the aid of distilled water from a wash bottle to a 15 ml pyrex conical end centrifuge tube. Centrifuge and discard the supernatant liquid. The 90 ml centrifuge tube is washed twice with 2 ml of 6 M hydrochloric acid and the washings added to the 15 ml centrifuge tube to dissolve the bismuth phosphate.

The bismuth phosphate solution is diluted to 5 ml and 0.5 ml of lanthanum solution, (0.5 mg La^{+3}/ml) added. The solution is stirred with a platinum rod while 0.5 ml of 13-15 N hydrofluoric acid is added. The lanthanum fluoride is centrifuged down and transferred as previously described.

5. Evaluation of Methods

The various procedures which were described previously have been used by independent groups to determine plutonium in urine specimens. Due to the urgency for the experimental results no one group was able to undertake a thorough comparative study of all the methods. The only attempts made to evaluate a few of the methods were in establishing the most reliable and rapid procedure to use. In each case the procedure adopted by the group has been the one which they were more familiar with. Each procedure has its advantages and disadvantages and on this basis we will attempt to discuss each method.

5.1 Adsorption Technique. This method of analyzing natural urine has the advantage of being applicable to mass analysis with a minimum of personnel and equipment. The most recent results, previously given, indicate that the method is reliable to the extent of 80 per cent recovery. However, for large volumes of urine insufficient data has been collected for the method to be recommended for use without further investigation.

The anion exchange adsorption procedure is apparently dependent on the concentration of certain urinary constituents for efficient recoveries. The urine used in developing the method, all from one individual, was of such a nature that over 90 per cent of the plutonium was always recovered. When other individuals supplied urine, the recoveries were erratic. The method is not recommended for use.

5.2 Cupferron-Chloroform Extraction Procedure. Considerable information has been obtained on the conditions for extracting the plutonium cupferride complex into chloroform from aqueous salt solutions. In the hands of an experienced technician, the method should prove quite reliable for the determination of

plutonium in ashed urine samples. The method appears longer than is necessary and the cupferron extraction can be eliminated provided the initial precipitation is altered. The procedure can be relied upon to give better than 80 per cent recovery.

5.3 T.T.A. Extraction Procedure. This method has not been widely used, but there are several unique features which make it appear attractive. The final deposit on the counting plate contains very little solid and therefore mass absorption of the alpha particles is at a minimum. Recovery of the plutonium in practically all tests have been above 80 per cent with the majority of the results being above 88 per cent. The only objection which might be raised is the manner in which the plutonium is mounted. The evaporation of 10 ml of nitric acid solution on a small flat plate is quite tedious and time consuming. However, a dropping pipette might be constructed to deliver the solution to the plate at the rate it is evaporated and thereby eliminate this objection. The method is reliable.

5.4 Lanthanum Fluoride Coprecipitation. The analysis of urine solutions or solutions of the ashed urine by coprecipitating plutonium with lanthanum fluoride is limited by (1) the volume of urine, 40 ml in the case of natural urine, and (2) the salt concentration of the dissolved ash. The method is only recommended for use where it is necessary to rapidly determine plutonium in small volumes of urine with an accuracy of 80 per cent.

5.5 Calcium Oxalate and Bismuth Phosphate Coprecipitation Procedures. Both of these methods appear to be satisfactory. The limitations, such as using fresh urine at 25°C. for the precipitation of calcium oxalate, may be objectionable as it is likely that the urine specimens may be stored before being analyzed. No recovery data have been reported for this method, however it is stated that

good recovery is consistently obtained. The method apparently is useful where ashing facilities are not available.

The bismuth phosphate method has been investigated quite extensively. The method has been tested under various conditions for analysis of urine for plutonium. It is not recommended for use on unashed urine though a few tests have given good results. On ashed urine the method will give consistent results of 90 per cent or better recovery.

6. Summary

The three general techniques, adsorption, solvent extraction, and coprecipitation, used in the separation of plutonium from undesirable constituents have been briefly discussed in connection with the analysis of urine solution for plutonium. A detailed outline of each analytical method is given with a brief discussion of the applicability of the method.

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