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LA-376 c. 3

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SERIES B

August 29, 1945 This document contains 9 pages

DETERMINATION OF PLUTONIUM IN HUMAN FECES

WORK DONE BY:

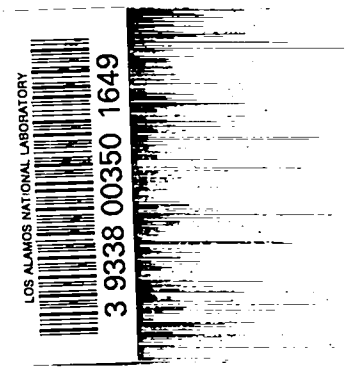
Robert Fryxell

Elizabeth Maxwell

REPORT WRITTEN BY:

Wright H. Langham

Elizabeth Maxwell



ABSTRACT

A detailed description is given of a method for determining plutonium in human feces. The essential features of the method are as follows: The dried sample is ashed in a muffle furnace and the ash dissolved in 2N HCl. The reduced plutonium is carried from an aliquot of the feces ash solution with calcium oxalate. The calcium oxalate precipitate is digested with fuming HNO_3 and taken up in 2N HCl. Ferric iron is added as a carrier and the plutonium is extracted into $CHCl_3$ as the cupferride. The cupferride complex is destroyed with $HClO_4$. The plutonium is carried with LaF_3, slurried to a platinum plate and counted in an alpha counter. Results with both mock and actual human feces ash solutions show the recovery of plutonium by this method to be 80 percent or better.

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DETERMINATION OF PLUTONIUM IN HUMAN FECES

INTRODUCTION

The toxic effects of plutonium on the human body depend on a considerable number of physical and biological factors. One of the most important biological factors is the rate of elimination of plutonium from the body.

The ratio of fecal to urinary excretion of plutonium by the rat is of the order of ten to one. This is indeed, a favorable ratio. Preliminary information, however, indicates that the excretion ratio for the human is much less favorable.

It is imperative that the fecal excretion of plutonium by the human and the ratio of fecal to urinary output be carefully determined. Information on these factors is extremely limited at the present time, partially because of the difficulty of analyzing human feces samples for extremely small amounts of plutonium.

This report presents a relatively accurate and consistent method of analyzing human feces for trace amounts of plutonium and some of the experiences of this laboratory during the process of developing such a method.

METHODS

Collection of Sample

Since there has been no attempt to date to put the analysis of human feces samples for plutonium content on a routine basis, a set method for collecting and handling samples has not been established. A desirable method might be to collect and pool four days' excretion under conditions which would prevent external contamination, to completely emulsify the entire sample in 2N HCl, and to take for analysis an aliquot representing a day's excretion.

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Ashing and Solution of Sample [redacted]

After trying several variations of both wet- and dry-ashing techniques, the following procedure was selected. The sample is transferred to a large porcelain casserole and placed on a steam bath. When dry the material is transferred as completely as possible to a 250-ml porcelain crucible and placed under an infrared lamp for further drying. When completely dry, and partially charred, the sample is heated over a Bunsen burner until a dark grey ash remains. The dry material remaining in the original casserole is washed into the crucible containing the ash using a little conc. HNO_3. The HNO_3 is evaporated off, and the sample is again heated over a burner. When there is no further evidence of charring and ashing over the flame, the sample is placed in a muffle furnace at 800°C for 8 to 15 hours. The resulting ash varies in color from white to a reddish white. The red color is believed to be due to iron.

Solution of the ash has proved to be a rather difficult problem, and several methods have been tried. The following procedure, however, has proved satisfactory. About 60 ml of 2N HCl is added to the crucible containing the ash. The slurry is heated under an infrared lamp for about 15 minutes. The partially dissolved sample is transferred to a 200-ml centrifuge bottle and the insoluble portion is centrifuged out. The supernatant is transferred to a volumetric flask of a size such that the final solution will contain 2 to 4 g of ash per 100 ml. The insoluble portion is digested almost to dryness with about 10 ml of aqua regia. Twenty-five ml of 6N HCl is added and the portion remaining undissolved is centrifuged out and discarded. The supernatant is added to the volumetric flask, and the sample is made up to volume so that the final solution is approximately 2N in HCl. The insoluble residue which is discarded probably consists mainly of silica. For some time this was fumed with HF and H_2SO_4 and added to the solution. However, good recoveries have been obtained on feces samples spiked at the first step of the ashing

procedure and carried through the entire process in which the insoluble residue is discarded. It is therefore thought unnecessary to attempt to dissolve the residue and to include it in the final solution.

Determination of Plutonium in Feces Ash Solutions

A number of methods for determining plutonium in feces ash solutions have been tried. These will not be described in detail since they have all proved inferior to the method finally adopted.

The first method attempted consisted of a hydroxide precipitation followed by a cupferron extraction. The chloroform phase from the extraction was wet-ashed to destroy the cupferron. Finally a LaF_3 precipitation was carried out and the LaF_3 was transferred to a platinum plate and counted in an alpha counter. This method was entirely unsatisfactory.

A LaF_3 precipitation using 20 mg La^{+3} per 100 ml of solution was substituted for the original hydroxide precipitation. This method was fairly satisfactory, but little or no separation from iron was obtained in the first LaF_3 precipitation and the precipitate was very difficult to dissolve. Separation of the aqueous and chloroform phases in the cupferron extraction which followed was not always clear cut.

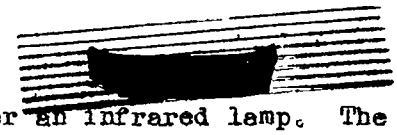
Direct extraction of plutonium from small aliquots of feces ash solutions using both hexone and TFA (trifluoroacetylacetone) were tried. Both reagents gave unsatisfactory results.

A $BiPO_4$ precipitation followed by a LaF_3 precipitation was satisfactory when tried on mock feces ash solutions, but gave inconsistent recoveries from actual feces ash solutions. Recoveries were better but still inconsistent, when a cupferron extraction was inserted between the two precipitations. About the same results were obtained when a partial hydroxide precipitation was used instead of the $BiPO_4$.

Direct cupferron extractions were carried out on various sized aliquots of ash solutions. About 75 percent recovery could be obtained from small aliquots. However, the size of the aliquot which could be tolerated seemed to vary from sample to sample and was too small to give adequate sensitivity.

A lanthanum oxalate precipitation from feces ash solutions adjusted to pH of 0.4 to 0.7 gives good separation of plutonium from iron and probably from phosphate. The oxalate precipitate is destroyed by digesting and taking to dryness with fuming HNO_3. The residue which remains is readily soluble in 2N HCl. Good recoveries of plutonium were obtained when this solution was extracted with cupferron followed by a LaF_3 precipitation. It was found, however, that commercially obtained lanthanum salts contain a radioactive impurity (probably thorium) which follows the plutonium throughout the procedure and causes a high blank value. Since it is necessary to determine extremely small amounts of plutonium a high blank cannot be tolerated. Attempts were made to purify the lanthanum. These were partially successful. It was found, however, that a calcium oxalate precipitation carried reduced plutonium quite successfully. The addition of calcium to the ash solution is not necessary as the natural calcium content of feces ash is adequate. Following is a description of the method which was finally selected.

A 50-ml aliquot containing 1 to 2 g of feces ash is transferred to a 200-ml centrifuge bottle. The solution is adjusted to a pH 0.4 to 0.7 using methyl violet indicator. One ml of 20 percent hydroxylamine hydrochloride is added. The solution is heated under an infrared lamp for about two hours to facilitate the reduction of plutonium. The pH is readjusted using the same indicator. Twenty-five ml of 10 percent oxalic acid is added. A drop of ammonium hydroxide is sometimes necessary to start the precipitation. The solution is left standing overnight to insure complete carrying of the plutonium. The precipitate is centrifuged out and washed once with one percent oxalic acid. About 10 ml of fuming



HNO_3 is added, and the solution is taken to dryness under an infrared lamp. The residue is dissolved in 25 ml of 2N HCl and transferred to a 125 ml separatory funnel. Five drops of 20 percent hydroxylamine and one mg of iron are added. The acidity of the solution is adjusted so that a bright green color is obtained with methyl violet indicator. After allowing one-half hour for reduction of the plutonium, about one ml of 6 percent cupferron solution is added. Four or five extractions using about 2 ml of chloroform for each extraction are carried out. More extractions are necessary if all the iron has not been removed from the aqueous phase. The chloroform phases are collected in a 40-ml pyrex centrifuge cone. The cone is placed in a water bath and the chloroform evaporated off. One ml of conc. HNO_3 and one ml of 72 percent $HClO_4$ are added to the residue. The cone is then placed in an oil bath at about 100°C. The temperature of the oil bath is allowed to rise to about 180°C over a period of one hour. At the end of this time about one ml of a clear or straw colored $HClO_4$ solution remains. This is diluted to 5 ml with distilled water. Two drops of 20 percent hydroxylamine are added and the solution allowed to stand one-half hour. Two hundred micrograms of La^{+3} and one-half ml of 27N HF are added. The LaF_3 precipitate is centrifuged out, transferred to a platinum plate and counted in an alpha counter for 30 minutes.

It is quite possible that the calcium oxalate precipitation can be substituted for the LaF_3 precipitation in the California method which uses TTA (Thiophenyltrifluoracetone) as the extracting agent.

RESULTS

Recovery by the above procedure has been tested by recovering known amounts of plutonium from both mock and actual human feces ash solutions. The results are presented in Tables I and II. The results in Table III were obtained from samples of human feces to which plutonium was added before beginning the ashing procedure. They therefore represent over-all recovery. The average recovery was 85 percent with a mean deviation of 9.5 percent.

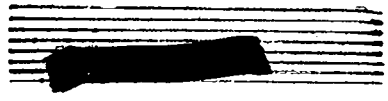


TABLE I. -- Recovery of Known Amounts of Plutonium From Mock Feces Ash Solutions

counts/minute added	counts/minute recovered	percent recovered
150	145	97
150	140	93
150	125	83
150	131	87
Mean percent recovery		90

TABLE II. -- Recovery of Known Amounts of Plutonium From Human Feces Ash Solutions

counts/minute added	counts/minute recovered	percent recovered
150	127	85
150	120	80
150	117	78
150	116	77
150	119	79
150	110	73
100	82	82
100	86	86
Mean percent recovery		80
Maximum deviation from mean		7.0
Mean deviation from mean		3.8

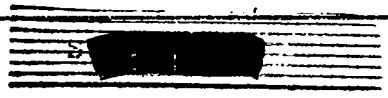


TABLE III. -- Recovery of Known Amounts of Plutonium From Aliquots of Ashed Samples to Which Plutonium Was Added at the Beginning of the Ashing Procedure

sample number	c/m added to entire sample	c/m in aliquot taken	c/m recovered	percent recovered
1	500	125	125	100
		125	118	94
2	500	125	129	103
		125	108	85
3	500		252	100
4	500	125	96	77
		125	79	63
5	500	250	204	82
6	208	52	39	75
		52	38	73
		52	43	82
		52	42	81
7	208	52	50	96
		52	47	90
		52	40	76
		62	48	93
Mean percent recovery				85
Maximum deviation from mean				22
Mean deviation from mean				9.5

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