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Subject: The Quantitative Determination of Plutonium in
Biological Materials

Part II. Analysis of Stools

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To: _____

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Practically all of the research and experimental tests reported here is the work of Mr. Harold Delaney with contributions by Mr. Ercole Motta.

E. R. Russell

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It was pointed out in Part I that it was desirable to have adequate means of estimating the plutonium content of the body. Since only a small fraction of the plutonium which enters the intestines is absorbed, a routine survey of the fecal plutonium excretion would not give accurate information as to the body content. However, valuable information could be gained from such a survey as it would be possible to estimate the exposure of the individual.

Experiments on humans indicate a daily excretion of plutonium in the feces of 0.004% of that contained in the body. This would require an analytical procedure capable of detecting 0.0004 gram of Pu or about 0.5 alpha counts in approximately 250 grams of feces.

In the procedures which are described, the limit of detection was set at 1 alpha count per minute due to plutonium for a 24-hour fecal output. The problem consisted of two phases: (1) developing an ashing method which would result in the complete solution of the material, and (2) extracting the plutonium from this solution for counting. Preliminary experiments had shown that simply the ordinary wet and dry ashing procedures were not satisfactory.

2. Ashing of Feces

2.1 Wet Ashing: The sulfuric acid-peroxide method of ashing organic material was considered because plutonium in concentrated sulfuric acid solutions is readily recovered. Fuming

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nitric acid and peroxide causes considerable frothing and the final residue is not completely soluble in either nitric or hydrochloric acids. The insoluble residue contains up to 30% of the plutonium. Ashing with ammonium nitrate and nitric acid gives a completely soluble residue but the technique is dangerous to use as a violent reaction usually takes place. In some cases small fecal specimens can be converted to a white ash soluble in dilute nitric acid by alternate treatments of the oven dried sample with concentrated nitric acid and peroxide.

2.2 Dry Ashing: Ordinarily fecal specimens are dry ashed in a muffle furnace at 800°C after the moisture has been removed. The residue is dissolved in acid only after fusion with pyrosulfate. Such a procedure does not allow complete recovery of the plutonium. The low recovery is probably due to fusion of the plutonium in the walls of the ashing vessel. Ashing at a lower temperature, 600°C does not permit plutonium to react with the walls of the vessel but leaves an incompletely ashed material. Some tests have shown that plutonium may be recovered quantitatively from this ash but the results are not consistent. Taking into consideration the advantages and disadvantages of each ashing method a combination of the two seems to give the most reliable results.

2.3 Adopted Ashing Procedure: The entire fecal specimen is dried for 24 to 48 hours in an oven at 100°C. until the sample is brittle, it is then transferred to a large porcelain crucible lined with three layers of ashless filterpaper. The crucible,

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partially covered by a lid, is placed in a muffle maintained at 600°C and allowed to remain for 24 hours. After removing the crucible from the furnace and allowing it to cool, from 25-50 ml of fuming nitric acid are added and evaporated to dryness. This procedure is repeated once more and the residue dissolved in 25ml of 2 M nitric acid by warming. The small amount of residue is centrifuged out and the supernate transferred to a 90 ml centrifuge tube. The ashing vessel is washed with 25 ml of 2 M hot nitric acid and this is slurried with the residue from the previously centrifuged solution to leach any plutonium which may remain. It is then centrifuged and the supernate added to the solution in the 90 ml tube. Tests have shown that the undissolved material contains less than 1% of the plutonium and that less than 1% remains in the ashing vessel.

3. Extraction of the Plutonium

3.1 Hexone Extraction: The ashed feces solution is made 1 M in ammonium hydroxide and the precipitate centrifuged out. This precipitate carries the plutonium. The precipitate is dissolved in a minimum of nitric acid and is nearly saturated with aluminum or ammonium nitrate. The solution is made just pink with potassium permanganate and extracted with hexone which was previously treated with permanganate. The two liquids are separated by freezing the aqueous layer with dry ice and the plutonium extracted back into an aqueous solution saturated with SO₂.

For small amounts of feces, this method is fairly satisfactory

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since not much residue is carried through the extraction process. For large specimens, the procedure has not been applied successfully.

3.2 Thiophenyltrifluoroacetone (T.T.A.): The procedure in which T.T.A. is employed in the extraction of plutonium from the ash of biological material was developed by K. S. Scott at Berkeley. The essential features are given below.

The fecal ash is dissolved in 2 M nitric acid which is 0.1 M in hydroxylamine hydrochloride (0.1 gram of solid per ml of solution.) The plutonium is coprecipitated with about 40 mg of lanthanum as the fluoride, the precipitate dissolved in a 1.5 M aluminum nitrate solution and the plutonium brought to the +4 oxidation state with sodium nitrite by heating to 80°C. After cooling, the plutonium is extracted with 10 ml of a 0.2 M solution of T.T.A. in benzene. The benzene is separated and evaporated on a platinum plate (2 inches diameter), flamed and counted. If desired, it is possible to extract the plutonium back to an aqueous solution of nitric acid and either count an aliquot of this solution directly or perform a lanthanum fluoride precipitation. Since the benzene solution contains only a minute quantity of inorganic matter, direct counting of this solution is quite feasible.

With one extraction, tests in this laboratory have shown better than 80% recovery of the plutonium. Unfortunately, the

lanthanum available in the laboratory contained alpha active contaminants which did not allow the application of the method to specimens containing less than 2 alpha counts per minute of plutonium. Where alpha free lanthanum can be obtained, the method is quite satisfactory.

3.3 Zirconium Phosphate-Lanthanum Fluoride: It was known that plutonium under certain conditions is carried by a zirconium phosphate precipitate² and that it could be easily separated from this material. Since a direct lanthanum fluoride precipitation is not feasible in the presence of large amounts of calcium, it is necessary for the analysis of plutonium that a preliminary separation of the plutonium and calcium be made. Tests on the carrying of plutonium by zirconium phosphate from ashed feces solution showed very erratic results. Some samples showed less than 40% carrying. Many factors may account for the varied results. It is possible that iron may interfere, particularly at concentrations greater than $10^{-4}M$. Conditions might be worked out whereby the method would give consistent results.

3.4 Bismuth Phosphate-Lanthanum Fluoride: The 50 ml of 2 M nitric acid solution containing the fecal ash is diluted to 80 ml in a 90 ml centrifuge tube. The procedure is identical to that described in Part I for urine ash.

The method has been applied to specimens weighing as much as 300 grams and containing as little as 1 alpha count per minute of plutonium. Experimental tests on human stools have shown an average recovery of 88% while dog stools have shown

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greater than 90% recovery.

4. Remarks and Summary

It is understood that the problem of detecting very minute quantities of plutonium is dependent on the counting apparatus as well as the procedure adopted for the isolation of the element. For any method to be successful in detecting 1 alpha count per minute of plutonium it is essential that the analysis be carried out under such conditions that atmospheric contamination as well as contamination from other sources be eliminated.

The methods which have been described are based on many experimental tests. The T.T.A. and bismuth phosphate have given the most consistent results. All of the methods make use of a preliminary ashing of the samples. The combination wet and dry ashing procedure appears to be the most satisfactory. Though many fundamental facts concerning each procedure need investigating, the methods as adopted have served well the purpose for which they were designed.

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