

THE JOURNAL

OF

BIOLOGICAL CHEMISTRY

FOUNDED BY CHRISTIAN A. HERTER AND SUSTAINED IN PART BY THE CHRISTIAN A. HERTER
MEMORIAL FUND

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VOLUME 172

BALTIMORE

1948
REPOSITORY DOE - Chicago Ops - Center
FOR Human Radiobiology

COLLECTOR HRP/Plutonium DOES

BOX No. 2952

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DETERMINATION OF PLUTONIUM IN HUMAN FECES*

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(Received for publication, September 24, 1947)

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 10:1. 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 was extremely limited, partially because of the difficulty of analyzing human feces 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—Fecal specimens, representing from 1 to 4 days excretion, are pooled and completely emulsified in 2 M HCl by heating on a steam bath with rapid stirring. The weight of HCl used is about twice that of the feces. A suitable aliquot by weight is taken for analysis. The size of the aliquot chosen depends both on the expected radioactivity and on the total weight of the sample. In general, not more than 250 gm. of the emulsified sample should be used in any one analysis. Two aliquots of each sample are analyzed.

Ashing and Solution of Sample—The aliquot taken for analysis is transferred to a large porcelain crucible and placed in an oven at 110°. When completely dry, after about 24 hours, the sample is heated over a Bunsen burner until a dark gray ash remains. When there is no further evidence of charring and ashing over the flame, the sample is placed in a muffle

* This paper is based on work performed under contract No. W-7405-Eng-36 with the Manhattan Project at the Los Alamos Scientific Laboratory of the University of California.

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furnace at 800° for 8 to 15 hours. The resulting ash varies in color from white to a reddish white.

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 4 M HCl are added to the crucible containing the ash. The slurry is heated under an infra-red lamp for about 15 minutes. The partially dissolved sample is transferred to a 200 ml. centrifuge bottle and the insoluble portion is centrifuged. The supernatant is transferred to another 200 ml. centrifuge bottle. The insoluble portion is washed once with 4 M HCl, the wash being added to the original solution, and is transferred to a platinum crucible. About 10 ml. of concentrated HF are added, and the slurry is taken to dryness under an infra-red lamp. The residue is taken up in about 5 ml. of 4 N HCl. The part still remaining undissolved is centrifuged and discarded. Many unsuccessful attempts were made to find an easy method of dissolving the residue. However, good recoveries have been obtained on feces samples with known amounts of plutonium added 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 Solutions of Feces Ash—A number of methods for determining plutonium in solutions of feces ash 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 hydroxide precipitation followed by cupferron extraction. The chloroform phase from the extraction was wet-ashed to destroy the cupferron. Finally LaF₃ precipitation was carried out and the LaF₃ was transferred to a platinum plate and counted in an α-counter. This method was entirely unsatisfactory.

Direct cupferron extractions were carried out on aliquots of ash solutions of various size. About 75 per cent 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.

It was found that 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. A description of the method which was finally selected follows.

The ash solution is adjusted to pH 0.4 to 0.7 with methyl violet indicator. 1 ml. of 3 M hydroxylamine hydrochloride is added. The solution is heated under an infra-red lamp for about 2 hours to facilitate the reduction of plutonium. The pH is readjusted with the same indicator. 25 ml. of

0.8 M oxalic acid are necessary to start night to insure co is centrifuged and fuming HNO₃ are infra-red lamp. Tferred to a 125 ml. mg. of iron are ad bright green color i for reduction of the added. Four or five extraction are carr.

Recovery of Known A

Added
counts per min.
150
150
150
150

Mean

* A solution whose a 50 gm. fecal sample.

iron has not been re are collected in a 4 water bath and the and 1 ml. of 72 per placed in an oil ba allowed to rise to a time about 1 ml. of is diluted to 5 ml. amine are added an and 0.5 ml. of 27 transferred to a pl

Recovery by th amounts of pluton

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 25 ml. of

0.8 M oxalic acid are 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 and washed once with 0.1 M oxalic acid. About 10 ml. of fuming HNO₃ are added, and the solution is taken to dryness under an infra-red lamp. The residue is dissolved in 25 ml. of 2 M HCl and transferred to a 125 ml. separatory funnel. 5 drops of 3 M hydroxylamine and 1 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 ½ hour, for reduction of the plutonium, about 1 ml. of 6 per cent cupferron solution is added. Four or five extractions with about 2 ml. of chloroform for each extraction are carried out. More extractions are necessary if all of the

TABLE I
 Recovery of Known Amounts of Plutonium from Solutions of Artificial Feces* Ash by Calcium Oxalate-Cupferron Procedure

Added counts per min.	Recovered counts per min.	Recovered per cent
150	145	97
150	140	93
150	125	83
150	131	87
Mean		90

* A solution whose mineral composition was that which might be expected from a 50 gm. fecal sample.

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. 1 ml. of concentrated HNO₃ and 1 ml. of 72 per cent HClO₄ are added to the residue. The cone is then placed in an oil bath at about 100°. The temperature of the oil bath is allowed to rise to about 180° over a period of 1 hour. At the end of this time about 1 ml. of a clear or straw-colored HClO₄ solution remains. This is diluted to 5 ml. with distilled water. 2 drops of 20 per cent hydroxylamine are added and the solution allowed to stand ½ hour. 200 γ of La⁺⁺⁺ and 0.5 ml. of 27 M HF are added. The LaF₃ precipitate is centrifuged, transferred to a platinum plate, and counted in an α-counter for 1 hour.

Results

Recovery by the above procedure has been tested by adding known amounts of plutonium to both artificial and actual solutions of human

* of Human Feces Ash by
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deviation from the mean was 3.8 per cent.

TABLE IV
Recovery of Known Amounts of Plutonium from Samples of Human Feces by Calcium Oxalate-Cupferron Procedure

Recovered
per cent
85
80
78
77
79
78
82
88
80
7.0
3.8

ing procedure.

the Procedure

Deviation from mean

0.97
0.17
0.03
0.23
0.33
0.27
0.03
0.23
0.03
0.73
0.43

0.42

used to plutonium.
Subtracted from each re-

II. When known
ash resulting from
80 per cent. The

Pu added counts per min.	Pu recovered* counts per min.	Recovery per cent
48.2	38.5	79.9
48.2	40.0	83.0
48.2	41.0	85.1
48.2	27.1	56.2
48.2	31.0	64.3
48.2	23.3	48.3
48.2	36.9	76.6
48.2	41.7	86.6
48.2	37.9	78.6
48.2	36.0	74.7
48.2	25.1	52.1
48.2	42.5	88.2
48.2	42.3	87.8
48.2	48.1	99.8
48.2	43.3	89.8
48.2	46.4	96.3
48.2	42.4	88.0
48.2	45.3	94.0
48.2	48.1	99.8
48.2	37.5	77.8
48.2	41.7	86.6
48.2	83.9	86.7
96.8	64.4	66.6
96.8	83.0	85.7
96.8	68.2	70.5
96.8	82.2	84.9
96.8	77.1	79.6
96.8	157.1	81.0
194		80.3
Mean		9.9
" deviation from mean		32.0
Maximum deviation from mean		

* A counter background and a blank value of 0.93 count per minute have been subtracted from each result.

Feces samples were collected from persons having never been exposed to plutonium. Analysis of these blank samples by the calcium oxalate-cupferron procedure gave a small positive value even after correction for the background of the α -counter. The data are given in Table III. The



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mean blank value was 0.93 count per minute, and mean deviation from the mean 0.42 count per minute. This positive value may result from one or all of three factors: (1) α -activity in the feces as a result of the presence of naturally occurring α -emitters in the body and in the food consumed, (2) presence of naturally occurring α -emitters in the reagents, and (3) contamination of the sample during analysis.

The results given in Table IV were obtained when known amounts of plutonium were added to aliquots of human feces samples before ashing. They, therefore, represent the over-all recovery. These data show a mean recovery of 80.3 per cent. The maximum deviation from the mean was 32.0 per cent and the average deviation was 9.9 per cent.

SUMMARY

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 4 M 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 HNO₃ and taken up in 4 M HCl. Ferric iron is added and the plutonium is extracted into CHCl₃ as the cupferride. The cupferride complex is destroyed with HClO₄. The plutonium is carried with LaF₃, transferred to a platinum plate, and counted in an α -counter. Results with solutions of both artificial and actual human feces ash show the recovery of plutonium by this method to be 80 per cent or better, with a mean deviation from the mean of 9.9 per cent.

ON THE NATURE OF LIPIDES OF CABBAGE LEAVES AND A PHOSPHOLIPID

By DONALD

(From the Division of Physiological Chemistry)

(Received ...)

In 1927 Chibnall and ... cabbage leaves. Although ... was obtained from fresh ... cabbage leaves were first ... containing lipide isolated ... content. These observations ... carrot (2, 3), contain a ... role at its ester lin ... phoric acid grouping. ... leaves, and some of its ...

Isolation

From Fresh Cabbage ... ground and 1000 gm. of ... flask. A sufficient amount ... provide 3 cc. of solvent ... for 12 to 14 hours at 55 ... the cabbage residue sub ... alcohol-ether solvent. ... and in the presence of ... concentrated at 55-60 ... material was then re ... (b.p. 30-60°) and the ... volume of about 10 cc ... in an atmosphere of ... washed twice with 0.1 N ...

* The research which ... Committee on Food Research ... the Armed Forces. The ... authors. They are not ... ment of the War Department ...