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PLUTONIUM IN THE EXCRETA OF THREE SUBJECTS [redacted] DAYS AFTER INJECTION

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Substantial amounts of ^{239}Pu were found in the daily excreta of two subjects who had been injected intravenously with plutonium citrate (^{239}Pu) 10^4 days previously. The urine of a third subject injected intramuscularly with ^{238}Pu contained just measurable amounts of this nuclide.

Introduction

[redacted] persons who had received injections of plutonium in 1945–1947 were hospitalized on a metabolic ward in [redacted]. Complete collections of urine and feces were made for periods of 8 to 14 days, and these excreta were shipped to ANL for plutonium analysis. Two of the individuals received intravenous injections of about 0.3 μCi of plutonium (IV) citrate; the third individual received an intramuscular injection of 0.095 μCi of plutonium (VI) nitrate. The intravenous injections were of ^{239}Pu, while the intramuscular injection was of ^{238}Pu.

The intramuscular injection was made in the [redacted] muscle of a [redacted] having a [redacted] days after the injection, the [redacted] Analysis of a 69-g sample of tissue from what was described as the "injection site" showed that it contained 0.044 μCi. Because of the possibility that tissue adjacent to the "injection site" also contained unabsorbed plutonium, it is impossible to establish an accurate value for the initial systemic burden.

This report is confined to the description of the methods used for the analyses of these unique and important samples, together with the results. Interpretation will be presented elsewhere. For a description of the early experiments and their results, the reader is referred to the extensive review prepared by Durbin.[1] Some pertinent details of the three subjects are set out in Table 1.

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TABLE 1. Some Details of the Three Subjects Who Survived Their Primary Diseases.

CHR case No.	Literature[a] case No.	Sex	Original diagnosis	Age in [redacted] yr	Amount injected, μCi
[redacted]					0.095 (^{238}Pu) 0.301 (^{239}Pu) 0.331 (^{239}Pu)

[a] Literature case numbers are those in Reference 1.

Urine: Sample Treatment, Aliquoting, and Analysis

During each 24-hr collection period the individual urine specimens were transferred to a polyethylene bottle; at the end of the collection period the urine was frozen. The samples were shipped to ANL and kept frozen until they were aliquoted.

To aliquot a 24-hr urine specimen, it was thawed and transferred, along with several concentrated nitric acid washes of the original container, to a tared mixing cylinder. The amount of nitric acid used was such that the final acidity of the urine was about 2.0 N. After the urine had been mixed with the acid and the mixing cylinder reweighed, the solution was apportioned about equally to 12 tared polyethylene bottles. The bottles were then retared and their contents frozen. These portions were individually analyzed; the fraction factor for each portion was calculated from the weight of each portion and the total weight of acidified urine.

The plutonium content of the urine was determined by alpha spectrometric-isotope dilution analysis using ^{242}Pu as the spike isotope. The aliquot was thawed, the ^{242}Pu spike was added, the urine was transferred, along with nitric acid washes of the container, to an erlenmeyer flask and the urine was wet-ashed. The ashing was considered to be complete if the salt residue was white when evaporation was carried to dryness. The salts were then dissolved in 2 N nitric acid.

The plutonium was separated from the other inorganic constituents of the urine by first coprecipitating it with cerous fluoride and then subjecting it to an anion exchange separation procedure. Hydroxylamine was added to the

nitric acid solution, the solution was heated to reduce the plutonium to the trivalent state, cerous nitrate was added, and cerous fluoride was precipitated by the addition of hydrofluoric acid. After separation of the cerous fluoride by centrifugation, it was dissolved by heating with 8 N nitric acid that had been saturated with aluminum nitrate. This solution was passed through a column of Dowex 1 × 8, and the column was washed, first with 8 N nitric acid and then with 12 N hydrochloric acid. The plutonium was eluted from the column with 0.1 N hydrochloric acid-0.01 N hydrofluoric acid.

The plutonium was transferred from solution to the surface of a polished stainless steel planchet for alpha spectrometric assay by an electrodeposition procedure. Sulfuric acid was added to the eluant solution, the solution was evaporated to fumes of sulfuric acid, diluted with water, and neutralized with ammonia gas to a pH of 2.0. The electrodeposition was carried out for 1.5 hr at 1.2 amp. The planchets were counted until about 300 counts had been accumulated in the ^{239}Pu peak. The amounts of activity in the aliquots ranged from about 0.3 pCi to 0.75 pCi; the counting efficiency was about 35%.

The alpha spectrograms ranged in quality from good to excellent, a "good spectrum" being defined as one in which the FWHM of the ^{242}Pu peak is 0.12 MeV and an "excellent spectrum" as one in which the FWHM is the same as that obtained in the electrodeposition of standards, i.e., 0.06 MeV.

As the analysis of several aliquots of the urine from case [redacted] showed that there was too little plutonium for measurement, the aliquots that had been made from each of three 24-hr collection periods were recombined and analyzed. In the alpha spectrograms, integration of the ^{238}Pu peak at 5.48 MeV was impeded by the presence of a peak at 5.43 MeV. The radionuclide producing this peak was identified as ^{228}Th. By counting the plates after 3.62-day ^{224}Ra had reached secular equilibrium with its ^{228}Th parent and integrating the counts in the ^{224}Ra peak at 5.68 MeV, we could calculate the ^{228}Th contribution to the ^{228}Th–^{238}Pu peak. This contribution ranged from 20 to 25% of the total. It was subsequently established that ^{228}Th as well as ^{230}Th and ^{232}Th were present in the reagents. The hydrochloric acid wash of the anion exchange column, although extensive, had not been sufficient to wash

all the thorium away from the plutonium.

Feces: Sample Treatment and Analysis

At the time the fecal samples were obtained they were bagged and frozen. They were kept in this condition until the time of analysis.

To prepare the samples for analysis, they were thawed, the ^{242}Pu spike was added, and the organic matter destroyed by first dry-ashing them for 16 hr at 500°C and then wet-ashing by repeated additions of nitric acid and evaporation to dryness. When the residues from the nitric acid treatment were judged by their appearance to contain no residual organic material, they were dissolved by adding concentrated hydrochloric acid and heating to 80°C. These solutions were analyzed by the radiochemical procedure described above for the urine samples.

For 22 of the 24 samples analyzed, the ^{242}Pu recovery ranged from 66 to 100%. Although the recoveries in two of the analyses were only 10%, the ^{239}Pu excretion rates obtained did not appear to be significantly different from the rates obtained where the recoveries of ^{242}Pu were much higher. From this it is inferred that isotopic exchange between the ^{239}Pu and ^{242}Pu had been established in all the samples during the operations used to destroy the organic material.

Results

To establish the precision of the analysis three aliquots from each of three urine samples were analyzed, and the values were compared. In each comparison all values were within the 95% confidence limits calculated from the average value and the number of counts in the ^{239}Pu peak.

The amounts excreted in the 24-hr urine samples are summarized in Table 2, while the results for the fecal samples are given in Table 3. One aspect of the entries in these tables calls for comment. For cases [redacted] and [redacted] the statistical errors on the results in Table 3 are all substantially lower than on those in Table 2, yet the numbers are lower in Table 3. This is because only small aliquots (5–10%) of the 24-hr urine samples were analyzed,

while the whole of each fecal sample was assayed.

Day-to-day variations in the urinary output of plutonium-239 were comparatively small; the ratio of highest to lowest daily output was 1.48 for case [redacted] and 1.36 for case [redacted] There were much larger sample-to-sample variations in the fecal output. The number of days of excretion represented by the sample was determined by identifying the beginning and end of each of two periods when a carmine dye appeared in the stool. For case [redacted] the results for the two periods were in complete agreement, and the daily fecal excretion was 38% of the mean daily urinary excretion. The results for case [redacted] were not so straightforward; the mean daily fecal excretion was substantially higher in the first period than in the second period, and a sample voided just before the start of the first period contained a remarkably large amount of plutonium (sample 2, Table 3). This patient had been suffering from [redacted] which ended the day before sample 1 was collected. It seems likely that the high excretion rate of plutonium just prior to and during part of the first marker period reflected the voiding of feces containing plutonium which had continued to be secreted into the gastrointestinal tract during the period of constipation. The mean daily excretion during the second period may thus be our best estimate of the true fecal elimination rate; it was 42% of the mean daily

TABLE 2. Plutonium in the 24-hr Urine Samples.

Day	Plutonium content of urine samples, pCi/day		
	Case [redacted] (a) (^{238}Pu)	Case [redacted]	Case [redacted]
1	-	6.50 ± 0.24	4.62 ± 0.25
2	-	9.00 ± 0.34	3.94 ± 0.28
3	-	8.23 ± 0.21	4.56 ± 0.26
4	-	7.91 ± 0.25	5.33 ± 0.26
5	0.062 ± 0.005	7.63 ± 0.54	4.42 ± 0.32
6	-	7.72 ± 0.37	4.90 ± 0.28
7	-	7.47 ± 0.39	5.35 ± 0.34
8	-	7.38 ± 0.38	4.46 ± 0.25
9	0.059 ± 0.005	6.59 ± 0.34	
10	0.055 ± 0.010	7.37 ± 0.47	
11	-	8.41 ± 0.49	
12		7.77 ± 0.38	
13		6.09 ± 0.43	
14		8.05 ± 0.39	
Weighted mean ± S.E.	0.060 ± 0.003	7.60 ± 0.21	4.68 ± 0.17
Time since injection, days	9474	9934	10,008

(a) Small aliquots did not provide sufficient ^{238}Pu for analysis of samples from case [redacted] only 3 of the 11 samples were analyzed in toto.

TABLE 3. Plutonium in the Fecal Samples from the Two Patients Who Received ^{239}Pu

Sample No.	Case [redacted] [a] Wet weight, g	pCi	Case [redacted] [a] Wet weight, g	pCi
	Weights and plutonium contents of fecal samples			
1	20	1.94 ± 0.06	33.5	0.43 ± 0.02
2	222	18.7 ± 0.4	50.5	0.77 ± 0.03
3	135.5	9.18 ± 0.30	178.5	1.87 ± 0.06
4	75	2.92 ± 0.11	217	2.09 ± 0.08
5	167	4.96 ± 0.16	269.5 [b]	1.46 ± 0.08
6	161.5	6.27 ± 0.10	90 [b]	0.91 ± 0.06
7	95.5	2.79 ± 0.11	98	2.21 ± 0.09
8	170	3.90 ± 0.10	53	0.85 ± 0.03
9	94.5	3.10 ± 0.15	125	1.72 ± 0.06
10	83	2.51 ± 0.08	132.5	2.29 ± 0.10
11	324	7.34 ± 0.50		
12	54	2.18 ± 0.10		
13	143	3.30 ± 0.10		
14	53.5	1.35 ± 0.08		
Mean for period I		5.22 pCi/d (5 days)		1.78 pCi/day (4 days)
Mean for period II		3.17 pCi/d (6 days)		1.77 pCi/day (4 days)

[a] The horizontal lines indicate the starts and stops of time periods defined by the appearance of a dye marker in the stool.

[b] Combinations of 2 or 3 smaller samples voided at short intervals.

urinary excretion. This is similar to the result for case [redacted]

Because of the importance of these analyses, large numbers of aliquots of the urine samples were analyzed by two of us independently, and also by the Bio-Analytical and Chemical Section of the Industrial Hygiene Group at the Los Alamos Scientific Laboratory. With only two exceptions all the values from the aliquots of one 24-hr urine sample agreed within the statistics of counting. The averages of the three sets of values also agreed within this limit.

Reference

1. Durbin, P. W. [redacted] Ed. B. J. Stover and W. S. S. Jee. The J. W. Press, Salt Lake City, pp. 469–530, 1972.