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THE RADIOCHEMICAL DETERMINATION OF AMERICIUM IN THE PRESENCE OF PLUTONIUM IN URINE

MASTER

by

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ABSTRACT

The procedure is based on the coprecipitation of americium with bismuth phosphate from a nitric acid - digested urine sample. The bismuth phosphate is wet-ashed, dissolved in 6N HCl and the americium coprecipitated with lanthanum fluoride. The lanthanum fluoride is metathesized to the hydroxide and the precipitate dissolved in 2N nitric acid. Removal of concurrently metabolized plutonium is accomplished by liquid-liquid extraction of the nitric acid solution with 0.1 M di(2-ethylhexyl)phosphoric acid (D2EHPA) in chloroform. The purified americium is carried on lanthanum fluoride. The precipitate is slurried onto a stainless steel planchet and counted in a low-background proportional alpha counter. The method is effective for quantitative separation from plutonium and uranium. Quantities of the order of 0.5 dpm of americium can be detected in a urine sample.

INTRODUCTION

This procedure was developed to meet the need for a routine sensitive and reliable differential chemical analysis for the determination of Am^{241} in the presence of plutonium in urine. There existed no americium urinalysis which met the above requirements.

The existing potential for simultaneous exposure to these nuclides in a plant handling aged plutonium emphasizes the need for the quantitation of metabolized Am^{241} in urine free from plutonium and uranium interference. The data obtained from routine urinalysis may be used for evaluation of possible low level exposures, estimation of Am^{241} body burden(1), and as an effective guide for medical therapy. The handbook value for a maximum permissible body burden of Am^{241} is 0.05μc (bone)(2).

The chemical method described in this paper ultimately yields a thin sample which can be counted without appreciable absorption of the alpha particles by solid materials and is free of other important alpha emitters.

Procedures have been reported for americium urinalyses(3,4). However, thorium and plutonium are carried through these processes. Other workers report very good separations of americium and plutonium by extraction of plutonium(IV) cupferrate into chloroform(5,6). Results obtained at Rocky Flats from attempted adaptation of this technique to urinalysis were quite variable and exhibited a decontamination factor of insufficient magnitude at the ultramicro activity levels encountered in urinalysis. Chetham-Strode, Jr.(7) has used 2-thenoyltrifluoroacetone (TTA) for simultaneous extraction of americium and plutonium followed by selective stripping of americium from the TTA with 0.5 M nitric acid. However, the requisite pH of 4.8 for initial extraction is difficult to maintain, even with buffers, and quite often leads to the formation of emulsions in many systems. A variation of this technique was attempted. TTA was used to remove plutonium preferentially from a solution 1 M in nitric acid (optimum acidity). Satisfactory plutonium decontamination was achieved but americium recoveries averaged only 25-40%. Horner and Coleman(8) conducted an extensive investigation of plutonium extraction from acid nitrate solutions by amines and organophosphorous compounds. Di(2-ethylhexyl)phosphoric acid (D2EHPA) was found to extract plutonium(IV) much more strongly than either amines or phosphine oxides. In one instance, the extraction coefficient (E_a^o)for americium was in the neighborhood of 10^{-2} as compared to approximately 10^4 for plutonium.

This study suggested that an effective radiochemical separation procedure for americium from plutonium in urine could be devised through use of this reagent.

DISCUSSION

Principle of Method

The extraction mechanism(8) appears to be extraction of a simple cation or cationic complex arising from plutonium-hydrogen cation exchange. The order of extractability is Pu(IV) > Pu(VI) > Pu(III).

Variables such as hydrogen ion concentration, extraction rate, concentration of sample constituents, D2EHPA concentration and choice of organic solvent could be expected to affect markedly the distribution coefficient obtained in a solvent extraction of Pu with D2EHPA. These parameters were examined to determine conditions for the extraction which would insure quantitative removal of plutonium in a urinalysis procedure.

EXPERIMENTAL

Purification of Plutonium Stock

Alpha pulse-height analysis of the Pu^{239} stock solution used in this study revealed that approximately 8% of the total alpha activity was due to Am^{241}. Measurement of high plutonium extraction coefficients and decontamination factors for this process would be severely affected by contamination of plutonium with even very small amounts of the poorly extractable americium. Therefore, the americium was effectively eliminated by extraction of the plutonium from 1 M HNO_3 with 0.1 M D2EHPA + 0.1 M TOPO (tri-n-octylphosphine oxide) in Gulf BT. The extracted plutonium was scrubbed twice with 1 M HNO_3 and stripped twice with 1 M Na_2CO_3. The combined strip solutions were then acidified to give a stock solution which was 1 M in HNO_3, and 1 M in $NaNO_3$. Am^{241} activity in this purified solution was too low for detection by alpha pulse-height analysis.

Choice of Solvent

Chloroform was the solvent of choice since it possessed the desirable properties of density, non-flammability, miscibility with D2EHPA, and low cost. Preliminary experiments also indicated satisfactory extraction of plutonium(IV) with D2EHPA from nitric acid into solvent. The higher density of this solvent is a desired feature since it permits successive extractions of a single aqueous portion with the complexing agent.

Hydrogen Ion Concentration

Previous studies(8) have shown that, as expected on the basis of the previously suggested reaction mechanism, extraction coefficients for plutonium(IV) decrease with increasing acidity over most of the nitric acid concentration range. However, these investigations were carried out in a kerosene-type diluent (Amsco 125-82). Therefore, similar studies in chloroform were conducted in order to ascertain the most favorable conditions for its use (Figure 1). Sodium nitrate had little effect as a salting agent on the extraction except at nitric acid concentrations less than 0.5 M.

Extraction Rate of Plutonium(IV) with D2EHPA

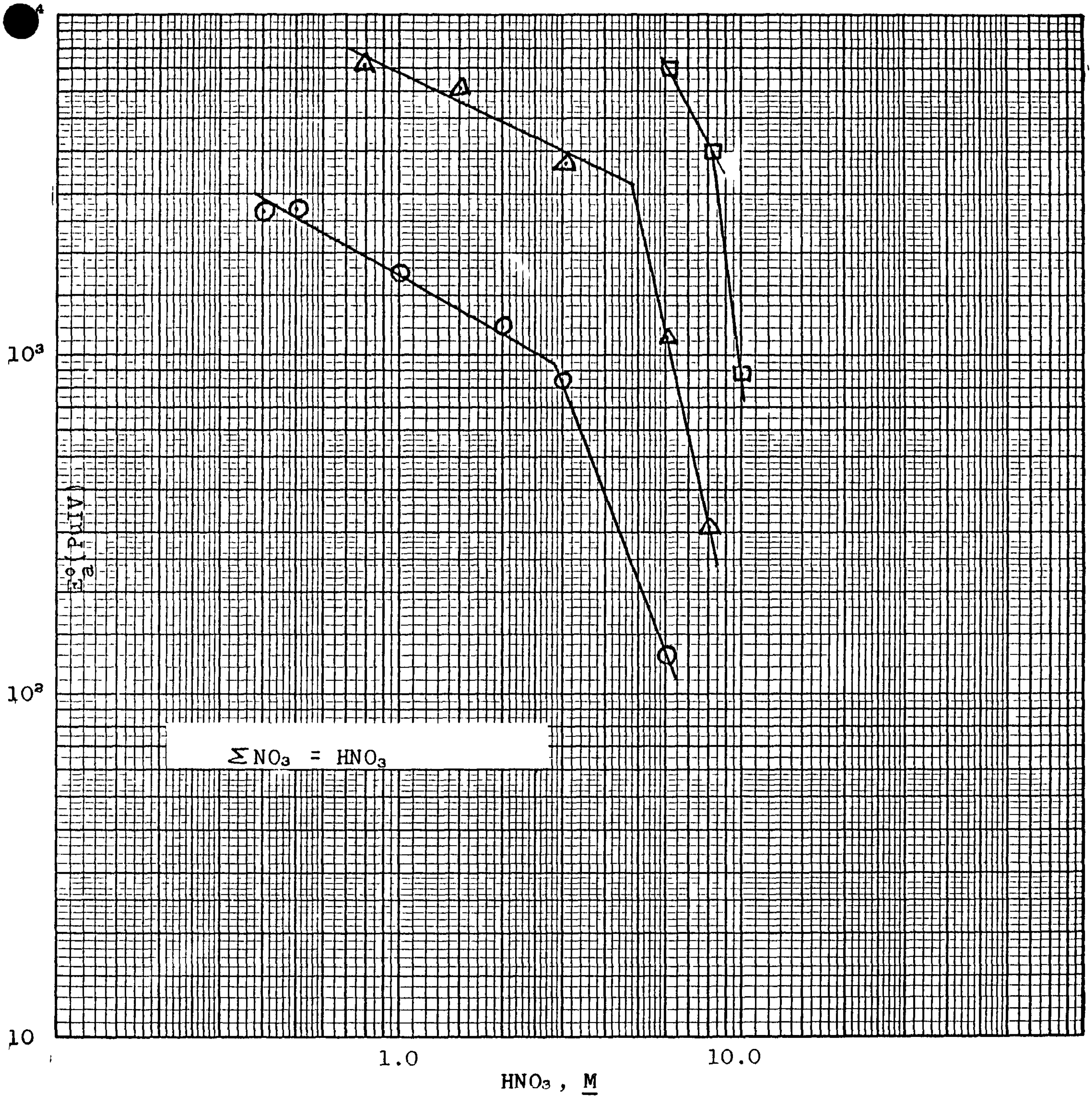
The extraction rate was studied by preparing an aqueous solution of 2 M nitric acid containing a known tracer concentration of plutonium(IV) and extracting aliquots of this solution for different lengths of time with a solution of D2EHPA-chloroform. Phase ratios were aqueous/organic = 2:1. The extractions were carried out in separatory funnels, and a mechanical shaker provided good mixing of the phases.

It was observed that the extraction rates for both 0.05 M and 0.1 M D2EHPA in chloroform were extremely high and that extraction was quantitative within 2 - 3 minutes.

RESULTS

This procedure was investigated using urine collected from nonexposed personnel for spikes, control samples and blanks.

FIGURE 1



Plutonium(IV) Extraction by D2EHPA:
Effect of Nitric Acid Concentration
○ = 0.01 M D2EHPA
△ = 0.05 M D2EHPA
□ = 0.1 M D2EHPA
Chloroform diluent

Since 1200 ml is considered as an average single-day void at Rocky Flats, mixed urine samples were divided into portions of this volume for experimentation. Spike samples consisted of pure americium and plutonium in known ratios while controls were urine samples to which either pure americium or pure plutonium were added at an activity level corresponding to its respective value in the matching spike sample. A blank was carried with each set of spikes and controls.

The americium or plutonium on the resultant sample planchet was determined by alpha counting. Plutonium decontamination was based on comparison of the alpha counts found on the control planchet with plutonium originally added to the control sample. A sensitive test for completeness of plutonium removal was made by alpha analysis of spike planchets with the Model H-100(9) alpha energy analyzer. (Figures 2 and 3). With this instrument, about 2% of plutonium alphas can be determined in the presence of americium. In every case, the americium was free of plutonium. Recovery of americium in the aqueous layer after extraction is shown in Table 1.

FIGURE 2

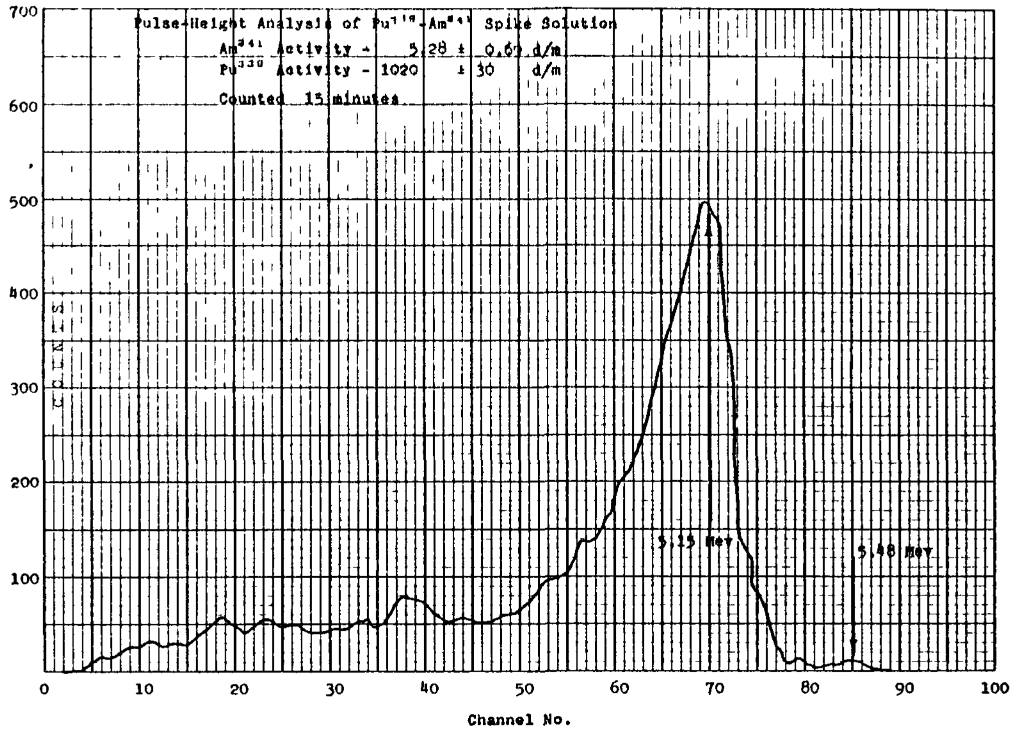


FIGURE 3

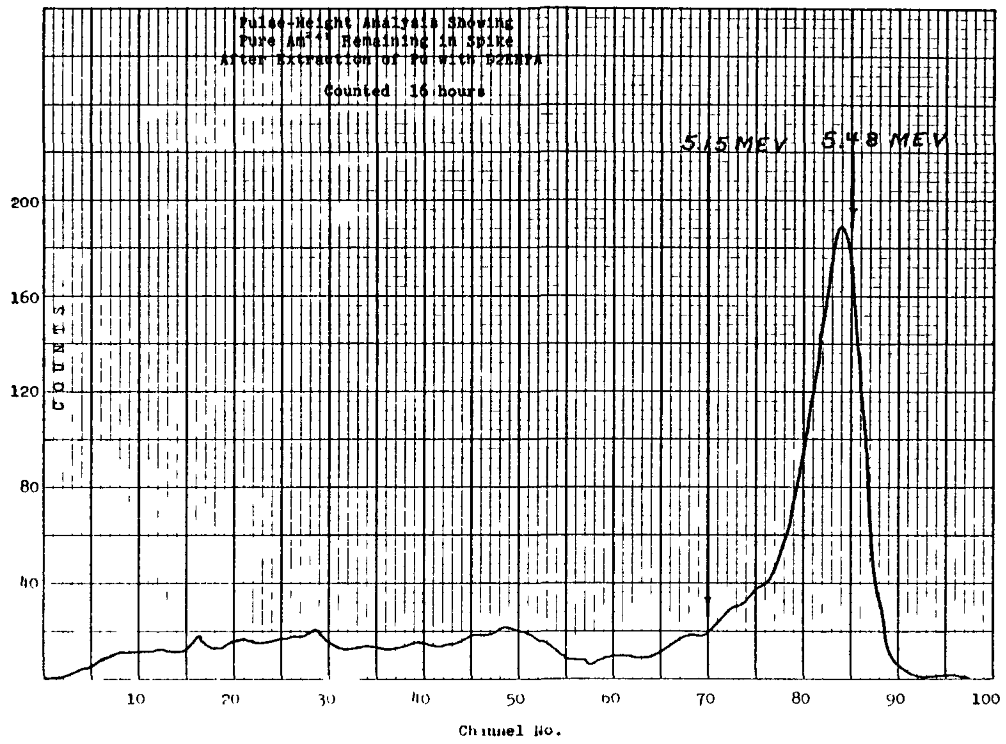


TABLE 1

Spike and Control Recoveries*

Sample	No. of Samples	Activity Added (d/m/1.2 liter)		Counting Time (min.)	Mean Alpha Activity Recovered (d/m)	Mean Recovery, %
		Am^{241}	Pu^{239}			
Am-Pu	2	1200 ± 32	1020 ± 30	9	967 ± 26	80.6 ± 3.41
Am control	2	1200 ± 32	--	9	935.3 ± 28	78 ± 3.54
Pu control	2	--	1020 ± 30	100	Background	--
Am-Pu	3	560 ± 17	1020 ± 30	15	432 ± 15	77.1 ± 4.1
Am	3	560 ± 17	--	15	405 ± 14	72.3 ± 3.9
Pu	3	--	1020 ± 30	150	Background	--
Am-Pu	10	5.28 ± 0.69	1020 ± 30	90	3.71 ± 0.58	70.2 ± 15.3
Am	10	5.28 ± 0.69	--	90	3.90 ± 0.57	73.9 ± 15.2
Pu	10	--	1020 ± 30	150	Background	--
Am-Pu	7	0.74 ± 0.10	1020 ± 30	150	0.48 ± 0.16	64.9 ± 25.6
Am	7	0.74 ± 0.10	--	150	0.42 ± 0.16	56.8 ± 25.6
Pu	7	--	1020 ± 30	150	Background	--

* Corrected for background and blank values at 95% confidence interval

PROCEDURE

Reagents

Bromthymol Blue Indicator Solution -

Dissolve one gram of reagent grade indicator in 500 ml of distilled water made alkaline with one pellet of sodium hydroxide.

Bismuth Nitrate Solution -

Dissolve 231.2 g of bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$-AR] in 660 ml of concentrated HNO_3 and dilute to one liter with distilled water. This solution contains 0.1 g of bismuth per milliliter.

4 N HCl -

Add 344 ml of concentrated hydrochloric acid to approximately 500 ml of distilled water in a volumetric flask and make up to one liter with distilled water.

6 N HCl -

Dilute 510 ml of concentrated hydrochloric acid to one liter in a volumetric flask.

8 N HCl -

Dilute 688 ml of concentrated hydrochloric acid to one liter in a volumetric flask.

Lanthanum Nitrate Solution

$La(NO_3)_3$, as received from the Lindsey Chemical Company, West Chicago, Illinois, is freed from actinum alpha emitting impurities on a Dowex-50X12 cation exchange resin column by the method of Farabee(10). The lanthanum nitrate stock solution obtained is used to prepare working solutions containing 25 mg of La^{+3}/ml. Only solutions containing 0.05 d/m or less of alpha activity per mg of La^{+3} are used.

2M Hydroxylamine Hydrochloride -
Dissolve 139.0 g of C.P. grade hydroxylamine hydrochloride and dilute to one liter. Store in brown bottle.

2N Sodium Nitrite Solution
Dissolve 13.8 g of sodium nitrite ($NaNO_2$-AR) in distilled water in a 100-ml volumetric flask and make to volume with distilled water. Prepare fresh before use.

0.1M D2EHPA -
Add 32.3 g of di(2-ethylhexyl)phosphoric acid (Union Carbide Chemical Company) to chloroform-AR in a 1-liter volumetric flask and make to volume with chloroform.

8N KOH -
Dissolve 65.3 g of potassium hydroxide (KOH 86%-AR) in distilled water and dilute to one liter.

All other chemicals are either of reagent or C.P. quality.

Sample Pretreatment

The volume of a "24-hr equivalent" urine sample (two morning and two evening voidings) is measured and the sample transferred to a 2-liter beaker. The volume and the liquid level are denoted on the beaker with a china-marking pencil or marking pen. Several glass beads, one ml of octyl alcohol and 200 ml of concentrated nitric acid are added. The beaker is covered with a Speede-Vap and placed over an asbestos pad on a hot plate at high heat. The sample is digested by gentle boiling until it attains a clear appearance.

$BiPO_4$ Coprecipitation

A stirring bar is added to the cooled solution and rapid stirring initiated over a magnetic stirring motor. Approximately 130 ml of concentrated ammonium hydroxide are added cautiously, followed by one ml of bromthymol blue indicator solution. Neutralization is completed by addition of concentrated ammonium hydroxide to the yellow-green endpoint. If necessary, the sample volume is readjusted to its original value with distilled water. Concentrated nitric acid is added to make the solution 0.15 M in HNO_3 (Table 2). 500 mg of hydroxylamine hydrochloride are added to the solution and the beaker placed in a steam bath heated to 80 ±5 C. Concentrated phosphoric acid is then added to a concentration of approximately 0.09 M (Table 2). An amount of bismuth nitrate solution, equivalent to 60 mg bismuth per 100 ml, is added dropwise to the heated, stirred solution.

The precipitate is digested by an additional hour of stirring at 80 ± 5 C. The sample beaker is removed from the water bath and allowed to stand undisturbed for a minimum of three hours. The supernatant solution is carefully aspirated off (avoid disturbing precipitate) and the precipitate transferred to a 90-ml Pyrex centrifuge tube with a distilled water rinse. The precipitate is centrifuged for 5 minutes at 2000 rpm and the supernate carefully discarded. The sample beaker walls are then rinsed down with 4N HCl from

TABLE 2

Solution Requirements for $BiPO_4$ Precipitation

Urine Volume (ml)	Conc. HNO_3 for 0.15 M (ml.)	H_3PO_4 (ml)	$Bi(NO_3)_3$ soln. (ml)
500	4.8	3.0	3.0
600	5.9	3.6	3.6
700	6.8	4.2	4.2
800	7.5	4.8	4.8
900	8.7	5.4	5.4
1000	9.6	6.0	6.0
1100	10.5	6.6	6.6
1200	11.6	7.2	7.2
1300	12.45	7.8	7.8
1400	13.50	8.4	8.4
1500	14.4	9.0	9.0
1600	15.0	9.6	9.6
1700	16.4	10.2	10.2
1800	17.3	10.8	10.8
1900	18.5	11.4	11.4
2000	19.2	12.0	12.0

a wash bottle and the rinse transferred to the 90-ml tube. The final volume in the tube should be approximately 50 ml.

Wet-ashing of Bismuth Phosphate

Several drops of octyl alcohol are added to the HCl solution in the 90-ml tube; it is placed in an aluminum block at approximately 100 C and the solution taken to dryness. The dried sample is then repeatedly wet-ashed with several drops of concentrated nitric acid in a block heated to 350 C. After the sample has ashed to whiteness, it is evaporated twice with 8N HCl.

Lanthanum Fluoride Coprecipitation

The bismuth chloride ash is dissolved in 8 ml of 8N HCl and the solution is transferred to a 25-ml conical centrifuge tube. The walls of the 90-ml tube are rinsed with an additional 2 ml of 4N HCl and the rinse added to the centrifuge cone. After addition of 0.1 ml of $La(NO_3)_3$ solution, the tube contents are mixed thoroughly. Two ml of concentrated hydrofluoric acid (27M) are then added, and the solution stirred with a platinum stirrer. The tube is allowed to stand for 5 minutes and then centrifuged at 2000 rpm for 3 minutes. The supernatant is carefully aspirated and the precipitate dissolved in 2 ml of concentrated HCl.

Following the addition of 2 ml of distilled water, LaF_3 is reprecipitated by addition of 2 ml of 27 M HF. The preceding digestion and centrifugation steps are repeated. Five ml of 8N potassium hydroxide are added to the precipitate and carefully heated to boiling. After cooling, the mixture is centrifuged for 3 minutes.and the supernate carefully drawn off.

D2EHPA Extraction

Following solution of the precipitate in 6 ml of 2 N HNO_3, one ml of 2M hydroxylamine hydrochloride is added, and the sample heated in a water bath at 70 C for 5 minutes. The tube is then removed from the water bath and 2 ml of 2M sodium nitrite solution are added with swirling. When bubble evolution ceases, the solution is transferred to a 30-ml separatory funnel. The centrifuge tube is rinsed once with 3 ml of 2N nitric acid and the rinse added to the separatory funnel. The aqueous layer is then extracted thrice with 5-ml portions of 0.1 M D2EHPA in chloroform for 5 minute periods. The chloroform extracts are removed and the aqueous layer is shaken for 3 minutes with a 5-ml portion of toluene. The aqueous portion is then withdrawn through the funnel stem into another 25-ml conical centrifuge tube. Lanthanum fluoride is precipitated by addition of 2 ml of 27M HF. The solution is allowed to stand 5 minutes, centrifuged at 2000 rpm for 3 minutes and the supernatant drawn off and discarded. Shake the precipitate with 10-15 ml of 1:100 hydrofluoric acid wash solution and centrifuge at 2000 rpm for 5 minutes.

Sample Planchetting

Aspirate the supernatant and invert the centrifuge cone quickly over absorbent tissue. Drain 15 minutes. Slurry the precipitate with distilled water and transfer to a stainless steel planchet with a disposable capillary pipette. Dry the disc under an infrared lamp and flame the dried planchet to red heat. The alpha activity is then counted with a low-background proportional counter for 150 minutes.

SUMMARY AND CONCLUSIONS

The analysis requires a maximum of two working days from the time a sample is received until the result is available. Refinements in the procedure resulting in an increased sensitivity would allow use of a smaller sample with accompanying decrease in sample collection time. In view of the large number of manipulations required in the procedure, differential analysis of a urine sample by means of an alpha energy analyzer would provide results requiring a minimum of elapsed time. However, the instrument time required for the pulse-height method in the case of low activity samples would disallow the possibility of conducting a differential analysis by this means on a routine basis. Hence, a differential chemical analysis of this type provides results in a relatively short period of time.

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