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URINALYSIS FOR CURIUM BY ELECTRODEPOSITION

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ABSTRACT

A urinalysis method has been developed for the determination of curium by electrodeposition. The urine is wet ashed, and the curium coprecipitated with bismuth phosphate, then lanthanum fluoride, and finally lanthanum hydroxide. The curium is separated from the lanthanum carrier using Dowex-50 colloidal ion exchange resin. Electrodeposition on a stainless steel or platinum disc gives a uniform film suitable for pulse-height analysis or low-background proportional counting. Final analysis of weak samples is done by radioautography. Curium recoveries of approximately 45% are obtained. Quantities of the order of 0.2 dpm can be detected by this method.

INTRODUCTION

Urinalyses for curium have been routinely accomplished by coprecipitation with bismuth phosphate and lanthanum fluoride, followed by counting in a low-background proportional counter.[1,2] Because of the greater sensitivity achieved by radioautography, a track plate method following electrodeposition has been developed utilizing the curium-lanthanum fluoride precipitate. Curium is separated from the lanthanum carrier by an ion exchange method developed by Hoff et al.[3] Electrodeposition is done according to a method of Coops.[4] Radioautography of the sample gives a quantitative measurement of curium,[5-8]

with recoveries of 45 ± 10% being obtained. Quantities of 0.26 dpm can be readily detected in a 24-hour specimen.

PROCEDURE

The urine specimen is initially treated according to the Argonne procedure[1] for alpha contamination, using bismuth phosphate and lanthanum fluoride. (This procedure is outlined in detail in the Appendix.) Curium is separated from the lanthanum fluoride carrier and electroplated as follows (see Fig. 1): The lanthanum fluoride is dissolved in 3 ml saturated boric acid – 6M hydrochloric acid, and lanthanum hydroxide precipitated with 10 ml of 28% ammonium hydroxide. This step requires heating: 20 minutes in an oil bath at 80°C. The lanthanum hydroxide is centrifuged for 5 minutes at 2000 rpm, and washed twice with approximately 1 ml of water and centrifuged for 2 to 3 minutes at 2000 rpm each time. The wet precipitate is then dissolved with HCl gas, yielding about 3 drops of liquid.

The ion exchange column is prepared as follows (see Fig. 2): The tip of a 10-cm × 3-mm-i.d. glass column is plugged with glass wool. A slurry of Dowex-1 × 10 resin is introduced and allowed to settle to 1 cm. The supernatant is discarded. A slurry of Bio-Rad AG 50 × 12 colloidal resin is then introduced carefully to form a distinct line of separation of the two resins, and is allowed to settle to a column of 6 cm. The resins are washed with 1 ml of 6M HCl and then several ml of 13M HCl. The column should be free of air bubbles.

The 3 drops of solution from the lanthanum hydroxide step are loaded onto the column. The transfer is completed with 3 drops of 13M HCl. As soon as the sample is loaded onto the column, counting of effluent drops begins. When the sample is completely in the resin, 1 ml of 13M HCl is used

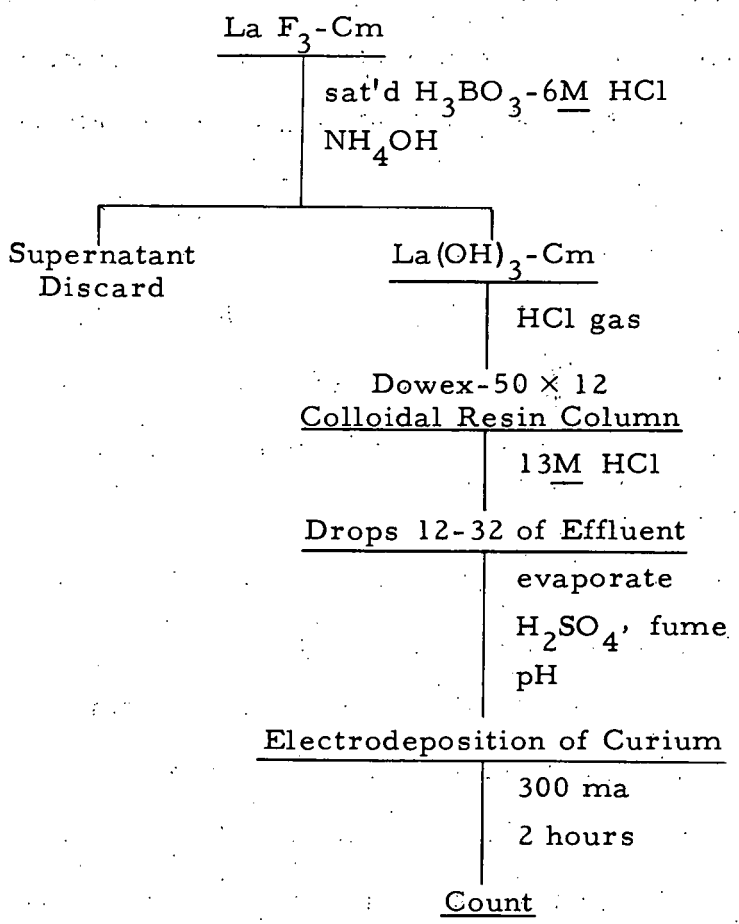

Fig. 1. Procedure for the electrodeposition of curium.

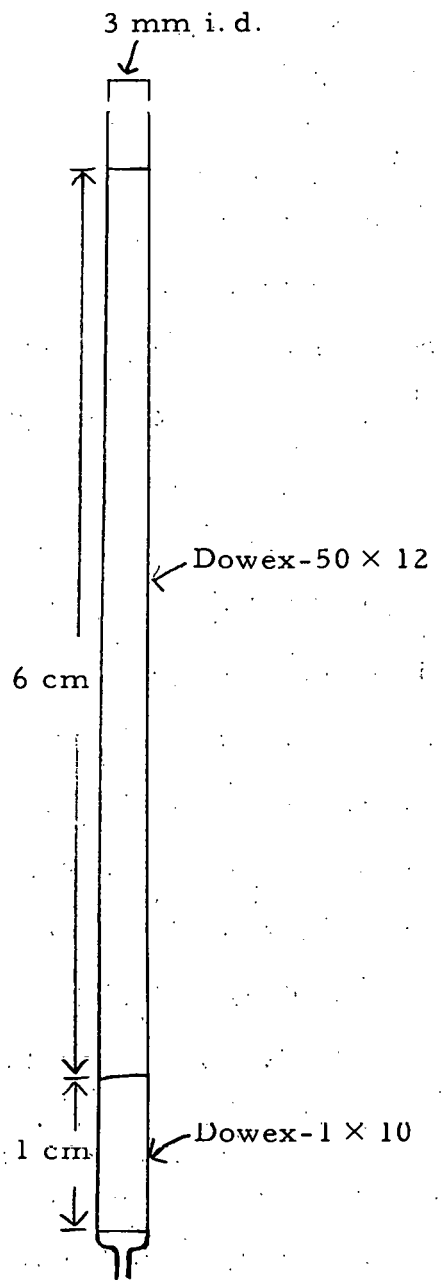

Fig. 2. Ion exchange column.

to elute the column at a rate of 1 drop each 90 seconds (air pressure may be required to attain this rate). Drops 12 to 32 are collected for electrodeposition (Fig. 3). The effluent is evaporated to dryness, 0.3 ml concentrated sulfuric acid is added, and the sample heated to dense SO_3 fumes. The solution is cooled pending preparation for electroplating.

An "Electro" power supply and a specially built 6-cell electrodeposition apparatus are used. The electrodeposition cell described by the Hanford group[6] is used. The sample disc is cleaned by electropolishing in a 40% solution of citric acid in 30% sulfuric acid.[7]

The solution for electrodeposition is transferred quantitatively to the electrolytic cell using approximately 5 ml of water. The total volume of solution should not exceed 6 ml. Two drops of 1% methyl red indicator are added. The solution is then titrated with 28% ammonium hydroxide to just yellow; then 1.5M sulfuric acid is added until the solution is 1 drop on the red side. The cell is placed on the electrodeposition apparatus and electroplated for 2 hours at 300 ma. Just prior to turning off the current, 1 ml of 28% ammonium hydroxide is added to prevent the dissolution of the electroplated material by the plating solution. The supernatant is decanted, and the cell rinsed twice with distilled water. The disc is removed from the cell, rinsed in acetone, dried under an infrared lamp, and then ignited to a cherry red in a Bunsen flame.

For immediate evaluation, the plated disc can be counted in an alpha counter. For final evaluation, the disc is placed in a brass camera designed by the Hanford group[6] and exposed routinely for 1 week to Ilford E 1, 25 (or 50) mμ, nuclear track emulsion plates.

Development of the nuclear track plates[9] is outlined in Table I. The D-19 stock solution and acid fixer solution should be replaced every 1 to 2

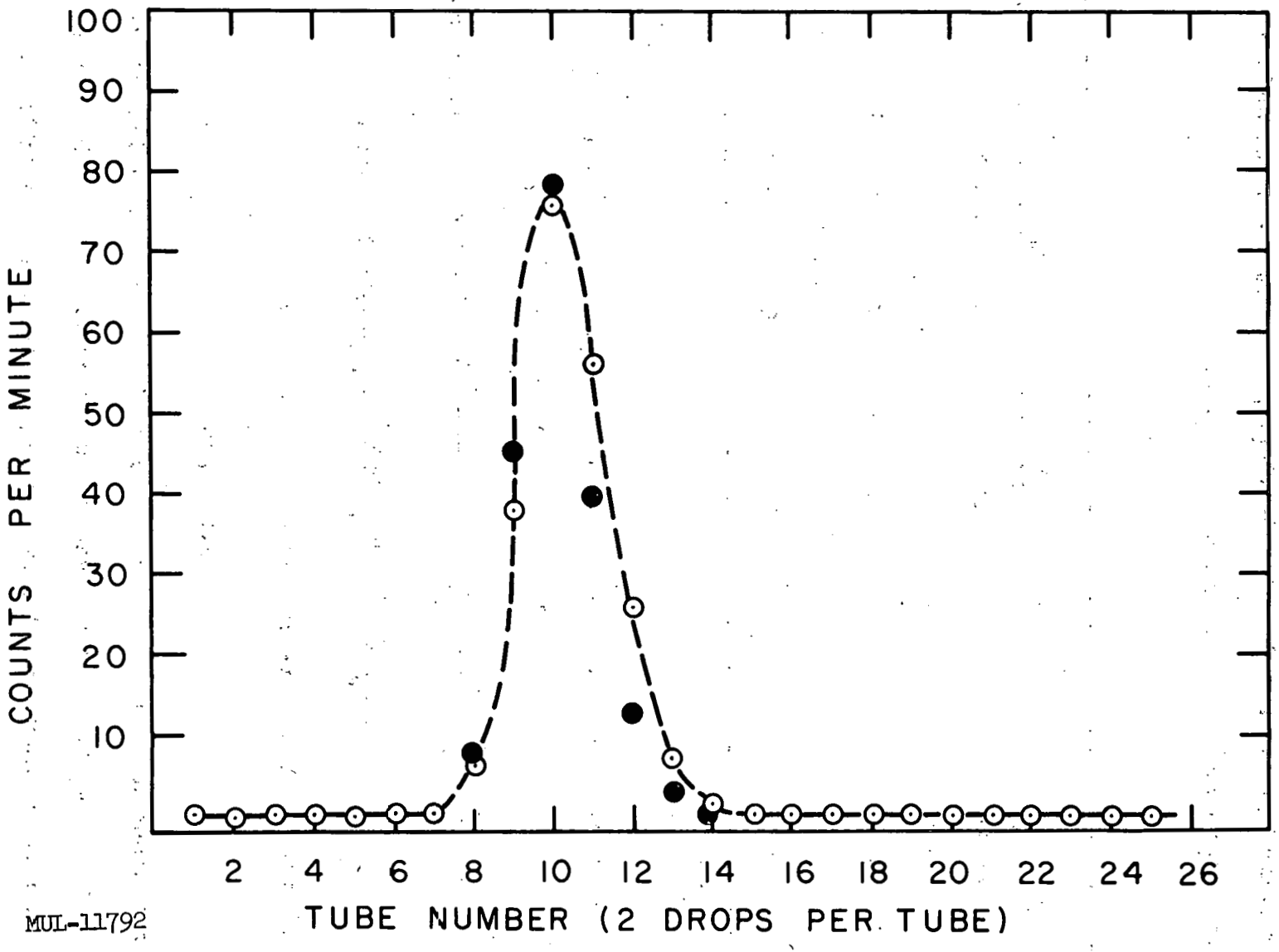

Fig. 3. Recovery of curium from the ion exchange column.

months. The 1:6 D-19 solution is freshly prepared each time. The development of the slides is simple and requires no special equipment or techniques. Plastic centrifuge tubes rather than developing tanks can be used, and a Dewar flask is a good constant-temperature water bath.

Table I. Developing procedure.

Operation	Time* (min)	Solution
Presoak	1	De-ionized H_2O
Develop	15	6:1 D-19
Stop	1	0.5% acetic acid
Fix	40-50	Kodak acid fixer (powder)
Wash	15	Distilled H_2O

*Temp = 20°C.

The nuclear tracks are counted using a microscope equipped with a Whipple counting disc. Calculation of the results is as follows:

$$\frac{(\text{total tracks counted}) \times (\text{total plated area} - 38.5\ \text{mm}^2)}{(\text{area scanned})} = \text{total tracks per plate}$$

$$\frac{(\text{tracks per plate})}{(\text{minutes of exposure}) \times (\text{efficiency})} = \text{dpm/sample} .$$

The total tracks counted are corrected for background.

DISCUSSION

In aqueous solutions, curium and americium exist in the trivalent state, thus making lanthanum fluoride a satisfactory carrier. Conversion of the curium-lanthanum fluoride to the hydroxide provides an acid-soluble compound for curium-lanthanum separation by Dowex-50. The trivalent actinides

elute ahead of the trivalent lanthanides from Dowex-50 with 13M HCl.[10] Bismuth impurities are adsorbed on Dowex-1. However, at high concentrations of hydrochloric acid, the adsorption is decreased.[11] Therefore it is important to remove any excess bismuth in the preparation of the lanthanum fluoride. Curium, and also americium, has little tendency to adsorb onto the Dowex-1 from hydrochloric acid.[10]

To determine the elution rate of the column, curium spikes were put through the procedure beginning at the lanthanum fluoride precipitation step. Effluent drops were collected 2 drops per tube. These fractions were counted in a proportional counter, and the curves in Fig. 3 show the results. The highest count rate appeared at the 19-20th drops, and drops 12 through 32 contained essentially all of the activity.

Spectrochemical analysis of the fractions eluted from the column showed that boron from the boric acid is eluted in the (0-12)-drop fraction; curium, as well as any bismuth contamination, is eluted in the (12-32)-drop fraction, and lanthanum is eluted in the 32-plus fraction.

The electrodeposition step was evaluated with regard to efficiency and optimum plating time. Figure 4 shows the recovery as a function of time; in one hour approximately 65% is recovered; in 2 hours, 88%, and in 3 hours, 89%. Because of the little difference in recovery obtained between 2 and 3 hours, a plating time of 2 hours is used routinely.

The recovery efficiency of each of the four basic steps of the procedure has been shown to be: the lanthanum fluoride step — 70%, conversion of the fluoride to the hydroxide and transfer to the column — 72%, column elution — 95%, and electroplating — 88%. The estimated over-all recovery is 42%.

The results of the urine spikes covering the range 0.30 to 5.88 dpm are included in Table II. To simulate a 24-hour sample, 1.5 liters of pooled urine was used in each instance. The average recovery of the 67 spikes is 45 ± 10%.

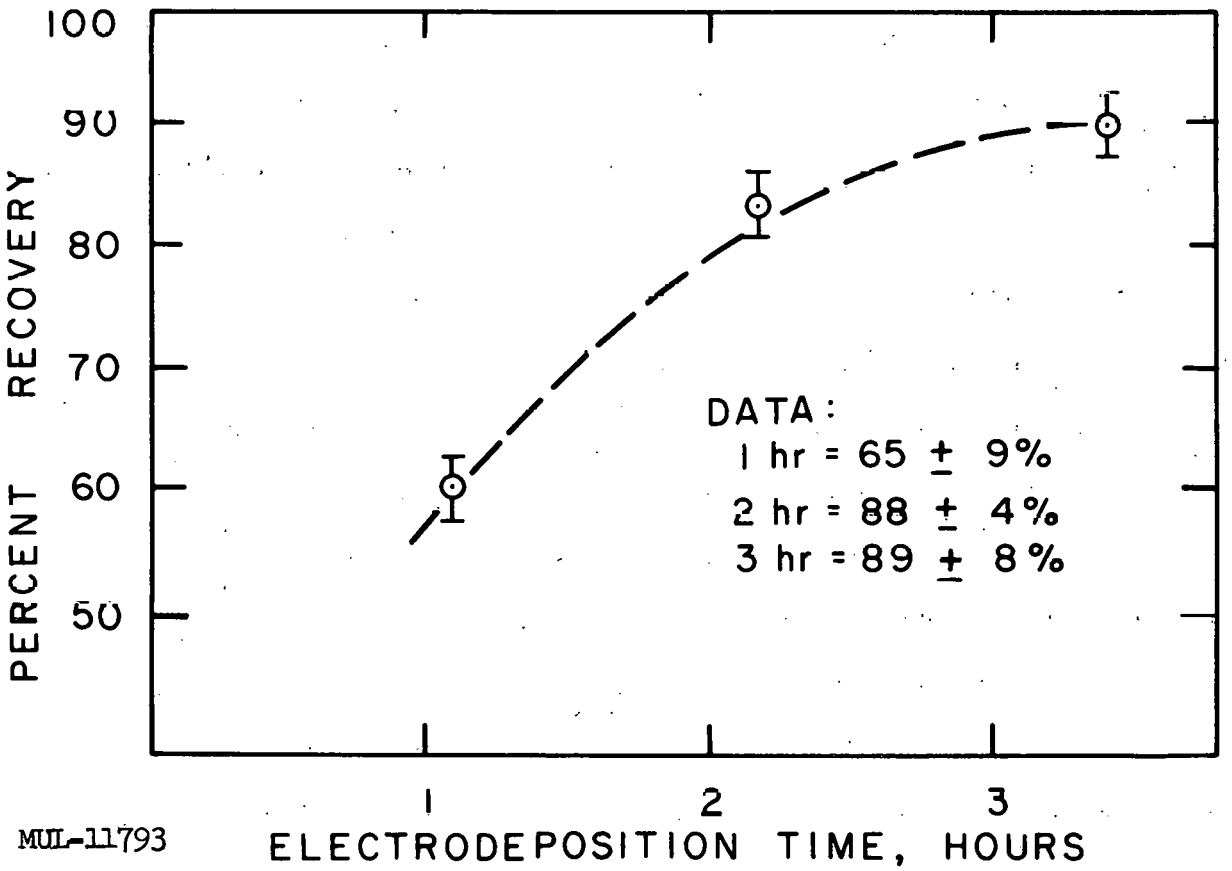

Fig. 4. Recovery of curium by electrodeposition as a function of time (effect of time on recovery).

Table II. Spike recovery of curium.

Spike/1.51 (dpm)	No. samples	% Recovery	% Standard deviation
0.30	9	53	12
0.56	23	43	10
1.44	9	40	14
2.68	10	43	6
5.88	16	45	10
Blanks, urine	20	0.030 dpm	0.018 dpm

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APPENDIX

I. Reagents

(All chemicals used are reagent grade)

Concentrated Nitric Acid – HNO_3 70%, sp. gr. 1.42

N-Octyl Alcohol – $CH_3(CH_2)_6 CH_2OH$, practical

Boiling Chips – Carborundum

Sulfurous Acid – 6%

Concentrated Phosphoric Acid – H_3PO_4 (Orthophosphoric Acid) 85%, sp. gr. 1.71

Concentrated Hydrochloric Acid – HCl 36%, sp. gr. 1.19

50% Sodium Hydroxide Solution – 50 g of NaOH (AR) pellets dissolved in 50 ml of distilled water.

Bismuth Nitrate: Dissolve 231.2 g bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$-AR) in 660 ml conc. nitric acid and dilute to 1 liter with distilled water. 100 mg Bi/ml.

Lanthanum Nitrate: Dissolve 1.56 g lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$-AR) in 63 ml conc. nitric acid and dilute to 1 liter with distilled water. 1 mg La/ml.

Concentrated Hydrofluoric Acid – HF 48%

1% Hydrofluoric Acid – Add 1 cc of 48% HF to 99 ml distilled water.

Saturated Boric Acid – 6M hydrochloric acid – dissolve an excess (6-7 g) of boric acid (H_3BO_3-AR) in 100 ml 6M HCl.

13M HCl – Bubble HCl gas into 12M HCl.

HCl gas – Lecture-Size Cylinder

Acid Fixer – Eastman Kodak – Powder

D-19 Developer – Eastman Kodak

0.5% Acetic Acid – Dilute 5 ml of acetic acid – to 1000 ml.

Electrolyte Solution – Dissolve 200 grams of citric acid ($H_3C_6H_5O_7 \cdot H_2O$) in 200 ml distilled water and add 57.5 ml conc. sulfuric acid slowly with stirring.

II. Equipment

Electrodeposition Apparatus

Electrodeposition Cells

← 1/2-inch stainless steel discs

← 10-cm × 3-mm Ion Exchange Columns with a (20 to 30)-ml reservoir

A Brass Camera

Bausch-Lomb Binocular Microscope

Whipple Counting Disc

Ilford El Nuclear Track Plates, 25 mμ thick.

III. Details of the Procedure

Gross Alpha Determination

1. A 24-hour urine specimen is transferred to a 2-liter beaker and the original container rinsed with 2N HNO_3. Add 200 ml of conc. nitric acid, cover the beaker with a speedyvap and evaporate to dryness on a hot plate. Carborundum chips and octyl alcohol are used to minimize bumping and foaming.

2. Cool sample sufficiently to add enough nitric acid to cover the salts. Evaporate to dryness.

3. Repeat step 2 until the salts are white when cool. In some cases, such as when feces are wet ashed, H_2O_2 in 5-cc amounts with 100 ml conc. nitric acid is used to obtain white salts.

Analytical

4. Add 30 ml of water and 5 ml of conc. nitric acid to the salts. Heat gently on hot plate to help dissolution.
5. Transfer the solution to a 90-ml round-bottom centrifuge tube. Centrifuge at 2500 rpm for 5 minutes.
6. Decant the supernatant into a 250-ml beaker.
7. Repeat step 4 to dissolve any remaining salts in the original beaker.
8. Transfer the solution to the 90-ml centrifuge tube. Centrifuge for 5 minutes at 2500 rpm.
9. Add the supernatant to the original 250-ml beaker.
10. Add 1/2 ml conc. nitric acid and 2 ml water to the salts in the centrifuge tube. Heat over a Bunsen burner. Cool. Centrifuge for 5 minutes at 2500 rpm.
11. Add supernatant to the main solution.
12. Add 2 ml of sulfurous acid. Stir. Let stand for 5 minutes.
13. Adjust the pH to 1.7.
14. Transfer the solution to two (2) 90-ml centrifuge tubes; place the tubes in a constant-temperature oil bath (80°C). Stir continuously with a stirring motor. After 15 minutes add 1 ml of conc. phosphoric acid and 1 ml bismuth nitrate.
15. Allow the bismuth phosphate precipitate to digest for 1 hour with stirring.
16. Terminate stirring, remove tubes from bath, centrifuge for 5 minutes at 2500 rpm.
17. Remove the supernatant through a glass tube attached to a water aspirator.

18. Transfer the precipitate in a water slurry from the first 90-ml tube to a 40-ml conical centrifuge tube. Centrifuge for 5 minutes at 2000 rpm. Pour off supernatant.

19. Repeat steps 16 and 17 with the second 90-ml tube to the same 40-ml tube.

20. Wash down each 90-ml tube with 2 ml of conc. HCl followed by 2 ml of water.

21. Add liquid from each 90-ml tube to the 40-ml tube. Stir with a glass rod until the precipitate dissolves. If a gelatinous precipitate exists, centrifuge and decant quantitatively the supernatant into another 40-ml centrifuge tube.

22. Add 0. 3 ml lanthanum nitrate to the solution; mix by swirling and add 1 ml of 48% hydrofluoric acid. Mix.

23. Let stand for 5 minutes, then centrifuge for 5 minutes at 2000 rpm. Discard the supernatant. Wash the precipitate with 10 ml of 1% hydrofluoric acid. Centrifuge 5 minutes at 2000 rpm. Discard washing.

24. Invert the centrifuge tube on several thicknesses of Kimwipes. Drain for 20-30 minutes.

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