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THE RADIOCHEMICAL SEPARATION OF ACTINIUM AND ITS DAUGHTERS BY MEANS OF LEAD SULFATE

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DISCLAIMER

ABSTRACT

A method has been developed for separation of Ac^{227} and its radioactive daughters from rat urine by means of precipitated lead sulfate. Individual activities may be determined by counting and by application of calculations involving differential decay techniques. Approximately 90% of the activity in rat urine can be recovered. The method requires about eight hours. In the absence of large quantities of phosphorus the method should be applicable to the analysis of other biological materials.

INTRODUCTION

A method[1] has been described for determination of small amounts of radium in uranium ores by separating the radioactivity on precipitated lead sulfate. This method[2] was adapted, with slight modifications, for the separation of small amounts of radium from large volumes of human urine.

The technique of using lead sulfate as a carrier for radioactivity was suggested as a method for separation of actinium and its daughter elements from rat urine containing these substances. Experiments were conducted, using radioactive lanthanum-140 as a stand-in for actinium, to determine if lead sulfate could be used to precipitate an actinium-like activity from urine salts. The results of these experiments, as determined by alpha-counting techniques, were low and inconsistent. The difficulty was overcome by precipitating the lead as the sulfate in hot solutions instead of in ice-cold solutions as recommended. Excellent results were obtained after this modification was made and actinium in equilibrium with its daughters was determined satisfactorily.

Actinium-227, a beta emitter with a 22-year half-life, decays to thorium-227, radium-223, and a number of short-lived products including lead, bismuth, and polonium. Because the chemical properties of these decay elements are dissimilar, it is thought that the ability of lead sulfate to serve as a carrier for radioactivity can be attributed to a mass absorption effect rather than to a similarity of chemical properties.

METHOD

GENERAL

The method described herein for the separation and determination of actinium and its daughter products in rat urine containing radioactive substances requires about eight hours. The radioactivity is coprecipitated from hot solution with lead sulfate, and the precipitate containing the activity is separated from the soluble urine salts by centrifugation. The lead is removed by precipitation as a sulfide or by electrolysis, leaving the activity in solution. The actinium fraction is free of interfering salts except for a small quantity of urine salts coprecipitated with the lead sulfate. This residue amounts to less than 50 milligrams by weight in a typical sample. Approximately 90 per cent of the total activity can be recovered from rat urine salts and more than this amount can be recovered if corrections are made for counting losses resulting from absorption. Individual activities may be quantitatively determined by alpha counting and calculations involving differential decay[3] techniques.

PROCEDURE

To a sample of rat urine in a 250-milliliter boiling flask add 60 milliliters of concentrated nitric acid. Enclose the flask in an electric heating mantle and evaporate nearly to dryness. Add small portions of concentrated nitric acid until the urine salts are clear and free from all organic matter, and evaporate to dryness.

Dissolve the dried urine salts with dilute nitric acid and transfer quantitatively to a clean 150-milliliter beaker. Evaporate to dryness, take up the salts in 100 milliliters of 0.1-normal nitric acid, and slowly add 3.0 milliliters of concentrated sulfuric acid. Heat to 70°C on a hot plate with mechanical stirring and add dropwise 100 milligrams of lead in carrier solution (dissolve 32 grams of lead nitrate in 100 milliliters of distilled water; each milliliter contains 200 milligrams of lead). Maintain the temperature at 70°C and stir for thirty minutes. Rinse stirring rod and thermometer with sufficient water to bring the volume of the solution to 100 milliliters. Cover the beaker with a watch-glass and let digest in a warm place for at least four hours, or preferably, overnight, and stir occasionally.

Cool the beaker and contents to room temperature and centrifuge. Rinse the beaker thoroughly with portions of the supernatant liquid, add to the centrifuge tube, and centrifuge until the supernatant liquid is clear. If there are "floaters" on top of the solution, add a drop of 5 per cent aerosol (5% aqueous solution of Aerosol-OT, dioctyl sodium sulfosuccinate) and centrifuge again. Discard the supernatant liquid which contains the inactive urine salts. The major portion of the radioactivity has been precipitated with the lead sulfate. Set aside the original 150-milliliter beaker for use in the next step.

Two methods may be used for the removal of lead from solution. The lead, using either method, is almost completely removed and less than 2 per cent of the radioactivity is lost through its removal. The weight of the final residue is slightly lower if the sulfide method is used, but this method has the disadvantage of being tedious and time-consuming.

LEAD SULFIDE METHOD

To the lead sulfate precipitate add 15 milliliters of concentrated hydrochloric acid and transfer to the original 150-milliliter beaker. Heat on a steam bath with stirring until the residue is dissolved and then evaporate to dryness. Add dilute hydrochloric acid dropwise to the residue until it dissolves and make up to 50 milliliters with distilled water. Adjust the acidity with dilute ammonium hydroxide so that it is weakly acid (pH 3.0 - 3.5) to alkacid paper. Heat almost to boiling and saturate the solution with hydrogen sulfide. Add 50 milliliters of cold distilled water and continue to pass in hydrogen sulfide until the solution is clear and the precipitate settles to the bottom of the beaker. Centrifuge and wash the precipitate twice with 5-milliliter portions of hydrogen sulfide water. Dissolve the lead sulfide precipitate in hot concentrated hydrochloric acid, evaporate to dryness, dissolve in dilute hydrochloric acid, and reprecipitate. Combine the two supernatant solutions, heat almost to boiling and test for completeness of precipitation by saturating with hydrogen sulfide. Evaporate the combined solution to dryness. Dissolve residue in 10 milliliters of concentrated nitric acid, reduce the volume of the solution to 2 to 3 milliliters by evaporation. Cool, and rinse the sides of the beaker with nitric acid, followed by a second rinsing with distilled water. Again reduce the volume by evaporation to 2 to 3 milliliters. Transfer solution to a clean 10-milliliter volumetric flask, using small portions of distilled water to wash the contents of the beaker into the flask. Fill the flask to the mark and mount on slides as described below.

ELECTROLYTIC METHOD

To the lead sulfate precipitate add 15 milliliters of concentrated hydrochloric acid. Heat on steam bath with stirring until dissolved and evaporate to dryness. Take up the residue in 10 milliliters of concentrated nitric acid. Transfer quantitatively from the centrifuge tube to the original 150-milliliter beaker with 90 milliliters of distilled water. Heat if necessary to put all of the lead in solution. Connect a clean platinum gauze to the positive terminal of an electro-analyzer. A heavy-gauge platinum spiral wire placed within the gauze serves as the cathode. Place the 150-milliliter beaker containing the lead on a magnetic stirrer and bring the assembly beneath the electrodes. Adjust the heighth of the beaker so that the platinum gauze anode is at least two-thirds immersed. Turn on the current and adjust to a value of 0.5 to 1.0 ampere at 2 volts or more. Electrolyze for two hours with stirring. Test for completeness of deposition by adding a little water and note if any deposit is formed on the freshly-immersed gauze after the electrolysis has continued for thirty minutes. When deposition is complete, lower the beaker slowly and with the current still on, wash the electrodes thoroughly with a fine stream of water. Catch the wash solution in the same beaker. Add 10 milliliters of concentrated nitric acid to the solution and evaporate nearly to dryness on the steam bath. Dissolve the lead plating on the anode by immersing in dilute nitric acid which contains about 0.5 milliliter of 30 per cent hydrogen peroxide. Discard the solution.

Rinse the sides of the beaker containing the residue with about 10 milliliters of concentrated nitric acid. Reduce the volume of the solution to 2 to 3 milliliters by evaporation. Cool, and rinse the sides of the beaker again with nitric acid, followed by a second rinsing with distilled water. Again reduce the volume by evaporation to 2 to 3 milliliters. Transfer solution quantitatively to a clean 10-milliliter volumetric flask, using small portions of distilled water to wash the contents of the beaker into the flask.

DETERMINATION OF ACTIVITY

Fill the flask to the mark and mount an appropriate aliquot on a round 2-inch stainless steel slide. For best results, the volume of the mounted aliquot should be selected so as to produce an alpha count within the range of 1,000 to 50,000 counts per minute. When the mount on the slide is nearly dry, lower the heat lamp and heat strongly until all excess sulfuric acid has been volatilized. Flame the slide with a Bunsen burner to drive off the short-lived daughter elements, and count the slide. Counting data obtained over a period of several weeks are used for the differential decay[8] calculations for the quantitative estimation of individual activities.

RESULTS

Table I shows the total activity recovered from rat urine with one lead sulfate precipitation. Varying amounts of actinium in equilibrium were added to the urine to produce between 5,700 to 4,800,000 counts per minute. Losses of activity in the urine salts and the separated lead carrier are shown.

A study was made to determine which of the three major activities of actinium in equilibrium were lost through chemical separations. Mounted slides of both urine salts and separated lead carrier were counted at regular intervals for 30 days. Data from these counts show that the radioactivity lost was predominately thorium-227. However similar data collected from slides mounted with the final residue, column "Total Activity Recovered" in Table I, shows no appreciable growth or decay over a period of 30 days, indicating that the actinium recovered was in equilibrium with its daughters.

TABLE I

TOTAL ALPHA ACTIVITY RECOVERED FROM RAT URINE

LEAD CARRIER (mg Pb)	TOTAL ACTIVITY ADDED (cts/min)	ACTIVITY LOST IN URINE SALTS (%)	ACTIVITY LOST IN PbS (%)	ACTIVITY LOST IN LEAD PLATING (%)	TOTAL ACTIVITY RECOVERED (cts/min)	ACTIVITY RECOVERED (%)
100	4,800,000	2.30	1.50	-	4,358,000	91
100	4,500,000	0.52	2.30	-	3,812,000	85
200	4,500,000	0.18	0.41	-	3,932,000	87
200	4,500,000	0.31	1.88	-	3,954,000	88
200	900,000	0.04	1.65	-	756,000	84
200	900,000	0.21	2.10	-	775,000	86
100	900,000	0.60	1.96	-	763,000	85
100	900,000	0.15	-	0.34	792,000	88
100	225,000	2.00	-	0.75	206,800	92
100	66,000	0.38	-	0.51	59,600	90
100	66,000	0.30	-	2.70	56,400	86
100	21,000	1.20	-	2.30	19,640	94
100	21,000	0.57	-	0.71	20,400	97
100	5,700	-	-	-	5,020	88
100	5,700	-	-	-	5,825	102
100	5,700	-	-	-	5,120	90

CONCLUSIONS

The method described provides a convenient means for the removal of actinium-227 and its daughters from rat urine. In the absence of large amounts of phosphorus, which interferes with the quantitative precipitation of lead sulfate, the procedure can be applied to the separation of radioactivity from other biological materials.

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