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THE DETERMINATION OF LANTHANUM IN PLUTONIUM METAL AND IN PLUTONIUM NITRATE SOLUTIONS

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AEC RESEARCH AND DEVELOPMENT REPORT

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CHEMISTRY--SEPARATION PROCESSES FOR PLUTONIUM AND URANIUM
(M-3679, 16th ed.)

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CHEMISTRY--SEPARATION PROCESSES FOR PLUTONIUM AND URANIUM
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ABSTRACT

A colorimetric method for the determination of lanthanum in plutonium alloys or solutions was developed. The method was designed for samples containing up to 50 milligrams of plutonium and from 25 to 1000 micrograms of lanthanum (a range of 0.05 to 2.0 percent for the lanthanum-plutonium ratio). It was found necessary to separate lanthanum from a solution of the two elements by oxidizing plutonium to Pu(VI) with perchloric acid or ammonium persulfate and precipitating lanthanum as the fluoride. The lanthanum fluoride was dissolved in fuming perchloric acid and precipitated with 8-quinolinol. Lanthanum 8-quinolinate dissolved in 0.1 N hydrochloric acid was used for photometric measurements at 365 millimicrons with a Beckman spectrophotometer. For 40 to 200 micrograms of lanthanum the standard deviation for a single measurement was 3 micrograms. An attempt to separate a few micrograms of americium which was present with the plutonium by oxidation to Am(VI) was partially successful. Thorium interfered with the determination of lanthanum in plutonium-containing samples.

INTRODUCTION

Spectrochemical methods have been developed for the determination of lanthanum in both high-purity plutonium metal(10) and concentrated solutions of plutonium nitrate in nitric acid (Hanford nitrate solutions).(9) For these two methods the accuracy and precision of spectrochemical determinations is approximately the same. They have a range of about 50 to 10,000 p.p.m. of lanthanum with respect to plutonium, an average recovery of 117 percent, and a standard deviation of about 20 percent.

For some plutonium-lanthanum samples, particularly those containing 0.05 to 2.0 percent lanthanum (500 to 20,000 p.p.m.), the reproducibility of the spectrochemical methods is not always adequate. Consequently, the possibility of determining lanthanum in plutonium-containing samples by chemical methods was investigated. It was recognized that very probably a chemical method would require an initial separation of microgram amounts of lanthanum from milligram quantities of plutonium, since methods for determining lanthanum are not specific. For example, Sandell(11) describes two colorimetric methods for lanthanum: formation of a lake with alizarin, and an indirect determination in which lanthanum is precipitated as the phosphate and the phosphorus in the dissolved precipitate is determined by the molybdenum blue method. In both of these methods many other metals, including plutonium, will react and interfere.

In looking for a separation method it was recalled that quantitative precipitation of lanthanum has been used in plutonium radiochemical work continuously from the beginning of the Plutonium Project.(6) Lanthanum, added to plutonium solutions and precipitated with hydrofluoric acid, serves as a carrier for Pu(III) and Pu(IV). Plutonium as Pu(VI), however, does not coprecipitate with lanthanum fluoride. If a plutonium-lanthanum solution is treated with a suitable oxidizing agent and only hexavalent plutonium is present during the formation of lanthanum fluoride, a separation of the two elements should result. If possible, the oxidizing agent should also convert any americium accompanying the plutonium to a hexavalent compound, but it should not lead to the introduction of a substance which precipitates with lanthanum and interferes in any subsequent method of determination.

APPARATUS AND REAGENTS

Apparatus

Spectrophotometer. Beckman Model DU was used with 1-cm. Corex cells.

Centrifuge. International Clinical Model.

Heating Block. This aluminum block, 25 x 50 x 132 mm., has six 14.5 x 42 mm. holes drilled into the 25 x 132 mm. side at a 10° angle to the horizontal position for heating 12 x 100 mm. test tubes. The block should be heated with an electric hot plate, similar to a Fisher Autemp heater.

Text tube. Quartz, 12 x 100 mm.

Filter funnel. Pyrex, 15 ml., medium porosity fritted disc.

Bell jar, micro. Pyrex, Corning No. 6880.

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Volumetric flask. Pyrex, 10 ml.

Reagents

Plutonium metal, high-purity.

Perchloric acid, A.R., 70 percent.

Hydrofluoric acid, A.R., 48 percent and 1 N.

Hydrochloric acid, A.R., 0.1 N.

Acetic acid, A.R., 2 N.

Ammonium hydroxide, A.R., 1 and 10 percent.

Lanthanum nitrate, $La(NO_3)_3.6H_2O$, C.P., A. D. Mackay.

Ammonium persulfate, A.R.

Thymol blue indicator, E. K. No. 753. A 0.05 percent solution was prepared by mixing 100 mg. of reagent with 4.3 ml. of 0.05 N NaOH in a mortar, transferring the solution to a 200-ml. volumetric flask, and diluting to volume with distilled water.

8-Quinolinol, E. K. No. 794. A 1 percent solution in 2 N acetic acid and a 3 percent solution in ethanol were used.

RECOMMENDED METHOD

CAUTION

Work with plutonium-containing materials should always be done in laboratories designed for adequate protection of the worker and under approved conditions. Health-Safety Rules of the Laboratory for protection from radioactive material must be strictly followed in employing any of the analytical procedures which are described in this report.

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Sample Preparation

For the determination of lanthanum an individual sample of either plutonium metal or plutonium nitrate solution should contain between 40 and 200 micrograms of lanthanum and may contain as much as 50 milligrams of plutonium. Samples containing as little as 25 micrograms of lanthanum can be analyzed with some loss of precision. If samples contain more than 200 micrograms of lanthanum, the final solution of lanthanum 8-quinolinate in 0.1 N hydrochloric acid should be diluted to some suitable, known volume greater than 10 milliliters before measuring absorbance with a spectrophotometer.

If necessary, samples containing 100 milligrams of plutonium can be analyzed with the recommended procedure, but special care must be taken. For example, with larger samples of fine metal turnings, there is a possibility that the dissolving reaction with perchloric acid will become too violent and cause the formation of some plutonium dioxide. A third fluoride precipitation may be advisable with large amounts of plutonium.

The volume of any nitrate solution sample should be as small as possible to avoid time-consuming evaporations. Quartz test tubes, 12 x 100 mm., used in the analysis will not conveniently hold samples larger than 5 milliliters; samples with volumes in excess of this quantity should be evaporated in other containers before transfer to the quartz tube.

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Procedure

The directions to be followed for steps 1 to 5 depend upon the nature of the analytical sample; thus, select either A. Metal Samples or B. Nitrate Solution Samples for these directions.

A. Metal Samples

1. Weigh the sample accurately to the nearest 0.1 mg. and transfer it quantitatively to a quartz test tube (12 x 100 mm.).

2. Place the round-bottom end of the quartz tube under water in a beaker to prevent an excessively rapid dissolving reaction. Add 0.3 to 0.4 ml. of 70 percent perchloric acid to the tube, but avoid contact between the acid and quartz near the open end of the tube. Immediately close the tube with a stopper made from a portion of a Kleenex tissue.

3. When all reaction between metal and acid has ceased, remove and discard the Kleenex stopper.

4. Transfer the quartz tube to an aluminum heating block and heat at 225° C for 10 minutes. Perchloric acid fumes should be evolved during the last few minutes of heating. Then remove the tube from the heating block and allow the quartz container and contents to cool to room temperature.

5. To the green solution or crystallized sample add 3 ml. of distilled water, rinsing down the inner wall of the tube during this addition. Dissolve all material by stirring the solution with a platinum wire stirrer and allow the stirrer to remain in the tube. Any insoluble material at this point may cause interference.

6-41. Perform steps 6-41 under B. Nitrate Solution Samples.

B. Nitrate Solution Samples

1. Transfer the solution sample, as an accurately known volume or weight aliquot with a maximum volume of 5 ml., to a quartz test tube (12 x 100 mm.).

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2. Add 0.4 ml. of 70 percent perchloric acid to the tube and carefully evaporate the solution to a volume of about 0.5 ml. An infrared lamp may be used for this evaporation but loss of material due to boiling or too-rapid heating must be avoided.

3. Transfer the quartz tube to an aluminum heating block and heat at 225° C for 7 to 10 minutes. Perchloric acid fumes should be evolved during the last few minutes of heating. Then remove the tube from the heating block and allow the quartz container and contents to cool to room temperature.

4. To the green solution or crystallized sample add 3 ml. of distilled water, rinsing down the inner wall of the tube during this addition. All material should dissolve during brief stirring with a platinum wire stirrer. If the sample dissolves readily, proceed to step 6; otherwise, it will be necessary to follow the directions in step 5.

5. If the initial nitrate solution sample contained sulfate, red plutonium(IV) sulfate crystals may form during the fuming with perchloric acid. Complete oxidation to a green plutonium(VI) solution or solid is prevented and plutonium sulfate crystals will not dissolve rapidly on addition of 3 ml. of water. In this case continue agitation until all material is dissolved. Add about 100 mg. of solid ammonium persulfate and two drops of thymol blue indicator solution to the quartz tube. Dissolve and mix with the platinum stirrer. Add 10 percent ammonium hydroxide, dropwise and with stirring, until excess acid is nearly neutralized. Then complete the neutralization with 1 percent ammonium hydroxide. The indicator changes from red to orange or yellow-orange. The solution volume should not exceed 5 ml. Rinse the stirrer with several drops of water on removing it from the solution. Heat the quartz tube and solution in an aluminum heating block at 85° C for 15 to 20 minutes. Remove from the heating block and replace the stirrer in the tube.

6. Add dropwise 0.4 to 0.8 ml. of concentrated hydrofluoric acid to the platinum stirrer in the quartz tube. If the acid is allowed to flow down the stirrer, direct contact between the reagent and quartz can be avoided. Stir the solution thoroughly and rinse the stirrer with a few drops of 1 N hydrofluoric acid when it is being removed from the tube.

7. Allow the quartz tube to stand for 10 minutes for complete precipitation of lanthanum fluoride.

8. Centrifuge the tube at maximum speed for 5 minutes.

9. Remove the tube from the centrifuge and dispose of all supernatant

[redacted]

liquid without disturbing the collected precipitate. The liquid may be conveniently transferred by suction to a container for disposal of radioactive solutions, inverting the tube to drain thoroughly and to avoid disturbing the precipitate as the last portion of liquid is removed.

10. Add 1 to 2 ml. of 1 N hydrofluoric acid, stir the mixture of precipitate and wash liquid with the platinum stirrer, and again rinse the platinum wire with 1 N hydrofluoric acid as it is withdrawn from the tube.

11. Again centrifuge the tube for 5 minutes.

12. Remove the tube from the centrifuge and discard the supernatant liquid by suction, with same procedure used in step 9.

13. Add 0.3 ml. of 70 percent perchloric acid to the precipitate in the quartz tube.

14. Heat the tube and contents in an aluminum heating block at 225° C for 7 or 8 minutes. Fumes of perchloric acid should be evolved during the last 3 or 4 minutes of heating.

15. Remove the tube from the heating block and allow the quartz container and contents to cool to room temperature.

16. Rinse the inner surface of the tube with 0.5 ml. of distilled water and collect all liquid at the bottom of the tube by centrifuging the tube briefly.

17. With a suitable pipet, transfer the solution quantitatively to another quartz test tube (12 x 100 mm.) which is reserved exclusively for work with solutions containing no more than microgram quantities of plutonium. Complete transfer of the solution can be assured by using three 0.7- or 0.8-ml. portions of distilled water to rinse the original tube and using the same pipet to carry each rinse to the new quartz tube.

18. Add about 100 mg. of solid ammonium persulfate and 2 drops of thymol blue indicator solution to the quartz tube. Dissolve and mix with a platinum stirrer. Add 10 percent ammonium hydroxide, dropwise with stirring, until excess acid is nearly neutralized. Then complete the neutralization with 1 percent ammonium hydroxide. The indicator changes from red to orange or yellow-orange. The solution volume should not exceed 5 ml. Rinse the stirrer with several drops of water on removing it from the solution.

19. Heat the quartz tube and solution in an aluminum heating block at 85° C for 15 to 20 minutes. Then remove the tube from the heating block and replace the stirrer in the tube.

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20. Add 0.4 ml. of concentrated hydrofluoric acid, allowing the reagent to first touch the platinum stirrer so that direct contact with the quartz tube is avoided. Use the last several drops of acid to rinse the stirrer after mixing the solution thoroughly.

21. Allow the quartz tube to stand for 10 minutes for complete precipitation of lanthanum fluoride.

22. Centrifuge the tube at maximum speed for 5 minutes.

23. Remove the tube from the centrifuge and dispose of all supernatant liquid by suction, without disturbing the collected precipitate. Invert the tube to collect the last drops of liquid.

24. Add 1 to 2 ml. of 1 N hydrofluoric acid, stir the mixture of precipitate and wash liquid with the platinum stirrer, and rinse the stirrer with several drops of 1 N hydrofluoric acid.

25. Again centrifuge the tube for 5 minutes.

26. Remove the tube from the centrifuge and discard the supernatant wash liquid by suction.

27. Add 0.3 to 0.4 ml. of 70 percent perchloric acid to the precipitate in the quartz tube.

28. Heat the tube and contents in an aluminum heating block at 225° C for 7 or 8 minutes. Fumes of perchloric acid should be evolved during the last 3 or 4 minutes of heating.

29. Remove the tube from the heating block and allow the quartz container and contents to cool to room temperature.

30. Rinse the inner surface of the tube with 1.5 to 2.0 ml. of distilled water.

31. Add 0.5 ml. of 8-quinolinol in 2 N acetic acid. More reagent may be necessary if the quantity of lanthanum is greater than 200 μg.

32. Add 10 percent ammonium hydroxide dropwise with stirring until the solution is neutralized. Neutralization is revealed by an increase in the intensity of the yellow solution and precipitation of lanthanum. Add several drops of the same ammonium hydroxide solution and mix thoroughly. Rinse the stirrer with water in removing it from the tube.

33. Heat the tube for 1 or 2 minutes at the temperature of a steam bath.

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34. Allow the precipitate to settle for 1 hour.

35. Collect the precipitate on a 15-ml., medium porosity, Pyrex filter funnel which is fitted to a Pyrex micro bell jar. Wash the quartz tube and precipitate on the funnel thoroughly, but with a minimum of distilled water. Discard all filtrate and washings; wipe the lower end of the filter funnel with a Kleenex tissue.

36. Place a 10-ml. volumetric flask under the filter funnel in the bell jar to collect the solution of dissolved precipitate.

37. Rinse the quartz tube with several milliliters of 0.1 N hydrochloric acid and add this rinse solution to the precipitate on the funnel.

38. Very carefully apply suction to the bell jar to draw the dissolved precipitate down into the volumetric flask without loss of solution. Rinse the funnel thoroughly with 0.1 N hydrochloric acid and transfer this rinse to the volumetric flask until the total volume is 8 or 9 ml.

39. Remove the flask from the bell jar, dilute to exactly 10 ml. with 0.1 N hydrochloric acid, and mix this solution thoroughly. If the lanthanum content of the sample is greater than 200 μg. it will be necessary to transfer this solution to a volumetric flask with a capacity greater than 10 ml. and dilute to the designated volume with 0.1 N hydrochloric acid.

40. Measure the absorbance of this solution at 365 mμ against a reference cell containing distilled water. Subtract any cell correction from the observed absorbance reading.

41. Determine the equivalent amount of lanthanum in micrograms for the corrected absorbance reading by reference to a calibration curve. (See below for the preparation of this curve.) Calculate the percent lanthanum in the sample from the weight of lanthanum.

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Calibration Curve

A calibration curve may be prepared by using the Recommended Procedure, beginning with the directions under A. Metal Samples, and 50-milligram samples of high-purity plutonium. After the metal has been dissolved (steps 1 to 4), a known aliquot of a standard lanthanum nitrate solution is added to each sample in place of a portion of the distilled water (step 5). The combined volume of standard lanthanum solution and distilled water should be 3 milliliters. When the procedure has been followed to the end of step 40, a calibration curve may be prepared with the corrected absorbance readings as ordinate and corresponding quantities of lanthanum in micrograms as abscissa.

A standard lanthanum nitrate solution containing 1 milligram of lanthanum per milliliter is convenient if weight aliquots are used in preparing a calibration curve. With either weight or volume aliquots, the solution can be standardized gravimetrically by transferring samples containing at least 10 milligrams of lanthanum to 100 milliliter beakers and diluting to about 30 milliliters. Heat to boiling, add 5 milliliters of 2 N acetic acid, and add an excess of 8-quinolinol reagent (5 percent 8-quinolinol in ethanol). Add ammonium hydroxide until no more precipitate is formed and a strong odor of ammonia is detected. After warming the solution for several minutes, allow it to stand for 1 hour before filtering on a tared, sintered-glass, filter crucible. Wash with warm water, dry at 130° C, cool, and reweigh the crucible.

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The factor for lanthanum in the dried lanthanum 8-quinolinate is 0.2433.

EXPERIMENTAL RESULTS

Methods for Determining Lanthanum

Selection of a method for determining lanthanum, to be used in conjunction with plutonium-lanthanum separations, was made after testing these three methods: (a) a gravimetric determination in which lanthanum 8-quinolinate is precipitated, dried at 130° C, and weighed,(8) (b) a volumetric method including precipitation of lanthanum oxalate and oxidation of the dissolved oxalate with standard ceric sulfate, and (c) a colorimetric method which includes precipitation of lanthanum phosphate and an indirect determination of lanthanum with the molybdenum blue procedure for phosphate.(1) The 8-quinolinol gravimetric method was very satisfactory for milligram quantities of lanthanum and was used in standardizing lanthanum nitrate solutions, but it was not practical for samples containing less than 1 milligram of lanthanum. Only a few analyses were made with the volumetric method in which lanthanum oxalate is titrated with ceric sulfate; it had no advantage in comparison with the 8-quinolinol procedure. The indirect colorimetric procedure with a photometric measurement of phosphate was sufficiently rapid and very nearly covered the range of lanthanum which was required in this project. It was found desirable to use a modification of the phosphate determination in which a colored phosphovanadomolybdate complex is formed, partially to avoid some interference from silica.(7) However, another indirect colorimetric method was finally selected in place of the phosphate procedure because there was too much variability in lanthanum phosphate composition, especially when the quantity of lanthanum was small. The method actually used in investigating plutonium-lanthanum separations is similar to an indirect magnesium determination described by Deterding and Taylor.(3) Lanthanum is first precipitated with 8-quinolinol. This part of the analysis has the advantage shown by gravimetric procedure; a compound with a definite composition is formed. The determination is concluded by dissolving the 8-quinolinate in dilute hydrochloric acid and making photometric measurements at 365 millimicrons with the 8-quinolinol solution.

Fluoride Separation of Lanthanum and Plutonium

An initial choice of perchloric acid as an oxidizing agent for the formation of hexavalent plutonium, before separating lanthanum as a fluoride, was made because this acid is also necessary for other purposes. Perchloric acid can be used in dissolving plutonium metal samples and it serves satisfactorily in the removal of nitric acid from a plutonium nitrate solution sample. Oxidation with perchloric acid ordinarily does not lead to the formation of other substances which will interfere with the precipitation of lanthanum fluoride in the presence of a soluble plutonyl compound. The only interference

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noted was the partial precipitation of silver, due to chloride from reduction of perchloric acid, when at times this metal ion was added with ammonium persulfate as another oxidizing agent. The only reagents which were used extensively for the formation of plutonyl ion were perchloric acid and ammonium persulfate. A few tests were made with dichromate ion as a holding agent which would prevent any reducing agent in hydrofluoric acid from forming plutonium(IV) during the precipitation of lanthanum. Dichromate added for this purpose did not noticeably change the degree of separation for plutonium-lanthanum mixtures and its use was not continued.

Conditions normally used for precipitation of lanthanum fluoride included maintaining the solution at least 1 N with respect to both hydrofluoric acid and a strong acid like perchloric. Even with as little as 25 micrograms of lanthanum, there was no difficulty in obtaining quantitative separations by centrifuging the insoluble fluoride from 3 or 4 milliliters of solution unless some extraneous material such as paper fibers was inadvertently added to the precipitating solution. Except in this case, lanthanum fluoride collected by centrifuging will adhere strongly to the bottom of a test tube. The tube can be inverted to allow the last trace of solution to drain away from the precipitate and be collected by suction without danger of disturbing the precipitate. This manner of separating precipitate and solution is essential for complete removal of plutonium from lanthanum in two successive precipitations.

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The success of a particular series of operations, including one or more fluoride precipitations, in separating plutonium was usually determined by dissolving the final fluoride precipitate in perchloric acid, diluting the solution to 10 milliliters, and determining the plutonium content of this solution by radioanalysis. Frequently, it was necessary for this analysis to include separate determinations of plutonium and americium. Although only a few micrograms of Am^{241} may be found in a 50-milligram sample of plutonium, this element is more difficult to oxidize to the hexavalent state than plutonium. Therefore, microgram amounts of alpha-emitting americium may remain unseparated from lanthanum. The disintegration rate of Am^{241} is about 50 times greater than the rate for Pu^{239}. A radioanalysis which measures only total alpha emission from a lanthanum sample will be misinterpreted if the alpha particles are assumed to originate only from plutonium. It is possible to make a correction for unseparated radioactive material in a lanthanum 8-quinolinate determination by means of radioanalysis; however, this is true only if the radioanalysis is for plutonium and americium.

During the investigation of fluoride separations it became apparent that a combination of one oxidation step and one precipitation would not result in the necessary degree of decontamination for lanthanum. Two successive oxidation-precipitation steps were necessary. Initially this repetition of separation steps resulted in lanthanum samples con-

[redacted]

taining no more than 1 or 2 micrograms of plutonium and americium. At times it was as little as 0.1 microgram of plutonium and 0.15 microgram of americium. In each case the original plutonium-lanthanum sample included 50 milligrams of plutonium. After repeated analyses with the same equipment there was a gradual decrease in the degree of separation until the final lanthanum solutions were contaminated with as much as 8 micrograms of plutonium and americium, although no change in procedure had been made. It was concluded that at least some of this increase was due to accidental contamination of the final solution by either the reagents or the equipment used. This possibility was removed and separations were again more successful when the first part of the recommended procedure (steps 1 to 17) was performed in a separate drybox and the last part (steps 18 to 41) was performed after the quartz tubes and sample solutions were transferred to a second drybox, with reagents and equipment reserved only for low-level radioactive samples.

Some of the first fluoride separations, made only with Pyrex equipment, were investigated not only by radioanalysis but also by lanthanum 8-quinolinate colorimetric measurements. The former analyses showed no unusual contamination, but the colorimetric results were about 10 percent too high. This consistent positive error was eliminated by changing from Pyrex to quartz test tubes after it was found that handling fluoride solutions in Pyrex containers introduced material which was precipitated by 8-quinolinol and produced a positive error.

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Plutonium Nitrate Solution Samples

Fluoride separation experiments were usually begun with 50-milligram metal samples. After dissolving the plutonium in acid, lanthanum was added as an aliquot of a standard lanthanum nitrate solution. When the starting material was a concentrated plutonium nitrate solution containing nitric acid (Hanford nitrate solution), it was necessary to modify the procedure to avoid certain difficulties. If the nitrate solution volume was much more than 0.1 milliliter, it was impossible to add the required volume of perchloric acid (0.4 milliliter) and then place the quartz tube directly into an aluminum heating block at 225° C. This was normally done with metal samples, but with nitrate samples a portion of the solution sample was lost from the quartz tube by violent bumping of the solution before it was concentrated and produced perchloric acid fumes. To avoid this loss, the solution sample and added perchloric acid was evaporated more slowly under an infrared lamp before transfer to the heating block. When these nitrate solution samples contained both nitric and sulfuric acid, the evaporation and fuming at 225° C did not convert all of the 50-milligram plutonium sample to the hexavalent state, even though additional perchloric acid was used and heating at 225° C was continued for 12 to 18 hours. During the first phase of evaporation, removal of water causes the formation of plutonium(IV) sulfate crystals, on account of the low solubility of this substance in concentrated perchloric acid. When

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the acid becomes more concentrated and the solution temperature is high enough to result in a slight evolution of fumes from the tube, there is a rapid oxidation of plutonium(IV) which is revealed by a sudden, momentarily vigorous evolution of perchloric acid fumes. Examination of the solution immediately after this vigorous evolution of fumes will show a green plutonyl solution instead of the brown plutonium(IV) solution. However, the solid plutonium(IV) sulfate crystals are almost completely unaffected under these conditions and are dissolved and oxidized very slowly. It was more practical to dissolve this solid plutonium(IV) material in water and oxidize the soluble plutonium compound with ammonium persulfate instead of using prolonged heating with perchloric acid.

Reliability of Lanthanum Determinations

Estimates of the reliability of lanthanum determinations were made both for pure lanthanum solutions and for lanthanum-plutonium mixtures which were first subjected to a fluoride separation. In this manner the effect of a fluoride separation on subsequent lanthanum determinations was observed. No plutonium-lanthanum alloys of known composition were available for making reliability estimates.

In the case of solution samples containing only lanthanum nitrate, the analytical procedure which was followed was essentially the same as

[redacted]

steps 31 to 41 in the Recommended Procedure. These determinations began with weight aliquots of a standard lanthanum nitrate solution which were transferred to quartz tubes, treated with a few drops of perchloric acid, and diluted to about 2 milliliters with distilled water before beginning with step 31. Plutonium-lanthanum samples were prepared by dissolving 50-milligram pieces of pure plutonium metal in perchloric acid and adding weight aliquots of a standard lanthanum solution. Analysis followed according to the Recommended Procedure. All of the data obtained in this manner are shown in Table I.

The lanthanum nitrate solution used in preparing both types of samples was standardized gravimetrically with 8-quinolinol as the precipitant. It contained 1.039 milligrams of lanthanum per gram of solution, with a standard deviation of 0.23 percent for five determinations. Since the weight aliquots of this standard solution were weighed by difference to 0.1 milligram, errors in weight of lanthanum added to individual samples were less than 0.5 microgram.

In making a statistical analysis of the data in Table I, it was found that the best straight lines for the experimental data, calculated by the method of least squares, have intercepts of -0.001 and -0.003 absorbance units for lanthanum samples and lanthanum-plutonium samples respectively. A "t" test with the intercept and the standard deviation of the intercept confirmed the conclusion that these values do not differ from zero more than can be accounted for by the analytical

[redacted]

[redacted]

Table I

RELIABILITY DATA FOR LANTHANUM DETERMINATIONS

Lanthanum Samples		Plutonium-Lanthanum Samples	
Lanthanum, µg.	Corrected absorbance	Lanthanum, µg.	Corrected absorbance
38	0.140	39	0.140
49	0.180	49	0.195
49	0.181	71	0.267
50	0.205	91	0.329
64	0.240	101	0.405
90	0.334	117	0.428
99	0.374	120	0.453
109	0.395	128	0.468
119	0.445	130	0.505
123	0.446	149	0.579
136	0.510	151	0.572
154	0.578	157	0.610
172	0.650	187	0.698
174	0.641	209	0.794
180	0.677	221	0.845
191	0.737		
208	0.769		

errors. Therefore, all further calculations were made for straight lines passing through the origin. These calculations are summarized in Table II. They indicate that the presence of plutonium in lanthanum samples and the fluoride separation which is used to remove plutonium do not materially affect the lanthanum determinations which are made after such a separation. There is only a negligible change in the absorbance units per microgram of lanthanum when plutonium is also present in the initial sample. To confirm this conclusion the slopes of the two

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Table II

STATISTICAL DATA FOR LANTHANUM DETERMINATIONS

Sample Contains:	La	La and Pu
No. of determinations	17	15
Standard deviation of single measurement of absorbance	0.010	0.012
Slope, absorbance/μg. La	0.00374	0.00380
Standard deviation of slope	0.000019	0.000023

lines were compared. The variance for the difference between slopes (from the pooled variance which was calculated from the estimate of the variance available from each line) was used to determine a value for t; it was equal to 1.95. Since the critical value for t is 2.75, at 1 percent level and 30 degrees of freedom, no difference in the slopes is demonstrated.

Calibration Curve

The data in Table I for lanthanum-plutonium samples and the corresponding slope, shown in Table II to be equal to 0.00380, are typical of the results obtained in preparing a calibration curve. A curve based on these data is shown in Figure 1. The deviations of the individual points in this figure from the line drawn with a slope of 0.00380 were calculated. The average value for these deviations, in micrograms, is 3.2 and the maximum deviation is 6 micrograms.

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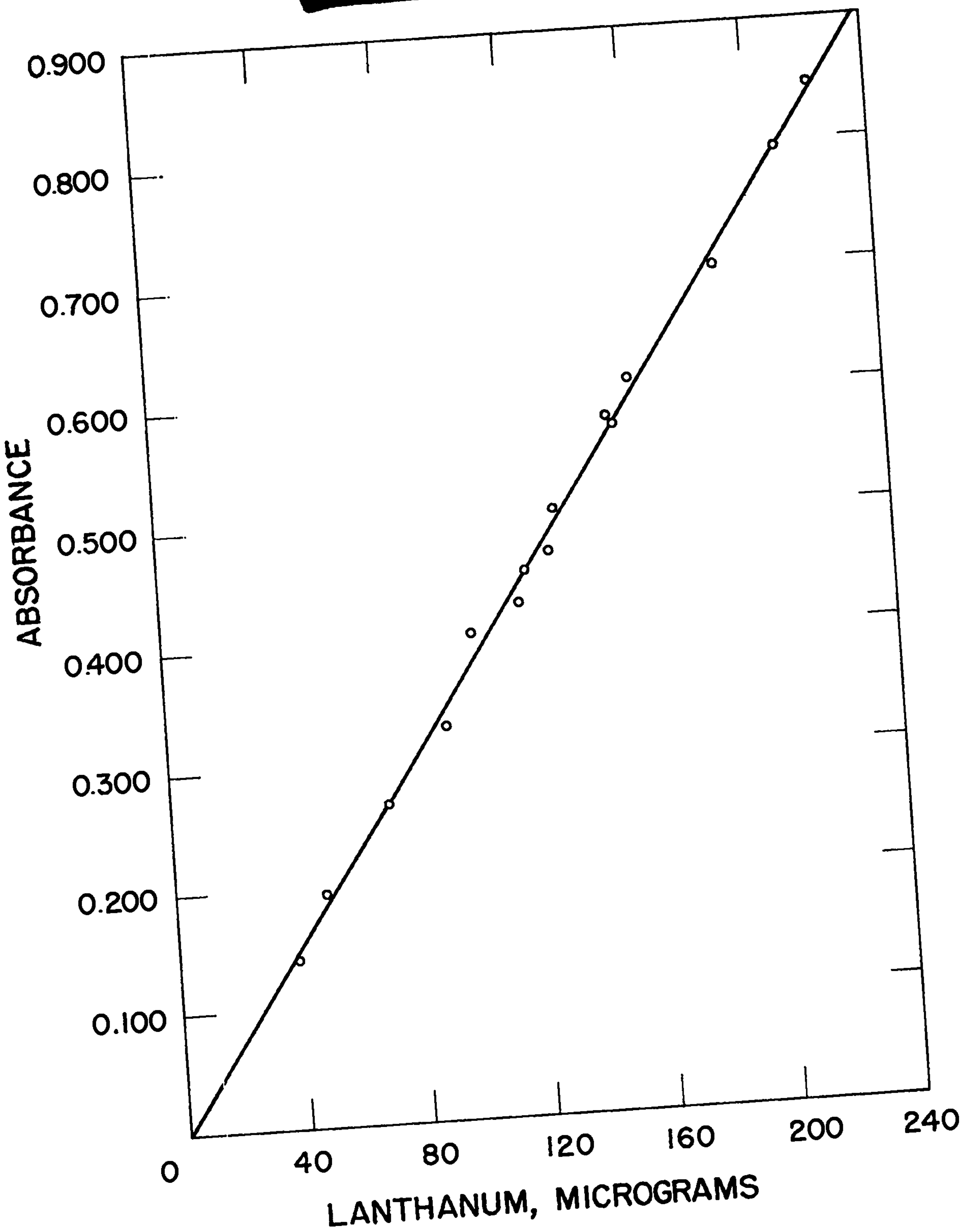

Figure 1. Calibration curve for plutonium-lanthanum data.

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The range of lanthanum for which the calibration curve applies is approximately 40 to 200 micrograms, with a standard deviation for a single measurement equal to 3 micrograms. The range can be extended to 25 micrograms of lanthanum, but greater attention must be given to certain sections of the procedure such as precipitation and handling of lanthanum 8-quinolinate. There is a tendency for this substance to appear as a colloidal dispersion in a precipitation volume of 3 or 4 milliliters. Excess ammonium hydroxide should be avoided in step 32 when first precipitating the 8-quinolinate, and more than 1 hour may be required for complete precipitation in step 34. Samples containing less than 25 micrograms might be precipitated from volumes considerably smaller than 4 milliliters. The final photometric measurement could then be made more sensitive by making observations at 252 instead of 365 millimicrons.(12)

Lanthanum samples in the range of 200 to 1000 micrograms can be handled readily by diluting the dissolved lanthanum 8-quinolinate to volumes larger than 10 milliliters before making photometric measurements. For example, seven determinations were made with 1-milligram lanthanum samples and the 8-quinolinate was dissolved and diluted to 100 milliliters. The standard deviation for these determinations was 2.3 percent.

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Interferences

During the determination of lanthanum in plutonium-containing samples with the recommended procedure, removal of interfering elements must be achieved either by the fluoride precipitation or by some added analytical operation, since precipitation by 8-quinolinol in an alkaline solution is not specific for lanthanum. This organic reagent actually precipitates most metals. The formation of insoluble lanthanum fluoride will not separate other rare earths, cerium(IV), uranium(IV) americium(III) or (IV), thorium, or the alkaline earths.

An extensive study of interfering elements was not made because the recommended procedure was designed for samples of relatively pure plutonium metal or plutonium nitrate solution. Only thorium and americium interference was investigated. Incidental observations revealed that gallium which might be present in some plutonium samples had no effect on lanthanum determinations. Also, when silver was added as a catalyst for persulfate oxidations, it was essential that this metal as an insoluble chloride did not accompany the insoluble lanthanum fluoride; otherwise, silver would interfere in the determinations with 8-quinolinol.

An attempt was made to separate thorium from lanthanum, after first removing plutonium with the usual fluoride precipitation, by precipitating thorium as an iodate with zirconium added as a carrier. The difficulty which finally lead to a rejection of this procedure was a consistent

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loss of lanthanum. In preliminary experiments this loss was at first concealed by some zirconium remaining with the lanthanum. When removal of zirconium and thorium iodate was made complete, the recovery of lanthanum varied between 50 and 80 percent. A more promising method was found in a brief investigation of thorium-lanthanum separation by extraction with cupferron and ethyl acetate from a 1:9 hydrochloric acid solution.(5) Thorium is soluble in the organic phase. Work with plutonium solutions was not attempted.

A separation of thorium from cerite earths with 8-quinolinol has been reported recently.(4) Careful control of the pH for a thorium-lanthanum separation is required. When this method was tried with the quantities of material which are of interest to this project (20 micrograms of thorium and 100 micrograms of lanthanum), a satisfactory separation did not appear to be feasible.

It was concluded that with small amounts of interfering thorium in a plutonium-lanthanum sample, probably the best procedure is to determine thorium in a separate sample or aliquot and correct the lanthanum results for this interference. In this connection it was found experimentally that 1 microgram of thorium is almost exactly equivalent to 1 microgram of lanthanum (factor is 0.997). Lanthanum does not interfere with the determination of thorium in plutonium.(2)

Complete separation of americium was sought, not only to avoid inter-

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ference by this element, but also to assist in discovering optimum conditions for oxidizing plutonium. Both of these radioactive elements can be oxidized to hexavalent compounds where they are not precipitated by hydrofluoric acid, but americium is less readily converted in this manner. It was convenient to make some tests with microgram amounts of americium taken from a relatively pure americium nitrate solution. Use of the complete lanthanum procedure was avoided and results could be observed more quickly by measuring alpha activity (in this case due only to americium) after a fluoride precipitation. All but 10 percent of a 0.7-microgram americium sample could be oxidized and thereby separated from lanthanum in repeated experiments. There were, however, some cases where the unoxidized americium accompanying the lanthanum would be 20 to 60 percent of the amount added, although no changes in oxidizing conditions were made. No explanation for these variations was found. These results emphasize the need for determining the americium and plutonium in the final solution of lanthanum 8-quinolinate by radioanalysis if very careful lanthanum determinations are to be made. In many cases, however, the presence of 2 or 3 micrograms of unseparated plutonium and americium will not be significant in lanthanum analyses.

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CONCLUSIONS

Colorimetric determinations of lanthanum in plutonium-containing samples are possible if the two elements are brought into solution and separated by oxidizing plutonium to Pu(VI) and precipitating lanthanum as a fluoride. This separated lanthanum is redissolved and precipitated with 8-quinolinol; an acid solution of the lanthanum 8-quinolinate is used for photometric measurements at 365 millimicrons. The initial sample, either as an alloy or an aqueous solution, may contain from 0.05 to 2.0 percent lanthanum with respect to plutonium. For samples containing 50 milligrams of plutonium and 40 to 200 micrograms of lanthanum the standard deviation for a single measurement is 3 micrograms. Microgram quantities of thorium and, to some extent, americium will interfere in the lanthanum determinations.

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