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LOS ALAMOS SCIENTIFIC LABORATORY

of

THE UNIVERSITY OF CALIFORNIA

LA-1082

March 16, 1950

This document consists of 31 pages

[redacted]ries A

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LANL Classification Group
11/8/95

COMPARISON OF DIRECT EVAPORATION AND LANTHANUM FLUORIDE METHODS FOR PLUTONIUM RADIOCHEMICAL ANALYSIS

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ABSTRACT

A comparison of two methods for the radiochemical analysis of plutonium was made with analytical samples that were either simulated or actual plant control solutions. Of the two methods employed, the direct evaporation procedure involved little or no separation of plutonium from other sample components, while the lanthanum fluoride procedure usually separated the plutonium from all other substances in the original sample. The direct evaporation procedure was satisfactory when no more than 300 micrograms of salt or other non-volatile substances was contained in the sample that was transferred to the counting plate. The lanthanum fluoride procedure was satisfactory for samples in which the 300-microgram limit was exceeded, or for all analyses of ethylene glycol-phosphoric acid mixtures. However, the concentration of potassium in the sample should not exceed 0.05 M just before precipitation of the LaF_3.

A determination of the errors due to salt absorption of alpha particles in the radiochemical analysis by the direct evaporation procedure was made for a series of sixteen salts at varying concentrations. The absorption errors generally were less than those predicted by the equation that has been proposed by Bradford, Roberts, and Wahl. For the salts that were studied, it was not possible to predict absorption errors on the basis of weight of salt in the analysis sample.

COMPARISON OF DIRECT EVAPORATION AND LANTHANUM FLUORIDE METHODS FOR PLUTONIUM RADIOCHEMICAL ANALYSIS

INTRODUCTION

Radiochemical analyses of plutonium solutions, especially for plant control and development purposes, have, in the past, been made by means of a relatively simple method which can be designated as the "Direct Evaporation Procedure". The development of this method of analysis (begun in November, 1946 and carried through August, 1947), a description of the equipment used, and some indication of its accuracy have been reported.(1) Briefly, the procedure involves the transfer of a properly diluted aliquot of the plutonium solution to a glass plate and evaporation of the solution to dryness on an electric hot plate at 60 - 80°C, followed by counting in the chamber of a linear amplifier. No separation of plutonium from other components of the sample is made, other than what is involved in the evaporation to dryness on the glass plate. At times the probable errors are quite high, especially when a low counting rate is obtained after diluting the sample sufficiently to avoid excessive quantities of salts on the counting plate.

It seemed desirable to re-study this method of radiochemical analysis in comparison with the "Standard Lanthanum Fluoride Procedure"(2,3,4) in which a chemical separation of plutonium from other sample constituents is made prior to counting. The specific problem considered in this investigation is the analysis of several plant control solutions by the two methods. As the investigation progressed, it was apparent that the errors due to absorption of alpha particles by some inorganic salts, in the direct evaporation procedure, were not so great as those predicted by the equation that had been proposed by Bradford, Roberts, and Wahl.(1) Consequently, the study of absorption errors for the direct evaporation method was continued by determining the errors caused by varying concentrations of sixteen separate inorganic salts.

RADIOCHEMICAL ANALYSIS BY THE DIRECT EVAPORATION METHOD

In making this comparative study of the direct evaporation and lanthanum fluoride methods, all the analyses by the first method have been made by the technicians of the Radiochemical Laboratory. They followed their normal analysis procedure which is briefly described here.

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Experimental Procedure for Direct Evaporation Method

In the direct evaporation procedure, an aliquot of the sample, about 30 microliters in volume, is transferred either directly to a one-inch-square microscope cover glass, No. 2 thickness, or to a flask for dilution. This dilution is made in various volumetric flasks from 1 to 100 ml in volume, depending upon the estimated plutonium content of the sample. If dilution is necessary, another pipet of about 30 microliters is used to transfer an aliquot of the diluted sample to a glass plate. For all volume measurements and transfer of solutions, semimicro pipets of about 30 microliters are used. These pipets, calibrated with mercury to contain, are so designed that they can be readily rinsed by addition of a suitable liquid at the end of the pipet opposite to that used for drawing in the sample. The rinsings, normally made with 3 - 5 drops of 5 N HNO_3, are forced through the pipet and are, of course, added to the original measured volume.

After transfer of the measured aliquot and rinsings to the glass plate, the solution is allowed to slowly evaporate to dryness at 60 - 80° C on a small electric hot plate. Under these conditions, some salts remaining on the plate will exist as hydrates; acids, such as sulfuric or phosphoric, and ammonium salts will not be removed. The glass plate is placed in a small cardboard sample box until counted. Care must be exercised in handling the prepared sample to prevent mechanical loss. Each sample is counted twice, or as many times as is necessary to obtain two results that agree within certain stated limits. These maximum allowable counting variations are listed in Table I. When samples show 800 counts per minute or less, the counting time is eight minutes; above this figure, the counting time is four minutes.

In reporting the results for a given sample, the average count per minute for the two counts is corrected for coincidence and for background. The background is determined and the counting equipment is checked with a standard sample, once for every two samples. Normally, all routine solutions submitted for determination of plutonium are analyzed in duplicate and are reported on the basis of these two results. If the duplicate analyses differ widely, the plutonium content of the solution is redetermined.

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Table I

MAXIMUM ALLOWABLE COUNTING VARIATIONS

Counts/Minute for Sample	Maximum Difference	Counts/Minute for Sample	Maximum Difference
Under 25	3	800 - 900	16
25 - 50	5	900 - 1100	17
50 - 100	6	1100 - 1300	18
100 - 200	8	1300 - 1400	19
200 - 300	9	1400 - 1600	20
300 - 400	10	1600 - 1800	21
400 - 500	11	1800 - 2000	22
500 - 600	12	2000 - 2100	23
600 - 700	14	2100 - 2300	24
700 - 800	15	2300 - 2500	25

RADIOCHEMICAL ANALYSIS BY THE LANTHANUM FLUORIDE METHOD

For most of the analyses made by the lanthanum fluoride method, the recommended procedure for total plutonium(5) was used with only slight modifications. The procedure usually followed in this investigation is described below. Whenever a change in it was made, a statement of the modification is given along with the analytical data.

Experimental Procedure for Lanthanum Fluoride Method

(1) Add aliquot to be analyzed to a 3-ml Pyrex centrifuge cone. Rinse the pipet in which the aliquot is measured three times with 1 N HNO_3, delivering the rinses into the centrifuge cone. The total volume of aliquot and rinses should not exceed 0.6 ml.

(2) Add 0.1 ml (2 drops) of lanthanum nitrate solution, containing 250 mg of La(III) per 100 ml of solution.

(3) Add 0.2 ml (4 - 5 drops) of 10 N HCl and 0.1 ml (2 drops) of 2.5 M $NH_2OH \cdot HCl$. Dilute to 1 ml with water, mix thoroughly with a platinum wire, and allow to stand at room temperature for ten minutes.

(4) Add 0.1 ml (2 drops) of 20 N HF dropwise, and again

[redacted]

mix thoroughly with the platinum wire.

(5) Allow the solution and precipitate to stand at room temperature for five minutes.

(6) Centrifuge the cone and contents for five minutes at the top speed of a clinical centrifuge.

(7) Remove and discard the supernatant, using a transfer pipet with a capillary tip which enables the removal of almost all the liquid.

(8) Wash the precipitate by agitation with 1 ml of 1 N HCl-1 N HF solution. Centrifuge for five minutes, remove and discard the wash liquid.

(9) Repeat the washing of the precipitate with 1 ml of 1 N HNO_3-1 N HF solution.

(10) Add 0.05 ml (1 drop) of 1 N HNO_3, agitate with a platinum wire, and transfer the resulting slurry with a capillary-tipped pipet to the center of a platinum plate.

(11) Rinse the centrifuge cone twice with 0.05 ml (1 drop) of 1 N HNO_3, stirring the rinse solution thoroughly with the same platinum wire, and transfer it to the platinum plate with the same capillary-tipped pipet.

(12) In the same manner, use a third rinse of 0.1 ml (2 drops) of 1 N HNO_3, but centrifuge the cone for just a moment before withdrawing the rinse to the platinum plate to bring down any drops adhering to the sides of the cone.

(13) All 1 N HNO_3 transfer liquid and rinses should be delivered to the central portion of the platinum plate without stirring the slurry on the plate. This procedure results in a uniform distribution of the lanthanum fluoride over approximately the same area for each sample.

(14) Evaporate the liquid at a moderate rate under an infrared lamp placed about 12 cm above the platinum plate.

(15) Flame the platinum plate in the flame of a Fisher burner, to just red heat.

(16) After cooling, place the plate in a cardboard sample box until counted.

The platinum plates, one-inch square and 0.005 inch in thickness, are counted in a manner identical with that used for the glass plates. After a platinum plate has been used, it is cleaned and decontaminated by placing in boiling concentrated sulfuric acid for several hours. For this purpose, a 25-mm-diameter Pyrex tube, 15 cm in length, is cut with about 30 slots at a slight angle to a plane that is perpendicular to the

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axis of the tube. In this manner, the platinum plates can be held in the tube slots with the tube standing on end. A glass hook on the top of the tube permits lowering the tube and plates into a 5 x 38 cm Pyrex tube containing the sulfuric acid. After cooling and rinsing with distilled water, the plates are given a second cleaning in sulfuric acid. Then, after rinsing and drying, the plates are checked for contamination. Plates showing five counts per minute or more are not used for analysis. They are recleaned and rechecked.

For purposes of comparing the two radiochemical methods in analyzing various plant-control solutions, it was not considered necessary to make corrections for the self-absorption of the lanthanum fluoride. From the work of Clifford and Koshland,(2) this absorption error was judged to be 1 - 2 % with a maximum of 0.25 mg of La(III) spread over 2 cm^2 of the platinum plate. Several experimental determinations of the absorption error indicated a value of about 1 %. Also, the specific activity of plutonium was considered to be the same on glass and platinum plates.

COMPARISON OF DIRECT EVAPORATION AND LANTHANUM FLUORIDE METHODS

A. Preparation of Synthetic Plant Control Solutions

In making a comparison of the two methods of radiochemical analysis for plutonium, two synthetic plant-control solutions were prepared; this readily permits the addition of known quantities of plutonium as well as variation of the concentration of any solution component.

1. Magnesium nitrate solution: 40.0 g of $Mg(NO_3)_2$ and 5.0 g of $Ca(NO_3)_2$ per 100 ml of solution which is 2N with respect to HNO_3. Reagent-grade chemicals were used.
2. Iodide solution: The following quantities of reagent grade chemicals were added to 100 ml of water in the order listed and, after dissolving, the resulting solution was diluted to exactly 200 ml. The concentrations of the various components in the 200 ml of solution are also given:

Components	Concentrations
3.6 ml conc. nitric acid (Sp. gr., 1.42)	0.29 N HNO_3
1.1 ml 5 N sulfuric acid	0.028 N H_2SO_4
2.54 g oxalic acid	0.20 N $H_2C_2O_4$
8.28 ml conc. hydriodic acid (Sp. gr., 1.5)	0.23 N HI
1.52 g iodine	0.03 M I_2

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B. Analysis of Synthetic Plant-Control Solutions

As a first approach to the problem of radiochemical analysis for plutonium in these synthetic solutions, the accuracy of the direct evaporation procedure was determined by using aliquots of the magnesium nitrate solution without previous dilution. Then, by successively greater dilutions of the magnesium nitrate solution, it was determined at what concentration the direct evaporation procedure would give quantitative results, i.e., within 95% of the actual plutonium content. For these purposes, 2-ml portions of the magnesium nitrate solution, and of other solutions prepared by diluting the magnesium nitrate stock solution with water by known ratios, were placed in small flasks. To these 2-ml samples, known quantities of a plutonium chloride solution were added. Previous analyses had shown that this plutonium solution, with dilute hydrochloric acid as solvent, was equivalent to 102,900 counts per minute for a 30-microliter aliquot. However, a knowledge of the exact plutonium content of these various 2-ml samples was obtained by including in the analysis series a 2-ml sample of 1N HNO_3 to which no magnesium nitrate was added. Although the volumes of plutonium solution added varied slightly from 30 microliters for each different sample, the analysis data have been recalculated on the basis of adding exactly 30 microliters of the active solution, to facilitate comparison of the results.

These flasks containing 2 ml of solution were given to the Radiochemical Laboratory. Each solution was analyzed twenty times by the direct evaporation procedure. The aliquots varied from 29.59 to 31.12 microliters, but the resulting counts per minute were recalculated on the basis of using exactly 30 microliters for each analysis. At the same time, 10 aliquots of the stock magnesium nitrate solution, to which no plutonium was added, were analyzed to determine possible contamination of pipets, reagents, etc. The results showed little or no such contamination. The data for this series of analyses are given in Table II. In this table, the percent recovery has been calculated by taking the average count per minute for solution No. 1 as being the correct plutonium concentration for all solutions.

This same magnesium nitrate stock solution was used for analysis by the lanthanum fluoride procedure, with samples prepared in a slightly different manner. Only the most concentrated magnesium nitrate solution was analyzed, and the quantity taken for a sample was over three times as much as was placed on a glass plate in the direct evaporation analyses. However, the plutonium content of the sample remained about the same as in individual samples taken for direct evaporation analysis.

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Table II

RADIOCHEMICAL ANALYSIS OF MAGNESIUM-CALCIUM NITRATE SOLUTIONS

(Direct Evaporation Procedure)

Solution Number	1	2	3	4	5	6	7*
Technician	A	A	B	B	B	B	A
Salt Concentration							
$Mg(NO_3)_2$ mg/ml	0	400	200	100	40	10	400
$Ca(NO_3)_2$ mg/ml	0	50	25	12.5	5	1.3	50
No. of determinations	20	20	20	20	20	20	10
Average c/min.	1533	156	591	863	1087	1468	5
Lowest c/min.	1493	72	462	566	763	1403	2
Highest c/min.	1573	255	744	1095	1344	1528	10
Average Deviation (percent)	1.2	23	12	15	12	1.8	---
Percent Recovery	---	10.1	38.4	56.1	70.7	95.4	---

*Approximately 30-microliter aliquots of the stock magnesium nitrate solution, with no plutonium solution added, were analyzed to determine any possible contamination of equipment

A 100-microliter portion of the magnesium nitrate stock solution was placed in a 3-ml Pyrex centrifuge cone. To this was added 31.09 microliters of a plutonium solution. Six identical samples were prepared in this manner, along with two control samples (Nos. 7 and 8), each containing 100 microliters of 1N HNO_3 and 31.09 microliters of the same plutonium solution. Some variations in the lanthanum fluoride procedure were made with these samples, as noted along with the data in Table III.

The only appreciable change was made for samples Nos. 5 and 6. Here, after only one wash with 1N HNO_3 - 1N HF solution, the lanthanum fluoride precipitate was dissolved in 0.5 ml of zirconium nitrate solution (approximately 0.25 mg of Zr per ml in 1N HNO_3) and 0.5 ml of 1N HNO_3. Then, after adding 0.15 ml (3 drops) of 20N HF, the resulting precipitate was centrifuged and washed twice with 1N HNO_3 - 1N HF solution.

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Table III

RADIOCHEMICAL ANALYSIS OF MAGNESIUM-CALCIUM NITRATE SOLUTION

(Lanthanum Fluoride Procedure)

Solution No.	LaF_3 Procedure Modification	Analysis Result (counts/minute)	Percent Recovery
1	1	1029	98.6
2	1	965	92.4
3	2	1034	99.0
4	2	1030	98.7
5	3	1013	97.0
6	3	1016	97.3
7	1	1036	---
8	1	1051	---

Percent recovery is calculated by taking the average result for solutions Nos. 7 and 8, 1044 counts per minute, as the correct measurement of the plutonium added to each of the eight samples

Lanthanum fluoride procedure modifications:

(1) Replace 1N HCl-1N HF wash with 1N HNO_3-1N HF wash

(2) Replace 1N HCl-1N HF wash with three 1N HNO_3-1N HF washes

(3) Dissolve LaF_3 in zirconium nitrate solution as described in text

A similar comparison of the two methods under consideration was made with the iodide solution. Again, 2-ml portions of the iodide solution, and of other solutions resulting when aliquots of the iodide were diluted with measured amounts of water, were treated with plutonium dissolved in dilute hydrochloric acid. After thorough mixing, these samples were analyzed, the data from this series of determinations being given in Table IV.

In the case of the iodide solutions, the lanthanum fluoride procedure was followed without modifications. Six equal aliquots of a plutonium chloride solution were taken, four being transferred to 3-ml

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Table IV

RADIOCHEMICAL ANALYSIS OF IODIDE SOLUTION

(Direct Evaporation Procedure)

Solution Number	1	2	3	4
Technician	A	B	A	B
Dilution of Iodide (vol. of iodide/vol. of water)	0:1	1:0	1:9	1:39
No. of determinations	20	20	20	20
Average c/min.	1538	1479	1567	1531
Lowest c/min.	1493	1286	1369	1306
Highest c/min.	1573	1569	1647	1666
Average Deviation (percent)	1.2	4.7	2.4	4.0
Percent Recovery*	---	96.2	101.9	99.5

*Percent recovery is calculated by taking the average count per minute for solution No. 1, to which no iodide solution had been added, as the correct measurement of the plutonium added to each solution

Pyrex centrifuge cones and two being transferred directly to platinum plates. In two of the centrifuge cones, 100-microliter portions of the undiluted iodide solution were added. The results from the counting of the platinum plates on which the plutonium solution was placed directly are taken as the actual plutonium content of the aliquots used in each of the six samples. The data for these lanthanum fluoride analyses are shown in Table V.

C. Analysis of Actual Plant Control Solution

A sample of a plant control solution (2BM31), similar to the synthetic iodide solution, was obtained for further study. Preliminary measurements showed that the plutonium concentration was too high to use aliquots directly for analysis without dilution. Therefore, in the following work this solution was first diluted by transferring a 30-microliter aliquot to a 1-ml volumetric flask, diluting to volume, and using 30-microliter portions of this diluted solution for analysis. Three different series of determinations were made with this solution by two

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Table V

RADIOCHEMICAL ANALYSIS OF IODIDE SOLUTION

(Lanthanum Fluoride Procedure)

Solution No.	Description of Solution	Analysis Result (counts/minute)	Percent* Recovery
1	100 microliters of iodide and Pu	2726	96.3
2	100 microliters of iodide and Pu	2770	97.8
3	Pu solution	2808	99.2
4	Pu solution	2702	95.4
5	Pu solution - direct transfer to Pt plate	2854	---
6	Pu solution - direct transfer to Pt plate	2819	---
7	100 microliters of iodide	8	---
8	100 microliters of iodide	9	---

*Percent recovery is calculated by taking the average count per minute for solutions Nos. 5 and 6, 2836 c/min., as the correct measurement of the plutonium added to each of solutions Nos. 1 to 6

Radiochemical Laboratory technicians using the direct evaporation procedure. In all cases, only four aliquots were withdrawn from the 1-ml volumetric flask in which dilution of the original sample had been made. Then the remaining diluted solution was discarded and another 1-ml diluted sample was prepared from the original solution for further analyses. The data are given in Table VI.

The lanthanum fluoride procedure was used for several samples of this plant-control solution, with the results shown in Table VII.

In order to simulate the analysis of other plant-control solutions, this same iodide solution (2BM31) was neutralized with potassium hydroxide. When 1-ml portions of the iodide solution had been pipetted into 5-ml centrifuge cones, 10 N KOH was added until the solution was just alkaline to phenolphthalein. After centrifuging, the supernatant

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Table VI

RADIOCHEMICAL ANALYSIS OF PLANT-CONTROL SOLUTION (2BM31)*

(Direct Evaporation Procedure)

Technician	A	B	A
Aliquot added to 1-ml flask, microliters	28.79	28.79	30.97
Aliquot of diluted solution, microliters	27.97	29.59	30.92
Number of determinations	16	20	16
Average c/min.	647	638	734
Lowest c/min.	605	570	714
Highest c/min.	680	773	761
Average Deviation (percent)	3.4	4.7	1.7
Average c/min./ml of original sample	803,000	749,000	767,000

*Composition of this plant-control solution is similar to iodide solution described on page 8

Table VII

RADIOCHEMICAL ANALYSIS OF PLANT-CONTROL SOLUTION (2BM31)

(Lanthanum Fluoride Procedure)

Count/minute, Sample No. 1	654
Count/minute, Sample No. 2	663
Count/minute, Sample No. 3	645
Average c/min.	654
Average deviation (percent)	0.9
Avg. c/min./ml of original sample*	767,000

*A 29.20 microliter aliquot of the original sample, similar in composition to iodide solution described on page 8, was diluted to 1 ml, and 29.20 microliter aliquots of the diluted solution were used for analysis

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liquid was separated from the solid residue, transferred to a 25-ml volumetric flask, and diluted to volume. The residues, dissolved in 1 N HNO_3, were transferred to 10-ml volumetric flasks and diluted to volume. These solutions were analyzed in duplicate by both methods, with the average results, calculated in terms of the volume of the original 2BM31 sample, given in Table VIII.

Table VIII

RADIOCHEMICAL ANALYSIS OF PRODUCTS
FROM NEUTRALIZED PLANT SOLUTION (2BM31)

Direct Evaporation Procedure	Residue	Supernatant	Total
Technician A			
Sample No. 1	759,000	9,000	768,000
Sample No. 2	752,000	15,000	767,000
Technician B			
Sample No. 1	730,000	8,000	738,000
Sample No. 2	753,000	8,000	761,000
Lanthanum Fluoride Procedure			
Sample No. 1	752,000	11,000	763,000
Sample No. 2	725,000	17,000	742,000
All data are given in counts per minute per ml of original sample (2BM31), which is similar in composition to iodide solution described on page 8			

The next products to be analyzed by both procedures are obtained by acidifying other preparations of the potassium hydroxide supernatant liquid, obtained in the manner just described, adding aluminum nitrate, and again forming a precipitate and supernatant liquid by potassium hydroxide neutralization. Before proceeding with this series of determinations, it was decided to "spike" the first potassium hydroxide supernatant liquid, when it had been acidified, since it retained only 1.1 to 2.3% of the plutonium in the original iodide solution. This low retention in the supernatant liquid resulted in analysis samples showing only 10 - 20 counts per minute.

Four 1-ml portions of the iodide solution (2BM31) were transferred with a volumetric pipet to 5-ml centrifuge cones. After adding 10 N KOH

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until the solution was just alkaline to phenolphthalein, the solid residues and the supernatant liquids were separated. The four residues were dissolved in acid and analyzed. To each of the four supernatant liquids, after acidification with 10 N HNO_3, equal aliquots of a plutonium solution (equivalent to a count per minute of 104,000) were added. Two of these "spiked" supernatant liquids were diluted in volumetric flasks and analyzed as controls. The other two samples were transferred to centrifuge cones, and 25 microliters of a solution containing 1 mg of aluminum (as aluminum nitrate) was added to each. These two solutions were neutralized with potassium hydroxide to a pH of about 7. The resulting aluminum hydroxide precipitates and solutions were centrifuged and separated for analysis, with the precipitates being dissolved in nitric acid. All solutions were transferred to volumetric flasks that were as small as possible. All samples were analyzed in duplicate and, from the average counts per minute, the data shown in Table IX were calculated.

D. Discussion of Results from Comparative Study

It is very evident from the data shown in Tables II and III that the lanthanum fluoride procedure is superior for the analysis of solutions with high magnesium nitrate concentrations. Where the direct evaporation method gave, on the average, only 10.1% of the actual plutonium content, the lanthanum fluoride procedure, with three times as much $Mg(+Ca)(NO_3)_2$ present, gave recoveries that, in all but one case, were above 97%.

A corresponding difference between methods is not apparent for the iodide solution (Tables IV and V). A closer agreement between methods is to be expected since a 30-microliter aliquot of the undiluted iodide solution leaves only 420 micrograms of material (H_2SO_4 and $H_2C_2O_4 \cdot 2H_2O$) on the glass plate, while an equal volume of the magnesium nitrate stock solution leaves 12 mg of solid. When the amount of $Mg(+Ca)(NO_3)_2$ is reduced to near 420 micrograms, the average results are 95.4% (for solution No. 6, a 30-microliter aliquot contains 340 micrograms of salt).

In the analysis of the plant iodide solution and the various products obtained from it, there is little difference between the results from the two methods (Tables VI to IX). In general, the difference between separate analyses of the same sample by the direct evaporation method, or differences between average results for two technicians, are as large as or larger than differences between the two procedures for determining plutonium. One possible exception is the analysis of the "spiked"

Table IX

RADIOCHEMICAL ANALYSIS OF PRODUCTS FROM PLANT IODIDE SOLUTION (2BM31)

Direct Evaporation Procedure	1 First KOH Residue	2 First Supernatant + Plutonium	3 $Al(OH)_3$ Precipitate	4 $Al(OH)_3$ Supernatant	5 Total 3 + 4
Technician A					
Sample No. 1	732,000	102,000	--	--	--
Sample No. 2	736,000	102,000	--	--	--
Sample No. 3	732,000	---	108,000	5,000	113,000
Sample No. 4	737,000	---	93,000	10,000	103,000
Technician B					
Sample No. 1	728,000	98,000	--	--	--
Sample No. 2	702,000	103,000	--	--	--
Sample No. 3	719,000	---	110,000	4,000	114,000
Sample No. 4	748,000	---	101,000	12,000	113,000
Lanthanum Fluoride Procedure					
Sample No. 1	723,000	116,000	--	--	--
Sample No. 2	709,000	115,000	--	--	--
Sample No. 3	730,000	---	112,000	5,000	117,000
Sample No. 4	740,000	---	102,000	13,000	115,000

All data are given in counts per minute per ml of original sample (2BM31) which is similar in composition to iodide solution described on page 8.

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supernatant solution (column 2 in Table IX). All four direct evaporation results are less than the known amount of added plutonium (104,000 counts per minute). This is also shown by the fact that the totals (column 5), after further treatment of the supernatant liquid, are greater than the amount of plutonium in the supernatants which have not undergone the further treatment (column 2). These discrepancies do not occur in the results from the lanthanum fluoride procedure.

SALT ABSORPTION ERRORS IN DIRECT EVAPORATION PROCEDURE

In the report by Bradford, Roberts, and Wahl(1) on "Radioassay of Plutonium", an equation is given for the absorption of alpha particles by salts in the direct evaporation procedure: $A = 1.5\ \gamma^{1/2}$, where A is the percent absorption and γ is the amount of salts (up to 300 micrograms) on the glass plate. Referring to the data for solution No. 6 (Table II), a 30-microliter sample would place 340 micrograms of salt on the glass plate. Assuming that any deviation from 100% recovery is due only to salt absorption, the average salt absorption error is experimentally 5.6%. The highest absorption error in 20 determinations is 8.2% (lowest counts/minute is 1403). But when the salt absorption error is calculated with the above equation, for 340 micrograms of salt, the estimated figure is 27.6%. This same equation would predict an absorption error of 5.6% from only 14 micrograms of salt instead of the experimental 340 micrograms.

If the results obtained in the direct evaporation analysis of the magnesium-calcium nitrate solutions are typical of many salts, then the proposed equation, $A = 1.5\ \gamma^{1/2}$, is grossly in error. To determine the accuracy with which this equation describes the absorption errors for other salts and to determine any relationship between type of salt and the errors caused in the direct evaporation analysis, a group of sixteen salts was investigated. For each salt, four to six solutions of varying concentration were prepared by adding accurately measured aliquots from a concentrated salt solution of known composition to 5-ml volumetric flasks. These concentrated salt solutions were prepared so that the amount of salt in the 5-ml flasks could be varied, usually from 5 to 200 grams per liter of anhydrous salt. To each 5-ml flask was added an equal volume of a plutonium solution. After dilution to volume with 1 - 5 N HCl or HNO_3 and mixing, each of these 5-ml solutions was analyzed twenty times by the direct evaporation procedure. Equal volumes of the same plutonium solution also were added to 5-ml flasks containing no salt and, after dilution to volume, the amount of

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plutonium actually added was determined by twenty direct evaporation analyses. The aliquots taken from the 5-ml volumetric flasks as samples varied from 24.93 to 32.24 microliters. However, the experimental results have all been multiplied by the proper factor to obtain the counts per minute that would have been obtained from a 30-microliter aliquot, assuming that this volume change would not have altered the percent error. These calculated results, together with the average deviation and the percent recovery, are given in Table X. The percent recovery has been calculated as the ratio of the average of the twenty analyses of the solution containing salt and plutonium to the average of twenty analyses of the solution containing only plutonium. In Figs. 1, 2, 3, and 4, these data for percent recovery and salt concentration are shown graphically, along with the curve for the equation $A = 1.5 \gamma^{1/2}$.

In most of these investigations, the amount of plutonium added to each 5-ml flask has been equivalent to about 1220 counts per minute for a 30-microliter analysis sample. To determine the effect of decreasing the added plutonium to an equivalent of 116 counts per minute per 30 microliters, additional series of 20 analyses were made with some of the salts. The final salt concentration was, in each case, 5 grams per liter. The percent recoveries were slightly lower than the corresponding figures when the plutonium added was equivalent to 1220 c/min. (Table X), but these slight increases in absorption error were not considered significant. It was concluded that the ten-fold decrease in plutonium concentration did not change the percent error due to salt absorption.

The curve for the equation, $A = 1.5 \gamma^{1/2}$, has been added to Figs. 1 through 4 to facilitate comparison with the experimental data. It can be seen that this equation predicts the absorption error most accurately in the case of chlorides and sulfates (Figs. 1 and 3). But even with these types of salts, there are cases where the agreement is not close. At 10 grams per liter, potassium chloride has an average error of 11%, but the calculated value from the equation for this concentration is 26%. At the same concentration, the average error found experimentally for ammonium sulfate is 5% and for potassium sulfate is 14%. For nitrates at 10 grams per liter, the average error is as low as 3% (mercuric nitrate). At best the equation can serve only to calculate the maximum absorption errors.

It is apparent from these data that no prediction of error due to absorption of alpha particles in the direct evaporation analysis procedure can be made simply on the basis of the weight of salt in the analysis sample. In general, nitrates cause the least absorption error.

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Table X

PERCENT RECOVERY IN PLUTONIUM RADIOCHEMICAL ANALYSIS OF UNI-SALT SOLUTIONS AT VARYING CONCENTRATIONS

(Direct Evaporation Procedure)

Salt	Salt Conc. g/liter	Avg. c/min./30λ (20 Analyses)	Lowest c/min./30λ	Highest c/min./30λ	Avg. Dev. (Percent)	Percent Recovery
NaCl	5	1004	847	1114	5.2	83
	10	938	837	1108	4.3	77
	40	795	639	972	8.8	65
	100	783	607	871	6.7	64
	200	599	422	797	11.0	49
KCl	5	1180	1117	1258	1.8	97
	10	1084	909	1160	3.9	89
	40	886	727	1015	7.1	73
	100	754	603	993	8.2	62
	200	648	510	864	12.6	53
$CaCl_2$	5	1148	1063	1236	3.1	94
	10	1111	983	1190	3.0	91
	40	857	673	981	8.1	71
	100	613	406	848	15.2	50
	200	485	359	706	17.7	40
$AlCl_3$	5	1081	962	1197	3.7	89
	10	1065	813	1152	5.7	88
	40	508	220	700	22.6	42
	100	462	319	591	12.8	38
	200	262	170	399	21.4	22

Table X (continued)

Salt	Salt Conc. g/liter	Avg. c/min./30λ (20 Analyses)	Lowest c/min./30λ	Highest c/min./30λ	Avg. Dev. (Percent)	Percent Recovery
Na_2SO_4	5	1068	931	1143	4.0	87
	10	983	743	1122	7.1	80
	40	638	541	819	10.5	52
	100	454	210	820	28.6	37
	200	362	117	516	20.6	30
K_2SO_4	5	1162	1067	1200	2.5	96
	10	1119	1058	1190	3.1	92
	40	793	380	997	15.7	65
	100	461	277	710	25.9	38
	200	270	62	538	40.0	22
$(NH_4)_2SO_4$	10	1160	1067	1412	4.4	95
	40	1025	885	1120	3.9	84
	100	789	477	948	11.7	65
	200	224	106	380	28.6	18
$Al_2(SO_4)_3$	5	986	808	1097	5.6	81
	10	939	893	1031	2.9	77
	40	651	487	778	11.7	54
	100	591	322	756	18.8	49
	200	481	260	689	23.8	40
$Cr_2(SO_4)_3$	5	1063	889	1121	3.9	87
	10	915	712	1117	9.7	75
	40	716	593	979	8.0	59
	100	642	476	675	12.9	53
	200	401	199	603	22.3	33

Table X (continued)

Salt	Salt Conc. g/liter	Avg. c/min./30λ (20 Analyses)	Lowest c/min./30λ	Highest c/min./30λ	Avg. Dev. (Percent)	Percent Recovery
$NaNO_3$	5	1096	1013	1208	3.5	90
	10	1088	977	1162	3.0	89
	40	986	867	1244	5.9	81
	100	809	645	917	5.6	66
	200	784	582	910	10.1	64
KNO_3	5	1173	1115	1221	1.8	97
	10	1147	1103	1190	1.6	95
	40	994	912	1116	4.4	82
	100	838	682	916	6.6	69
	200	682	502	799	9.6	56
$Ni(NO_3)_2$	10	1151	1099	1213	2.1	92
	40	1030	948	1082	3.0	83
	100	916	855	966	3.4	74
	200	651	523	770	5.4	52
$Hg(NO_3)_2$	10	1181	1141	1242	1.5	97
	40	1108	1032	1196	3.2	91
	100	1092	1007	1175	3.5	90
	200	899	809	1026	5.0	74
NaH_2PO_4	5	1092	993	1188	3.0	90
	10	1034	893	1116	4.0	85
	40	901	807	992	4.3	74
	100	683	556	814	6.7	56
	200	453	151	621	13.7	37

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Table X (continued)

Salt	Salt Conc. g/liter	Avg. c/min./30λ (20 Analyses)	Lowest c/min./30λ	Highest c/min./30λ	Avg. Dev. (Percent)	Percent Recovery
KH_2PO_4	5	1185	1117	1224	2.1	98
	10	1155	941	1361	4.4	95
	40	1034	981	1079	1.9	85
	100	862	700	1001	6.8	71
	200	646	480	768	9.4	53
$H_2C_2O_4$	5	1130	1021	1243	5.2	93
	10	1103	937	1235	5.4	91
	40	952	764	1078	6.0	78
$K_2C_2O_4$	5	1123	941	1219	4.8	92
	10	1107	1001	1235	2.8	91
	40	863	537	1117	9.4	71

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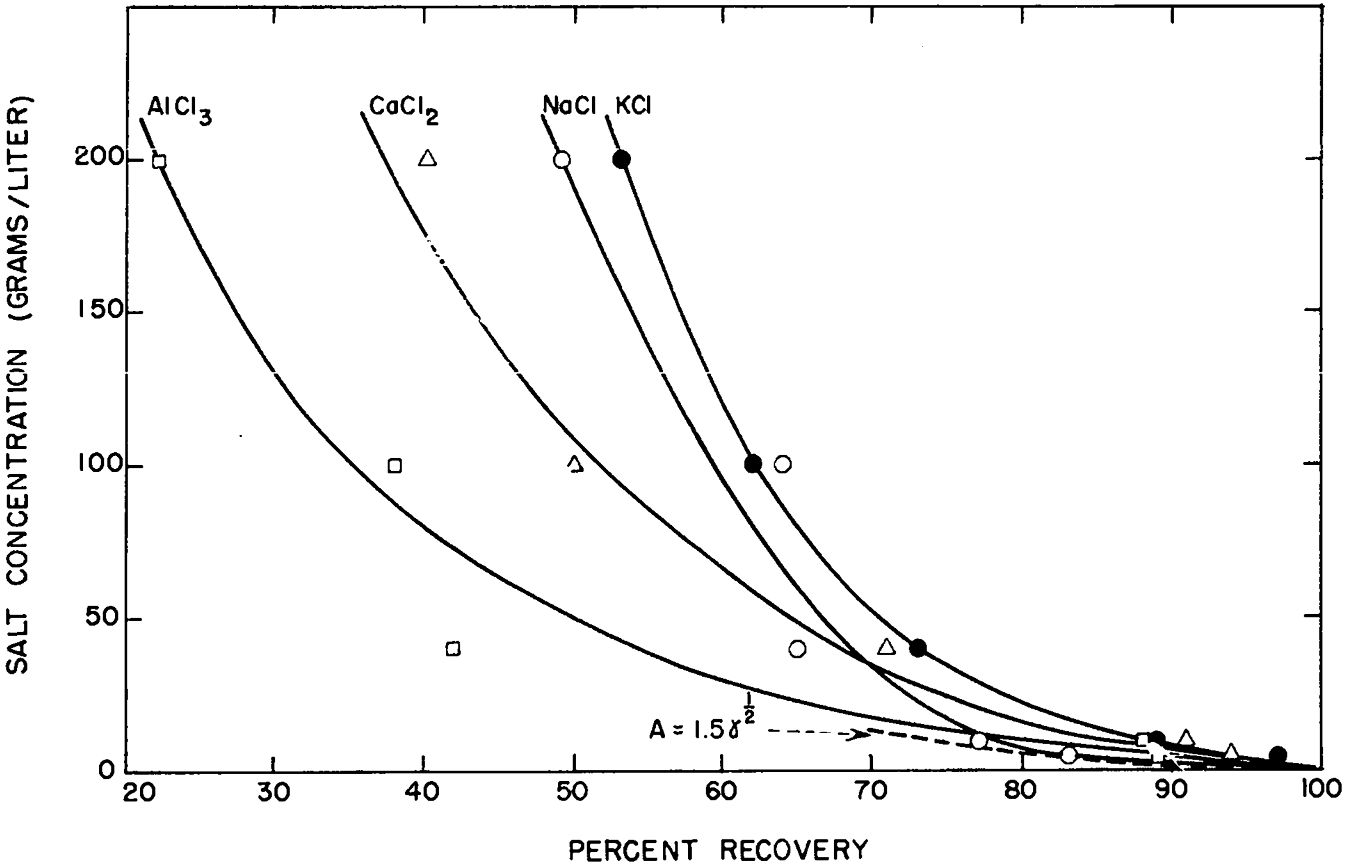

Fig. 1 Salt Concentration - Percent Recovery Curves for NaCl, KCl, CaCl$_2$, and AlCl$_3$

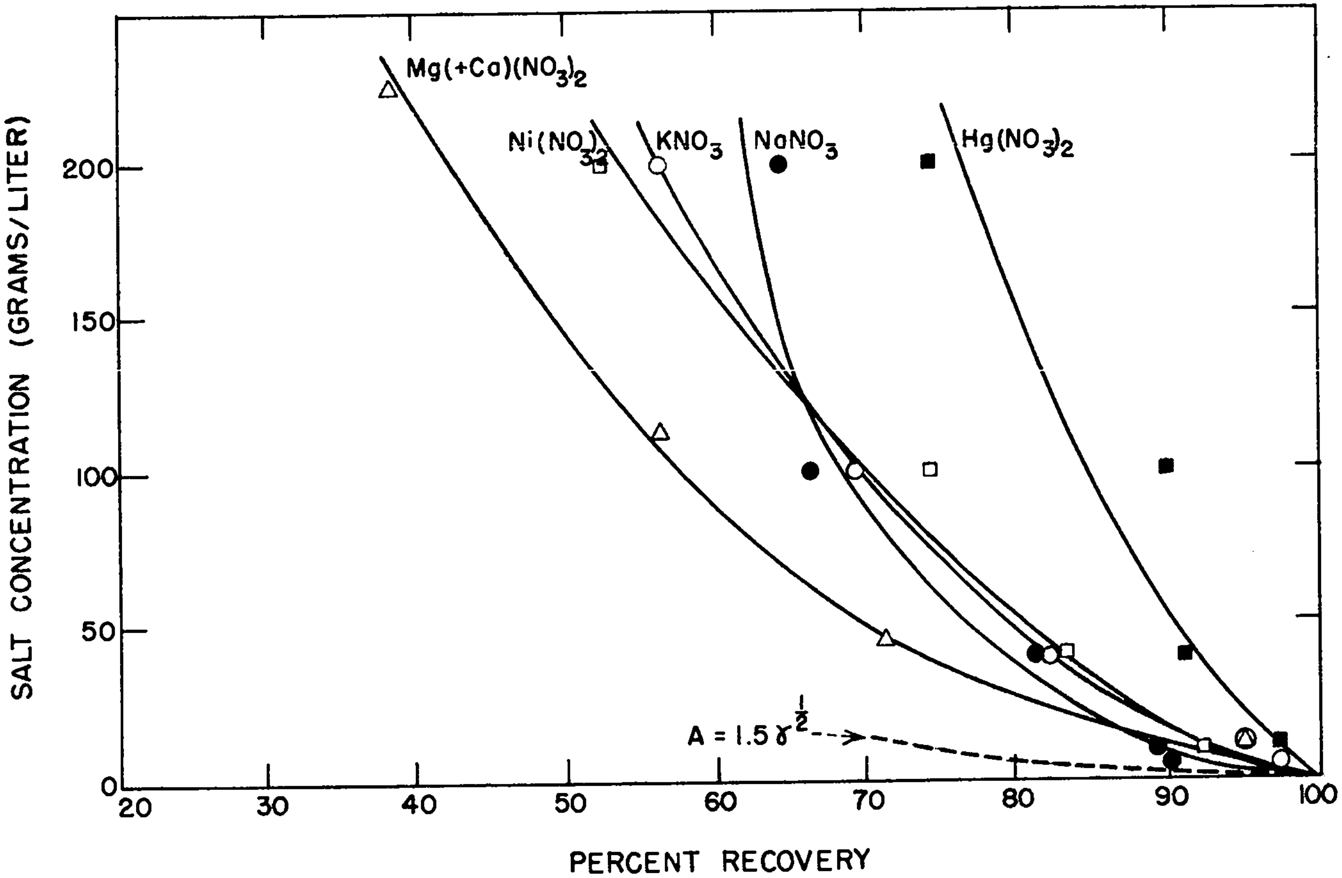

Fig. 2 Salt Concentration - Percent Recovery Curves for $Mg(+Ca)(NO_3)_2$, $NaNO_3$, KNO_3, $Ni(NO_3)_2$, and $Hg(NO_3)_2$

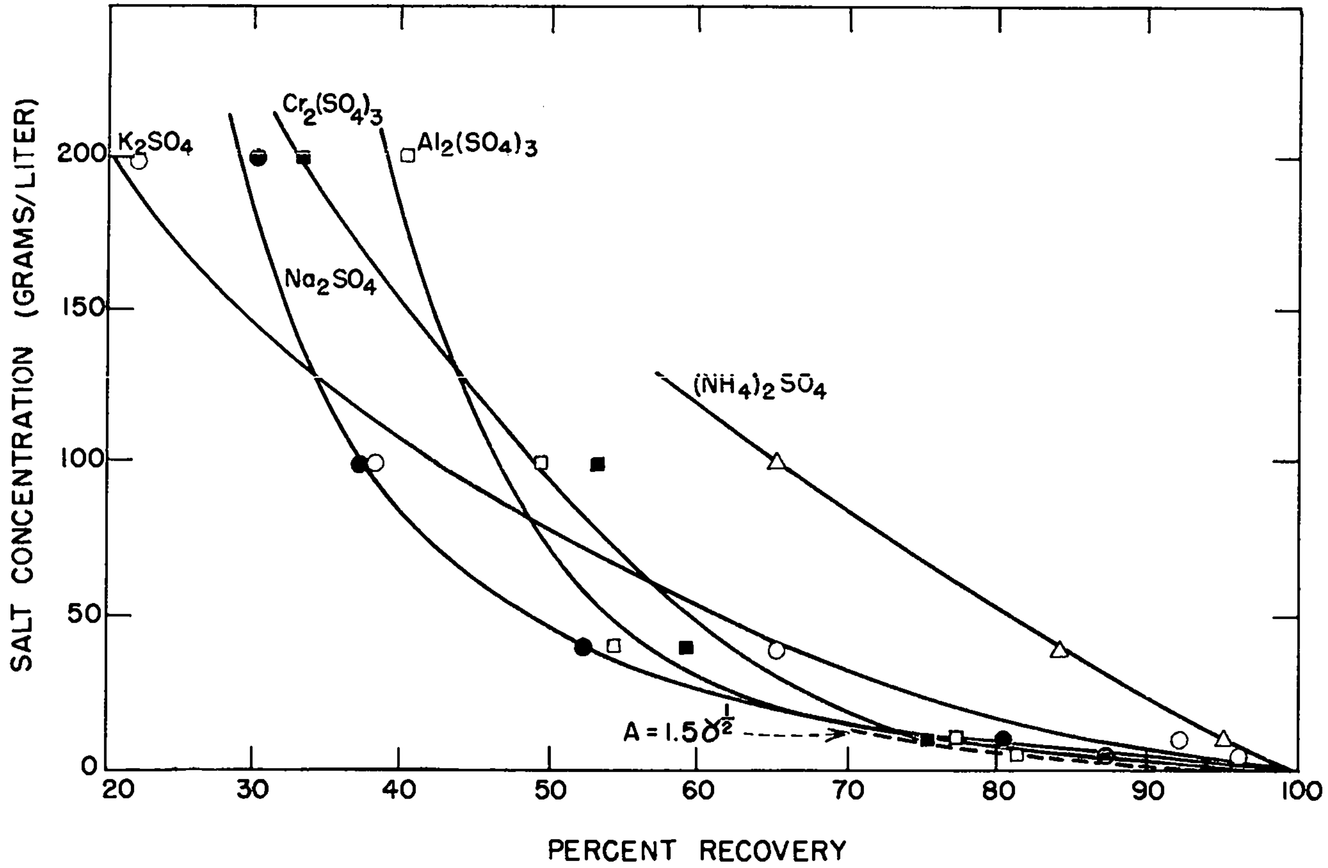

Fig. 3 Salt Concentration - Percent Recovery Curves for Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $Cr_2(SO_4)_3$, and $Al_2(SO_4)_3$

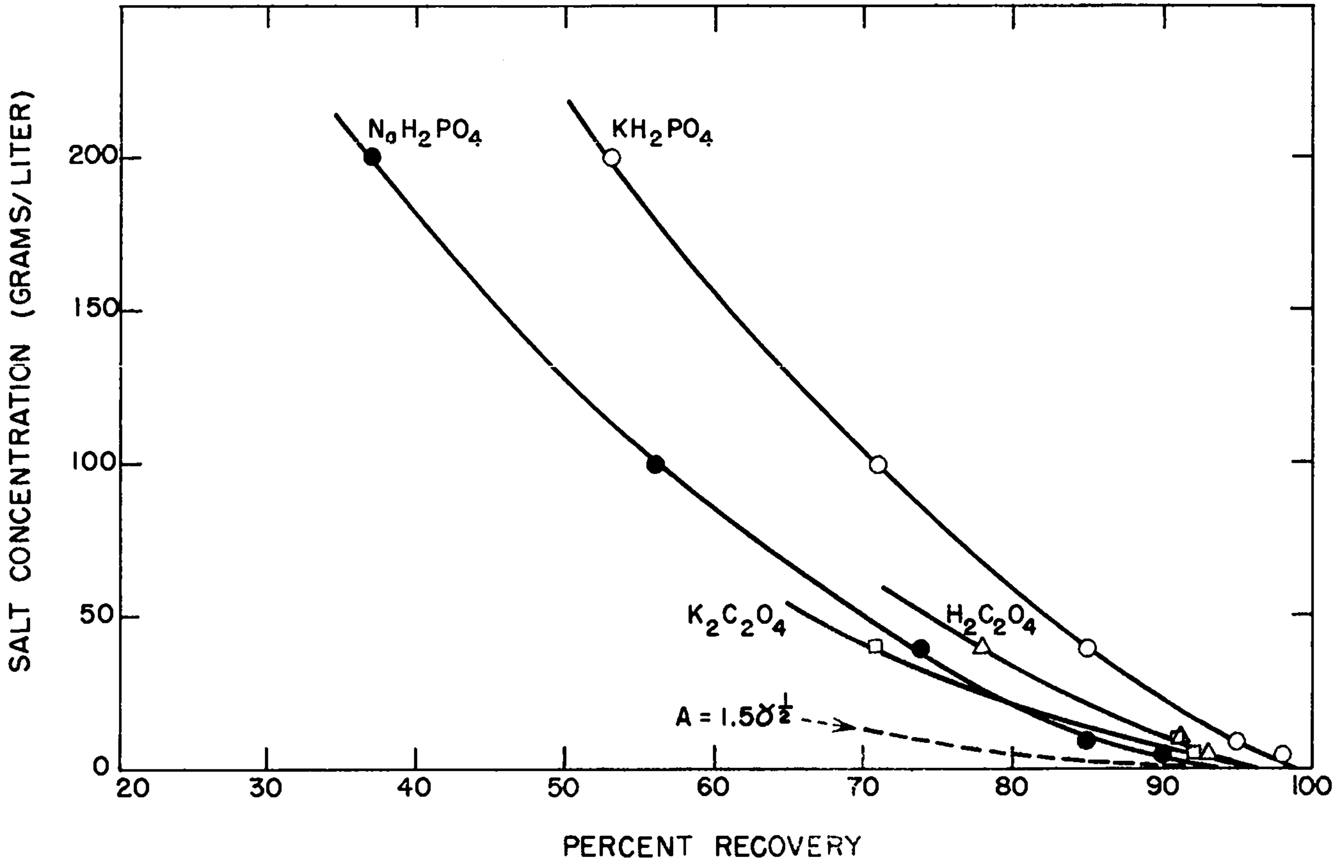

Fig. 4 Salt Concentration - Percent Recovery Curves for NaH_2PO_4, KH_2PO_4, $K_2C_2O_4$, and $H_2C_2O_4$

However, there is no obvious relationship between absorption error and some characteristic of the salt present in the analysis sample. Such variations as the amount of moisture left on the glass sample plate after drying at 60 - 80°C, the distribution of the salt on the plate, and the size of the salt crystals may be more significant than the type or amount of salt added to the sample plate.

FURTHER APPLICATION OF THE LANTHANUM FLUORIDE PROCEDURE

A. Analysis of Ethylene Glycol-Phosphoric Acid Mixture

The analysis of a mixture of ethylene glycol and phosphoric acid by the direct evaporation method did not seem possible, especially if the plutonium content of the sample would be so low that dilution of the sample would be impractical. In the direct evaporation procedure, neither component of the mixture would be removed from the glass plate by evaporation. Consequently, the analysis of such a mixture was briefly investigated with the lanthanum fluoride procedure.

A 1:1 mixture, by volume, of ethylene glycol and 90% phosphoric acid was prepared. Then 0.1-ml portions of the mixture were placed in centrifuge cones and to several of them 31.09-microliter aliquots of a plutonium solution were added. The same aliquot of plutonium solution was added to cones without the ethylene glycol-phosphoric acid mixture, to determine the actual count for the active material added. Using the standard lanthanum fluoride procedure, the results shown in Table XI were obtained. Apparently this procedure can be successfully used with such a mixture.

B. Radiochemical Analysis of Salt Solutions Containing Potassium Ions

The standard lanthanum fluoride procedure was shown by Johnson, Koshland, and Smith(6) to be satisfactory for the analysis of solutions that are 0.05 M or less with respect to potassium ions, at the time of LaF_3 precipitation. Consequently, it was not surprising that the standard procedure gave low results for a solution that was 3.9 M $Mg(NO_3)_2$, 4.7 M $NaNO_3$, and 1.5 M KNO_3. In using a 0.1-ml analysis sample of this solution, the potassium ion concentration at the time of LaF_3 precipitation is 0.15 M. The precipitate obtained was abnormally large, and the analysis showed only 58% of the actual plutonium content of the sample. Even when the acetic acid modification(6) of the standard lanthanum fluoride procedure was employed, the results were much the same as with the standard procedure, with large amounts of precipitate which

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Table XI

RADIOCHEMICAL ANALYSIS OF ETHYLENE GLYCOL-PHOSPHORIC ACID MIXTURE

(Lanthanum Fluoride Procedure)

Solution Number	Description of Solution	Analysis Results (c/min.)
1	0.1 ml of mixture + 31.09 microliters Pu	1035
2	0.1 ml of mixture + 31.09 microliters Pu	1020
3	31.09 microliters of Pu solution	1044
4	31.09 microliters of Pu solution	1047

would not adhere satisfactorily to the platinum plate. However, when the amount of sample was reduced to 25 microliters (instead of 0.1 ml) with a reduction of potassium ion concentration to a value below the limit of 0.05 M, the analysis by the standard lanthanum fluoride method proceeded in a normal manner in agreement with the results of Johnson, Koshland, and Smith.

It is possible that the excessive amount of LaF_3 precipitate, using the 0.1-ml portions of the salt mixture, could be avoided before transferring to a platinum plate by dissolving the first precipitate in a zirconium nitrate solution. Then, after dilution to 1 ml, a second precipitation with HF might give a normal LaF_3 precipitate.

It is of interest to note the maximum potassium ion concentration in the analysis of the plant-control iodide solution that was discussed earlier. A 1-ml sample of the iodide solution required 0.135 ml of 10 N KOH for neutralization. The resulting supernatant liquid was transferred and diluted to 5 ml. This analysis solution, therefore, was 0.27 M in potassium ions. Even if a 0.1-ml sample were used for analysis by the lanthanum fluoride procedure, the concentration at the time of LaF_3 precipitation would be only 0.027 M, less than the maximum of 0.05 M. Therefore, the results for lanthanum fluoride analysis in Table IX should not have been unfavorably influenced by the potassium ions present in the solution.

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RECOMMENDED PROCEDURES

As a result of the study made of the two methods for radiochemical analysis of plutonium solutions, the following recommendations are offered for routine analyses in the Radiochemical Laboratory.

1. The direct evaporation procedure for radiochemical analysis ordinarily should be used. Its use is satisfactory when no more than 300 micrograms of salts and non-volatile substances are placed on a glass plate to obtain a sample that will show at least 50 - 100 counts per minute. Consequently, the solution from which 30-microliter aliquots are to be withdrawn for analysis may contain up to 10 grams per liter of substances that will not be removed from the counting plate by evaporation.
2. When the amount of material remaining on the glass plate would exceed 300 micrograms, the lanthanum fluoride procedure for radiochemical analysis should be used. This same procedure should be employed for all analyses of ethylene glycol-phosphoric acid mixtures.
3. When using the lanthanum fluoride method, the concentration of potassium ions in solution just before precipitation should not exceed 0.05 M.
4. Use of the equation, introduced by Bradford, Roberts, and Wahl, for the relation between salt absorption error and weight of salt on the counting plate should be discontinued.

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(2) J. H. Clifford and D. E. Koshland, Jr., "Development of Radiochemical Analytical Procedures for Plutonium" - (1) "Synthetic Solutions", CN-2040, September 23, 1944.

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(4) D. E. Koshland, Jr., "Development of Radiochemical Analytical Procedures for Plutonium". "Analysis of Fluoride and Phosphate Solutions", CN-2042X, June 30, 1945.

(5) Reference 3, pages 37-8.

(6) G. L. Johnson, D. E. Koshland, Jr., and C. W. Smith, "Development of Radiochemical Analytical Procedures for Plutonium". "Analysis of Potassium and Sodium Solutions", CN-2043X, June 30, 1945.

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