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THE SPECTROPHOTOMETRIC DETERMINATION OF GALLIUM IN PLUTONIUM

by

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TECHNOLOGY - PLUTONIUM

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ABSTRACT

A spectrophotometric method using 8-hydroxyquinoline for the determination of gallium in plutonium metal is described. The metal is dissolved in hydrochloric acid and the plutonium complexed with citric acid. Gallium is then extracted into chloroform as gallium quinolate, and the concentration of the metal is determined by colorimetric measurement. The effects of numerous variables are discussed, including the interference of foreign ions. The precision is ± 1 % of the gallium content on samples containing from 0.5 to 1.5 milligrams of gallium. This represents a distinct improvement over the previously available procedure.

INTRODUCTION

The gravimetric method of Pepkowitz[3] has been used in this laboratory for the determination of gallium in plutonium. Briefly, this method consisted of isolating the gallium by iso-propyl ether extraction from a 7 N acid solution, re-extracting into water at pH 7, and precipitating it with 8-hydroxyquinoline. The small amount of gallium necessitated weighing the precipitated quinolate on semi-micro balances.

The first improvement made in the method was the substitution of a colorimetric procedure for the final weighing. 8-hydroxyquinoline was still used as the reagent, but the complex was extracted into chloroform and the color measured at 390 mμ. Oxine had been used in a fluorimetric test for gallium[4] but at that time there was no published data on its colorimetric use. In a recent article, Moeller and Cohen[2] discuss the colorimetric properties of both gallium and thallium quinolates in chloroform solutions. The present procedure is a further simplification resulting from an effort to eliminate the tedious ether extraction steps for the separation of the metals.

APPARATUS AND REAGENTS

250 ml glass stoppered pyrex bottles.

Automatic pipets.

Beckman Spectrophotometer, Model DU, with accessories

Absorption Cells, 1.0 cm, Corex.

Citric acid, C.P. 5 % aqueous filtered.

8-hydroxyquinoline, Eastman White Label, 1 % in ethanol.

Sodium acetate, C.P. 20 % aqueous filtered.

Chloroform, C.P.

RECOMMENDED PROCEDURE

Place the weighed sample containing from 0.5 to 1.5 mg of gallium in a 250 ml bottle and treat with approximately 1 ml of concentrated HCl. After making certain that any oxide has completely dissolved, add the following reagent solutions: 5 ml of citric acid, 10 ml 8-hydroxyquinoline, and 10 ml sodium acetate. (The solutions may be added individually, or they may be mixed in the proper ratio and added in one 25 ml portion.) Swirl the bottle to mix the solutions. At this point the pH must be adjusted to 5.0 to 8.0. This may conveniently be done as follows: The acid solution is greenish grey in color and usually contains a precipitate. Add concentrated NH_4OH dropwise with swirling until the color changes to clear deep red. Tip the bottle so a thick layer may be viewed. A sample containing 100 mg of plutonium and 1 ml of HCl ordinarily requires 4 to 6 drops of NH_4OH. If too much NH_4OH is added so that a permanent red precipitate forms, add a drop or two of HCl to cause solution. Add 100 ml of chloroform, shake the bottle vigorously for 15 seconds, and allow to stand overnight.

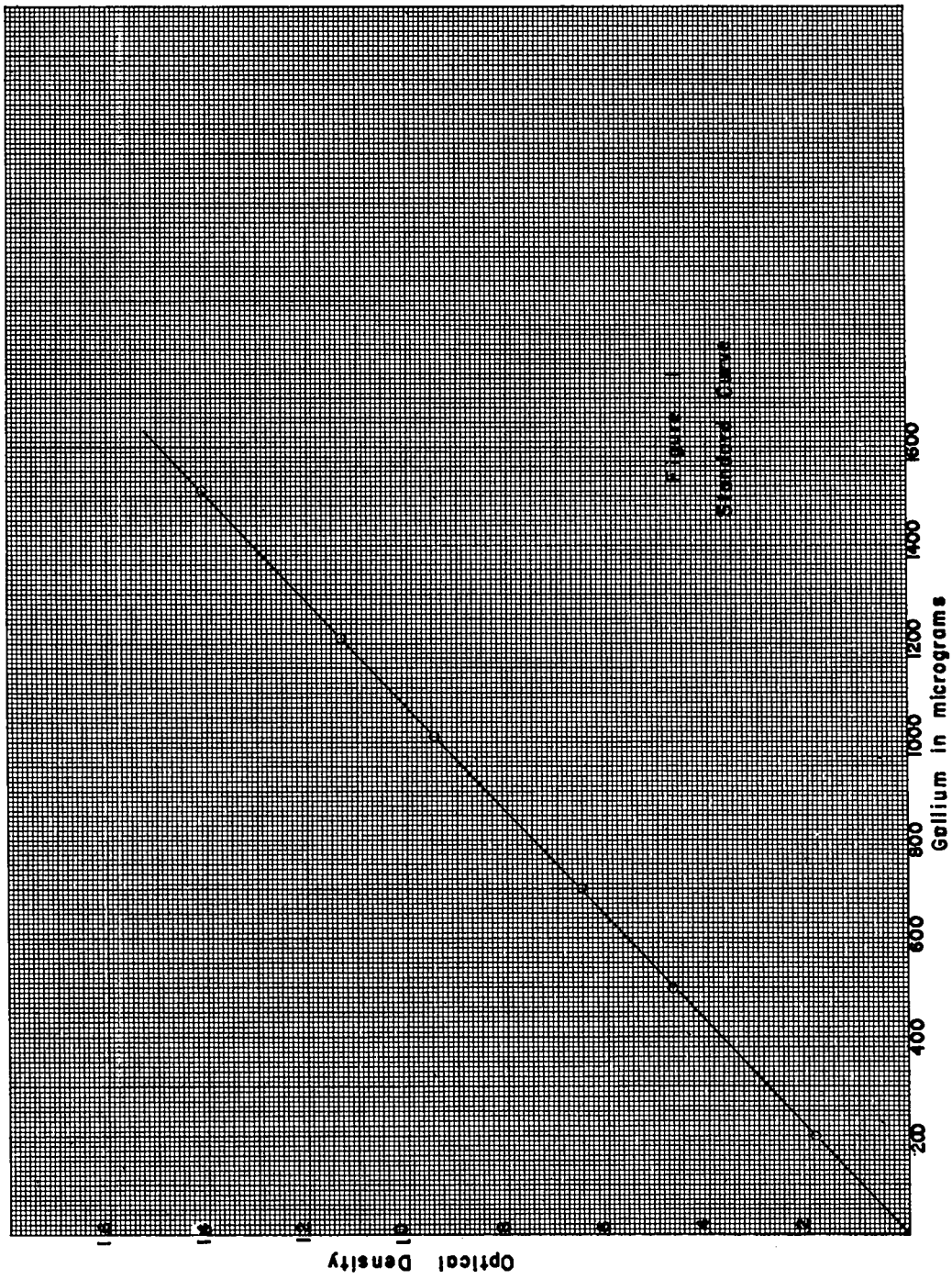
When the phases have separated completely, withdraw a portion of the chloroform solution with a syringe pipet (See Figure 4) and fill a 1 cm absorption cell. Measure the optical density at 390 mμ and at 500 mμ, using for reference a blank which contains the citric acid, buffer, oxine and chloroform. Make the necessary cell corrections at both wavelengths, and subtract the value at 500 mμ from that at 390 mμ. Obtain the weight of gallium from a standard curve prepared by using known amounts of gallium and calculate the percent gallium in the original sample.

EXPERIMENTAL

Standard solutions of gallium were prepared by weighing the pure (99.9 %) metal and allowing it to dissolve in concentrated HCl at room temperature. A stock of gallium-free plutonium metal was available. This was dissolved in HCl as necessary, and added to the gallium aliquots. Solutions of La, Mg, Al, etc., were prepared by dissolving the chlorides of these metals in water.

The Standard Curve

The standard curve shown in Figure 1 was prepared from the analysis of known amounts of gallium, containing sufficient plutonium to make the gallium approximately 1 % of the total weight. The curve is a compilation of the results of analyses of two different gallium standards, each run in duplicate and repeated on a different day.



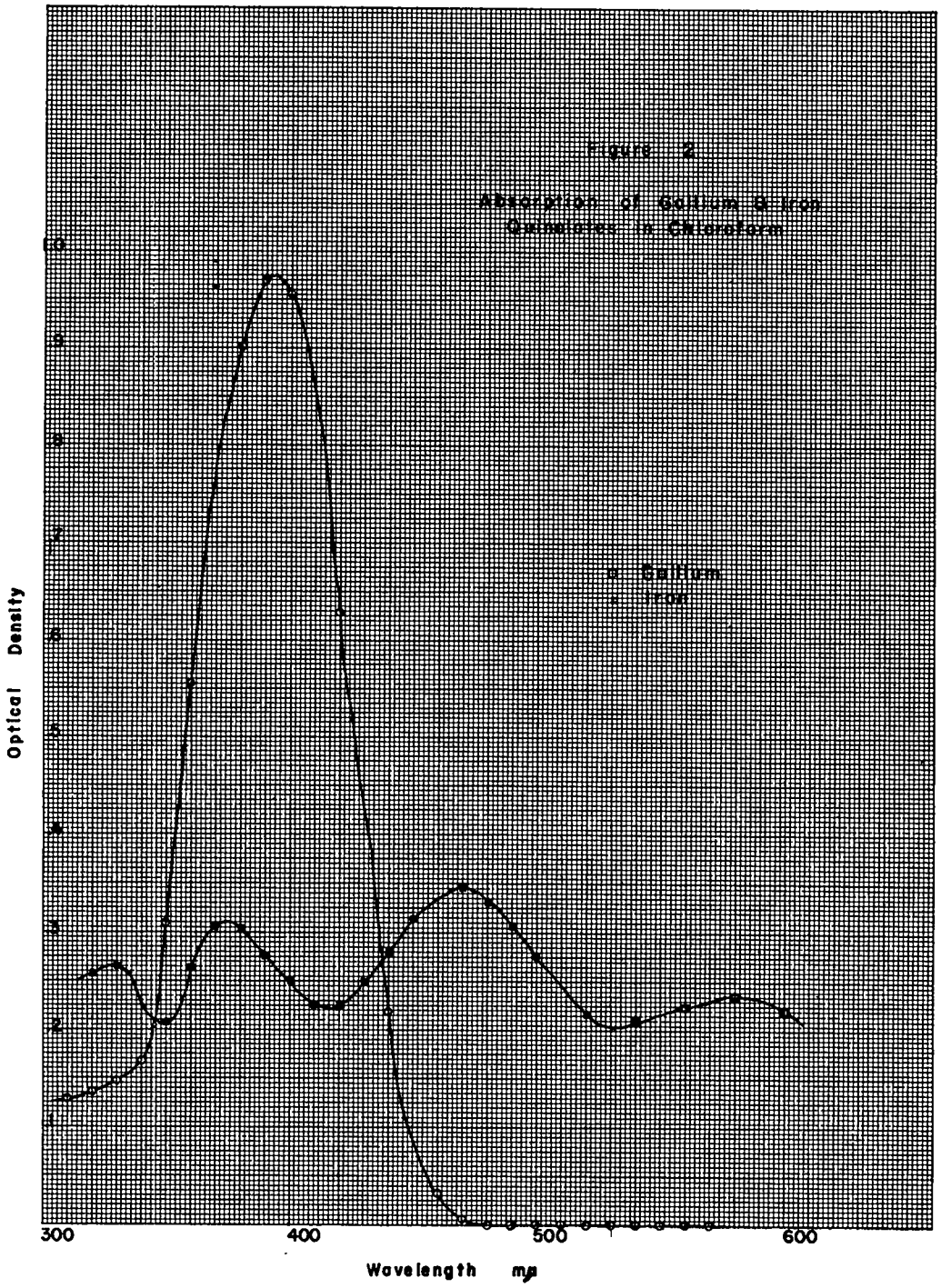
Effect of Iron

It was found that under the conditions of the procedure, iron quinolate is extracted along with the gallium. Figure 2 shows the absorption curve of 1 mg of gallium in 100 ml of chloroform. The absorption curve for 500 micrograms of iron in 100 ml of chloroform is shown in the same figure. It is readily seen that if 390 mμ is used for the measurement of gallium, a correction for iron will be necessary. It can also be seen that the absorption of gallium quinolate is negligible above 480 mμ, and this conclusion has been checked by careful measurements. Since the absorption of iron quinolate is the same at 390 mμ and at 500 mμ (See Table I), the iron contribution to the gallium reading can be corrected by measuring the density at 500 mμ and subtracting from that at 390 mμ.

Table I

Comparison of Optical Density Readings for Iron at 390 mμ and 500 mμ

Micrograms of Iron	390 mμ	500 mμ	Difference
5	.007	.015	+ .006
10	.021	.019	- .002
10	.021	.027	+ .006
12.5	.026	.032	+ .006
25	.070	.070	.000
50	.137	.140	+ .003
50	.151	.157	+ .006
100	.339	.334	- .005
100	.360	.361	+ .001



Effect of pH

The pH dependence of the extraction of plutonium from solutions containing only plutonium and the usual reagents was tested over the range from 3.0 to 10.5. In this interval the amount of plutonium passing into the chloroform is negligible. At lower pH values the separation of phases is very slow, while at pH greater than 9.0 the plutonium can be extracted more or less completely to the chloroform.

With gallium alone under the same conditions, extraction of the complex was unvarying from pH 5.0 to 9.0. With increasing acidity the gallium becomes insoluble in the chloroform phase. The buffering action of the salts present is quite strong, so that adjustment of the pH is not difficult. Samples which have been adjusted in the manner described in the procedure have been found to fall quite uniformly between 5.5 and 6.5.

Effect of Valence of Plutonium

Citric acid forms a complex with both + 3 and + 4 plutonium, and neither one is extracted into chloroform. The addition of hydrogen peroxide to the original $PuCl_3$ solution had no effect on the reading obtained for gallium. It may be observed that in any case all the plutonium is oxidized by the time the phases have separated.

Extraction of Plutonium

Figure 3 shows the absorption curve of plutonium quinolate in chloro-

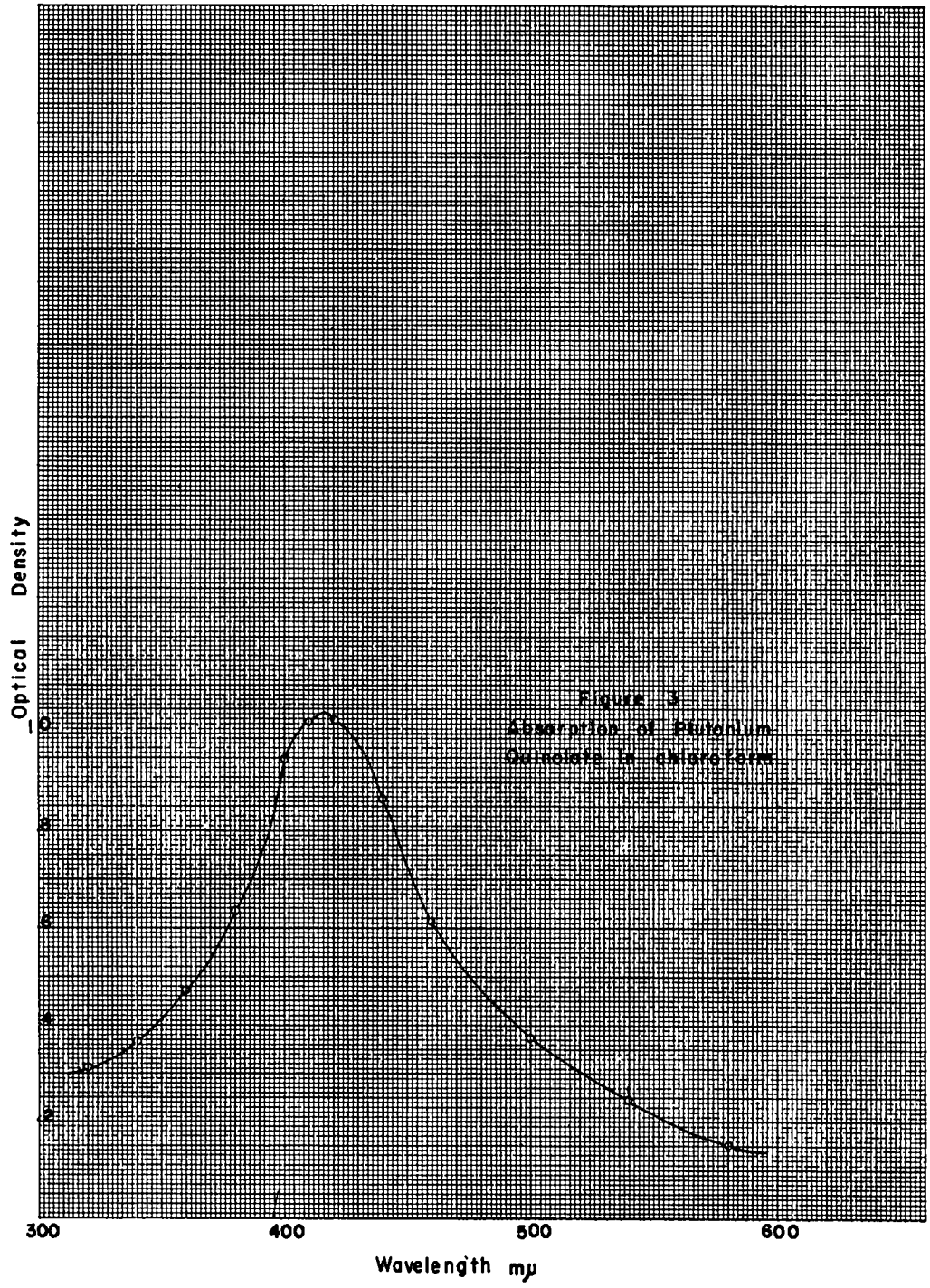


Figure 3
Absorption of Plutonium
Quinolate in chloroform

form. One milligram of plutonium metal was used, so the absorption at 390 mμ is quite strong. The reading at 500 mμ would correct for approximately one-half this absorption in addition to the iron.

The amount of plutonium extracted from citric acid solution as a function of the total amount present was investigated in a series of samples. Table II shows the amount of plutonium present and the results observed. No gallium was used. It is clear that the amount extracted is extremely small and nearly constant over the range in which it is proposed to work. Even the small amount shown is largely corrected by the preparation of the standard curve with samples containing plutonium.

Table II

The Extraction of Plutonium

Pu Present	Resulting Error at 390 mμ
32.2 mg	.005 (optical density)
55.2	.007
90.3	.007
196.4	.010

Since the amount of plutonium extracted appears to be nearly independent of the quantity present, and since the standard curve was constructed with samples in which the gallium was approximately 1 % of the plutonium weight, samples of low gallium content would give biased results. The magnitude of this effect was measured on two sets of six determinations in which the gallium content was made only 0.2 %. The

results at this extreme were found to be 2 % high, so the error is of no concern for routine work.

Effect of Order of Addition of Reagents

Variations in the order of addition of reagents have no effect on either the color intensity or the time required for its development. For example, samples in which the citric acid was withheld until all the other reagents, including the chloroform, had been added, showed no difference from controls in which the citric acid was added first.

Measurement of Reagents

A variation of ± 10 % in the amount of 8-hydroxyquinoline added produced no change in the final result. The allowable variation in the amount of citric acid and of the buffer solution is at least as great. The chloroform should be measured with care however, and the amount of ethanol added with the oxine should be controlled because it is partitioned between the water and chloroform phases about equally.

As suggested in the procedure, the 8-hydroxyquinoline, citric acid, and sodium acetate may be mixed in the proper proportion and added at once. A Machlett pipettor has been found very useful. The effects of such mixing on possible aging of the oxine solutions has been checked with negative results up to 10 days storage. The permissable age limit of the oxine solution has not been determined beyond that time since it is used up rapidly.

Effect of Foreign Elements

The method has been developed for the determination of gallium in quite pure plutonium metal. In Table III some of the more common contaminants are listed and their effects on the analysis shown. The quantities used are approximately ten times those normally encountered. The tests were run as follows: A group of samples containing 504 micrograms of gallium each were measured out from a standard solution, and approximately 50 mg of plutonium were added to each. Ten of these were set aside for controls, (one sample was subsequently lost), and the remainder, in groups of five, received the amounts of the various metals shown. The amounts of these ions are calculated to ppm on a 50 mg sample.

Table III

Effect of Foreign Ions

Element	No. of Samples	Ave. Gallium Recovery in Micrograms
None	9	504
100 ppm Li	5	505
100 ppm Mg	5	505
100 ppm Al	5	506
100 ppm Na	5	502
20 ppm B	5	505
1000 ppm La	5	504

Statistical analysis of these data indicates that there are no significant differences among these results.

Figure 4
Transfer Pipet

Color Development and Stability

While the routine procedure is designed to allow the natural separation of the chloroform, a centrifuge may be used to advantage for quick analyses. One hour is a sufficient time for full development of the color, and the solution may then be centrifuged and the optical density measured. The chloroform solutions of gallium quinolate show very slight change upon standing. The data of Table IV are typical.

Table IV

Color Stability of Gallium Quinolate in Chloroform

	Time of Standing		
Sample No.	1 Day	3 Days	10 Days
B1	.189	.190	.214
B2	.954	.957	.962
B3	1.427	1.437	1.437

These samples were aged at room temperature in the glass-stoppered bottles in which the test was run. The increase shown by B1 between the third and tenth days is probably not the result of a color change at all, but is due to the loss of chloroform. Such loss is slowed by the water layer over the chloroform, and no difficulty from this source has ever been observed with samples stored two or three days. When stored for 3 weeks in sealed tubes a slight decrease in absorption was noted.

Purity of the 8-hydroxyquinoline

It has been found that different bottles of 8-hydroxyquinoline produce measurably different results. Table V shows the results of analyses run with material from nine different bottles of Eastman White Label reagent and indicates also the improvement obtained by recrystallizing. Each result shown is the average of triplicate determinations.

Table V

Variation in Gallium Recovery
With Different Bottles of Reagent

Bottle No.	Untreated	Recrystallized
1	99.8 %	101.0 %
2	99.8	99.8
3	100.6	100.0
4	99.8	
5	99.3	100.0
6	98.9	99.8
7	98.7	100.0
8	98.7	99.6
9	99.6	100.1

The recrystallization is made from alcohol as follows: Dissolve 5 grams of the salt in 50 ml of warm 190 proof ethanol, and filter the solution if necessary. Precipitate the oxine by the addition of 200 ml of distilled water while stirring the solution vigorously. Collect the crystals on a fritted glass filter and wash once with water. After sucking them as dry as possible, heat at 50 to 60° C for about 8 hours. The recovery is approximately 80 %.

It is desirable to check each recrystallized batch by analyzing a known gallium sample, and if the purification is done in 25 gram lots this is not much trouble.

PRECISION OF THE RESULTS

A series of replicate samples were analyzed with the results shown in Table VI. Each contained 504 micrograms of gallium and 50 mg of plutonium.

Table VI

Recovery of Gallium from Known Samples (in Micrograms)

502	504	500	502	504
504	501	506	500	501
504	502	512	503	500
504	508	505	503	508
504	509	505	502	504
502	505	505	505	504
509	503	503	508	504
502	505	510	506	

The mean weight of gallium recovered was 504 micrograms. The standard deviation was 2.8 micrograms, so that 95 % of the individuals in any series of determinations may be expected to differ from their true mean value by no more than 1 %.

In Table VII are shown the results of 40 analyses made on one sample of plutonium-gallium alloy. The mean value of the gallium assay was 1.05 %, and the standard deviation of .01 % is approximately 1 % of

that figure.

Table VII

Gallium Content of Plutonium Metal
(in Percent)

1.07	1.06	1.04	1.05	1.05
1.06	1.05	1.06	1.04	1.05
1.05	1.05	1.06	1.06	1.06
1.05	1.06	1.05	1.05	1.05
1.06	1.06	1.06	1.06	1.06
1.05	1.05	1.07	1.06	1.04
1.06	1.05	1.05	1.06	1.05
1.05	1.06	1.07	1.07	1.05

COMPARISON OF THE METHODS

One rather important criterion in evaluating an analytical method is the amount of time required per analysis, since this has a direct relationship to the personnel, equipment, and space required. The gravimetric method requires the full attention of one operator for eight hours to complete 18 determinations. Colorimetrically, 90 determinations with the associated cleaning and book work can be done in 8 hours though not on the same day.

The precision obtained is, of course, the prime consideration, and the two methods have been exhaustively compared in this respect.

The author prepared 20 samples of 504 micrograms from a gallium stand-

ard solution, and added to each approximately 100 mg of gallium-free plutonium. Ten of these were analyzed colorimetrically and 10 were analyzed by the method of Pepkowitz, following his procedure except that the oxine was recrystallized. The variances of the two series of results were compared by Fisher's test (as described by Brownlee[1], and it was found that the value of the variance ratio was 144. The variance ratio table given by Brownlee gives 10.4 for the .001 significance level with 9 degrees of freedom in each set. There is, therefore, a virtually certain difference in the reproducibility of the two methods, and the colorimetric method is the more reproducible.

To avoid any possible bias of the author, the rest of the data reported here will be taken from the work of other individuals.

Six different plutonium-gallium samples were analyzed by both methods. The analyst who performed the gravimetric determinations had 2 years experience with the procedure. The data are shown in detail in Table VIII as Series B. Using the method of Brownlee the variances in all the gravimetric results were averaged and compared with the averaged variance of the colorimetric results. In this case the value of the variance ratio is 5.01. In the variance ratio tables for the .01 significance level, we find 6.9. From the point of view of the statistician, the experiment was not well designed since the colorimetric data have too few degrees of freedom. However, the rather interesting conclusion may be drawn that about 95 % of the time dupli-

cate colorimetric analyses will offer as good precision as averaging 8 gravimetric analyses.

Table VIII

Comparison of Methods in Series B

	1	2	3	4	5	6
Gravimetric	1.09	1.07	1.08	1.02	1.12	1.09
	1.07	1.07	1.12	1.01	1.08	1.08
	1.08	1.04	1.07	1.02	1.11	1.07
	1.10	1.13	1.10	.99	1.08	1.09
	1.06	1.08	1.05	.96	1.07	1.07
	1.10	1.00	1.05	.99	1.05	1.07
	1.05	1.04	1.08	.97	1.11	.98
	1.08	1.02	1.33	.99		1.09
Colorimetric	1.12	1.04	1.05	.98	1.08	1.09
	1.11	1.10	1.06	.99	1.11	1.11

The analyses shown in Table IX as Series C are taken in sequence from the last analyses performed by the gravimetric method. Series D in Table X shows the results of duplicate colorimetric analyses on the same type samples. If the assumption is made that these samples are essentially the same, and no reason to doubt this is known, we may calculate the difference between duplicates in each set and apply Fisher's significance test. The ratio of the variances turns out to be 73.0/1.3, and there are 71 degrees of freedom associated with each member of the ratio. The value 57.5 for the ratio is compared with the value 1.9 from the table of variance ratios at the .001 level of sig-

nificance. There is therefore no doubt that a significant difference exists, and that the colorimetric method is more reproducible.

Table IX

Comparison of the Methods in Series C

(Gravimetric)

.98	1.03	1.06	1.08	1.11	1.31	1.21	1.28
1.02	1.12	1.02	1.27	1.05	1.33	1.29	1.34
1.33	1.16	1.03	1.16	1.42	1.26	1.25	1.21
1.33	1.36	.99	1.05	1.40	1.16	1.30	1.20
.89	1.36	.97	1.04	.99	1.20	.96	1.25
.94	1.29	.97	1.05	1.00	1.21	.89	1.05
1.12	1.15	1.18	1.36	.91	1.22	1.24	1.66
1.03	.99	1.34	1.30	.92	1.17	1.30	1.49
1.10	1.27	1.12	1.34	1.45	1.30	1.37	1.14
1.00	1.24	1.18	1.26	1.38	1.24	1.18	1.02
1.10	1.18	1.13	1.09	.93	1.04	1.04	1.26
1.13	1.10	1.10	1.23	.96	1.12	1.04	1.29
1.35	1.38	.97	1.00	.99	1.23	1.05	1.32
1.28	1.26	.99	1.05	.95	1.32	1.00	1.29
.94	1.00	1.07	1.24	1.00	1.29	.81	1.52
.97	1.07	.92	1.33	.98	1.19	.77	1.58
.99	1.41	.94	1.22	1.09	1.14	1.47	1.15
1.00	1.43	1.10	1.13	1.04	1.20	1.45	1.09

$$\text{Variance} = \frac{5276 - \frac{81^2}{72}}{71} = 73.0$$

Table X

Comparison of the Methods in Series D

(Colorimetric)

1.01	1.05	.94	1.38	1.15	1.11	.94	.96
.99	1.05	.92	1.34	1.15	1.13	.93	.98
.89	1.09	.93	1.05	1.11	.98	1.06	.96
.89	1.14	.94	1.01	1.13	.99	1.04	.95
.92	.94	1.42	1.24	1.26	.91	.97	1.04
.91	.96	1.42	1.24	1.27	.93	.97	1.03
1.15	1.11	.93	.99	1.11	1.24	1.15	1.21
1.16	1.08	.94	.99	1.11	1.23	1.16	1.20
1.24	1.09	1.11	1.21	1.07	1.04	1.08	1.30
1.25	1.06	1.11	1.24	1.06	1.04	1.10	1.28
1.25	1.08	.97	.82	1.04	.99	.98	.96
1.25	1.08	.97	.84	1.02	1.02	.99	.98
.94	.93	.94	1.06	.94	.99	1.18	1.22
.94	.93	.94	1.06	.97	.98	1.17	1.25
1.10	1.12	.58	.93	1.08	1.08	1.18	1.20
1.08	1.09	.62	.94	1.08	1.09	1.16	1.18
1.19	1.20	1.29	1.50	1.33	1.17	1.34	1.33
1.16	1.18	1.33	1.53	1.32	1.14	1.32	1.31

$$\text{Variance} = \frac{130 - \frac{54^2}{72}}{71} = 1.27$$

Pepkowitz offers a table of typical analytical results in LA-425. Making the same assumption that there is no essential difference in the sample material (again there is no reason to suppose otherwise), the variances of this set of results may be compared with Series D. In this

case the variances are calculated to 12.1 (gravimetric) and 1.3 (colorimetric), and they have 15 and 71 degrees of freedom respectively. The numerical value of the ratio is 9.6, and from the table for the .001 significance level we obtain 3.3. Again, there is definite indication of the superior precision of the colorimetric method.

The difference in reproducibility between the two procedures is definite but hardly surprising. In the iso-propyl ether extraction of the older method no fewer than 6 phase separations must be made, and this must be followed by the precipitation, filtration, washing and weighing of a minute amount of gallium quinolate. In the colorimetric procedure on the other hand, once the solid sample has been transferred to the reaction bottle, no further manipulation is required except to withdraw a portion of the chloroform for measurement of its optical density.

CONCLUSIONS

A simple and precise determination of gallium in plutonium is possible by forming the citric acid complex of the plutonium and separating the gallium as quinolate in a single pass extraction with chloroform. The concentration of gallium may then be determined by measuring the absorption of the chloroform solution at 390 mμ. In the high purity plutonium metal for which the procedure is intended, the only element known to interfere is iron, and a correction is easily applied. The

precision, or reproducibility, of the method is ± 1 % of the gallium content over the range recommended.

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