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THE SPECTROPHOTOMETRIC DETERMINATION  
OF TRACE AMOUNTS OF GALLIUM  
IN HIGH-PURITY PLUTONIUM METAL

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THE SPECTROPHOTOMETRIC DETERMINATION  
OF TRACE AMOUNTS OF GALLIUM  
IN HIGH-PURITY PLUTONIUM METAL

by

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#### ABSTRACT

The rhodamine B method for the spectrophotometric determination of gallium has been modified and applied to the determination of trace amounts of gallium in high-purity electrolytic plutonium metal. In this method the plutonium is dissolved in hydrochloric acid and the chlorogallate-rhodamine B complex is extracted into a 3:1 mixture of chlorobenzene and carbon tetrachloride without any preliminary separation of the plutonium. The absorbance of the extract is measured at 562 m $\mu$ . Forty-two determinations made on plutonium solutions containing from 0.5 to 100 ppm of gallium showed a standard deviation of 2% relative or 0.1 ppm, whichever was larger. Some care is necessary to assure that the volume and acidity of the aqueous phase is reproduced each time, but the manipulations are simple and little time is required. Interference from plutonium and from other elements commonly found in high-purity plutonium metal was found to be negligible.



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## INTRODUCTION

The recent development of new methods for the production of high-purity plutonium metal has made necessary the development of more sensitive methods for determining the impurities present. Gallium is of particular interest because of its strong effect in modifying the physical properties of the plutonium.

In this Laboratory, gallium in plutonium-gallium alloys is determined by a spectrophotometric measurement of the gallium-oxine complex extracted into chloroform. The procedure was developed by Henicksman,<sup>(2)</sup> specifically for macro amounts of gallium. More recently a modification was introduced to permit use of the method in determining gallium as an impurity in plutonium metal. This modification consisted of starting with a larger sample and making a preliminary separation of the gallium by anion exchange on Dowex 1 resin in a hydrochloric acid medium. This was followed by the usual extraction and spectrophotometric measurement. The limit of detection was thus extended downward to about 20 parts per million. The high-purity metals currently being produced usually contain less than 20 parts per million of gallium, so the present study was undertaken to lower the limit of detection to the less-than-one part

per million range. Methods considered for doing this were the use of even larger samples with smaller volumes for the extraction, and the use of a more sensitive color reagent such as rhodamine B.

#### EXPERIMENTAL

Direct extraction of small amounts of gallium as the oxinate from highly concentrated aqueous plutonium solutions was tried, out of a desire to keep the procedure as simple as possible. This was unsuccessful, probably because of the difficulty in controlling the pH of the concentrated plutonium solution.

Next, attention was given to the ion-exchange separation of gallium. The distribution coefficients of gallium and Pu(III) in hydrochloric acid medium are extremely favorable for a separation of the two metals. Such a separation permits the use of much larger samples, but it is time-consuming and it was found to contribute a significant and variable blank to the absorbance measurement of the gallium. All efforts to eliminate this blank were unsuccessful, though it was reduced and made somewhat more constant by using hydrochloric acid that had been purified by passage through a similar column. The ion-exchange separation was used throughout this study to obtain gallium-free plutonium.

Culkin and Riley<sup>(1)</sup> modified the usually-recommended rhodamine B method<sup>(3)</sup> for gallium by extracting the colored complex into a 3:1 mixture of chlorobenzene and carbon tetrachloride instead of benzene. They claimed 100 percent extraction in one pass. This method was tried with a known solution of gallium and found to be more than 10 times as sensitive as the oxine method, although 100 percent extraction was not achieved.

After choosing conditions that seemed appropriate to a plutonium sample, a series of 15 known solutions containing 0.1 to 5 micrograms of gallium was analyzed for a calibration curve. The standard deviation of these values amounted to 16 percent. Culkin and Riley recommended filtering the organic phase through a pledget of glass wool in the funnel stem, but it was observed that the fibers were brightly colored after this operation. The use of glass wool (or any filter) turned out to be unnecessary, and its elimination resulted in an increase in sensitivity of about 30 percent while the standard deviation dropped to 8 percent.

The spectrophotometer cells being used, which were old and somewhat etched, held the dye so strongly that they had to be washed with hydrochloric acid and acetone after each reading. A new set of Vycor cells proved easier to rinse clean, and the standard deviation improved to about 2 percent.

The mixed solvent (3 parts chlorobenzene to 1 part carbon tetrachloride) has a density of about 1.2 grams per milliliter. A dilute aqueous solution therefore floats on it. A high concentration of plutonium in the aqueous phase (e.g. 1 gram in 5 milliliters) will cause the organic layer to float. If the densities of the two phases are too near each other there is a tendency for an emulsion to form, so phase separation is slower and poorer. The optimum sample size for 5 milliliters of solution was found to be about 200 milligrams. Attempts to increase the sample size while maintaining the difference in density were made by increasing the volume of the aqueous phase and by increasing the ratio of carbon tetrachloride in the mixed solvent. In both cases there was a loss in sensitivity due to poorer extraction.

#### INTERFERENCES

Sandell<sup>(3)</sup> lists antimony, gold, thallium, and iron as the elements that will interfere in the procedure. Reduction of these elements to lower valences Sb(III), Au(0), Tl(I), Fe(II) prevents most of the interferences, but the author states it is more satisfactory to separate gallium from these and most other elements by ether extraction before applying the rhodamine B reaction.

Under the conditions described in this report, a preliminary separation was not necessary. The dissolution of plutonium metal in hydrochloric acid provides an effective reducing atmosphere, and the addition of

titanous chloride makes any subsequent oxidation unlikely. No attempt was made to verify Sandell's list of interferences. However, analytical reports of high-purity plutonium metal samples which had been analyzed in this Laboratory in recent months were studied, and the elements which were commonly found as impurities were checked for interference in the gallium procedure. These elements were added individually to a sample solution of plutonium which had been found to contain 5.7 parts per million of gallium. The gallium was then redetermined. The results are shown in Table I.

Table I  
Effect of Foreign Ions on Gallium Determination

<u>Element added</u>	<u>Amount added, ppm</u>	<u>Ga present, ppm</u>	<u>Ga found, ppm</u>
-	-	5.7	5.7
Fe	100	5.7	5.9
Al	100	5.7	5.7
Cu	50	5.7	5.9
Ni	50	5.7	5.8
Th	100	5.7	5.8
W	100	5.7	5.9
Si	50	5.7	5.6

The amount of foreign element added in each case was appreciably more than is usually found in the samples for which this procedure is intended, and since the variation was less than the precision claimed for the method, it was concluded that any interference was negligible.

Since no high-purity americium was available for the preparation of knowns, a study was made of the analytical results from a series of twenty-six samples analyzed by this method for gallium, and radio-chemically for americium. A complete lack of correlation between the gallium and americium leads to the conclusion that americium could not cause a serious interference in the procedure.

#### APPARATUS AND REAGENTS

##### Apparatus

Flasks, volumetric, 25-ml.

Funnels, separatory, 60-ml.

Pipets, volumetric, 5-ml. and 0.5-ml.

Spectrophotometer, Beckman Model DU, with 1-cm. Vycor cells.

##### Reagents

Gallium solution, standard. Dissolve a weighed portion of pure metallic gallium in hydrochloric acid and dilute with 6.5 N hydrochloric acid to contain 1  $\mu$ g. of gallium per ml.

Mixed solvent, Mix 3 parts of Eastman White Label chlorobenzene with 1 part of reagent grade carbon tetrachloride.

Plutonium metal, Gallium-free plutonium metal was prepared from electrolytically refined metal by passage through a column of Dowex 1 resin.

Rhodamine B solution. Dissolve 0.5 gram of solid reagent in 100 ml. of 6.5 N hydrochloric acid. Filter.

Titanous chloride, solution, 20%, reagent grade.

### RECOMMENDED PROCEDURE

Place a weighed portion (about 1 gram) of the plutonium sample in a 25-ml. volumetric flask and add 2 ml. of concentrated hydrochloric acid to dissolve the metal. Make the flask to volume with 6.5 N hydrochloric acid. Place a 5-ml. aliquot of the sample solution in a 60-ml. separatory funnel and add 2 drops of the titanous chloride solution and 0.5 ml. of the rhodamine B solution. Mix thoroughly. Add 5 ml. (measured accurately) of mixed solvent and shake vigorously for 1 minute. Allow 10 minutes for the phases to separate. Drain the organic phase into a spectrophotometer cell after discarding a small portion which might contain a drop or two of aqueous solution. Measure the absorbance at 562  $\mu$  against a reagent blank. If the absorbance reading is more than 0.700 (about 2.5  $\mu$ g. of gallium) repeat the determination with a smaller aliquot of the sample solution, keeping the volume of the aqueous phase at 5 ml. by adding 6.5 N hydrochloric acid as needed. Compare the absorbance to a calibration curve prepared by analyzing known mixtures of plutonium and gallium containing 0.5, 1.0, and 2.0  $\mu$ g. of gallium. It is important to always adjust the volume of the aqueous phase to 5 ml. with 6.5 N hydrochloric acid.

### RELIABILITY

Using this procedure, several series of analyses were made on known solutions. Plutonium metal was dissolved, purified by ion exchange, and combined with standard gallium solution to make 0.5 to 100 parts per million of gallium with respect to the plutonium. The results are shown in Table II. It will be noted that down to a concentration of 5 parts per million the relative standard deviation is quite constant at about 2 percent of the gallium present. At concentrations lower than 5 parts per million the reproducibility is about 0.1 part per million.

Table II

## Recovery of Gallium from Known Solutions

<u>No. of determi- nations</u>	<u>Ga added, ppm</u>	<u>Ga found average, ppm</u>	<u>Standard deviation, ppm</u>
6	100	98	2
6	50	48.9	1
6	25	24.4	0.6
6	10	9.9	0.2
6	5	5.0	0.1
6	1	1.00	0.04
6	0.5	0.58	0.08

The plutonium used in this study had been previously analyzed and reported to contain less than 20 parts per million of gallium. Analyzed by this procedure, it was found to contain 10.2 parts per million. After purification by ion exchange it still seemed to contain 0.1 part per million when measured against a reagent blank. It was not determined whether this was actual gallium still present or was due to extraction of a slight amount of plutonium.

Several recent high-purity plutonium metal samples which were analyzed by the old method and reported to contain less than 20 parts per million of gallium have been reanalyzed by this method and found to contain only a few tenths of 1 part per million.

Further extension of the sensitivity of this method is probably possible. Chlorobenzene alone might be used as the solvent in the extraction if sufficient plutonium were used to increase the density of the water phase to a point at which the chlorobenzene would separate well on top. Also,



the sensitivity of the final measurement might be increased<sup>(3)</sup> by measuring the fluorescence instead of the absorbance of the extracted complex.

#### SUMMARY

A spectrophotometric method using rhodamine B as the color forming agent has been modified and applied to the determination of trace amounts of gallium in plutonium metal. The method as developed is rapid, precise, and very sensitive. The time required for an analysis is about one-fourth of that needed for the less sensitive oxine method with an ion exchange separation. The sample is dissolved in hydrochloric acid, the reagents are added, and the chlorogallate-rhodamine B complex is extracted into a mixture of chlorobenzene and carbon tetrachloride where its absorbance is measured. No preliminary separation is needed, as none of the usual contaminants of electrorefined plutonium metal interfere. The standard deviation is about 2 percent relative in the concentration range 5 to 100 parts per million and about 0.1 part per million where the gallium content is less than 5 parts per million.

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