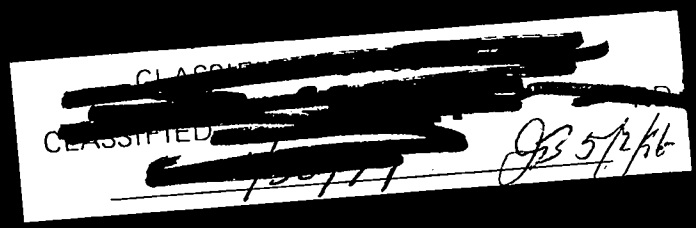
LA--425
Copy 13



[redacted] UNCLASSIFIED

LA-425

[redacted]

October 10, 1945

This document contains 10 pages

MICROGRAVIMETRIC DETERMINATION OF GALLIUM IN PLUTONIUM-GALLIUM ALLOYS

WORK DONE BY:

L. P. Pepkowitz

REPORT WRITTEN BY:

L. P. Pepkowitz

[redacted]

ABSTRACT

A microgravimetric procedure for the determination of gallium in gallium-plutonium alloys is presented. The gallium is separated from plutonium by extraction of chlorogallic acid with isopropyl ether. The gallium is re-extracted from the ether by shaking with water and is determined gravimetrically as the 8-hydroxyquinolate, $Ga(C_9H_6ON)_3$.

[redacted]

MICROGRAVIMETRIC DETERMINATION OF GALLIUM IN PLUTONIUM-GALLIUM ALLOYS

The use of 8-hydroxyquinoline as a reagent for the determination of gallium was first suggested by Moser and Brukl[1]. The procedure was improved and applied to indium as well as gallium by Geilmann and Wrigge[2]. Gallium has also been determined electrolytically[3], potentiometrically by titration with ferrocyanide[4], and as the oxide after precipitation with tannin[5]. A colorimetric method has been described[6], and the use of cupferron has been advocated[7].

In the present case, a method which would permit the determination of 1-mg quantities of gallium with an accuracy of 5 percent or better was required. The gravimetric 8-hydroxyquinoline procedure, while it had not been applied to amounts of gallium below 3 mg[2], was selected for study since it seemed likely that this procedure could be made to meet the requirements. An extremely good factor is involved (0.1389) and the precipitate is of constant composition and can be weighed directly as $Ga(C_9H_6ON)_3$. The use of the 2-bromo-8-hydroxyquinoline has been advocated[8]. Results obtained with this reagent were not satisfactory. High recoveries were obtained because of the relative insolubility of the reagents. In addition, rigorous conditions for the quantitative precipitation are required which make the procedure difficult for routine work.

---

1) Moser, L., and Brukl, A. 51, 75 (1929)
2) Geilmann, W. and Wrigge, Fr. W., Z. Anorg. Allem. Chem. 209, 129 (1932)
3) Reichel, E., Z. Anal. Chem. 87, 321 (1932)
4) Kirshman, H. D., and Ramsey, J. R., J. Am. Chem. Soc. 50, 1632 (1928)
5) Moser, L., and Brukl, A. Monatsh 50, 181 (1928)
6) Willard, H. H., and Fogg, H. C., J. Am. Chem. Soc. 59, 40 (1937)
7) Moser, L., and Brukl, A., Monatsh 51, 329 (1929)
8) Gastinger, E., Z. Anal. Chem. 120, 373 (1944)

Reagents Required

1. Isopropyl ether, shake with alkaline permanganate and redistill.
2. Mercury, c.p.
3. Hydrochloric acid, 12 N, standardized.
4. Sodium acetate solution, 20 per cent.
5. Alcoholic 8-hydroxyquinoline, 5 per cent.
6. Ammonium hydroxide, conc.
7. Phenolphthalein indicator.

Discussion

In order that quantitative results may be obtained in the extraction procedure, the acidity must be carefully adjusted to 7.3 N. At this normality the distribution ratio of gallium between isopropyl ether and water is at a maximum[9]. On either side of this value, the distribution ratio falls off abruptly. In order to obtain this normality, the following factors must be taken into consideration.

1. Hydrogen ion used in the solution of the metal.

$$2\ Pu + 6\ H^{+} \rightarrow 2\ Pu^{+++} + 3\ H_2$$

The equivalent weight of Pu is therefore 239/3 = 79.7. If W is the weight of the sample in mg and N is the normality of the HCl, the volume in ml of acid necessary to dissolve the metal is W/(79.7)(N).

2. The volume of N-normal HCl necessary to make 1 ml of 7.3 N HCl is 7.3/N ml.

The total acid necessary, therefore, to dissolve the metal sample and produce 1 ml of 7.3 N HCl is

$$V_a = \left[\frac{W}{(79.7)(N)} + \frac{7.3}{N}\right] ml$$

9) Batchelder, M. C., Nachtrieb, N. H. and Weidig, R. S., LA-417 (1945)

and the water required for 1 ml of solution is

$$V_w = (1.00 - V_a) \text{ ml}$$

A number of approximations have been made in these calculations. For example, the volume change on dissolving the metal is neglected, V_a and V_w are assumed to be additive, and the sample weight is not corrected for the gallium content. However, the results of many determinations have indicated that these corrections can be neglected.

The most common interfering element found in the alloy is iron. This, if present in the solution in the oxidized state, will be extracted as ferric chloride. Ferrous chloride, however, is not extracted by isopropyl ether. On this basis, iron is prevented from interfering in the determination by shaking the solution vigorously with elemental mercury before and during the ether extraction.

$$Fe^{+++} + 2Hg^{o} \rightarrow Fe^{++} + Hg_2^{++}$$

Table I gives some typical recoveries of gallium by the proposed method. An indication of the precision to be expected is given in Table II. The data contained in Table II were obtained from actual runs on unknowns and indicate the precision obtained under regular operating conditions.

Procedure

1. Extraction and re-extraction.

Extreme care should be used in handling and dissolving plutonium samples. See LA-416 for precautions and hazards involved.

Calculate for a metal sample containing approximately 1 mg of gallium,

the volume of acid required to dissolve the metal and to produce, upon the addition of a calculated volume of water, 1.00 ml of solution 7.3 N in HCl. Pipet the calculated volume of water into the shaking tube and drop in the metal sample. Add the calculated volume of acid slowly from a 1-ml buret. The reaction will start immediately upon the addition of the first drop of acid. Keep the tube inclined to prevent the possibility of spray emerging from the tube. If metal turnings or filings are used, immerse the shaking tube in an ice-water bath while adding the acid to slow down the vigorous reaction that will result.

When the sample has dissolved and the solution is clear, add 4 drops of mercury to reduce the iron present and stopper the tube with a well greased (silicone stopcock grease) ground glass stopper. Shake for five minutes.

Remove the tube from the shaking machine and add 1 ml of isopropyl ether, being careful to wash down the stopper with the first portion added. Re-grease the stopper if necessary and shake for twenty minutes.

After shaking, allow the Pu-Hg layer to separate from the ether and swirl the tube gently so that a sharp separation takes place. Transfer the ether layer to a second shaking tube by means of the transfer pipet. Wash the pipet by drawing up an equal volume of ether and add the ether washings to the second tube. The same pipet should be used for any given sample through all the subsequent operations.

Add 1 ml of isopropyl ether to the first tube, stopper (greasing stopper, if necessary), and shake for another twenty-minute interval. Transfer the ether layer to the second tube, add a small quantity of ether to the first tube, invert several times to wash the sides of the tube and transfer this ether layer to the second tube.

Using the same pipet, add 5 ml of water to the second tube. Add a glass bead, stopper with a well-greased stopper, and shake for ten minutes.

Transfer the lower aqueous layer by means of the pipet to a 30-ml beaker containing 5 ml of 20 percent sodium acetate, 1 drop of concentrated ammonium hydroxide and 1 drop of phenolphthalein indicator. While the pipet is passing through the upper ether layer, expel air through the pipet so that no ether is permitted to enter. Fill the pipet with water and add the washings to the beaker. Repeat the re-extraction procedure with another 5 ml of water.

After transferring the second 5 ml of water to the beaker, add a small quantity of water to the first shaking tube, stopper, and invert several times to wash the sides of the tube. Add these washings to the beaker as before. The total volume of solution in the beaker should now be between 15 and 20 ml.

2. Precipitation

Cover the beaker with a watch glass and heat below the boiling point until most of the pink color of the indicator has disappeared. Wash down the cover glass and add, dropwise, 15 drops of the alcoholic 8-hydroxyquinoline (5 percent) waiting between drops for the yellow precipitate to form. Place on the steam bath and digest for one hour.

3. Transferring, Washing and Drying of the Precipitate.

Transfer the precipitate to a tared 10-ml platinum Munroe crucible using hot water to wash out the precipitate. Transfer as much as possible by washing before using a policeman. Extreme care must be taken in the transfer since the precipitate is difficult to handle because of its tendency to crawl and become finely dispersed. Wash the precipitate in the crucible 3 times with hot water. Inspect the beaker with a magnifying glass to see that all the

precipitate has been transferred.

Dry in an electric oven at 120°C for one hour. Cool and weigh as $Ga(C_9H_6ON)_3$ F = 0.13885.

TABLE I.

RECOVERIES OF GALLIUM BY THE PROPOSED METHOD

Ga taken mg	Ga found mg	Percent Recovered
0.811	0.808	99.63
	0.830	102.34
	0.802	98.89
	0.798	98.40
	0.836	103.08
1.380	1.377	99.78
	1.392	100.87
1.490	1.491	100.07
	1.490	100.00
	1.507	101.14
	1.492	100.13
	Average	100.39

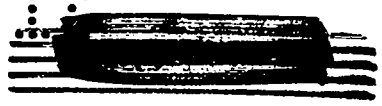


TABLE II

DUPLICATE RESULTS OBTAINED FROM ACTUAL ANALYSES INDICATING THE PRECISION OF THE METHOD

Sample No.	Gallium percent	Deviation of Duplicates percent
7140	1.08 1.04	3.85
7144	1.11 1.04	6.73
7155	1.01 1.04	2.97
7159	1.09 1.08	0.93
7177	1.07 1.08	0.93
7241	1.09 1.11	1.83
7131	0.65 0.65	0
7267A	0.91 0.91	0
7267B	0.95 0.93	2.15
7276	0.97 0.99	2.06
7298	0.78 0.81	3.85
7273	0.97 1.01	4.12
7154-C-3	1.04 0.99	4.92
7140	1.08 1.04	3.84

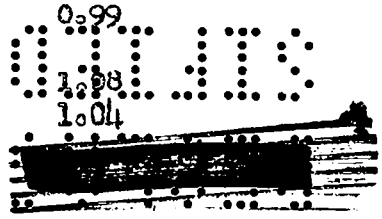


TABLE II (continued)

Sample No.	Gallium	Deviation of Duplicates
7161	1.03 1.07	3.88
7205	1.05 1.09	3.81
	Average.....	2.88