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THE DETERMINATION OF GALLIUM
IN PLUTONIUM BY ATOMIC ABSORPTION

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IN PLUTONIUM BY ATOMIC ABSORPTION

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June 7, 1968

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THE DETERMINATION OF GALLIUM
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A. G. Miller
Atlantic Richfield Hanford Company

Gallium in plutonium has been determined for many years by a fluorimetric measurement of the gallium 8-quinolinolate in chloroform.¹ Since the precision routinely obtainable by this method has become somewhat unsatisfactory (between four and five percent relative standard deviation at the 95 percent confidence level), a more precise substitute method was desired. The most promising method appeared to be atomic absorption with a maximum precision obtainable of 0.2 percent relative.² A Perkin-Elmer model 303 atomic absorption spectrophotometer had recently been placed in service. The installation had been specifically designed so that radioactive, including plutonium, samples could be analyzed.

A suitable separation, preferably by solvent extraction, of the gallium from most of the plutonium was necessary. Besides the 8-quinolinol-chloroform method mentioned above, a literature search suggested several other promising methods. Nachtrieb and Fryxell³ extracted gallium from hydrochloric acid systems with both ethyl ether and isopropyl ether. Good and Holland⁴ investigated the extraction of gallium and indium from chloride systems with long chain alkyl amines and quaternary salts in toluene. They measured extraction coefficients approaching 1,000 for gallium. Seeley and Crouse⁵ conducted a similar investigation of 58 elements but with diethylbenzene as a diluent. They obtained an extraction coefficient for gallium of 10,000 with tricapryl monomethyl ammonium chloride (Aliquat 336*). Orlandini, Wahlgren, and Barclay⁶ studied the distribution of 45 elements between 83 percent 2-ethylhexanol - 17 percent petroleum ether and hydrochloric acid solutions. An optimum gallium extraction coefficient of between 100 and 1,000 was obtained. Gallium is also quantitatively extracted from hydrochloric acid media by methyl isobutyl ketone as described by Goto, Kakita, and Ichinose.⁷

Since the desired method of determining gallium was by an atomic absorption measurement on the organic phase, a number of limitations were imposed upon the choice of an extraction system. These are important because the organic solvent must have suitable burning characteristics in a laminar flow burner which requires a very quiet flame. This requirement eliminates chloroform and carbon tetrachloride from consideration (including the 8-quinolinol-chloroform method) since they do not burn in the air-acetylene flame and do disturb the flame when a standard burner head is used. The solvent must also have a low viscosity to provide adequate aspiration rate and thus sensitivity, but the viscosity must not be too low or a fuel-rich flame, atom dilution, and perhaps light absorption by the flame will result. The final consideration is that the solvent be such that a stable signal from the element of interest is obtained.

* Aliquat 336 is a tradename of General Mills, Inc.

Considering these requirements, an extraction utilizing Aliquat 336, which was being used in other applications, was viewed as being the most promising.

EXPERIMENTAL

Equipment

A Perkin-Elmer 303 atomic absorption spectrophotometer equipped with a recorder readout accessory and a Brown Elektronik variable-span recorder was adopted for analyzing plutonium-bearing solutions by enclosing the Perkin-Elmer laminar flow burner in a specially designed fume hood. A Westinghouse gallium hollow cathode lamp was used.

Reagents

All chemicals and solvents were reagent grade. The Aliquat 336 (tricapryl monomethyl ammonium chloride with the carbon chains a mixture of C₈ and C₁₀) was used as received from the manufacturer. The average molecular weight is 442.

The relative sensitivity of the various resonance wavelengths was determined for the Westinghouse lamp in the Perkin-Elmer instrument using a 91.4 mg/l Ga standard and a seven angstrom spectral band width. (See Table I.)

TABLE I
Gallium Analytical Lines

<u>Wavelength</u>	<u>Sensitivity</u> ⁸	<u>P.E. 303 Gain</u> <u>Setting (Relative)</u>	<u>% Absorption</u> <u>91.4 ug/ml Ga</u>
2874	2.3 ppm	7.0	29.3
2944	2.5 ppm	6.7	33.0
4033	6.2 ppm	6.6	14.5
4172	4.7 ppm	6.4	23.5

With this particular combination of equipment, the 2944 angstrom line is seen to be the most sensitive. This line also requires less photomultiplier gain and subsequently a lower noise level is obtained.

In choosing a solvent system for the Aliquat 336, the first approach was to find one compatible with the standard Perkin-Elmer single slot burner head that was available. Iso-amyl alcohol (iAA1) was found to perform well but the sensitivity was low due to a high viscosity. Consequently, the alcohol was diluted by 25 percent with xylene which provided a 38 percent increase in sensitivity. When this combination of solvents was used to make a five percent (by volume) solution of Aliquat 336

(approximately 0.1M), extraction coefficients for gallium approaching 1,000 were obtainable under optimum conditions. Although the ethers have extremely low viscosities, they are unsuitable for AAS because they produce a flame too fuel-rich and too unstable to be used.

A Boling burner head (three slot head) was purchased to produce greater sensitivity and allow less viscous and more volatile solvents such as xylene and methyl iso-butyl ketone to be used. Methyl iso-butyl ketone (MIBK), one of the best organic diluents for atomic absorption, was investigated both from the standpoint of use as a diluent for Aliquat 336 and a primary extractant.⁷ The extraction of 0.9 g/l Ga from 6M HCl produced an extraction coefficient of 80. The sensitivity of gallium in this solvent was greatly increased, but the signal begins with a sharp spike and rapidly decreased (Figure I). Conversely, the iso-amyl alcohol (iAAI) and xylene solution produces an increasing signal with the Boling head. Different ratios of MIBK to iAAI were compared, each being spiked with equal quantities of gallium and aspirated using the Boling head. The scan produced is shown in Figure I. The solvent producing the best signal is obviously the 50/50 mixture. Sensitivity is comparable with that of 100 percent MIBK.

The problem arising with the 50/50 mixture is graphically demonstrated in Figure II. After contact of an organic solution containing gallium and iAAI with 6M HCl, the signal dropped to about 30 percent of its original value with no measurable loss of gallium to the aqueous phase. No explanation is presently available. Due to this effect, the use of 100 percent MIBK as a solvent for Aliquat 336 was developed.

The distribution coefficients for 0-100 percent MIBK in iAAI were measured. This relationship is graphed in Figure III. Extraction coefficients greater than 4,000 could not be measured by AAS.

The distribution coefficients of 100 percent MIBK (Figure IV) and five percent Aliquat 336 in MIBK were determined for various concentrations of hydrochloric acid. The distribution coefficients for five percent Aliquat 336 in MIBK were too high to measure, being in excess of 5,000. A further attempt to measure the distribution coefficient was made by contacting an equal volume of this organic with 12.8 g/l Ga in 6M HCl. The extraction coefficient was still too high to measure, being greater than 20,000.

The effect of impurities that might be present and interfere with the extraction and subsequent determination of gallium was studied for the five percent solution of Aliquat 336 in MIBK. Tables II and III list the extraction coefficients of these elements including plutonium, the principle element of the sample. Iron and uranium, the only elements to extract significantly, are seldom present in more than trace quantities of a few hundred parts per million. Thus, any interferences observed in this study would be much reduced if it

should occur in a sample. All gallium extraction coefficients in the presence of these impurities were shown to be greater than 2,000. The extractable impurities do have an effect on the AAS signal of the extracted gallium as shown in Figure V. This effect should be negligible because iron and uranium levels in the usual sample are on the order of one percent of the concentrations studied here.

TABLE II
Distribution Coefficients of Common Metallic Impurities

<u>Al</u>		<u>Ca</u>		<u>Fe(III)</u>		<u>Mg</u>	
<u>mg</u>	<u>D</u>	<u>mg</u>	<u>D</u>	<u>mg</u>	<u>D</u>	<u>mg</u>	<u>D</u>
0.93	0.04	0.80	2×10^{-4}	1.12	>50	0.77	0.04
1.87	0.05	1.59	4×10^{-4}	2.24	>50	1.55	0.02
4.67	0.07	3.98	6×10^{-4}	5.60	>50	3.87	0.01

TABLE III
Distribution Coefficients of U and Pu

<u>U(VI)</u>		<u>Pu(III)</u>	
<u>mg</u>	<u>D</u>	<u>mg</u>	<u>D</u>
4.65	>20	7.42	2×10^{-3}
9.30	>40		
23.3	5.2		

PROCEDURE

Samples are diluted to volume with 6M HCl, five percent hydroxylamine-hydrochloride. One-half ml of sample is added to 1.5 ml of 6M HCl in an 18 ml vial. Exactly 2.0 ml of five percent Aliquat 336 in MIBK is added and stirred vigorously for three minutes. After the phases separate, the organic phase is analyzed by AAS. The following atomic absorption instrumental conditions are used:

TABLE IV
Instrumental Conditions

Boling burner head*
 Fuel: 2 l/min acetylene
 Oxidant: 18 l/min air
 Lamp Current: 16 ma
 Recorder Response Time: 15 seconds minimum
 aspiration time

* The Boling burner head must be allowed to thermally equilibrate before beginning the AAS measurements.

The sample and standards were aspirated until the signal reached a maximum. Two standards for each four samples are prepared by extracting approximately 180 and 250 ug of gallium each from four ml of 6M HCl into four ml of the organic extractant producing 45 and 62 ug/ml standards. The order of aspiration used was 45 ug/ml standard, one sample, and 62 ug/ml. This continuous restandardization method produces the best precision.

RESULTS AND DISCUSSION

The extraction of gallium by five percent Aliquat 336 in methyl iso-butyl ketone has been demonstrated to be quantitative for any conditions encountered or likely to be encountered in this application. Strongly extracted impurities do not interfere with the gallium extraction. However, caution must be exercised when the extractable impurities exceed the gallium concentration (Figure V). This effect is probably produced by the nebulization efficiency decreasing as the concentration of extractable elements increases. The decreasing nebulization efficiency reduces the rate of atom production in the flame and hence the signal.

At least two gallium complexes are possible because of the use of two organic extractants of gallium. Aliquat 336, a quaternary amine chloride, forms an organometallic salt that may be formulated as follows:

The methyl iso-butyl ketone complex may be formulated as:

The following analytical data was collected for calculation of the precision possible for this method.

TABLE V
Analytical Results

Sample	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
g/l Ga	0.222	0.108	0.110	0.235
	0.227	0.122	<u>0.104</u>	0.245
	<u>0.232</u>	<u>0.111</u>		0.240
				0.231
				0.245
				<u>0.241</u>
Average	0.227 g/l	0.114 g/l	0.107 g/l	0.240 g/l
Average				
Deviation	± 0.003 g/l	± 0.006 g/l	± 0.003 g/l	± 0.004 g/l

The standard deviation calculated from these results with nine degrees of freedom is 0.0059 g/l or 2.5 percent relative. At the two sigma level, the

relative deviation is 0.013 g/l or 5.4 percent. The conclusion that must be reached is that because the precision is not as good as that possible with the fluorimetric method, the fluorimetric determination will be retained.

FIGURE-II

Distribution Coefficient vs. % MIBK in Solvent

Effect of Extracted Fe(III) and U(VI) on the 62 ug/ml Ga AAS Signal

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