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SPECTROPHOTOMETRIC DETERMINATION OF ALUMINUM IN PLUTONIUM-ALUMINUM ALLOYS

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Abstract

The method described involves the spectrophotometric determination of aluminum in plutonium-aluminum alloys following the separation of the excess plutonium and small amounts of iron from the aluminum by extraction of the cupferrate into chloroform. The aluminum concentration is determined on a Beckman Model DU spectrophotometer by measuring the optical density of the aluminum 8-hydroxyquinolate in chloroform at 385 millimicrons (mμ). A correction is made for the small amount of plutonium which carries through the cupferron extraction and forms plutonium 8-hydroxyquinolate along with aluminum. This is done by reading the optical density at 500 mμ and 650 mμ and using these values to correct the 385 mμ optical density reading.

1. Introduction

Several methods have been proposed for the determination of aluminum in various alloys. A critical evaluation of these methods is given by Parks and Lykken[1]. In the present case, it was desired to determine aluminum in the presence of a large excess of plutonium, thus necessitating a preliminary separation. The problem may then be divided into two separate operations: (a) preliminary removal of plutonium, and (b) determination of aluminum in the remaining solution.

Two methods were considered for the removal of plutonium; namely, precipitation with oxalic acid and precipitation (or extraction) with cupferron[2,3]. The oxalate precipitation approach had to be abandoned when it was found that the excess oxalate interfered by complexing the aluminum. A direct extraction with cupferron was unsatisfactory since part of the aluminum was removed with the plutonium. It was found experimentally, however, that a quantitative separation could be made by first precipitating the plutonium with an aqueous solution of cupferron and then shaking with chloroform to simultaneously dissolve and extract the plutonium cupferrate, and extract any coprecipitated aluminum back into the aqueous layer. The present method is based on this procedure.

Because of the small quantities of sample that must be used, a colorimetric method was considered most practical for the determination of aluminum. The classic method employing aurin tricarboxylic acid was tried, but impure reagent caused erratic results. Other investigators[1] had noted this difficulty with the reagent. Recrystallization of the reagent gave no improvement in results; consequently, no further work was done on this method.

There are numerous references in the literature[1,2,4,5,6,7,8,] to the colorimetric determination of aluminum as the aluminum 8-hydroxyquinolate in chloroform. The color produced is independent of time and temperature, and Beer's law is obeyed in the range 0.2-1.2 micrograms Al/ml[5]. Further investigation of this method proved it to be well suited for the present determination.

2. Conclusions

Aluminum, in the range of 0-600 micrograms, may be determined in the presence of 50 mg of plutonium by removing most of the plutonium with cupferron, forming the aluminum complex of 8-hydroxyquinoline, and extracting this complex into chloroform. The optical density of the chloroform solution is read at 385 mμ, and then at 500 mμ and 650 mμ to correct for any plutonium that may still be present. At the 95% confidence level, the precision is 5% in the vicinity of 500 micrograms of aluminum.

3. Apparatus

The cupferron extractions are conveniently carried out in 125-ml separatory funnels and the aluminum 8-hydroxyquinolate complex may be formed in 250-ml glass-stoppered bottles. All optical density measurements may be taken on a Beckman Model DU spectrophotometer using 1-cm Corex cells. The buffered 8-hydroxyquinoline solutions and the chloroform are added to the 250-ml bottles from 25-ml and 100-ml Machlett automatic burets respectively. After development of the color, a portion of the chloroform layer containing the green aluminum complex is added to the 1-cm Corex cells with a transfer pipet.

4. Reagents

a. Buffered 8-hydroxyquinoline solution:

0.1 g recrystallized[†] 8-hydroxyquinoline, 10 ml

[†] The 8-hydroxyquinoline is recrystallized as follows: Ten grams of 8-hydroxyquinoline (Baker) are dissolved in 100 ml of warm 95% ethanol. To this solution is added with stirring 400 ml of distilled water. The solution is filtered through a fritted glass filter and the crystals are washed with distilled water, partially dried by suction, and then dried in an oven at 55°C for 8 hours.

ethyl alcohol, 15 ml water, 2.1 g sodium acetate per sample.

b. Cupferron solution:

0.10 g ammonium cupferrate (Baker) per 1 ml water. This solution should be prepared fresh daily.

c. Iron reagent:

3.0 g $FeCl_3$ per liter.

d. Chloroform, reagent grade.

e. Toluene, reagent grade.

5. Procedure

A 50 ± 5 mg sample from a 1% aluminum-99% plutonium alloy is added to a 125-ml separatory funnel and dissolved in 1 ml of concentrated HCl. After the sample has dissolved, 25 microliters of the iron reagent is added to the separatory funnel and rinsed down with 1-2 ml of water. Six ml of the freshly prepared cupferron reagent is quickly added with swirling of the separatory funnel. The separatory funnel is shaken vigorously for exactly 2 minutes. Approximately 15 ml of chloroform is quickly added and the funnel is shaken vigorously for 1 minute. The chloroform layer is discarded, and 10 ml of fresh chloroform is added to the separatory funnel for another 15-second extraction. This chloroform is discarded and 15 ml of toluene is added for a final 15-second extraction of the aqueous layer. After allowing the layers to separate, the aqueous layer is drained into a 250-ml bottle; and the remaining toluene is washed once with 10 ml of water, which is added to the bottle.

Twenty-five ml of the buffered 8-hydroxyquinoline reagent is added to the bottle, followed by 100 ml of chloroform. The bottle is stoppered, shaken vigorously for 30 seconds, and allowed to stand at least 30 minutes, or if convenient, overnight.

After the layers have separated, a pipet is immersed through the aqueous layer into the chloroform layer and 3 ml of the chloroform layer is carefully removed and transferred to a 1-cm Corex cell. The optical density is measured at 385 mμ, 500 mμ, and 650 mμ, using a reference blank containing 25 ml of buffered 8-hydroxyquinoline reagent, 100 ml of chloroform, 65 microliters of concentrated HCl, and 15 ml of water. The necessary cell corrections are made at the three wave lengths and the net optical density at 650 mμ is multiplied by 1.4. This value is subtracted from the optical density at 500 mμ. The resulting corrected value at 500 mμ is multiplied by a factor of 7.5 to get the contribution it gives to the optical density at 385 mμ. This value is subtracted from the corrected reading at 385 mμ to get the new optical density due to aluminum 8-hydroxyquinolate. The weight of aluminum corresponding to this optical density is obtained from a standard curve prepared by using known amounts of aluminum, and the percent aluminum in the metal alloy is calculated.

6. Experimental

5.1 Standard Curve

The standard curve shown in Fig. 1 was obtained by determining the mean result of at least six samples at each of six different aluminum contents ranging from 0 to 600 total micrograms aluminum. Each sample contained 50 mg of plutonium, the designated amount of aluminum, 75 micrograms of iron, and 1 ml of concentrated HCl. The optical density of each sample was determined at wave lengths of 385 mμ, 500 mμ, and 650 mμ. Necessary corrections, as explained in the procedure, were made on the 385 mμ reading and a statistical analysis was made on the results. The slope and y-intercept of the curve, as determined by the least squares method, were determined to be 0.00207 O.D. units/microgram Al and 0.055 O.D. units respectively. From a statistical analysis of 41 samples, the standard deviation of the regression of x on y was found to be constant at 11.51 micrograms. Therefore, the results for samples containing 500 micrograms of aluminum may be expected to vary by no more than 5% at the 95% confidence level. The large y-intercept of 0.053 O.D. units may be explained on the basis that the optical densities of all samples were determined using a reagent blank which was not carried through the cupferron extraction and contained only acid, 8-hydroxyquinoline, and chloroform. Synthetic samples containing no aluminum were carried through the procedure and had an average corrected optical density of 0.058 O.D. units when compared with the above reagent. The difference between the 0.053 y-intercept and the 0.058 reading was found to be statistically insignificant.

5.2 Effect of Foreign Ions

For the type of sample discussed in this report, only the interference due to iron and plutonium need be considered. To determine the effect of iron, varying amounts of ferric chloride were added to the samples which were then carried through the standard procedure. The results are given in Table I.

TABLE I
EFFECT OF ADDED IRON

Al Added (Micrograms)	Fe Added (Micrograms)	Net O.D.[≠]	Al Found (Micrograms)	Standard Deviation (Micrograms)
250	0	0.395	164	
250	0	0.405	169	
250	0	0.599	262	
250	0	0.491	210	
250	0	0.606	268	49
250	30	0.590	257	
250	75	0.605	265	
250	75	0.606	268	
250	75	0.609	269	
250	75	0.590	257	6
250	150	0.597	261	
250	300	0.579	252	
500	0	0.781	350	
500	0	0.705	312	
500	0	1.139	522	
500	0	0.569	249	
500	0	1.152	530	
500	0	1.144	526	126
500	75	1.14	523	
500	75	1.17	537	
500	75	1.13	518	
500	75	1.16	532	
500	75	1.19	546	
500	75	1.22	560	
500	75	1.18	542	14

[≠] Optical density readings are uncorrected for plutonium interference.

Iron in amounts up to 300 micrograms causes no interference; in fact, better reproducibility was obtained from samples to which iron was added (see Table I). Presumably, the iron suppresses the cupferron extraction of aluminum; even though the iron is itself extracted, as will be shown later. For this reason, it is thought advisable to add 75 micrograms of iron to each sample before the cupferron extraction.

In order to completely remove the interfering plutonium, it is necessary to perform the cupferron extraction at a pH that will permit quantitative removal of the plutonium without any extraction of aluminum. Reinschreiber et al[3]. report that the optimum normality of acid for this separation is 0.82; consequently, a normality of 0.80-0.85 was selected for the initial investigation described below.

Synthetic samples containing 500 micrograms of aluminum were prepared and carried through the cupferron extraction as explained in the procedure. To determine the amount of plutonium remaining in the aqueous layer, 100-microliter samples of this layer were mounted on counting discs and the total alpha count determined. The data are given in Table II.

TABLE II
CUPFERRON EXTRACTION OF PLUTONIUM

Mg Pu Originally Present	Mg Pu in Aqueous After Extraction	%Pu Extracted Into Organic Layer	Optical Density
50	3.38	93.2	2.00
50	0.180	99.6	1.08
50	0.129	99.7	1.11
50	0.120	99.8	1.01
50	0.463	99.1	1.14
50	0.456	99.1	1.11

The amount of plutonium remaining in the aqueous layer varies considerably and was far greater in the first sample than in the others. This sample formed a brownish color upon addition of the reagent and had a much higher optical density than the solutions containing less plutonium. In order to eliminate this occasional interference, it was necessary to devise a scheme for correcting the optical density values.

Spectrophotometric curves of optical density versus wave length for the aluminum, plutonium, and iron complexes of 8-hydroxyquinoline are shown in Fig. 2. Examination of these curves reveals the following:

1. The plutonium 8-hydroxyquinolate has an absorption maximum at the same wave length as the aluminum 8-hydroxyquinolate maximum, namely 385 mμ.
2. At 500 mμ, the optical density of the aluminum 8-hydroxyquinolate is essentially zero, while that of the plutonium complex is approximately 2/15 of the value at 385 mμ. The

iron complex has approximately the same optical density at both wave lengths.

3. At 650 mμ, only the iron complex has an optical density, this being about 0.7 of its value at 500 mμ.

By reading all samples at these three wave lengths, it is possible to eliminate the interference due to small amounts of plutonium. By subtracting the reading at 650 mμ (generally very small) from the reading at 500 mμ, the optical density at 500 mμ due to plutonium can be obtained. This value, when multiplied by 7.5, gives the optical density of the plutonium complex at 385 mμ; and subtraction of this value from the experimental optical density at 385 mμ gives the optical density of the aluminum 8-hydroxyquinolate alone. If there is an appreciable reading at 650 mμ, this reading should also be subtracted from the 385 mμ reading to correct for the iron absorption at 385 mμ. Usually this correction is unnecessary. If the plutonium were present in amounts greater than 5 or 6 mg, it could contribute an appreciable optical density reading at 650 mμ which would cause a false correction if subtracted from the 500 mμ optical density value. However, if 5 mg of plutonium were present after the cupferron extraction, it would be impossible to determine the optical density of the chloroform layer because of the dense brown color of the plutonium 8-hydroxyquinolate. Thus, the correction is valid for any sample whose optical density can be determined.

At one time it was thought feasible merely to read the samples at 385 mμ and 500 mμ and discard those samples that had appreciable readings (optical density over 0.010) at 500 mμ. Investigation showed, however, that this method, when applied to the standard curve data, gave a regression curve with a standard deviation of 21.76 micrograms, almost twice that of the corrected curve. Furthermore, the samples re-run ration would be much higher because of the necessity of discarding values.

5.3 Effect of Extraction Time with Cupferron

In order to determine the optimum extraction time for the cupferron, a series of samples was prepared containing 500 micrograms of aluminum, 1 ml of concentrated HCl, 75 micrograms of iron, and 50 mg of plutonium. These samples were extracted for varying times with 6 ml of cupferron solution and chloroform. The data, given in Table III, shows the optimum time of extraction is 2-3 minutes.

TABLE III
EXTRACTION TIME

Shaking Time (Min)	Optical Density Total	Optical Density Due to Al[≠]	Optical Density Error	Mg Pu Present Before Extraction	Mg Pu Present After Extraction	% Pu Extracted
1/2	2.30	1.09	1.11	50	4.53	90.9
1/2	2.65	1.09	1.56	50	7.02	86.0
1	1.07	1.09	-0.02	50	0.463	99.1
1	1.26	1.09	0.17	50	0.456	99.1
2	1.14	1.09	0.03	50	0.116	99.8
2	1.11	1.09	0.01	50	0.115	99.8
3	1.05	1.09	-0.04	50	0.126	99.7
3	1.12	1.09	0.03	50	0.109	99.8
5	1.01	1.09	-0.08	50	0.120	99.7

5.4 Stability of the Aluminum 8-Hydroxyquinolate Color

To determine the stability of the aluminum complex, synthetic samples were carried through the procedure. The optical density of these samples was then determined over a 96-hour period, and the results are shown in Table IV.

[≠] 500 micrograms of aluminum gives a corrected value of 1.09 ± 0.008 optical density units. This value was calculated from the regression equation.

TABLE IV
COLOR STABILITY OF ALUMINUM HYDROXYQUINOLATE

Micrograms of Al	Optical Density				
	15 Min	1 Hr	7 Hr	24 Hr	96 Hr
500	1.20	1.19	1.20	1.20	1.23
500	1.21	1.20	1.21	1.21	1.21
500	1.20	1.19	1.18	1.18	1.20

Samples were compared with a pure chloroform blank.

No significant difference was found in the values obtained from 15 minutes to 96 hours.

5.5 Effect of pH on Extraction of Aluminum 8-Hydroxyquinolate

Considerable difference of opinion exists in the literature concerning the optimum pH for the extraction of the aluminum 8-hydroxyquinolate into chloroform. Moeller[4] states that complete extraction occurs only in the pH range 4.3-4.6, whereas Margenum et al[8]. report complete extraction only at a pH above 4.5. Parks and Lykken[1] used Moeller's value of 4.3-4.6. Gentry and Sherrington[6] give the optimum range as 4.5-6.5; and the range is extended by Wimberley and Bassett[9], who report that anywhere within the pH range 4.9-9.4 is satisfactory. Sprain and Banks[5] recommend that the extraction be carried out at pH 5.

In order to arrive at the correct pH for this extraction, a series of synthetic samples was made up containing 500 micrograms of aluminum, 6 ml of water, (corresponding to the 6 ml of cupferron solution used with actual samples), and 25 ml of the 8-hydroxyquinoline reagent solution. The pH of each solution, as determined on a Beckman Model G pH meter, was adjusted to the desired value with concentrated HCl and/or 20% NaOH. Then 100 ml of chloroform was added to each sample, followed by shaking for 15 seconds. The samples were allowed to stand overnight and the optical density of the chloroform layer of each was determined the next day with the Model DU spectrophotometer. The results are given below.

TABLE V
VARIATION OF EXTRACTION WITH PH

pH	Net O.D.	pH	Net O.D.
3.0	0.078	4.8	1.12
3.0	0.096	4.8	1.08
4.0	1.17	5.0	1.22
4.0	1.13	5.0	1.26
4.2	1.11	6.0	1.20
4.2	1.12	6.0	1.32
4.4	1.13	7.0	1.26
4.4	1.04	7.0	1.25
4.6	1.05	8.0	1.22
4.6	1.10	8.0	1.26

These values indicate complete extraction in the pH range 5.0-8.0. A pH of 5.0-5.1 was chosen for the extraction employed in this procedure.

7. Discussion

Below is given a table of micrograms of aluminum found for a series of synthetic samples containing 500 micrograms of aluminum run over three different days.

TABLE VI

486	496	515	510	520	500
486	496	496	496	505	510
515	496	510	496	525	486
491	505	500	471	525	500

The mean of these values is 501 micrograms, and the standard deviation is 2.6%. Thus, the limit of error is 5%; so that in 95% of the determinations, the value obtained would not differ from the true mean value by more than 5%.

A statistical analysis of duplicate results on seventeen individual samples run over a period of several weeks shows a standard deviation of 0.022% with a mean aluminum content of 1.10%.

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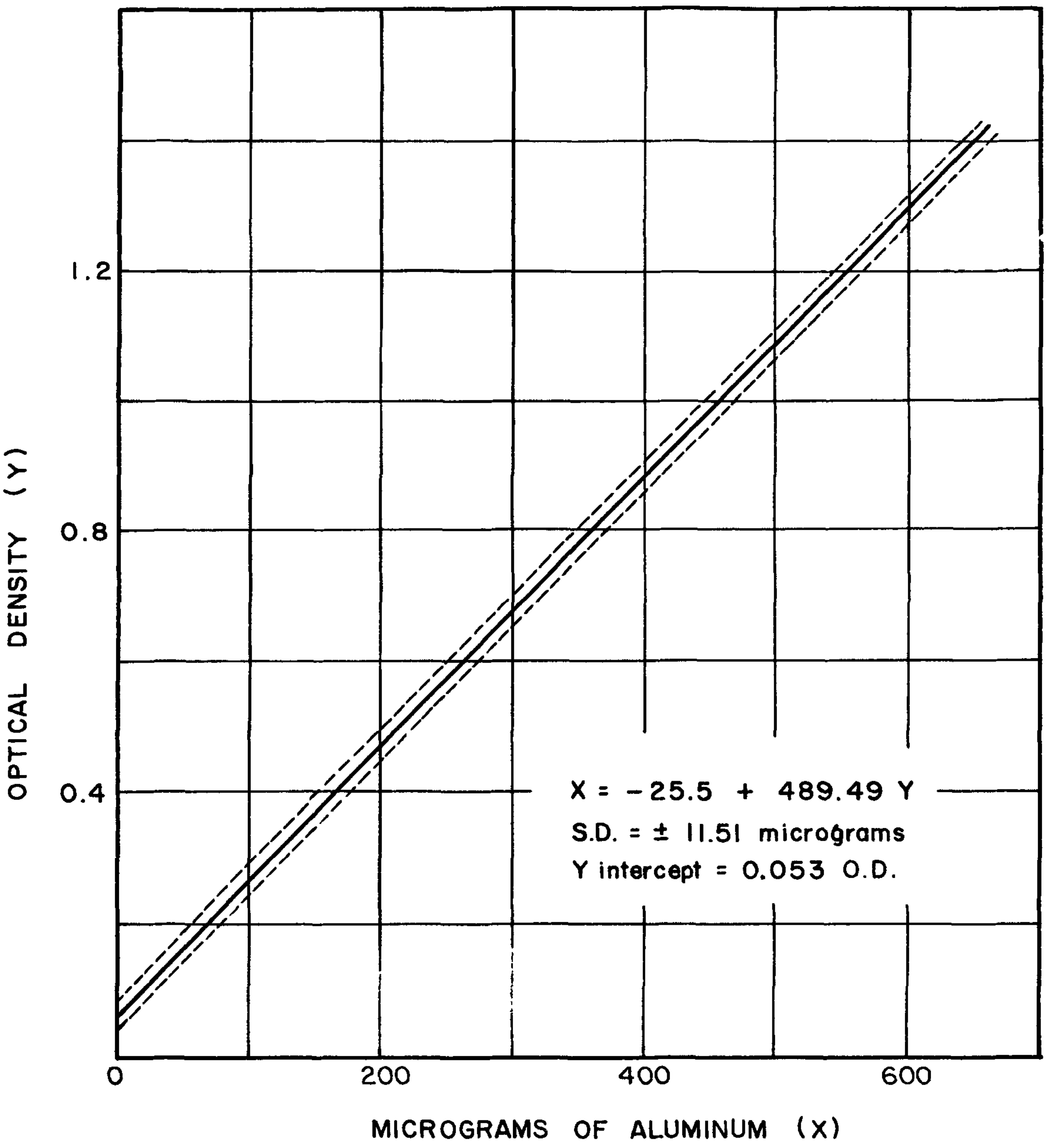
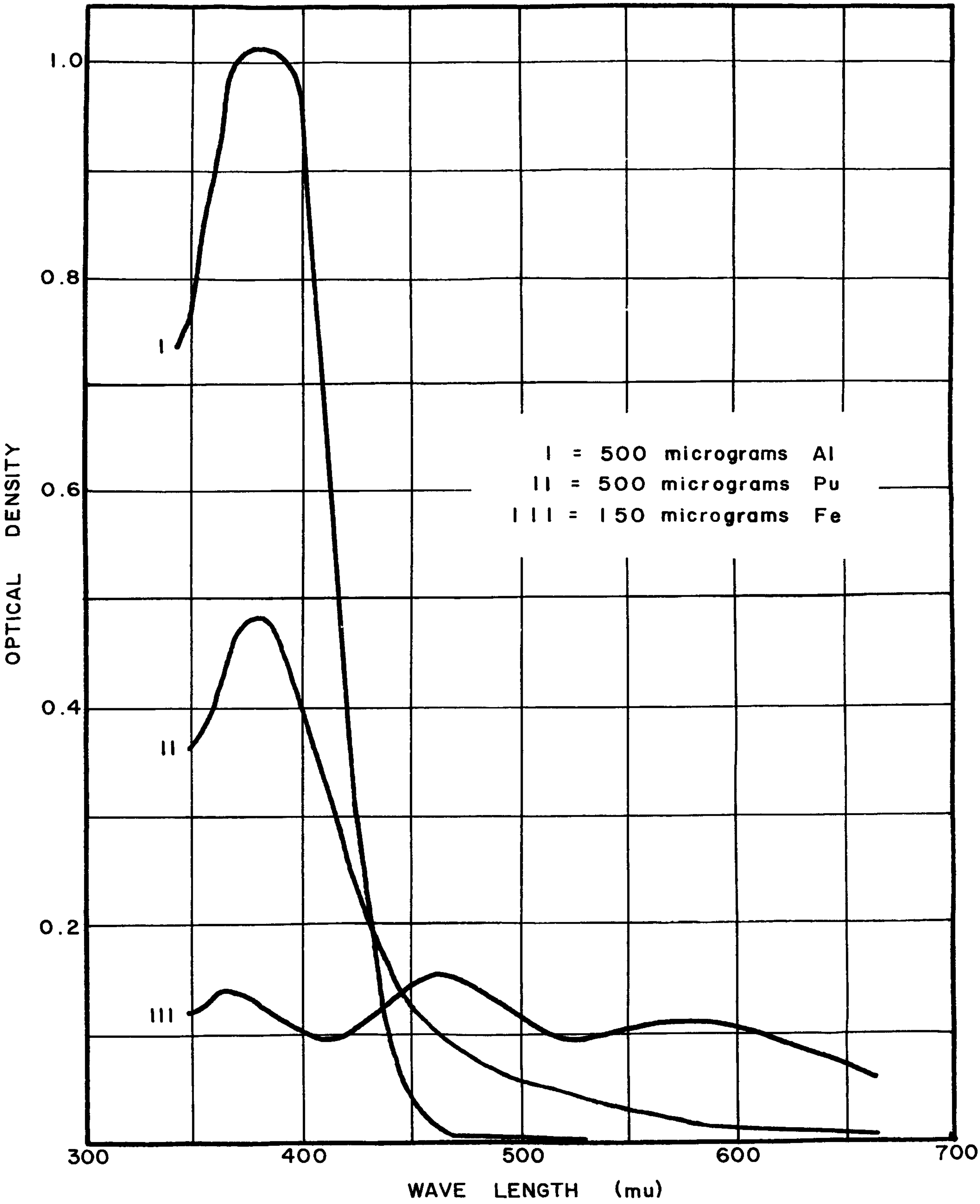

1.2
0.8
0.4
OPTICAL DENSITY (Y)
0
200
400
600
MICROGRAMS OF ALUMINUM (X)
X = −25.5 + 489.49 Y
S.D. = ± 11.51 micrograms
Y intercept = 0.053 O.D.


1.0
0.8
0.6
0.4
0.2
OPTICAL DENSITY
I
II
III
I = 500 micrograms Al
II = 500 micrograms Pu
III = 150 micrograms Fe
300
400
500
600
700
WAVE LENGTH (mu)