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DEPARTMENT OF MINES AND TECHNICAL SURVEYS  
MINES BRANCH

# THE DETERMINATION OF ALUMINUM BY THE FLUOROPHOTOMETRIC METHOD

by

J. B. ZIMMERMAN  
RADIOACTIVITY DIVISION



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## CONTENTS

	<u>Page</u>
Introduction .....	1
Theory .....	1
Outline of method .....	2
Reagents and apparatus .....	3
Fluorimeter .....	3
Procedure .....	4
Discussion of method .....	7
Conclusion .....	9
References .....	10

## ILLUSTRATIONS

Figure 1 - Calibration curve for aluminum 8-hydroxyquinolate in chloroform .....	11
Figure 2 - Quenching curve for iron on the fluorescence of aluminum 8-hydroxyquinolate in chloroform .....	12



### Abstract

A method is described by which a large range of aluminum concentrations may be determined speedily and with approximately  $\pm 5$  per cent accuracy for samples containing less than 1.0 per cent aluminum.

Samples are taken into solution and impurities precipitated with sodium hydroxide. An aliquot containing the soluble sodium aluminate is adjusted to pH 4.6, 8-hydroxyquinoline is added and the complex aluminum 8-hydroxyquinolate extracted with chloroform and measured fluorimetrically at 560 m $\mu$ . Various materials containing aluminum such as iron, steel, ores, aluminum powder and base metal alloys varying in aluminum content from 0.001 per cent to 99.0 per cent have been determined using a dilution technique.

The fluorescent procedure has proved superior to gravimetric and colorimetric methods especially for low aluminum values in the presence of iron or phosphates.



# THE DETERMINATION OF ALUMINUM BY THE FLUOROPHOTOMETRIC METHOD

## INTRODUCTION

A fast and accurate method of analysis of low-value aluminum samples was needed to meet the constant demand for such analysis in connection with research and development projects. The existing gravimetric and colorimetric methods are fairly satisfactory, but the former is difficult and lengthy, and the latter falls off in accuracy at low aluminum concentrations.

The method described herein is fast and accurate and is particularly adapted to low-value aluminum concentrations. The aluminum 8-hydroxyquinolate complex fluoresces brilliantly when dissolved in chloroform and irradiated with ultra-violet light.

## THEORY

8-hydroxyquinoline under varying conditions precipitates many of the metals as 8-hydroxyquinolates, a property which has been used extensively in analytical chemistry. In its metal salts, the metal ion associated with the oxygen of the phenol group usually forms a co-ordination bond with the nitrogen of the pyridine ring and a 5-membered ring is formed (1).





The non-ionic character of these salts is shown by their solubility in many organic solvents especially in chloroform.

The colorimetric determination of aluminum depends upon the yellow colour given to chloroform by aluminum 8-hydroxyquinolate. During an investigation of this means for determining aluminum, C. H. R. Gentry and L. G. Sherrington (2) first mentioned that the solution fluoresced when irradiated with ultra-violet light and suggested that this might be a means of assaying aluminum ores. Using this approach, successful methods for assaying aluminum in phosphate rocks were developed by F. S. Grimaldi & H. Levine (3) and for determining small amounts of aluminum in beer by T. U. Tulls, W. T. Stringer, and G. A. F. Harrison (4).

The method used at the Mines Branch, Radioactivity Division, follows in the main that outlined by Grimaldi & Levine.

#### OUTLINE OF METHOD

The present method is based on the following facts. Aluminum forms the complex salt aluminum 8-hydroxyquinolate, which is completely extracted by chloroform at a pH of 4.6. The resultant solution fluoresces strongly with a greenish-yellow colour when exposed to ultra-violet light. The fluorescent output of the solution is linear with aluminum concentration in a range of less than one gamma of aluminum to at least 50 gamma of aluminum in 30 ml of solution. Interference from other ions notably iron, manganese, and chromium may be encountered if they are present in sufficient quantity. These, however, may be readily removed either by a preliminary separation with the mercury cathode or by precipitation with sodium hydroxide.

REAGENTS AND APPARATUS

8-hydroxyquinoline - Dissolve 15 grams of 8-hydroxy-quinoline in 1 litre of 2M acetic acid (3).

Buffer Solution - Mix equal volumes of 2M acetic acid and 2M ammonium acetate (3).

Chloroform - reagent grade chloroform, redistilled if necessary.

Dilute ammonium hydroxide - 10 per cent  $v/v$

Dilute sulphuric acid - 10 per cent  $v/v$

Calcium sulphate - reagent grade.

pH meter

60 ml separatory funnels

Two 100 ml burettes

Florence flasks

1, 2, 5, 10, 25, ml pipettes.

FLUORIMETER

The fluorimeter is a Lumetron model 402EF fluorescence meter. This instrument has an  $AH_4$  mercury vapour lamp for an ultra violet light source. Primary filter Corning No. 5874 transmits strongly in the region of 365  $m\mu$  and the secondary filter Corning No. 3385 has peak transmission at approximately 560  $m\mu$ . The glass cells are rectangular, having one end made of thin glass in order to diminish the absorption of ultra-violet light.

## PROCEDURE

### Solid samples

A suitable amount of samples, 0.15 to 2.0 grams, depending upon the aluminum concentration, is accurately weighed and taken into solution.

At this point an estimate of the aluminum content is of great value. If no estimate is available, a trial run has to be made and an appropriate change made in the volume of sample if the fluorescence is off the linear scale.

Separation of any interfering elements is now carried out either by the mercury cathode method or by a sodium hydroxide method.

### Mercury cathode method

The elements that can be quantitatively deposited in the mercury cathode (5) are Cr, Mo, Re, Fe, Co, Ni, Cu, Zn, Ga, Ge, Rh, Pb, Ag, Cd, In, Sn, Ir, Pt, Au, Hg, Tl, Bi, and Po.

The elements partially deposited in the mercury cathode are Mn, Ru, Sb, As, Se, Te, Os, and Pb.

If there is an estimate of the aluminum, a double dilution of the sample is calculated so that 1 to 10 ml of the second dilution contains somewhat less than 11.1 gamma of aluminum, the amount in the standard.

### Example

A sample is estimated to contain approximately 4 per cent aluminum. Weigh one gram of sample which would, therefore, contain 0.04 grams aluminum. After sample is in solution dilute to 1000 ml. One ml, however, would now contain 0.00004 grams of aluminum. With a

second dilution of 5 ml/50 ml of the first dilution, one ml would contain 0.000004 grams Al or 4 gamma of Al and 2 ml of this second dilution, would contain 8 gamma Al, which is within the limits for the extraction process.

Make up the first dilution in 1-2 per cent  $H_2SO_4$  and transfer 25 to 200 ml depending upon the size of the cell to the mercury cathode. Electrolyze for the period required to eliminate iron and other impurities. After this treatment there are not as a rule any elements left which can seriously affect the fluorescence of aluminum in chloroform.

After electrolyzing the sample, pipette an aliquot into a 50 ml volumetric flask and make up to volume with distilled water.

Pipette 25 ml of the second dilution into a 50 ml beaker and adjust the pH to approximately 3.5 with ammonium hydroxide, using a pH meter, noting the amount of  $NH_4OH$  added, as this constitutes a third dilution.

Example

2.0 ml of  $NH_4OH$  was used to adjust the pH of 25 ml of solution to approximately 3.5. The third dilution would be 25/27.

After adjusting the pH, pipette 2 ml into a 60 ml separatory funnel which contains 1 ml of prepared 8-hydroxyquinolate reagent; add 3 ml of buffer solution, 16 ml of distilled water and 30 ml of chloroform. The amount of water added would vary, depending upon the size of sample aliquot taken. The total volume in the separatory funnel should be 51 ml. Shake for 10 seconds and allow the chloroform to settle. Run off the chloroform layer into a 100 ml Florence flask containing approximately 1 gram of calcium sulphate. The

calcium sulphate will remove any water carried down with the chloroform. Decant the chloroform into a 30 ml rectangular glass cuvette and using the fluorescence meter compare the fluorescence of the sample to the standard.

Example of complete calculation

Sample read 65 per cent of 11.1 gamma Al (standard).

Weight of Al in 2 ml aliquot = 7.22 gamma

Per cent Al in original sample:

<u>gamma Al</u>		<u>1st Dil.</u>		<u>2nd Dil.</u>		<u>3rd Dil.</u>		<u>Per Cent</u>	
$\frac{7.22}{2}$	X	$\frac{1000}{1}$	X	$\frac{50}{5}$	X	$\frac{27}{25}$	X	$\frac{100}{10^6}$	= 3.89 per cent Al
aliquot								gamma/gm	

If a sample is too low in aluminum to warrant a second dilution, 25 ml of solution may be used directly from the mercury cathode for pH adjustment.

Sodium hydroxide method

Elements that are either completely precipitated or nearly so, from solutions by adding sodium hydroxide (5) are Mg, Sr, Ti, Y, Zr, La, Hf, Ac, Th, Pa, U, Cr, Mn, Fe, Co, Ni, Cu, Ag, Cd, In, and Tl.

The sodium hydroxide method is particularly adapted to acid-soluble materials such as iron and steel, metal alloys, and solutions.

Calculate as in the mercury cathode method the size of aliquot to be extracted. Weigh 0.5 to 2 gram of sample and dissolve in HCl or H<sub>2</sub>SO<sub>4</sub>. After solution is effected, make the sample 10 per cent W/v with NaOH and boil 5 minutes. Make the caustic solution containing the precipitate and soluble sodium aluminate up to volume, mix well, and allow it to stand until the precipitate has settled or separate the mixture by filtering or centrifuging. The procedure is

then the same as that outlined for the mercury cathode except that the pH adjustment is made with dilute  $H_2SO_4$ .

### Solutions

Add sodium hydroxide 10 per cent  $w/v$  directly to the sample and boil the solution for 5 minutes. The procedure is then the same as for the caustic treatment of solid samples.

### DISCUSSION OF METHOD

The method outlined has proved most successful, good agreement having been obtained on standard samples and on samples analyzed by other methods. Care must be taken when using the caustic process if chromium is present. If present as chromate, reduction is necessary for precipitation as the hydroxide. Soluble chromium salts are extracted with the aluminum, and increase the fluorescence output of the sample.

Iron and manganese have a quenching effect on the fluorescence due to aluminum. These elements, however, are removed easily in either the mercury cathode or by the caustic precipitation.

The quenching effect of iron was investigated, and it was found that all iron must be removed for a 100 per cent recovery of aluminum.

### Figure 1.

The calibration curve in Figure 1 shows the linearity of fluorescence output from an aluminum standard for low aluminum concentrations. The Lumetron is a null point instrument and the fluorescence from a known amount of standard is set at 100 per cent. A blank containing the reagents in the same proportion as the standard

is set for zero fluorescence and samples are then read as a percentage of a known amount of aluminum. In Figure 1 and for subsequent work the fluorescence output from 11.1 gamma Al was taken as 100 per cent.

Iron was the only element of those known to quench the fluorescence of aluminum which was investigated. Figure 2 shows the effect of increasing the iron to aluminum ratio with three different amounts of aluminum standard. The curves are exponential, indicating adherence to Beer's law. The apparent fluorescence is proportional to the iron to aluminum ratio, showing the necessity for complete removal of iron.

The following table compares the aluminum assays obtained by the fluorescent method with Bureau of Standards samples and external samples for various types of materials. The fluorimetric assays shown are for a single determination.

Comparative Analyses of Standard and Other Samples

Sample	Bureau of Standards Assay	Fluorimetric Mercury Cathode	Fluorimetric Caustic	Fluorimetric Acid Solution Only	Other Method. Chemical
	Al Per Cent	Al Per Cent	Al Per Cent	Al Per Cent	Al Per Cent
B. S. #26 Iron ore	0.54	0.55	0.57		
B. S. #22c Steel	0.116	0.12	0.12		
B. S. 55b Open hearth iron	0.002	0.002	0.0018		
B. S. 64a Ferrochromium	0.01	0.011	-		
B. S. 63b Phosphor bronze	0.05	0.045	-		
B. S. 94a Zinc base	3.90	3.93	3.92		
Luxor aluminum powder #3090		0.056	0.052	99.2	99
Precipitate b			<u>7.70</u>		8.1
2-476 Solution			0.0015 g/l		Trace
2-477 Solution			0.0016 g/l		N.D.

CONCLUSION

The results of this work indicate that the fluorimetric method for assaying aluminum is speedy, accurate and well adapted for a routine laboratory method.



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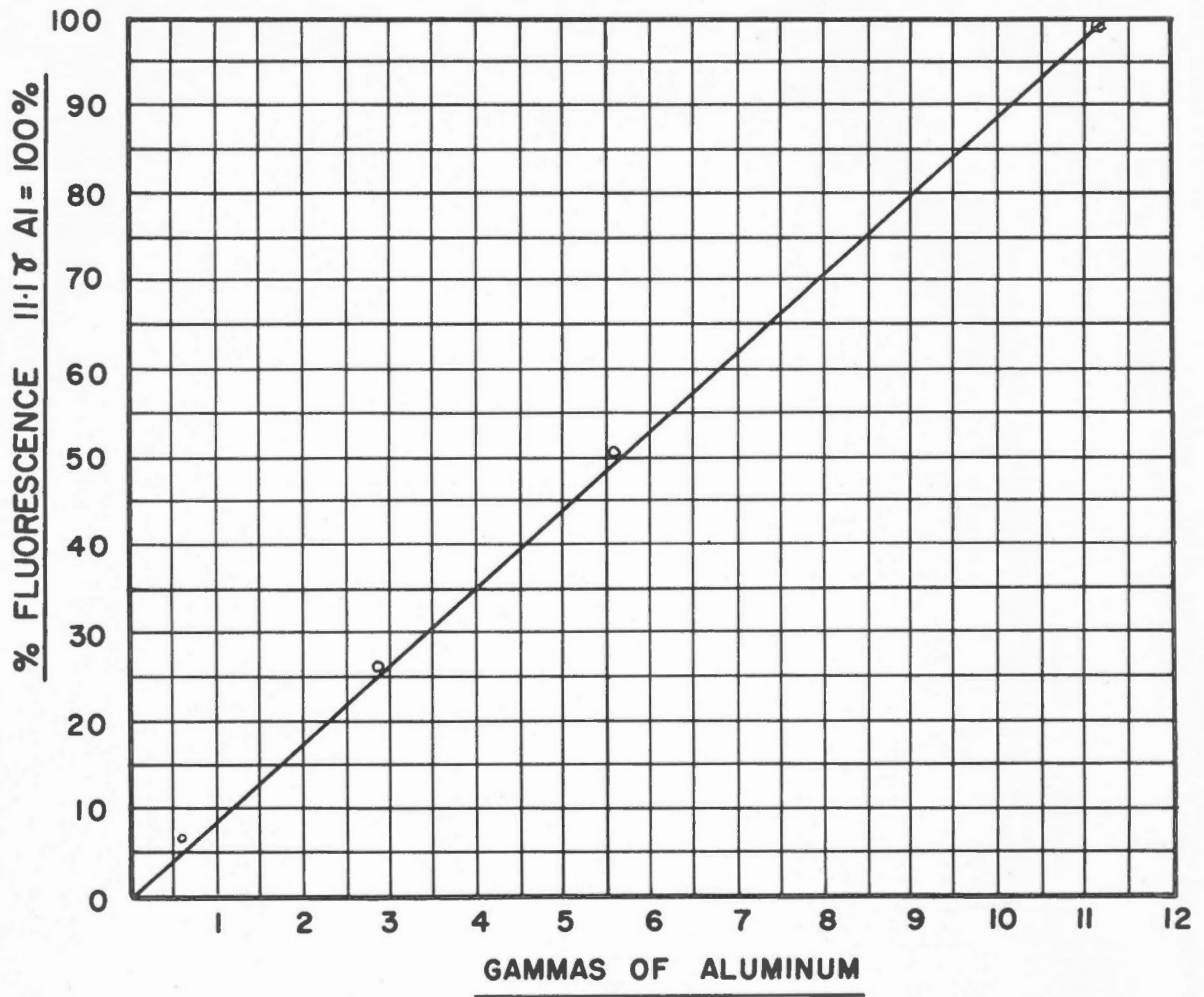


FIGURE 1 - CALIBRATION CURVE FOR ALUMINUM  
8-HYDROXYQUINOLATE IN CHLOROFORM

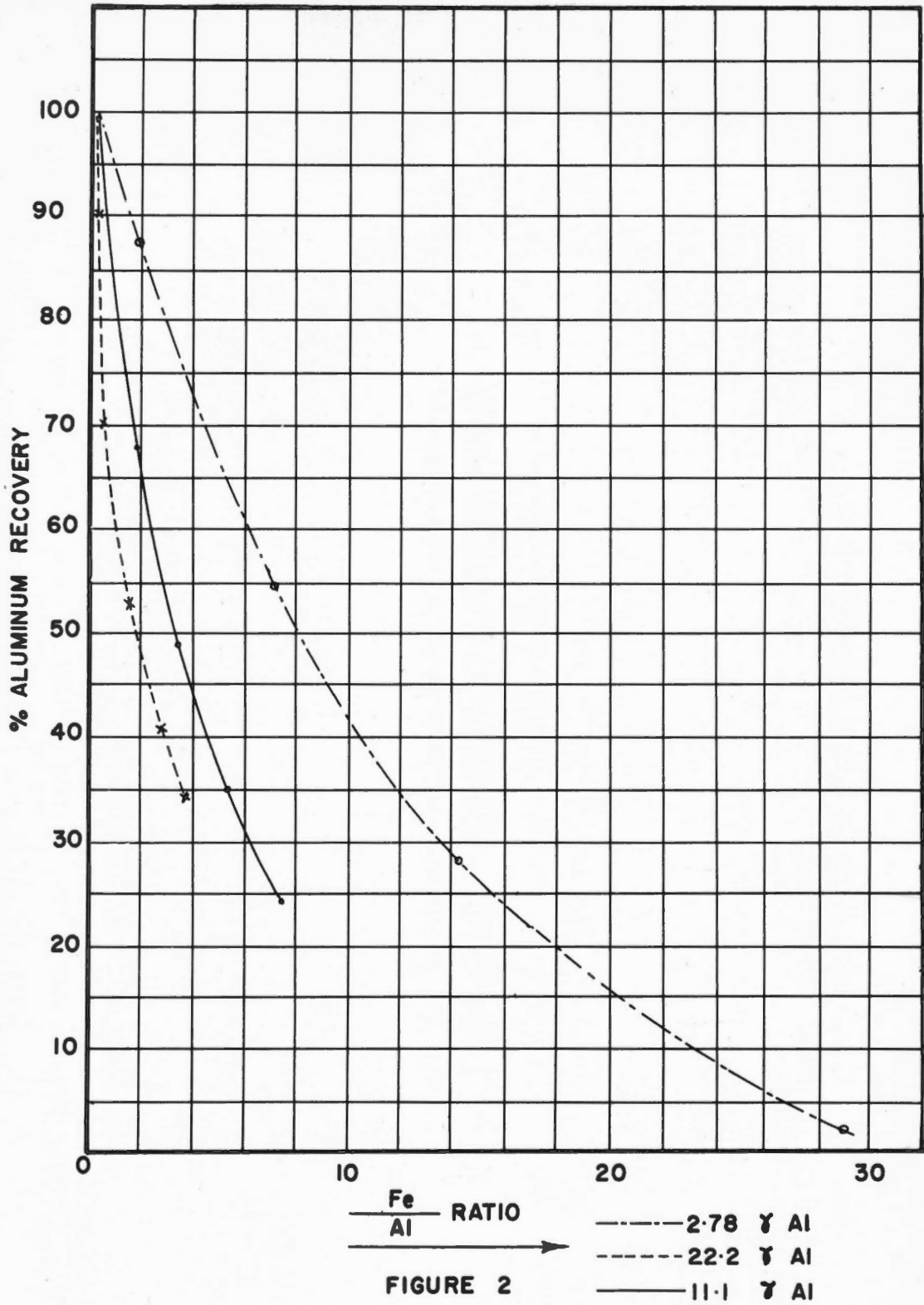


FIGURE 2 - QUENCHING CURVE FOR IRON ON THE FLUORESCENCE OF ALUMINUM 8-HYDROXYQUINOLATE IN CHLOROFORM.

