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# A COMBINED SPECTROPHOTOMETRIC-FLUORIMETRIC METHOD FOR THE DETERMINATION OF ALUMINUM IN PRODUCTS FROM WET-PROCESS PHOSPHORIC ACID MANUFACTURE

by

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#### ABSTRACT

This report describes methods for the determination of aluminum in products obtained during the manufacture of wetprocess phosphoric acid from Florida land-pebble phosphate ore. The methods feature a combination of spectrophotometric and fluorimetric techniques to permit the determination of aluminum over a wide range of concentration.

# RÉSUMÉ

Cette étude décrit les méthodes utilisées pour le dosage de l'aluminium dans les produits obtenus au cours de la fabrication d'acide phosphorique par voie humide à partir des nodules de minerai phosphaté de l'intérieur de la Floride. Ces méthodes utilisent une fluorométriques qui permet le dosage de l'aluminium dans un large éventail de concentrations.

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## INTRODUCTION

Conversion of imported phosphate ore into superphosphate for fertilizer has long been a favoured method for disposing of by-product sulphuric acid. In a significant new development, the Dow Chemical Company has worked out a flow-sheet for the conversion of by-product hydrochloric acid from Canada's burgeoning chlorinated organic chemicals industry into economically important calcium chloride and phosphoric acid by reacting it with Florida land-pebble phosphate ore. The leaching step of this process was recently the subject of an extensive pilot-plant program carried out by the hydrometallurgy section of the Mines Branch's Extraction Metallurgy Division, in Ottawa. The combination of calcium, aluminum and fluoride in the ore resulted in precipitation of calcium fluoaluminate, which created certain operating problems and made it necessary to carry out large numbers of aluminum determinations rapidly.

A literature survey made by the writer indicated that the chloroformaluminum 8-quinolinate extraction method, currently being used at this Mines Branch laboratory, was still the most generally suitable method for aluminum determination. In the modification used at the Mines Branch up to the present, aluminum has been determined fluorimetrically. This has the advantage of providing the high sensitivity necessary for dealing with the small quantities of sample available from bench work, but has many disadvantages. These disadvantages include the necessity for large dilutions when dealing with macro-amounts of aluminum, and comparatively less precision because of contamination from apparatus and reagents. In other published modifications of this procedure (4, 8, 11), the final measurement is made spectrophotometrically. In this way, the high sensitivity is sacrificed but the relative effect (loss of precision) due to contamination is correspondingly reduced.

Because, in the literature survey, no indication was found of a chloroformaluminum 8-quinolinate extraction method in which the same basic procedure is employed with either fluorimetric or spectrophotometric finish (depending on the aluminum content observed in the final aliquot), experiments were carried out in the Extraction Metallurgy Division by the writer to establish the conditions necessary to permit this combination of techniques to be used. Such a method would eliminate the necessity to dilute a sample or repeat an analysis in which the aluminum content varied greatly from that expected. At the same time, a brief investigation was undertaken to establish the optimum working conditions and to find suitable methods for eliminating certain common interferences.

## REAGENTS AND APPARATUS

## Reagents

8-Quinolinol solution 1%  $\gamma$ --Dissolve 1 gram of 8-quinolinol in 2 ml 6N hydrochloric acid and dilute to 100 ml with distilled water.

Aluminum stock solution -- Dissolve 1.000 gram of aluminum metal 99.99% pure, which has been cleaned with acetone, in 40 ml hydrochloric acid (1:1) and dilute to 1 litre with distilled water.

Standard aluminum working solutions -- (1) For fluorimetric curve, 5 ml of stock solution diluted to 2 litres with distilled water, 1 ml = 2.5  $\mu$ g A1. (2) For spectrophotometric curve, 10 ml of stock solution diluted to 1 litre with distilled water, 1 ml = 10  $\mu$ g A1.

Buffer solution -- Dissolve 193 g of ammonium acetate in distilled water and dilute to 1 litre. Adjust the pH to 5.8 with hydrochloric acid (1:1).

Chloroform -- Reagent grade

Sodium sulphate -- Na<sub>2</sub>SO<sub>4</sub>, anhydrous, reagent grade

Acetone -- Reagent grade

Quinine sulphate solution -1 mg of quinine sulphate dissolved in 1 litre of 0.1 N H<sub>2</sub>SO<sub>4</sub>.

Ammonium Hydroxide --10% v/v.

#### Appar atus

pH meter: EIL Model 23

Separatory funnels: Squibb's pear-shape with Teflon plugs.

Pipettes: 1, 2, 3, 4, 5, 10, 25 ml sizes.

Erlenmeyer flasks: 50 ml size

Stoppers, polyethylene: Nalgene, No. 2

#### Fluorimeter;

A General Electric Model H-100 A4 Lamp (stabilized by a Sola constant-wattage 100 watt transformer) in a water-cooled housing, illuminates the solutions contained in Corex fluorimeter cell in a Cat.No. 2980 Beckman Fluorescence Attachment through a filter which isolates the 3650 Å mercury line. The fluorescent light from the sample, passed through a yellow filter to remove reflected ultra violet light, is picked up by a Farrand Electron Multiplier Photometer. This latter unit consists of a detector unit containing a 1 P21 photomultiplier tube, and its power supply. A Leeds and Northrup 10,000-ohm Aytron shunt and a spot-light galvanometer are used to measure the output of the photomultiplier tube.

Fluorimeter cells:

Corex, 1 cm light path, with transparent bases.

Spectrophotometer:

Beckman Model B.

Spectrophotometer cells: 1 cm light path.

Mercury cathode:

e.g. Eberbach Dyna-Cath.

#### PREPARATION OF CALIBRATION CURVES

Measure out aliquots of standard solution, into 100-ml beakers, to contain 0, 2, 4, 8, 10, 25, 50, 75 and 100  $\mu$ g of aluminum, and dilute them each to 20 ml with distilled water. Add 2 ml of 8-quinolinol reagent, 5 ml of buffer, stir, and allow the solutions to stand for 5 minutes. Then adjust the pH to 5.6 to 5.7 with dilute NH<sub>4</sub>OH, using a pH meter. Transfer the solutions to 60 ml separatory funnels with a minimum amount of distilled water (2 to 3 ml) and shake each solution with a 25 ml portion of chloroform for one minute. Let the layers separate, draw the chloroform layers into separate 50 ml flasks containing 1 to 2 g of sodium sulphate, and cap with plastic stoppers. For the fluorimetric curve, measure the 0 to 10  $\mu$ g aluminum extracts fluorimetrically as described below under "Fluorimetric Operation". Plot a curve of average fluorescent readings, corrected for the blank, against  $\mu$ g of aluminum. For the spectrophotometric curve, read the 0 to 100  $\mu$ g aluminum extracts on a spectrophotometer at 387 m $\mu$  and plot these values, corrected for the blank, against aluminum concentrations.

## RECOMMENDED PROCEDURES

# A. Preliminary Treatment

## (1) Rock and Recycle Liquors

Choose an aliquot containing 0.2 to 2 mg Al and pipette it into a 250 ml Teflon beaker. Add 15 ml of concentrated nitric acid, and 10 ml concentrated perchloric acid, and evaporate to fumes at low hot plate heat. Wash the inside surface of the beaker with distilled water and fume to near dryness. Add 20-30 ml of distilled water and warm to dissolve.

#### (2) Ores

Accurately weigh a sample containing 0.2 to 2 mg Al into a 250 ml Teflon beaker. Add 30 ml nitric acid (1:1) and 10 ml of concentrated hydrofluoric acid. Evaporate to dryness on the hot plate at low heat. Add 20 ml nitric acid (1:1), 5 ml concentrated hydrofluoric acid, and 15 ml of concentrated perchloric acid. Evaporate nearly to dryness, cool, and wash the inside surface of the beaker with a jet of water. Add 5 ml of concentrated perchloric acid and again evaporate nearly to dryness. Add 30 ml of distilled water and warm to dissolve. Filter the sample through a Whatman No. 541 paper, and wash the residue with hot distilled water. (In decomposing phosphate ores, the residues which remain undissolved after treatment with the above acids contain only a negligible amount of aluminum.)

(3) Residues

Accurately weigh a sample containing 0.2 to 2 mg of Al into a 250 ml Teflon beaker. Add 20 ml of nitric (1:1) and 10 ml of concentrated perchloric acid, and evaporate to fumes. Wash the inside surface of beaker with a jet of water and evaporate nearly to dryness; add 30 ml of distilled water and warm to dissolve. Filter a Whatman No. 541 paper, and wash the residue with hot water.

# B. Removal of Interfering Elements

(1) Rock and Recycle Liquors

Dilute the solution to 100 ml with distilled water, adjust the acidity by adding 5 ml of 6 N sulphuric acid, and transfer to a mercury cathode cell. Electrolyze at 10 to 15 amperes until a negative test for iron is obtained using the following spot test: (one-half hour is usually adequate). Place a drop of a standard solution containing l microgram of ferrous iron per ml and a drop of the solution in the cell on a white hot plate. To each of these, add one drop of 10% hydroxylamine hydrochloride. After waiting about a minute, add 2 drops of 20% ammonium acetate, followed by 2 drops of 0.1% o-phenanthroline solution. If the solution shows less iron than the standard solution, by comparison of the orange colours formed, remove it from the electrolytic cell.

Transfer the solution to a 250 ml volumetric flask and dilute to the mark with distilled water.

# (2) Residue Samples

Dilute the filtrate from the acid treatment directly to 250 ml in a volumetric flask, omitting the preliminary mercury cathode separation. Take a 5 ml aliquot, transfer it to a 100 ml beaker, and dilute to 15 ml with distilled water. Treat the solution with 1 ml of 10% hydroxylamine hydrochloride solution and 5 ml of 0.1% o-phenanthroline solution and allow it to stand 2 to 3 minutes. Carry on the procedure as given under C, from the point indicated by the asterisk.

#### C. Extraction of Aluminum 8-quinolinolate

(N.B. Carry two blanks through the procedure from this point)

Transfer a suitable aliquot (5 ml will contain from 4 to  $100 \mu g$  of Al based on the original weight) to a 100 ml beaker and dilute to 20 ml with distilled water\*. Add, in order, 2 ml of 8-quinolinol reagent, and 5 ml of buffer. Mix, and allow to stand for 5 minutes. Adjust the pH to 5.6 to 5.7 with dilute ammonium hydroxide by means of a pH meter, and transfer to a 60 ml separatory funnel with a minimum of distilled water (2-3 ml). Extract with 25 ml of chloroform for one minute. Run off the chloroform into a 50 ml Erlenmeyer flask containing 1 to 2 g of anhydrous sodium sulphate, and cap with a plastic stopper. Depending on the aluminum content observed in the chloroform extract, complete the determination fluorimetrically or spectrophotometrically.

#### D. Fluorimetric Finish

## (1) Fluorimetric Operation

Turn on the water supply to the lamp-housing of the fluorimeter. Turn on the ultra-violet lamp, and leave it on 15 minutes to ensure stable operation. Set the Ayrton shunt at position 0.01 and turn on the galvanometer and power supply. Zero the galvanometer.

## (2) Scale Adjustment and Sample Reading

Use the quinine sulphate solution (1  $\mu$ g per ml) as the standard for comparison; put this solution, the two blanks and a sample each in a separate 1 cm Corex fluorimeter cell. Place the holder in the fluorimeter and replace the cover. Move the quinine sulphate solution into the light path and open the photomultiplier shutter. With the Ayrton shunt set at 0.01, adjust the power supply control so that the galvanometer reads 500. (The galvanometer scale is 10 cm in length graduated in millimeters, and the actual reading is the galvanometer reading in cm taken to the nearest 0.05, divided by the shunt setting.) Move the blanks and sample successively into the light path and record their respective readings. Leave the number one cell filled with the quinine sulphate solution. Refill the three remaining cells with the next samples and repeat the scale adjustment and reading operation.

Correct the fluorimeter reading by subtracting the average value obtained for the two blanks. Read the  $\mu$ g of Al per final aliquot from the prepared calibration graph.

#### E. Spectrophotometric Finish

Measure the sample against a blank in 1 cm cells on the spectrophotometer at 387 m $\mu$ . Record the absorbance and read the  $\mu$ g of Al per final aliquot from the prepared calibration curve.

## F. Calculations

•	g/1A1 =	$\mu$ g Al per final aliquot x 10 <sup>-6</sup> x	250 final alqt		
	% A1 =	$\mu$ g Al per final aliquot x 10 <sup>-6</sup> x	250	x <u>100</u>	
	· · ·		final alqt	sample wt., g	

#### EXPERIMENTAL

#### A. Effect of pH

The effect of the pH of the aqueous phase upon the percentage of aluminum extracted as 8-quinolinolate into the chloroform phase was investigated, since there is some disagreement in the literature concerning the proper conditions for the extraction. Moeller (1) found complete extraction only in the pH interval 4.3 to 4.6, while Gentry and Sherrington(2) reported that recovery was complete over the pH range 4.5 to 11.5, except between pH 6.5 and 8 where incomplete extraction was found. Margerum, Sprain and Banks (3) report the optimum range to be between pH 4.7 and 5.0.

The procedure used to investigate the amount of aluminum extracted in relation to pH was as follows: into a 50 ml beaker were added 10  $\mu$ g aluminum standard, 1 ml 1.5% 8-quinolinol reagent, 5 ml of 2.5 M ammonium acetate, and sufficient dilute hydrochloric or ammonium hydroxide to attain the desired pH. The solution was transferred to a 60 ml separatory funnel, diluted to 20 ml with distilled water, and extracted once with 25 ml chloroform. The fluorescence of this solution was measured, along with that of a reagent blank at the same pH. The exact pH of the aqueous phase was measured after the extraction, since it was found to decrease by about 0.2 pH units from the initial setting, due to dilution.

Figure 1 shows the fluorimeter readings of the extract, plotted against the final pH of the extracted aqueous layers. Extractions are seen to be complete over a pH range of 5.5 to 7. These fluorimetric results check reasonably well with results of spectrophotometric measurements of Middleton (4) who found, in working with the same amounts of aluminum, that the extraction was complete over a pH range of 5 to 6.

The pH range selected for use in all subsequent work was 5.6 to 5.7. To adjust and maintain the pH at the desired value during the course of the procedure the sample, buffer and 8-quinolinol reagent are diluted to 20 ml, the pH is adjusted, and the solution is transferred to a separatory funnel with a minimum of water (2-3 ml). No further dilution is made.



Figure 1. The Effect of the pH of the Aqueous Phase on the Amount of Aluminum Extracted into Chloroform, Based on Fluorimetric Measurements.

## B. Effect of 8-quinolinol Concentration

The theoretical ratio of 8-quinolinol to aluminum required for extraction is given by the ratio of the solubility of aluminum 8-quinolinolate in chloroform to its solubility product in water saturated with chloroform; at equilibrium, this ratio is large, about  $9 \times 10^{30}$ , and it is predicted that when 10 equivalents of 8-quinolinol are present for 1 equivalent of metal, a single chloroform extraction will completely remove the aluminum 8-quinolinolate from the aqueous phase (5). The effect of increasing the amount of 8quinolinol from the theoretical 10:1 equivalents ratio was investigated to find out (a) whether better reproducibility could be obtained, and (b) whether the same concentration of 8-quinolinol could be used for extraction of small amounts of aluminum which were to be measured fluorimetrically, as for the larger amounts of aluminum which were to be determined spectrophotometrically.

Excess 8-quinolinol caused lowered fluorescence readings but improved the stability and reproducibility, as was also found by Goon et al (6). Increased amounts of reagent in solutions taken for spectrophotometric measurements resulted in an increase in the blank absorbency but also a proportional increase in the sample values and, provided that the 8quinolinol concentration in the initial solution (prior to extraction) is the same in the sample as in the blank, the net reading (sample minus blank) is the same regardless of the absolute value of the reagent concentration (within practical limits). Two ml of 1% 8-quinolinol reagent gave reproducible results, both fluorimetrically and spectrophotometrically. In the proposed procedure, over 35 equivalents of 8-quinolinol are added for each equivalent of aluminum.

# C. Effect of Ammonium Acetate Buffer Concentration

The concentration of buffer used to stabilize the pH at 5.6 to 5.7 was varied. Solutions containing 10 and 50  $\mu$ g Al, 2 ml of 1% 8-quinolinol reagent, and 2.5, 5 and 10 ml of 2.5 M ammonium acetate were extracted at pH 5.6 and the corresponding fluorescence and absorbance were measured.

Fluorimetrically, maximum readings were obtained with 2.5 and 5 ml of buffer, whereas 10 ml resulted in a decrease in fluorescence of about 10%. The spectrophotometric measurement of 50  $\mu$ g of aluminum showed an increase in absorbency with increased amounts of buffer but also a proportional increase in the blank value. A 5 ml quantity of buffer was chosen as the amount sufficient to stabilize the pH and to give maximum fluorescence.

## D. Effect of Time of Standing

Both the fluorescence measurements and the absorbancies of the aluminum extracts were measured after standing one-half hour, and one hour. There was no difference between either of the two sets of measurements.

### E. Fluorimetric Calibration Curve

Based on the above study of conditions, the following procedure was used for the preparation of a calibration curve. One-hundred-millilitre beakers containing 0, 2, 4, 8, 10 and 12  $\mu$ g of aluminum in a volume of 20 ml were treated with 2 ml of 1% 8-quinolinol reagent and 5 ml of 2.5 M ammonium acetate buffer (adjusted to pH 5.7), and the solutions were adjusted to pH 5.6 to 5.7 with dilute ammonium hydroxide solution by means of a pH meter. The solutions were then transferred to 60 ml separatory funnels and extracted once with 25 ml of chloroform for one minute.' The chloroform layers were drained into 50 ml flasks containing 1 to 2 g of sodium sulphate and capped with plastic stoppers.

The extracts were measured fluorimetrically, using the apparatus previously described under "Recommended Procedure". The solution fluoresces over a wave length range of 470 to 550 mµ (11). Figure 2 shows the calibration curve obtained. This curve is linear over the range 2 to  $10 \mu$ g Al flattening off at higher concentrations.

#### F. Spectrophotometer Calibration Curve

The wave length of maximum absorption for aluminum 8-quinolinolate has been reported to be 389 mµ (7) and 395 mµ (2). To establish the optimum wave length for maximum absorption under the extraction conditions employed, the absorbance of 50 µg of aluminum extract was measured against an extracted reagent blank over a wave length range of 350 to 450 mµ on a calibrated Beckman DK Recording Spectrophotometer. The curve obtained is shown in Figure 3, the maximum being observed at 387 mµ.







Figure 2. Calibration Curve for the Fluorimetric Determination of Aluminum.

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The absorbance values, for aluminum extracts containing 0, 10, 25, 50, 75 and 100  $\mu$ g Al, obtained by the procedure described under "Preparation of Calibration Curve" were measured at this wavelength. The results are shown in Figure 4. The curve is linear over the entire range measured.

## G. Sources of Contamination

The degree of purity of the reagents and the contamination from the apparatus were next investigated.

The effects of the reagents on the blank value are shown in Table 1. There was no measurable fluorescence from the chloroform used (Test No. 1). or from a solution of 8-quinolinol in chloroform (Test No. 2). The distilled water showed negligible fluorescence and aluminum content (Tests No. 7 and 8). No appreciable increase in the blank value was found due to the acetate buffer (Test No. 6). A comparison of Tests 1, 2 and 7 with Tests 5 and 6, suggests that the typical blank readings obtained in these latter tests arise neither from the instruments, nor from any of the reagents, but instead are due to the extraction step itself. This is confirmed in Test'8, which shows that a second blank extract gives virtually the same fluorescence as the first, whereas had the blank been due to contaminants, the second extract should have given a significantly lower value. Hence it is concluded that the blank readings are due largely to the small amount of 8-quinolinol which is extracted from the aqueous solution into the chloroform layer. Ionized 8-quinolinol (9) has been reported to have an absorption peak at 372 m $\mu$ , and it is possible that this absorption is accompanied by fluorescence in the same manner as it is in the case of the metal complex. The blank was found to increase with an increase in the amount of acetic acid used in making up the 8-quinolinol solution (Tests No. 3 and 4), whereas dissolving the 8-quinolinol reagent in 0.1 M HCl resulted in a decrease in the blank reading (Test No. 5). The anhydrous sodium sulphate used for drying the extract contributed to a slightly higher blank reading (Tests No. 5 and 9). However, the moisture present in some of the extracts not treated with  $Na_2SO_4$ resulted in abnormally high absorbance readings, and the drying step was therefore included in the procedure.

It was suspected that some aluminum contamination might arise from the use of glassware in dissolving samples, particularly where hydrofluoric acid was employed in the initial attack and in the removal of silica. Accordingly, tests were carried out to establish the magnitude of such contamination. Platinum, Teflon, Pyrex and Hysil beakers were treated with 10 ml concentrated nitric, 10 ml concentrated perchloric, 1 ml 48% hydrofluoric acids, and evaporated to dryness. The residues were analysed for aluminum; the recoveries from platinum and Teflon was negligible, but those from Pyrex and Hysil was of the order of 5 mg of aluminum. Hence, the use of Teflon beakers for sample dissolution is considered mandatory.



Figure 4. Spectrophotometric Calibration Curve: Absorbance vs. Aluminum Concentration at 387 mµ on Beckman "B" Spectrophotometer.

#### TABLE 1

## The Effects of the Reagents on the Blank Value

.

Test	Rescents Present	FLUORIMETRIC READING (instrument set at 500)		SPECTROPHOTOMETRIC READING (absorbance read against chloroform)	
No.		Average scale reading	No. of determinations	Average absorbance	No. of determinations
1	Chloroform (Mallinckrodt A.R.).	4	(2)	0:000	(2)
2	Chloroform and 8-quinolinol (0.02 g per 25 ml chloroform)	. 4	(2)	0.004	(2)
3	25 ml chloroform extract from 2 ml 8-quinolinol (1% in 1 M acetic acid), 5 ml buffer and 20 ml of distilled water.	140	(4)	0.049	(4)
4	25 ml chloroform extract from 2 ml 8-quinolinol (1% in 0.25 M acetic acid), 5 ml buffer and 20 ml of distilled water.	95	(4)	0.038	(4) .
5	25 ml chloroform extract from 2 ml 8-quinolinol (1% in 0.1 M HCl), 5 ml buffer and 20 ml of distilled water.	66	(4) '	0.025	(4)
6	25 ml chloroform extract from 2 ml 8-quinolinol (1% in 0.1 M HCl) and 20 ml of distilled water at pH 5.6. No buffer added.	60	(2)	,	
7	Distilled water; no extraction.	3	(2)		· · · ·
8	20 ml of distilled water, pre-treated by addition of 2 ml 8-quinolinol (1% in 0.1 M HCl) and 5 ml buffer followed by extraction with chloroform. The aqueous phase was then treated with 2 ml of 8-quinolinol and extracted with 25 ml of chloroform	58	(2)		
9	25 ml chloroform extract from 2 ml 8-quinolinol (1% in 0.1 M HCl), 5 ml buffer and 20 ml of distilled water (the extract was dried over 1 g of anhydrous sodium sulphate before ; reading).	79 	(4)		

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## H. Interfering Elements in Samples

The elements that may be found in samples obtained during the production of wet-process phosphoric acid from Florida land-pebble phosphate ore and that will seriously interfere with this extraction procedure are fluorine and iron. Phosphate, which is present in large concentrations in most samples, also causes difficulties; the order of addition of reagents, and the time of standing before extracting with chloroform, have a serious effect on the intensity of the colour in the presence of phosphate ion. It is not separated from aluminum in the course of analysis. The large amounts of calcium that may be present in these samples was found not to interfere. Large amounts of acetate, chloride, nitrate, sulphate and perchlorate are without effect, but citrate and tartrate interfere by reducing the amount of aluminum extracted (8).

## I. Methods for Eliminating Interferences

#### (1) FLUORIDE

The strong complex formed by fluoride and aluminum interferes seriously. The fluoride is removed by fuming samples with sulphuric or perchloric acid in Teflon beakers.

#### (2) IRON

## a) Mercury Cathode Separation

A mercury cathode electrolysis (8, 11) will give an effective separation of aluminum from iron, as well as from such elements as chromium, molybdenum, cobalt, nickel, copper, zinc, antimony, and tin, but not from manganese, zirconium, titanium, niobium, tantalum, uranium, vanadium, or thorium. Niobium and tantalum do not interfere in the present procedure, because they can be removed almost completely in the dissolution step by fuming with perchloric acid. The electrolysis can be done in the presence of perchloric or sulphuric acids (11).

To establish the effectiveness of these steps in eliminating interferences present in the samples, a synthetic standard was made up to simulate the composition of the residues from the phosphoric acid leaching process. These residues, which had the highest concentration of interfering elements encountered in this work, were simulated by a mixture of equal parts of NBS standard sample 69a (Bauxite) and NBS standard sample 79 (Fluorspar). The resultant mixture contained 27.5% Al<sub>2</sub>O<sub>3</sub> (14.6% Al), 47.4% CaF<sub>2</sub>, 2.98% Fe<sub>2</sub>O<sub>3</sub>, 3.95% SiO<sub>2</sub>, 1.39% TiO<sub>2</sub>, and 0.04% P<sub>2</sub>O<sub>5</sub>. This standard was put into solution and analysed for aluminum by the recommended procedure, including the mercury cathode separation. On four determinations, the aluminum content averaged 14.3%, as compared with the calculated value of 14.6%.

## b) Sodium Hydroxide Separation

This separation is often used to separate aluminum from other elements. It will remove such elements as iron, chromium, manganese, cobalt, nickel, copper, titanium, zirconium, uranium and rare earths, but not vanadium, molybdenum, zinc, antimony, and tin (13). Table 2 compares the effectiveness of the sodium hydroxide precipitation with the mercury cathode separation. For the removal of moderate amounts of most interfering elements, the mercury cathode separation is faster, introduces fewer impurities, and leaves the aluminum in a dilute acid solution ready for the extraction step.

#### TABLE 2

## A Comparison of Sodium Hydroxide and Mercury Cathode Separations for the <u>Removal of Iron in the Determination of Aluminum on Typical Calcium</u>-<u>Aluminum-Fluoride Precipitates</u>

Sample	NaOH Separation, % Al found	Mercury Cathode Separation, % Al found
(a)	3.19	3.38
(b)	1.36	1.27
(c)	2.47	2.67
(d)	1.59	1.70

#### c) Use of Complexation

It is reported that the interference due to a small amount of iron can be eliminated by the use of o-phenanthroline (3). To confirm this, small amounts of iron were added to solutions containing known amounts of aluminum. The solutions were treated with 1 ml of 10% hydroxylamine hydrochloride solution and 5 ml of 0.1% o-phenanthroline solution, and were then allowed to stand two to three minutes; 8-quinolinol reagent and buffer were added, the pH adjusted, and the aluminum extracted with chloroform. The aluminum content was read fluorometrically and the results are shown in Table 3.

## TABLE 3

## Results of Complexing Iron Interference with o-phenanthroline

Amount Fe	Treatment	μgAl	µg Al
added, µg		added	found
30 30 60 60	Fe complexed No o-phenanthroline Fe complexed No o-phenanthroline	5.0 5.0 5.0 5.0 5.0	4.8 3.0 5.2 1.8

The orange-coloured iron o-phenanthroline complex remained in the aqueous phase and did not interfere. Thus, it may be possible to determine the iron present in the aqueous layer spectrophotometrically during the course of the aluminum determination.

Since the calcium aluminum fluoride precipitates obtained during the course of the pilot-plant investigation contained only iron (about 1%) as an interfering element after the dissolution step, the aluminum content of one such sample was also determined after the dissolution step by complexing the iron with o-phenanthroline and using the fluorimetric finish. The result is compared, in Table 4, with that obtained when iron was removed by a mercury cathode separation.

## TABLE 4

## Determination of Aluminum in Calcium Aluminum Fluoride Residue

Treatment	% Al Determined
Fe Complexed with o-phenanthroline	3.3%
Mercury Cathode Separation of Fe	3.4%

# (3) PHOSPHATE

As noted previously, when phosphate is present the order of addition of reagents and the time of standing before extracting with chloroform affect the intensity of the colour. If the 8-quinolinol reagent is added to the sample, the acidity initially adjusted to a pH of about 5.2 with dilute  $NH_4OH$  and the buffer added, phosphate will interfere seriously: results will be low by about 50%. It was found that the effect can be overcome if the 8-quinolinol reagent and buffer are added successively to the sample at pH 1 to 3 and the solution is allowed to stand 5 minutes. Dilute NH4OH is then added to give a pH of 5.6 and solution extracted.

Results obtained using the recommended procedure on standard aluminum solutions with phosphate added in the ratio present in the phosphoric acid samples showed no appreciable interference. These results are given in Table 5.

#### TABLE 5

## Percentage Recovery of Aluminum from Standard Solutions Containing Phosphorus

Measurement	Alμg present	P mg added	% Al recovered (aver. of 3 determinations)
Fluorimetric	10	0.4	92
Spectrophotometric	50	2.0	98
Spectrophotometric	100	4.0	98

## (4) CALCIUM

Large amounts of calcium were present in most of the samples received from the pilot plant. Calcium was added to prepared solutions in the same concentration as in the actual samples and was found not to interfere with the proposed method. These results are given in Table 6.

# Percentage Recovery of Aluminum from Standard Solutions Containing Calcium

Measurement	Al μg present	CaO mg added	% Al recovered (aver. of 3 determinations)
Fluorimetric	10	1	94
Spectrophotometric	50	5	103
Spectrophotometric	100	10	99

#### J. Precision

The standard deviations were calculated for two concentrations of aluminum, determined fluorimetrically, in samples received from the pilot plant leach circuit. They are shown in Table 7.

#### TABLE 7

#### Precision of Fluorimetric Method

Level	No. of Sets	No. in Set	Average Range*	Standard Deviation
0.15 g/1	1	5	0.04	+ 0.017
3.0%	2	5	0.23	± 0.098

\* The range of the observations is the difference between the greatest and least value, and the range is converted to a measure of dispersion independent of the number of observations (12).

The precision of the spectrophotometric part of the method is similar to that shown in Table 8, as calculated from values obtained by Dagnall, West and Young (14).

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## TABLE 8

#### Precision of Spectrophotometric Method

Level	No. of Sets	No. in Set	Average Range*	Standard Deviation
0,04	· 1	5	0.014	, <del>*</del> 0.006
0,13	1	5	0.017	<u>+</u> 0.007

\* The range of the observations is the difference between the greatest and least value, and the range is converted to a measure of dispersion independent of the number of observations (12).

#### K. Speed

The time required to analyse three samples in duplicate by the recommended procedure, including a mercury cathode separation, would be 3 to 4 hours.

#### CONCLUSIONS

The proposed method permits the determination of aluminum over a wide range of concentrations with adequate speed and good precision. It is applicable to the various types of samples obtainable from the phosphoric acid process. The fluorimetric finish, with its high sensitivity, is particularly suitable in dealing with small quantities of sample or with samples of low aluminum content, but the spectrophotometric finish will give better precision and accuracy.

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