F.R.I. 47.

WCU/C/115

BRANDSTOFNAVORSINGSINSTITUUT

VAN SUID-AFRIKA.

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA.

ONDERWERP:
SUBJECT:_____THE DETERMINATION OF SMALL AMOUNTS OF ALU-

___MINIUM OXIDE IN MAGNETITES AND IRON CATALYSTS.___

AFDELING:
DIVISION:_____CHEMISTRY.

NAAM VAN AMPTENAAR:
NAME OF OFFICER:_____F.H. KUNSTMANN AND E.F.E. MÜLLER.

THE DETERMINATION OF SMALL AMOUNTS OF ALUMINIUM OXIDE IN MAGNETITES AND IRON CATALYSTS.

by: F.H. Kunstmann and E.F.E. Müller.

Aluminium oxide, among other substances, is used as a "structural promoter" in iron catalysts (1). The following method makes possible the determination of the relatively small amounts of aluminium in iron catalysts.

It is customary in mineral analysis to determine alumina indirectly by determining Fe_2O_3, TiO_2 and P_2O_5 and subtracting their sum from the total oxides precipitated by ammonia. When, however, the amount of iron is greatly in excess of the aluminium, as in these catalysts which consist mainly of iron oxides, the indirect aluminium determination is not sufficiently accurate.

When small quantities of a constituent are to be determined it is often convenient to carry out the determination colorimetrically. Therefore, as a first attempt, a colorimetric method worked out by Bannerjee and Colliss (2) for the determination of aluminium in coal ash was applied to the iron catalysts. The procedure is based on the prevention of the interference of ferric iron by means of thioglycolic acid (mercaptoacetic acid) and the formation of a coloured complex of aluminium with ammonium aurintricarboxylate (aluminon) (3).

With synthetic mixtures of aluminium and iron, where the relative amounts are in the ratio normally found in coal ash ($Al_2O_3/Fe_2O_3 \sim 5/1$), the method proved to be adequate, but during analysis of some of the magnetites (ratio $Al_2O_3/Fe_2O_3 \sim 1/50$) unsatisfactory results were obtained. Therefore, it was felt advisable to separate the iron from the aluminium by some means. A short discussion of various separations may be found in the textbook of Sandell (3). C. Howard Craft and G.R. Makepeace (4)

describe/........

describe a method where isopropyl ether (or ethyl ether) is used to extract the iron from hydrochloric acid solutions. As it is inconvenient to use highly inflammable chemicals in an analytical laboratory where naked flames are often used, it was decided to try some other separation and keep the ether separation as a last resort. The electrolytic separation of iron with the mercury cathode (3, 5, 6) was studied and found very suitable. A method for the determination of aluminium, where iron is separated electrolytically, is described below. The electrolysis cell used, shown in fig. 1, was taken from the textbook of Hillebrand and Lundell (5). The analysis is carried out according to the method of Howard Craft and Makepeace (4)

Solutions Required.

Ammonium Aurintricarboxylate (aluminon), 0.10%. Dissolve 0.10g. of the salt in water, add 10ml. of 10% benzoic acid in methyl alcohol and dilute to 100 ml. Allow to stand three days before using.

Gelatin, 1%. Dissolve 1g. of gelatin in hot water, cool, add 10ml. of 10% benzoic acid in methyl alcohol and dilute to 100ml.

Buffer Solution. Mix 470ml. of 15 N ammonium hydroxide and 430ml. of glacial acetic acid, cool to room temperature, and add more acid or base as required, to give a pH of 5.25 - 5.35 when diluted 1 in 20. Dilute to 1 litre.

Composite Reagent Solution. Mix equal volumes of each of the above solutions. The composite may be prepared from freshly dissolved aluminon, but then the mixture should not be used until after three days.

NOTE: When mixing the three components a turbidity, which was found to be due to the gelatin was formed. The turbidity could not be removed by filtration. It had no effect on the accuracy, however, as it dissapeared during the process of analysis.

Sodium/..........................

<u>Sodium Hydroxide Solution.</u> Make up a solution of approximately 1 N strength.

<u>Procedure.</u>

Dissolve 0.1g. of finely ground magnetite or catalyst sample in 5ml. of concentrated hydrochloric acid, evaporate to dryness on a sandbath.   Cool, add ca. 5ml. water and 1.2ml. concentrated sulphuric acid, evaporate to white fumes so as to expel chlorides. Cool, carefully add some distilled water to dissolve the ferric sulphate, transfer the solution quantitatively to 100ml. measuring flask and dilute to the mark.   Shake well, pipette 20ml. into the mercury cathode cell, electrolyze for 1 hour with 0.5 amps. (6V), run the electrolyzed solution and rinsings into a beaker, filter into 100ml. measuring flask, wash beaker and filter paper a few times with distilled water, make up to 100ml. and mix.   Take a 5ml. aliquot for the aluminium determination.   To the aliquot in a test-tube (ca $\frac{3}{4}$" x 6") add a drop of phenolphthalein indicator, and then add 1 N sodium hydroxide to the first red colour.   Add 15ml. of composite aluminon reagent.   A blank containing the same amount of sulphuric acid as the sample solution is run at the same time.   Immerse the test-tubes in a water bath ($90-100^{\circ}$C) for 10 minutes, remove and allow to stand at room temperature for 10 minutes. Dilute to exactely 100ml. and measure the absorption in a spectrophotometer at a wavelength of 525mμ and a slit width of 0.045 mm. The blank serves as reference solution.   Read off the aluminium oxide content from a calibration curve.   The calibration curve is obtained by taking aliquots from 0 to 50 μg Al$_2$O$_3$ of a standard aluminium solution and treating as above.

By electrolysis/........

By electrolysis with a mercury cathode the elements Al, Ti, Zr, P, V and U can be separated from Cr, Fe, Co, Ni, Cu, Zn, Ga, Ge, Mo, Rh, Pd, Ag, Cd, In, Sn, Re, Ir, Pt, Au, Hg, Tl and Bi, which are deposited on the cathode (5).

Of the elements that are not separated from aluminium by electrolysis and that may interfere in the determination, titanium, phosphorus and possibly calcium and magnesium have to be reckoned with. Their effect on the determination of Al with aluminon was determined.

I Effect of Titanium

Table 1 shows the effect of titanium on the aluminium determination with ammonium aurintricarboxylate. Assuming that a catalyst has an aluminium content of 2.5% then 25 μg Al_2O_3 corresponds to 1000 μg of catalyst. The addition of 20 μg TiO_2 would, in this case, correspond to a 2% titanium content of the catalyst. The table shows for each of two Al_2O_3 concentrations (5 and 25 μg or 0.5 and 2.5%) the effect of three concentrations of TiO_2 (5,20 and 50 μg or 0.5, 2.0, and 5.0%).

From the table it can be seen that the presence of TiO_2 depresses the Al_2O_3 values. The influence of TiO_2 at the concentration in question is not sufficiently large to force a separation which would invariably complicate matters.

It should be mentioned here that the gelatin in the reagent not only acts as a protective colloid for the aluminium lake, but, it was found, also has the effect of minimising the influence of titanium.

Table I/. . . . .

TABLE 1.

μg Al_2O_3 present	μg TiO_2 added	μg Al_2O_3 found	Average.
5	-	5.1	
5	-	4.9	5.0
5	-	5.0	
5	5	5.1	
5	5	4.9	5.0
5	5	5.0	
5	20	4.8	
5	20	5.0	4.9
5	20	5.0	
5	50	5.0	
5	50	4.9	4.9
5	50	4.9	
25	-	25.0	
25	-	25.0	25.0
25	-	25.0	
25	5	25.0	
25	5	25.2	25.1
25	5	25.0	
25	20	25.0	
25	20	24.8	24.9
25	20	25.0	
25	50	24.0	
25	50	24.0	23.9
25	50	23.7	

II Effect of Phosphorus.

As before if the Al_2O_3 content of a catalyst is 2.5% then $25 \mu g$ Al_2O_3 corresponds to 1000 μg catalyst and therefore, 50 μg P_2O_5 corresponds to a 5% P_2O_5 content.

TABLE 2.

μg Al_2O_3 present	μg P_2O_5 added	μg Al_2O_3 found	Average
5	-	5.3	
5	-	4.9	5.1
5	-	5.1	
5	5	5.2	
5	5	4.9	5.0
5	5	5.0	
5	50	5.1	
5	50	4.9	5.1
5	50	5.3	
25	-	25.0	
25	-	25.2	25.1
25	-	25.0	
25	5	25.0	
25	5	25.0	25.0
25	5	25.0	
25	50	25.0	
25	50	25.0	24.9
25	50	24.8	

As can be seen from Table 2, phosphorus, in the concentrations shown, has no marked influence on the determination of aluminium with aluminon.

III Effect of Calcium and Magnesium.

Table 3 shows that the aluminium determination is not affected by calcium and magnesium at the concentration given below.

TABLE 3

μg Al_2O_3 present	μg CaO added	μg MgO added	μg Al_2O_3 found	Average
5	–	–	5.0	
5	–	–	5.0	5.0
5	–	–	5.1	
5	25	–	5.0	
5	25	–	5.3	5.1
5	25	–	5.0	
5	–	25	5.0	
5	–	25	5.3	5.1
5	–	25	5.0	
5	25	25	5.0	
5	25	25	4.9	5.0
5	25	25	5.0	
25	–	–	25.0	
25	–	–	24.8	24.9
25	–	–	25.0	
25	25	25	25.0	
25	25	25	24.8	25.0
25	25	25	25.2	
25	50	50	25.0	
25	50	50	25.0	25.0
25	50	50	25.0	

Relative/..............

Relative Accuracy of the Method.

To determine the relative accuracy of the analysis, three different samples were examined. Six portions of each were dissolved, electrolyzed and the Al_2O_3 content determined. Table 4 gives the results.

TABLE 4.

Sample No.	1	2	3
Al_2O_3 found per cent.	0.17	0.81	2.19
	0.15	0.81	2.19
	0.17	0.77	2.14
	0.17	0.81	2.16
	0.20	0.77	2.14
	0.15	0.78	2.12
Average	0.17	0.79	2.16

The Al_2O_3 content of Sample No. 1 is too low for this method to give sufficiently accurate results.

Absolute Accuracy of the Method.

A catalyst sample with a 5% Al_2O_3 content was prepared in the laboratory - Sample A. A series of composites were also prepared by mixing sample A with Millscale. These samples were dissolved electrolyzed and analyzed. The results are given in Table 5.

Table 5.

Composites		Al_2O_3 content found (%)	Al_2O_3 content calculated (%)
Sample A (g).	Millscale (g)		
0.000	1.000	0.11	-
0.217	0.783	1.15	1.17
0.435	0.565	2.14	2.24
0.652	0.348	3.19	3.30
0.870	0.130	4.33	4.36
1.000	0.000	4.99	5.00

References/..........

References.

1) The Fischer Tropsch and Related Syntheses - H.H. Storch,
    N. Golumbic and R.B. Anderson 1951, p. 37 (John Wiley and
    sons)

2) Rapid Analysis of Ash from Coal and Oil Shale by Colorimetric
    Methods - N.N. Bannerjee and B.A. Colliss - Fuel Vol. 34,
    April 1955 Supplement p. S71.

3) Colorimetric Determination of Traces of Metals - E.B. San-
    dell 1950, pp. 141 - 144 (Interscience Publishers.)

4) Colorimetric Estimation of Aluminium in Aluminium Steel -
    C. Howard Craft and G.R. Makepeace - Ind. Eng. Chem. (Anal.
    Ed.) Vol. 17, 1945, p. 206.

5) Applied Inorganic Analysis - Hillebrand and Lundell - Second
    Edition, revised by Lundell, Bright and Hoffman, 1953, p. 138.

6) A Textbook of Quantitative Inorganic Analysis (Second Edition)
    - A.I. Vogel, 1951, p. 514.

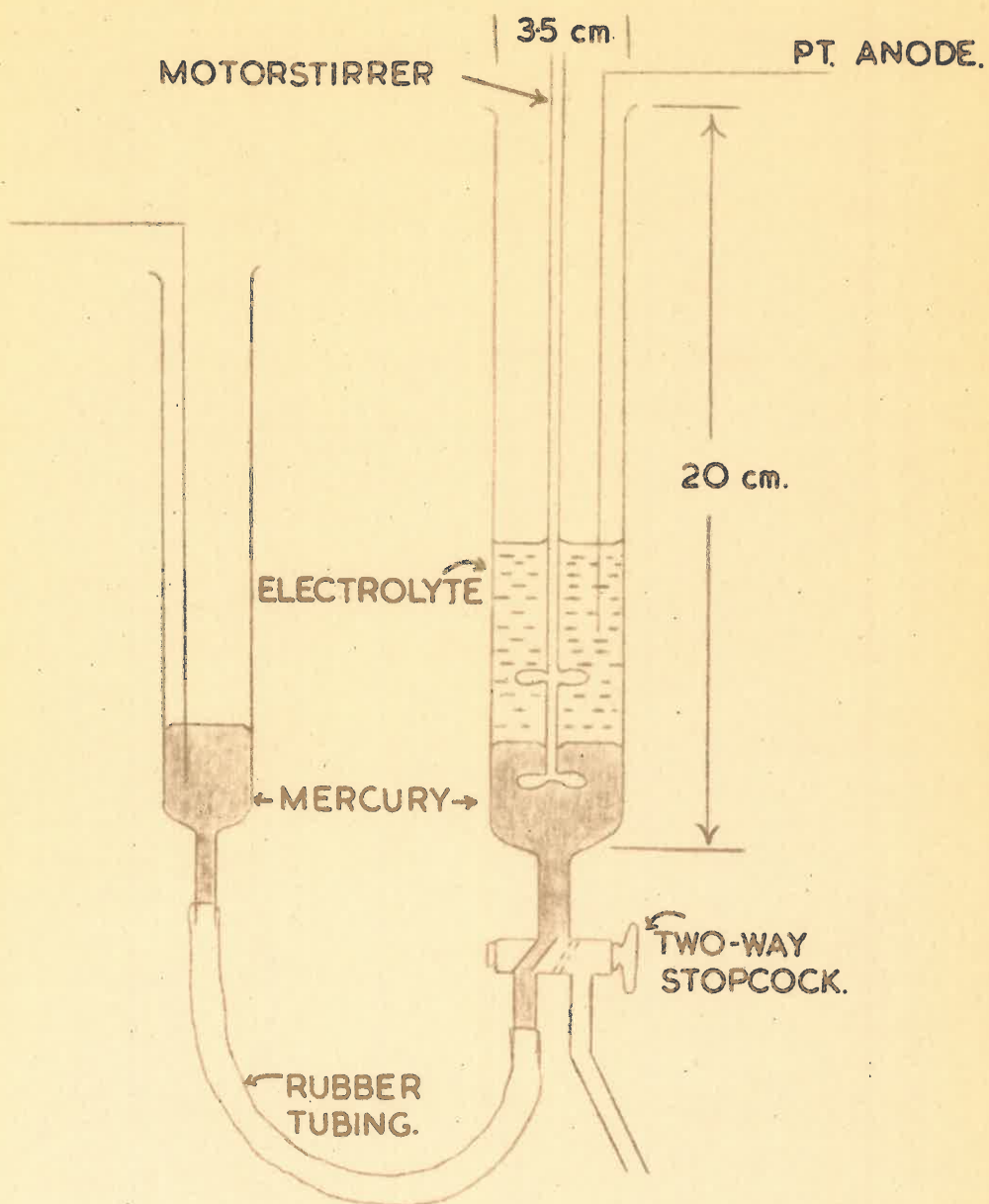MOTORSTIRRER

35 cm

PT. ANODE.

20 cm.

ELECTROLYTE

MERCURY

TWO-WAY
STOPCOCK.

RUBBER
TUBING.

FIGURE I.

APPARATUS FOR ELECTROLYSIS.