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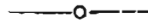
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THE VOLUMETRIC DETERMINATION OF ALUMINA
IN CLAYS AND RELATED MATERIALS

BY

DAVID FERDINAND BOLTZ



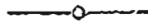
A

THESIS

submitted to the Faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
DEGREE OF
MASTER OF SCIENCE, CHEMISTRY MAJOR

Rolla, Mo.

1940



Approved by

W.T. Schrenkel
Head, Department of Chemical Engineering and Chemistry.

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THE VOLUMETRIC DETERMINATION OF ALUMINA
IN CLAYS AND RELATED MATERIALS

INTRODUCTION

The primary purpose of this thesis was to develop a direct method for the determination of alumina in certain silicates. The classical gravimetric procedure for the analysis of alumina in clays and related materials has often been regarded as being too lengthy and troublesome, especially when only the percentage of alumina was desired. The correct determination of alumina is undoubtedly one of the most unsatisfactory of the chemical constituents of siliceous materials, and therefore the development of a direct volumetric method for the determination of this constituent was made the main objective of this research.

The use of the organic reagent, 8 hydroxyquinoline, for the quantitative precipitation of aluminum as aluminum quinolate was employed in certain analyses in 1927 by Berg.¹ The precipitate was usually weighed as aluminum quinolate or as alumina after ignition. The principle of quantitatively brominating the dissolved quinolate precipitate was known and applied with

¹Berg, R., New Method for Determining and Separating Metals with Aid of O-Hydroxyquinoline. Determination and Separation of Aluminum; Z. Anal. Chem., 71, 369-80 (1927).

varying degrees of success.² The work of these investigators indicated, however, a need for further study in the application of the method to other materials. The methods of decomposing the sample and of separating aluminum from interfering elements, such as iron and titanium, would then become a definite part of the problem. After considerable experimental work a procedure was developed which gave consistent and accurate results.

²Fleck, H. R., Greenan, F. J., and Ward, A. M., Determination of Metals by Means of 8 Hydroxyquinoline; *Analyst*, 59, 325, (1934).

Knowles, H. B., Use of 8 Hydroxyquinoline in the Determination of Aluminum, Beryllium, and Magnesium; *J. Research, National Bur. Standards*, 15, 87-96, (1935).

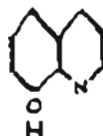
Koenig, E. W., Direct Determination of Alumina in Certain Silicates; *Ind. Eng. Chem., Anal. Ed.*, 11, 532, (1939).

Robitschek, V., The Use of 8 Hydroxyquinoline for the Chemical Analysis of Silicates; *J. Am. Ceram. Soc.*, 11, 587-94, (1928).

REAGENTS8 Hydroxyquinoline

This organic reagent is obtainable in a pure form from the Eastman Laboratories. It has a molecular weight of 145.06,

melts at 76° C. and has the following structural formula:



Although it is slightly soluble in water it readily dissolves in either acetic acid or ethanol. Often 8 hydroxyquinoline is referred to in the literature as "oxine." In reacting with an element the H of the OH radical is replaced by an equivalent of that element. Precipitation may be carried out either in a properly buffered acid solution or in an alkaline medium.³ The following common ions may be precipitated completely in an acetic acid—acetate solution: Al, Fe, Ti, Hg, Ag, Zn, Cu, Ni, Co, and Bi, while Cr, Mn, Sn, and Sb are partially precipitated. The degree of alkalinity or acidity determines the completeness of precipitation.

The necessity of controlling the pH and its importance in the separation of various ions has only recently been realized. There is only a limited amount of information available concerning the solubility of the quinolate precipitates in solutions of different pH values.

³Lundell, G. E. F., and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*; New York, J. Wiley, 1938, p. 113.

There are several reasons why 8 hydroxyquinoline is a desirable precipitating reagent. First, the precipitate obtained is crystalline and is easy to filter and wash. Secondly, the amount of metal found in the precipitate is small. Aluminum quinolate contains only 5.87 percent of the metal by weight. This is of considerable importance when dealing with small amounts of metallic ions. Because a quinolate can be dried at 110° C. and weighed, it is quite suitable for use in gravimetric analysis. Finally, the quinolate precipitate may be dissolved and quantitatively brominated to give a di-bromo substitution compound enabling volumetric determinations which are faster than gravimetric procedures.

The use of an alcoholic solution of 8 hydroxyquinoline is not as desirable as an acetic acid solution because the alcohol has a solvent action on the precipitate. In this work a 5 percent solution of this reagent in 1N acetic acid was used. Usually 12.5 grams of 8 hydroxyquinoline was dissolved in 15 cc. hot glacial acetic acid and the solution diluted to 250 cc. with distilled water. This solution was stable and did not decompose after standing for long periods.

Potassium Bromate Solution (0.1N)

This solution was prepared by dissolving 5.568 grams of potassium bromate, which was previously dried at 150° C., in two liters of distilled water.

Arsenious Oxide Solution (0.1N)

Dissolve 4.9455 grams of reagent grade arsenious oxide in 50 cc. of 1N sodium hydroxide solution. It was neutralized with dilute hydrochloric acid and several grams of sodium bicarbonate added. This solution was transferred to a one-liter flask and diluted to the mark with distilled water at 20° C.

Iodine Solution (approximately 0.1N)

Weigh out approximately 12.5 grams of reagent grade iodine and place together with 50 grams of potassium iodide, which must be iodate free, in a beaker containing 25 to 50 cc of water. Stir until dissolved, transfer to a glass-stoppered bottle, and dilute to one liter with distilled water. This solution should be kept well stoppered and away from direct sunlight.

Buffer Solution

Dissolve 150 grams of ammonium acetate in one liter of water and place in a glass-stoppered bottle.

Starch Solution

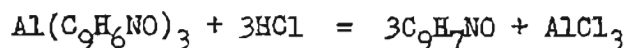
A 1-gram sample of starch was treated with 5 to 10 cc. of distilled water to form a suspension and diluted to a volume of 500 cc. with hot water. This solution was boiled for about 15 minutes and set aside to cool. The clear supernatant liquid was decanted into a glass-stoppered bottle and kept in a cool place.

Sodium Hydroxide

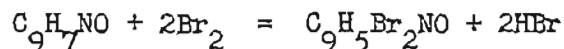
Baker's C. P. pellets were used.

A STUDY OF THE BROMINATION OF 8 HYDROXYQUINOLINE

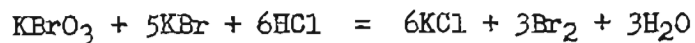
An aluminum quinolate precipitate when dissolved in hydrochloric acid forms 8 hydroxyquinoline in accordance with the following equation



This equation definitely shows that aluminum is equivalent to three molecules of 8 hydroxyquinoline, each molecule of which may be brominated to give a di-bromo substitution product consuming two molecules of bromine per molecule of the reagent. Therefore, aluminum being equivalent to three molecules of 8 hydroxyquinoline possesses a hydrogen equivalent of 12. This is illustrated by the following equation

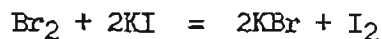


The bromine consumed in this reaction was obtained from a standard potassium bromate-bromide solution by a reaction with the excess hydrochloric acid used in dissolving the aluminum quinolate as illustrated by the following equation



In practice an excess of the potassium bromate solution is added, and it is therefore necessary to measure the excess bromine in order to find the exact amount of bromine consumed by the 8 hydroxyquinoline.

The procedure generally used measures the excess bromine by adding sufficient potassium iodide so that the iodine may be replaced by the more active bromine, thus



The iodine thus liberated is titrated with a standardized sodium thiosulfate solution, the amount of sodium thiosulfate being equivalent to the brominating solution added in excess,



The author tested this recommended procedure for the volumetric determination of aluminum by 8 hydroxyquinoline and obtained satisfactory results in few instances. In general the results were erratic and unsatisfactory. This led to an investigation of a number of factors which might cause deviations, such as pH value, amount of potassium iodide added, volume of solution, and losses due to volatilization.

The hydrogen ion concentration was important inasmuch as different amounts of reagent were consumed depending on the acidity. Buffering the solution with sodium acetate before addition of the sodium thiosulfate and just after liberation of the iodine gave fairly constant results.

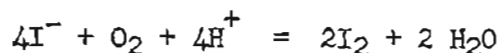
When the effect of the amount of potassium iodide added was studied only enough potassium bromide was present to react with the potassium bromate to liberate bromine. Keeping all other factors constant the sodium thiosulfate solution was standardized adding different amounts of potassium iodide. The data in Table 1 indicate that there is a tendency for the normality of the sodium thiosulfate to decrease as the ratio of potassium iodide to iodine increases.

In an analysis this variation in normality would give either positive or negative errors, depending on the amount of potassium iodide present in standardization. Later it was found that the effect of the potassium bromide was similar to that of the potassium iodide. This gave basis for an explanation which will be mentioned later. As previously stated, in all of the above work the volume was kept constant in each case, (100 cc). If the aforementioned facts were true the normality of the sodium thiosulfate should increase as we increase the total volume, keeping the amount of potassium iodide, acidity, and amount of excess bromine constant. This was found to be true experimentally. Should the amount of potassium iodide be increased proportionally to the increase in volume the normality remained practically the same.

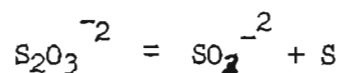
Table 1. Effect of Potassium Iodide

Amount KI in grams per 100 cc of solution	N. of $\text{Na}_2\text{S}_2\text{O}_3$
0.05	0.01652
.07	.01634
.08	.01623
.10	.01606
.20	.01598
.30	.01594
.40	.01589
.50	.01589
.60	.01589
.70	.01581
.80	.01579
.90	.01572
1.00	.01561
3.00	.01556

Several explanations might be given for these differences in normalities of the sodium thiosulfate solution. First in respect to acidity it is possible that at a high hydrogen ion concentration the action of atmospheric oxygen is appreciable in accordance with the following equation⁴



It is also reported that even in a moderate concentration of hydrogen ions that the following reaction may become fast enough to introduce an error⁵



The first reaction would require more sodium thiosulfate to react with the iodine than should be necessary to give a lower normality. The second reaction increases the normality as one mole of sulfite will reduce only one mole of iodine whereas two moles of thio-sulfate are necessary for reduction of one mole of iodine.

The fact that the use of a sodium acetate buffer solution gave more consistent results would indicate that the acidity had an appreciable effect. Although more consistent results were obtained they tended to run high, as illustrated in Table 2.

⁴Town, G., Hall, N. F., and Meloche, Quantitative Chemical Analysis; Ann Arbor, Mich., Edward Brothers, Inc., 1936, p. 86.

⁵Ibid. p. 81.

Partington, J. R., Textbook of Inorganic Chemistry; London, Mac-Millan, 1937, p. 491, 527.

Table 2. Effect of Buffer Solution

Al taken, mg	Al found, mg	Deviation in mg
11.37	11.56	+ 0.13
11.37	11.47	+ .10
11.37	11.43	+ .06
11.37	11.49	+ .12
11.37	11.47	+ .10
11.37	11.41	+ .04

A feasible explanation for these high results is that some bromine or iodine was lost through volatilization. Bromine has a high vapor pressure and if some were allowed to escape less iodine would be replaced, less sodium thiosulfate would be used, and consequently a larger amount of potassium bromate would be necessary for the bromination. This could give high results. The fact that increasing amounts of potassium bromide or iodide gave lower normalities also provides further evidence because larger amounts of these salts should reduce the tendency of the bromine to escape. The most likely place in the procedure where bromine might escape would be when the buffer solution and potassium iodide were added. Even if the flask were kept stoppered the addition of the above reagents would force out some of the air within the flask which in all probability contained some bromine vapor.

The next problem was to develop a procedure eliminating any loss of bromine. To accomplish this it was decided to use a standard arsenite solution and back titrate the excess bromine immediately. This would not necessitate the addition of either potassium iodide or a buffer solution and should therefore prevent loss of bromine. If this standard arsenite solution were added in excess, the amount consumed could readily and accurately be determined by back titrating with a standardized iodine solu-

tion. It would be necessary to neutralize the acid solution with sodium bicarbonate before titrating with the iodine. Such a procedure was tried and satisfactory results were obtained, as shown in Table 3.

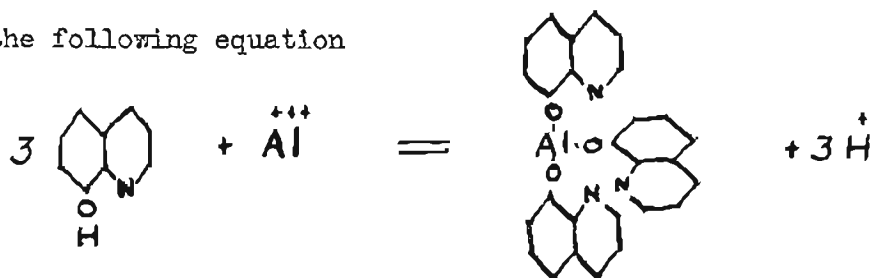
From the results shown in Table 3 it was concluded that this procedure for measuring the excess bromine was satisfactory and that it eliminated some of the errors detected in the course of this study.

Table 3. Efficiency of New Procedure

Al taken, mg	Al found, mg	Deviation in mg
1.80	1.79	- 0.01
3.41	3.40	- .01
4.83	4.81	- .02
5.75	5.75	
11.43	11.45	+ .02
14.66	14.65	- .01

PRECIPITATION OF ALUMINUM BY 8 HYDROXYQUINOLINE

The reagent 8 hydroxyquinoline was first used by Berg⁶ in 1927 and since then numerous modifications and applications of his original experimental work have appeared in the literature. Berg precipitated aluminum by two different procedures. The reaction taking place in both precipitations may be represented by the following equation



In the first procedure $\text{Al} (\text{C}_9\text{H}_6\text{NO})_3$ was precipitated from an acetic—acetate medium by addition of 8 hydroxyquinoline according to the following procedure: To a 100 cc. weakly acetic acid solution containing 3 to 5 grams of sodium acetate a 2.5 percent solution of 8 hydroxyquinoline was added until an orange color appeared. Vigorous stirring must accompany the addition of the 8 hydroxyquinoline to prevent adsorption. The solution was then heated to 60° — 70° C. and the fine yellow crystalline precipitate filtered and washed with hot water until the filtrate was colorless. This precipitate was used to determine the aluminum either gravimetrically or volumetrically.

⁶Berg, R., New Method for Determining and Separating Metals with Aid of O-Hydroxyquinoline. Determination and Separation of Aluminum; *Z. Anal. Chem.*, 71, 369-380, (1927).

The second procedure provides for the precipitation of aluminum in an ammoniacal solution. The slightly acid solution containing the aluminum, 5 to 10 grams of ammonium chloride, and sufficient tartaric acid to prevent precipitation of aluminum hydroxide, was neutralized with ammonium hydroxide and heated to 60° C. A 2.5 percent solution of 8 hydroxyquinoline was then added until an orange-yellow color was apparent. About one cc. of ammonium hydroxide was added and the solution heated for at least five minutes, after which it was filtered, washed, dried and weighed; or dissolved and determined volumetrically.

In using these procedures it was found that the pH played an important part in the success of the analysis. Aluminum will precipitate as the quinolate in a solution with a pH 3--12. Low results were obtained at either extremity of this range and best results were obtained in the acetic--acetate procedure possessing a pH 4 to 5.5 and in the ammonia-tartrate procedure about 7 to 8.

The purpose of heating the solution containing the aluminum quinolate was mainly to form a more crystalline and filterable precipitate. It was the experience of the author, however, that it was better practice to first heat the solution to about 70° C., then precipitate the aluminum quinolate, and allow it to stand for approximately one hour without further heating. Another recommended modification in the precipitation in an acid medium is

that the 8 hydroxyquinoline always be added first and followed by the slow addition of the buffer solution with constant stirring. This eliminates the danger of precipitating any aluminum in the form of basic acetate. Cold water was just as effective in washing the precipitate as hot water.

The procedure used in this work for the precipitation of aluminum as the quinolate was as follows: The hydrochloric acid solution containing the aluminum was heated to approximately 75° C. and a 5 percent solution of 8 hydroxyquinoline in 1N acetic acid was added. One cc of this 8 hydroxyquinoline solution was sufficient to precipitate five mg. of alumina. A 2N sodium or ammonium acetate solution was added with continual stirring until a precipitate formed and then an excess of 15 to 20 cc. added. The solution was set aside to cool and occasionally stirred. The precipitate was then filtered on a Gooch crucible, and washed with a total of about 100 cc. of cold water. The precipitate was then ready to be dissolved in hydrochloric acid for the volumetric procedure as previously given.

SOLUTION OF SAMPLES

A number of reagents may be used in opening silicates depending on their composition. In general samples having less than 40 percent of silica may be put into solution with hot concentrated hydrochloric acid. Alkali carbonates are sometimes satisfactory. A potassium pyro-sulfate fusion is used on refractory materials as is sodium peroxide depending on whether the sample is basic or acidic. For this work, however, sodium hydroxide was selected as it not only dissolved the sample but also formed sodium aluminate which would be of importance in extracting the aluminum from impurities. The procedure employed was as follows: A 0.2 to 0.3 gram sample was placed in a nickel crucible and about 4.5 grams of sodium hydroxide pellets added. The crucible and its contents was slowly heated to drive off moisture and finally the temperature was raised to dull red heat for 5 or 10 minutes. A rotary motion applied to the crucible assists in securing a more uniform melt and complete solution of the sample. The crucible was placed in a casserole and its contents dissolved in about 100 cc. of cold distilled water. The crucible was removed, polished, and washed thoroughly. The solution was then ready for the separation of the aluminum from interfering elements.

SEPARATION OF ALUMINUM FROM INTERFERING ELEMENTS

As in all previous work on the analysis of aluminum the presence of iron and certain other elements proved a source of difficulty. The fact that titanium was usually present made a sulfide separation inadvisable. Iron may be precipitated as the quinolate in an acid solution containing the tartrate ion whereas the aluminum will not, but the difficulty again confronted was that when the aluminum quinolate was precipitated in the alkaline range co-precipitation of certain alkaline earth metals occurred.⁷ Certain other organic reagents⁸ were considered but it was finally upon the amphoteric property of aluminum that a separation was made. In a sodium hydroxide solution the iron and nickel precipitate as hydroxides, whereas the titanium forms an insoluble sodium titanate. Care must be taken in washing the precipitated hydrous oxides with dilute sodium hydroxide solution since the titania may become colloiddally dispersed and pass through the filter if water were used. Heating of the alkali solution before filtering caused low results if considerable sodium silicate was present due to the formation of insoluble

⁷Berg, R., Separation of Iron from Aluminum, Manganese, and the Alkaline Earths; *Z. Anal. Chem.*, 76, 191 (1929).

⁸Koenig, E. W., Direct Determination of Alumina in Certain Silicates; *Ind. Eng. Chem., Anal. Ed.*, 11, 532 (1939).

aluminum compounds. Sodium silicate and sodium aluminate being soluble in an alkali solution pass through the filter. The soluble silicic acid does not interfere in the aluminum precipitation unless the solution is made strongly acid. After acidifying the filtrate, aluminum was precipitated with 8 hydroxyquinoline thus separating it from magnesium, calcium, and any beryllium that was present.

This method was tried and proved efficient. Details of the procedure will be given in the next section.

APPLICATION OF METHOD

In the previous sections mention was made of (1) precipitation of aluminum by 8 hydroxyquinoline, (2) of bromination of the 8 hydroxyquinoline, (3) solution of samples, and (4) separation of alumina from interfering elements. The results obtained from these investigations were incorporated into a direct procedure for the volumetric determination of alumina in clays and related materials. The procedure developed does not necessitate the removal of the silica and separate determinations of titanium and iron as does the classical indirect method.

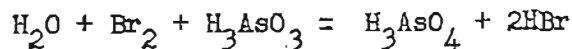
The new method consists essentially of (1) an alkali fusion to effect solution of sample, (2) separation of aluminum from certain interfering elements by extracting as sodium aluminate, (3) precipitation of aluminum as aluminum quinolate by 8 hydroxyquinoline, and (4) bromometric determination of the dissolved aluminum quinolate.

The exact procedure as applied to the analysis of clays was as follows: A 0.2 to 0.3 gram sample was fused with approximately 4.5 grams of sodium hydroxide pellets in a nickel crucible. In fusing it was advisable to heat gently at first to expel moisture and then heat at dull red heat for 5 to 10 minutes. After cooling, the crucible and its contents were placed in a casserole and 75 to 100 cc. of water added. On complete solution of the melt the nickel crucible was removed, polished, and washed thoroughly.

The solution was then filtered through a fine filter paper and the precipitate washed repeatedly with cold 1N sodium hydroxide. The filtrate was acidified with hydrochloric acid and transferred to a 250-cc. volumetric flask and diluted to the mark. An aliquot portion of this solution, usually 25 or 50 cc., was taken depending on the amount of aluminum present. A good indication of the amount present may be obtained by noting the quantity of aluminum hydroxide formed on the acidification of the original filtrate containing sodium aluminate. To this aliquot portion water was added to bring the solution to a volume of about 75 cc. It was then heated to 65° — 75° C. and a 5 percent solution of 8 hydroxyquinoline in 1N acetic acid was added. One cc of this solution for every five mg. of alumina was sufficient. Usually no more than 5 cc. was added. A 2N solution of ammonium acetate was slowly added with constant stirring until a yellow precipitate formed, and then an additional 15 or 20 cc. to ensure complete precipitation of the aluminum quinolate. This gives a pH of 4 to 5.5 which was necessary for complete precipitation. The solution containing the precipitated aluminum quinolate was set aside to cool and allowed to stand for about one hour. The precipitate was then filtered through a Gooch crucible and washed repeatedly with small portions of water until at least a total volume of 100 cc. was used. The crucible and

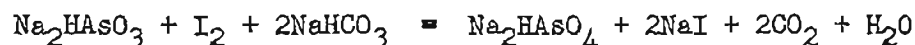
its contents was placed in the beaker in which the original precipitation of the aluminum quinolate was made and 50 cc. of 1:3 hydrochloric acid added. The acid was heated to dissolve the precipitate and the crucible removed and washed with 1:5 hydrochloric acid. The washings were added to the solution containing the dissolved quinolate. The dissolved precipitate regenerates 8 hydroxyquinoline in an acid solution.

This solution was then transferred to an Erlenmeyer flask and one gram of potassium bromide added. A 2-hole stopper was used to close the flask. Through one of these holes the tip of the burette containing a standard potassium bromate solution was inserted. The bromate solution was added slowly with continual shaking of the flask. An addition of an excess of bromate solution was indicated by an orange color imparted by the free bromine. The burette containing the standard arsenite solution was next inserted and enough arsenite solution added to remove the excess bromine as illustrated by the following equation



Generally only 5 or 10 cc. of the arsenite solution was necessary. The removal of the excess bromine was indicated by a transition in color from orange to light yellow. The flask was shaken and allowed to stand for a few minutes. The solution was then poured

very slowly with continual stirring into a 600 cc. beaker containing 100 cc. of saturated sodium bicarbonate and about 10 grams of solid sodium bicarbonate to ensure complete neutralization of the hydrochloric acid. Next five cc. of the starch solution was added and the standardized iodine solution added dropwise until a blue coloration appeared. The following equation represents the chemical reaction involved:



The reaction goes to completion in a neutral or alkaline medium. For calculation of amount of aluminum present in the aliquot portion this expression may be used:

$$\text{Wt. alumina} = 0.000425 \left\{ \text{N of KBrO}_3 \times \text{cc. added} - \left[(\text{cc. As}_2\text{O}_3 \times \text{N As}_2\text{O}_3) - \text{N I}_2 \times \text{cc. I}_2 \right] \right\}$$

$$\text{Percent alumina} = \frac{250 \times (\text{weight of alumina in aliquot})}{(\text{cc. of aliquot}) \times (\text{weight of sample})}$$

In order to check this method, several analyzed samples secured from the U. S. Bureau of Standards were used. The results obtained compared with the recommended values and are summarized in Tables 4 and 5.

Table 4. Analysis of Standard Samples

Sample	Al ₂ O ₃ taken, mg.	Al ₂ O ₃ found, mg.	Error in Al ₂ O ₃ , mg.	Percent error
Bauxite	22.02	22.03	+ 0.01	+ 0.04
Feldspar	10.84	10.85	+ .01	+ .09
Soda-feldspar	15.25	15.24	- .01	- .06
Burnt-refractory	13.56	13.59	+ .03	+ .22
Plastic-clay	15.32	15.38	+ .06	+ .39
Flint-clay	15.51	15.50	- .01	- .05

Table 5. Comparison of Analyses of Standard Samples

Sample	Al ₂ O ₃ present, percent (U S Bu. Stds.)	Al ₂ O ₃ found, percent	Deviation in Al ₂ O ₃ , percent
Bauxite	55.06	55.08	+ 0.02
Feldspar	18.03	18.08	+ .05
Soda-feldspar	19.06	19.05	- .01
Burnt-refractory	37.67	37.74	+ .07
Plastic-clay	25.54	25.64	+ .10
Flint-clay	38.77	38.76	- .01

From these analyses it was concluded that the method was reliable. In case of the bauxite sample there was also present 5.66 percent of Fe_2O_3 , 3.07 percent TiO_2 , 6.32 percent SiO_2 , and 0.55 percent MnO . The plastic clay contained 59.11 percent of SiO_2 , 2.05 percent of Fe_2O_3 , and 1.43 percent of TiO_2 , while the flint clay had 42.87 percent of SiO_2 , 0.98 percent of Fe_2O_3 , 2.38 percent of TiO_2 , 0.1 percent of CaO , 0.26 percent of MgO , and 0.25 percent of ZrO_2 . The burnt refractory had 54.68 percent of SiO_2 , 2.38 percent of Fe_2O_3 , 2.21 percent of TiO_2 , 1.58 percent of MgO , and 0.27 percent of CaO . The feldspar and soda-feldspar were characteristic in that they contained 68.66 and 66.66 percent of SiO_2 , respectively.

The accurate values obtained for Al_2O_3 in the analysis of these samples proved the feasibility of the method for the separation of aluminum from interfering elements.

The results showed that the direct determination of alumina in clays and related substances was possible and that the analysis could be accomplished in a relatively short time. It was therefore concluded that the primary objective of this thesis had been attained.

To further test the new method, however, a topaz sample containing 53.45 percent of Al_2O_3 and about 13.7 percent F was run to check for any effect of fluorine on the analysis. A value of 53.36 percent of Al_2O_3 was obtained indicating that the method was valid even when fluorides were present.

Other samples of unknown alumina content were analyzed in duplicate by this procedure and the results are tabulated and compared in Table 6.

For routine analyses one change in the procedure is recommended. The use of smaller samples would eliminate the necessity of transferring the filtrate to a volumetric flask and the taking of aliquot portions. This change would result in a saving of time. When a 0.1N potassium bromate solution is used the amount of alumina in each sample should not exceed 0.02 gram.

The author would also like to suggest the possibility of further research on this method. One should be able to take the precipitate obtained when extracting the sodium aluminate and develop a procedure for the determination of iron and titanium. This was included in the original program but had to be postponed due to lack of time.

There also remains the possibility of using the 8 hydroxy-quinoline filtrate for the determination of calcium and magnesium. A colorimetric method for silica, if developed, should be applicable by the use of a new aliquot portion.

Table 6. Analysis of Clays and Related Materials

Sample		Al ₂ O ₃ found, mg.	Al ₂ O ₃ , per- cent	Deviation in Al ₂ O ₃ , mg.	Deviation in Al ₂ O ₃ , percent
English	A	15.42	38.54		
China clay	B	15.40	38.49	0.02	0.05
Zadock	A	8.52	21.31		
Clay	B	8.51	21.27	.01	.04
Fulton	A	15.07	37.68		
Plastic clay	B	15.10	37.75	.03	.07
Diaspore	A	12.90	64.51		
Clay	B	12.94	64.69	.04	.18
Bauxite	A	19.73	49.33		
	B	19.75	49.39	.02	.06
Kaolin	A	15.33	38.34		
	B	15.29	38.23	.04	.11
Beryl	A	10.48	17.47		
	B	10.58	17.64	.10	.17
Spodumene	A	10.17	16.95		
	B	10.14	16.89	.03	.06

SUMMARY

1. The behavior of 8 hydroxyquinoline was studied in respect to its application to analytical chemistry and found highly satisfactory for the precipitation of aluminum.

2. A study of methods for measurement of the bromination of 8 hydroxyquinoline resulted in the development of a method which proved superior to other methods used.

3. A procedure embodying these findings was developed and numerous analyses made on a variety of clays and related materials.

4. The results of the analyses indicated that this new direct method is accurate, fast, and entirely satisfactory in the determination of alumina in clays.

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