

A SEMI-MICRO ANALYSIS OF SILICATE ROCKS FOR

Ca, Mg, Fe, AND Al EMPLOYING E. D. T. A.

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A rapid, accurate analysis of total iron, aluminum, calcium and magnesium in silicate rocks using EDTA as the analytical reagent has been developed using semi-micro techniques. This analysis will be a great aid to the geologist and geochemist since it is time-saving, accurate, and gives approximately 80% of the composition of the average igneous rock other than SiO_2 . Another advantage of this method is the fact that a relatively small sample (0.2 g) is needed in order to make this determination. A sample can be fused, diluted to volume and analyzed for these elements in approximately 3 hours. If several samples are fused at the same time, as many as eight determinations can be made in a eight hour day.

INTRODUCTION

Since the development of Ethylene-Diamine-Tetra-Acetic acid (EDTA) as an analytical reagent by Schwarzenbach (1) in 1945, its applications and uses have spread into many fields of research. The determination of over 40 cations and numerous anions employing EDTA has been reported up to the present time, and separations based on the EDTA complex formation have become very important in the determination of various other ions. EDTA has been used extensively as an analytical reagent in the fields of chemistry, biology, agriculture and, to a certain extent, in geology. Materials analyzed by EDTA range from milk (2), through fertilizers (3), to sedimentary rocks (4) and includes many substances.

Calcium and magnesium in igneous rocks have been determined by various investigators using EDTA (5) (6) (7). However the author could find no information in the literature on the determination of iron and aluminum in igneous rocks other than ores, and developed the method discussed in this paper for the determination of Ca, Mg, Al, and Fe in igneous rocks employing EDTA as the analytical tool following methods or modifications of methods already in the literature for the determinations of these ions in other substances. The following report discusses the method developed by the author, and includes, in order, a section on the preparation of the sample for analysis, analysis of the sample solution, and results of the analysis of various known rocks.

PREPARATION OF SAMPLES

Samples of silicate rocks were crushed and powdered and approximately 0.2 g of the powdered sample was weighed out into a platinum crucible using a Beckman chainomatic balance. 1.5 g of sodium carbonate was added to the crucible, thoroughly mixed with the igneous rock sample, and a small amount of sodium carbonate was placed upon this mixture. The crucible was covered and the mixture was slowly heated over a meeker burner until it became red hot. The heating was continued until the molten mixture became quiet and had ceased to evolve carbon dioxide. Once the molten mass had become quiet, the heat was shut off and the mixture was swirled in the crucible so that a portion of the hot mass adhered to the side of the crucible thus enabling the fused mass to dissolve faster, in the following step, because of the larger surface area. The fusion process takes 10 to 30 minutes.

The cooled crucible was placed in dilute (2:5) hydrochloric acid and heated slowly until the fused mixture dissolved. A clear solution was seldom obtained since silicic acid separated from the solution almost immediately. This did not

interfere with following steps and an analysis of the silicic acid which precipitated from the solution showed no appreciable coprecipitation of Ca, Mg, Fe and Al. After the melt had dissolved, the solution was cooled and the platinum crucible was rinsed several times. The resulting solution was added to a volumetric flask and diluted to 200 ml.

ANALYSIS OF SOLUTION

The EDTA analysis of the final solution was accomplished by carefully controlling the pH and by the utilization of masking agents to eliminate interference from interfering substances. Various size aliquots of the final solution, from one to ten ml., were used in the analysis. The aliquot size was determined by the various concentrations of the elements present.

The solution was analyzed for calcium, magnesium, iron and aluminum using methods similar to those in the literature. Those unfamiliar with EDTA, its nature and uses, and the principals involved in EDTA titrations, should refer to Welcher (8) or other books on the subject. Total Ca-Mg was determined at a pH of approximately 10 using an ammonium hydroxide-ammonium chloride buffer and Erichrome Black T as the indicator. Calcium was determined at a pH of 12.5 using potassium hydroxide as a high pH buffer and Calver II or a Murexide-Napthol Green B mixture as the indicator. Total iron was determined at a pH of approximately 2.4 using salicylic acid as the indicator. Total iron plus aluminum was determined by back titration of a hot 40% acetone solution of dithizone as the indicator at a pH of 4.5. The following flow sheet will serve as a guide to the EDTA determination of Ca, Mg, Fe, and Al in silicate rocks. The determination of each of the elements is discussed in greater detail in the following paragraphs.

0.200g			
pH scale		dissolve sample dilute to volume store in plastic bottle	
12	10	4.5	2.4
Calcium	Ca-Mg	Fe-Al	Iron
KOH buffer	pH 10 buffer	Na Ac buffer	HCL-NaAc buffer
Calver II	Erichrome Black T	Dithizone	Salicylic acid
or			
Murexide			

Calcium was determined using an 8N solution of KOH as a high pH buffer. The KOH eliminated interference of magnesium by precipitating it as the hydroxide, and from aluminum by converting it to the aluminate ion which does not interfere with the EDTA titration. Potassium cyanide was added to remove interference from any heavy metals which might be present by tying up the metal as the cyanide. If the rock contained large amounts of iron, triethanolamine was added to complex the iron. Sodium tartrate was added to the solution before the high pH buffer in order to prevent coprecipitation of the calcium with the magnesium hydroxide. Hydroxylamine was added to prevent oxidation of the indicator, and if small amounts of ferric iron are present they will be reduced to the ferrous stage which will be masked by the cyanide.

The order of addition of reagents is very important in the calcium determination. Sodium tartrate must be added before the solution is made basic to prevent coprecipitation of the calcium. Hydroxylamine must be added before the potassium cyanide so that small amounts of ferric iron can be converted to ferrous iron, and obviously it must be added before the indicator to prevent oxidation of the indicator. Potassium cyanide must be added after the solution is made basic in order to prevent liberation of cyanide gas which is given off when cyanides are placed in acid solutions. The indicator is always added after all the masking agents have been added and after the pH adjustment has been made.

Three different indicators were tried and the sharpest endpoints and most accurate results were obtained using Calver II (Hack Chemical Company) and a Murexide-Naphthol Green B mixture (9). Murexide was tried but the endpoint was not ideal and much harder to detect than those of either of the other two indicators. Calcium forms purple complexes with these indicators and when EDTA ties up the calcium the indicators turn blue.

Total calcium plus magnesium was determined at a pH of approximately 10 using an ammonium hydroxide-ammonium chloride buffer. Interference of the heavy metals plus iron and aluminum was eliminated by potassium cyanide and triethanolamine. Triethanolamine will tie up the aluminum ion in ammoniacal solution by the formation of an aluminum-ammonium-triethanolamine complex. If ferric iron is present, it will interfere by oxidizing the indicator. However, this can be overcome by the addition of hydroxylamine which reduces the iron and prevents oxidation of the indicator.

The order of adding reagents is not quite as important in the total calcium-magnesium determination as in the calcium determination but two things must be remembered. First, make sure the solution is basic before adding the cyanide, and secondly, do not add the indicator until all the adjustments on the solution have been made.

Two indicators were tried in this determination. Erichrome Black T was preferred since, in general, it appeared to be much more sensitive to small quantities of magnesium than the second indicator, Erichrome Blue Black R (as Calcon). The endpoints with both indicators were very sharp, changing from red to blue as the calcium and magnesium is tied up by the EDTA. The indicators were used in solid form in approximately 1:50 ratio using ammonium chloride for a filler as suggested by Hammon and Neuman (10). The ammonium chloride serves as a carrier and a source of the ammonium ion for the buffer. The number of mls. of EDTA required for titration of calcium was subtracted from the number of mls. required for total calcium plus magnesium. This difference represented the number of mls. required for the magnesium titration.

Total iron was determined at a pH of 2.4-2.6 using salicylic acid as the indicator. Ammonium persulfate was added to the solution to oxidize any ferrous iron to ferric iron. The pH was adjusted to approximately 2.5 using sodium acetate and hydrochloric acid. The endpoint was very sharp with the indicator changing from a deep violet to a yellow or colorless solution upon titration. If the concentrations of iron were high the solution usually changed to a yellow color. Thiocyanate was also tried as an indicator and performed equally well at a lower pH. Reagent grade indicators were used in the solid form.

No attempt was made to calculate ferrous and ferric iron separately although this is entirely possible providing none of the ferrous iron is oxidized during the fusion. Kolthoff and Sandell (11) have described a carefully controlled sodium carbonate fusion whereby ferrous iron is not oxidized to ferric iron. Ferric iron in the presence of ferrous iron can be titrated under CO_2 at a pH of 2.4-2.6 with EDTA by using salicylic acid as the indicator. Total iron can then be determined by adding ammonium persulfate which oxidizes the ferrous iron to ferric iron. Total iron is then determined and ferrous iron is found by difference. Since this determination is carried out at a low pH most divalent cations do not interfere (12). The author has not tried this method but recognizes that it would frequently be very desirable.

Total iron plus aluminum was determined by a modification of a back titration method originally proposed by Vanninen and Ringbom (13) in which a known volume of EDTA is added to a known volume of unknown solution and the excess EDTA is back-titrated with zinc sulfate using diphenyl-thio-carbonozone as the indicator. In their original work the EDTA-unknown solution was made 40-50% alcoholic to serve as a solvent for the indicator. This process was modified by using acetone in place of alcohol as proposed by Banks and Bisque (14) and back titrating with zinc chloride rather than zinc sulfate. The indicator (Eastman Kodak Co.) was prepared by dissolving 0.75 g of the indicator in 200 ml of reagent grade alcohol rather than absolute alcohol as proposed in the original work.

It is very important that the indicator be made up every few days.

The procedure of analysis varies from the original work (13) in that total iron and aluminum is determined by oxidizing all the iron to the ferric state (if not already in that form) and then heating the solution of EDTA and unknown for three to five minutes on a hot plate. Acetone, which has also been warmed, is then added until the solution is between 40-60% acetone. The pH is adjusted to between 4.4-4.6 using the hot sodium acetate and hydrochloric acid. The pH is kept in this range throughout the titration. After adjusting the pH, the indicator is added and the solution is titrated with zinc chloride from a greenish-blue to a bright pink color. The solution is heated because, in cold solutions, aluminum and EDTA complex quite slowly but, if the solution is hot, the complex forms rapidly.

The number of mls. of zinc solution required for titration was recorded and the equivalents of EDTA used up by the unknown solution was calculated. The amount of EDTA required for the total iron determination was subtracted from this and the number of equivalents required for the aluminum titration was determined.

EDTA solutions were made up using the disodium salt of ethylene-diamine-tetra-acetic acid and standardized against a carefully prepared 0.01 M calcium chloride solution. Approximately 1 gram of magnesium chloride 6-hydrate was added for each 40 grams of the disodium salt. The magnesium salt was added to sharpen the Erichrome Black T endpoint in case only very small amounts of magnesium were present. This was added before the solution was standardized. 0.01 and 0.001 M solutions were made up and used in the titrations.

RESULTS OF THE ANALYSIS

Four samples from the National Bureau of Standards were selected for analysis. Three of them; the Chelmsford Granite, the Graniteville Granite, and the Columbia River Basalt, were selected as typical igneous silicate rocks and the fourth, a standard dolomite was run because it is a rock in which the calcium and magnesium predominated over the iron and aluminum. Table I shows the CaO results obtained by EDTA compared with the Bureau of Standards analysis. Table II shows the same for MgO, and tables III and IV illustrate this for Al_2O_3 and Fe respectively. The EDTA results are an average of several runs. The per cent difference is calculated; it is assumed that the Bureau of Standards analysis is the correct analysis.

From the results of the analyses it can easily be seen that the EDTA determination in no case seriously disagreed with the Bureau of Standards analysis. The per cent difference in no case exceeded 5% and in only three cases did it exceed 3%. This, in itself, is very remarkable considering the small sample used and the relative speed of the determination in comparison to standard methods of determination. However it must be added, in all fairness, that the determinations were very closely watched and the attention given to these samples from the Bureau of Standards would probably be slightly above that which would be given most rocks during routine laboratory analysis. Work with standard solutions, made up by dissolving the salts of Ca, Mg, Fe and Al in water or acid and then determining the actual content with the speed and technique one normally employs in the laboratory, showed that percentage of error was about the same as in the carefully controlled fusions of the Bureau of Standards samples. Attempts to correlate beds of volcanic rock, on the basis of chemical content, in which only normal attention was given to the sample, showed that the actual variations did not exceed that expected for normal variations of the analyzed component within volcanic flows.

The limit of sensitivity for detecting the various ions varies. Ca and Mg are very easy to detect in small amounts with a high degree of accuracy. Iron was also quite easy to detect in small amounts with a high degree of accuracy. However, in the case of the Standard Dolomite, the aliquot size had to be increased and the original sample size also was larger. Aluminum was much harder to detect in small amounts. The lower limits of detection, for which the high degree of accuracy discussed in the foregoing paragraphs may be

expected, are about 0.1-0.2% sample weight for Calcium and Magnesium and about 0.4% for iron and aluminum providing one follows the scheme outlined in this paper and employs normal laboratory technique. However, the limits of detection may be lowered further by increasing the size of the sample or the size of the aliquot.

Table I
CaO
%

Sample	Bureau of Standards	EDTA	% Difference
Graniteville Granite	0.65	0.67	3.1
Chelmsford Granite	0.76	0.77	1.3
Columbia River Basalt	9.03	9.01	0.2
Standard Dolomite	30.49	30.52	0.1

Table II
MgO
%

Graniteville Granite	0.08	N. D.	---
Chelmsford Granite	0.24	0.25	4.0
Columbia River Basalt	4.76	4.81	1.1
Standard Dolomite	21.48	21.65	0.8

Table III
Al₂O₃
%

Graniteville Granite	12.30	12.28	0.2
Chelmsford Granite	13.59	13.66	0.5
Columbia River Basalt	13.04	13.10	0.5
Standard Dolomite	.067	N. D.	---

Table IV
Fe
%

Graniteville Granite	1.22	1.16	4.9
Chelmsford Granite	0.81	0.82	1.2
Columbia River Basalt	11.08	11.26	1.6
Standard Dolomite	0.058	0.057	1.7

Modifications in methods of fusion have been studied by the author and two significant conclusions resulted. The first of these is the fact that, for most igneous rocks with normal iron content, the method of fusion described in this paper was the most practical if the determinations were sought, fusions with sodium hydroxide in nickel crucibles were faster and just as accurate. In the case of rocks, which are high in iron, it was found that the sodium carbonate fusion was not completely successful because a certain amount of iron alloyed to the platinum crucible. The only alternative, in this case, was to dissolve the sample in hydrofluoric acid, which, of course, increased the time necessary for analysis.

As a general conclusion, it may be stated that the method of analysis outlined in this paper is, for most geological and geochemical work, faster and as accurate as most other published methods.

ACKNOWLEDGEMENTS

The work herein reported was supported in part by the Atomic Energy

Commission under contract AT(11-1)-689-Correlation and Chronology of Ore Deposits and Volcanic Rocks. I would like to thank the members of the Geochemical Section of the Geochronology Laboratories of the University of Arizona for their helpful advice. I am especially grateful to Mr. Carl E. Hedge for his great interest in the project and for aid in the development of the fusion technique.

A special note of thanks goes to Prof. Paul E. Damon, who heads the Geochemistry Laboratory, for his encouragement of this work. Prof. Damon and Prof. J. W. Anthony kindly read this report. Also, the author would like to thank Dr. Raymond Bisque for first introducing him to many of the techniques involved in the EDTA titrations.

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