

Determination of Sodium and Potassium in Silicates

An Improved Method

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The use of hydrofluoric and perchloric acids as a decomposition mixture was investigated. It was shown that, by the use of this mixture, the major difficulties of both the Berzelius and the J. Lawrence Smith methods of decomposition could be avoided and most of their advantages retained. A procedure was devised whereby the solution obtained from the acid decomposition could be purified preparatory to an alkali analysis. Data were obtained on synthetic and National Bureau of Standards samples.

THE problem of an alkali analysis by the J. Lawrence Smith method may be divided into two parts. The first part concerns the preparation of a solution containing the alkalis along with some or all of the other metallic elements found in the sample. This is followed by an appropriate purification by which a mixture of the alkalis is separated from all the other metallic elements. The second part concerns a separation of the alkalis (usually only sodium and potassium) one from the other. This paper deals directly with the first problem. The work was conducted and the proposed method devised on the basis that the G. F. Smith (13) method would be employed for the separation of the individual alkalis, the second of the above two problems.

Sodium may be determined directly by the triple acetate method in the presence of many of the metals. The method of Barber and Kolthoff (1) employs the zinc salt, while Caley (4) did most of the work on the magnesium salt. These methods are well adapted to the determination of small amounts of sodium but are not desirable for large amounts. Potassium may be determined directly by the perchlorate method without the removal of aluminum, calcium, magnesium, sodium, and other metals according to the method of Willard, Liggett, and Diehl (18) in which the distillation of hydrofluosilicic acid is employed. (An excellent review of the methods for the determination of the alkali metals is given by Willard and Diehl, 17.)

The use of ammonium fluoride as a flux for the decomposition of refractory silicates, according to the method of Shead and Smith (12), was not attempted in this investigation, since it seemed to offer no particular advantage over a direct attack by means of perchloric and hydrofluoric acids.

At present two procedures are in general use for decomposition of a mineral structure preparatory to an alkali analysis.

The older procedure, published in 1824 by Berzelius (2), involves the use of the acid decomposition mixture hydrofluoric-sulfuric acids. The second and by far the more popular procedure, the J. Lawrence Smith method (14), breaks down the silicate structure by sintering the ground material with a calcium carbonate-ammonium chloride mixture.

The Berzelius method depends upon sulfuric-hydrofluoric acid mixture to open up the silicate structure, followed by heating to volatilize and eliminate the silica as silicon tetrafluoride, and subsequent fuming of the sulfuric acid to eliminate all fluorides. The inherent disadvantage of this method is the introduction of sulfate into the analysis, which must be removed before sodium and potassium can be successfully separated. The removal of sulfate can be accomplished but requires the use of barium ion in excess, which in turn must be removed by carbonate ion. The entire procedure is long and involved, and is used very little at the present time.

With the advent of the J. Lawrence Smith method of silicate decomposition the disadvantage of the Berzelius procedure was

avoided, and at the same time there was provided a solution of the alkalis requiring but little purification. The main difficulty encountered in the J. Lawrence Smith procedure is the necessity of grinding an already weighed sample, a procedure rather difficult to maintain quantitative. At least one attempt has been made at correcting this disadvantage by grinding the sample with the calcium carbonate-ammonium chloride mixture under ethanol (16). In addition, a number of other modifications of the original method have been published (3, 5, 6, 7, 9, 10, 11, 15). However, the recommended changes have not improved upon the fundamental basis of the method and consequently have retained its main disadvantage.

This research was undertaken to attempt to combine the desirable features of both the Berzelius and the J. Lawrence Smith methods of decomposition. It was found that mixed hydrofluoric-perchloric acid could be substituted for mixed hydrofluoric-sulfuric acid as an acid decomposition mixture, and that iron, aluminum, and magnesium (as in the J. Lawrence Smith method) could be removed simultaneously by a suitable procedure.

When mixed hydrofluoric-perchloric acid is used for the decomposition of a silicate, the solution obtained, after the removal of excess hydrofluoric acid by fuming, contains the perchlorates of the metals present in the mineral with possibly some fluoaluminates. Evaporation yields, in the case of a typical mineral, a solid mixture of the perchlorates of sodium, potassium, magnesium, calcium, iron, and aluminum. The thermal decomposition of the perchlorates in this mixture provides a means for the separation of sodium, potassium, and calcium from magnesium, iron, and aluminum in one step.

A qualitative test on the aqueous extract from the thermal decomposition of the perchlorates gave no test for fluorides, indicating that complex fluoaluminates are decomposed by such treatment. Tests further indicate that less than 1 mg. of fluoride remains after the decomposition.

Thermal decomposition studies on sodium, potassium, lithium, calcium, magnesium, iron, and aluminum perchlorates were made by Marvin and Woolaver (8) in order to determine the temperature at which decomposition occurs and the products of such a decomposition. The thermal decomposition of the perchlorates of sodium, potassium, and calcium gives the corresponding chlorides and the evolution of oxygen. On the other hand, the perchlorates of magnesium, iron, and aluminum are hydrolyzed by the water of hydration contained in the molecule to yield perchloric acid, water, and the corresponding oxide. Sodium, potassium, and calcium are separated from magnesium, iron, and aluminum by making use of the difference in solubility existing between the chlorides and oxides formed. By leaching the decomposed perchlorates with hot water made slightly alkaline with ammonium hydroxide (to repress the solubility of magnesium oxide), a solution is obtained containing essentially only sodium, potassium, and calcium chlorides. Thus, at this point, the solution is exactly similar to one obtained by the J. Lawrence Smith method of decomposition. Only the removal of calcium and ammonium salts from this solution is required to obtain a solution to which the G. F. Smith method of alkali analysis can be applied.

The use of mixed hydrofluoric-perchloric acid retains the ease of manipulation of an acid decomposition procedure as compared to a sintering method, and introduces no interfering ions. At the same time it is possible to remove from the solution by one

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operation a number of interfering metals. These facts greatly simplify the purification of a sample in preparation for an alkali analysis.

PROCEDURE FOR SYNTHETIC SAMPLES

Nine synthetic samples were prepared by mixing one 25-ml. portion of each of six stock solutions. A stock solution was prepared for each metallic element (sodium, potassium, calcium, magnesium, iron, and aluminum as chlorides) desired in the sample. The concentration of four of these solutions—calcium, magnesium, iron, and aluminum—was 50 ± 10 mg. per 25 ml. The concentration of sodium and potassium was accurately determined by precipitating the chloride with silver and weighing the residue; their approximate concentrations were 100 mg. per 25 ml. Suitable aliquots were taken to obtain smaller quantities. The total sodium chloride plus potassium chloride in the samples was calculated from the chloride analyses (Table I). In addition to the six primary elements listed above, sample 1 contained 10 ± 2 mg. each of titanium, manganese, lead, and barium; sample 2 contained 10 ± 2 mg. of phosphorus; and sample 3 contained 10 ± 2 mg. of arsenic.

Table I. Analyses on Synthetic Samples^a

Sample No.	NaCl and KCl Added	NaCl and KCl Found
	Gram	Gram
1	0.1912	0.1920
	0.1912	0.1918
2	0.1912	0.1846
	0.1912	0.1851
3	0.1912	0.1914
	0.1912	0.1913
4	0.2162	0.2167
	0.2162	0.2171
5	0.0432	0.0432
	0.0432	0.0439
6	0.0108	0.0102
	0.0108	0.0105
7	0.0021	0.0029
	0.0021	0.0022
8	0.1015	0.1019
	0.1015	0.1017
9	0.0992	0.0993
	0.0992	0.0993

^a Results were obtained by procedure outlined with due care to observe usual precautions for securing a residue free of impurities.

The samples were placed in 250-ml. tall-form beakers, 5 ml. of 60 to 70% perchloric acid added, and the solutions slowly evaporated to dryness. The dry residues were baked for a short time on a gas hot plate. After being covered with watch glasses, the beakers were placed in a muffle furnace regulated at 550°C . for 30 minutes. This temperature was high enough to ensure the complete decomposition of all the perchlorates present. The decomposition proceeded very smoothly with no tendency to spatter. After cooling, the residue was carefully crushed and leached with two successive 50-ml. portions of hot water each containing 5 ml. of ammonium hydroxide solution (sp. gr. 0.90), followed by two 10-ml. portions. This step must be carefully followed to ensure complete extraction of all sodium and potassium salts. The washings were filtered, the filtrates heated to just below boiling, and 10 ml. of 0.5 *N* ammonium oxalate solution added. The solutions were allowed to stand for one hour and then filtered. The filtrates were reheated to about 60°C . (no higher) and 5 drops of a 5% 8-hydroxyquinoline solution in dilute acetic acid (1 to 10) added.

After standing for one hour at room temperature, the solutions were filtered, and the filtrate was acidified with hydrochloric acid and evaporated to dryness. (It is possible these two precipitations might be incorporated and performed together, but this was not tried.) The residues were treated with 25 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, covered with watch glasses, and vigorously boiled. After the initial reaction had subsided, and 25 ml. of hydrochloric acid had been added, the solutions were again boiled and finally evaporated to dryness. The beakers were cautiously heated over a free flame to drive off any remaining ammonium salts or organic matter. The soluble material was dissolved in distilled water and

filtered into weighed 100-ml. tall-form beakers. A few milliliters of concentrated hydrochloric acid were added and the solutions evaporated to dryness. The residues were cautiously heated to drive off any moisture, cooled, and weighed. The results are tabulated in Table I.

PROCEDURE FOR BUREAU OF STANDARDS SAMPLES

From the long list of samples available, the following set of six was chosen as best representing the field of alkali silicate analysis:

B. of S. Sample No.	Material
70	Feldspar, potash
89	Glass, lead-barium
91	Glass, opal
93	Glass, high-boron
80	Glass, soda-lime
99	Feldspar, soda

One-gram amounts of each sample were weighed into flat-bottomed platinum dishes (Payne form), and 15 ml. of 60 to 70% perchloric acid and 10 ml. of 47% hydrofluoric acid were added. The mixtures were very cautiously heated on an electric hot plate until the volume of each was substantially reduced. The dishes were placed under a heating unit suspended over an electric hot plate and the heating was continued to copious fumes of perchloric acid. When the solutions had almost reached dryness they were removed and 5 ml. of perchloric acid added. The dishes were returned to the overhead evaporator and the heating was continued until the solutions were again almost dry. The solutions and any precipitate were washed into individual 250-ml. tall-form beakers and slowly evaporated to dryness on an electric hot plate. After being covered with watch glasses, the beakers were placed in a muffle furnace regulated at 550°C . for 30 minutes. This temperature was high enough to ensure the complete decomposition of all perchlorates present. The decomposition proceeded very smoothly with no tendency to spatter.

After cooling, the residue was carefully crushed and leached with two successive 50-ml. portions of hot water each containing 5 ml. of ammonium hydroxide solution (sp. gr. 0.90), followed by two more 10-ml. portions. This step must be carefully followed to ensure complete extraction of all sodium and potassium salts. The washings were filtered, the filtrates heated to just below boiling, and 10 ml. of 0.5 *N* ammonium oxalate solution added. The solutions were allowed to stand for one hour and then filtered. The filtrates were reheated to about 60°C . (no higher) and five drops of a 5% 8-hydroxyquinoline solution in dilute acetic acid (1 to 10) added. After standing for one hour at room temperature, the solutions were filtered, and the filtrate was acidified with hydrochloric acid and evaporated to dryness. (These two precipitations might be performed together, but this was not tried.)

The residues were treated with 25 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, covered with watch glasses, and vigorously boiled. After the initial reaction had subsided, and 25 ml. of hydrochloric acid were added, the solutions were again boiled and finally evaporated to dryness.

Table II. Analyses of Bureau of Standards Samples^a

Sample No.	Weight of Chlorides Theoretical	Weight of Chlorides Found
	Gram	Gram
70	0.2439	0.2439
	0.2439	0.2442
89	0.2406	0.2412
	0.2406	0.2408
91	0.2112	0.2009
	0.2112	0.2116
93	0.0810	0.0810
	0.0810	0.0798
80	0.3145	0.3147
	0.3145	0.3147
99	0.2088	0.2042
	0.2088	0.2088

^a As a test of applicability in the hands of an expert analyst the above procedure was used by E. B. Read for analysis of Bureau of Standards Sample 70 and 0.2353, 0.2354, and 0.2363 gram of chloride obtained. This degree of agreement between the theoretical value of the chlorides and the values obtained is considered to be within the limits of manipulative error for an analyst using this method for the first time.

The beakers were cautiously heated over a free flame to drive off any remaining ammonium salts or organic matter. The soluble material was dissolved in distilled water and filtered into weighed 100-ml. tall-form beakers. A few milliliters of concentrated hydrochloric acid were added and the solutions evaporated to dryness. The residues were cautiously heated to drive off any moisture, cooled, and weighed. The results obtained (total weight of sodium chloride plus potassium chloride) are tabulated in Table II.

DISCUSSION

Perhaps the most attractive feature of the J. Lawrence Smith method of silicate decomposition is the simultaneous removal of most of the nonalkali basic constituents. The hydrofluoric-perchloric acid decomposition, as used above, accomplishes the same purpose. The perchlorates of magnesium, iron, and aluminum all form oxides upon thermal decomposition, thus rendering them insoluble. The sodium, potassium, and calcium salts, however, form soluble chlorides which can readily be dissolved away from the insoluble oxides. Inasmuch as the special equipment required for the hydrofluoric-perchloric acid decomposition is a platinum dish, and the operation of grinding an already weighed sample may be avoided, this method has certain advantages over the J. Lawrence Smith method.

Examination of Tables I and II shows that satisfactory results are obtained in all cases except where phosphorus is present in the solution, and one value for Bureau of Standards Sample 91. The presence of phosphorus apparently ties up the alkalis in a form which cannot be extracted out of the solid mass of perchlo-

rate decomposition products. No attempt was made to investigate this matter further. Sulfates are incompatible with the principle involved in this method. They would interfere seriously and if present in the original material this method is not applicable in the present form.

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Agar-Streak Method for Assaying Antibiotic Substances

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The agar-streak method for assaying antibiotic substances is rapid, does not require a sterile sample, permits testing unknown substances against several bacteria or fungi at one time, and can be used to test substances in nonaqueous solutions. Although it is less precise and less rapid than some other methods, it has marked advantages, especially in screening tests with a large number of organisms and in isolation procedures of the antibiotic substances.

IT HAS long been recognized that the results of assaying bacteriostatic and bactericidal substances depend largely upon the methods employed. Such results may vary considerably, and are influenced by the species of test organism used, the composition and reaction of the medium, and the time and temperature of incubation. Although standard conditions can be established for accurate evaluation of a single substance or of a crude preparation containing a single antibiotic agent, the results may not be very reliable when several antibiotic substances are compared, since substances may vary greatly not only in their selective action upon different bacteria, but also in their mode of attack upon the same organisms; this is especially true of crude products which may contain either a mixture of widely different types of antibiotic substances or a group of closely related modifications of the same general type of substance.

In selecting a method for measuring quantitatively the activity or potency of an antibiotic substance, it is essential to recognize several pertinent facts, which bear upon the nature and antibacterial properties of antibiotic substances in general.

Antibiotic substances are primarily bacteriostatic in their action; they are bactericidal to only a limited degree, although some substances may possess marked bactericidal properties.

Antibiotic substances are selective in their action; they are able in very low concentrations to prevent the growth of some bacteria, whereas much larger amounts are required to prevent the growth of other bacteria; some bacteria may not be inhibited at all by a particular substance even in very high concentrations.

The conditions for the bacteriostatic activity of different antibiotic substances vary greatly; some are not active at all or their activity is greatly reduced in certain media, because of the antagonistic action of some of the constituents of the media upon the antibiotic substance; others require for their activity the presence of certain specific chemical compounds in order to become effective.

The mechanism of action of antibiotic agents varies; some interfere with bacterial cell division, some affect bacterial respiration, still others interfere with the utilization of essential metabolites by the bacteria, either by replacing or combining with a substance necessary for the nutrition of the organisms.

Many antagonistic organisms produce more than one antibiotic substance; the culture filtrate of the organism may differ, therefore, in the nature of its activity from that of the active fractions obtained from it.

These facts have an important bearing upon the methods used for measuring the activity of or assaying an antibiotic substance. Methods already developed include:

1. The serial dilution or titration method (2, 7)
2. The agar diffusion or cup (cylinder plate) method and its modifications (1, 4, 7, 8)
3. The agar-streak method (10, 14)
4. The turbidimetric method (3)
5. A variety of other methods (9)

Considerable precision may be obtained with the serial dilution and cup methods. For special purposes, as for measuring the concentration of the antibiotic in body fluids, special methods may have to be devised.