

301. *The Determination of Sodium and Potassium in Insoluble Silicates.*

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WHEN a silicate containing sodium and potassium oxides is decomposed according to the standard procedure of Lawrence Smith, and the cold sintered mass is extracted with water, the solution ordinarily contains, in addition to the chlorides of sodium and potassium, a large excess of calcium as chloride and hydroxide, and a little sulphate. Potassium has been determined in such a solution, without removal of calcium and sulphate (U.S. Geol. Surv. Bull. No. 700, p. 215), but, as a knowledge of the amounts of both of the alkali constituents is usually required, it is customary to separate and weigh the alkali chlorides, and then determine potassium directly, and sodium by difference. In view of the methods now available for separating sodium as complex triple acetates (see, *e.g.*, Mitchell and Ward, "Modern Methods in Quantitative Analysis," 1932, p. 130), one may, however, avoid not only its indirect determination, but also the preliminary removal of radicals such as calcium and sulphate. For instance, Caley and Foulk (*J. Amer. Chem. Soc.*, 1929, **51**, 1664) used sodium magnesium uranyl acetate for this purpose, and Guthrie and Miller (*Min. Mag.*, 1933, **23**, 405) used the corresponding zinc complex salt, the results being comparable with those based on difference methods. As there is a dearth of critical studies relating to simplified procedures for the determination of the alkalis in silicates, we have now examined more fully the methods of determining soda and potash directly in the aqueous extracts obtained from silicates decomposed according to Lawrence Smith's procedure, weighing sodium finally as sodium zinc uranyl acetate and potassium as its perchlorate.

By direct experiment, the aqueous solution obtained after decomposing 0.5 g. of a sulphur-containing silicate with the same weight of ammonium chloride and 4 g. of calcium carbonate was found to contain calcium equivalent to 1.2 g. of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and 1.4 mg. of sulphate. In such extracts, since the proportion of sodium in sodium zinc uranyl acetate is very much less than that of potassium in potassium perchlorate, sodium was determined in one-fifth or one-tenth of the solution, according as the amount was small or large, and potassium in the remainder. This meant that, for the determination of sodium, silicates containing 0.25—11% of soda and 0.8—14% of potash gave rise to solutions containing 0.5—10 mg. of sodium chloride and 0.24 or 0.12 g. of calcium chloride, with a maximum of 22 mg.

of potassium chloride and a trace of sulphate; and, for the determination of potash, solutions containing 5—100 mg. of potassium chloride, about 1 g. of calcium chloride, a trace of sulphate, and a maximum of nearly 100 mg. of sodium chloride.

Sodium.—Barber and Kolthoff (*J. Amer. Chem. Soc.*, 1928, 50, 1625) and Kolthoff and Lingane (*ibid.*, 1933, 55, 1871) have shown that amounts of potassium chloride of the order indicated above do not interfere with the determination of sodium as sodium zinc uranyl acetate in 1 ml. of solution. According to Barber and Kolthoff, 0.83 g. of hydrated calcium chloride is similarly without influence, but they record only one result. Wiggins and Wood (B., 1935, 432) mention slight interference from calcium. No interference was anticipated from a trace of sulphate (cf. Barber and Kolthoff). We found that calcium chloride does interfere in the determination of sodium by Barber and Kolthoff's method, positive errors being consistently recorded, with one exception, as shown in cols. 3 and 7 of Table I. The results have been corrected for a trace of sodium impurity in the calcium chloride. In the experiment where 1 mg. of sodium chloride was precipitated in presence of 12 g. of calcium chloride, the negative error might not have been incurred had the precipitate been allowed to settle overnight (cf. Kolthoff and Sandell, *J. Physical Chem.*, 1933, 37, 443), instead of for less than an hour, as in the other experiments. Impure precipitates could not be freed from contaminants by further washing, but were purified by reprecipitation, as indicated in cols. 4 and 8 of the table.

TABLE I.

| Initial volume of solution, 10 ml. | | | | Initial volume of solution, 1 ml. | | | |
|--|-----------|-----------|----------------|--|-----------|-----------------|-------|
| CaCl ₂ ·6H ₂ O added, g. | NaCl, mg. | NaCl, mg. | | CaCl ₂ ·6H ₂ O added, g. | NaCl, mg. | NaCl, mg. | |
| | | taken | found, 1 pptn. | | | found, 2 pptns. | taken |
| 12.0 | 10.00 | 10.81 | 10.07 | 1.0 | 14.40 | 14.70 | 14.42 |
| | | 10.74 | 10.07 | | | 14.78 | 14.44 |
| 12.0 | 1.00 | 0.79 | — | 0.12 | 10.00 | 10.10 | 9.98 |
| 5.0 | 10.00 | 10.60 | — | 0.12 | 5.00 | 10.12 | 9.97 |
| | | 10.79 | — | | | 5.14 | — |
| 1.0 | 10.00 | 10.16 | — | 0.24 | 1.00 | 5.12 | — |
| | | 10.16 | — | | | 1.04 | — |
| 0.0 | 10.00 | 9.95 | — | 0.24 | 0.50 | 1.06 | — |
| | | 9.98 | — | | | 0.56 | 0.48 |
| | | 9.86 | — | | | 0.56 | 0.50 |

The data recorded in the second part of the table signify that, in determining soda in silicates without prior removal of calcium chloride, a double precipitation should be made.

The experiments made with 12 g. of calcium chloride, in presence of which 10 mg. of sodium chloride were completely precipitated in less than an hour, and 1 mg. was not, had a bearing on the determination of the sodium content of calcium carbonate, which is almost entirely responsible for the introduction of a little sodium impurity, necessitating the application of a correction, in careful silicate analyses. Caley (*Ind. Eng. Chem., Anal.*, 1929, 1, 191) determined the sodium content of calcium carbonate by dissolving 2 g. in acid, evaporating to remove the excess of acid, and separating and weighing the sodium as sodium magnesium uranyl acetate. There is no means of assessing the accuracy of his results. Correspondingly, but adopting the zinc uranyl acetate method with two precipitations, we determined sodium in 5 g. of calcium carbonate, adding 10 mg. of sodium chloride to ensure complete precipitation of the triple salt within an hour. The amount of sodium found corresponded to 0.6 mg. of sodium chloride. This result was practically identical with that found in "blank" experiments made with the carbonate treated in the same way as in the actual silicate analyses. The agreement was not unexpected, since the additional reagents required in the "blank" experiments were only ammonium chloride and water, which are easily obtained pure, and platinum apparatus was used, except in the filtration of the sodium-containing extracts. The direct determination of sodium in calcium carbonate is therefore recommended as a substitute for the "blank" experiment associated with our sodium extractions.

Sodium was determined in certain silicates obtained from the U.S. Bureau of Standards;

they were dried as instructed, and the results (Table II) have been corrected for sodium in the reagents.

TABLE II.

| Silicate. | Na ₂ O found, %. | Mean, %. | Bureau of Standards' value, %. |
|--------------------------------|-----------------------------|----------|--------------------------------|
| Opal glass, No. 91 | 8.39, 8.50, 8.32 | 8.40 | 8.46 |
| Feldspar, No. 70 | 2.35, 2.33 | 2.34 | 2.38 |
| Burnt refractory, No. 76 | 0.19, 0.17; 0.20, 0.20 | 0.19 | 0.38 |
| Plastic clay, No. 98 | 0.25, 0.25 | 0.25 | 0.27 |

All the separate determinations, with the exception of those for "opal glass," which was known to be difficult to decompose, agree well with each other, and the maximum deviations from the mean are within the limits allowed by Washington ("The Chemical Analysis of Rocks," 1930, p. 142). The only figures not in good agreement with the Bureau of Standards' value are those for the "burnt refractory," so further duplicate determinations were made with a more finely ground sample, but no marked increase in the Na₂O content was found (see table). There is no reason to suppose that the figures given are seriously in error. It is significant that the results for potash subsequently found (p. 1393) are high by amounts roughly equivalent to those by which the results for soda are low, as referred to the certificate values.

Potassium.—Three methods of determining potassium in solutions of the composition mentioned on p. 1390 were examined and compared for speed and accuracy.

Method 1. After precipitation of the trace of sulphate with a slight excess of barium chloride, sufficient perchloric acid was added to form the perchlorates of all the metallic radicals. From the dry mixture, the perchlorates of calcium, sodium, and barium were twice extracted with an anhydrous mixture of ethyl acetate and *n*-butyl alcohol (Smith and Ross, *J. Amer. Chem. Soc.*, 1925, **47**, 1020), and the residual potassium perchlorate was weighed.

Method 2. The mixture of the dry chlorides and a trace of sulphate was extracted with a little anhydrous *isoamyl* alcohol, which dissolved the bulk of the calcium chloride without appreciably affecting the potassium salt. From the residue, sulphate was then removed as barium sulphate, and potassium was separated as before from the remaining metallic radicals, and weighed as its perchlorate.

Method 3. Potassium was separated as potassium sodium cobaltinitrite from sulphate and the bulk of the calcium chloride. A small amount of calcium contaminates the precipitate (Guthrie and Miller, *loc. cit.*). After dissolution in perchloric acid and evaporation to dryness sodium, cobalt, and calcium perchlorates were removed as before, and the residual potassium perchlorate was weighed.

The results obtained are shown below. All the mixtures contained 0.1 g. of sodium chloride, 1.2 g. of calcium chloride hexahydrate, and 5 mg. of sodium sulphate, in addition to potassium chloride.

| KCl used, mg. | KCl found, mg. | | |
|------------------|----------------|-----------|-------------|
| | Method 1. | Method 2. | Method 3. |
| 100.0 | 100.2, 100.2 | 100.0 | 100.1, 99.9 |
| 50.0 | 50.2 | — | 49.6, 49.8 |
| 5.0 | 5.4, 4.8, 5.3 | 4.7, 5.2 | 5.0, 4.9 |

There appears to be little to choose between the three methods in regard to results. There were, however, definite objections to the first method, for calcium chloride had a slight solvent effect on barium sulphate, causing 0.4—1 mg. to remain behind and contaminate the potassium perchlorate. The removal of sulphate after the extraction of the bulk of the calcium perchlorate was not successful, owing to adsorption of potassium perchlorate by barium sulphate. The expulsion of the excess of perchloric acid from the mixed perchlorates was very troublesome, and the calcium-rich extract was extremely slow-filtering. In the second method, the filtration of the *isoamyl*-alcoholic solution of calcium chloride was tedious. The third method was preferred as being, on the whole, the quickest.

The three methods were applied to the silicates mentioned in Table II. For practice in

the determination of a small amount of potash, a rock, Inchcolm picrite, which had been analysed by Day (*Trans. Geol. Soc. Edin.*, 1924—1931, **12**, 236), was examined by the second and the third method. The results are shown below.

| Silicate. | K ₂ O found, %. | | | Bureau of Standards' value, %. |
|------------------------|----------------------------|--------------------------|-----------------------|--------------------------------|
| | Method 1. | Method 2. | Method 3. | |
| Feldspar | 12.56 | 12.38, 12.59 | 12.69, 12.60 12.57 | 12.58 |
| Opal glass | — | — | 3.34, 3.39 | 3.24 |
| Plastic clay | 3.12, 3.30 | 3.26, 3.25 3.24, 3.35 | 3.25, 3.23 | 3.20 |
| Burnt refractory..... | 1.60, 1.65 | 1.51, 1.55 | 1.61, 1.60 | 1.37 |
| Inchcolm picrite | — | 0.41, 0.56 | 0.41, 0.42 | (0.49) * |

* Day's value.

The mean percentages obtained by the three methods are in fair agreement with the certificate values, but it is noteworthy that in the third method alone do the maximum deviations from the mean lie consistently within the limits allowed by Washington (*op. cit.*). The general tendency to slightly high figures for potash, as compared with the certificate values, is balanced by the slightly low figures obtained for soda (Table II). This is particularly noticeable for "burnt refractory." The certificate values are based on the use of standard procedures involving the weighing of the alkali chlorides. We are unable to account for the discrepancy.

EXPERIMENTAL.

Reagents.—As far as possible the reagents employed were of A.R. quality. Organic solvents were purified and dehydrated according to standard methods. Hydrochloric and perchloric acids were redistilled. Sodium chloride (Kahlbaum's "mit Garantieschein") and potassium chloride (recrystallised) were dried and heated to fusion before use. Kahlbaum's calcium chloride hexahydrate, "mit Garantieschein," was examined spectroscopically for sodium by Dr. S. Judd Lewis, and guaranteed to contain not more than 0.0002%. Specially washed calcium carbonate was prepared for us by Messrs. Hopkin and Williams.

Apparatus.—Pyrex and Jena glassware were used throughout, and pipettes and volumetric flasks were calibrated. Jena sintered-glass filtering crucibles, Nos. 10 G 3 and 10 G 4, and small immersion filters, G 4, with a disc of 30-mm. diameter and the minimum capacity above it, were used as far as possible. Silicates were decomposed in narrow platinum crucibles of 25-ml. capacity, and evaporations were made in 200- and 100-ml. platinum basins. Small basins (60 ml.) were used in extraction processes and for weighing small residues. Evaporations were carried out on a gas-heated steam-bath or electrically. A thermostat fitted with a wire tray and with clamps for holding bottles was kept at about 20°, and used in connection with sodium determinations.

Determination of Sodium as Sodium Zinc Uranyl Acetate.—Small amounts of sodium chloride were measured by weighing accurately prepared solutions. The solution of mixed chlorides (10 or 1 ml.) was treated with 10 volumes of a zinc uranyl acetate solution saturated with the triple salt, which had been prepared according to Barber and Kolthoff's (*loc. cit.*) directions, and mechanically stirred and filtered before use. After 15 mins.' stirring and not less than 15 mins.' settling, the precipitate was collected on a glass crucible (10 G 3), and washed with the precipitant (5 × 2 ml.), 95% aqueous ethyl alcohol saturated with the triple salt (5 × 2 ml.), and finally with a little ether. All operations were conducted at constant temperature. The precipitate was dried at 40° for 10 mins., cooled, and weighed. When two precipitations were required, the washings with ether were omitted, and those with alcohol reduced in number. The precipitate was then dissolved in 10 ml. of 0.1N-hydrochloric acid, the solution evaporated to 2 ml., and reprecipitation effected as before. Because negative errors were of frequent occurrence, more retentive crucibles (10 G 4), were subsequently used, or a thin layer of asbestos was put on the others (10 G 3). The results in Table I referring to two precipitations were obtained in this way.

Determination of Sodium in Calcium Carbonate.—5 G. of calcium carbonate in a platinum basin were dissolved in 20 ml. of 6.7N-hydrochloric acid, and the solution was evaporated to dryness on an electric boiler. Water was added to make a total volume of 7—8 ml., and 100 ml. of the zinc uranyl acetate reagent were employed to wash the solution into a beaker containing 10 mg.

of sodium chloride. Two precipitations of the sodium triple salt were made in the customary manner, and from the amount of sodium chloride deduced that added initially was deducted.

Decomposition of Silicates and the Determination of Sodium.—0.5 G. of the dried, powdered silicate was decomposed with 0.5 g. of ammonium chloride and 4 g. of calcium carbonate, exactly as described by Washington (*op. cit.*, p. 222). The filtered aqueous extract of the cold sintered mass was made slightly acid with hydrochloric acid, and diluted accurately to 250 ml. 25 or 50 ml. were then evaporated in a platinum basin to remove hydrochloric acid, washed with the minimum of water into a small beaker, and evaporated to 1 ml. Sodium zinc uranyl acetate was precipitated twice under the appropriate conditions. In "blank" experiments made in absence of the silicate in order to find the sodium content of the reagents, the total aqueous extract was evaporated to dryness in a platinum basin, dissolved in water, and added to 10 mg. of sodium chloride, the subsequent procedure corresponding to that outlined in the preceding section.

Determination of Potassium as Perchlorate in Solutions containing Potassium, Sodium, and Calcium Chlorides, and a Little Sulphate.—*Method 1.* To the neutral solution (100 ml.) in a platinum basin 2 ml. of a 1% aqueous solution of barium chloride were added to precipitate the sulphate. The solution was evaporated to 10 ml., and filtered cold, through either a very small paper (Schleicher and Schüll's No. 589, blue band) or a tiny quartz filtering crucible. The precipitate was washed with cold water. To the filtrate was added 2–3 times the quantity of perchloric acid required to convert all the chlorides into perchlorates, and it was evaporated to dryness. After dissolution in a little hot water, the solution was re-evaporated to dryness, and the residue, which was broken up with a flat-ended glass rod, was digested near the b. p. for 2–3 mins. with 10 ml. of a mixture of equal parts of ethyl acetate and *n*-butyl alcohol. With the aid of the immersion filter, the liquid containing sodium and calcium perchlorates was removed by suction, and the residue was washed with the solvent (5×1 ml.). The residue adhering to the filter was washed back into the basin with hot water, which also dissolved the residue in the basin, and the evaporation and extraction processes were repeated. Again the filter was washed free from potassium perchlorate, and the solution in the basin was evaporated to dryness, heated for a few minutes at 150°, and then for 10 mins. at 350°. The basin was cooled and weighed in order to obtain the weight of potassium perchlorate.

Method 2. The solution was evaporated to dryness in a platinum basin, and, with the aid of the immersion filter, extracted as described above with 10 ml. of *isoamyl* alcohol. As it was not essential to remove the last traces of calcium chloride, but important to prevent loss of potassium chloride by solution in the alcohol, washing of the residue was omitted. From the residual chlorides, traces of alcohol were removed, and, after dissolution in 10 ml. of water, sulphate was removed as barium sulphate, the filtrate being collected in a small weighed platinum basin. The treatment with perchloric acid and the subsequent procedure were as previously described.

Method 3. Hamid's method (*Analyst*, 1926, 51, 450) of precipitating potassium as potassium sodium cobaltinitrite was selected in preference to more recent methods (*e.g.*, Piper, *J. Soc. Chem. Ind.*, 1934, 53, 392r), because complete precipitation was effected without leaving the precipitate to settle over-night, and no correction was required for potassium in the sodium cobaltinitrite solution, which was prepared according to Hamid's instructions and filtered just before use. To the neutral solution of chlorides in a 250-ml. beaker, 10 ml. of the reagent were added, and the whole was evaporated to dryness. The residue was stirred with *N*-acetic acid, the liquid removed with the aid of the immersion filter, and the residue washed with a freshly saturated, filtered, aqueous solution of potassium sodium cobaltinitrite, as recommended by Piper. The cobaltinitrite precipitate was dissolved by gentle warming in a three-fold excess of perchloric acid, and the solution transferred to a small weighed platinum basin, in which evaporations and extractions were carried out as already described. Potassium perchlorate was finally weighed.

Determination of Potassium in Silicates.—200 or 225 ml. of the slightly acid aqueous extract obtained after decomposing a silicate (above) were evaporated to dryness, and potassium was determined as perchlorate by one of the methods cited.