

## VOLUMETRIC DETERMINATION OF BORON IN NATURAL BOROSILICATES

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A rapid and simple method was suggested for the separation of boron from a series of associate elements, which interfere with the subsequent volumetric determination. After the decomposition of the mineral by sintering with a mixture sodium carbonate–zinc oxide, most of the interfering elements are separated by leaching the sinter with water. Ions, which are transferred to the aqueous extract, are separated from boric ions by static action of a strongly acidic cation exchanger added in a sufficient excess. Simultaneously the solution is neutralized by hydrogen ions formed by the exchange reaction. Boron is determined in the deionized solution acidimetrically by titration of complex mannitoboric acid.

The presence of most cations interferes with gravimetric and volumetric determinations of boron. During the analysis of a complex material, boron must be therefore separated either by distillation in the form of methyl ester, or with the application of pyrolysis, extraction, or chromatography<sup>1</sup>. Most of the separation procedures based on ion exchange can be easily employed, if the material is well soluble in water or in acids. The column separation procedure is usually applied: boron is separated from a slightly acidic or neutral medium by passing through a cation exchanger column in the hydrogen cycle. Some authors use also the static procedures of separation<sup>2,3</sup>.

Natural borosilicates (tourmaline, axinite, dumortierite *etc.*) are virtually insoluble in mineral acids and must be decomposed by fusion or sintering<sup>4</sup>. With both of these procedures, however, solutions of the melts are obtained containing a high excess of neutral salts and additional ions, which makes the subsequent separation and determination of boron more difficult. We attempted therefore to separate the interfering ions with a cation exchanger in a weakly alkaline – carbonate medium. At the same time we examined the efficiency of decomposition of natural borosilicates by sintering with a mixture sodium carbonate–zinc oxide, and the completeness of extraction of the anions formed into the aqueous phase.

## EXPERIMENTAL AND RESULTS

### Chemicals

The sintering mixture  $\text{Na}_2\text{CO}_3\text{-ZnO}$  (4 : 1) was used. Dowex 50-W X8, 50–100 mesh, served as the cation exchanger in the hydrogen cycle. The dry exchanger was sieved, repeatedly washed with 4M-HCl and then with water until the wash liquid gave a neutral reaction, and finally dried in a thin layer at 80°C for 12 h. 0.05M and 0.1M solutions of carbonate-free sodium hydroxide were prepared by diluting a 40% solution of NaOH with boiled redistilled water; they were kept in an atmosphere with a minimum content of carbon dioxide. Standard solutions of 0.1M-HCl and 0.05M- $\text{Na}_2\text{B}_4\text{O}_7$  and solid D-mannitol whose aqueous solution exhibited a neutral reaction were also used.

### *Decomposition of Natural Borosilicates by Sintering*

A mixture of sodium carbonate and zinc oxide was used as the sintering agent. The reaction in the solid phase occurring during the decomposition yields low-soluble zinc silicates and, in addition, hydrates and carbonates of a series of cations, which can be so separated from the  $\text{BO}_2^-$ ,  $\text{F}^-$ , and other ions by leaching the sinter with water. For the test of the completeness of decomposition and for the determination of the amount of interfering components transferred to the extract, we decomposed three standard rock materials with different contents of silicon dioxide and aluminium oxide<sup>5</sup> and one tourmaline with higher contents of ferrous and manganous oxides<sup>6</sup>. Repeated results showed that the contents of silicate and aluminate in the extract after the sintering are approximately proportional to their original contents in the material. The fraction of the extracted silicic acid lies in the range of 4–8%, that of aluminium oxide amounts to 25–50% rel. Manganese is transferred to the extract almost quantitatively. The other cations of the silicates, including the zinc added, remain quantitatively in the insoluble residue.

The completeness of decomposition was examined on a sample of schorl by comparing the content of fluorine in the original material and in the extract. The content of fluorine found in the latter (average of eight determinations  $\bar{x} = 0.463\%$ ,  $S = 0.003$ ) is in a good agreement with the direct determination (four determinations with the average  $\bar{x} = 0.459\%$ ). In the precipitate of carbonates and hydroxides, boron was found only in traces after thorough washing. From these findings it follows that during the sintering procedure as described below, the silicate lattice decomposes quantitatively and the anions released are transferred completely into the aqueous extract.

### *Separation of Boron by Static Action of a Cation Exchanger*

Solid, strongly acidic cation exchanger was added in excess to synthetic solutions containing an amount of sodium carbonate as corresponds to the sintering conditions. The exchange rate was followed for 6–24 h. After the exchange equilibrium established

the exchanger was filtered off, washed with water, and the content of borate in the filtrate was determined volumetrically as described below.

It was proved that the action of the exchanger in the static arrangement on carbonate solutions containing, in addition to borate, a series of anions, can be employed for a quantitative separation of boron from aluminium, manganese(II), uranyl, chromate, and alkali metal ions. Due to the action of protons formed the carbonate is decomposed, so that the solution is at the same time neutralized and deionized. After the separation of cations, boric and silicic acids and fluoride ions remain in the solution. Fluorides and silicates were found not to interfere with the subsequent volumetric determination of boric acid up to the content of 100 mg in the solution titrated. The results of the separation of boron from some ions are given in Table I.

#### Procedure

A weighed portion of finely ground borosilicate sample (0.3 g) is mixed in a platinum crucible with 2.0 g of the sintering mixture and covered with additional 0.5 g of the latter. The covered crucible is heated for 30 minutes at the temperature of dark red glow and the decomposition is finished at an enhanced temperature of a Mecker burner during 10 minutes. The sinter formed is released mechanically, transferred to a teflon beaker, 50 ml of water is added and the mixture is kept in a drier at 80°C. The solid phase is occasionally ground with a rod to speed up the decomposition process. Simultaneously the residue in the crucible is digested with several ml of water. After finishing the extraction, the solution together with the precipitate is transferred to a 100 ml volumetric flask, cooled, made up to the mark, and shaken. A portion of the solution is filtered over a dry filter (the first millilitres of the filtrate are not used) and from the clear filtrate 50 ml is pipetted into a polypropylene beaker. To this solution 10 g of the dry cation exchanger is added in portions under a glass. The resin is allowed to act with occasional mixing for 12 h. After that period the exchanger is filtered off over a medium fine filter and washed with water so that the overall volume of the filtrate be approx. 100 ml. The filtrate is collected in a conical flask.

TABLE I

Results of the Separation of Boron from Associate Elements Obtained on the Action of a Cation Exchanger

17.32 mg of B<sub>2</sub>O<sub>3</sub> given in all cases.

Element	Amount mg	B <sub>2</sub> O <sub>3</sub> found %
Al <sup>3+</sup>	50—100	99.64 ± 0.16
Cr <sup>3+</sup>	20—50	99.76 ± 0.05
UO <sub>2</sub> <sup>2+</sup>	10	99.60
Mn <sup>2+</sup>	5—10	99.76 ± 0.14
F <sup>-</sup>	10—50	100.29 ± 0.23
Na <sup>+</sup>	1 000—2 000	100.75 ± 0.25
SiO <sub>2</sub>	100—250	99.51 ± 0.15

To the combined filtrates in a titration flask with a ground joint, 2 drops of methyl orange are added. The solution is slightly acidified with 0.1M-HCl, and then boiled under a reflux condenser for some 5 minutes to remove CO<sub>2</sub> dissolved. The condenser is washed with a small amount of water and the solution is perfectly cooled. A stream of a CO<sub>2</sub>-free gas is then introduced into the solution and the latter is neutralized to pH 7.5 with 0.1M-NaOH; the pH is measured with an electrode pair glass electrode-s.c.e. 7 g solid *d*-mannitol is added and the complex mannitoboric acid formed is titrated with a titrant solution of 0.05 or 0.1M-NaOH. Starting from pH ~ 6 the titrant is added in regular portions (0.1 ml) and the whole shape of the titration curve is recorded. The titration end point is evaluated graphically.

The titre of the titrant solution of the hydroxide is determined by using a standard 0.05M-Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> solution. During that test determination all the operations are performed as during the normal boron determination, including digestion with the sintering mixture and separation using the cation exchanger, as described above.

## DISCUSSION

The application of the suggested procedure of decomposition and static action of the ion exchanger leads to a virtually complete isolation of borate. The cation exchanger acts in this case as an acid, neutralizing the slightly alkaline solution and at the same time removing the ions present in the aqueous extract of the sintered material. The exchange procedure is expressed by the equations as follows:



where [RSO<sub>3</sub>] is the solid phase.

The exchange is virtually quantitative if a sufficient excess of the exchanger and offtake of the reaction product are applied. The solution is practically deionized on the static action of the exchanger: during the volumetric determination followed with a glass electrode a minimum salt error of the latter occurs, and the potential changes near the equivalence point are rather high.

The procedure suggested was tested on samples of natural borosilicates — schorl with predominating ferrous component and enhanced contents of manganese, and axinite; results were obtained as follows:

tourmaline						
B <sub>2</sub> O <sub>3</sub>	$\bar{x}$	<i>n</i>	<i>s</i>	<i>V</i> , %	check determination	
	9.124	8	0.049	0.54	9.03,	9.07
axinite						
	5.253	8	0.030	0.57	5.10,	5.14

These results are in a good agreement with check gravimetric determinations performed after distillation separation of boron in the form of methyl ester. The values of standard deviations indicate that the procedure suggested is well applicable for routine analyses.

## REFERENCES

1. Vláčil F., Drbal M.: Chem. Listy 62, 1371 (1968).
2. Danilova V. V.: *Metody Khimicheskogo Analiza*, p. 66. Izd. Akad. Nauk SSSR, Inst. Geokhim. Mineralogii Rud. Mestorozhd. IGEM, Moscow 1967.
3. Fleet M. E.: Anal. Chem. 39, 253 (1967).
4. Doležal J., Povondra P., Šulcek Z.: *Decomposition Techniques in Inorganic Analysis*. Iliffe Books, London 1968.
5. Grassmann H.: Z. Angew. Geol. 12, 368 (1962).
6. Povondra P.: Geochem. Meth. Data, in press.

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