Laboratory and Computing Methods

DETERMINATION OF SILICON IN BORON

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Determination of small amounts of silicon in boron by direct AAS method with flame atomization in concentrations of Si 1–15 μg/ml in hydrochloric acid at the 1000-fold weight excess of boron (c = 1 mg/ml) was described.

Decomposition of the sample (0.1 g) was performed by melting with addition of solid sodium hydroxide and sodium chlorate in a silver or a gold crucible and dissolving the melt after cooling down in hydrochloric acid. No effect of boron on the silicon signal was observed under given conditions. Maximum of silicon atoms absorption at a 251.6 nm line is at concentration of hydrochloric acid 0.2–0.35 mol/l.

The results obtained by AAS method were compared with those achieved by a spectrophotometric determination of silicon as a blue silicomolybdate complex. Although the differences between the AAS results and the spectrophotometric results are not statistically significant, the atomic absorption method is more suitable with respect to a significant saving of time needed for determination.

INTRODUCTION

AAS has found extensive application in the analysis of Si and has been selected as the preferred technique for the determination of silicon in various matrices (minerals, coal ash, cement, steel, iron ores etc.) [1–3].

Determination of small amounts of silicon is possible by direct AAS method with flame atomization but several depression of silicon absorbance has been observed in dependence of the type of matrix [4].

We have aimed to develop the AAS method for the determination of low concentrations (0.05–2.00% w/w) of silicon in samples of pure boron and technical-grade boron. Dependences of the silicon signal on acidity of the solution and on the content of boron as well as NaCl in the solution were studied.

EXPERIMENTAL

Reagents and apparatus

hydrochloric acid conc., purified by subboiling distillation in the quartz apparatus
hydrochloric acid (1+4)
sulfuric acid (1+1)
ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$, solution 2% w/w, pH = 7.8
sodium acetate, solution 30% w/w
ascorbic acid $C_6H_8O_6$, solution 5% w/w
silicon stock solution, 100 mg Si/l

The silicon stock solution: 0.2139 g of pure silica was weighed into a platinum crucible, 1.2 g of anhydrous sodium carbonate was added, mixed and fused until a clear melt was obtained. Cooled melt was leached with 200 ml of water and after dissolution the solution was transferred into a 1000 ml volumetric flask, diluted, mixed and transferred into a plastic bottle. The true concentration was determined by evaporation with perchloric acid.

All chemicals were of analytical grade purity. Redistilled water was used.

All solutions were stored in polyethylene bottles.

The measurements were made on an atomic absorption spectrometer Varian SpectrAA30 with deuterium background correction and on a spectrophotometer Pulfrich with Elpho equipment fy Zeiss Jena (Germany).

Decomposition of sample [5]

The finally ground sample (50–100 mg) and 1.0 g of solid sodium hydroxide were weighed into a silver or a gold crucible. The mixture in the crucible covered with a lid was heated to the melt and afterwards solid $NaClO_3$ was stepwise added (in approximately 5 mg portions) so long as the dark flux turned bright. After cooling down the melt was dissolved in 20 ml of concentrated HCl and evaporated to the volume of 5 ml. Then the solution was cooled down and diluted to 100 ml in a volumetric flask.

Method

a) Determination of Silicon by Atomic Absorption Spectrophotometry

Table I

Determination of silicon in boron - comparison of the results obtained by AAS and spectrophotometrical method

	Silicon content			
	AAS		Spectrophotometry	
	$\bar{x} \pm s\frac{t_\alpha}{\sqrt{n}}$	s	$\bar{x} \pm s\frac{t_\alpha}{\sqrt{n}}$	s
technical-grade boron				
sample 1	0.54±0.02	0.016	0.55±0.03	0.028
sample 2	0.47±0.01	0.008	0.45±0.02	0.016
pure boron				
sample 1	0.11±0.02	0.016	0.14±0.02	0.016
sample 2	0.06±0.02	0.016	0.07±0.02	0.016
sample 3	0.13±0.02	0.020	0.17±0.02	0.016

$\bar{x} \pm s\frac{t_\alpha}{\sqrt{n}}$ .... reliability interval ($n = 6$, $\alpha = 0.05$)
s .... standard deviation
A set of 6 paralel determinations was performed for every sample

Silicon solution after decomposition (content of silicon from 1 mg/l to 15 mg/l) was measured at a 251.6 nm line. Flame N_2O-acetylene was used for the atomization of the sample and integrated absorbances were measured (suitable) measurement time is 3 s). The deuterium background correction was applied. Optimum concentration of HCl in solution was in 0.20–0.35 mol/l range. Calibration graph was prepared with standard silicon solutions adjusted to the same acid concentration used in sample solution.

b) Determination of Silicon by Spectrophotometric Method

For the spectrophotometric determination of silicon a method of reduced silicomolybdate complex [6] was used.

The ammonium molybdate solution (2 ml) was added to the solution of sample containing from 5 to 100 μg of silicon. Acidity of the solution was adjusted precisely to pH = 1.1–1.2 using HCl(1+4) or acetate solution according initial acidity of solution.

After 6 minutes 5 ml of H_2SO_4 and 1 ml freshly prepared 5% solution of ascorbic acid were added. The mixture was diluted to 100 ml after 30 minutes the absorbances were measured at a 720 nm line. The calibration curve was measured in the same way using the silicon stock solution 100 mg Si/l.

RESULTS AND DISCUSSION

Both methods – direct AAS and the spectrophotometric method – were used for the determination of silicon in 5 samples of technical grade and pure boron. The obtained results are summarized in Table I. With the AAS method we studied the dependence of the silicon signal on acidity of the solution (Fig. 1) and we have found optimum concentration range of 0.20–0.35 mol HCl/l for this method. We verified that sodium chloride up to concentration 20 mg NaCl/l and boron

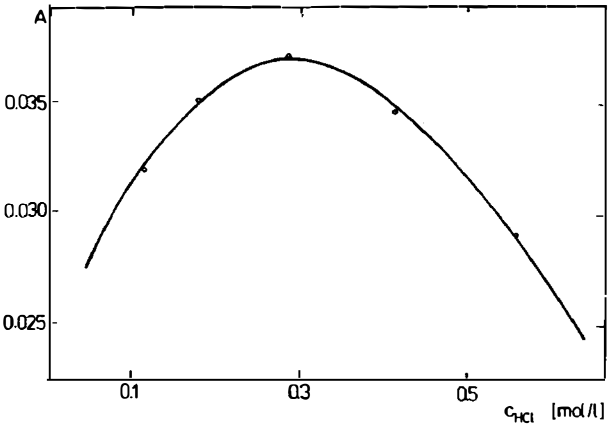

Fig. 1. Plot of the silicon absorbance against acidity of the solution. (c = 8.5 mg Si/l, working conditions: N_2O – C_2H_2 flame, lamp current 10 mA, slit width 0.2 nm, wavelenght 251.6 nm).

up to concentration 1000 mg B/l do not affect silicon signal at a 251.6 nm line.

Fig. 2 shows the calibration graph of the determination of silicon by the AAS method under this working conditions.

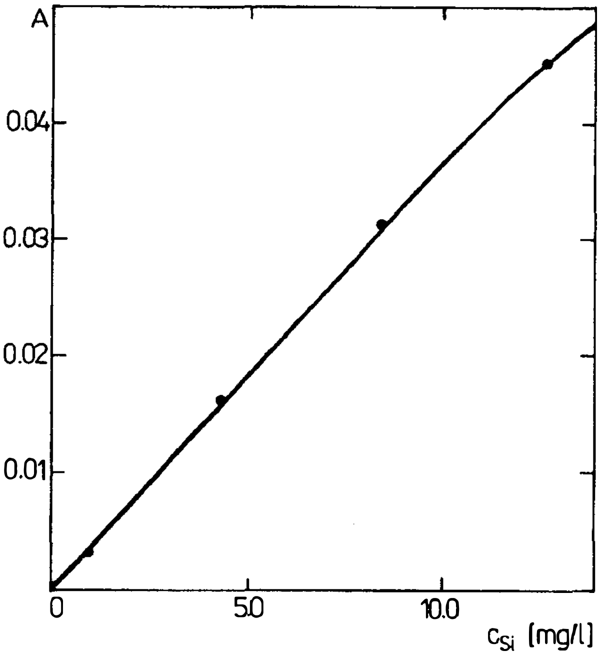

Fig. 2. Calibration curve Si (working conditions are the same as for the Fig. 1).

Table II

Statistical evaluation of the obtained results

AAS	Spectrophotometry	$D_i = x_A - x_B$	$(D_i - \bar{D})^2$
0.54	0.55	0.01	1.44×10^{-4}
0.47	0.45	0.02	0.04×10^{-4}
0.11	0.14	0.03	0.64×10^{-4}
0.06	0.07	0.01	1.44×10^{-4}
0.13	0.17	0.04	3.24×10^{-4}

Student's test $t_\alpha = 2.776$ $\alpha = 0.05$

$\nu = 4$

$$t = |\bar{x} - \bar{x}_B| \sqrt{\frac{k(k-1)}{\sum (D_i - \bar{D})^2}} = 2.40$$

$k = 5$

$$\boxed{t < t_\alpha}$$

The same verification was performed for the spectrophotometric method and we found that these results were not affected by NaCl and boron in the range mentioned above. We found that in the presence of boron the acidity of the dyeing solution has an remarkable effect on the spectrophotometric determination of silicon. This fact requires accurate electrometric checking of the pH value in a very narow range of 1.1–1.2.

The statistical evaluation [7] of the results obtained by both these methods is given in Table I and II. A set of 6 parallel determinations was performed for every sample. The comparison of the results of AAS and spectrophotometric method was made by Student's test and the results are presented in Table II. It is evident that differences between the AAS results and the spectrophotometric results are not statistically significant.

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Je popsáno stanovení nízkých obsahů křemíku v boru metodou plamenové AAS v koncentračním rozmezí 1–15 μg Si/ml v prostředí kyseliny chlorovodíkové ($c = 0.25$ mol/l) v přítomnosti 1000 násobného přebytku boru ($c =$ 1 mg/ml). Rozklad vzorku (0,1 g) se provádí ve zlatém nebo stříbrném kelímku tavením s 1 g NaOH za přídavku pevného $NaClO_3$.

Maximum absorbance atomů křemíku při vlnové délce 251.6 nm je při koncentraci HCl 0,20–0,35 mol/l, tj. za těchto podmínek je dosaženo maximální citlivosti. Ovlivnění signálu křemíku přítomností boru jsme za těchto podmínek nezjistili.

Výsledky stanovení křemíku získané AAS metodou byly srovnány s výsledky spektrofotometrického stanovení křemíku jako silikomolybdenové modři ve vzorcích čistého a technického boru. Přestože se výsledky dosažené

oběma metodami statisticky významně neliší, je metoda AAS vhodnější s ohledem na významnou úsporu času při stanovení.

Obr. 1. Závislost absorbance křemíku na koncentraci kyseliny chlorovodíkové ($c = 8,5$ mg Si/l). Pracovní podmínky: plamen N_2O–C_2H_2, žhavící proud lampy 10 mA, šířka štěrbiny 0,2 nm, vlnová délka 251,6 nm.

Obr. 2. Kalibrační křivka křemíku (pracovní podmínky stejné jako u obr. 1).