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ARTICLES

A Procedure of ICP-AES Analysis of Silicon Using Microwave Digestion and Preconcentration

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Abstract—A combined procedure has been developed for the analysis of high-purity silicon with preliminary vapor-phase digestion and preconcentration in a microwave oven using inductively coupled plasma atomic emission spectrometry (**ICP-AES**). Liners for high-pressure vessels of microwave oven ensuring the simultaneous distillation of matrices from 3–4 samples without their contact with the acid solution have been designed and manufactured. The procedure ensures the determination of up to 30 elements: Ag, Al, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hf, In, K, Li, Mn, Mo, Na, Nb, Ni, P, Rb, Sb, Sn, Sr, Ta, V, W, Zn, and Zr with the limits of detection 10^{-8}–10^{-6} wt %.

Keywords: atomic emission spectrochemical analysis, inductively coupled plasma, high-purity silicon, multielemental analysis, preconcentration of impurities, limits of detection

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Silicon is one of the main materials of present-day microelectronics. It is widely used for the production of integrated circuits, solar batteries, particle detectors in nuclear physics, etc. The possibility of using monocrystalline silicon in these fields is caused primarily by the chemical composition of the material, which substantially affects the main electronic and optical properties [1, 2]. For the control of the quality of silicon and the development of new technologies for its production and purification, one should constantly improve the methods of quantitative chemical analysis on the basis of modern analytical equipment. The requirements to the methods of chemical analysis for the set of test impurities and the limits of their detection are determined by the functions of silicon (metallurgic, solar, and semiconductor). As a rule, these methods should be highly informative, i.e., multielemental and provide low limits of detection for analytes. For example, for the analysis of semiconductor silicon of the 5N brand, the methods must ensure the determination of more than 20 impurities at a level of 10^{-6} wt % and lower.

It is known [3] that multielemental neutron activation analysis and solid-state mass spectrometry are the most efficient methods in the analysis of silicon, however, these methods are not widespread because of the complexity and high prices of the analytical equipment. The greatest number of publications deals with description of methods of silicon analysis using ICP-AES and inductively coupled plasma mass spectrometry. In most of AES methods of analysis, a sample is dissolved in a mixture of HF with HNO_3 and then the matrix is distilled as SiF_4 [4, 5]. However, because the volume of acids required for the digestion reaction is more than 10 times greater than the sample portion, the contamination of the concentrate with impurities present in the reagents used is unavoidable. This leads to the high values of the blank experiment and restricts the limits of detection for the analytes. The digestion of samples by acids vapor in sealed high-pressure vessels became widespread because of its simplicity and the possibility of a substantial decrease of the blank value [6, 7]. Nevertheless, this kind of sample preparation requires special equipment and is time consuming; in most of the known methods vapor-phase digestion takes from 8 to 40 h [8]. For the control of pressure and temperature inside such vessels, special sensors are required, and the absence of these can create safety hazard. Therefore, the digestion of samples in a microwave oven is one of the best techniques of sample preparation to the analysis of high-purity substances, silicon among them. In a microwave oven samples are digested in sealed high-pressure vessels with controlled temperature and pressure, which ensures the minimization of the value of the blank experiment because of the minimization of the amount of reagents.

In the present work, we propose a procedure of vapor-phase digestion of silicon and the preconcentration of trace impurities using a standard microwave

system. The procedure is based on the distillation of silicon as SiF_4 in a stream of HF and HNO_3 vapors obtained in a high- pressure vessel with a special lining under the impact of microwave radiation. The performance characteristics of the developed analytical procedure were evaluated and the accuracy of the results of analysis was tested.

EXPERIMENTAL

Equipment and reagents. The measurements were performed on an ICP ICAP 6500 spectrometer (Thermo Scientific) with a cyclone type nebulizing chamber and a SeaSpray type pneumatic nebulizer. The registered range of wavelengths was from 166 to 847 nm. To achieve low limits of detection for impurities, an axial method of the registration of analytical signal was used, which ensures the highest intensities of the analytical bands. Solutions of concentrates were supplied to the ICP using a peristaltic pump with a flow rate of 0.7 mL/min. The conditions of instrumental ICP-AES analysis are presented in Table 1.

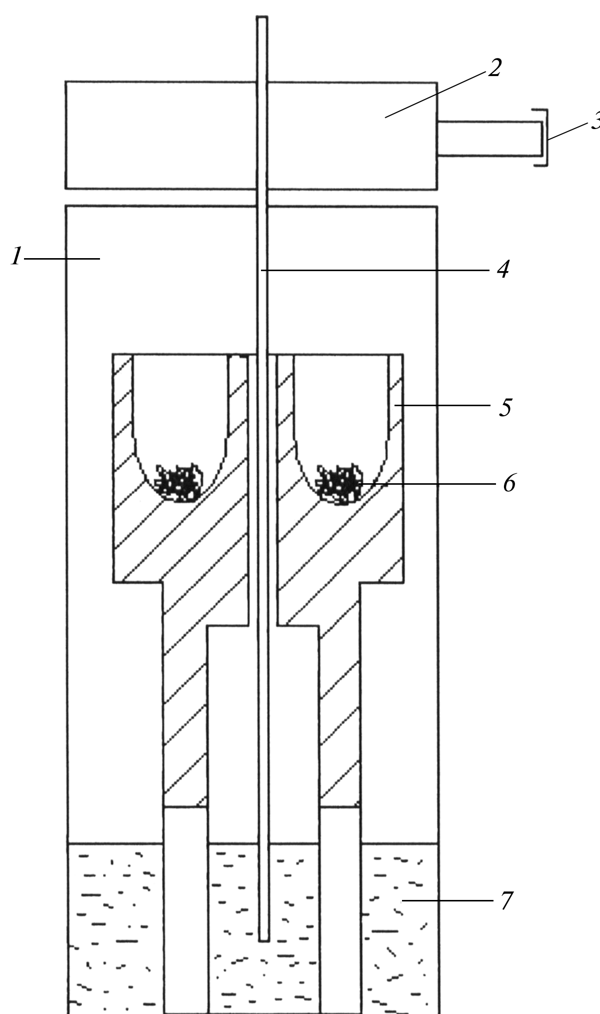
Table 1. Parameters of ICP-AES instrumental analysis

Parameter	Value
Plasma power, W	1150
Diameter of injector, mm	3.0
Nebulizer brand	SeaSpray Nebulizer
Cooling flow rate, L/min	12
Auxiliary flow rate, L/min	0.5
Nebulizer flow rate, L/min	0.7
Plasma scanning	Axial
Sample flow rate, mL/min	0.7

For the digestion and distillation of the samples matrix, we used a MARS 5 microwave oven (CEM, Mattews) and XP-1500 Plus high-pressure vessels for which special liners were developed. A scheme of a liner in a standard XP1500 Plus high-pressure vessel is presented in the figure. With this liner 3 samples and one blank sample could be placed in the vessel simultaneously. The liner was produced from polytetrafluoroethylene, which is stable in the reaction mixture, withstands temperature up to 200°C, is hydrophobic, and is easily cleaned by boiling in a mixture of HCl with HNO_3.

All operations were done using deionized water (Direct-Q3, Millipore) with the relative resistivity >18 Megohm/cm. HNO_3 and HF of the 27-5 high purity grade were used. The test and standard solutions were prepared using 14 M HNO_3 of the 27-5 high purity grade additionally purified by sub-boiling distillation on a DuoPUR (Milestone) setup. Reference samples were prepared by the consecutive dilution of multielemental solutions (**MES**) from Scat (Novosibirsk) with 1 M HNO_3.

Procedure. Portions of HF (10 mL) and HNO_3 (5.0 mL) were placed in XP-1500 Plus high-pressure vessels. Precisely weighed silicon samples (~300 mg) were placed into sockets for samples of the liner. To obtain reproducible results of analysis, pieces of silicon 20–40 mg in weight should be selected for digestion, because larger pieces have not enough time to be digested during the cycle of microwave digestion, while small pieces cause vigorous proceeding of the decomposition reaction, which can lead to underestimated results of analysis. Distilled concentrated H_2SO_4 (50 μL) was added to each sample to prevent the formation of a poorly soluble white silicon-containing precipitate [7] and distil silicon more com-



Scheme of a high-pressure vessel with a liner for the vapor-phase digestion and preconcentration of samples: *1*, high-pressure vessel XP-1500 Plus; *2*, vessel lid; *3*, pressure sensor; *4*, temperature sensor; *5*, polyfluoroethylene liner; *6*, sockets with samples; *7*, reagents mixture (HF and HNO_3).

Table 2. Limits of detection (wt %) of trace impurities in silicon by the method of microwave vapor-phase digestion and preconcentration (**MVPC**) and by methods [4] and [5] ($P = 0.95$)

Analyte	MVPC	[5]	[4]	Analyte	MVPC	[5]	[4]
Ag	2×10^{-7}	2×10^{-7}	6×10^{-8}	Mn	8×10^{-8}	9×10^{-8}	1×10^{-7}
Al	5×10^{-6}	5×10^{-6}	2×10^{-6}	Mo	1×10^{-7}	2×10^{-6}	ND
Be	1×10^{-8}	1×10^{-8}	ND*	Na	4×10^{-6}	6×10^{-6}	ND
Bi	3×10^{-6}	3×10^{-6}	6×10^{-7}	Nb	2×10^{-7}	2×10^{-7}	ND
Ca	4×10^{-6}	2×10^{-5}	5×10^{-6}	Ni	3×10^{-7}	7×10^{-7}	2×10^{-6}
Cd	2×10^{-8}	2×10^{-8}	2×10^{-7}	P	8×10^{-7}	8×10^{-7}	ND
Co	3×10^{-8}	3×10^{-8}	6×10^{-6}	Rb	7×10^{-7}	1×10^{-6}	ND
Cr	2×10^{-8}	3×10^{-7}	2×10^{-6}	Sb	5×10^{-7}	8×10^{-7}	6×10^{-6}
Cu	5×10^{-7}	5×10^{-7}	1×10^{-7}	Sn	1×10^{-7}	1×10^{-7}	2×10^{-6}
Fe	2×10^{-6}	4×10^{-6}	2×10^{-6}	Sr	6×10^{-8}	7×10^{-8}	ND
Ga	2×10^{-7}	2×10^{-7}	ND	Ta	4×10^{-7}	4×10^{-7}	ND
Hf	1×10^{-7}	1×10^{-7}	ND	V	7×10^{-8}	7×10^{-8}	ND
In	8×10^{-7}	8×10^{-7}	ND	W	2×10^{-7}	2×10^{-7}	ND
K	4×10^{-6}	6×10^{-6}	ND	Zn	6×10^{-8}	8×10^{-7}	2×10^{-5}
Li	4×10^{-8}	4×10^{-8}	ND	Zr	1×10^{-7}	1×10^{-7}	ND

* Not detected

pletely [5]. The liner with samples was placed in a high-pressure vessel and sealed according to the operational manual of XP-500 Plus high-pressure vessels in a microwave oven and then exposed to microwave impact. In this version, the reagents did not contact with the samples, the digestion of silicon occurred though the reaction in acids vapors and, as a consequence, the contaminants from the reagents did not enter the samples. The microwave treatment of silicon with acid vapors gave a volatile compound of SiF_4; therefore, along with the digestion of samples the distillation of the matrix took place. The treatment of samples in a microwave oven was performed at 400 W in three stages; the time of heating and holding were as follows: at the first stage, heating was up to 100°C for 10 min and holding for 30 min; at the second stage, heating was up to 160°C for 20 min and holding for 60 min; and, at the third stage, heating was up to 180°C for 10 min and holding for 30 min. The design of the liner ensures the use of regular temperature and pressure sensors of the MARS 5 microwave oven; this ensures the control of vapor-phase digestion and distillation of the samples. After opening the high-pressure vessels were cooled; the concentrates representing solutions of acid mixture were removed from the liner sockets with a micropipette and transferred into clean 5-mL polypropylene tubes, and diluted to 2 mL with 1 M HNO_3. The blank experiment was performed in parallel with the digestion and preconcentration of samples in an empty socket of the liner. Scandium used as an internal standard (1 ng/mL) was added to all solutions. Calibration curves were obtained by the consecutive dilution of MES solutions with 1 M HNO_3. The residual concentration of silicon in the analyzed solutions did not exceed 0.1 wt %.

RESULTS AND DISCUSSION

Evaluation of the limits of detection. For the evaluation of the limits of detection for impurities (c_{min}), we used the 3s test, where s is the standard deviation of the impurity concentration detected in the blank sample (c_c), $c_{min} = c_c + 3s$.

Table 2 presents the limits of detection for analytes calculated for 300-mg of sample portions ($n = 10–15$) and also the limits of detection by the earlier reported methods [5] and GOST [4]. It can be seen that the attained limits of detection for abundant impurities of Ca, Cr, Fe, K, Mn, Mo, Na, Ni, Sb, Sr, and Zn were 1.5–10 times lower than those obtained by the method [5] and 10–100 times lower than the limits of detection by the GOST method [4]. Method [5] includes standard sample preparation: the dissolution of silicon samples in a mixture of acids followed by the distillation of the matrix as SiF_4 on the addition of H_2SO_4 and an ICP-AES analysis. According to the GOST method, the impurities were concentrated on a graphite powder to which NaCl is added and then analyzed by AES with direct current arc. Such significant differences in the limits of detection are caused by the absence of a contact of samples with an acid solution during vapor-phase digestion and matrix distillation. As can be seen from Table 2, the method ensures the determination of up to 30 elements with the limits of detection (wt %) in the range from 1×10^{-6} to 1 ×

Table 3. Results (wt %) of analysis of a high-purity silicon sample according to MVPC and method [5] ($P = 0.95$)

Analyte	Method [5]	MVPC	Analyte	Method [5]	MVPC
Ag	$(7.9 \pm 2.4) \times 10^{-6}$	$(1.2 \pm 0.2) \times 10^{-5}$	Mn	$(2.7 \pm 0.2) \times 10^{-5}$	$(2.4 \pm 0.3) \times 10^{-5}$
Al	$(3.5 \pm 0.2) \times 10^{-5}$	$(3.5 \pm 0.4) \times 10^{-5}$	Mo	$(2.4 \pm 0.1) \times 10^{-5}$	$(2.4 \pm 0.3) \times 10^{-5}$
Be	$(8.9 \pm 0.8) \times 10^{-6}$	$(8.8 \pm 0.9) \times 10^{-6}$	Na	$(1.8 \pm 0.3) \times 10^{-4}$	$(1.5 \pm 0.2) \times 10^{-4}$
Bi	$(1.6 \pm 0.1) \times 10^{-5}$	$(1.2 \pm 0.4) \times 10^{-5}$	Nb	$(2.6 \pm 0.1) \times 10^{-5}$	$(2.8 \pm 0.5) \times 10^{-5}$
Ca	$(2.3 \pm 0.2) \times 10^{-4}$	$(2.0 \pm 0.3) \times 10^{-4}$	Ni	$(2.0 \pm 0.2) \times 10^{-5}$	$(2.0 \pm 0.2) \times 10^{-5}$
Cd	$(2.2 \pm 0.1) \times 10^{-5}$	$(2.0 \pm 0.3) \times 10^{-5}$	P	$(1.9 \pm 0.5) \times 10^{-4}$	$(1.2 \pm 0.3) \times 10^{-4}$
Co	$(2.0 \pm 0.2) \times 10^{-5}$	$(2.2 \pm 0.1) \times 10^{-5}$	Rb	$(3.5 \pm 0.4) \times 10^{-5}$	$(3.0 \pm 0.3) \times 10^{-5}$
Cr	$(2.6 \pm 0.1) \times 10^{-5}$	$(2.3 \pm 0.3) \times 10^{-5}$	Sb	$(2.2 \pm 0.2) \times 10^{-5}$	$(2.3 \pm 0.2) \times 10^{-5}$
Cu	$(2.1 \pm 0.2) \times 10^{-5}$	$(2.1 \pm 0.1) \times 10^{-5}$	Sn	$(2.2 \pm 0.2) \times 10^{-5}$	$(2.2 \pm 0.2) \times 10^{-5}$
Fe	$(1.0 \pm 0.2) \times 10^{-3}$	$(8.2 \pm 1.7) \times 10^{-4}$	Sr	$(3.3 \pm 0.7) \times 10^{-5}$	$(2.9 \pm 0.4) \times 10^{-5}$
Ga	$(2.0 \pm 0.2) \times 10^{-5}$	$(2.0 \pm 0.2) \times 10^{-5}$	Ta	$(2.6 \pm 0.1) \times 10^{-5}$	$(2.7 \pm 0.4) \times 10^{-5}$
Hf	$(2.7 \pm 0.2) \times 10^{-5}$	$(2.7 \pm 0.4) \times 10^{-5}$	V	$(2.2 \pm 0.2) \times 10^{-5}$	$(1.6 \pm 0.4) \times 10^{-5}$
In	$(2.7 \pm 0.3) \times 10^{-5}$	$(2.7 \pm 0.2) \times 10^{-5}$	W	$(2.3 \pm 0.1) \times 10^{-5}$	$(2.3 \pm 0.4) \times 10^{-5}$
K	$(1.1 \pm 0.1) \times 10^{-3}$	$(9.4 \pm 0.8) \times 10^{-4}$	Zn	$(2.3 \pm 0.1) \times 10^{-5}$	$(2.0 \pm 0.3) \times 10^{-5}$
Li	$(1.1 \pm 0.1) \times 10^{-5}$	$(1.0 \pm 0.1) \times 10^{-5}$	Zr	$(2.0 \pm 0.2) \times 10^{-4}$	$(2.2 \pm 0.4) \times 10^{-4}$

10^{-5} for Al, Bi, Ca, Fe, K, and Na; from 1×10^{-7} to 1×10^{-6} for Ag, Cu, Ga, Hf, In Mo, Nb, Ni, P, Rb, Sb, Sn, Ta, W, and Zr, and 1×10^{-8} to 1×10^{-7} for Be, Cd, Co, Cr, Li, Mn, Sr, V, and Zn.

Evaluation of the accuracy of the analytical procedure. The preservation of impurities in the concentrate and the accuracy of the results of ICP-AES analysis were tested by comparing the results of analysis of a silicon sample with spiked impurities obtained by the proposed and independent methods [5]. The results in Table 3 demonstrate that, under the selected conditions, 30 analytes, Ag, Al, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hf, In, K, Li, Mn, Mo, Na, Nb, Ni, P, Rb, Sb, Sn, Sr, Ta, V, W, Zn and Zr, were reliably preserved in the concentrate. The data in Table 3 were obtained from 3–4 independent experiments; the error depended on the analyte and varies from 2 to 30%.

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