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Capillary electrophoretic determination of silicon in plants

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ABSTRACT

A very limited number of methods for the determination of silicon are used. The classic analytical methods (gravimetric, photometric) and modern methods ICP-MS and ICP-AES are applied for the determination of silicon in plants, whereas the latter has an advantage because the sample preparation is not necessary. However, the reliability of the results obtained by ICP-AES is disputable. Conventional methods of sample preparation for silicon determination are time-consuming and difficult to perform; therefore, there is a critical need for development of more effective sample preparation procedures. Herein, we report the improved method of sample preparation for determining of silicon in plant materials. The method includes dry ashing, followed by oxidative degradation in $HClO_4$ and dissolution of formed silica in a mixture solution of potassium hydroxide and NaEDTA. Proposed method of sample preparation is more reliable and rapid (40 min). We employ the capillary electrophoresis (CE) for determination of silicon in plants, which to the best of our knowledge has not been done before. The dynamic concentration range of determination is 0.05–2 mg/l, detection limit — 0.02 mg/l. Analysis of different plant samples showed that the method is suitable for determination of silicon in plant materials down to trace amounts (0.1 mg/g) with satisfactory validity. Overall analysis time is 50–52 min.

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1. Introduction

Silicon is the second most abundant element in the Earth's crust. For a long time silicon compounds have been considered to be biologically inactive [1]. However, it was demonstrated that silicon plays an important role in biological processes, primarily it provides mechanical strength and elasticity to cell walls [2]. The soil is a source of silicon for plants because they dissolve silicates in rocks (basalt, rhyolite, quartz and diorite) [3]. The silicon content in the dry biomass of plants varies from 1 up to 100 mg/g [4,5]. The highest silicon content among terrestrial plants is found in horsetails as in the oldest plants [6]. Silicon is present in plant tissue in three major forms, such as water-soluble, organic-soluble, and insoluble polymeric compounds (polysilicon acid and amorphous silica) [6]. Monomeric orthosilicic acid H_4SiO_4 dominates the water-soluble forms of silicon in plants [7]. Orthosilicic acid undergoes polymerization to form polysilicic acids, and finally passes into a soluble state when the total concentration of silicon in the cell sap of plants exceeds 0.1 g/l [8]. Other forms of the existence of silicon in plant tissues were not established reliably.

A very limited number of methods for the determination of silicon are described in literature. The gravimetric and photometric methods are still widely used for the determination of silicon [9,10]. The gravimetric method of silicon determination is based on the precipitation of polymerized silicic acid followed up by drying, calcining, and weighing in the form of anhydrous silica. The photometric method is based on the conversion of silicon into yellow or blue form of silicomolybdic acid. Electric arc and spark is used for AES determination of silicon. The powdered sample is placed on the electrodes or blown through the atomizer with air flow. The detection limit of ICP-AES method is up to 0.03 mg of silicon without decomposition of the sample [11]. Mass spectrometry with inductively coupled plasma (ICP-MS) was used for the determination of silicon in beer [12]. The most abundant isotope ^{28}Si was determined using ICP-MS. Nitrogen is the major interfering component, therefore nitric acid is not recommended for use in sample preparation [13].

Method CE was used for determination of silicon in rivers [14] and geothermal waters [15]. Background solutions of sodium chromate were used as photometric reagent and cationic surfactant ($pH = 11.0 \pm 0.1$). Injection of the sample was hydrostatic, applied voltage was −20 and −15 kV, and the indirect UV detection was at 254 nm. The analysis time was 9 and 5.5 min, respectively. The method detection limits were 0.037 and 0.15 mg/l, respectively as well. Several samples of river water from the Galicia Coast and two samples of geothermal water from deposits taken from Los Humeros, Mexico were analyzed. Concentrations at the level of $n \cdot 1$ mg/l were found. The application of CE methods for the determining of silicon in plant materials is limited by LOD. Moreover, the methods of sample preparation described in the articles mentioned are not suitable for plant analysis.

A single paper [11] is dedicated to the determination of silicon in plant materials without sample preparation. The results obtained generally correlate with those of conventional methods with sample preparation, but the mean silicon content in 9 out of 10 samples is lower than those obtained by usual methods. This disagreement can be

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explained by differences in atomization efficiency of the reference material (cellulose + silicate) and sample plants.

A number of sample preparation methods have been applied for the quantitative determination of silicon in plants. Classical dry ashing procedures are time-consuming (more than 5 h) [16]. Acidic decomposition using hydrofluoric acid takes from 1 [17] to 8 [18] h. It can be reduced to 2 h by means of microwaves [16] and autoclaves [18]. Alkaline decomposition by lithium metaborate melt [19] takes 6–7 h. Autoclave-induced decomposition is applied to reduce the time of sample preparation to 1 h with the aid of sodium hydroxide/hydrogen peroxide [20] and for at least up to 2 h with the aid of Tiron [19].

Currently, there is a lack of modern, sufficiently rapid, and accurate and reliable methods for silicon determination in plant materials. Therefore, there is a crucial need for the development of CE method for the determination of silicon in plants.

2. Experimental

2.1. Apparatus

A Capel-105 capillary electrophoresis system (Lumex, Russia) equipped with a fused silica capillary with an external protective polyimide coating (inside diameter 75 μm; external diameter 365 μm; total length 60 cm; effective length 50.5 cm; applied voltage −20 kV; and temperature 20.0 °C) was used. The capillary was consecutively washed with concentrated $HClO_4$, H_2O, 4 M NaOH, H_2O, and background solution (treatment times 15, 5, 10, 5, 15 min, respectively) daily before use. The sample was injected on the cathode side at a pressure of 30 mbar for 5 ÷ 30 s. Electrophoregrams were recorded by means of indirect UV detection (271 nm) immediately in the capillary. The signal of the device was measured in millivolt. The spectral data were obtained using UV mini-1240 spectrophotometer (Shimadzu, Japan).

2.2. Sample preparation

Samples of plant were collected at Sergievka Park in Peterhof and St. Petersburg Botanical Garden. Air-dried samples were crushed with a grinding mill. The samples were stored in PP containers in a dark place. The proposed method of sample preparation of plant materials is as follows: 0.1 g of powdered sample (particles size less than 1 mm) is heated for 10 min in glassy carbon crucible at a temperature of 300–350 °C. Residue should not contain significant amounts of organic matter to prevent excessively rapid decomposition during subsequent processing. After cooling, the black residue was evaporated to dryness with 1 ml concentrated perchloric acid 3 times. The resulting residue should be white, yellowish or a light brownish color. 1 ml of 20% KOH and 2 ml of 0.05 M NaEDTA solutions (to avoid $CaSiO_3$ precipitate formation during further dilution) were added and the mixture was heated to 100 °C for 10 min. The mixture was diluted with water, then filtered, quantitatively transferred to a 100 ml PP volumetric flask and analyzed by CE (or photometric) method.

2.3. Chemicals and procedures

All chemicals were of analytical grade. Optimal background solution for CE was prepared as follows: 5 ml of 10 mM solution of the ammonium salt of cinnamic acid and 1 ml of 10 mM tetradecyltrimethylammoniun bromide solution were mixed, and then NaOH solution was added so that the pH = 10.5 (pH-meter). Then the solution was placed into a 25 ml volumetric flask and was diluted to the mark with distilled water. Only fresh buffer solutions were used.

Silicon in the samples was determined by reference photometric method. The following modification of the conventional colorimetric procedure [21,22] was used: 5–10 ml of sample solution was added by 1 M $HClO_4$ up to pH = 1.5 (pH-meter); the solution was quantitatively transferred to a 25 ml PP volumetric flask and added by 5 ml of 5% ammonium molybdate solution, 5 ml of 20% tartaric acid and distilled water to the mark. When using the blue form of silicomolybdic complex, 2.5 ml of the solution of 1% ascorbic acid was added before dilution to a final volume. The solution was mixed well and allowed to stand for 10 min. The absorbance was measured at 400 nm (for yellow form) or 811 nm (for blue form) with a 1 cm path length in a spectrophotometer. The optical densities were converted into silicon concentration using calibration curves constructed previously. LODs are 0.03 and 0.3 mg/l for the used photometric methods with blue and yellow silicomolybdic complex, respectively.

3. Results and discussion

Indirect photometric detection is the only acceptable method for silicon detection in CE due to the fact that orthosilicic acid and silicate ions do not absorb visible and UV light. Since silicon exists in anionic form in alkali solutions, it is necessary to choose the absorbing reagent among anions. Anions of cinnamic, 4-hydroxybenzoic, 3-nitrobenzoic and 3,5-dinitrobenzoic acids have been considered. The molar absorption coefficients of these substances are as follows: 13,600 (λ = 271 nm), 11,100 (λ = 250 nm), 7100 (λ = 266 nm), 9700 (λ = 240 nm). Cinnamic acid was selected as the absorbing substance since it has a maximum extinction coefficient and therefore provides potentially the lowest detection limit for CE determination of silicon. Reversion of electroosmotic flow in the presence of cationic surfactants is commonly used in CE analysis of anions [23]. Tetradecyltrimethylammonium bromide $CH_3(CH_2)_{13}N(CH_3)_3Br$ was applied for this purpose in the work.

The migration time of silicon varies from 1400 to 500 s for background electrolytes with pH = 9–11. Migration time changed slightly (500–700 s) at the pH = 10–11. The areas of peaks regularly decrease by more than threefold at increasing pH of the background electrolyte, from 9 to 11. However, the height of the silicon peak passes through a maximum at the pH = 10.0–10.5. Therefore, the height of the silicon peak at pH = 10.5 has been selected as an analytical signal for further work.

At the fixed pH = 10.5 the varying concentrations of cinnamic acid in the range of 1–8 mM cause a fourfold variation in the heights of the peaks. The maximum height of the silicon peak was obtained with 2 mM cinnamic acid. Thus, optimal conditions for the CE determination of silicon are the following: background electrolyte 2 mM cinnamic acid + 0.4 mM tetradecyltrimethylammoniun bromide, pH = 10.5, U = −20 kV, and sample injection duration for 20 s. The peak with migration time of 500–700 s corresponds to the silicon. The dependence of the analytical signal of silicon versus the concentration under optimum

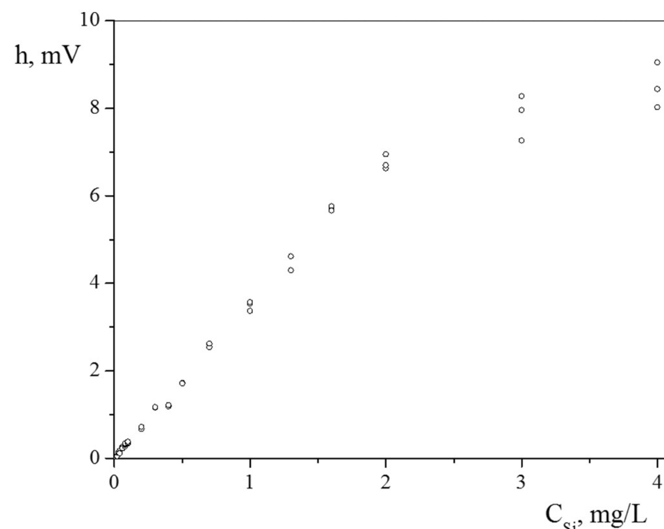

Fig. 1. Concentration dependence for CE determination of silicon.

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