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Short communication

Determination of silicate in water by ion exclusion chromatography with conductivity detection

Hua-Bin Li, Feng Chen*

Department of Botany, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong

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Abstract

A novel method for the direct determination of silicate in water by ion exclusion chromatography with conductivity detection is reported. The method is simple and sensitive with good precision. The calibration graph was linear from 0.1000 $\mu\text{mol l}^{-1}$ to 1000.0 $\mu\text{mol l}^{-1}$ for silicate with a correlation coefficient of 0.997 ($n=6$). The detection limit was 0.02 $\mu\text{mol l}^{-1}$. The method was successfully applied to the determination of silicate in mineral water, tap water, distilled water and seawater. The recovery was from 93 to 104% and the relative standard deviation was in the range of 1.1 to 4.4%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Conductivity detection; Silicate

1. Introduction

Silicon has an important role for animals and plants, and is an essential trace element for humans [1–3]. The total human ingestion has been estimated to be 30 mg Si per day with 60% of this from cereals and 20% from water and drinks and with the latter providing silicon in its most bioavailable form as silicic acid [4]. In the literature, several methods including spectrophotometry [5,6], atomic absorption spectrometry [7], atomic emission spectrometry [8] and high-performance liquid chromatography

(HPLC) [9], have been proposed for the determination of silicate. There are also reports on the determination of silicate by ion exclusion chromatography, with detection by postcolumn reaction [10]. The first report about the direct determination of silicate by ion exclusion chromatography was a combination of ion exclusion chromatography and inductively coupled plasma mass spectrometry [11]. Although the technique has the required sensitivity and accuracy, it is not easily accessible due to the high level of specialization needed and the high cost involved. In this paper, we report a novel method for the direct determination of silicate by a combination of ion exclusion chromatography with conductivity detection. The proposed method is simpler and more sensitive. The determination of silicate in mineral water, tap water, distilled water and seawater was

*Corresponding author. Tel.: +852-2859-1945; fax: +852-2858-3477.

E-mail address: sfchen@hkusua.hku.hk (F. Chen)

performed to validate the proposed method with real samples.

2. Experimental

2.1. Apparatus

The HPLC system used throughout this study consisted of a Waters 510 pump (Waters, Milford, MA, USA), a sample injector (Rheodyne, Cotati, CA, USA) with a 20- μ l loop, and a Waters 432 conductivity detector. Evaluation and quantification were made on a Millennium chromatography data system (Waters). The column used was an Aminex HPX-87H ion exclusion column (300 mm \times 7.8 mm I.D., Bio-Rad, Hercules, CA, USA).

2.2. Reagents

All solutions were prepared with analytical-reagent grade compounds and stored in polyethylene bottles. Reverse osmosis-Milli-Q water (18 M Ω) (Millipore, USA) was used for all solutions and dilutions. The silicate stock solution was 0.1000 mol l⁻¹ which was prepared by dissolving 2.121 g of sodium metasilicate pentahydrate (Fluka, Switzerland) in 100 ml of 0.2% sodium hydroxide (BDH, UK) solution. The working solutions were prepared by suitable dilution of the stock solutions with water. The sulphuric acid (BDH) solution, ammonium molybdate (Merck, Germany) reagent, oxalic acid (Sigma, USA) solution and ascorbic acid (Sigma) solution were prepared according to Grasshoff and Ehrhardt [12]. All other solutions were prepared by dissolving appropriate commercially available chemicals in water.

Tap water and distilled water were obtained from our laboratory. Mineral waters, which were manufactured in Hong Kong, France and Italy, respectively, were purchased from a local market. Seawater was obtained from Victoria Harbour in Hong Kong.

2.3. Procedure

All chromatographic separations were carried out at ambient temperature. The water sample was

filtered through a 0.45- μ m membrane filter before injection and the injection volume was 20 μ l. The mobile phase was water and the flow-rate was 1.00 ml min⁻¹, except 0.5 ml min⁻¹ for seawater. The column eluate was monitored with a conductivity detector.

3. Results

3.1. Chromatographic conditions

An Aminex HPX-87H column was chosen for the separation of silicate from the other ions in water. The mobile phase was water and flow-rate was 1 ml min⁻¹, except 0.5 ml min⁻¹ for seawater. Under these conditions, the representative chromatograms of silicate in standard solution, mineral water and seawater are shown in Figs. 1–3, respectively. The chromatograms of silicate in tap water and distilled water were similar to that of mineral water (data not shown).

3.2. Analytical parameters

The calibration graph obtained was linear from 0.1000 μ mol l⁻¹ to 1000.0 μ mol l⁻¹ for silicate with a correlation coefficient of 0.997 ($n=6$). The detection limit ($S/N=3$) was 0.02 μ mol l⁻¹. The relative standard deviation (RSD) was 2.0% for determination of 100.0 μ mol l⁻¹ silicate standard solution ($n=8$).

3.3. Effect of foreign ions

The interference of a number of different ions was studied by spiking 50.00 μ mol l⁻¹ of silicate with known quantities of foreign materials and analyzing it by the present method. No interference (relative error less than $\pm 5\%$) was observed at ratios (m/m) of 1000/1 for K⁺, Na⁺, NH₄⁺, NO₃⁻, SCN⁻, Cl⁻, Br⁻, SO₄²⁻ and PO₄³⁻, and 100/1 for HCO₃⁻, H₂BO₃⁻, Ca²⁺, Mg²⁺, Cu²⁺, Zn²⁺, Fe³⁺, Al³⁺ and AsO₄³⁻. That ion exclusion affords a separation of the silicate not only from the major water cations but also from potentially interfering anions has been described in the literature [11]. But, it should be

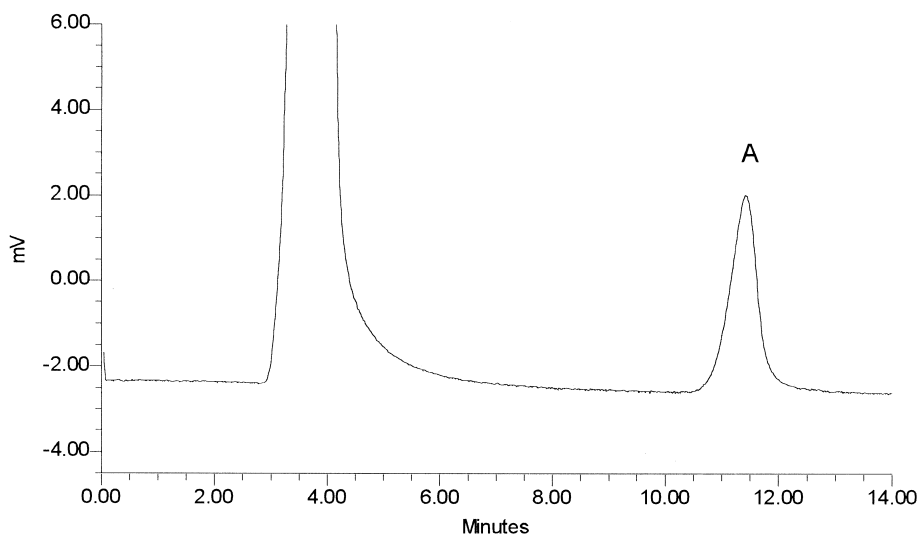


Fig. 1. Chromatogram of silicate standard at $100 \mu\text{mol l}^{-1}$. Conditions: column, Aminex HPX-87H; eluent, water; flow-rate, 1.00 ml min^{-1} ; detection, conductivity; injection volume, $20 \mu\text{l}$; peak, A=silicate.

given that when the total concentration of foreign ions is high, such as in seawater, chromatographic peaks of foreign ions would overlap with that of silicate at a flow-rate of 1.00 ml min^{-1} . Thus, a flow-rate of 0.50 ml min^{-1} was chosen for seawater. In this case, the chromatographic peaks of foreign ions were well separated from that of silicate.

3.4. Determination of silicate in real samples

The present method was applied to determine silicate in mineral water, tap water, distilled water and seawater. Results are given in Table 1. The recovery was from 93 to 104% and the RSD was in the range of 1.1 to 4.4%. Results agreed with those

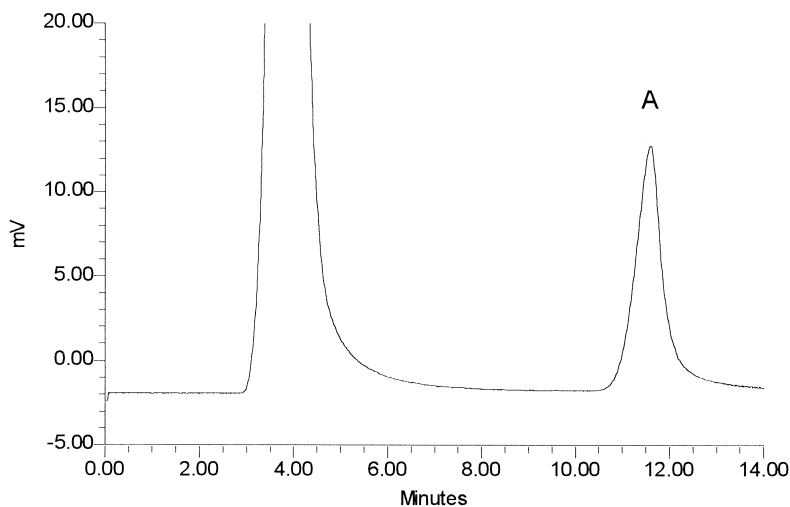


Fig. 2. Chromatogram of silicate in mineral water. Conditions: column, Aminex HPX-87H; eluent, water; flow-rate, 1.00 ml min^{-1} ; detection, conductivity; injection volume, $20 \mu\text{l}$; peak, A=silicate.

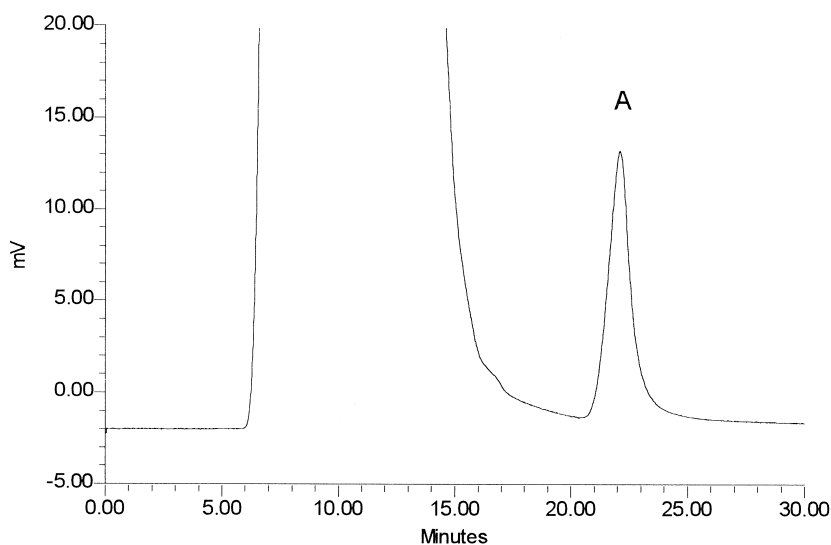


Fig. 3. Chromatogram of silicate in seawater. Conditions: column, Aminex HPX-87H; eluent, water; flow-rate, 0.50 ml min^{-1} ; detection, conductivity; injection volume, $20 \mu\text{l}$; peak, A=silicate.

obtained by spectrophotometry with blue silicomolybdc complex [12]. The *t*-test proved that no significant difference between the proposed method and the spectrophotometry could be observed at the 95% probability level.

4. Discussion and conclusion

Compared with the HPLC [9], the proposed method is more sensitive, i.e., the detection limits are $0.02 \mu\text{mol l}^{-1}$ (0.56 ng ml^{-1} as Si) in the present method and 10 ng ml^{-1} in the literature [9]. The present method is also simpler because derivatization

reaction and extraction are not needed. Compared with the previous ion exclusion chromatography with chemiluminescence detection by postcolumn reaction [10], the proposed method is simpler and more sensitive, i.e., the detection limits are $0.02 \mu\text{mol l}^{-1}$ (0.56 ng ml^{-1} as Si) in the present method and 50 ng ml^{-1} in the literature [10]. Furthermore, the proposed method does not require postcolumn reaction, and is direct determination of silicate. The proposed method can be more widely used than that by chemiluminescence detection because conductivity detection is more widely used than chemiluminescence detection for ion chromatography. Compared with the previous ion exclusion chromatography with

Table 1
Determination of silicate in water^a

Samples	Found silicate ($\mu\text{mol l}^{-1}$)	RSD ^b (%)	Added silicate ($\mu\text{mol l}^{-1}$)	Recovery ^b (%)	Comparison method [11] ($\mu\text{mol l}^{-1}$)
Distilled water	58.90	3.1	0.10	99	56.75
Tap water	70.54	3.7	0.10	102	72.34
Mineral water 1	132.44	4.4	1.00	93	128.52
Mineral water 2	318.50	2.9	1.00	104	320.17
Mineral water 3	400.19	1.1	1.00	98	401.28
Seawater	425.97	3.8	1.00	96	423.69

^a Average of five determinations.

^b $n=8$.

inductively coupled plasma mass spectrometry method [11], the proposed method is simpler and more sensitive, i.e., the detection limits are $0.02 \mu\text{mol l}^{-1}$ in the present method and $0.08 \mu\text{mol l}^{-1}$ in the literature [11]. The proposed method is also easily accessible because it does not need high levels of specialization or high costs.

A new method for the direct determination of silicate in water by ion exclusion chromatography with conductivity detection is described. The conductivity detection of silicate has not been reported previously, although conductivity detection is used widely in ion chromatography. The method is simple and sensitive with good precision. The present method is simpler and more sensitive than the previous HPLC [9] and ion chromatography methods [10,11]. The present method has been successfully applied to the determination of silicate in mineral water, tap water, distilled water and seawater. The proposed method can be adopted as a routine analytical method for the determination of silicate in water, such as mineral water, tap water, distilled water and seawater.

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