Spectrophotometric Determination of Trace Silica in Water After Enrichment on Polyurethane Foam and Complexation with Rhodamine B

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Abstract

A highly sensitive spectrophotometric method has been developed for the rapid determination of nanogram amounts of silica in pure water. The method involves the formation of yellow molybdosilicate in nitric acid medium, its extraction on polyether based polyurethane foam, elution in acetone, formation of ion associate between molybdosilicate and Rhodamine B (RB) in nitric acid and finally measurement of absorbance at 596 nm. The detection limit was found to be 0.05 ng mL^{-1} Si. The method obeys Beer's law over the concentration range 0.1 – 5 ng mL^{-1}. The molar absorptivity was found to be 1.4043 x 10^{6} L mol^{-1} cm^{-1}. The proposed method was successfully applied for the determination of silica in highly purified water samples.

1. Introduction

Many water supplies contain silica. This is not surprising since silicon is the second most abundant chemical element in the earth. In the form of silicates it is present in most natural water supplies. Typical concentrations lie between 1 and 30 mg L^{-1} Si. Higher concentrations may exist in brackish waters and brines. Silica content of water should be determined prior to its use in a variety of industrial applications. Silica can form a harmful scale on the equipment and heat transfer surfaces, particularly steam turbine blades. The cleaning and etching processes in the manufacturing of high technology products such as semiconductors, data storage media, printed wiring board etc. consume significant amounts of highly purified water. The use of purified water helps to fulfill two main objectives, namely production of high quality materials and minimization of rejects. Consequently, the need for more sensitive and accurate measurements of impurities in pure water has seen a rapid increase. Silicate is one of the most important substances for silicon surface reaction. The desired impurity level for silicon in pure water used for high-technology products is currently less than 1 ng mL^{-1}. Therefore, the analytical methods employed should accurately determine 0.1 ng mL^{-1} of Si.

Jolles and Neurath developed a colorimetric method for the determination of silica based on the reaction of silica and molybdate to form yellow molybdosilicate in 1898 [1]. Spectrophotometry using molybdenum blue based on the reduction of heteropolymolybdate ion, developed by Deniges in 1920 [2] is the most frequently used method for the determination of silica in water samples. However, the direct application of this method is

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limited due to insufficient sensitivity. Therefore, either pre-concentration or an increase in light path length is generally required to enhance the sensitivity of spectrophotometry in the detection of silica. Motomizu et al. developed several spectrophotometric methods based on the formation of ion associate between molybdosilicate and Malacite Green for highly sensitive determination of silica [3-6]. Takaku et al. [7] developed High Resolution ICP-MS method for the determination of silica in ultra-high-purity water. Takeda et al. [8-9] applied ICP-MS for the determination of ultra-trace elements in water. Yoshimura and Hase [10] reported a flow analysis for the determination of silica in highly purified water. Recently, Sabarudin et al. reported a sensitive method for determination of trace silica in pure water using Rhodamine B [11]. However, in these methods sample preparation were time consuming and complicated.

Since pure water contains ultra-trace quantities of silica, water samples had to be concentrated / evaporated to at least 10-fold to achieve satisfactory quantitative measurement. Takeda et al. [8-9] used non-boiling evaporation technique for pre-concentration of ultra-trace elements prior to their determination. Yoshimura and Hase [10] applied adsorption technique to pre-concentrate silicate using Sephadex LH-20 gel. Chu and Balazs [12] developed ICP-AES, ICP-MS and colorimetric techniques for the determination of silicate in pure water and applied 10-fold and 20-fold concentration of the sample.

In this work polyurethane foam (PUF) has been used for the enrichment of trace amounts of silica present in water. Resillient open-cell polyurethane foam (PUF) has successfully been used for the enrichment/preconcentration of traces of elements prior to their determination [13-14]. Owing to membrane like structure, outstanding rapid sorption and mass transfer properties, PUF has enabled the replacement of liquid-liquid extraction systems by the open-pore quasi-spherical solid-liquid system with enhanced separation and pre-concentration efficiency. Enrichment of silica on PUF in the form of molybdosilcate and its spectrophotometric determination was done by Roy and Kundu [15-16]. In this study, polyurethane foam (PUF) was applied for the enrichment of ultra-trace amounts of silica in pure water. Sensitivity of this method had further been increased by the formation of an ion associate between molybdosilicate and cationic dye Rhodamine B (RB) before spectrophotometric determination of silica. The method is based on the extraction of molybdosilicate on solid solvent polyurethane foam (PUF), elution of molybdosilicate from PUF in acetone, formation of an ion associate of molybdosilicate with RB and spectrophotometric measurement of absorbance of the complex at the wavelength of 596 nm. The method is simple, rapid and highly sensitive.

2. Experimental

2.1. Reagents

All chemicals used were of analytical reagent grade or highest quality commercially available grade. Water used for experiments was purified by reverse osmosis with an Elix 3 system followed by deionization with an 18 MΩ cm^{-1} deionised Milli-Q system (Millipore, USA). All laboratory materials were cleaned with acid (2 mol L^{-1} HNO$_3$), rinsed with Milli-Q water and stored in a laminar flow cabinet.

Hexaammonium heptamolybdate tetrahydrate (Merck, Germany) and suprapure grade nitric acid (Merck, Germany) were used. Acetone from Merck, Germany was used.

A commercially available silicon standard solution for AAS (1000 mg L^{-1} Si, Merck, Germany) was used. The working solutions were prepared daily by accurate dilution with pure water.

Molybdate solution 0.05 mol L^{-1} was prepared from Hexaammonium heptamolybdate tetrahydrate $(NH_4)_6(Mo_7O_{24}).4H_2O$ in water.

Polyvinyl alcohol (PVA) 0.1% w/v was prepared in water. Before use, PVA solution was filtered through a cellulose membrane filter (pore size, 0.45 µm; diameter, 2.5 cm).

Rhodamine B solution, 12×10^{-7} mol L^{-1} was prepared in 0.1 mol L^{-1} nitric acid. Open-pore polyether-type polyurethane foam (PUF) with a bulk density of 22 kg m^{-3} was cut into small cylindrical plugs of 5 mm $\varnothing \times 10$ mm length and was used. The foam plugs were first squeezed in acetone for 30 min to open their pores, washed with water and dried at 80°C in an oven. The dried foam plugs were then soaked in 2 mol L^{-1} hydrochloric acid solution for 2 h to remove all inorganic impurities, washed with water until the washing was acid free and neutral, and later dried at 80°C in an oven. The dried plugs were soaked in acetone for 30 min to remove all organic impurities. The foam was then pressed between filter papers to remove excess acetone and dried at 80°C and stored for further use.

2.2. Apparatus

An UV-VIS spectrophotometer (Perkin Elmer, Lamda 45) was used for absorbance measurement. All pH measurements were done with Orion 720A+ pH meter. A Soxhlet apparatus was used for cleaning of polyurethane foam.

3. Procedure

A suitable aliquot of silicon solution containing 0.1 – 5 ng mL^{-1} Si was taken in 50 mL PTFE beaker. Molybdosilicate was formed at 1 mol L^{-1} nitric acid and 16×10^{-3} mol L^{-1} molybdate [15, 16]. Molybdosilicate formed was extracted on PUF by adding 5-6 foam plugs and squeezing with a plastic plunger. After 15 min the foam plugs were washed with water and the sorbed molybdosilicate was eluted in acetone into 25 mL calibrated flask. Ion associate between molybdosilicate and RB was formed at 0.03 mol L^{-1} nitric acid and 6×10^{-7} mol L^{-1} RB. To the mixture 2.5 mL of 0.1% PVA was added. The volume was made with water. The absorbance was measured at 596 nm against reagent blank.

4. Results and Discussion

In our previous work [15-16], it was observed that yellow silicomolybdate complex formed in nitric medium could be sorbed selectively on PUF within a short period of time (< 15 min). The sorbed complex on foam matrix could be eluted with acidified acetone. In order to increase the sensitivity of the method, the eluted molybdosilicate complex was further allowed to form an ion associate with RB. The possible reaction mechanism is:

$$H_2SiO_3 + molybdate \rightarrow H_4SiMo_{12}O_{40}$$

$$H_4SiMo_{12}O_{40} + RB^+ \rightarrow (RB^+)(H_3SiMo_{12}O_{40}^-)$$
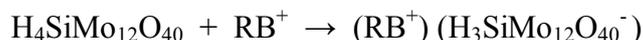
The absorption spectrum of this ternary complex showed an absorption maxima at 596 nm. This observation leads to further investigation for establishing different parameters affecting the quantitative formation of ion association complex of molybdosilicate with RB.

4.1. Effect of experimental variables for the formation of ion association complex

Optimum conditions for the concentration of molybdate, nitric acid, amount of solid solvent (PUF) and time of extraction of molybdosilicate on PUF, which were obtained in the previous work [15-16], were adopted in the present study. Medium acidity for the formation of ion associate of molybdosilicate with RB was examined by using sulfuric acid and nitric

acid. Nitric acid for medium acidity was selected because of lower value of reagent blank, a higher absorbance signals and better linearity of a calibration graph.

The effect of nitric acid concentration on the formation of ion associate of molybdosilicate with RB was examined and the results obtained are shown in Fig. 1. The best linearity of the calibration graph and highest value of the absorbance was achieved when 0.03 mol L^{-1} nitric acid was used. Therefore, 0.03 mol L^{-1} nitric acid was adopted. Higher concentration of nitric acid resulted in lower absorbances because RB is converted into a protonated orange cation by an excess of nitric acid which resulted in decrease in absorbances.
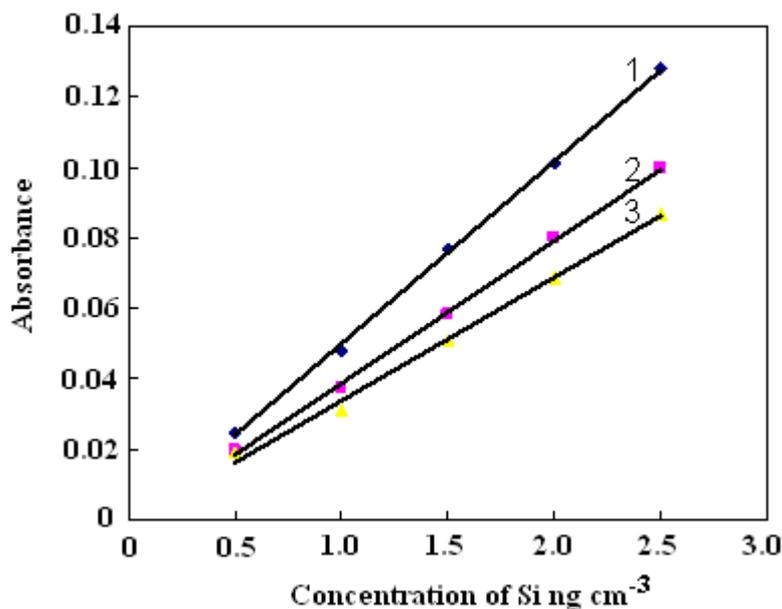
Fig. 1. Effect of nitric acid concentration. RB : 6 x 10^{-7} mol L^{-1}, PVA : 0.01 % (w/v)
(1) 0.03 mol L^{-1} HNO_3, linear correlation coefficient 0.999
(2) 0.05 mol L^{-1} HNO_3, linear correlation coefficient 0.998
(3) 0.10 mol L^{-1} HNO_3, linear correlation coefficient 0.995

Spectrophotometric method of silicate [17] based on the formation of an ion associate between molybdosilicate anion and a cationic dye is very sensitive. The ion associate formed between molybdate and RB tends to precipitate and the base line become very noisy and linearity of the calibration graph is poor. To prevent the precipitation of the complex and to avoid the base line drift, PVA was added to stabilize the ion associate. In this paper, 0.01% PVA was chosen at an optimum concentration with respect to the linearity of the calibration graph and low base line noise. On increasing the concentration of PVA (> 0.01%), the solution became more viscous resulting in reduced stability of background and poor linearity of the calibration graph.

The effect of RB concentration was investigated by varying the concentrations from 3 x 10^{-7} to 9 x 10^{-7} mol L^{-1}. The results showed that with the increase in RB concentration (Fig.2) there is increase in absorbances. But with high RB concentration, the base line became noisy and therefore 6 x 10^{-7} mol L^{-1} RB was considered to be the optimum concentration.
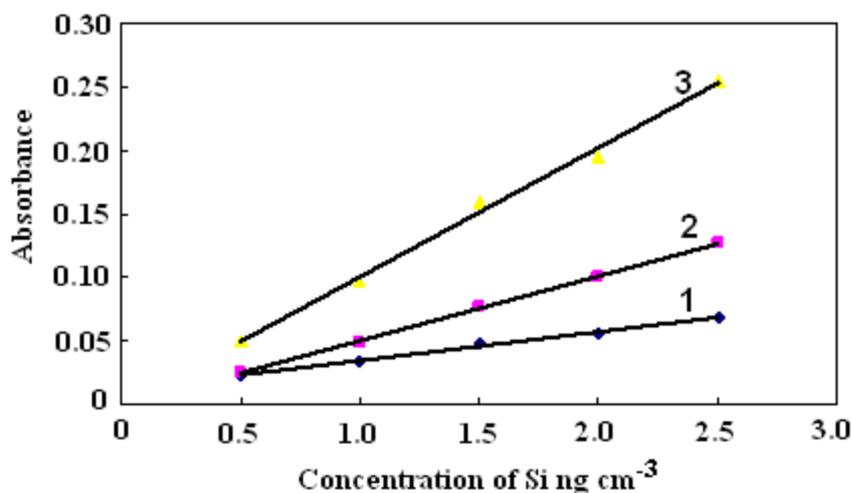
Fig. 2. Effect of Rhodamine B (RB) concentration. HNO_3 : 0.03 mol L^{-1}, PVA : 0.01% (w/v)
(1) 3 x 10^{-7} mol L^{-1} RB, linear correlation coefficient 0.992
(2) 6 x 10^{-7} mol L^{-1} RB, linear correlation coefficient 0.999
(3) 9 x 10^{-7} mol L^{-1} RB, linear correlation coefficient 0.995

5. Analytical parameters

5.1. Calibration

The calibration graph was constructed from 0.1 to 5 ng mL^{-1} Si using standard silicon solution to determine the features of the method. The calibration graph showed a good linearity. Beer's law was obeyed in the concentration range 0.1 to 5 ng mL^{-1} Si. The molar absorptivity at the wavelength corresponding to maximum absorbance at 596 nm was calculated by measuring the absorbance of solution at different concentration level of silicon. The mean value of the molar absorptivity was found to be 1.4043 x 10^6 L mol^{-1} cm^{-1}, which indicates that the method is sensitive. The correlation coefficient was found to be 0.999. The detection limit attained by the proposed method was 0.05 ng mL^{-1} Si.

5.2. Interference study

Normally, the amounts of interfering ions present in high purity water are very small and generally tolerable. The concentrations of some anions e.g. Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-} in high purity water are in the range 0 – 9 pg mL^{-1}. The range of concentrations of some metals, such as Li, Na, Mg, Al, Cr, Mn, Fe, Co, Ni, Cu and Pb is 0.034 – 0.94 pg mL^{-1} while K, Ca and Zn are present in the range 4.4 – 6.8 pg mL^{-1} [18]. From these data, it can be expected that there is no interference from co-exsisting ions in high purity water.

Phosphate and arsenate form molybdophosphate and molybdoarsenate and also form ion associate with RB. The effect of phosphate can be eliminated by the addition of oxalic acid, which decomposes any molybdophosphate formed. Effect of arsenate can be removed by reducing As(V) to As(III) on addition of hydrazine sulfate so as to prevent the formation of molybdate.

5.3. Application

Having established suitable conditions to detect silica, the proposed method, has been verified for pure water and distilled water samples (Table 1). The process stages for water purification are as follows :

Pure water A : pre-filtration → reverse osmosis → ion-exchange → UV irradiation → ultra-filtration → 1st filtration → 2nd filtration

Pure water B : pre-filtration → ion-exchange → UV irradiation → ultra-filtration

Doubly distilled water : pre-filtration → ion-exchange → 1st distillation → 2nd distillation → filtration

Distilled water : pre-filtration → ion-exchange → distillation → filtration

Quantitative recoveries were obtained for spiked pure water samples. Trace silica at ng mL^{-1} levels was detected in the doubly-distilled water and distilled water. Silicon present in water samples were tested in ICP AES and the results were compared with those obtained by the present method. The proposed method is found to be highly reliable and accompanied by good precision.

Table 1. Analytical results for the determination of silica in water samples.

Sample	Si added (ng mL^{-1})	Si found^{a} (ng mL^{-1})	Recovery (%)	ICP-AES^{b} (ng mL^{-1})
Pure water A	---	n.d.	---	---
	2.0	1.9 ± 0.06	95	1.8 ± 0.05
	4.0	1.9 ± 0.06	105	4.1 ± 0.07
Pure water B	---	0.15 ± 0.004	---	0.13 ± 0.003
Doubly distilled water	---	2.9 ± 0.06	---	3.0 ± 0.07
Distilled water	---	4.8 ± 0.09	---	4.6 ± 0.06

a : Mean ± sd (n=5)
b : concentration factor 10 fold
n.d. : not detected

6. Conclusion

In the present method, a new technique for the enrichment of ultra-trace silicate on PUF has been successfully introduced. Sensitivity of the method has been increased by the formation of ternary complex of molybdosilicate with RB. The method described in this study has useful application in the determination of ultra-trace silicon in water.

Acknowledgements

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