Sensitive Spectrophotometric Detection of Silicic Acid in Pure Water with Slab Optical Waveguide Absorption Detector

Kin-ichi Tsunoda,* Eiichi Yamamoto, and Hideo Akaiwa
Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376

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Blue silicomolybdate anion was adsorbed onto a glass slab optical waveguide (SOWG) surface as an ion associate with cetyltrimethylammonium cation and was detected with the SOWG absorption detector using a semiconductor laser (780 nm) as a light source. The sensitivity of the SOWG method for 2 cm^3 of a pure water sample was ca. 20 times higher than that of conventional spectrophotometry at 3 ppb Si level, and the detection limit was ca. 0.2 ppb Si (S/N=3).

Recently, the necessity of ultrapure water is increasing dramatically in advanced industries such as atomic power stations and semiconductor industry. Since silicon (Si) is one of the most difficult elements to remove in the process of its preparation, an analysis of pure water for Si is often demanded. However, it is not an easy task even today. For example, ICP-MS, one of the most sensitive analytical methods for various elements, does not show remarkable sensitivity for Si due to the interference from molecular ions such as N_2^+ and CO^+. Thus, the development of a simple and sensitive analytical method for Si in pure water is an important research subject for analytical chemists. Among various analytical techniques for Si, molybdenum blue spectrophotometry is still one of the most common analytical methods for Si (silicic acid) in water samples, although it is rather classical. To improve its sensitivity, various types of the analytical systems have been proposed, e.g., gel-phase absorptiometry,[1,2] the use of membrane filter preconcentration[3] and so on.

On the other hand, we have been applying a glass slab optical waveguide (SOWG) to a visible absorption detector of flow analysis to detect trace amounts of several dyes and iron(II).[4-6] In this technique, the concentration and detection of analytes were achieved at the same time with the SOWG detector, thus, it could be a simple and highly sensitive analytical method.

In the present study, the glass SOWG absorption detector was applied to the determination of Si (silicic acid) in pure water by flow analysis based on molybdenum blue spectrophotometry.

All reagents used were of analytical grade. Deionized water produced with a Milli-Q Labo (Millipore,U.S.A.) was used throughout. Stock standard solution of Si (1000 ppm) was purchased from Wako, Japan.

Glass SOWGs having tapered velocity coupler, which was originally proposed by Itoh and Madou, were used in this study to enhance the sensitivity of the SOWG measurements.[7] A K^+ doped glass SOWG was fabricated first by an ion-exchange process on borosilicate glass slide (n_D = 1.474, 25 x 70 mm) in molten KNO_3 at 723 K for 90 min. Then, a thin film (ca. 1.5 μm thick, 10 mm wide) of Corning 7059 glass, which had tapered slopes at both ends, was deposited onto the center of the K^+SOWG by a radio frequency (rf)-sputtering method. Sputtering conditions were as follows; a Corning 7059 glass target (80 mmϕ) was placed in a custom-made rf sputtering apparatus (Veetech, Japan) and was sputtered at 200 W forward rf power (27.13 MHz) for 3 h. A stainless steel mask which had a hole of 20 x 8 mm was placed between the target and the substrate (K^+SOWG) (6 mm above the substrate) to make the tapered sensing thin film. The partial pressures of the working gases, oxygen and argon, were 5 and 15 mTorr, respectively.

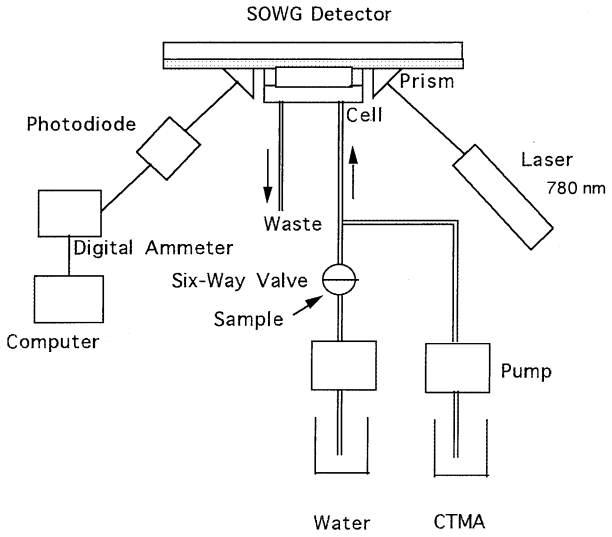

Figure 1. Schematic diagram of the present system. CTMA; cetyltrimethylammonium ion (1 μmol dm^{-3}).

The schematic diagram of the flow system is shown in Figure 1. The SOWG detector used in this study was basically the same as that in the previous paper,[6] except that a semiconductor laser (wavelength; 780 nm, the maximum power; 30 mW, and random polarization) was used as a light source. The flow cell was placed on the SOWG with a polytetrafluoroethylene (PTFE) block and a PTFE spacer (0.5 mm thick). The physical cell length was 1.0 cm, and the cell volume was ca. 15 mm^3. Deionized water as a carrier and a cetyltrimethylammonium (CTMA) bromide solution (1 μmol dm^{-3}) were pumped with an SNK DMX-2300T double plunger pump (Sanuki Industry, Japan) at 0.6 $cm^3 min^{-1}$. Blue color developed silicomolybdate standard solutions (0.1 to 2.0 cm^3) were introduced into the carrier stream via a Rheodyne 5020 loop injector (Cotati, U.S.A.). Those standard solutions were prepared according to reference 2. The mixing coil was ca. 50 cm long.

When the silicomolybdate standard solution alone was introduced to the SOWG detector, its adsorption onto the SOWG surface was not observed at all, probably because silicomolybdate ion is highly water-soluble. Thus, the ion-pair formation between silicomolybdate ion and quaternary ammonium ion was investigated, which was utilized for the preconcentration of silicomolybdate ion in pure water samples on a membrane filter by Kasahara et.al.[3] Various kinds of

quaternary ammonium ion such as tetraethylammonium, cetyltrimethylammonium (CTMA), tetradecyldimethylbenzylammonium ion and so on were tested as counter ions. As CTMA gave the best sensitivity for Si among them, it was used throughout the following experiments. Then, the concentration of CTMA ion was optimized. When the concentration of CTMA was too high compared with that of silicomolybdate ion, aggregate formation inside the mixing coil was observed, which interfered with the SOWG measurements. Thus, 1 μmol dm^{-3} CTMA solution was used for the concentration range lower than 100 ppb Si.

The various types of glass SOWGs were compared with one another, i.e., a K^+ doped glass SOWG, an octadecylsilane (ODS) coated K^+ doped glass SOWG,[4-6] a glass SOWG having tapered velocity coupler and so on. The glass SOWG having tapered velocity coupler gave ca. 5 times higher sensitivity than the ordinary K^+ doped SOWG. Moreover, ODS coating did not improve the sensitivity. Thus, the glass SOWG having tapered velocity coupler was used without any surface treatment.

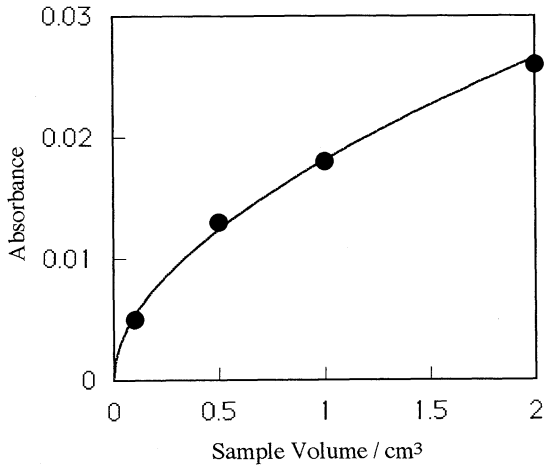

Figure 2. Dependence of absorbance upon the sample volume in the SOWG measurements. The concentration of a molybdosilicate standard solution used is 3 ppb Si.

Figure 2 shows that the absorbance signal (peak height) increases along with the increase in sample volume. This means that increasing sample volume is effective for improving the sensitivity of this method. In other words, although the sample volume tested in this study was upto 2 cm^3, further improvement of the sensitivity may be expected with the use of larger sample volume. The calibration curve for Si with the SOWG method is shown in Figure 3, when the sample volume of 2 cm^3 was applied. In either figure, however, linear response to the sample volume or the concentration of Si was not obtained, probably because the adsorption process of the analytes onto the SOWG surface may be governed by Freundlich isotherm. From Figure 3, the absorbance signal with the SOWG method is ca. 20 times greater than that with conventional spectrophotometry for 3 ppb of Si. The detection limit of the SOWG method for Si was about 0.2 ppb (S/N=3), which was mainly limited by the contamination of Si in deionized water used in this study (about

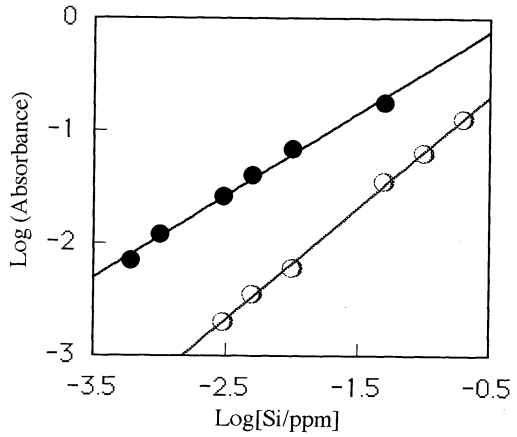

Figure 3. Calibration curve for silicic acid by the SOWG method. The sample volume of 2 ml was applied. ● ; the present method, ○ ; conventional molybdenum blue spectrophotometry.

0.7 ppb). The reproducibility of the SOWG measurements was typically about 10% at 0.6 ppb Si.

In conclusion, the SOWG method can be used to determine subppb level of Si in pure water. The present method itself showed the comparable sensitivity with other spectrophotometric methods combining various preconcentration processes.[1-3] In the present method, the concentration and detection of analytes were achieved simultaneously with the SOWG detector. Thus, a simple, rapid and sensitive analysis for Si in pure water could be realized by this technique. Finally, it is fair to add that some problems remain unsolved. One is that the conditions of the SOWG surface, which we can still not control entirely, affect the analytical performance of the method, e.g., the desorption of the analyte, i.e., the ion pair of silicomolybdate ion and CTMA, was often incomplete and baseline did not returned to the initial level after the measurement was done. Now we are continuing our study to solve such problems.

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References and Notes

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