Spectrofluorimetric Determination of Submicrogram Silicate with Benzoin and Mannitol

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A method for the determination of 5 ng - 10 μg (as Si) of silicate based on the formation of a fluorescent complex among silicate, benzoin and mannitol in a strongly alkaline formamide medium has been established. To reduce the blank value and to improve the reproducibility, sodium dithionite is added as a reducing agent; this prevents the oxidation of benzoin. The silicate in the solution can be determined over a very wide range by the same chemical procedures only by changing the sensitivity range of the spectrofluorimeter. The relative standard deviation of the method at a level of 0.5 μg Si is 2.7%. Phosphate and arsenate can be tolerated up to 4000-fold amounts.

Keywords Silicate determination, spectrofluorimetry, silicate-benzoin-mannitol ternary complex

Determination of traces of silica in high purity water such as that used in the electronics industry or as boiler feed-water is very important. In recent years, the atomic absorption spectrometry and the ICP emission spectrometry are applied in this field. But, generally speaking, photometric methods based on the formation of molybdosilicic acids (yellow or blue) are the standard methods. For samples of sub-ppm level some concentration process is needed.¹

Elliott *et al.* found that silicate ion forms a fluorescent complex with benzoin and mannitol in alkaline formamide media, during the course of their investigations of the fluorimetric method for the determination of boron with benzoin², and devised a method for the determination of silica.³ Although their method is not so sensitive as a fluorimetric method ($\geq 2 \mu\text{g}$ Si), it arouses interest because it is based on reactions entirely different from the molybdosilicic acid methods or other conventional ones and because it has the advantage of high tolerance for phosphate and arsenate. But, no further information has been given since their brief report appeared. In order to establish a more sensitive and precise method, the conditions for the reaction are examined in detail, together with the use of a spectrofluorimeter equipped with a high intensity xenon lamp.

Experimental

Apparatus

A JASCO model FP-550 spectrofluorimeter with a 10-mm $\times$ 10-mm quartz cell and a circulating thermo-

static cell-holder was used for all the fluorescence measurements. Temperature for the reaction and measurement were regulated by a Thomas model TRL-N11 thermostatic water bath.

A Sanei model PAU-850AN clean air bench was used in the determination of silica amounts lower than 0.1 μg Si.

Reagents

Distilled water was further purified by passing through an active carbon, high-purity ion-exchanger column and a 0.2 μ -filter (Barnstead NANO pure II).

Standard silicate solution. After ignition to a constant weight, 0.2139 g of a high-purity reagent of silicon dioxide (99.999%; Soekawa Chemical Co.) was fused with 2 g of sodium carbonate in a platinum crucible. The cake was dissolved in water and diluted to 1 l in a volumetric flask (100 $\mu\text{gSi ml}^{-1}$). Working solutions were prepared by appropriate dilutions. All these solutions were stored in polyfluorinated ethylenepropylene bottles.

A special high-purity reagent of sodium hydroxide monohydrate (99.9%; Merck, Suprapur) was used.

Formamide redistilled under reduced pressure (85–90°C/2–4 mmHg) with addition of a few pellets of sodium hydroxide was used. Formamide can be recovered from waste solutions of the procedure by distillation (two times).

Benzoin was recrystallized first from benzene, then twice from high-purity methanol (NF-SOL, Kanto Chemical Co.) before use. It was dissolved in ethanol to saturation and the mixture was stored in an amber glass bottle.

Sodium dithionite aqueous solution (13% in w/v) must be prepared directly before use.

Other chemicals were of reagent grade and were used without further purification.

Recommended procedure

Take 1 ml of a sample solution in a 25-ml polypropylene volumetric flask. Add 0.5 ml of 8 mol l⁻¹ sodium hydroxide aqueous solution and 40 mg of mannitol to it, then dissolve the content by adding about 15 ml of formamide. Add 3 ml of the saturated benzoin solution and 0.2 ml of the 13% sodium dithionite solution. Mix well and dilute to a mark with formamide. Place the flask in a water-bath regulated at 25±0.2°C for 100±2 min.

Measure the fluorescence intensity of the solution at 390 nm for excitation and 499 nm for emission at 25±0.2°C.

Results and Discussion

Effect of solvents

We wanted the best medium for developing the fluorescence, so we examined the reaction in various solvents miscible in water. In ethanol no fluorescence appeared, although high fluorescence intensity was obtained in it with the boron-benzoin system.² *N,N*-Dimethylformamide and dioxane were almost immiscible with a concentrated aqueous solution of sodium hydroxide and gave no fluorescence. By use of *N*-methylformamide, the fluorescence intensity was comparable with that in formamide. But the blank value was much higher and a longer time was needed to develop the maximum fluorescence intensity than in formamide. After all, none of the tested solvents have any advantage over formamide.

The quality of the formamide reagent affects the fluorescence intensity of the system considerably. The AnalaR reagent from BDH Chemicals gave the best results as received. Several kinds of reagent grade formamide were purified by fractional distillation under the conditions already described in the Experimental section with addition of sodium hydroxide. Constant results almost the same as that from the BDH's AnalaR were obtained by use of the purified reagents. Formamide could be recovered from the waste reaction-solutions by two distillations as above, although the blank was a little higher when the recovered solvent was used.

Effect of reducing agents

Elliott *et al.*³ reported that benzoin is extremely sensitive to oxygen in the presence of sodium hydroxide and explained that the high blank readings are derived mainly from the fluorescent oxidation products of benzoin. They used hydroxylamine hydrochloride as a reducing agent to reduce the blank value and to stabilize the sample readings.

Benzil is known as an oxidation product of benzoin. The fluorescence spectra of benzil in alkaline formamide media were measured and compared with those of the blank solution without reducing agents. The excitation (max. 350 nm) and emission (max. 380 nm) bands almost coincided with each other. In addition, the emission spectrum of benzil at the excitation wavelength of 390 nm, which is an excitation maximum of the silicate-benzoin-mannitol complex (see a later part of this section), was almost the same as that of the blank solution without reducing agents (between 450 and 500 nm). Their fluorescences were attenuated by the addition of hydroxylamine, but did not completely disappear. Moreover, when the amount was increased, the fluorescence of silicate-benzoin-mannitol complex decreased significantly, as Elliot *et al.*³ have mentioned. This effect may be due to the acidity of hydroxylammonium cation.

The effect of several reducing agents on the fluorescence of the blank solution and of the sample solution containing 6 µg (as Si) of silicate was investigated and is shown in Table 1. Sodium dithionite reduced the blank reading sufficiently without affecting the sample readings as hydroxylamine hydrochloride does and gave the largest net fluorescence intensity among the tested reducing agents.

Table 1 Effects of some reducing agents

Reducing agent	Fluorescence intensity		
	Blank	6 µg Si	Net
Hydroxylamine hydrochloride	1.8	38.8	37.0
Ascorbic acid	3.8	50.7	46.9
Sodium dithionite	1.7	60.1	56.4
Sodium thiosulfate	9.4	21.7	12.3

Fig. 1 Effect of the amount of sodium dithionite on the relative fluorescence intensity of the system. ○ Blank, ● 1 µg Si. The volume of the Na₂S₂O₄ solution was kept constant at 0.2 ml.

The fluorescence spectra of the sample containing 1 μg (as Si) of silicate by use of sodium dithionite have the excitation maximum at 390 nm and the emission maximum at 499 nm. The maximum of the excitation spectrum was shifted a little from 374 nm when hydroxylamine was used, whereas that of the emission spectrum was not changed.

The effect of the amount of sodium dithionite is shown in Fig. 1. The high sample and low blank readings were obtained with addition of more than 6.5 mg of it. The addition of 0.2 ml of 13% (w/v) sodium dithionite solution was adopted to minimize the effects of added water (see the next section) and of the aerial oxidation of the reagent.

Effect of water

While the fluorescent reaction in the present method takes place in formamide media, water is inevitably added to the reaction system as the sample and reagent solutions. So the effect of water contents on the reaction must be examined. The maximum fluorescence intensity and the time to reach it increased as the water contents in the reaction solutions decreased, as shown in Fig. 2. The amounts of the aqueous reagent solutions were determined as the irreducible minimum, that is, 0.2 ml for sodium dithionite and 0.5 ml for sodium hydroxide. Then, the volume of the sample solution was determined as 1 ml, because further decrease would lower the net sensitivity

Effect of concentration of sodium hydroxide

The alkalinity of the solution also affected the reaction markedly. When the volume of the sodium hydroxide solution was restricted to be 0.5 ml as already stated, the effect on the development of the fluorescence was investigated by changing the concen-

Fig. 2 Effect of water content on the development of the fluorescence. Si 4 μg . Total volume: 25 ml. 25°C. The volumes of the aqueous reagent solutions were kept constant at 0.2 ml of 13% $\text{Na}_2\text{S}_2\text{O}_4$ and 0.5 ml of 8 M NaOH. The volumes of aqueous sample solutions: Δ 1.8 ml, $\bullet$ 1.3 ml, $\circ$ 1.0 ml, $\blacksquare$ 0.8 ml, $\square$ 0.5 ml.

tration of the sodium hydroxide solution added. With increasing the concentration, the maximum fluorescence intensity increased, while a longer time was required to reach it. The maximum fluorescence intensities became constant with an addition of more than 8 mol l^{-1} NaOH solution. Taking into account the difficulty of pipetting a viscous solution precisely, 0.5 ml of 8 mol l^{-1} sodium hydroxide solution was added.

Almost all the commercially available reagents of sodium hydroxide showed high reagent blanks ($\geq 10^{-4}\%$ Si) and raised the detection limit of the method appreciably. Elliott *et al.*³ purified it by the electrolysis with an anion-permeable membrane. The special high-purity sodium hydroxide monohydrate from Merck (Sparapur) has a very low silicate content and can be used as received.

Effects of amount of benzoin and its solvent

Elliott *et al.* used 0.5 ml of a saturated solution of benzoin in methanol.³ The sensitivity of the method increased with increasing the amount of benzoin. On the other hand, the fluorescence became unstable when more than 1 ml of methanol was added (Fig. 3). Ethanol did not harm the stability of the fluorescence, although the solubility of benzoin in it is lower than in methanol. The addition of 3 ml of the saturated solution of benzoin in ethanol brought about an appreciable increase in the sensitivity.

Effects of amount of mannitol and of standing time

Without mannitol, no fluorescence appeared; the fluorescence intensity increased with the increase in the amount of mannitol up to 40 mg, but decreased by an addition of 60 mg.

With the rise in the temperature for the reaction and measurement, the fluorescence intensity attenuated a little. To secure reproducible results, the temperature for the reaction and measurement was fixed at $25 \pm 0.2^\circ\text{C}$.

Fig. 3 Effect of methanol on the development of the fluorescence. The added amounts of the saturated solution of benzoin in methanol: $\bullet$ 0.5 ml, $\circ$ 2.0 ml. Si 6 μg .

As shown in Fig. 4, the maximum fluorescence intensity was observed after about 90 min and could be maintained for 15 min by the operating conditions established above. Then, the fluorescence was measured at 100 ± 2 min after the solution had been mixed.

Precision and detection limit of the method

A linear relationship between the fluorescence intensity and the silicate concentration below $1 \mu\text{g}$ as Si was obtained with a relative standard deviation of 2.7% at a level of $0.5 \mu\text{g}$ Si. The limit of detection, defined as the three times the standard deviation of the blank value, was $0.05 \mu\text{g}$.

Although the sensitivity of the method established above was remarkably higher than that of Elliott's method, further improvement might be naturally expected from the sensitivity of the spectrofluorimeter used. The determination of silicate below $0.1 \mu\text{g}$ Si was attempted by increasing the applied voltage of the photomultiplier (changing the range selector). The calibration line was linear, but with poor reproducibility in this concentration range. It was thought that contamination from the atmospheric dust would seriously affect the determination of such a low level of silicate. All the experimental procedures were, therefore, carried out in a clean bench. The satisfactory results were obtained and the detection limit was lowered to 5 ng Si . It turned out that the main source of the contamination was from the adhesion of dusts on plastic-ware due to electrostatic charges. A remarkable feature of the proposed method is the fact that the silicate in the solution, over a very wide range from 5 ng to $10 \mu\text{g}$, can be determined by the same procedures by merely changing the sensitivity range of the spectrofluorimeter.

Effect of diverse ions

The effects of ions coexisting with $0.5 \mu\text{g}$ of silicate as Si are listed in Table 2. Phosphate and arsenate can

be tolerated at 4000-fold amounts. Borate, germanate and aluminum give positive errors in the presence of 10-fold amounts. Ferric iron and some heavy metal ions interfered at 50- to 100-fold level because of the coprecipitations of silicate with their hydroxides.

Application and some additional remarks

Silica contents in some water samples were determined by the proposed method (Table 3). The reproducible results were obtained with a wide range of silicate contents. Ten samples can be analyzed within 3 h.

In order to investigate the behavior of the colloidal silica in the proposed method, an aged geothermal-water sample was analyzed with and without the treatment by sodium carbonate⁴ (Table 4). The results were similar to those of the molybdosilicic acid methods^{4,5}: colloidal silica did not react with benzoin and mannitol and boiling with alkali is needed to determine it by the proposed method.

Table 2 Effect of diverse ions (silicate taken: $0.50 \mu\text{g Si}$)

Ion	Added as	Amount added/ μg	Silicate found ($\mu\text{g as Si}$)
None			0.50 ± 0.05^a
SO_4^{2-}	Na_2SO_4	2000	0.46
NO_3^-	NaNO_3	2000	0.48
Cl^-	NaCl	2000	0.51
PO_4^{3-}	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	2000	0.51
AsO_4^{3-}	$\text{Na}_2\text{HAsO}_4 \cdot 2\text{H}_2\text{O}$	2000	0.50
F^-	NaF	20	0.50
Br^-	KBr	20	0.51
I^-	KI	20	0.48
Borate	H_3BO_3	10	0.57
		1.0	0.46
Germanate	$\text{GeO}_2(\text{soluble})$	14 ^b	1.00
		1.4 ^b	0.53
Al^{3+}	$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	10	0.57
		1.0	0.51
Mg^{2+}	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	50	0.42
Ca^{2+}	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	50	0.46
Fe^{3+}	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	50	0.44
Zn^{2+}	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	50	0.52
Cu^{2+}	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	100	0.48

a. $3s$, s : standard deviation ($n=5$).

b. Calculated as GeO_2 .

Table 3 Determination of silicate in some water samples ($n=3$)

Tap water ^a	Si concentration/ $\mu\text{g ml}^{-1}$	
	Rainwater ^a	Distilled water ^b
11.5 ± 0.5	0.056 ± 0.008	0.008 ± 0.004

a. Collected at Tokyo Institute of Technology.

b. With a copper distillation boiler.

Fig. 4 Effect of standing time for the recommended procedure. Si $1 \mu\text{g}$. 25°C .

Table 4 Determination of colloidal silica (sample: aged geothermal water, Hatcho-baru, Oita Pref.)

Alkali treatment ^a	With	Without	Without ^b
Si found ($\mu\text{g ml}^{-1}$)	113	42.8	43.5

a. Boiled for 1 h with 10% Na_2CO_3 .

b. Determined by a molybdosilicic acid spectrophotometry.⁴

The reaction among silicate, mannitol and benzoin was presumed to lead to the formation of a ternary complex.⁶ Attempts to determine the composition of the complex were unsuccessful. First, more than a thousand-fold excesses in molar concentration of both benzoin and mannitol were necessary to develop the fluorescence in the method. Therefore, the molar ratio or continuous variation method could not be applied in this case. Methods based on the measurement of the

UV-absorption spectrum of the complex were also interfered with by the absorption of the excess reagents. Secondly, formamide is hydrolyzed in the strongly alkaline media and the acid titration method was also interfered with.

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