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Determination of Silicate by Ion-Exclusion Chromatography with Luminol Chemiluminescence Detection

Hiroyuki SAKAI,† Terufumi FUJIWARA, and Takahiro KUMAMARU*
Department of Chemistry, Faculty of Science, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima 724
† Laboratory of Inorganic Materials, Railway Technical Research Institute, 2-8-38, Hikari-cho, Kokubunji, Tokyo 185

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An increased chemiluminescence (CL) emission was produced upon mixing an acidified solution of silicate with a basic solution of luminol and hydrogen peroxide. The new CL reaction was used to develop a simple and rapid post-column detection system for selective determination of silicate after separation by ion-exclusion chromatography (ICE). Separation of silicate from other anions like phosphate, nitrite, sulfide or carbonate ion was achieved using a low-capacity cation-exchange column and a dilute perchloric acid solution as an eluent. Also, the present method has an advantage of eliminating interferences from ionic metal species. The detection limit of 50 ng cm^{-3} and a linear calibration graph with a dynamic range from 100 ng cm^{-3} to 30 μg cm^{-3} was obtained for silicon(IV). The proposed ICE-CL method was applied to the determination of silicate in tap and river water samples.

In the maintenance operation of concrete structures, particularly bridges and tunnels, an accurate knowledge of the silicate levels in the water seeping out of these structures is of great importance. Besides that, industrial, biological and clinical interests in silicon(IV) studies have well documented.[1,2] Thus, there has been an increased interest in the development of a simple and accurate method for the determination of silicon(IV) at trace levels.

For the determination of silicon(IV) spectrophotometrically, detection based on the molybdenum blue reaction,[3—5] has been used. However, the formation of exact or similar heteropolymolybdate analogues by phosphorus (V), arsenic (V), etc. reduces the specificity of the method. Recently, a molybdenum blue post-column detection system has been developed for the determination of those oxoanions using flow injection (FI) techniques.[6—9] However, the reaction of silicate was considered to be kinetically too slow for use in chromatographic detection. To resolve this problem, an increase in reaction temperature and/or the length of reaction coil was required.[8,9]

Chemiluminescence (CL) reactions are usually rapid, and the instrumentation used is simple and inexpensive. The CL methods have the advantages of wide dynamic range and high sensitivity. Thus CL systems are considered to be useful for a post-column chromatographic detection.[10] However, only a few CL systems have been presented for the determination of silicon(IV).[11] In the CL method reported,[12,13] silicate reacts with molybdate for quite a long period of time (ca. 10 min) before its final reaction with the CL reagent. In the present work, an increase in the CL emission resulting from the luminol-hydrogen peroxide reaction was first observed when an acidified solution of silicate was mixed with a basic solution of the CL reagent.

In inorganic trace analysis, a major problem associated with luminol CL methods is interference from other species, particularly transition metal ions.[11,14—17] Therefore, the separation of analyte is usually required before CL analysis.[18] An effective separation by chromatographic performance has been successfully demonstrated by several workers using low-capacity ion-exchange columns and various eluents.[14,19—22] Ion-exclusion chromatography (ICE) actually involves the chromatographic separation of molecular species rather than ions although an ion-exchange column is generally used.[23] Since silicate ion is an anion of weak acid, in the acidic medium it would be present in the form of a molecular acid, i.e. silicic acid, which is suitable for the present CL detection. When a dilute perchloric acid solution was used as an eluent in the ICE system, silicate was converted to silicic acid which was eluted from the column, and the CL detector responded well to silicic acid rather than to the eluent. This allowed the development of an FI system based on the direct combination of the ICE separation with the CL detection. One of the advantages of ICE is its ability to remove ionic interferents like transition metal ions. Silicic acid was also separated by the ICE from other weak acids which would otherwise interfere with the silicate determination.

Conductivity detector is widely used for ICE.[23] However, conductivity dectection signals are generally low owing to the small degree of the ionization of weak acids. A relatively small increase in a high background signal of the eluent is measured and therefore the sensitivity of the detection is very low. In this work, it was demonstrated that when combined with the CL detection, the ICE separation technique is an effective mean to improve selectivity and to enhance sensitivity. In addition, the advantages of FI analysis were incorporated into the present method to provide automated, rapid and reproducible analysis. Satisfactory results were obtained for the determination of silicate in tap and river water samples by the proposed ICE-CL method.

Experimental

Reagents and Standards. Luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) was purchased from Aldrich Chemical Co. (Milwaukee, WI, U.S.A.) and used without further purification. Other chemicals of analytical-reagent grade, were obtained from Kanto Chemical Co. (Tokyo, Japan), and were used as received. All solutions were prepared with high-quality deionized water obtained from a Yamato Kagaku (Tokyo,Japan) Model WAR-560 water purification system.

A 0.50 $\mathrm{mol\,dm^{-3}}$ hydrogen peroxide solution was prepared daily by diluting a stock solution of 10 $\mathrm{mol\,dm^{-3}}$ hydrogen peroxide with water. The CL reagent solution of 0.10 $\mathrm{mmol\,dm^{-3}}$ luminol and 5.0 $\mathrm{mmol\,dm^{-3}}$ hydrogen peroxide in 5.0 $\mathrm{mmol\,dm^{-3}}$ potassium hydroxide was prepared daily. The pH of the reagent solution was 11.4. Silicon(IV) working standard solution were prepared by serial dilution of the stock solution of 1000 $\mathrm{\mu g\,cm^{-3}}$ silicon (IV) in 0.5 $\mathrm{mol\,dm^{-3}}$ potassium hydroxide. Working standard solutions of other acid anions used here were prepared by dissolving potassium sulfate, sodium sulfide, potassium dihydrogenphosphate, sodium nitrite, and potassium hydrogencarbonate with water. Metal working solutions were prepared by serial dilution of the corresponding 1000 $\mathrm{\mu g\,cm^{-3}}$ stock standards solutions available commercially in 0.1 $\mathrm{mol\,dm^{-3}}$ nitric or hydrochloric acid, except for iron(II) standard which was prepared by dissolving iron(II) chloride in 0.1 $\mathrm{mol\,dm^{-3}}$ hydrochloric acid.

Instrumentation and Procedures. The batch measurements of luminescence resulting from the CL reaction were made with a Hitachi (Tokyo, Japan) Model F-2000 fluorescence spectrophotometer using a 1-cm cell. In the cell, 1.0 $\mathrm{cm^3}$ of the CL reagent solution was placed and an equal amount of a sample was injected quickly into the cell by using a plastic syringe.

A schematic diagram of the flow system used for the ICE separation and CL detection is given in Fig. 1. A Yokogawa Electric (Musashino, Japan) Model IC 100 ion chromatograph, with a 100-$\mathrm{mm^3}$ sample loop, was employed. A Tokyo Rikakikai (Tokyo, Japan) Model MP-3 peristaltic pump was used for elution. For separation, a 200-mm×4.9-mm i.d. cation-exchange column (SCX1, Yokogawa Electric) was employed. Dilute (4.4 $\mathrm{mmol\,dm^{-3}}$) perchloric acid was used as an eluent. PTFE tubing (0.5-mm i.d.) was used throughout in the flow system. Samples were introduced into the eluent stream of perchloric acid. The CL reagent was uniformly delivered to the system via a pump of the chromatograph device.

The column effluent from the ICE was mixed directly with the CL reagent in a 70-$\mathrm{mm^3}$ coiled flow cell housed in front of the photomultiplier tube of a Niti-on (Funabashi, Japan) Model LF-800 bio-chemiluminescence monitor. When entering the flow cell, pH of the resulting mixture of the CL reagent stream and the eluent stream was 10.7 which was optimum for CL. The CL signals produced were recorded on an ordinary strip-chart recorder. Even when the CL reagent and the column effluent containing no silicic acid were mixed, a relatively high baseline signal was obtained. The peak height of the CL signal was read against the reagent blank. Therefore, the flow system was optimized for a stable and constant baseline signal, which is important for obtaining a low dectection limit and better reproducibility. The constant flow rates for the eluent and reagent solutions were set at 1.0 and 2.0 $\mathrm{cm^3\,min^{-1}}$, respectively.

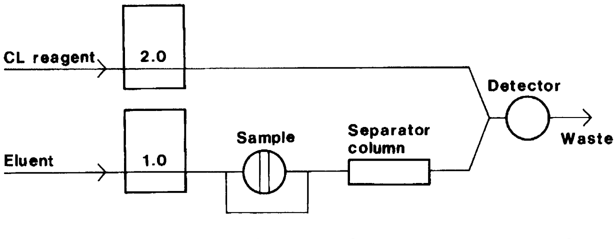

Fig. 1. Flow system for the ICE separation and CL detection.

The analyte solution was prepared as follows: To 100 $\mathrm{cm^3}$ of a water sample in a 100-$\mathrm{cm^3}$ PTFE beaker, 0.2 g of sodium hydrogencarbonate was added. After heating in a boiling water bath for 20 min, the resulting solution was cooled to room temperature on standing and then filtered through a No. 5C Toyo Roshi (Tokyo, Japan) filter paper. The final solution was made up to 100 $\mathrm{cm^3}$ with water and was immediately analyzed.

For the silicate determination in water samples, parallel measurements by flame atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) were also performed. A Hitachi Model Z-6000 polarized Zeeman effect atomic absorption spectrometer with a nitrous oxide–acetylene flame at 251.6 nm and a Kyoto Koken (Kyoto, Japan) Model UOP-1S high-resolution ICP atomic emission spectrometer at 251.611 nm (Si I) were used, respectively.

Results and Discussion

Silicic Acid–Luminol-Peroxide Chemiluminescence. An increased CL emission resulted when potassium silicate in a dilute acid was mixed with a basic solution of luminol and hydrogen peroxide. Figure 2 shows a typical profile of CL intensity vs. time. The CL signal reached very rapidly to a maximun and was observed for about 3 s. On the other hand, dilute perchloric acid gave a low CL signal with the reagent solution (Fig. 2). Also, no increase in the CL emission was observed when an unacidified solution of the silicate was mixed with the CL reagent solution. Similar to the batch measurements, CL was observed in a post-column flow cell using an FI system. By removing the separation column from the system shown in Fig. 1, it was possible to conduct FI studies to select the pH of the medium required for sensitive detection. Figure 3 shows the dependence of CL emission intensity on the pH of the silicate solution injected. At pH higher than 3.5, no increased CL emission was observed. However, when the pH was decreased, the CL intensity increased and reached its maximum at around pH 2.6.

Aqueous solutions of silicate contain $[\mathrm{SiO_2(OH)_2}]^{2-}$ as confirmed through Raman spectra[24] but tetrameric and other polymerized species could also be present at different pH and concentrations.[25] Although the

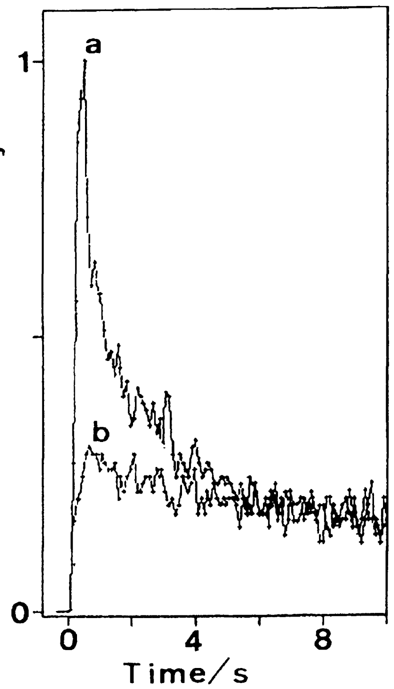

Fig. 2. Peak shapes for CL signals obtained from the luminol–hydrogen peroxide reaction with dilute perchloric acid solutions in the presence (a) and absence (b) of silicon(IV). Si(IV), 1.0 µg cm^{-3}; $HClO_4$, 4.4 mmol dm^{-3}; luminol, 0.10 mmol dm^{-3}; KOH, 5.0 mmol dm^{-3}; H_2O_2, 5.0 mmol dm^{-3}.

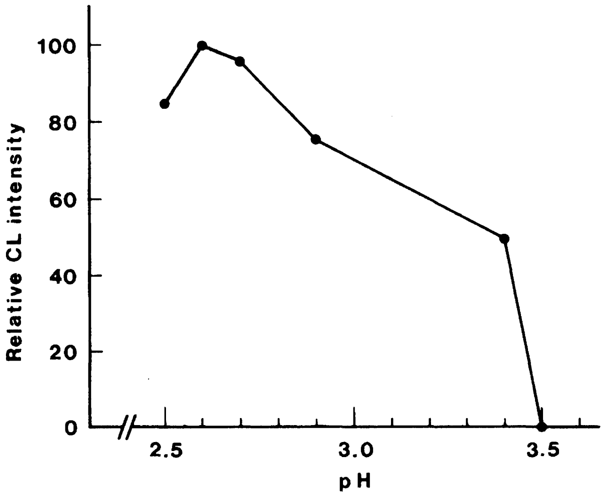

Fig. 3. Variation of the CL intensity with pH of the perchloric acid solution containing 1.0 µg cm^{-3} silicon(IV). Luminol, 0.10 mmol dm^{-3}; KOH, 5.0 mmol dm^{-3}; H_2O_2, 5.0 mmol dm^{-3}.

composition of the oxygen compound of silicon(IV) is unclear,[26] it behaves as a weak acid.[27] Silicate can be readily converted into molecular acid as is the case when the anion of weak acid is acidified. This indicates that in the acidic medium silicic acid is produced, which then plays an important role in the enhancement of the CL emission. At the moment the involvement of silicic acid in the luminol CL could not be explained. Using the aforementioned FI system and optimum reagent conditions for silicic acid, a comparative inquiry on CL behavior were carried out for anions of other acids such as phosphoric acid, nitrous acid, sulfuric acid, carbonic acid, and hydrogen sulfide. The results are summarized in Table 1. Sulfuric acid in the acidic medium produced a comparable CL signal while the CL intensities with other acids were 4—5 times lower than that with silicic acid.

Chromatographic Separation. Anions of weak acids were separated as molecular acids by ICE using a high-capacity cation-exchange column with water[28] or dilute solutions of strong acids[29] as eluents. Strong acid anions such as nitrate and chloride ions pass rapidly through the column and elute first as a group. Weak acids exist as the molecular acids which are free to partition into the occluded solvent within the resin and are therefore separated from the anions and from one another. When a high-capacity cation-exchange column was used in the ICE system as in general use, silicic acid could not be eluted from the column even with a concentrated strong acid solution. In addition, a high baseline CL signal was caused by using such a concentrated strong acid solution as an eluent. Therefore, a low-capacity cation-exchange column and dilute perchloric acid as an eluent were preferably used in this work.

Retention times for anions of several acids separated on the column at various concentration of perchloric acid are given in Table 2. Under the elution conditions used here, silicate ion was obviously separated from phosphate, nitrite, sulfide, and carbonate ions. In spite of a strong acid anion, sulfate ion was always eluted very close or in admixture with the silicate ion. Factors other than partition, like size effect,[23] might alter the chromatographic behavior. Unlike the CL signal for the eluting silicate, however, the CL signal for the eluting sulfate became extremely broad and its magnitude was ca. 100 times less than that of the silicate signal. Thus, an overlapping CL-profile containing sharp and broad

Table 1. Relative CL Intensities for Acid Anions with Luminol–Hydrogen Peroxide

Anion[a)]	Concentration µg cm^{-3}	Relative CL intensity[b)]
SiO_3^{2-}	1.0	100
CO_3^{2-}	10	223
NO_2^-	10	ND[c)]
PO_4^{3-}	10	286
S^{2-}	10	252
SO_4^{2-}	10	791

a) All solutions were prepared in 4.4 mmol dm^{-3} perchloric acid. b) Luminol, 0.10 mmol dm^{-3}; KOH, 5.0 mmol dm^{-3}; H_2O_2, 5.0 mmol dm^{-3}. c) ND=Not detected.

Table 2. Effect of Perchloric Acid Concentration on the Retention Time for Acid Anions Separated by ICE[a)]

$[HClO_4]$	Retention time/min					
(mmol dm^{-3})	PO_4^{3-}	CO_3^{2-}	NO_2^-	S^{2-}	SO_4^{2-}	SiO_3^{2-}
1.5	5.34	5.33	5.44	5.55	8.14	8.27
2.2	4.46	4.49	4.52	4.64	6.56	6.57
3.3	3.59	3.64	3.63	3.88	4.78	5.11
4.4	3.36	3.37	3.37	3.38	4.43	4.46
5.5	3.16	3.15	3.18	3.10	4.08	4.06

a) 200-mm×4.9-mm i.d. cation-exchange column and a flow rate of 1.0 cm^3 min^{-1} was used.

peaks obtained for silicate and sulfate ions, respectively, could be easily identified from the broad peak CL-profile of sulfate alone.

Optimization Studies. When a lower perchloric acid concentration was used, CL intensities for the eluting anions formed broader peaks and the retention times were longer (Table 2). However, the higher was the perchloric acid concentration, the higher baseline signal was obtained as mentioned above. As a result of the optimization of the elution conditions for rapid separation with acceptable resolution and lower blank emission, 4.4 mmol dm^{-3} perchloric acid was chosen as an eluent for all subsequent studies of experimental conditions. The eluent pH was very close to that of the acidic medium required for the most sensitive detection in the FI system.

The CL reagent conditions were optimized using a 1.0 μg cm^{-3} silicon(IV) standard solution. Maximum CL intensity occurred at luminol and hydrogen peroxide concentrations of 0.10 and 5.0 mmol dm^{-3}, respectively, chosen as optimal for the system. With an increase in the concentration of potassium hydroxide the CL signals also increased and attained the maximum intensity at around 5.0 mmol dm^{-3}. Therefore 5.0 mmol dm^{-3} was chosen as the optimum potassium hydroxide concentration.

When a 100-mm^3 sample was injected in this system, calibration graph obtained under the optimized conditions was linear above 100 ng cm^{-3} and the working range was extended to 30 μg cm^{-3} silicon (IV). The detection limit (DL) obtained by this method was 50 ng cm^{-3} silicon (IV), where the DL is defined as the concentration producing a signal-to-noise ratio of two. The relative standard deviation of 4.4% was obtained for five replicate measurements of 500 ng cm^{-3} silicon (IV). The present DL is not superior to that obtained by the batch CL measurements based on the heteropoly acid reaction with luminol (ca. 10 ng cm^{-3} silicon (IV)[12)]). However, the kinetics of the heteropoly acid CL reaction is more complicated and more reagents are needed, and thus the CL system is not suited as a detector for an FI technique. The major advantages of the present CL detection system come from the use of a single post-column reagent stream and a simple post-column reaction manifold for the chromatographic technique. Figure 4 shows a typical chromatogram resulting from the injection of a mixture of 1.0 μg cm^{-3} silicon (IV) and 10 μg cm^{-3} carbonate. The two species were completely resolved from each other.

Interference Studies. Metal ions, especially transition metal ions, interfere because of their catalytic effect on the luminol CL reaction in aqueous CL analysis.[11,14—17)] Interference studies were performed using 5.0 μg cm^{-3} silicon(IV) solutions containing 100 μg cm^{-3} of various metal ions such as chromium(III), manganese(II), iron(II), iron(III), cobalt(II), nickel(II), copper(II), and zinc(II). Before use, the solutions were treated with sodium hydrogencarbonate in the same manner as practical sample solutions mentioned below. These metal ions were not eluted from the ion-exchange column used with the eluent of dilute perchloric acid in the present ICE system. The results presented in Table 3 showed that these metals gave no interference, indicating almost complete removal of these ions with the ICE separation system.

Acids such as phosphoric acid, nitrous acid, sulfuric acid, carbonic acid, and hydrogen sulfide, also caused a small increase in the CL emission (Table 1). The anions of these acids except sulfate ion were separated from silicate ion (Table 2) to such an extent that interferences from the anions were eliminated. For sulfate ion, negligibly positive interference at a concentration of sulfate in 20-fold excess over that of silicate was observed. This might be due to broadening of the sulfate signal as mentioned above.

Analytical Applications. This method was applied to the determinations of silicate in tap and river water samples. Silicates are present in water in different forms, such as monomeric and polymeric silicates.[25,26)] One of these species, probably monomeric silicate ion,

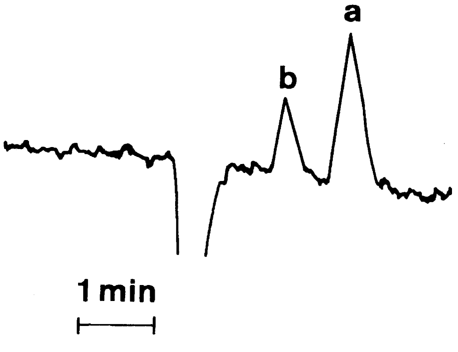

Fig. 4. Chromatogram for a synthetic mixture (100-mm^3) of silicate (a) and carbonate (b) ions obtained with a 200-mm×4.9-mm i.d. cation-exchange column and the flow rates of 1.0 and 2.0 cm^3 min^{-1} for the eluent and reagent solutions, respectively. Si(IV), 1.0 μg cm^{-3}; CO_3^{2-}, 10 μg cm^{-3}; luminol, 0.10 mmol dm^{-3}; KOH, 5.0 mmol dm^{-3}; H_2O_2, 5.0 mmol dm^{-3}.

Table 3. Effect of Metal Ions Tested for Interference on the Silicate CL Intensity in the ICE-CL Analysis[a)]

Metal[b)]	Relative CL intensity
None	100
Cr (III)	107
Mn (II)	104
Fe (II)	97
Fe (III)	105
Co (II)	96
Ni (II)	107
Cu (II)	100
Zn (II)	107

a) Conditions: luminol, 0.10 mmol dm^{-3}; KOH, 5.0 mmol dm^{-3}; H_2O_2, 5.0 mmol dm^{-3}; $HClO_4$ eluent, 4.4 mmol dm^{-3}; a 200-mm×4.9-mm i.d. cation-exchange column and the flow rates of 1.0 and 2.0 cm^3 min^{-1} for the eluent and reagent solutions, respectively, were used. b) Metal ions, 100 μg cm^{-3}; Si(IV), 5.0 μg cm^{-3}.

is assumed to be eluted in the form of silicic acid and then increases the CL emission in the present system. Other polymeric silicates should be converted into the monomeric species by digesting the sample with sodium hydrogencarbonate.[30)] A chromatogram obtained for the river water sample, A, was shown in Fig. 5. Analysis using a conductivity dectector indicated sulfate contents of 50—110 μg cm^{-3} for all water samples. As seen in Fig. 5, however, no signal for sulfate ion appeared and a single peak resulted for silicate ion, except for another sharp one for carbonate ion. The broadening behavior of the sulfate signal led to a sufficient elimination of interference from sulfate. The results of direct determination of silicate using a calibration curve method are given in Table 4. In order to investigate the possibility of accurate silicate determination by the present method, recovery tests on the tap water sample, A, to which a certain amount of silicate was added were performed. The results indicated good recovery of silicon(IV) (Table 4). Furthermore, to verify the results, measurements by flame AAS or ICP-AES were performed for the same water samples. These results were consistent with those obtained by the present CL method (Table 4).

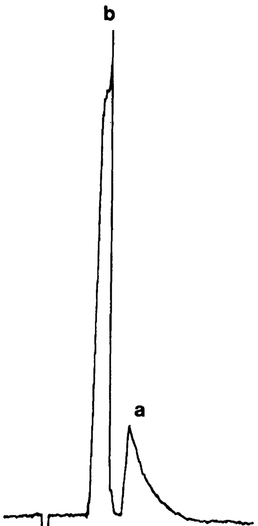

Fig. 5. Chromatogram obtained for river water sample A (100-mm^3) containing silicon (IV) (a) and carbonate (b) ions by using a 200-mm×4.9-mm i.d. cation-exchange column and the flow rates of 1.0 and 2.0 cm^3 min^{-1} for the eluent and reagent solutions, respectively. Luminol, 0.10 mmol dm^{-3}; KOH, 5.0 mmol dm^{-3}; H_2O_2, 5.0 mmol dm^{-3}. Analysis, by conductivity detection, indicated a sulfate content of 110 μg cm^{-3}.

Table 4. Determination of Silicate in Water Samples

Sample	Si (IV) (μg cm^{-3})		
	This method[a)]		Other method
Tap water			
A (Kokubunji)	12.6,	13.3	13[b)]
A + 10 μg cm^{-3} Si (IV)	23.0,	24.4	—
B (Kudamatsu)	4.6,	5.1	6.4[c)]
C (Higashi-Hiroshima)	5.6,	5.9	5.5[c)]
River water			
A (Saijo)	5.1,	5.5	5.1[c)]
B (Kurose)	6.6,	7.0	7.3[c)]

a) Conditions: luminol, 0.10 mmol dm^{-3}; KOH, 5.0 mmol dm^{-3}; H_2O_2, 5.0 mmol dm^{-3}; $HClO_4$ eluent, 4.4 mmol dm^{-3}; a 200-mm×4.9-mm i.d. cation-exchange column and the flow rates of 1.0 and 2.0 cm^3 min^{-1} for the eluent and reagent solutions, respectively, were used. b) AAS. c) ICP-AES.

The analytical results indicated that the proposed ICE-CL method applicable to the determination of silicate in the samples such as tap and river waters is valid and rapid. The CL system is simple, inexpensive and thus suited as a sensitive dectector for the ICE. The problem of possible interferences from metal ions and acid anions in the CL analysis was sufficiently eliminated by the ICE. This ICE-CL method would also be applicable to the determination of silicon(IV) in the environmental and biological samples, although the possibility needs to be investigated. Further investigation to use the proposed method for the analyses of other anions is now in progress. To improve sensitivity, current work is also aimed at a sufficient understanding of the present CL system.

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