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Selective fluorometric determination of indium(III) by high-performance liquid chromatography with 2-methyl-8-quinolinol based on a ligand-exchange reaction of silanol groups

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Abstract

The decomposition of metal chelates due to silanol groups in the high-performance liquid chromatography (HPLC) column was applied for the selective determination of indium(III) by HPLC. The decomposition of metal chelates developed with the ligand-exchange reaction between metal chelates and silanol groups. Among seventeen elements [Bi(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ga(III), In(III), Mg(II), Ni(II), Pd(II), Pb(II), Sc(III), V(V), Y(III) and Zn(II)], only indium(III) and zinc(II) were detected with 2-methyl-8-quinolinol as a pre-column derivatizing agent with fluorometric detection by using the decomposition reaction. The fluorescent 2-methyl-8-quinolinol chelates of Cd(II), Ga(III), Mn(II), Pb(II), Sc(III) and Y(III) were decomposed by silanol groups in the HPLC column. The baseline separation between indium(III)– and zinc(II)–2-methyl-8-quinolinol chelates were performed on a TSK gel ODS-80 column (250 mm×4.6 mm I.D.) with an eluent consisting of $4 \cdot 10^{-3}$ mol dm^{-3} 2-methyl-8-quinolinol and $2 \cdot 10^{-3}$ mol dm^{-3} hexamethylenetetramine in aqueous (20%, v/v) methanol solution. The detection limit ($S/N=3$) of indium(III) was $1.4 \cdot 10^{-8}$ mol dm^{-3}. The thermodynamic studies on the coordinating function of the silanol group were also discussed.   © 1997 Elsevier Science B.V.

Keywords: Silanol groups; Derivatization, LC; Indium; Metal chelates; Methylquinolinol

1. Introduction

High-performance liquid chromatography (HPLC) with pre-column derivatization has been one of the most powerful methods in the determination of trace amounts of metal ions. This method possesses high sensitivity, multi-component detectability, high reproducibility and simplicity. Many kinds of analytical reagents such as 8-quinolinol derivatives [1,2], azo dyes [3,4], β-diketones [5,6], hydrazones [7,8] and dithiocarbamate [9,10] etc., have been examined as pre-column derivatizing agents. Several

review articles [11–16] have published on the determination of metal ions by HPLC.

The multi-component detectability of HPLC has been stressed for the simultaneous determination of inorganic species such as metal ions. On the other hand, the selective determination method with HPLC has also been recently reported [17–19]. Hoshino and cowokers [18,19] determined nickel(II) and beryllium(II) selectively using the eluents containing no chelating agent. The labile chelates were decomposed in migrating in the separation column due to a lack of ligand in the eluent. Therefore, the stable chelates were only detected, selectively. They studied the use of a HPLC system for flow-analysis

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with spectrophotometry equipped with a decomposition device that was a separation column. A decomposition function developed with a separation function of a HPLC column, indirectly.

We reported [20] that the silanol group in the ODS column decomposed the gallium(III)–2-methyl-8-quinolinol chelate. The decomposition of the gallium(III) chelate was due to the ligand-exchange reaction between gallium(III) chelate and the silanol groups based on the coordination function of the silanol groups. A separation column will be able to become an active decomposition device on the basis of a ligand-exchange reaction of the silanol groups directly. Therefore, a new selective determination method with HPLC will be possible using the active decomposition function of the column. For this purpose, in this paper, we screened chelating agents among 8-quinolinol derivatives and HPLC columns. It was found that indium(III) was determined by the fluorometric detection using 2-methyl-8-quinolinol as a derivatizing agent, selectively. The mechanism of the selectivity was discussed thermodynamically.

2. Experimental

2.1. Apparatus

The HPLC system used consisted of a Shimadzu LC-6A pump (Kyoto, Japan), a Japan Spectroscopic 870-UV spectrophotometer (Tokyo, Japan), a Shimadzu RF-535 fluorometric detection system, a Rheodyne 7125 loop injector equipped with a 200 μl sample loop and a Shimadzu R1231 recorder. The column used was a TSK gel ODS-80 (250 mm$\times$4.6 mm I.D., particle size 5 μm) obtained from Tosoh (Tokyo, Japan). The other columns used were as the same as those used in the previous work [20]. pH measurements were made with a Horiba Model F-13 pH meter. Metal concentrations were measured by a Hitachi Model Z-6100 polarized Zeeman atomic absorption spectrophotometer.

2.2. Materials

2-Methyl-8-quinolinol was obtained from Kanto

(Tokyo, Japan) and recrystallized from ethanol. The other 8-quinolinol derivatives used were synthesized in the laboratory. A stock solution ($5 \cdot 10^{-2}$ mol dm^{-3}) of 2-methyl-8-quinolinol was prepared with methanol.

Standard metal solutions ($1 \cdot 10^{-2}$ mol dm^{-3}) were prepared from nitrates and standardized by titration with ethylenediazninetetraacetic acid.

Distilled, deionized water was further purified by a Millipore Milli-Q system. Analytical-reagent grade methanol was passed through a Millipore filter (pore size 0.45 μm) after distillation. A silica gel (particle size 5 μm) used for thermodynamic study was a Cosmosil 5SL silica gel obtained from Nakarai Tesque (Kyoto, Japan). All other reagents used were of analytical-reagent grade.

2.3. Procedure

To a sample solution containing indium(III) ions in a 20 ml volumetric flask, 1 cm^3 of $5 \cdot 10^{-2}$ mol dm^{-3} 2-methyl-8-quinolinol solution, 2 cm^3 of 1.0 mol dm^{-3} Tris(hydroxymethyl)aminomethane buffer (pH 8.0) and 10 ml of methanol were added. After the solution had been diluted to the mark with water, an aliquot (200 μI) of the solution was injected into the HPLC system.

The eluent was an aqueous (20%, v/v) methanol solution containing $4 \cdot 10^{-3}$ mol dm^{-3} 2-methyl-8-quinolinol and $2 \cdot 10^{-3}$ mol dm^{-3} hexamethylenetetramine. The pH of the eluent was adjusted to 6.0 by the addition of hydrochloric acid prior to the addition of methanol. The flow-rate was 0.8 cm^3 min^{-1}. The excitation and emission wavelengths were set at 375 nm and 515 nm, respectively.

The thermodynamic studies on the reaction between silica gel and metal ion were done as follows: 0.02 g of silica gel (particle size 5 μm, specific surface area 300 m^2 g^{-1}) was added to 25 ml of metal ion solution $\{[M^{n+}]=2 \cdot 10^{-6}–1 \cdot 10^{-3}$ mol dm^{-3}, ionic strength=0.1 (NaNO$_3$)$\}$. After adjusting a suitable pH with sodium hydroxide or nitric acid, the solution was shaken for 24 h. Consequently, pH and the concentration of metal ion were measured with a pH meter and a flame atomic absorption spectrometry, respectively.

3. Results and discussion

3.1. Selective detectability due to silanol groups

Gallium(III)–2-methyl-8-quinolinol chelate was decomposed by the silanol groups in the HPLC column [20]. However, indium(III)–2-methyl-8-quinolinol chelate which had similar properties to the gallium(III) chelate was scarcely decomposed by the silanol group. The difference in the reactivity between the chelates will become a promising tool for the selective detection by HPLC. Various effects due to silanol groups, namely silanol effects have been regarded as negative actions on HPLC [21]. Besides, the silanol effects were unavoidable as long as the silica gel based columns were used, even if the end-capped treatment was completed. The positive use of silanol effects is an alternative method for HPLC [22] with the silica gel based column.

Considering the above, methylated 8-quinolinols and HPLC columns were screened for the selective detection by HPLC with fluorescence detection using the decomposition reaction due to the silanol groups. It was found that the selectivity of indium(III) appeared when 2-methyl-8-quinolinol as chelating agent and an inadequately end-capped ODS column were used, as shown in Table 1. 2-Methyl-8-quinolinol did not react with aluminum(III) ions in

aqueous media, so the HPLC system with 2-methyl-8-quinolinol did not detect aluminum(III). Using the other methylated 8-quinolinols and/or a fully end-capped ODS column, aluminum(III) and gallium(III) chelate were detected, but could not be separated. A TSK gel Octadecyl-4PW detecting a gallium(III) chelate was polymer gel column, with no silanol groups.

A typical chromatogram obtained for a solution containing seventeen metal ions [Bi(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ga(III), In(III), Mg(II), Ni(II), Pd(II), Pb(II), Sc(III), V(V), Y(III) and Zn(II)], which reacted with 2-methyl-8-quinolinol is shown in Fig. 1. Only zinc(II) and indium(III) chelates were detected, and they were well separated. The transition metal chelates were non-fluorescent, so they were not detected. Calcium(II) did not form a chelate with 2-methyl-8-quinolinol under the conditions studied. The fluorescent chelates of cadmium(II), magnesium(II), lead(II), scandium(III), yttrium(III) and gallium(II) were decomposed by silanol groups. These chelates eluted gradually with repeated decomposition by silanol groups on stationary phase and reformation in mobile phase. The response due to the elution of the chelates, therefore, was masked by the fluctuation of baseline noise. These chelates could not be detected, even though the concentration of 2-methyl-8-

Table 1

Peak shapes of trivarent metal chelates of 2-methyl-8-quinol and other methyl derivatives with commercially available columns

	2-Methyl-8-quinolnol			8-Quinolnol and methyl-derivatives[1]		
	Al	Ga	In	Al	Ga	In
Cosmosil 5 C_{18}^2	×	○	○	○	○	○
TSK gel OD580-TM[2]	×	×	○	○	○	○
TSK gel Octadecyl 4PW[3]	×	○	○	○	○	○
CAPCELL C 18SG-120[4]	×	△	○	○	○	○
L-Column ODS[2]	×	△	○	○	○	○
LiChrospher RP-18(e)[2]	×	×	○	○	○	○
Partisil 5ODS-3[2]	×	×	○	○	○	○
YMC R ODS-5[2]	×	×	○	○	○	○
YMC ODS-AM[2]	×	△	○	○	○	○

○: Sharp peak, △: broad peak, ×: no peaks.
HPLC conditions: see Section 2.3.
[1] 3-Methyl, 4-methyl, 5-methyl and 6-methyl.
[2] ODS column with end-capped.
[3] Polymer gel column having C_{18} group.
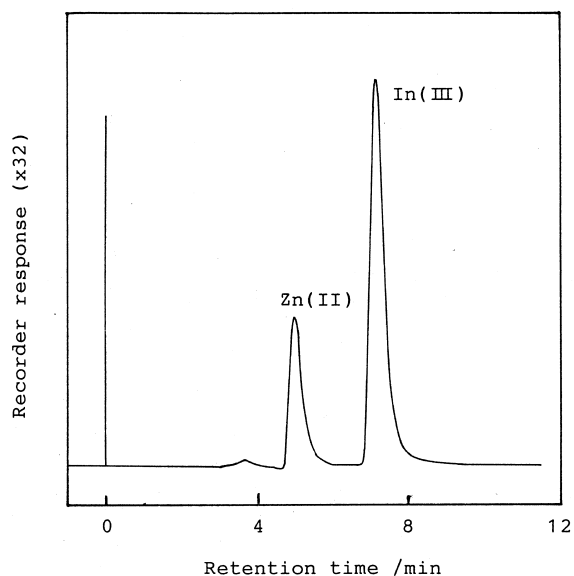[4] Polymer coated silica gel column having C_{18} group.

In(III)
Zn(II)
Recorder response (x32)
0
4
8
12
Retention time /min

Fig. 1. HPLC separation of 2-methyl-8-quinolinol chelates with fluorometric detection. Sample solution: [2-methyl-8-quinolinol] = $5 \cdot 10^{-3}$ mol dm^{-3}, [Ca and Mg] = $1 \cdot 10^{-3}$ mol dm^{-3}, [Cr, Co, Fe, Ga, Ni, Sc, V, Y and Zn] = $1 \cdot 10^{-4}$ mol dm^{-3}, [Bi, In, Pb and Pd] = $2.5 \cdot 10^{-5}$ mol dm^{-3}, [Cd and Cu] = $5 \cdot 10^{-6}$ mol dm^{-3}, pH 8.0 (0.1 mol dm^{-3} Tris–HCl buffer), 40% (v/v) aqueous methanol solution. Eluent: aqueous (20%, v/v) methanol solution containing $4 \cdot 10^{-3}$ mol dm^{-3} 2-methyl-8-quinolinol and $2 \cdot 10^{-3}$ mol dm^{-3} hexamethylenetetramine (pH 6.0). Column: TSK gel ODS-80 (250 m×4.6 mm I.D., particle size 5 μm). Flow-rate: 0.8 cm^3 min^{-1}. Detection wavelength: excitation 375 nm, emission 515 nm.

quinolinol in the eluent increased. Adding 2-methyl-8-quinolinol into the eluent stabilized the chelates thermodynamically, but it could not suppress the decomposition of the chelates kinetically.



3.2. Thermodynamic studies

The gallium(III)–2-methyl-8-quinolinol chelate decomposed in the HPLC column, but the indium(III) chelate survived and was detected. We discuss the coordinating function of silanol groups thermodynamically, to clarify the mechanism of the decomposition reaction in the HPLC column.

The ligand exchange reaction between metal chelates of 2-methyl-8-quinolinol and silanol group is expressed by Eq. (1).

$$MQ_3 + n\mathrm{HO-Si} \rightleftharpoons \mathrm{M(-O-Si)}_n + 3\mathrm{HQ} + (n-3)\mathrm{H}^+ \quad (1)$$
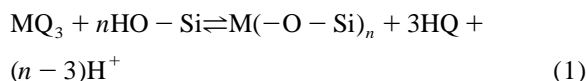
where MQ_3: metal–2-methyl-8-quinolinol chelate, HO–Si: silanol group, M(–O–Si)$_n$: metal–silanol complex, HQ: 2-methyl-8-quinolinol M: trivalent metal ion.

Eq. (1) can be divided into Eqs. (2) and (3) as follows:

$$M^{3+} + 3Q^- \rightleftharpoons MQ_3 \quad (2)$$

$$M^{3+} + \mathrm{HO-Si} \rightleftharpoons \mathrm{M(-O-Si)} \quad (3)$$
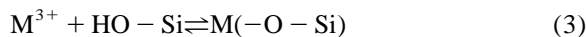
The thermodynamic data on the formation of 8-quinolinol chelates have not been reported, yet. However, Yotsuyanagi et al. [23] estimated the formation constants of 8-quinolinol-5-sulfonic acid and 2-methyl-8-quinolinol-5-sulfonic acid to evaluate the contribution of 2-methyl group against the formation constants. The data are summarized in Table 2. The differences of the formation constants ($\Delta\log\beta_3$) between 8-quinolinol-5-sulfonic acid and 2-methyl-8-quinolinol-5-sulfonic acid can be regarded as the contribution of 2-methyl group. The value of $\Delta\log\beta_3$ for gallium(III) is larger than that of indium(III). This can be explained as follows: the ionic radius of gallium(III) ion is smaller than that of indium(II), so that the steric hindrance of 2-methyl group against gallium(III) was stronger than against indium(II). The decline of the formation constant made the

Table 2
Stability constants (logarithm) of metal complexes of 8-quinolinol derivatives and silanol groups

Ligand		Al	Ga	In
8-Quinolinol-5-Sulfonic acid[1]	log β1	8.8	11.5	10.5
	log β2	17.6	23.1	20.5
	log β3	24.2	33.3	29.1
2-Methyl-8-quinolinol-5-sulfonic acid[1]	log β1	6.7	10.1	9.9
	log β2	13.9	20.9	20.1
	log β3	20.2	29.1	27.7
Δlog β3		4.0	4.2	1.4
Silanol		−0.78	0.62	−0.72

[1] Ref. [23].

gallium(III)–2-methyl-8-quinolinol chelate decompose easily in the column.

The reliability of thermodynamic data on the formation of metal–silanol complex on the surface of silica gel has not yet been reported. The equilibrium reactions at the surface of the metal oxides such as silica gel did not obey the mass-action law. This was due to the change of activity coefficients at the surface of metal oxides [24]. This effect made the analysis difficult. Tamura and Furuichi [25] analyzed the formation constants of surface hydroxyl groups with metal ions on the basis of the Frumkin adsorption. We could not analyze the formation of metal–silanol complex by Tamura's method, because of the low adsorption ability of silica gel and the complication in dealing with trivalent metal ions. Therefore, a mass-action law was assumed using Eq. (2), and the formation constant of Eq. (2) was estimated. The formation constant of metal–silanol complex (K_{M-O-Si}) was expressed by Eq. (4).

$$K_{M-O-Si} = \frac{[M-O-Si][H^+]}{[M^{3+}][HO-Si]} \quad (4)$$

Eq. (4) can be changed into Eq. (5)

$$\log \frac{[M-O-Si]}{[HO-Si]} = \log [M^{3+}] + \log K_{M-O-Si} + pH \quad (5)$$

Eq. (6) was calculated from the mass balance of silanol groups.

$$[M-O-Si] + [HO-Si] = Ns/2 \quad (6)$$

where Ns: the surface concentration of all silanol groups on the silica gel. A combination of Eqs. (5) and (6) resulted in Eq. (7)

$$\log\frac{[M-O-Si]}{Ns/2 - [M-O-Si]} = \log [M^{3+}] + \log K_{M-O-Si} + pH \quad (7)$$

[M–O–Si] could be calculated on the basis of a mass-balance of metal ion as Eq. (8), experimentally

$$[M-O-Si] = ([M^{3+}]_I - [M^{3+}])V/S \quad (8)$$

where $[M^{3+}]_I$: initial concentration of metal ion (mol

dm^{-3}), V: volume of solution (dm^{-3}), S: surface area of silica gel.

The theoretical mass balance for the metal ion was expressed as Eq. (9).

$$\begin{aligned}
[M^{3+}]_I &= [M-O-Si] + [M^{3+}] + [M(OH)^{2+}] \\
&\quad + [M(OH)_2^+] \\
&= [M-O-Si] + [M^{3+}] \\
&\quad \times (1 + \beta_{M(OH)^{2+}}[OH^-] + \beta_{M(OH)_2^+}[OH^-]^2)
\end{aligned} \quad (9)$$

$\beta_{M(OH)^{2+}}$ and $\beta_{M(OH)_2^+}$ are the stability constants between the M^{3+} and OH^- ions.

$$\beta_{M(OH)^{2+}} = \frac{[M(OH)^{2+}]}{[M^{3+}][OH^-]}$$

$$\beta_{M(OH)_2^+} = \frac{[M(OH)_2^+]}{[M^{3+}][OH^-]^2}$$

The free concentration of metal ion $[M^{3+}]$ could be calculated with Eq. (9). The adsorption isotherm of the gallium(III) ion is shown in Fig. 2. The analytical plots of gallium(III) with Eq. (7) are shown in Fig. 3. Some scatter of plots in Fig. 3 seemed to be due to the partial hydrolysis of the gallium(III) ion. The reactions between the silanol groups and the hydrolysis species of gallium(III) such as $[Ga(OH)^{2+}]$, $[Ga(OH)^{2+}]$ and $[Ga(OH)_3]$ were ignored for the simplification of analysis.
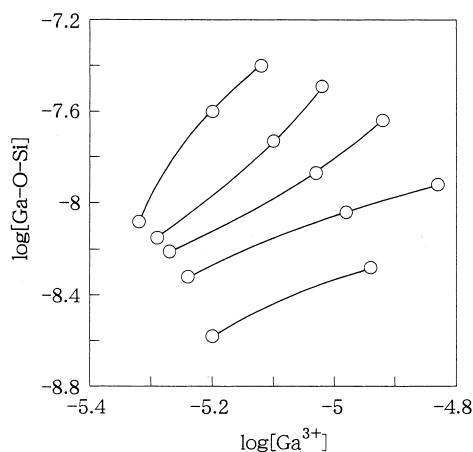

Fig. 2. Adsorption isotherm of the gallium(III) ion on silica gel with different pH at an ionic strength 0.1 (NaNO$_3$) and 25°C.
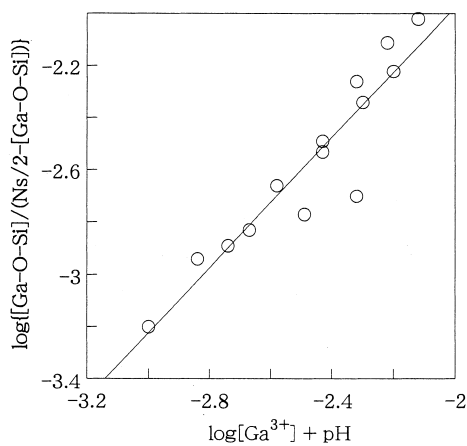
Fig. 3. Plots of log $\dfrac{[Ga - O - Si]}{Ns/2 - [Ga - O - Si]}$ vs. log $[M^{3+}]$+pH on the gallium(III) ion.

Fig. 4. Plots of retention time of metal chelates vs. methanol content of eluent. Other conditions as in Fig. 1.

The data of log K_{M-O-Si} as well as the stability constants of 2-methyl-8-quinolinol chelates are summarized in Table 2. From Table 2, the selective decomposition of gallium(III)–2-methyl-8-quinolinol with silanol group was due to the fact that the silanophilicity of the gallium(III) ion was larger than that of indium(III), and that the coordinating ability of 2-methyl-8-quinolinol declined compared with 8-quinolinol, qualitatively. The kinetic information for the decomposition reaction of the chelates by the silanol group is necessary for more quantitative discussion.

3.3. Optimization and performance

The HPLC parameters such as methanol content and 2-methyl-8-quinolinol concentration in the eluent were optimized for the determination of indium(III). The methanol content was an effective parameter to control the retention times and resolution of the chelates. Fig. 4 shows the effect of methanol content against indium(III) and zinc(II) chelates. A decrease of methanol content increased the retention times and the resolutions of indium(III) and zinc(II) chelates, but that broadened the peak shapes of the chelates. A baseline resolution was obtained under 80% of methanol content. The addition of 2-methyl-8-quinolinol into the eluent was necessary to prevent the dissociation of indium(III) chelate. Fig. 5 shows the effect of 2-methyl-8-quinolinol concentration in
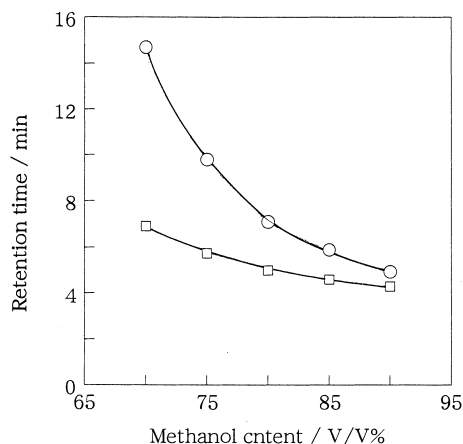
the eluent against the peak height of indium(III) chelate. Indium(III) chelate did not dissociate over $2 \cdot 10^{-4}$ mol dm^{-3} of 2-methyl-8-quinolinol concentration.

The column length was also an important factor for not only the resolution between the chelates but also the decomposition function of the column. Because the total amount of silanol group in the column was proportional to column length. The 25 cm column was best for the resolution and the decomposition function. An increase of injection
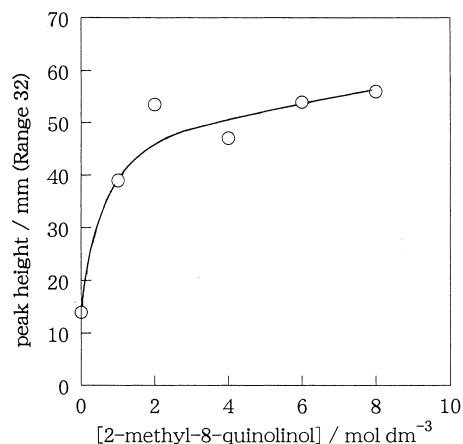

Fig. 5. Plots of peak height of indium(III) chelate vs. concentration of 2-methyl-8-quinolinol in eluent. Other conditions as in Fig. 1.

volume into the HPLC system was a simple and effective technique to improve sensitivity. There was a linear relationship between injection volume and peak height of indium(III) chelate up to 200 µl. The peak shape of the indium(III) chelate became broad at injection volumes greater than 200 µl.

Under the optimized conditions, the calibration curve for indium(III) based on the peak height was linear from $2 \cdot 10^{-8}$ mol dm^{-3} up to $2 \cdot 10^{-6}$ mol dm^{-3}. The detection limit ($S/N = 3$) was $1.4 \cdot 10^{-8}$ mol dm^{-3}. A blank peak of indium(III) was not observed. The detection limit might be improved, if the baseline noise was suppressed electrically.

The tolerance limits of foreign ions were tested by means of the molar ratio which gave not more than ±5% error in the determination of $1 \cdot 10^{-7}$ mol dm^{-3} indium(III). The tolerance limit of zinc(II) was 50-fold. The tolerance limits of the other transition metal ions were over 100-fold. Alkali and alkali-earth ions containing magnesium(II) and calcium(II) were tolerated 1000-fold of indium(III). The recovery of $1 \cdot 10^{-7}$ mol dm^{-3} indium(III) added to the river water as the real sample was quantitative.

Indium(III) was determined selectively by using a ligand-exchange reaction between metal chelates and silanol groups due to the coordinating function of the silanol groups. The consumption and discharge of indium which is an important material in the semiconductor industry has increased. The monitoring of indium(III) will become important: this method was applied for the determination of indium(III) in the river water sampled at the Kinu River (Tochigi, Japan), for example. The indium(III) concentration in the river water sample was much lower than that of the detection limit of the method. The further applications of the method are our future work.

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