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Determination of Aluminum in Water Samples and Its Speciation Approach by Fluorophotometric Flow Injection Analysis with 8-Quinolinol Coupled with Micelle Sensitization

Toshio Takayanagi[1,2,*], Kie Hojyo[2], Fumihiko Iwami[1], and Shoji Motomizu[1,2]

[1] Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530 Japan
[2] Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530 Japan

Abstract

Trace amounts of aluminum in water samples were determined by fluorophotometric flow injection analysis. Less harmful 8-quinolinol and Triton X-100 were used as a fluorophotometric derivatizing reagent for Al^{3+} and a micelle sensitizer, respectively. Even with the traditional and conventional reagents, a linear calibration graph was obtained for Al^{3+} at the concentration range of 10^{-7} mol/l level with a limit of detection at $2.8x10^{-9}$ mol/l. The sample throughput was 60 h^{-1}. The proposed method was applied to the analysis of a standard reference substance, and the analytical result agreed well with the certified value. The proposed system was also applied to the speciation analysis of tap water and river water samples; aluminum species of free Al^{3+}, hydrolyzed Al species, and Al in suspended particles were fairly evaluated. The recovery test of Al^{3+} to the water samples was in the ranges of 92–106%.

Keywords Aluminum ion; fluorophotometry; 8-quinolinol; micelle sensitization; speciation analysis

1. Introduction

Aluminum is one of the most abundant elements in the earth's crust, and it is easily dissolved in hydrosphere. Aluminum salts are also used in water treatment as coagulants to reduce organic matter, color, turbidity, and microorganism levels. While the benefit of the aluminum salts as coagulants are recognized, possible risks including potential neurotoxicity should be minimized. Therefore, aluminum level in tap water should be regulated. World Health Organization recommends the control level of aluminum in drinking water at 0.2 mg/l or less (< $7.4x10^{-6}$ mol/l) [1].

Various types of analytical methodologies have been proposed to realize the sensitive determination of aluminum in water samples [2,3]. Although atomic spectroscopy is specific for a particular element, the instruments and running costs are expensive. Conventional molecular spectroscopy would be more convenient to realize inexpensive analysis. 8-Quinolinol is one of the traditional fluorophotometric reagents for Al^{3+}, and it is available for the determination of aluminum in aqueous solution [4]. The detection sensitivity with 8-quinolinol, as well as 8-quinolinol-5-sulfonic acid, has been developed in hexadecyltrimethylammonium micelle [5], cetyltrimethyl-ammonium micelle [6], reversed micelle [7], microemulsion [8], cluod point extraction [9], and solvent extraction [10]. Aluminum in serum and urinary samples [11], injection solutions [12], and aluminum adhering to the gastric mucosa [13] were determined by fluorophotometric high performance liquid chromatography with 8-quinolinol. Fluorophotometric reagents of morin [14], lumogallion [15], and quercetin [16] were also used in fluorophotometric HPLC. The limits of detection reported are around 10^{-9} to 10^{-8} mol/l level [11-16]. Flow injection analysis (FIA) [17-21] and sequential injection analysis (SIA) [21-24] are more conventional alternatives for the determination of aluminum in aqueous solutions without separation column. Pre-injection concentration by cloud point extraction [25] and ion-exchange extraction [26], as well as in-line concentration [27], have also been proposed for the fluorophotometric determination of Al^{3+} by FIA. Advantage of FIA and SIA is their integrated chemical system optimized to the substance of interest.

Noticing that 8-quinolinol is one of the most traditional and conventional reagents for the determination of aluminum and that the risk control of the reagent is well established (LD_{50} = 1200 mg/kg: oral ingestion to rat, LD_{50} = 43 mg/kg: injection into the abdominal cavity to mouse, and no carcinogenic to human) [28], the present authors aimed at improving the limit of detection with less harmful 8-quinolinol. Micelle sensitization with Triton X-100 was also utilized in this study to improve the fluorescence. Risk control of Triton X-100 is also established (LD_{50} = 1800 mg/kg: oral ingestion to rat and no carcinogenic to human) [29]. Therefore, a sensitive but less harmful analytical system would be developed with the reagents system to meet Green Chemistry. With the detection system developed, the limit of detection reached down to $2.8x10^{-9}$ mol/l (3 sigma of the blank), and the proposed system was applied to the determination of aluminum in river and tap water samples, as well as to the speciation of aluminum in the water samples.

2. Experimental

2.1 Reagents

Water purified with Elix 3/Milli-Q Element (Nihon Millipore, Tokyo, Japan) was used throughout. A standard solution of Al^{3+} was prepared with $AlK(SO_4)_2 \cdot 12H_2O$ (analytical reagent grade, Kanto Chemical, Tokyo, Japan) in 0.50 mol/l H_2SO_4 to give $1.00x10^{-2}$ mol/l solution. The stock solution was used by dilution with the purified water or $1.0x10^{-3}$ mol/l HNO_3. A fluorophotometric reagent of 8-quinolinol (HQ) was purchased from Tokyo Chemical Industry (Tokyo, Japan) and was used after recrystallization from ethanol; it was dissolved in 2%(v/v) acetic acid solution to give $4.0x10^{-2}$ mol/l stock solution. Surfactants of Triton X-100 (TX-100) and cetyltrimethyl-ammonium bromide (CTAB) were from Wako Pure Chemical

*Corresponding author.
E-mail: takayana@cc.okayama-u.ac.jp

Industries (Osaka, Japan) and Tokyo Chemical Industry, respectively. The pH of the reagent solution was adjusted with HEPES (Dojindo Laboratories, Kumamoto, Japan) − HaOH buffer. Other reagents used were of analytical grade. Polyethylene bottles were immersed in 1 mol/l HNO_3 for several days and used after washing with the purified water.

2.2 Sample preparation

Sample solutions including tap and river water were filtered with a DISMIC 25AS020AN (pore size: 0.20 μm, Advantec Toyo Kaisha, Tokyo, Japan) membrane filter. The filtered solution was further acidified with dilute HNO_3 for the determination of dissolved aluminum.

2.3 Apparatus

An FIA system was assembled with a double plunger pump PD-4000 (F.I.A. Instrument, Tokyo, Japan), a six-way rotatory valve SVM-6M2 (Sanuki Kogyo, Tokyo, Japan), and an RF-10A_{XL} fluorescence detector (Shimadzu, Kyoto, Japan), and a flat-bet recorder FBR-251A (TOA-DKK, Tokyo, Japan). The system is schematically illustrated in Figure 1. Teflon tubing with its inner diameter of 0.5 mm was used throughout to connect the components. A Mettler Toledo (Mettler Toledo K. K., Tokyo, Japan) MP220 pH meter was used to adjust the pH of the buffer solution.

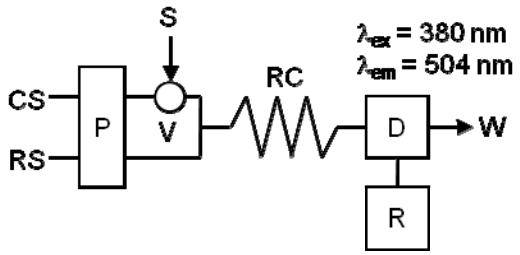

Fig. 1 Flow diagram for the fluorophotometric detection of Al^{3+} with 8-quinolinol.
CS: carrier solution ($1.0x10^{-3}$ mol/l HNO_3), RS: reagent solution ($2.4x10^{-4}$ mol/l 8-quinolinol, 1.0%(w/v) TX-100, 0.1 mol/l HEPES−NaOH buffer: pH 7.5), P: double plunger pump (1.0 ml/min each), V: six-way rotatory valve, S: sample injection (500 μl), RC: reaction coil (2.0 m x 0.5 mm i.d., room temperature), D: fluorophotometric detector, R: recorder, and W: waste.

2.4 Procedure

An aliquot of $1.0x10^{-3}$ mol/l HNO_3 was used as a carrier solution of the FIA system. A reagent solution containing $2.4x10^{-4}$ mol/l 8-quinolinol, 1.0%(w/v) Triton X-100, and 0.1 mol/l HEPES-NaOH buffer (pH 7.5). Two streams of the carrier and the reagent solutions were propelled using a double plunger pump at the flow rate of 1.0 ml/min each. A standard Al^{3+} solution or the sample solution of 500 μl was injected into the carrier stream via a six-way rotatory valve. The carrier stream was merged with the reagent stream using a tee connector, and the reaction proceeded in the reaction coil of 2.0 m length. The fluorescence intensity was continuously monitored by a fluorescence detector. The excitation and emission wavelengths of the detector were set at 380 nm and 504 nm, respectively.

3. Results and Discussion

3.1 Optimization of the FIA parameters

3.1.1 Fluorescence sensitization with surfactant micelles

It is well known that fluorescence intensity is enhanced in hydrophobic media according to the suppression of the heat inactivation, and therefore, organic solvents [10] or surfactant micelles [5,6] have been used as sensitizer. In this study, micelle sensitization was used to operate in a pseudo-homogeneous aqueous solution both in the complex formation reaction and for the fluorophotometric detection; the micelle media is suitable to solubilize the hydrophobic AlQ_3 complex in an aqueous solution. As micelle forming surfactant, we examined two types of surfactants: cationic CTAB and nonionic TX-100. The sensitization of the fluorescence intensity with the surfactants is shown in Figure 2. It can be seen that the FIA signal is much higher with TX-100 than with CTAB. The fluorescence signal for $1.0x10^{-6}$ mol/l Al^{3+} was sensitized by the degree of 6.2 times in the presence of 1.0%(w/v) TX-100, while the blank signal was not affected. Therefore, the concentration of TX-100 in the reagent solution was set at 1.0%(w/v).

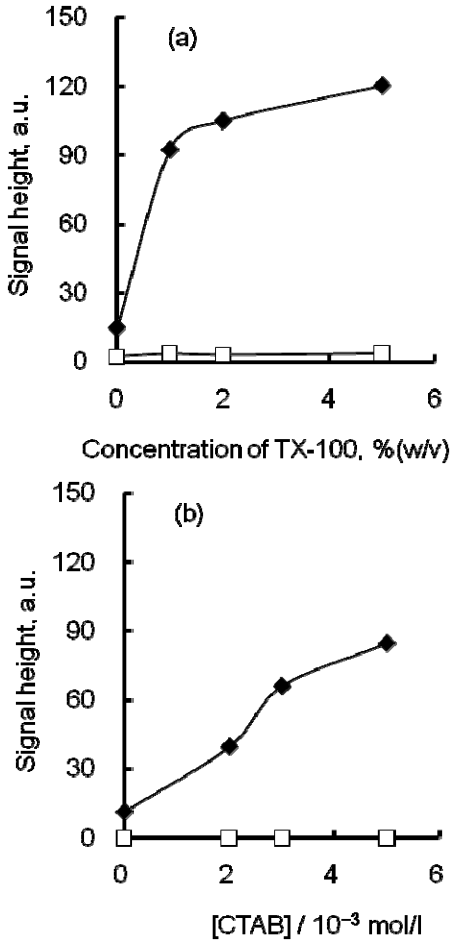

Fig. 2 Micelle sensitization on fluorescence intensity in the presence of (a) TX-100 or (b) CTAB in the reagent solution.
$[Al^{3+}]$: □, none; ♦, $1.0x10^{-6}$ mol/l.

3.1.2 Reagent concentrations

Concentration of 8-quinolinol in the reagent solution was examined at its concentration range from $1.0x10^{-4}$ mol/l to

$5x10^{-4}$ mol/l, where Al^{3+} concentration was at $1.0x10^{-6}$ mol/l. Enhanced fluorescence signals were obtained over $2.0x10^{-4}$ mol/l HQ, and the concentration of 8-quinolinol was set at $2.4x10^{-4}$ mol/l. Effect of pH conditions of the reagent solution was examined. Sensitive fluorescence signal was obtained in the pH range from 7.0 to 8.3 with stable baseline and small blank signals. Therefore, the pH of the reagent solution was adjusted at 7.5 with 0.1 mol/l HEPES−NaOH buffer. By using the HEPES−NaOH buffer, the pH of the reaction solution with the carrier stream was well controlled. When a 0.1 mol/l phosphate buffer (pH 7.5) was used, the fluorescence intensity drastically decreased to about 1/30.

3.1.3 Physical parameters of the FIA system

Adequate period of the reaction time is necessary to complete the reaction between Al^{3+} and 8-quinolinol. The coil length of the reaction tube was examined in the range between 0.5 m and 3.0 m for the blank solution and $5x10^{-7}$ mol/l Al^{3+}. The reaction coil was held at ambient temperature (25−30°C). Highest signals were obtained for the Al^{3+} solution with almost zero signals for the blank solution, when 2.0 m reaction tube was used. The signal height decreased with much longer reaction tube; it was because the sample zone diffused wider with the long reaction tube. The tube length of the reaction coil was set at 2.0 m. Relatively short reaction coil and reaction time at ambient temperature were enough for the fluorophotometric FIA with 8-quinolinol. The fast reaction has also been reported with chromotropic acid [21]: 60 cm coil length at 1.4 ml/min flow rate at ambient temperature, while reaction temperature at 80°C was required with lumogallion [26]. The mild and fast reaction conditions with 8-quinolinol is also advantageous to develop conventional FIA system.

Effect of the sample volume was examined with a 2.0 m reaction tube and $5x10^{-7}$ mol/l Al^{3+} in the volume range from 100 µl to 500 µl. The fluorescence signal increased with increasing sample volume up to 400 µl with small blank signals, and the signal for Al^{3+} became plateau over the volume. Therefore, the sample volume was set at 500 µl.

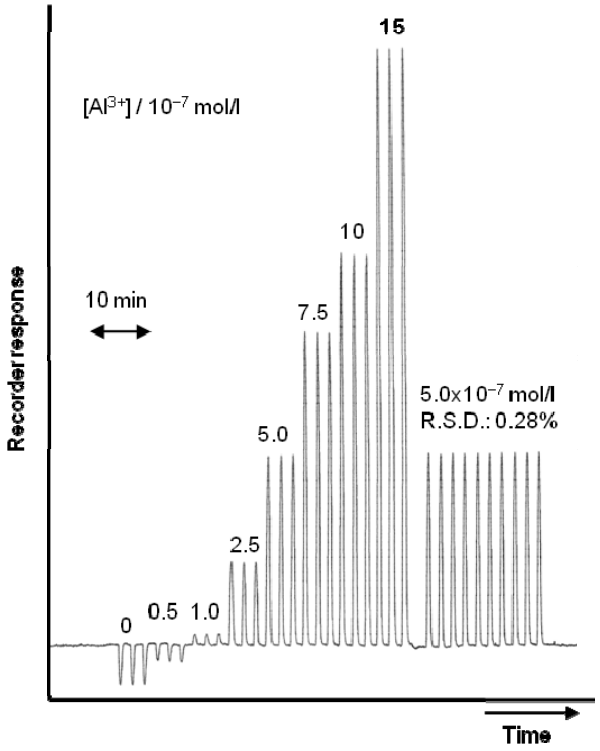

Fig. 3 Flow signals for Al^{3+}. The FIA system and its conditions are as in Fig. 1.

3.2 Calibration graph and the limit of detection

At the optimized conditions, a calibration graph for Al^{3+} was drawn at the concentration range of 10^{-7} mol/l level. The flow signals are shown in Figure 3. The calibration graph was linear at the concentration range examined. Negative signals at Al^{3+} concentration below $1.0x10^{-7}$ mol/l indicate that the concentration of Al^{3+} in the sample solution is lower than the

Table 1 Comparison of the analytical figures of merit

Detection reagent system	Detection method	Limit of detection	Water sample	Ref.
8-Quinolinol, Triton X-100 micelle	Fluorophotometric FIA	$2.8x10^{-9}$ mol/l, (0.08 µg/l)	River water, tap water	This study
Salicylaldehyde picolinoylhydrazone	Fluorophotometric reverse FIA	(1.9 µg/l)	Drinking water	[17]
N-o-vanillidine-2-amino-*p*-cresol, 50% Methanol	Fluorophotometric FIA	(0.057 µg/l)	River water, sea water	[18]
Eriochrome cyanine R	Photometric FIA	(16.6 µg/l)	Anti-perspirants	[19]
8-Quinolinol-5-sulfonic acid, Hexadecyltrimethylammonium micelle	Multisyringe - Fluorophotometric FIA	(0.5 µg/l)	Drinking water	[20]
Chromotropic acid	Fluorophotometric FIA Fluorophotometric SIA	(10 µg/l) (30 µg/l)	Pharmaceutical products	[21]
8-Quinolinol-5-sulfonic acid	Fluorophotometric SIA	(2.8 µg/l: LOQ)	Drinking water	[22]
Morin, Tween 20 micelle	Fluorophotometric SIA	(3 µg/l)	Drinking water	[23]
8-Hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid	Fluorophotometric SIA	(4 µg/l)	Drinking water	[24]
Chrome Azurol S, Benzyldimethyl-tetradecylammonium micelle	Cloud point preconcentration, Photometric FIA	$1.12x10^{-7}$ mol/l	Injection solutions	[25]
Lumogallion	Ion-exchange preconcentration, Fluorophotometric FIA	1−50 µg/l [a]	Soil extracts	[26]
Lumogallion, Brij 35 micelle	In-line concentration, Fluorophotometric FIA	$0.15x10^{-9}$ mol/l	Sea water	[27]
8-Quinolionol, $CHCl_3$	In-line extraction, Fluorophotometric FIA	(0.2 µg/l)	−	[30]

a. Determination range

carrier stream. Nitric acid added in the carrier solution contained a certain amount of Al^{3+}. The negative signals were not observed when the purified water was used as a carrier stream, or equal amount of HNO_3 was added in the sample solution. However, the reproducibility of the signal got worse in the absence of HNO_3 in the carrier stream, and $1x10^{-3}$ mol/l HNO_3 solution was used as a carrier solution. Limit of detection for Al^{3+} was estimated from the 3 sigma of the blank signal; it was $2.8x10^{-9}$ mol/l. The proposed FIA system showed enough sensitivity to the WHO guideline for aluminum: $7.4x10^{-6}$ mol/l (0.2 mg/l) [1] for tap water. The precision of the method was calculated as the relative standard deviation (R.S.D.) of the signal height for 10 replicate injections containing $5x10^{-7}$ mol/l of Al^{3+}; it was 0.28% as shown in Figure 3. The sample throughput was 60 h^{-1}. The analytical figures of merit in this study are compared with the previously reported ones applying FIA and SIA; they are summarized in Table 1. Although 8-quinolinol is a popular fluorophotomeric reagent for Al^{3+}, the limit of detection for Al^{3+} is superior to the reported ones. It would be noticed that special reagent such as salicylaldehyde picolinoylhydrazone [17], *N*-o-vanillidine-2-amino-p-cresol [18], Eriochrome cyanine R [19], or 8-hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid [24] are not necessary to achieve the limit of detection at 10^{-9} mol/l level. Such reagents may possess environmental risks, while the risk and environmental load of 8-quinolinol is well established, and the risk control would be easy. While the present FIA system does not employ any concentration technique, the limit of detection by the present study is comparable to the FIA systems that include concentration/enrichment [25, 26, 27, 30].

3.3 Effect of coexisting substances

Effect of coexisting ions was investigated by adding the substances to $1.0x10^{-6}$ mol/l standard Al^{3+} solution. The tolerable concentration of the coexisting ions was defined as maximum concentrations at which the signal change is within ±5%, compared with the signal obtained for the Al^{3+} solution. The maximum tolerable concentrations of the interfering ions are summarized in Table 2. When the present FIA system is supposed to the analysis of river water and tap water, the coexisting ions can be allowed. No masking reagent would be necessary for the analysis of river water.

Table 2 Effect of foreign ions on detection of Al^{3+} at $1.0x10^{-6}$ mol/l

Foreign ions	Added as	Conc. (mol/l)	[species] / $[Al^{3+}]$ [a]	Relative error (%)
Na^+	NaCl	$1.0x10^{-3}$	1000	+2.6
Cl^-	NaCl	$1.0x10^{-3}$	1000	+2.6
Mg^{2+}	$MgSO_4$	$1.0x10^{-4}$	100	+4.7
SO_4^{2-}	$MgSO_4$	$1.0x10^{-4}$	100	+4.7
K^+	KCl	$1.0x10^{-4}$	100	+3.9
Ca^{2+}	$CaCl_2$	$5.0x10^{-4}$	500	−0.6
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	$1.0x10^{-4}$	100	+1.8
I^-	KI	$1.0x10^{-5}$	10	0.0
Br^-	KBr	$1.0x10^{-5}$	10	+3.6
HPO_4^{2-}	Na_2HPO_4	$1.0x10^{-4}$	100	−1.8
NO_3^-	$NaNO_3$	$1.0x10^{-4}$	100	0.0
Zn^{2+}	$ZnCl_2$	$1.0x10^{-6}$	1	+3.4
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	$1.0x10^{-5}$	10	−0.9
Pb^{2+}	AAS std.**	$1.0x10^{-6}$	1	+2.5
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	$1.0x10^{-6}$	1	−2.9
Fe^{3+}	AAS std. [b]	$1.0x10^{-6}$	1	0.0

a. Tolerance limit of interfering ions for $1.0x10^{-6}$ mol/l Al^{3+} with the proposed method.
b. Standard solutions for Atomic Absorption Spectroscopy.

3.4 Application to practical samples

3.4.1 Determination of Al^{3+} in a standard reference substance

The proposed fluorophotometric FIA system was applied to the analysis of standard reference substance of river water. As a standard reference substance, JSAC 0301-1 from The Japan Society for Analytical Chemistry was used. The analytical result obtained by the present method was 20.1 ± 0.3 μg/l (n = 3); the result agreed well with the certified value of 19.9 ± 0.9 μg/l.

3.4.2 Effect of filtration on the determination of aluminum

Speciation of aluminum is one of the interest fields to investigate the dynamics of aluminum species in environment. Aluminum species in soil extracts have been reported by FIA [26], HPLC [31-33], and size exclusion chromatography [34]. The speciation analysis has also been performed on rain water [35].

In most cases, the aluminum species of interests are monomeric Al^{3+}, hydrolyzed $Al(OH)_n$ species, inorganic polyaluminum species, and Al complexes with organic substances such as fumic compounds. In this study, the authors aimed at the speciation of aluminum in river water and tap water samples. Natural water samples usually contain suspended particles even though the solution is clear, and the particles would contain a certain amount of aluminum. The suspended particles would be dissolved in the carrier stream containing $1x10^{-3}$ mol/l HNO_3 during flowing in the tube. The effect of filtration was examined with a tap water sample and two river water samples. The water samples were filtered or not with a membrane filter cartridge of 0.2 μm pore-size before injection; the analytical results are summarized in Table 3. Aluminum concentration in the water samples obviously decreased by the filtration, and an adequate portion of aluminum in suspended particles were removed by the filtration.

Table 3 Effect of filtration on the determination of aluminum in tap water and river water samples

Water sample	Filtration	$[Al^{3+}]$ found / 10^{-7} mol/l [a]
Tap water	—	4.0 ± 0.1
	Yes [b]	0.9 ± 0.1
Asahigawa Riv.	—	4.3 ± 0.1
	Yes [b]	1.9 ± 0.1
Zasugawa Riv.	—	9.0 ± 0.1
	Yes [b]	2.8 ± 0.1

a. Mean ± range (n = 6).
b. The sample solutions were filtered with a 0.20 μm pore-size membrane filter before injection.

3.4.3 Effect of addition of HNO_3 in the sample solution

Dissolved aluminum species in water samples is not only Al^{3+} but also hydrolyzed $Al_x(OH)_y^{m+}$ including polymeric species. The complex formation of the derivatizing reagents is generally fast with Al^{3+} and slow with the hydrolyzed species. Effect of the addition of HNO_3 at its final concentration at $1x10^{-3}$ mol/l was examined to decompose the hydrolyzed species to Al^{3+}. The results are shown in Figure 4. Aluminum concentration promptly increased by the addition of HNO_3 in the sample solution, and

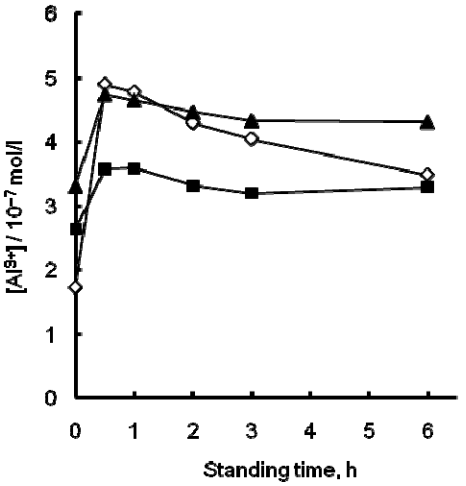

Fig. 4 Changes in concentration of Al^{3+} after the addition of HNO_3 in the sample solution at its final concentration of $1.0x10^{-3}$ mol/l.
Water samples: ▲, Zasugawa River; ■, Asahigawa River; ◊, tap water (Okayama City).

the concentration became stable after standing over 15 min. The hydrolyzed species dissolved in the sample solution were decomposed with HNO_3 added.

3.4.4 Analysis of practical river water and tap water samples

A practical tap water and two river water samples were taken, filtered, and acidified with $1.0x10^{-3}$ mol/l HNO_3. After allowing to stand for 30 min, the sample solutions were analyzed by the proposed fluorophotometric FIA; the results are summarized in Table 4. Aluminum concentrations at 10^{-7} mol/l level were determined in the practical sample solutions. As the result in the standard reference substance, the concentrations of aluminum in the sample solution would be reliable.

3.4.5 Standard addition method

Aluminum at the final concentration of $5.0x10^{-7}$ mol/l was added in the practical samples for the recovery test; the results are also summarized in Table 4. The recovery results are in the range between 92% and 106%; the results are satisfactory.

Table 4 Standard addition of Al^{3+} to the water samples

Water samples [a]	$[Al^{3+}]$ added / 10^{-7} mol/l	$[Al^{3+}]$ found [b] / 10^{-7} mol/l	Recovery / %
Tap water	0.0	3.5 ± 0.3	-
	5.0	8.8 ± 0.5	106
Asahigawa river	0.0	3.3 ± 0.3	-
	5.0	7.9 ± 0.4	92
Zasugawa river	0.0	4.3 ± 0.3	-
	5.0	9.6 ± 0.3	106

a. The water samples were filtered with a 0.20 μm pore-size membrane filter, and was acidified with $1.0x10^{-3}$ mol/l HNO_3.
b. Mean±range (n = 6).

4. Conclusion

This study demonstrated a sensitive determination of aluminum ion in water samples by fluorophotometric flow injection analysis using a conventional reagent of 8-quinolinol. Risk management would be one of the important factors on developing the analysis system; 8-quinolinol was thus used in this study for the sensitive detection of aluminum. The limit of detection reached down to $2.8x10^{-9}$ mol/l without any pre- or in-tube- concentrations. The proposed FIA system was applicable to the analysis of river water and tap water samples, as well as to the speciation of three types of aluminum species, free Al^{3+} ion, dissolved aluminum, and aluminum in suspended particles.

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