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On-line preconcentration using dual mini-columns for the speciation of chromium(III) and chromium(VI) and its application to water samples as studied by inductively coupled plasma-atomic emission spectrometry

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Abstract

On-line preconcentration system for the selective, sensitive and simultaneous determination of chromium species was investigated. Dual mini-columns containing chelating resin were utilized for the speciation and preconcentration of Cr(III) and Cr(VI) in water samples. In this system, Cr(III) was collected on first column packed with iminodiacetate resin. Cr(VI) in the effluent from the first column was reduced to Cr(III), which was collected on the second column packed with iminodiacetate resin. Hydroxyammonium chloride was examined as a potential reducing agent for Cr(VI) to Cr(III).

The effects of pH, sample flow rate, column length, and interfering ions on the recoveries of Cr(III) were carefully studied. Five millilitres of a sample solution was introduced into the system. The collected species were then sequentially washed by 1 M ammonium acetate, eluted by 2 M nitric acid and measured by ICP-AES. The detection limit for Cr(III) and Cr(VI) was 0.08 and 0.15 $\mu g\,l^{-1}$, respectively. The total analysis time was about 9.4 min.

The developed method was successfully applied to the speciation of chromium in river, tap water and wastewater samples with satisfied results.

Keywords: Speciation; Chromium; On-line preconcentration; ICP-AES; Chelating resin

1. Introduction

Speciation analysis of trace amounts of chromium(III) and chromium(VI) ions has become an important topic in environmental and biological sciences [1]. It is well known that the toxicological and biological properties of most elements depend upon their chemical forms. Therefore, the knowledge on the speciation of chromium is of particular necessity.

Chromium is widely used in various industries, such as plating, tanning, paint and pigment production, and metallurgy, which possibly contaminate the environment. Chromium(III) compounds are one of the essential trace nutrients in human bodies, and play an important role in the metabolism of glucose and certain lipids, whereas chromium(VI) compounds are toxic and carcinogenic [2–4]. The United State Environmental Protection Agency (USEPA) has regulated the permissible limit of 0.1 $mg\,l^{-1}$ of total chromium in drinking water. In Japan, the maximum tolerable concentration of chromium in wastewater is 0.5 and 0.05 $mg\,l^{-1}$ for total chromium and chromium(VI), respectively. However, World Health Organization (WHO) thought that the guideline value of 0.05 $mg\,l^{-1}$ of chromium(VI) is too high, compared with its high risk of carcinogenicity. Consequently, the development of sensitive method, as well as the speciation method of chromium, in environment is absolutely required.

A number of methods have been reported for the speciation of chromium in water samples. Liquid chromatography (LC) is a convenient method for the separation and determination of metal ions simultaneously. The LC methods coupled with atomic absorption spectrometry (LC-AAS) [5], inductively coupled plasma-atomic emission spectrometry (LC-ICP-AES) [6], and inductively coupled plasma-mass spectrometry (LC-ICP-

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MS) [7] were successfully applied to the speciation of chromium in water samples. Generally, the speciation of chromium is performed after the separation of one species of chromium(III) and (VI) by sorption [8–10], solvent extraction [11], and co-precipitation [12,13], followed by the instrumental analysis, and the another species is then determined after reducing or oxidizing the residual chromium contained in the sample solutions. Hirata et al. [9] used an iminodiacetate chelating resin for the collection/preconcentration of Cr(III) in seawater. Total chromium was determined after addition of the reducing agent to the sample, whereas Cr(VI) was determined by subtraction of total chromium with Cr(III). The concentration of Cr(VI) in waters is usually about one order of magnitude lower than that of Cr(III) and its determination as a difference between two much higher values may generate large errors.

Another option for the speciation of chromium is a simultaneous retention of Cr(III) and Cr(VI) by using dual column system. The dual column system can be constructed using the same sorbents [14–16] or different sorbents [17–19]. This system provide a good efficiency for the separation and preconcentration of Cr(III) and Cr(VI), which resulted in more accurate analysis when the species of chromium exist at very low level. The use of a dual column system, in which each species of chromium was retained on one column with their respective elution, was first reported by Naghmush et al. [17]. In this method, the effluent pH of the first column must be readjusted before it enters the other column, which makes the procedure somewhat complicated. This disadvantage was solved by Motomizu et al. [18] and Hashemi et al. [19]. However, the latter methods suffer from high concentration of matrix existing in water samples, which significantly reduced the sorption efficiency of chromium species on the column.

In this study, the on-line preconcentration system using dual mini-columns containing iminodiacetate chelating resin was proposed for the speciation of chromium(III) and chromium(VI). In this system, chromium(III) was collected on first column, whereas chromium(VI) was reduced to chromium(III) in the downstream and collected on the second column. Hydroxylamine was used as a potential reducing agent for the conversion of chromium(VI) to chromium(III). The collected species were sequentially eluted by 2 M nitric acid and measured by ICP-AES. The developed method permits the simultaneous measurement of both chromium(III) and chromium(VI) without need to readjust the pH of samples. The method was successfully applied to the speciation of chromium in environmental water samples.

2. Experimental

2.1. Instrumentation

The ICP-AES system (Vista Pro, Seiko Instrument, Japan) was used for the measurement of chromium. The optimized operating conditions of ICP-AES were summarized in Table 1. The flow diagram for the pretreatment of sample is shown in Fig. 1. The PTFE tubing (0.5 mm i.d.) was used for the assembling of flow lines in a flow injection pretreatment system. Peristaltic pumps (ALITEA, Sweden and SPETEC, Germany) were used to propel the solution of buffer, sample, reducing agent and eluent.

Table 1
Operating conditions of ICP-AES

ICP-AES:SII VISTA-PRO		
Plasma condition		
RF power	1.2 kW	
Plasma gas flow rate	15 l min^{-1}	Ar
Auxiliary gas flow	1.5 l min^{-1}	Ar
Nebulizer gas flow	0.75 l min^{-1}	Ar
Sample uptake rate	1.0 ml min^{-1}	
Nebulizer	Concentric glass nebulizer	
Torch	One-piece low flow extended torch in the axial view mode	
Data acquision		
Measurement mode	Time scan mode	
Emission line	267.716 nm	

2.2. Reagents and materials

A 100 mg l^{-1} stock standard solution of Cr(III) was prepared by dissolving chromium nitrate nonahydrate (analytical reagent grade: Wako Pure Chemicals, Osaka, Japan) in 0.01 mol l^{-1} nitric acid solution (ultrapure reagent grade: Kanto Chemical, Tokyo, Japan). A 100 mg l^{-1} Cr(VI) stock standard solution was prepared by dissolving sodium chromate tetrahydrate (analytical reagent grade: Kanto Chemical, Tokyo, Japan) in ultrapure water (resistivity $\geqq$ 18 MΩ cm^{-1}) prepared by an Elix3/Milli-Q Element System (Nihon Millipore, Japan).

Accurately diluted solutions of Cr(III) and Cr(VI) were prepared daily using the standard stock solutions. The reducing agent was prepared by accurate dilution of a stock solution of 10 (w/v)% hydroxylamine (Wako Pure Chemical, Osaka, Japan). The ammonium acetate solution was prepared by appropriate mixing of the electronic grade acetic acid and ammonia water (Mitsubishi Chemicals, Japan).

An iminodiacetate resin (Muromac A-1, 50–100 mesh: Muromachi Technos, Japan) was used for the collection and the preconcentration of Cr(III) species. The solid-phase columns was prepared by packing the resin into the PTFE tubing (5 cm × 2 mm i.d.) equipped with the plugs of quartz wool at both ends of the tubing to keep the resin in the column. The sample solutions were filtered through the membrane filter of nitrocellulose ester (0.45 μm, Advantec, Toyo, Japan) and adjusted to pH 3.3 before being injected to the system.

2.3. Column separation/preconcentration procedure

The schematic diagrams for the on-line separation/preconcentration of Cr(III) and Cr(VI) are shown in Fig. 1. The procedures involve the conditioning step (0.2 min), in which the iminodiacetate chelating resin in column was washed with ultrapure water, followed by the collection step (4.2 min; 5 ml of sample solution), where the chromium in water samples (pH

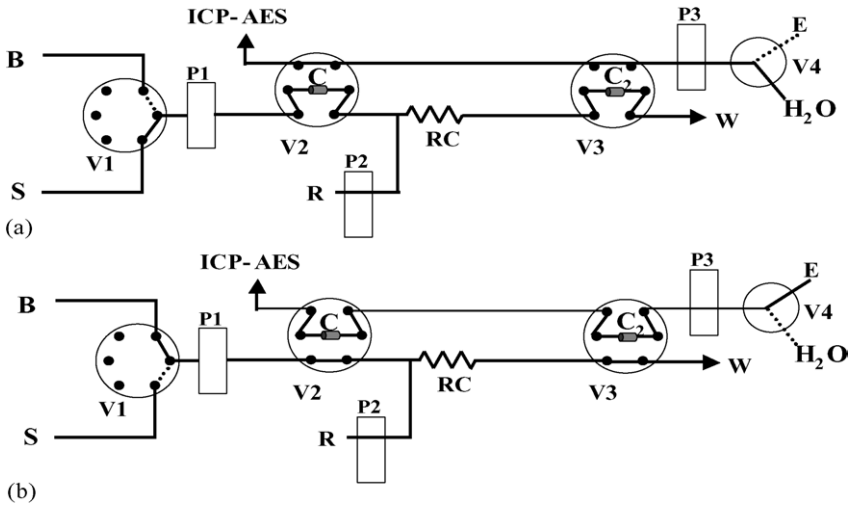

Fig. 1. Flow diagram of on-line dual column-ICP-AES system. P1, P2 and P3: Peristaltic pump; C_1 and C_2: column, PTFE tubing 5 cm × 2 mm i.d. packed with iminodiacetate chelating resin (Muromac A-1); S: sample, pH 3.3, flow rate = 1.2 ml min^{-1}; B: buffer, 1 M ammonium acetate, pH 3.3; E: eluent, 2 M HNO_3, flow rate = 1 ml min^{-1}; R: reducing agent, 100 mM hydroxyammonium chloride, flow rate = 0.2 ml min^{-1}; RC: reaction coil, PTFE tubing 5 m × 0.5 mm i.d.; (a) loading position; (b) inject position.

3.3) was collected in the resin column. In acidic regions, Cr(III) exists as cationic species, $Cr(OH)_n^{(3-n)+}$, whereas Cr(VI) exists as anionic species, $Cr\,O_4^{2-}$. Therefore, in the first column, only Cr(III) was collected, while unretained anionic Cr(VI) passed through the first column, and subsequently was reduced by hydroxyammonium Chloride to Cr(III), which was collected on the second column.

After the collection step of analytes, the valve V1 was switched (2.5 min) to introduce 3 ml of 1 M ammonium acetate buffer solution (pH 3.3) for removal of matrices, as well as analytes remaining in the tubing of the flow system. The collected Cr(III) and pre-reduced Cr(VI) were then subsequently eluted with 2 M nitric acid by switching the valve V2 for Cr(III) within 1.5 min, and thereafter switching the valve V3 for pre-reduced Cr(VI) within 1 min. The total analysis time was about 9.4 min when 5 ml of sample was used. The analytes zones eluted from the columns were introduced into ICP-AES for their measurement. The Cr signals obtained by ICP-AES using time scan mode measurement were transferred to Excel software, where the flow signals were graphically plotted. The peak area or peak height of the analytical signals was computed by using the Microcal Origin software. The examples of the peaks of Cr(III) and Cr(VI) were shown in Fig. 2.

3. Result and discussion

3.1. Effect of pH on the collection of chromium species

The effects of pH on the collection of chromium with the iminodiacetate resin were examined by using an off-line column procedure. As shown in Fig. 3, the chromium(III) (line A and B) was quantitatively collected at pH range of 3.0–3.5, whereas the anionic species of chromium(VI) was slightly retained on the resin (line C).

In acidic pH regions of 1–3, chromium(III) exists as $[Cr(H_2O)_6]^{3+}$, and it tends to be hydrolyzed at pH >4, as the pK_a of hydrolysis of Cr(III) is 3.85 [1,20,21], and eventually precipitated as $Cr(OH)_3$. Therefore, the pH dependence of the Cr(III) collection on the iminodiacetate resin column at acidic region seems to be due to its low hydrolysis.

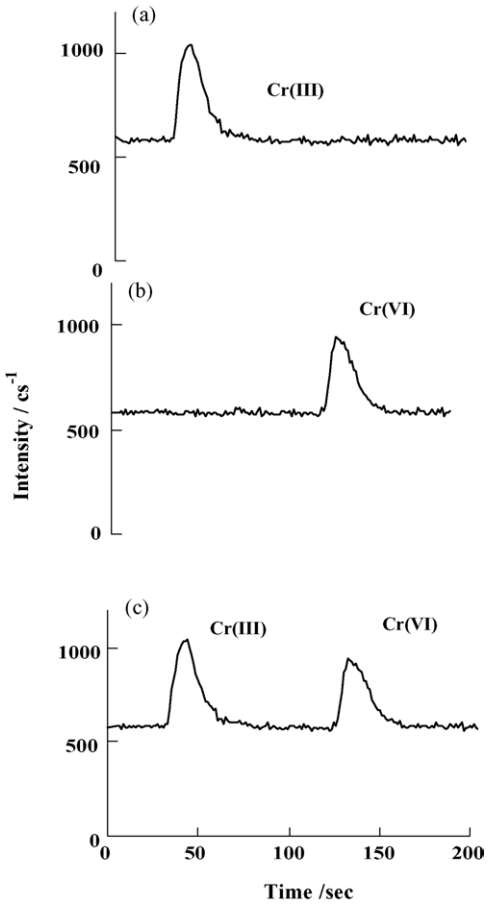

Fig. 2. Flow signals for solution of Cr(III) and Cr(VI) obtained by the proposed method. Sample solution: (a) 1 μg l^{-1} Cr(III), (b) 1 μg l^{-1} Cr(VI) and (c) 1 μg l^{-1} Cr(III) + 1 μg l^{-1} Cr(VI); pH 3.3; sample size, 5 ml; eluent: 2 M HNO_3.

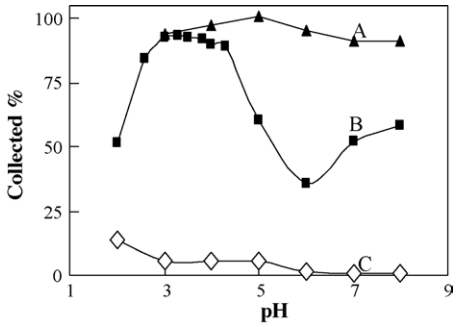

Fig. 3. Effect of pH on the collection of Cr. (A) Cr(III) sample without the addition of buffer solution; (B) Cr(III) sample with the addition of 1 M ammonium acetate buffer; (C) Cr(VI) sample with the addition of 1 M ammonium acetate buffer. Sample solution: 100 μg l^{-1}Cr(III) or Cr(VI); column procedure: off-line column containing iminodiacetate resin, Muromac A-1 (3 cm × 7mm i.d); eluent: 2 M HNO_3.

The Fig. 3 also showed that the collection of Cr(III) in sample solutions, in which 1 M ammonium acetate buffer solution (line B) was added, resulted in lower efficiency than the collection of Cr(III) without the addition of buffer (line A). Probably, the competition effect of other cations containing in the buffer solution is responsible to lower collection efficiency of Cr(III) at pH >4, where the loss of Cr(III) was obtained (see line B). In this work, the sample solution of pH 3.3 was adopted for the separation and the preconcentration of chromium species.

3.2. Reduction of Cr(VI) to Cr(III)

The effect of reducing agents were studied to obtain rapid conversion of Cr(VI) to Cr(III). In this work, some reducing agents, such as hydrazine sulfate, sodium sulfite, ascorbic acid, and hydroxyammonium chloride were examined. After adding a reducing agent solution to a Cr(VI) sample solution, and standing it for 30 and 60 min, the pH of the sample solution was adjusted to 3.3 with ammonia solution. Then, the sample solution was passed through the iminodiacetate resin column, followed by the elution of collected pre-reduced Cr(VI) and the measurement by ICP-AES. As shown in Table 2, hydroxyammonium chloride resulted in highest efficiency for the conversion of Cr(VI) to Cr(III).

The effect of the concentration of hydroxyammonium chloride on the conversion efficiency of Cr(VI) was examined by using the system in Fig. 1 and the results are shown in Fig. 4(a).

Table 2
Effect of reducing agents on the conversion of Cr(VI) to Cr(III)

	Conversion (%)	
	30 min	60 min
Hydrazine sulfate	49.5	49.5
Sodium sulfite	39.8	29.6
Ascorbic acid	40.0	42.0
Hydroxyammonium chloride	85.6	86.6

Sample solution: 100 μg l^{-1} Cr(VI); concentration of reducing agent in sample solution: 10 mM; column procedure: off-line column(3 cm × 7 mm i.d.); eluent: 2 M HNO_3.

Table 3
Effect of coexisting elements on the determination of Cr(III) after on-line column preconcentration

Element	Matrix solution concentration (mg l^{-1})	Cr concentration (μg l^{-1})	Recovery (%)[a] (n = 3)
Na	50	2	105 ± 0
K	50	2	103 ± 0
Ca	50	2	112 ± 0
Mg	50	2	105 ± 0
S1		1	100 ± 1
S2		1	100 ± 1
S3		1	110 ± 1
S4		1	120 ± 1
S5		1	113 ± 1
S6		1	171 ± 4

S1 (mg l^{-1}): Na 5, K 5, Ca 5, Mg 5; S2 (mg l^{-1}): Na 10, K 10, Ca 10, Mg 10; S3 (mg l^{-1}): Na 50, K 50, Ca 50, Mg 50; S4 (mg l^{-1}): Na 100, K 100, Ca 100, Mg 100; S5 (mg l^{-1}): Na 100, K 4, Ca 4, Mg 14; S6 (mg l^{-1}): Na 1000, K 40, Ca 40, Mg 140.

[a] The ratio of signal area of Cr(III) was obtained with and without coexisting ion.

As the results, the increase in the concentration of hydroxyammonium chloride from 30 to 100 mM resulted in an increase in the peak area of chromium signals. However, the chromium signals gradually decreased, when the concentration of hydroxyammonium chloride was higher than 100 mM. Therefore, 100 mM was selected as an optimal concentration of hydroxyammonium chloride.

The effect of the reaction coil length (3–5 m) on the reduction of Cr(VI) to Cr(III) was examined by flowing the 100 mM hydroxyammonium chloride at the flow rate of 0.2 ml min^{-1} and

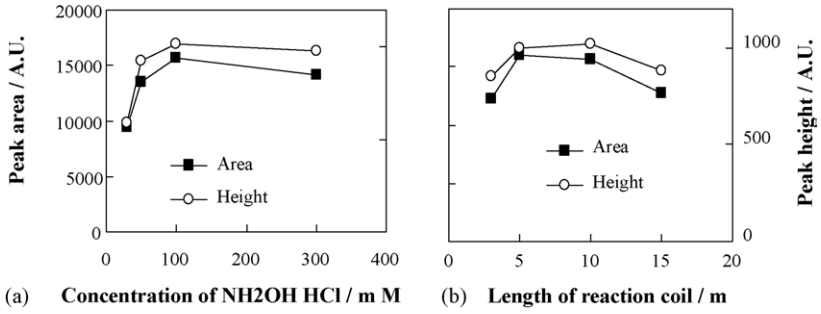

Fig. 4. Effect of concentration of hydroxyamine and length of reaction coil on the reduction of Cr(VI). Sample solution: 1 μg l^{-1}Cr(VI); pH 3.3; sample size, 5 ml.

Table 4
Determination of chromium species in River Water Reference Material SLRS-4 (National Research Council of Canada)

Added ($\mu g\,l^{-1}$)		Found ($n=3$) ($\mu g\,l^{-1}$)		Recovery (%)		Proposed method ($\mu g\,l^{-1}$)	Certified value ($\mu g\,l^{-1}$)
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr[a]	Total Cr
0	0	0.27 ± 0.01	0.07 ± 0.01	–	–	0.34 ± 0.01	0.33 ± 0.02
0.21	0.19	0.52 ± 0.03	0.24 ± 0.04	119 ± 4	89 ± 7	–	–

The volumes of sample solutions were 10 ml.
[a] Total Cr = Cr(III) + Cr(VI).

Table 5
Recovery of spiked tap sample

Added $\mu g\,l^{-1}$		Found ($n=3$) $\mu g\,l^{-1}$		Recovery (%)	
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
0	0	0.43 ± 0.03	0.37 ± 0.02	–	–
0	0.8	0.43 ± 0.03	1.15 ± 0.06	–	98 ± 7
1.7	0	2.18 ± 0.08	0.34 ± 0.03	103 ± 5	–
1.7	0.8	2.11 ± 0.01	1.16 ± 0.02	99 ± 1	99 ± 2

The volumes of sample solutions were 5 ml.

the sample at the flow rate of 1.2 ml min^{-1}. The results were shown in Fig. 4(b). The reaction coil length of 5–10 m, which corresponds to the reduction time of 0.8–1.6 min, resulted in about 73% conversion of Cr(VI) to Cr(III). It implies that the kinetics conversion of Cr(VI) to Cr(III) is fast. Then, the reaction coil of 10 m was selected as optimum condition.

3.3. Interferences

As the present method was intended to be applied to the determination of chromium in environmental water, the effect of interferences from various kinds of cations were examined. The cation matrices (Na, K, Mg and K), which are the most common ions in environment waters, can often affect the recovery of the target elements with chelate resins. Furthermore, alkali and alkaline earth metal matrices can easily release electron in the plasma, and the target metal ion can capture electrons released by the matrices.

In this work, the artificial sample solutions were prepared by addition of the cation matrices to the standard solution of 1–2 $\mu g\,l^{-1}$ Cr(III), and the pH of the sample solutions was adjusted to 3.3. The peak signals area with and without the addition of the cation matrices were compared to examine the recovery of chromium species. The results were shown in Table 3. The single matrix of each 50 mg l^{-1} of Na, K and Mg, as well as 5–10 mg l^{-1} mixed matrices (Na^+, K^+, Mg^{2+} and Ca^{2+}), did not give serious interferences with the recovery of Cr(III). Similarly, the mixed cation matrices did not interfere on the recovery of Cr(III). However, when the concentration of Na^+ is about 1000 mg l^{-1} in the mixed matrices, the positive error occurred.

3.4. Determination of chromium in standard reference material and recovery in spike water samples

The on-line dual columns system was validated through the determination of chromium in river water reference material, SLRS-4 (National Research Council of Canada). As shown in Table 4, the total chromium obtained by the proposed method was in good agreement with the certified value. The recovery test of spiked samples of SLRS-4 and tap water were also examined. By using the proposed method, the satisfactory results as shown in Tables 4 and 5, which were indicated by almost 100% recoveries of chromium species, were obtained.

The calibration graphs showed a good linearity in the concentration range of 0.2–2.0 $\mu g\,l^{-1}$. The detection limits using 5 ml of sample solutions, which corresponds to three times of the standard deviation of the blank solution, were 0.08 and

Table 6
Analysis of real water samples for Chromium speciation

Water sample	Proposed method ($n=3$) ($\mu g\,l^{-1}$)			Reduction method ($n=3$) ($\mu g\,l^{-1}$)
	Cr(III)	Cr(VI)	Total Cr[a]	Total Cr[b]
Kokubu River				
Middle stream[c]	0.14 ± 0.01	0.08 ± 0.01	0.22 ± 0.01	0.26 ± 0.01
Down stream[c]	0.13 ± 0.01	0.09 ± 0.01	0.22 ± 0.01	0.24 ± 0.01
Kagami River[c]	0.13 ± 0.02	0.08 ± 0.01	0.21 ± 0.02	0.24 ± 0.01
Tap water[d]	0.43 ± 0.03	0.37 ± 0.02	0.80 ± 0.05	0.85 ± 0.04
Wastewater[d] (metal plating after treatment)	0.23 ± 0.02	0.26 ± 0.01	0.49 ± 0.01	0.44 ± 0.01
Wastewater[d] (metal recycle after treatment)	1.16 ± 0.02	0.41 ± 0.02	1.57 ± 0.02	1.66 ± 0.04
Wastewater[c] (Industrial technology center)	0.20 ± 0.01	0.08 ± 0.01	0.28 ± 0.01	0.22 ± 0.01

[a] Total Cr = Cr(III) + Cr(VI).
[b] One hundred millimolar hydroxyammonium chloride was added to the water samples. After standing for 45 min, the pH of the solutions was adjusted to 3.3 with ammonia solution, and the concentrations of Cr were measured by the on-line column-ICP-AES system (Fig. 1).
[c] These values obtained by using 10 ml water sample solutions.
[d] These values obtained by using 5 ml water sample solutions.

0.15 μg l^{-1} for Cr(III) and Cr(VI), respectively. The sensitivity can be improved when the larger of sample volume was used. In standard procedure, 5 ml of water sample was injected to the system. However, due to very low concentration of Cr(VI) in SLRS-4 standard reference river water, the sample injected was 10 ml, which correspond to collection time of about 8.3 min.

3.5. Application of the proposed method to the determination of chromium in water samples

Water samples were collected from Kochi City, Japan. The samples were filtered through a membrane filter (0.45 μm), and were adjusted to pH 3.3 with ammonia solution or acetic acid solution prior to the injection of the samples in the system. The analytical results were summarized in Table 6. The results of the total chromium in all samples obtained by the proposed method were in good agreement with those obtained by the reduction method [9]. Similar to the analysis of chromium in SLRS-4 (Table 4), the volume of sample used for analysis of chromium in river water and wastewater (industrial technology center) was about 10 ml. According to the results of Tables 5 and 6 obtained in this work, the concentrations of the total chromium in all samples examined were much lower than the regulation values, which indicate the excellent environmental management. The concentration of Cr(VI) in tap water samples was found to be higher than river water samples, which means chlorine in tap waters, can readily oxidize Cr(III) to Cr(VI).

4. Conclusion

The on-line dual columns system coupled with ICP-AES for the simultaneous determination of Cr(III) and Cr(VI) was established. Hydroxyammonium chloride is found to be an effective reducing agent, which allows rapid reduction of Cr(VI) to Cr(III). The proposed system provides an on-line separation and preconcetration of Cr(III) and Cr(VI), which can determine both species simultaneously in a single injection of samples. Other advantages over common chromium determination techniques are: the developed method provides the sensitive determination of Cr(III) and Cr(VI) at sub-ng ml^{-1} level, rapid analysis (less than 10 min) of both chromium species without any interference from matrix ions. Furthermore, the detection limit of chromium was improved 10 times, when 5 ml of sample solution was used, compared with the direct measurement by ICP-AES.

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