

# Determination of Cr(III) and Cr(VI) at Sub-ppb Levels in Water with Solid-Phase Extraction/Metal Furnace Atomic Absorption Spectrometry

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A simple method using solid-phase extraction combined with metal furnace atomic absorption spectrometry was developed for the determination of Cr(III) and Cr(VI) at sub-ppb levels in water. A 500-ml water sample was adjusted to pH 3 with nitric acid and then passed through an iminodiacetate extraction disk placed on a cation-exchange extraction disk at a flow rate of 20–40 ml min<sup>-1</sup> for concentrating Cr(III). The filtrate was adjusted to pH 10 with aqueous ammonia and then passed through an anion-exchange extraction disk at a flow rate of 2 ml min<sup>-1</sup> for concentrating Cr(VI). The Cr(III) and Cr(VI) collected were eluted with 40 ml of 3 mol l<sup>-1</sup> nitric acid for Cr(III) and 40 ml of 1 g l<sup>-1</sup> diphenylcarbazide solution for Cr(VI). Each eluate was diluted to 50 ml with deionized water and injected into a U-type tungsten board on the metal furnace. The calibration curves of Cr(III) and Cr(VI) showed good linearity in the range of 0.1–0.5 ng. The detection limits corresponding to three times the standard deviation ( $n = 5$ ) of blank values were 8.1 pg for both Cr(III) and Cr(VI). The analytical value of total Cr (Cr(III) + Cr(VI)) in certified reference material of river water (JSAC 0302-3) was in good agreement with the reference value. The recovery test for 0.50 µg (1.00 µg l<sup>-1</sup>) of Cr(III) and Cr(VI) added to 500 ml of the water samples showed sufficient values (98.1–106%), except for river water sampled downstream due to relatively higher COD<sub>Mn</sub> value. The relative standard deviations ( $n = 5$ ) were less than 5% for both Cr(III) and Cr(VI).

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## Introduction

Chromium (Cr) is widely used in various industries, such as plating, leather, pigment, stainless-steel, and electrically-heated wire. Although Cr has several oxidation states, its species in water are mainly Cr(III) and/or Cr(VI). Chromium(III) is considered to be one of the essential trace elements in the human body because it has much to do with the metabolism of glucose. On the other hand, Cr(VI) is well known to have higher toxicity and carcinogenicity. An environmental quality standard (EQS) and an emission standard (ES) have been established in Japan for Cr(VI) because of its carcinogenicity. The standard value and regulation value of Cr(VI) in water are 0.05 mg l<sup>-1</sup> for EQS and 0.5 mg l<sup>-1</sup> for ES, respectively. Therefore, the determination of Cr(III) and Cr(VI) in water is of great importance; that is, its speciation is required.

The Japanese Industrial Standard (JIS) has prescribed diphenylcarbazide (DPC) absorptiometry for the determination of Cr(VI) and total Cr (Cr(III) + Cr(VI)); however, this method cannot be applied to the determination of Cr(III) and Cr(VI) at sub-ppb levels in water because the sensitivity is 2–50 µg for Cr.<sup>1</sup> The concentration of Cr in water is generally at sub-ppb levels; therefore, the combination of preconcentration (*e.g.*, coprecipitation,<sup>2</sup> solvent extraction,<sup>3</sup> and solid-phase extraction (SPE)<sup>4</sup>) and sensitive instrumental analysis (*e.g.*, atomic absorption spectrometry (AAS), inductively coupled

plasma-atomic emission spectrometry (ICP-AES), and inductively coupled plasma-mass spectrometry (ICP-MS))<sup>5</sup> is needed for the determination of Cr in water.

Recently, a number of methods using SPE combined with atomic spectrometry were reported for the determination of Cr(III) and Cr(VI) in water. Sule and Ingle<sup>6</sup> determined Cr(III) and Cr(VI) in tap water and humic acid solution with iminodiacetate chelating resin and anion-exchange resin columns by flame AAS (FAAS). Hirata *et al.*<sup>7</sup> preconcentrated Cr(III) and total Cr in seawater with iminodiacetate chelating resin column by ICP-MS and calculated Cr(VI) as the difference between total Cr and Cr(III). Motomizu *et al.*<sup>8</sup> developed an on-line flow injection system for the determination of Cr(III) and Cr(VI) in tap water, river water, and mineral drinking water with a cation-exchange extraction disk (CED) and an anion-exchange extraction disk (AED) by ICP-AES. Hashemi *et al.*<sup>9</sup> analyzed Cr(III) and Cr(VI) in tap water, river water, and wastewater with iminodiacetate chelating resin and anion-exchange resin columns by FAAS. Iwasaki *et al.*<sup>10</sup> determined Cr(III) and Cr(VI) in river water and lake water with cation- and anion-exchange resin in batch experiments by ICP-AES. Sumida *et al.*<sup>11,12</sup> preconcentrated Cr(III) and Cr(VI) in tap water, river water, wastewater, and seawater with iminodiacetate chelating resin column by ICP-AES. Furusho *et al.*<sup>13</sup> developed an automated pretreatment system for the determination of Cr(III) and Cr(VI) in tap water, river water, and mineral drinking water with iminodiacetate chelating resin and synthesized chitosan resin columns by ICP-AES. In this way, the iminodiacetate chelating resin was often used for the speciation of Cr in water; however, the chelate-forming reaction

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of Cr(III) with iminodiacetic acid is very slow at ordinary temperature, because the hydrated ion of Cr(III) is an inert complex. Therefore, the unreactive Cr(III) with iminodiacetic acid should be collected with another adsorbent (*e.g.*, cation-exchange resin) to recover the total amount of Cr(III) in water. Although Cr(III) was quantitatively recovered with only cation-exchange resin,<sup>10</sup> the combination of iminodiacetate chelating resin and cation-exchange resin is useful for the collection of Cr(III) in water containing a high concentration of coexisting ions, because iminodiacetate chelating resin has high selectivity for the concentrations of heavy metals and transition elements.

In general, the eluates of Cr(III) and Cr(VI) from solid phase are measured by AAS, ICP-AES, and ICP-MS. Metal and graphite furnaces are used as the atomizers of electrothermal AAS (ETAAS); the respective methods are therefore called metal furnace AAS (MFAAS) and graphite furnace AAS. In particular, MFAAS is effective because of the following advantages: (1) the rate of temperature increase is large, (2) the temperature distribution within the furnace is homogeneous, (3) the sample solution is not soaked into the furnace, (4) the lifetime of the furnace is longer than that of the graphite furnace, and (5) the repeatability is high.<sup>14,15</sup>

This paper describes a method for the determination of Cr(III) and Cr(VI) at sub-ppb levels in water using SPE combined with MFAAS. The method involves the preconcentration of Cr(III) and Cr(VI) with iminodiacetate extraction disk (IED), CED, and AED. Discussion will be extended to (1) calibration curve, (2) optimum pH, flow rate, and eluent volume, (3) elution of Cr(VI) with DPC solution, (4) separation of Cr(III) and Cr(VI), (5) effect of coexisting ions, and (6) validation of proposed method. The correlation between recoveries of Cr(III) and Cr(VI) and the chemical oxygen demand (COD), one of the organic pollution indexes, will also be discussed, because the dissolved organic matter (DOM) in water has the complexing and reducing abilities for Cr(III) and Cr(VI), respectively.<sup>16-19</sup> The proposed method was successfully applied to the determination of Cr(III) and Cr(VI) in tap water, rainwater, river water, hot-spring water, and mineral drinking water.

## Experimental

### Apparatus

An SAS-760 atomic absorption spectrophotometer (Seiko Instruments, Tokyo, Japan) was used in conjunction with a SAS-715 metal furnace atomizer (Seiko Instruments) and a U-type tungsten metal board (18 mm length, 7 mm width, and 1 mm depth). A Cr hollow cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) and a deuterium lamp (Hamamatsu Photonics) were used as the light source and the background correction, respectively. Pure argon (99.995%) and hydrogen were used as the carrier gas. The operating conditions are given in Table 1.

The sample solutions were injected into the metal board (30  $\mu$ l) within the metal furnace using an Eppendorf Model Reference-4900 pipette (10  $\mu$ l fixed volume, Eppendorf, Hamburg, Germany).

A Demi-Ace Model DX-15 deionizer (Kurita Water Industries, Tokyo, Japan) was used for preparing deionized water. An HM-30G pH meter (DKK-TOA, Tokyo, Japan) was used for pH control of the sample solution.

### Reagents and samples

A 1000 mg l<sup>-1</sup> Cr(III) stock standard solution was prepared by

Table 1 Instrumental conditions of atomic absorption spectrometry for Cr

Instruments Seiko SAS 760 AAS, SAS 715 metal furnace atomizer		
Instrumental condition		
Analytical line/nm	357.9	
Lamp current/mA	10	
Slit width/nm	1.08	
Absorbance	Peak area	
Ar gas flow rate/l min <sup>-1</sup>	5	
H <sub>2</sub> gas flow rate/l min <sup>-1</sup>	1	
Atomization condition		
Drying/ $^{\circ}$ C	150	Ramp 20 s
Pyrolysis/ $^{\circ}$ C	700	Hold 20 s
Atomizing/ $^{\circ}$ C	2300	Hold 2 s

dissolving chromium nitrate nonahydrate (analytical-reagent grade, Wako Pure Chemical, Osaka, Japan) in 0.1 mol l<sup>-1</sup> nitric acid (analytical-reagent grade, Junsei Chemical, Tokyo, Japan). A 1000 mg l<sup>-1</sup> Cr(VI) stock standard solution was prepared by dissolving potassium chromate (analytical-reagent grade, Junsei Chemical) in deionized water. The calibrating standard solutions of Cr(III) and Cr(VI) were prepared by accurate dilution of the stock standard solutions with deionized water. A 1 g l<sup>-1</sup> DPC solution was prepared by dissolving 1,5-diphenylcarbonohydrazide (analytical-reagent grade, Junsei Chemical) in a mixture of 50 ml of acetone and 50 ml of deionized water containing 0.1 mol l<sup>-1</sup> nitric acid. The DPC solution was prepared every time it was used because of its instability.<sup>20</sup> All other reagents used were of analytical-reagent grade.

The IED, CED, and AED (3M Empore<sup>TM</sup> extraction disk, 47 mm diameter, 0.5 mm thickness, 3M, St. Paul, MN) were used throughout the experiments. The certified reference material (CRM) of river water (JSAC 0302-3)<sup>21,22</sup> was used for validation of the proposed method.

The seven water samples were (1) tap water (Kawasaki, Kanagawa, Japan), (2) rainwater (Kawasaki, Kanagawa, Japan), (3) mineral drinking water (Hokuto, Yamanashi, Japan), (4) hot-spring water (Murayama hot-spring, Musashimurayama, Tokyo, Japan), (5) river water (upstream of Tamagawa River, Okutama, Tokyo, Japan), (6) river water (middlestream of Tamagawa River, Hamura, Tokyo, Japan), and (7) river water (downstream of Tamagawa River, Kawasaki, Kanagawa, Japan). The three river water samples were obtained on the same day and were filtered through a glass-fiber filter (GMF 150, 1.0  $\mu$ m pore size, 47 mm diameter, 0.73 mm thickness, Whatman, Kent, England) and immediately analyzed using the proposed method.

### Procedure

An IED was swollen with methanol and then conditioned successively with 20 ml of 3 mol l<sup>-1</sup> nitric acid, 100 ml of deionized water, and 50 ml of 0.1 mol l<sup>-1</sup> ammonium acetate solution (pH 5.6). A CED and an AED were successively conditioned with 10 ml of methanol, 10 ml of deionized water, 25 ml of 3 mol l<sup>-1</sup> nitric acid, and 30 ml of deionized water. A 500-ml water sample was adjusted to pH 3 with nitric acid and then passed through an IED placed on a CED at a flow rate of 20 - 40 ml min<sup>-1</sup> for collecting Cr(III). The filtrate was adjusted to pH 10 with aqueous ammonia and then passed through an AED at a flow rate of 2 ml min<sup>-1</sup> for collecting Cr(VI). IEDs placed on a CED and an AED were washed with 20 ml and 10 ml of deionized water, respectively. Chromium(III) and Cr(VI) as collected were eluted with 40 ml of 3 mol l<sup>-1</sup>

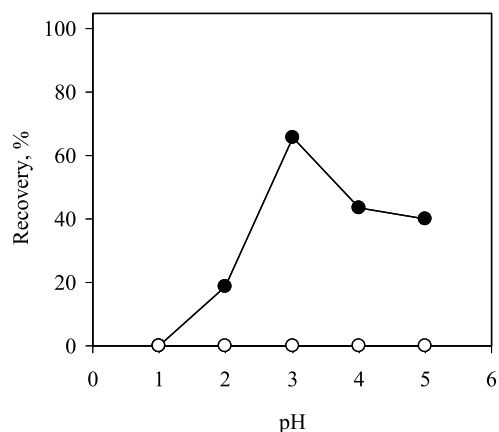


Fig. 1 Variations in the recoveries of Cr(III) (●) and Cr(VI) (○) with pH collected on IED. Cr(III),  $1 \mu\text{g l}^{-1}$ ; Cr(VI),  $1 \mu\text{g l}^{-1}$ ; sample volume, 500 ml; flow rate,  $2 \text{ ml min}^{-1}$ ; eluent, 40 ml of  $3 \text{ mol l}^{-1} \text{ HNO}_3$ .

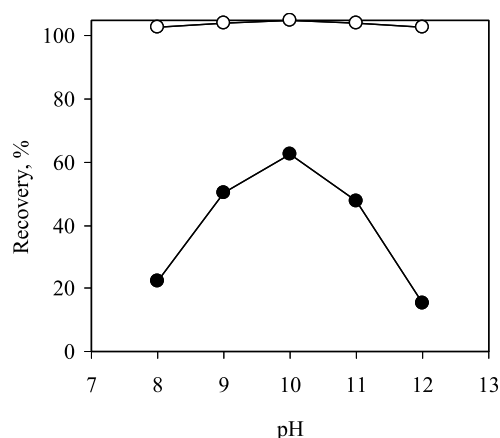


Fig. 2 Variations in the recoveries of Cr(III) (●) and Cr(VI) (○) with pH collected on AED. Cr(III),  $1 \mu\text{g l}^{-1}$ ; Cr(VI),  $1 \mu\text{g l}^{-1}$ ; sample volume, 500 ml; flow rate,  $2 \text{ ml min}^{-1}$ ; eluent, 40 ml of  $1 \text{ g l}^{-1} \text{ DPC}$  solution.

nitric acid and 40 ml of  $1 \text{ g l}^{-1} \text{ DPC}$  solution, respectively. Each eluate was diluted to 50 ml with deionized water and injected into a U-type tungsten metal board within the metal furnace. The concentrations of Cr(III) and Cr(VI) were calculated using calibration curves previously constructed with a suite of standard solutions.

The COD of the water samples was measured by potassium permanganate method at  $100^\circ\text{C}$  according to JIS K 0102.<sup>1</sup>

## Results and Discussion

### Calibration curve

Chromium(III) ion in diluted solution is adsorbed on a glass container at pH 4 - 12;<sup>23</sup> therefore, the calibrating standards of Cr(III) were adjusted to pH 1 with nitric acid prior to construction of the calibration curve. The calibration curves of Cr(III) and Cr(VI) showed good linearity in the range of 0.1 - 0.5 ng. The linear equations of the calibration curves of Cr(III) and Cr(VI) were  $Y = 1.736X + 0.229$  ( $r = 0.9996$ ) and  $Y = 1.741X + 0.222$  ( $r = 0.9998$ ), respectively, where  $X$ ,  $Y$ , and  $r$  are the absolute amount (ng), integrated absorbance, and correlation coefficient, respectively. The detection limits corresponding to three times the standard deviation ( $n = 5$ ) of blank values were 8.1 pg for both Cr(III) and Cr(VI). When Cr in CRM (JSAC 0302-3) was determined using these calibration curves to evaluate the accuracy of the calibration curve, the analytical values ( $10.0 - 10.3 \mu\text{g l}^{-1}$ ) obtained were in good agreement with the certified value ( $10.0 \pm 0.2 \mu\text{g l}^{-1}$ ).

### Optimum pH, flow rate, and eluent volume

The chemical species of Cr(III) and Cr(VI) in water depend on pH; especially, Cr(III) is known to be thermodynamically stable below pH 6 and Cr(VI) is stable above pH 7.<sup>24</sup> Therefore, the dependency on pH of the recoveries of Cr(III) and Cr(VI) collected on IED and AED was investigated. The pH of the sample solution was controlled with nitric acid and aqueous ammonia. Figure 1 shows the variations with pH in the recoveries of Cr(III) and Cr(VI) collected on IED. Cr(III) was recovered at 65.9% on an IED at pH 3, because the stability constant of mononuclear hydrated ion (*i.e.*,  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ) was slightly greater than that of the IED complex. Additionally, Cr(III) was recovered insufficiently with double layers of IED at

pH 3. Steiner *et al.*<sup>25</sup> collected Cr(III) with an IED, heated at  $100^\circ\text{C}$  for 30 min in water, and analyzed it by diffuse reflectance spectrometry. In reproducing the recovery test for Cr(III) at  $100^\circ\text{C}$  for 30 min, about 40% recovery was observed due to the deterioration of the IED by heating. Ohashi *et al.*<sup>26</sup> used sodium nitrite or sodium sulfite as the catalyst of chelatometric titration of Cr(III); however, this method was not investigated here, because sodium nitrite and sodium sulfite are an oxidant and a reductant for Cr(III) and Cr(VI), respectively. In this investigation,  $0.5 \mu\text{g}/500 \text{ ml}$  of Cr(III) was concentrated perfectly with an IED placed on a CED at pH 3 to recover the residual Cr(III) from the IED. Although Cr(VI) was not recovered with an IED at pH 1 - 5 because of oxoacid (*i.e.*,  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , and  $\text{CrO}_4^{2-}$ ), Cr(VI) was quantitatively recovered with an AED at pH 8 - 12, as shown in Fig. 2. On the other hand, about 50% of Cr(III) was recovered at pH 9 - 11 due to the formation of colloidal hydroxide (*i.e.*,  $\text{Cr}(\text{OH})_3$ ) or oxidation of Cr(III) to Cr(VI) by dissolved oxygen in water.<sup>27</sup>

As the flow rate of the sample solution increases, Cr(III) and Cr(VI) may pass through the solid phase prior to their adsorption. Therefore, the influence of flow rate on the recoveries of Cr(III) and Cr(VI) was investigated (Fig. 3). Chromium(III) was quantitatively recovered at a flow rate of 2 - 40  $\text{ml min}^{-1}$ . However, the recovery of Cr(VI) was insufficient for a flow rate above 20  $\text{ml min}^{-1}$  due to the slow ion-exchange rate of Cr(VI) with an AED.

An acid (*e.g.*, nitric acid<sup>6-8,11-13</sup> or hydrochloric acid<sup>9,10</sup>) solution has so far been used as the eluent for Cr(III). If hydrochloric acid is used for the elution of Cr(III), part of the Cr may evaporate as chromyl chloride (*i.e.*,  $\text{CrO}_2\text{Cl}_2$ ) prior to its atomization with ETAAS.<sup>28</sup> A  $3 \text{ mol l}^{-1}$  nitric acid was used as the eluent of Cr(III). On the other hand, a variety of eluents (*e.g.*, nitric acid,<sup>8,13</sup> hydrochloric acid,<sup>9</sup> potassium chloride solution,<sup>10</sup> and ammonium nitrate/ammonium hydroxide solution<sup>6</sup>) have been used for the elution of Cr(VI). If potassium chloride solution or ammonium nitrate/ammonium hydroxide solution is used as the eluent for Cr(VI), the molecular absorption and light scattering (*i.e.*, spectral interference) may give an error to the absorbance of Cr in the AAS. Chromium(VI) selectively reacts with DPC at around pH 1.<sup>29</sup> Kubota and Yamane<sup>30</sup> eluted only Cr(VI) from an activated alumina column with DPC solution. Therefore,  $1 \text{ g l}^{-1} \text{ DPC}$  solution containing

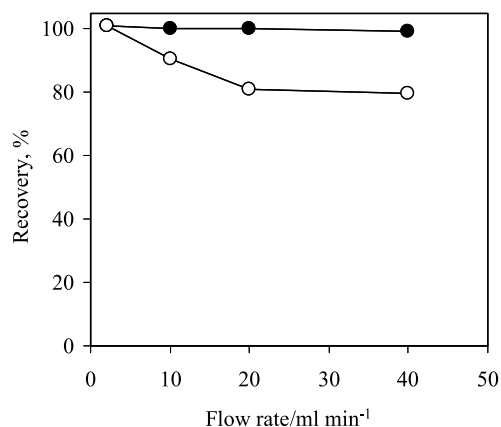


Fig. 3 Variations in the recoveries of Cr(III) (●) and Cr(VI) (○) with flow rate collected on a pair of IED placed on CED and AED, respectively. Cr(III),  $1 \mu\text{g l}^{-1}$ ; Cr(VI),  $1 \mu\text{g l}^{-1}$ ; sample volume, 500 ml; pH for Cr(III), 3; pH for Cr(VI), 10; eluent for Cr(III), 40 ml of  $3 \text{ mol l}^{-1} \text{ HNO}_3$ ; eluent for Cr(VI), 40 ml of  $1 \text{ g l}^{-1}$  DPC solution.

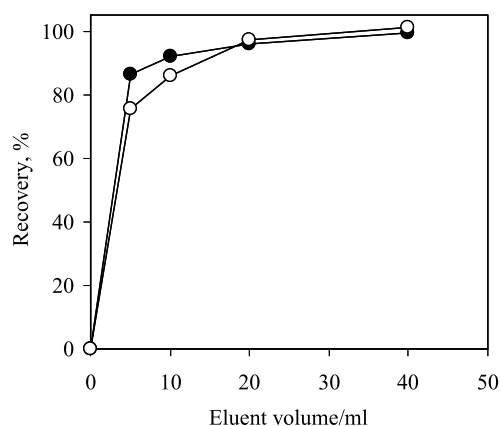


Fig. 4 Variations in the recoveries of Cr(III) (●) and Cr(VI) (○) with eluent volume collected on a pair of IED placed on CED and AED, respectively. Cr(III),  $1 \mu\text{g l}^{-1}$ ; Cr(VI),  $1 \mu\text{g l}^{-1}$ ; sample volume, 500 ml; pH for Cr(III), 3; pH for Cr(VI), 10; flow rate for Cr(III),  $20 - 40 \text{ ml min}^{-1}$ ; flow rate for Cr(VI),  $2 \text{ ml min}^{-1}$ ; eluent for Cr(III),  $3 \text{ mol l}^{-1} \text{ HNO}_3$ ; eluent for Cr(VI),  $1 \text{ g l}^{-1}$  DPC solution.

$0.1 \text{ mol l}^{-1}$  nitric acid was selected as the eluent of Cr(VI). Then, the eluent volumes for the recovery of Cr(III) and Cr(VI) were investigated (Fig. 4). We found that  $0.5 \mu\text{g}$  of Cr(III) and Cr(VI) are completely eluted using 40 ml of each eluent. When the eluate of Cr(VI) was clearly reddish-purple in color, its recovery was always quantitative. This test revealed that Cr(VI) is eluted as a Cr(III)-diphenylcarbazone complex with DPC solution. Consequently, the DPC solution is expected to be a novel eluent of Cr(VI) in environmental samples.

The optimum conditions for the determination of Cr(III) and Cr(VI) in water with SPE disk are given in Table 2.

#### Separation of Cr(III) and Cr(VI)

To separate Cr(III) and Cr(VI), we investigated the collection order of Cr species in a mixture of Cr(III) and Cr(VI) under the proposed conditions (Table 2). For 500-ml test samples containing  $0.50 \mu\text{g}$  of Cr(III) and Cr(VI), Cr(III) was collected first with an IED + CED at pH 3 and then Cr(VI) was collected with an AED at pH 10. The recoveries of Cr(III) and Cr(VI)

Table 2 Optimum conditions for the determination of Cr(III) and Cr(VI) in water with solid-phase extraction disk

Parameter	Cr(III)	Cr(VI)
Adsorbent	IED + CED	AED
Sample pH	3	10
Sample flow rate/ $\text{ml min}^{-1}$	20 - 40	2
Eluent	$3 \text{ mol l}^{-1} \text{ HNO}_3$	$1 \text{ g l}^{-1}$ DPC solution
Eluent volume/ml	40	40

IED: Iminodiacetate extraction disk.

CED: Cation-exchange extraction disk.

AED: Anion-exchange extraction disk.

DPC: Diphenylcarbazide.

Table 3 Analytical results of Cr(III) and Cr(VI) in the certified reference material of river water (JSAC 0302-3)

Sample	Concentration/ $\mu\text{g l}^{-1}$			
	Cr(III)	Cr(VI)	Total Cr	Certified value
JSAC 0302-3	10.1 (5.8) <sup>a</sup>	<0.8 <sup>b</sup>	10.1	$10.0 \pm 0.2$

Sample volume: 50 ml.

Total Cr: Cr(III) + Cr(VI).

a. Relative standard deviation, % ( $n = 5$ ).

b. Not detected.

were 100 and 98.1%, respectively. Conversely, when Cr(VI) was collected first with an AED at pH 10, followed by Cr(III) with an IED + CED at pH 3, the recoveries of Cr(III) and Cr(VI) were 33.8 and 174%, respectively. The decrease in the recovery of Cr(III) and the increase in that of Cr(VI) were caused by the formation of colloidal hydroxide or oxidation of Cr(III) to Cr(VI) at pH 10.<sup>27</sup> In subsequent collections, therefore, Cr(III) was concentrated with an IED placed on a CED at pH 3 and then Cr(VI) was concentrated with an AED at pH 10.

#### Effect of coexisting ions

The coexisting ions in water may decrease recoveries of Cr(III) and Cr(VI). The major ions in the Tamagawa River were selected as the coexisting ions.<sup>31</sup> When  $0.50 \mu\text{g}$  ( $1.00 \mu\text{g l}^{-1}$ ) of Cr(III) and Cr(VI) were added to 500 ml of artificial freshwater containing  $5 \text{ mg l}^{-1} \text{ Na}^+$ ,  $3 \text{ mg l}^{-1} \text{ K}^+$ ,  $5 \text{ mg l}^{-1} \text{ Mg}^{2+}$ ,  $50 \text{ mg l}^{-1} \text{ Ca}^{2+}$ ,  $10 \text{ mg l}^{-1} \text{ Cl}^-$ , and  $20 \text{ mg l}^{-1} \text{ SO}_4^{2-}$ , the recoveries of Cr(III) and Cr(VI) were 103 and 104%, respectively. The average concentration of major ions in freshwater did not interfere with the recoveries of Cr(III) and Cr(VI).

#### Validation of proposed method

The accuracy of the proposed method was evaluated using JSAC 0302-3. The analytical results are given in Table 3. Chromium in JSAC 0302-3 was prepared by adding potassium dichromate (*i.e.*, Cr(VI)) in  $0.1 \text{ mol l}^{-1}$  nitric acid;<sup>32</sup> however, Cr(VI) was not detected in this test. Chromium(VI) was probably reduced to Cr(III) by preserving JSAC 0302-3 at pH 1,<sup>33</sup> because Cr(VI) is thermodynamically unstable in acidic regions. However, the analytical value of total Cr (Cr(III) + Cr(VI)) obtained in JSAC 0302-3 was in good agreement with the certified value.

#### Application to water samples

The proposed method was applied to the determination of

Table 4 Analytical results of Cr(III) and Cr(VI) in water samples

Sample	Added/ $\mu\text{g l}^{-1}$		Found/ $\mu\text{g l}^{-1}$		Recovery, %		COD <sub>Mn</sub> /mg l <sup>-1</sup>
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	
Tap water (Kawasaki)	0	0	0.22 (5.4) <sup>a</sup>	0.13 (3.7) <sup>a</sup>			<0.5
	1.00	1.00	1.21 (2.2) <sup>a</sup>	1.12 (3.8) <sup>a</sup>	98.1	98.8	
Mineral drinking water (Hokuto)	0	0	0.25 (5.5) <sup>a</sup>	0.25 (3.9) <sup>a</sup>			<0.5
	1.00	1.00	1.25 (3.3) <sup>a</sup>	1.24 (2.7) <sup>a</sup>	99.4	98.5	
Hot-spring water (Musashimurayama)	0	0	<0.08 <sup>b</sup>	0.13 (4.8) <sup>a</sup>			0.5
	1.00	1.00	1.05 (3.1) <sup>a</sup>	1.16 (4.4) <sup>a</sup>	105	103	
Rainwater (Kawasaki)	0	0	<0.08 <sup>b</sup>	0.41 (4.1) <sup>a</sup>			0.7
	1.00	1.00	1.04 (3.3) <sup>a</sup>	1.42 (1.3) <sup>a</sup>	104	101	
River water (Okutama)	0	0	<0.08 <sup>b</sup>	0.31 (5.4) <sup>a</sup>			<0.5
	1.00	1.00	1.06 (4.4) <sup>a</sup>	1.31 (5.5) <sup>a</sup>	106	100	
River water (Hamura)	0	0	0.16 (3.0) <sup>a</sup>	0.16 (5.1) <sup>a</sup>			<0.5
	1.00	1.00	1.19 (4.4) <sup>a</sup>	1.20 (5.2) <sup>a</sup>	103	104	
River water (Kawasaki)	0	0	<0.08 <sup>b</sup>	<0.08 <sup>b</sup>			2.0
	1.00	1.00	0.60 (3.7) <sup>a</sup>	0.77 (5.8) <sup>a</sup>	60.3	76.8	

Sample volume: 500 ml. a. Relative standard deviation, % ( $n = 5$ ). b. Not detected.

sub-ppb levels of Cr(III) and Cr(VI) in water samples. The analytical results together with COD<sub>Mn</sub> values are given in Table 4. Each COD<sub>Mn</sub> value in Table 4 is the average of three measurements using 100 ml water samples; the relative standard deviations of COD<sub>Mn</sub> are less than 5%. The concentrations of Cr(VI) in water samples dropped much below the value (50  $\mu\text{g l}^{-1}$ ) of EQS for Cr(VI). The concentrations of Cr(III) were very low or below the detection limit. The accuracy of these analytical values was evaluated by testing the recoveries of Cr(III) and Cr(VI) in water samples. The recoveries of Cr(III) and Cr(VI) were satisfactory with the exception of recovery from downstream river water. The decreases in the recoveries of Cr(III) and Cr(VI) in downstream water are probably due to the complexing of Cr(III) and reduction of Cr(VI) by DOM in water. This result may be attributable to the discharge of water from several sewage disposal plants in the basin of Tamagawa River. Although the COD<sub>Cr</sub> method can oxidize almost any organic compound, the COD<sub>Mn</sub> method can quantitatively decompose only phenol and carbohydrate.<sup>34,35</sup> Therefore, even if the COD<sub>Mn</sub> of a certain water sample is estimated at a low value, Cr(VI) in its sample may be reduced easily to Cr(III) by DOM in water.

## Conclusions

A simple method using solid-phase extraction combined with metal furnace atomic absorption spectrometry was proposed for the determination of Cr(III) and Cr(VI) at sub-ppb levels in water. The iminodiacetate extraction disk and cation-exchange extraction disk were used for concentrating Cr(III). The anion-exchange extraction disk was used for concentrating Cr(VI). Chromium(III) and Cr(VI) could be determined without using an oxidant or a reductant by utilizing a difference in pH of the sample solution. The validation using JSAC 0302-3 indicated the usefulness of the proposed method. The recovery test for 1  $\mu\text{g l}^{-1}$  of Cr(III) and Cr(VI) in relatively clean water showed good recoveries (98.1 – 106%). This study revealed that Cr(VI) is eluted with diphenylcarbazine solution. In addition, the decreases in the recoveries of Cr(III) and Cr(VI) in downstream river water suggest that the complexing of Cr(III) and Cr(VI) or reduction of Cr(VI) tend to occur in organically polluted water.

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