

# On-line Electrochemical Oxidation of Cr(III) for the Determination of Total Cr by Flow Injection–Solid Phase Spectrophotometry

Shiro MATSUOKA,<sup>\*†</sup> Yu NAKATSU,<sup>\*\*</sup> Kô TAKEHARA,<sup>\*\*</sup> Sulistyo SAPUTRO,<sup>\*\*\*</sup> and Kazuhisa YOSHIMURA<sup>\*\*</sup>

<sup>\*</sup>*Department of Environmental Science, Faculty of Science, Niigata University, Ikarashi, Niigata 950-2181, Japan*

<sup>\*\*</sup>*Department of Chemistry, Faculty of Sciences, Kyushu University, Ropponmatsu, Chuo, Fukuoka 810-8560, Japan*

<sup>\*\*\*</sup>*Department of Mathematics and Natural Science Education, Faculty of Teacher Training and Education Sciences, Sebelas Maret University, Jl. Ir. Sutami No. 36A, Kentingan, Surakarta-57126, Indonesia*

A novel on-line oxidation method of ultra-trace Cr(III) dissolved in natural water has been developed using a flow electrolysis cell. This method was successfully applied to the determination of the total Cr concentration by flow injection–solid phase spectrophotometry using diphenylcarbazide as a coloring agent. With the applied potential of 1.35 V (*vs.* Ag/AgCl) and the flow rate of 0.80 cm<sup>3</sup> min<sup>-1</sup>, Cr(III) was quantitatively oxidized to Cr(VI) at room temperature. The total Cr concentration of sub- $\mu\text{g dm}^{-3}$  in 3–4 samples could be determined within 1 h using an aqueous sample volume of 7.1 cm<sup>3</sup>. The analytical values of the total Cr concentration in natural water were in good agreement with those obtained by ICP-MS. The detection limit of the proposed method was 0.014  $\mu\text{g dm}^{-3}$  ( $3\sigma$ ,  $n = 7$ ). This method could be applied to the specific determination of Cr(III) and Cr(VI) in river water samples.

(Received July 18, 2006; Accepted September 12, 2006; Published December 10, 2006)

## Introduction

Chromium is mostly present in two different oxidation states, Cr(III) and Cr(VI): Cr(III) is one of the essential trace elements, whereas Cr(VI) is very toxic to organisms. Since it has been demonstrated that Cr(VI) compounds are carcinogenic to humans, the routine monitoring of the Cr(VI) concentration in the environment has become significant. However, the specific determination of very low concentrations of Cr is very difficult, and for that reason, the total Cr concentration is used as a convenient alternative. For example, the current guideline value of 50  $\mu\text{g dm}^{-3}$  for total Cr in drinking water<sup>1</sup> has been accepted instead of Cr(VI) probably due to difficulties in the speciation of Cr(III) and Cr(VI). Recently, as the regulation of Cr content in water or in air is being tightened, it is expected that the need for not only a higher sensitivity but also a convenient analytical method for Cr will increase. In addition, the total Cr concentration in surface water was reported to be in the range of 0.02 to 2  $\mu\text{g dm}^{-3}$ ,<sup>2</sup> and there are great demands for routine analytical methods to determine such low total Cr in water samples in the research fields such as environmental chemistry or geochemistry.

A variety of methods for the determination of Cr have been proposed during the past ten years. The sensitivity of the methods using atomic absorption spectrometry (AAS) is not sufficient for the determination of Cr at  $\mu\text{g dm}^{-3}$  concentration

levels without some preconcentration procedures.<sup>3</sup> In some cases, the limit of detection (LOD) of 0.3  $\mu\text{g dm}^{-3}$  was obtained by direct determination using graphite furnace AAS.<sup>4</sup> The LOD's of flame emission spectroscopy<sup>5</sup> and inductively coupled plasma–atomic emission spectrometry (ICP-AES)<sup>6</sup> were reported to be on  $\mu\text{g dm}^{-3}$  levels, which are not sufficient for the direct determination of Cr in surface waters. Inductively coupled plasma–mass spectrometry (ICP-MS) is well known as a useful tool for the determination of trace elements whose concentrations are on the sub- $\mu\text{g dm}^{-3}$  levels. For chromium determination, however, it suffers from matrix effects due to molecular ion peaks such as <sup>40</sup>Ar<sup>12</sup>C and <sup>35</sup>Cl<sup>16</sup>OH for the <sup>52</sup>Cr analysis and <sup>37</sup>Cl<sup>16</sup>O for the <sup>53</sup>Cr analysis. Therefore, they also have to undergo some pretreatment steps for the sample solution in order to eliminate the matrix ions.<sup>7</sup>

Flow injection–solid phase spectrophotometry (FI-SPS) is a method in which the light absorption by the target chemical components that are concentrated in the solid phase packed in a flow-through cell is directly measured.<sup>8,9</sup> This flow method is more sensitive than the corresponding conventional solution method without using any expensive instrumentation. The FI-SPS using *syn*-diphenylcarbazide (DPC), which is known to be the most sensitive and selective coloring reagent for Cr(VI), has already been reported.<sup>10</sup> Furthermore, the total chromium concentration on a sub- $\mu\text{g dm}^{-3}$  level in natural water could be determined using peroxodisulfate as the oxidizing agent of Cr(III).<sup>11</sup> Although the LOD of this FI-SPS method was very low (0.015  $\mu\text{g dm}^{-3}$ ) when using a 7.9 cm<sup>3</sup> sample solution, the sample solution had to be heated for 20 min at 80°C together with the oxidizing agent for complete oxidation of Cr(III) when

<sup>†</sup> To whom correspondence should be addressed.  
E-mail: matsuoka@env.sc.niigata-u.ac.jp

a large amount of organic compounds is included in the samples. This time-consuming and troublesome oxidation procedure had to be made by a batch operation. If the on-line oxidation of Cr(III) can be performed, this FI-SPS method for Cr will become simple and its flexibility for routine analysis will be broadened.

For the oxidation of the target chemical component in a sample solution, an electrochemical method has the advantage for the oxidation of Cr(III) over other methods using oxidizing agents because it is free from any contamination by impurities in the oxidizing agents. Zanello and Raspi reported that Cr(III) could be electrochemically oxidized using a platinum electrode as the working electrode, and the detection limit by voltammetry was as low as  $0.2 \text{ mg dm}^{-3}$ .<sup>12</sup> Lin *et al.* described an electrochemical reactor for the on-line oxidation of Cr(III) to Cr(VI).<sup>13</sup> When using Au as the working electrode, however, the application of a constant potential caused a decrease in the response with an increased sample injection volume, probably due to the adsorption of oxidation products on the surface of the working electrode. As for the conversion efficiency of the proposed electrochemical reactor, moreover, only 40% of the Cr(III) could be oxidized to Cr(VI) even under their optimal experimental conditions, and this efficiency was critically dependent on the sample flow rate.

In the present study, a new on-line electrochemical oxidation method, using a vycor glass tube in which folded platinum mesh is used as the working electrode, was applied to the determination of total chromium at room temperature using FI-SPS with DPC as the coloring agent. In order to optimize the conditions for the on-line oxidation of Cr(III) in water, CV measurements of Cr(III) solution were applied first, and then both the validity and the practicability of the proposed system were examined. As the dilution of sample solution for the electrolysis did not affect the sensitivity of the FI-SPS detection system, this system could be effectively applied to the total Cr determination together with the specific determination of Cr(III) and Cr(VI) at sub- $\mu\text{g dm}^{-3}$  levels in river water samples.

## Experimental

### Reagents and chemicals

All chemicals used were of analytical grade.

Demineralized water prepared by the Milli-Q SP system (Millipore, Milford, MA, USA) was used throughout. All solutions were deaerated by means of an ultrasonic bath after heating at  $40^\circ\text{C}$ .

A standard Cr(VI) solution ( $1000 \text{ mg dm}^{-3}$ ) for atomic absorption spectrometry (Kishida, Osaka, Japan) was used. A standard Cr(III) solution ( $1000 \text{ mg dm}^{-3}$ ) was made from a Titrisol concentrate (Merck, Darmstadt, Germany). A sulfuric acid solution (about  $6.3 \text{ mol dm}^{-3}$ ) was prepared by diluting  $70 \text{ cm}^3$  of concentrated sulfuric acid with water up to  $200 \text{ cm}^3$ . A carrier solution for the sample solution was prepared by diluting  $1.6 \text{ cm}^3$  of the sulfuric acid solution with water up to  $1000 \text{ cm}^3$ . The coloring reagent solution was prepared by dissolving  $0.026 \text{ g}$  of DPC (Wako, Osaka, Japan) in the mixed solution of  $5 \text{ cm}^3$  of acetone and  $4.8 \text{ cm}^3$  of the sulfuric acid solution before diluting to  $500 \text{ cm}^3$  with water. A desorbing agent solution for the regeneration of the cation exchanger packed in a flow-through cell was prepared by mixing  $700 \text{ cm}^3$  of a  $3 \text{ mol dm}^{-3}$  nitric acid solution and  $300 \text{ cm}^3$  of acetone.

The Muromac 50W-X2 cation-exchange resin (100–200 mesh, Muromachi, Tokyo, Japan) was packed into a flow-through cell. The macroporous cation exchanger, AG MP-50

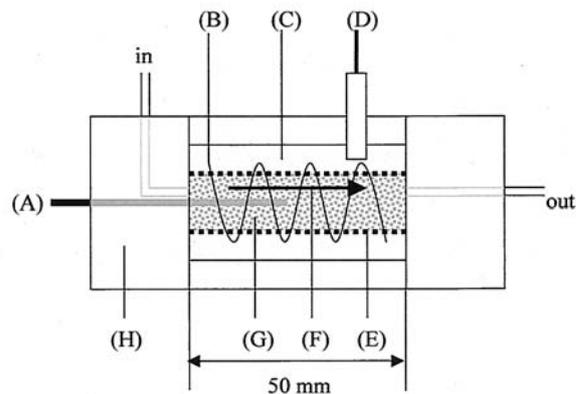


Fig. 1 Schematic illustration of the flow electrolysis cell for the on-line oxidation of Cr(III). (A) Glassy carbon rod for the electrical contact with Pt-mesh working electrode, (B) counter electrode wound around the vycor glass tube, (C) counter solution ( $0.1 \text{ mol dm}^{-3}$  KCl), (D) reference electrode (Ag/AgCl, satd. KCl), (E) vycor glass tube to separate the sample solution and counter solution, (F) sample flow, (G) Pt-mesh working electrode packed into the vycor glass tube, (H) teflon cell block.

(Bio-Rad, Richmond, CA, USA), was packed into a PTFE on-line column to remove the background cations such as calcium and magnesium ions.<sup>11</sup>

### Apparatus

Cyclic voltammetry (CV) was performed using a HECS972 potentiostat (Fuso, Kanagawa, Japan) and HECS321B potential sweep unit (Fuso). Ag/AgCl (satd. KCl) and a Pt wire were used as the reference electrode and the counter electrode, respectively. A glassy-carbon disk electrode ( $\phi 3.0 \text{ mm}$ ) or a Pt disk electrode ( $\phi 1.6 \text{ mm}$ ) was used as the working electrode.

The light measurements were made with a double-beam spectrometer (Model UVIDEC-320, Nippon Bunko, Tokyo, Japan). A perforated metal plate of attenuation 2 was inserted in a reference beam to balance the light intensities. It was mounted vertically and an internally mirrored tube was placed between the cell holder and the light detector window of the spectrophotometer.<sup>8,9</sup> A flow-through cell was supplied from GL Science (Tokyo, Japan). It was black-sided,  $10 \text{ mm}$  in length, and  $1.5 \text{ mm}$  in diameter.

The Model HX-301 flow electrolysis cell (Hokuto Denko Co., Tokyo, Japan) used for the online electrolysis of Cr in the flow system is shown in Fig. 1. For this electrolysis cell, a folded platinum mesh (80 mesh) was packed into the vycor glass tube and used as the working electrode. The counter electrode compartment was filled with a  $0.1 \text{ mol dm}^{-3}$  KCl solution. The sample volume of the electrolysis cell was  $0.90 \text{ cm}^3$ .

The total chromium concentration was also measured by ICP-MS with a Model PMS 2000 (Yokogawa, Tokyo, Japan) spectrometer located at the Center of Advanced Instrumental Analysis, Kyushu University, in order to evaluate the validity of the proposed method.

### Flow diagram

The FI-SPS system for total Cr determination is shown in Fig. 2. The applied potential and the flow rate were set at  $1.35 \text{ V}$  (vs. Ag/AgCl) and at  $0.80 \text{ cm}^3 \text{ min}^{-1}$ , respectively. For the determination of Cr(VI), the flow electrolysis cell was removed from this system and water was used as the carrier solution of the sample.

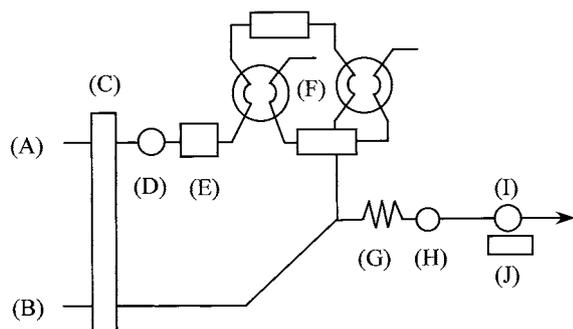


Fig. 2 Schematic flow system diagram for total Cr analysis using flow electrolysis cell. (A) Carrier solution:  $0.010 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ ; flow rate,  $0.80 \text{ cm}^3 \text{ min}^{-1}$ . (B) Coloring reagent solution:  $0.005\%$  (m/v) DPC,  $0.06 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ ,  $1\%$  (v/v) acetone; flow rate,  $0.45 \text{ cm}^3 \text{ min}^{-1}$ . (C) Pump. (D) PTFE six-way rotary valve for sample introduction with a  $7.1\text{-cm}^3$  PTFE tube loop. (E) Flow electrolysis cell. (F) PTFE double four-way valve with two PTFE tube loops ( $2 \text{ mm}$  i.d.,  $20 \text{ cm}$  long) packed with AG MP-50 cation exchanger ( $100\text{--}200$  mesh) in the hydrogen form. (G) Reaction coil, PTFE tube ( $1 \text{ mm}$  i.d.,  $1.5 \text{ m}$  long). (H) PTFE six-way rotary valve for desorbing agent solution introduction,  $2 \text{ mol dm}^{-3} \text{ HNO}_3$ ,  $30\%$  (v/v) acetone. (I) Flow-through cell packed with Muromac 50W-X2 cation exchanger ( $100\text{--}200$  mesh) in the hydrogen form. (J) Spectrophotometer.

#### Procedures for determination of the total chromium and for speciation of chromium dissolved in natural water

Some natural water samples were collected from surface streams in the town of Chikuho (Fukuoka, Japan), where metamorphic rocks such as phyllite with minor intrusions of amphibolite and serpentine occur. Eight sampling sites were selected in this area; 4 sites numbered from 1 to 4 were in a quarry and the others (numbered 5 to 8) were outside the quarry. Sample waters were filtered through  $0.20 \mu\text{m}$  membrane filters at the sampling sites and stored in PTFE containers. For the total chromium determination, sulfuric acid was added to the sample solution to make a  $0.01 \text{ mol dm}^{-3}$  final concentration at the laboratory. The samples ( $7.1 \text{ cm}^3$ ) containing  $0.5$  to  $25 \text{ ng}$  of Cr were directly introduced into the flow system. The measurements of the absorbance increase were made in a manner similar to that previously reported.<sup>11</sup> For the specific determination of Cr with a different oxidation state, the Cr(III) concentration was calculated by the difference between the values of the total Cr and Cr(VI).

#### Procedure for determination of chromium in rock

Mixed with  $1 \text{ g}$  of  $\text{Na}_2\text{CO}_3$  in a platinum crucible,  $0.100 \text{ g}$  of a powdered sample was decomposed by heating for  $1 \text{ h}$ . After cooling, the cake was added to the sulfuric acid solution in order to dissolve the cake and neutralize the  $\text{Na}_2\text{CO}_3$ . The hydrogen ion concentration was then adjusted to  $0.02 \text{ mol dm}^{-3}$  with sulfuric acid. After filtering, the solution was used for the Cr analysis in a way similar to that previously reported.<sup>11</sup>

#### Procedure for determination of chromium by ICP-MS

All the water samples were acidified to  $1.0 \text{ mol dm}^{-3}$  by adding highly purified concentrated nitric acid (Kanto Chemical, Japan); then they were stored in PTFE containers (Hagitec, Japan). The standard addition method was used for the determination of the total chromium using the  $^{53}\text{Cr}$  intensities in a way similar to that previously reported.<sup>11</sup>

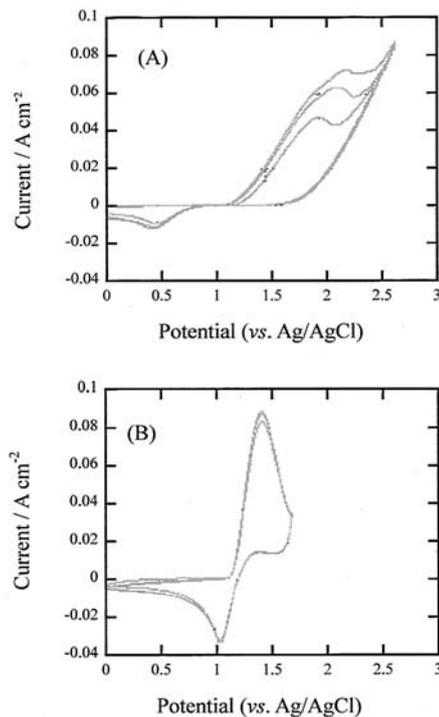


Fig. 3 Cyclic voltammograms of  $10^{-3} \text{ mol dm}^{-3} \text{ Cr(III)}$  in  $0.1 \text{ mol dm}^{-3} \text{ KCl}$  at pH 2. (A) Glassy carbon working electrode, (B) Pt working electrode.

## Results and Discussion

### CV measurements of chromium

In order to optimize the conditions for the electrolytic oxidation such as the applied potential or the type of working electrode using the flow electrolysis cell, CV measurements of Cr(III) solution was carried out. Figure 3 shows the cyclic voltammogram of  $0.1 \text{ mol dm}^{-3} \text{ Cr(III)}$  solution obtained by using a glassy-carbon disk (A) or a platinum disk (B) used as the respective working electrodes. The results show no anodic peak at electrode potentials up to  $1.5 \text{ V}$  when the glassy-carbon disk was used as the working electrode. This is probably due to the change in the surface property of the glassy-carbon electrode when sweeping to this over-potential. In contrast, a well-defined anodic peak corresponding to the oxidation of Cr(III) to Cr(VI) was observed at the potential of  $1.45 \text{ V}$  when the platinum disk was used as the working electrode. This peak was reproducible for several potential scan cycles. Therefore, platinum was used as the working electrode for the quantitative oxidation of Cr(III) to Cr(VI).

In our preliminary experiment, the oxidation of Cr(III) in natural waters containing a large amount of organic compounds by electrolysis was examined using an Ag/AgCl, a Pt wire and Pt mesh electrodes as the reference, the counter and the working electrodes, respectively.<sup>11</sup> Under the applied voltage of  $2.0 \text{ V}$ , only  $10\%$  of the Cr(III) in natural water could be oxidized. This electrolytic oxidation was carried out by the batch method using a  $50 \text{ cm}^3$  inner volume electrolysis cell and about a  $2 \text{ cm}^2$  Pt mesh electrode with magnetic stirring. Such a system might be inadequate for the slow oxidation reaction of the organic complexes of Cr(III), probably due to very small surface area of the Pt mesh working electrode for the sample solution volume of around  $50 \text{ cm}^3$ . To improve the oxidation efficiency, we then

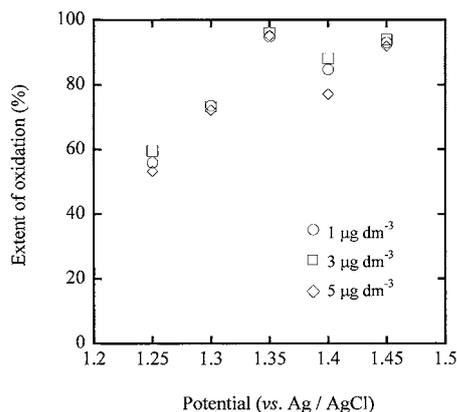


Fig. 4 Effect of the electrolysis potential on the oxidation efficiency of Cr(III) measured by using the flow electrolysis cell.

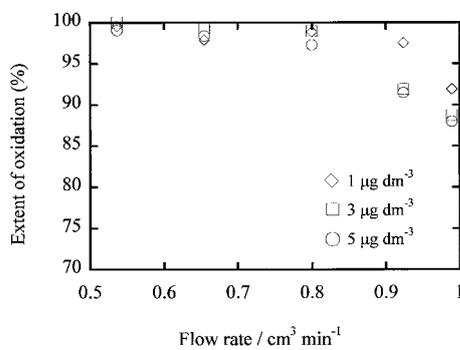


Fig. 5 Effect of the flow rate of sample solution on the oxidation efficiency of Cr(III) measured by using the flow electrolysis cell.

used in this study both a Pt working electrode of 80 mesh which is folded and packed into the vycor glass tube and a small volume flow-type electrolysis cell ( $0.9 \text{ cm}^3$ ) (Fig. 1).

#### Effect of the applied potential and the flow rate on the extent of Cr(III) oxidation

To determine the experimental conditions of the flow electrolysis, we examined the effects of the electrolysis potential and the sample flow rate on the oxidation efficiency of the Cr(III) oxidation. Figure 4 shows the effect of the applied potential on the efficiency of the oxidation of Cr(III) to Cr(VI) observed using the flow electrolysis cell. The oxidation efficiency increased with the applied potential up to 1.35 V (vs. Ag/AgCl) and then slightly decreased, which disagrees with the results that the maximum oxidation efficiency was obtained by the CV measurements at the applied potential of around 1.45 V (vs. Ag/AgCl). The water decomposition and oxygen generation reactions occurred at potentials higher than 1.35 V together with the oxidation reaction of Cr(III) to Cr(VI), which could have some effect on the oxidation efficiency of the proposed flow electrolysis system. The electrolysis potential of the proposed system was therefore set at 1.35 V. Figure 5 shows the effect of the flow rate on the oxidation efficiency at the applied potential of 1.35 V. The quantitative oxidation of Cr(III) was confirmed at flow rates less than  $0.80 \text{ cm}^3 \text{ min}^{-1}$  and the flow rate was set at  $0.80 \text{ cm}^3 \text{ min}^{-1}$  for the flow electrolysis.

The dilution of the sample solution decreases the sensitivity in a conventional FIA system. In contrast, the sample dilution did not affect the sensitivity of the FI-SPS system because the target

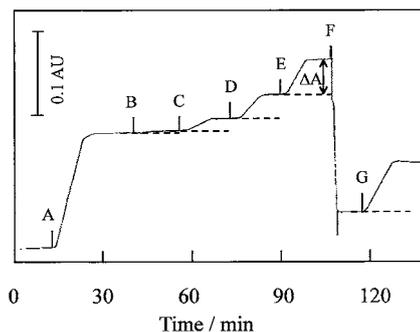


Fig. 6 Color-development profiles of Cr(III) obtained by FI-SPS with the electrochemical oxidation system. Sample volume introduced,  $7.1 \text{ cm}^3$ . (A) Applied voltage of 1.35 V (vs. Ag/AgCl), (B) blank, (C) 0.35 ng Cr(III), (D) 0.85 ng Cr(III), (E) 1.28 ng Cr(III), (F) desorbing agent solution, and (G) 1.92 ng Cr(III).

species were accumulated on the resin packed in the detection cell.

#### Color development profile and calibration

Figure 6 shows typical color development profiles obtained using the proposed FI-SPS system. With the application of 1.35 V at point (A) in the profile, the absorbance increased to a constant value even in the absence of the target species. The DPC that was continuously supplied by the pump may be partly oxidized at the applied voltage of 1.35 V. The colored oxidation product of DPC is distributed on the cation-exchange resin in the flow-through cell at a low distribution ratio, and the adsorption and elution of this oxidation product of DPC in the resin phase reach the steady state within a short time period.<sup>9</sup> This is why the increase and plateau of the absorbance were observed just after the application of the oxidation potential. After the light absorption becomes constant, each  $7.1 \text{ cm}^3$  sample solution of different concentrations was introduced at points (B) to (E) and (G) in the profile. The absorbance due to the reaction product of Cr(VI) with DPC proportionally increased with the concentration of Cr(III) in the sample solutions. The increase in the absorbance from the baseline ( $\Delta A$ ) can be expressed by the following equation:

$$\Delta A = (0.227 \pm 0.010)C + (0.002 \pm 0.002) \quad (1)$$

where  $C$  is the sample concentration in  $\mu\text{g dm}^{-3}$ . For 5 calibration curves prepared on different days, the standard deviations of the slope and intercept are also shown in Eq. (1). Because the ion exchange capacity of the solid particles in the flow-through cell decreases after long use, the deteriorated resin beads are required to be replaced by new ones. Then, fluctuations of the slopes of the calibration graphs were larger than those in Eq. (1). Anyway, the sensitivity similar to that in the previous report could be obtained even though the sample solution was diluted when using the flow electrolysis cell.

#### Recovery, precision and detection limit

In order to check the recovery, the standard addition method was carried out and the results are listed in Table 1. The water samples collected from the sites Nos. 2 and 5 were selected and the total chromium concentrations in the respective sample solutions were measured by the proposed FI-SPS system. Although the contents of the coexisting cations, such as  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ , in these sample solutions were at  $\text{mg dm}^{-3}$  or greater

Table 1 Standard addition method on the total chromium determination for natural water<sup>a</sup>

Sampling site No.	Cr added/ $\mu\text{g dm}^{-3}$	Cr found/ $\mu\text{g dm}^{-3}$	Recovery, %
2	0	$0.21 \pm 0.01$ ( $n = 4$ )	—
	0.71	0.91	98
	1.42	1.67	103
	2.13	2.27	97
5	0	$0.40 \pm 0.04$ ( $n = 5$ )	—
	0.49	0.87	96
	0.99	1.42	103
	1.47	1.92	101

a. 10 cm<sup>3</sup> of natural water samples were diluted to 25 cm<sup>3</sup> before measurement.

Chemical composition (No. 2, No. 5): water temperature (7.4, 9.4°C); pH (7.90, 9.89); Na<sup>+</sup> (4.9, 3.3 mg dm<sup>-3</sup>); K<sup>+</sup> (0.41, 0.28 mg dm<sup>-3</sup>); Mg<sup>2+</sup> (13.6, 58.3 mg dm<sup>-3</sup>); Ca<sup>2+</sup> (8.3, 2.0 mg dm<sup>-3</sup>); Cl<sup>-</sup> (5.6, 6.4 mg dm<sup>-3</sup>); SO<sub>4</sub><sup>2-</sup> (9.4, 8.2 mg dm<sup>-3</sup>); NO<sub>3</sub><sup>-</sup> (6.2, 7.9 mg dm<sup>-3</sup>); alkalinity (1.28, 4.80 mmol dm<sup>-3</sup>); SiO<sub>2</sub> (7.2, 1.8 mg dm<sup>-3</sup>).

levels, it is clear that the recovery for each sample solution was acceptable and the results show that the proposed system does not suffer from matrix effects.

To evaluate the accuracy of the proposed method, the Cr contents in three reference rocks, JA-1, JB-2 and JG-1 (Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology, Japan), were also determined. The results are listed in Table 2. The obtained values were in fairly good agreement with the respective certified values.<sup>14</sup>

In order to evaluate the LOD ( $3\sigma$ ), we repeatedly measured the blank signal. The obtained LOD was  $0.014 \mu\text{g dm}^{-3}$  ( $n = 7$ ), which was almost the same as that obtained by the batch-wise oxidation method using peroxodisulfate of  $0.015 \mu\text{g dm}^{-3}$ .<sup>11</sup>

#### Application to natural water

Table 3 shows the results on the total Cr in eight surface water samples. In order to evaluate the validity of the results, we also carried out ICP-MS measurements using the standard addition method. The total Cr concentrations in the natural water samples obtained by the proposed method essentially agreed with those obtained by ICP-MS; the reliability of the ICP-MS results cannot be very high because the blank signal of <sup>53</sup>Cr corresponded to the Cr concentration of  $0.4 \mu\text{g dm}^{-3}$ . These results show that both the on-line oxidation and the Cr(VI) determination were completely performed. Using the same flow system with and without the electrolysis flow cell made it possible to specifically determine the Cr(III) and Cr(VI) concentrations in various natural water samples, as shown in Table 3. Chwastowska *et al.* mentioned that the concentration of Cr(VI) in water samples was usually about one order of magnitude lower than that of Cr(III).<sup>4</sup> However, in our previous work using peroxodisulfate, our results were quite different; the predominant Cr species in natural water was Cr(VI).<sup>11</sup> Although the excellent selectivity of DPC for Cr(VI) is widely recognized and there should be no room for the Cr(VI) data to include systematic positive errors, the complete oxidation of Cr(III) in the sample solutions might not be made by peroxodisulfate, or relatively low concentrations of Cr(III) might produce large errors. In this study, therefore, we have applied the new on-line oxidation method to the specific determination of Cr in various natural waters collected near abandoned chromite mines, in which the Cr(III) concentration

Table 2 Determination of chromium in reference rock samples

Sample	Total Cr concentration/ $\text{mg kg}^{-1}$	Certified value/ $\text{mg kg}^{-1}$
JA-1	$8.29 \pm 0.34$ ( $n = 5$ )	7.83
JB-2	$27.9 \pm 1.7$ ( $n = 5$ )	28.1
JG-1	$51.8 \pm 1.3$ ( $n = 5$ )	53.2

Table 3 Speciation of chromium dissolved in natural water ( $n = 3$ )

Sampling site No.	Concentration/ $\mu\text{g dm}^{-3}$			
	Cr(III)	Cr(VI)	Total Cr	
			Proposed method	ICP-MS ( <sup>53</sup> Cr)
1	$0.16 \pm 0.01$	$0.27 \pm 0.01$	$0.43 \pm 0.01$	$0.34 \pm 0.04$
2	$0.01 \pm 0.04$	$0.44 \pm 0.03$	$0.45 \pm 0.03$	$0.44 \pm 0.03$
3	$0.09 \pm 0.06$	$0.46 \pm 0.04$	$0.55 \pm 0.04$	$0.56 \pm 0.08$
4	$0.12 \pm 0.03$	$0.67 \pm 0.02$	$0.79 \pm 0.02$	$0.81 \pm 0.04$
5	$0.43 \pm 0.04$	$0.65 \pm 0.03$	$1.08 \pm 0.03$	$0.98 \pm 0.05$
6	$0.04 \pm 0.03$	$0.65 \pm 0.02$	$0.69 \pm 0.02$	$0.77 \pm 0.04$
7	$0.10 \pm 0.04$	$0.77 \pm 0.03$	$0.87 \pm 0.03$	$0.95 \pm 0.02$
8	$0.02 \pm 0.01$	$0.57 \pm 0.01$	$0.59 \pm 0.01$	$0.67 \pm 0.04$

pH of respective sample solutions (from No. 1 to No. 8) was 8.59, 7.90, 7.94, 7.89, 9.89, 7.08, 7.65, 7.98.

was considered to be higher than that of Cr(VI). The results in Table 3 show that the Cr(VI) concentrations in these water samples were greater than or comparable to the Cr(III) concentrations. The predominant Cr species dissolved in well-aerated natural water samples may be Cr(VI).

## Conclusions

When a sample solution contains a high concentration of organic compounds, to oxidize Cr(III) into Cr(VI) using an oxidizing agent is difficult because a considerable amount of the oxidizing agent is consumed by the oxidation of the organic constituents. In such a case, the concentration of the oxidizing agent in a sample solution should be high, which may cause an increase in the blank signal. On the other hand, the concentration of oxidizing agent in the reduced form becomes higher as the oxidation reaction proceeds, which lowers the oxidation potential of the oxidizing agent and disturbs the quantitative Cr(III) oxidation. Based on this study, the application of the on-line electrochemical cell made it possible to quantitatively oxidize Cr(III) to Cr(VI) without any oxidizing agents and to measure the total Cr using FI-SPS with diphenylcarbazide as the coloring agent.

The sample dilution using the on-line electrochemical cell did not affect the sensitivity of the FI-SPS system because the target species were accumulated on the resin packed in the detection cell after the on-line oxidation. The proposed on-line oxidation method is also expected to be applicable for the differentiation of the oxidation states of trace metal ions using FI-SPS.

## Acknowledgements

The authors would like to express their sincere thanks to Dr. Jun

Aizawa of Fukuoka University for the geological information on an abandoned chromite mine near Fukuoka City.

## References

1. U. S. Department of Health and Human Services, Toxicological Profile for Chromium, **2001**, <http://www.atsdr.cdc.gov/toxprofiles/tp7.html>.
2. World Health Organization, "Chromium in Drinking Water", in Guidelines for Drinking-Water Quality, 2nd ed., **1996**.
3. H. F. Maltez and E. Carasek, *Talanta*, **2005**, *65*, 537.
4. J. Chwastowska, W. Skwara, E. Sterlińska, and L. Pszonicki, *Talanta*, **2005**, *66*, 1345.
5. J. Posta, A. Gáspár, R. Tóth, and L. Ombódi, *Microchem. J.*, **1996**, *54*, 195.
6. X. Zhu, B. Hu, Z. Jiang, Y. Wu, and S. Xiong, *Anal. Chim. Acta*, **2002**, *471*, 121.
7. Y. C. Sun, C. Y. Lin, S. F. Wu, and Y. T. Chung, *Spectrochim. Acta, Part B*, **2006**, *61*, 203.
8. K. Yoshimura, *Anal. Chem.*, **1987**, *59*, 2922.
9. K. Yoshimura and S. Matsuoka, *Laboratory Robotics and Automation*, **1993**, *5*, 231.
10. K. Yoshimura, *Analyst*, **1988**, *113*, 471.
11. S. Matsuoka, Y. Tennichi, K. Takehara, and K. Yoshimura, *Analyst*, **1999**, *124*, 787.
12. P. Zanello, *Anal. Chim. Acta*, **1997**, *88*, 237.
13. Y. Lin and G. G. Wallace, *Anal. Lett.*, **1990**, *23*, 1477.
14. N. Imai, S. Terashima, S. Itoh, and A. Ando, *Geostandards Newsletter*, **1995**, *19*, 135, <http://www.aist.go.jp/RIODB/geostand/welcome.html>.