Automated Pretreatment System for the Speciation of Cr(III) and Cr(VI) Using Dual Mini-Columns Packed with Newly Synthesized Chitosan Resin and ME-03 Resin

Yoshiaki FURUSHO,*¹ Akhmad SABARUDIN,*² Lukman HAKIM,*³ Koji OSHITA,*⁴ Mitsuko OSHIMA,*³ and Shoji MOTOMIZU*^{3†}

*¹ *GL Sciences Inc., 6-22-1 Nishi-shinjuku, Shinjuku, Tokyo 163-1130, Japan*

*² *Department of Chemistry, Faculty of Science, Brawijaya University, Jl Veteran, Malang 65145, Indonesia*

*³ *Department of Chemistry, Faculty of Science, Okayama University,
3-1-1 Tsushima-naka, Okayama 700-8530, Japan*

*⁴ *Department of International Conservation Studies for Cultural Properties, Faculty of Cultural Properties,
Kibi International University, 8 Iga-machi, Takahashi, Okayama 716-8508, Japan*

Chitosan resin possessing the 4-hydroxyphthalic acid moiety (CCTS-HPA resin) was synthesized. This resin could adsorb chromium(VI) at pH 3 to 5, whereas chromium(III) could not be retained in the acidic region. The CCTS-HPA resin was used for collecting chromium(VI), and ME-03 resin was used for collecting chromium(III) before their measurement by ICP-AES measurement. Both resins were packed in mini-columns and installed serially in a laboratory-assembled automated pretreatment system (Auto-Pret System). The system provides a highly sensitive and fully automated procedure for the speciation of chromium(III) and chromium(VI). The proposed system was successfully applied to speciation of chromium(III) and chromium(VI) using 5 ml of water samples. The detection limits ($S/N = 3$) of chromium(III) and chromium(VI) were 0.06 and 0.04 $\mu\text{g l}^{-1}$, respectively, along with an analysis time of 7 min 45 s for both chromium species. The lowest determinable concentrations for both chromium species were about 0.5 $\mu\text{g l}^{-1}$, which was enough for the speciation of chromium in water samples.

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Introduction

The speciation study of chromium is an important and exciting challenge for analytical communities in environmental, clinical, and biological research, and in the control of water system due to the growing awareness that the toxicity and biological activity of chromium are strongly dependent on their oxidation states.¹⁻³

Toxic chromium enters the water system from industrial effluent or waste-disposal sources, such as wastewater from steel works, electroplating, wood preservation, and tanning industries.^{4,5} The total chromium content in surface water is approximately 0.5 – 2 $\mu\text{g l}^{-1}$, of which 0.02 – 0.3 $\mu\text{g l}^{-1}$ exists in the dissolved form.⁶

The United State Environmental Protection Agency (USEPA) has regulated 0.1 mg l^{-1} of total chromium in drinking water.⁷ The maximum tolerable concentration of chromium in drinking water regulated in Japan as well as by World Health Organization (WHO) is 0.05 mg l^{-1} .^{8,9} Consequently, the development of accurate and sensitive analytical methods for the speciation of chromium is absolutely required.

The most widely employed procedures for the speciation of chromium in water samples are based on the retention of Cr(III) and Cr(VI) on the solid-phase materials prior to instrumental analysis. For these purposes, several speciation strategies have been reported so far. One is based on the use of an adsorbent

that retains both Cr(III) and Cr(VI), followed by sequential elution under different solvent conditions.¹⁰⁻¹² Chromium speciation is also possible by a collection method based on the retention of one chromium species on the ion-exchange or chelating resin, whereas the other species is oxidized or reduced and retained on the same resin. This strategy includes the adsorption of the chromium(III)-chelate complex on the ion-exchange resins, whereas Cr(VI) is reduced to Cr(III) for the adsorption and determination of total chromium.^{13,14} Similarly, the Cr(VI)-chelate complex can be adsorbed on the ion-exchange resins, while Cr(III) is oxidized to Cr(VI) before being collected on the resins.^{15,16} Another method is to use solid materials that selectively retain Cr(III), whereas Cr(VI) remains in solution. Chromium(VI) is reduced to Cr(III) and its concentration calculated on the basis of the difference between the two contents of chromium found before and after the oxidation.¹⁷⁻¹⁹ However, the concentration of Cr(VI) in water samples is usually about one order of magnitude lower than Cr(III), and therefore the contents of the Cr(VI) species obtained as a difference between two values may cause large errors.

The best option for the speciation of chromium(III) and (VI) is based on the individual collection of Cr(III) and Cr(VI) by using a dual-column system. The dual-column system was constructed using the same sorbents^{20,21} or different sorbents.^{6,22-24} When the same sorbent is used, a pre-oxidation or pre-reduction process is required, which makes the procedure somewhat complicated. The use of a different dual-column system for the on-line speciation of Cr(III) and Cr(VI) was first reported by Naghmush *et al.*²² A similar method was also reported by

† To whom correspondence should be addressed.
E-mail: motomizu@cc.okayama-u.ac.jp

Motomizu *et al.*⁶ and Hashemi *et al.*²⁴ However, these latter methods suffer from high concentrations of matrix existing in water samples, which significantly reduce the sorption efficiency of chromium species on the column.

In this work, chitosan cross-linked with ethyleneglycoldiglycidylether was chemically modified with 4-hydroxyphthalic acid (CCTS-HPA resin), and the adsorption behaviors of Cr(III) and Cr(VI), as well as other 60 elements, were investigated by using a mini-column method. It was found that CCTS-HPA resin showed excellent selectivity toward Cr(VI) at pH 3–5, whereas Cr(III) could not be adsorbed at an acidic region. Another chelating resin, ME-03, which is now commercially available, has a good adsorption ability for Cr(III), while Cr(VI) is hard to adsorb on the resin. Therefore, by exploiting the merit of CCTS-HPA and ME-03 resins, the speciation of Cr(III) and Cr(VI) was favorably developed. The Auto-Pret System with two mini-columns provides a highly sensitive and fully automated procedure for the speciation of Cr(III) and Cr(VI). In addition, the proposed method can provide less reagent consumption and high sensitivity (LOD: 0.06 $\mu\text{g l}^{-1}$ for Cr(III) and 0.04 $\mu\text{g l}^{-1}$ for Cr(VI)) in the use of 5 ml of samples, as well as good separation of the analytes from commonly existing matrices in water samples.

Experimental

Reagents and materials

The 4-hydroxyphthalic acid (HPA) and chitosan flake were purchased from Tokyo Kasei Co. Ltd. (Tokyo, Japan). Other reagents were of analytical reagent grade.

Multi-element standard solutions were prepared by the accurate dilution of a mixed stock solution containing 10 mg l^{-1} metal ions for ICP-MS, XSTC-13 and XSTC-1 (Spex CertiPrep, Metuchen, NJ, USA) and other single-element stock solutions (1000 mg l^{-1}) for AAS (Wako Pure Chemical, Osaka, Japan).

A 1000 mg l^{-1} stock standard solution of Cr(III) was prepared by dissolving chromium nitrate nonahydrate (Wako Pure Chemicals) in a 0.01 mol l^{-1} ultrapure-grade nitric acid solution (Kanto Chemical, Tokyo, Japan). A 1000 mg l^{-1} Cr(VI) stock standard solution was prepared by dissolving sodium chromate tetrahydrate (Kanto Chemical) in ultrapure water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}^{-1}$). Diluted standard solutions of Cr(III) and Cr(VI) were prepared daily by accurate dilution of the stock solutions with a 0.2 mol l^{-1} ammonium acetate solution (pH 3.5). The ammonium acetate solution was prepared by mixing electronic-grade acetic acid (96%) and ammonia water (29%) (Mitsubishi Chemicals, Japan).

The CCTS-HPA and ME-03 resins were packed in mini-columns made of PTFE tubing (2 mm i.d. $\times$ 4 cm length) equipped with quartz wool at both ends of tubing to keep the resins inside the columns. Sample solutions were filtered through a nitrocellulose ester membrane filter (0.45 μm , Advantec, Ehime, Japan). The CCTS-HPA resin was, for the first time, synthesized in our laboratory, and ME-03 resin was provided by GL Sciences Inc.

Apparatus

An ICP-AES system (Vista Pro, Seiko Instruments, Chiba, Japan) was used for the measurement of chromium at a wavelength of 267.716 nm. The operating condition of ICP-AES was similar to that in our previous work.^{6,20,21} The ICP-AES was coupled with a laboratory-assembled automated pretreatment system (Auto-Pret System), which consists of a syringe pump (SP: Cervo, San Jose, CA, USA) with a volume of 10 ml, an 8-port selection valve (SL: Hamilton, Reno, NV,

USA), an 8-way switching valve (SV-1: Hamilton), and a 6-way switching valve (SV-2: Hamilton). The Auto-Pret System was fully controlled by a computer using home-made software written by Visual Basic. The manifold of the Auto-Pret System is shown in Fig. 1. PTFE tubing (0.8 mm i.d.) was used for assembling all flow lines. A holding coil was prepared using PTFE tubing with a size of 5 m $\times$ 1.6 mm i.d. In this system, only water flows continuously by using a peristaltic pump fixed in ICP-AES, whereas the consumption of other reagents depends on the optimized volumes, which result in much less reagent consumption compared to the conventional flow-based method.

Infrared spectra (4000–400 cm^{-1}) were taken by a KBr pellet method using an FT/IR-4100 spectrometer, JASCO Co. (Tokyo, Japan). An automatic titration system, Model AT-510, Kyoto Electronics Manufacturing Co. (Kyoto, Japan), was used for acid-base titration to estimate the pK_a values of CCTS-HPA resin.

Synthesis of CCTS-HPA resin

CCTS-HPA resin was synthesized through two steps. In the first step, the cross-linked chitosan (CCTS) with the arm of chloromethyloxirane was synthesized in a similar manner as in our previous work.^{25–27} In the second step, 4-hydroxyphthalic acid (HPA; 10 g) was chemically bonded to CCTS (5 g) by coupling the hydroxyl group of HPA with the chloro terminal of the arm of CCTS. In this procedure, a 2 mol l^{-1} NaOH (40 ml) solution was added to a suspended mixture in 100 ml of dioxane, and it was refluxed for 3 h. Then, the final product (CCTS-HPA) was filtered on a glass filter and washed with methanol and water. The synthesis scheme is shown in Fig. 2.

Operating procedures for the speciation of chromium using an automated pretreatment system

The whole procedure involves 5 steps, as follows.

Step 1: Column conditioning. In this step, SV-1 is switched to position 2 (dotted lines in Fig. 1), whereas SV-2 is in position 1 (dotted lines in Fig. 1). SP is set up to aspirate 2000 μl (at a flow rate of 200 $\mu\text{l s}^{-1}$) of a 0.2 mol l^{-1} ammonium acetate solution (NH_4OAc , pH 3.5) into HC via port 1 of SL. It is then dispensed through port 5 at a flow rate of 50 $\mu\text{l s}^{-1}$ for conditioning both columns.

Step 2: Collection and preconcentration. The positions of SV-1 and SV-2 are the same as in step 1, whereas SP is set to aspirate 5000 μl of the samples into HC via port 2 of SL (flow rate, 300 $\mu\text{l s}^{-1}$), followed by flowing it into a column via port 5 (flow rate, 30 $\mu\text{l s}^{-1}$) for the collection and preconcentration of Cr(III) at MC-1 and Cr(VI) at MC-2, as well as removal of the matrices.

Step 3: Washing. After chromium samples are collected on the columns, 1000 μl of ultrapure water (W_1) is aspirated into a syringe (flow rate, 200 $\mu\text{l s}^{-1}$), and immediately afterwards dispensed to wash the columns via port 5 of SL (flow rate, 50 $\mu\text{l s}^{-1}$), while SV-1 and SV-2 are still in the same position as in the previous step.

Step 4: Elution of Cr(VI). In this step, the eluent (2 mol l^{-1} HNO_3 , 500 μl ; flow rate, 200 $\mu\text{l s}^{-1}$) is aspirated into HC via port 3, followed by aspirating ultrapure water (W_1) into the syringe (flow rate, 300 $\mu\text{l s}^{-1}$) to fill it up to 2500 μl . Then, SL is switched to port 5, while SV-1 is switched to position 1 (solid lines) and SV-2 is switched to position 2 (solid lines), as shown in Fig. 1. Afterwards, the zones in the HC, which consists of the zones of the 500 μl eluent (on the front side) and the zones of 2000 μl ultrapure water (in the back side), are dispensed to elute Cr(VI) collected on the CCTS-HPA column (MC-2) at a flow rate of 30 $\mu\text{l s}^{-1}$, followed by its detection with ICP-AES.

Step 5: Elution of Cr(III). Similar to step 4, the eluent (2 mol l^{-1} HNO_3 , 500 μl ; flow rate, 200 $\mu\text{l s}^{-1}$) is aspirated into HC via port 3,

Fig. 1 Automated on-line preconcentration system for the speciation of Cr(III) and Cr(VI). SP, syringe pump; HC, holding coil; SL, 8-port selection valve; SV-1, 8-way switching valve (position 1, solid lines; position 2, dotted lines); SV-2, 6-way switching valve (position 1, dotted lines; position 2, solid lines); MC-1, mini-column packed with ME-03 chelating resin for collection of Cr(III); MC-2, mini-column packed with CCTS-HPA resin for the collection of Cr(VI); PP, peristaltic pump fixed in the ICP-AES system.

Fig. 2 Synthesis scheme of CCTS-HPA resin. CCTS, cross-linked chitosan; HPA, 4-hydroxyphthalic acid; CCTS-HPA, cross-linked chitosan possessing 4-hydroxyphthalic acid.

followed by aspirating ultrapure water (W_1) into the syringe (flow rate, $300 \mu\text{l s}^{-1}$) to fill the syringe up to $2500 \mu\text{l}$. Then, SL is switched to port 5, while SV-1 and SV-2 are switched to position 2. Afterwards, the zones in the HC are dispensed to elute Cr(III) collected on the ME-03 column (MC-1) at a flow rate of $50 \mu\text{l s}^{-1}$, followed by its detection with ICP-AES.

The peak height was used as an analytical signal for preparing calibration graphs and measuring the analytes.

Results and Discussion

Fundamental characteristics of CCTS-HPA resin

The IR spectrum of CCTS-HPA resin, compared with cross-linked chitosan (CCTS), depicted an additional band at 1718.26 cm^{-1} , which is attributed to C=O stretching of the COOH group in the HPA moiety. This additional band is the key point, which

showed the existence of the HPA moiety in the resin.

Figure 3 shows the results of acid-base titration for the synthesized CCTS-HPA resin. There are two pK_a values that can be expected from the chemical structure of the CCTS-HPA resin. The pK_a value comes from $-\text{COOH}$ at the *-meta* and *-para* positions of the HPA moiety. For estimating pK_a of this resin, the pK_a values of phthalic acid, which are attributed to each $-\text{COOH}$ group (pK_{a1} : 2.94 and pK_{a2} : 5.43) can be referred.²⁸ As shown in Fig. 3, a pK_a value of 3.4 was clearly observed from the titration curve. This pK_a value can be attributed to the *meta* position of the $-\text{COOH}$ group. The pK_a value of the $-\text{COOH}$ group at the *para* position cannot be observed, because the neutralization reaction of the $-\text{COOH}$ group overlaps with the neutralization of HCl. In this experiment, 3 ml of 0.10 mol l^{-1} HCl was added to 30 ml of the resin sample solution before titration. Therefore, the pH of the HCl solution was about 2.2,

Fig. 3 Acid-base titration of CCTS-HPA resin. A sample for the titration consists of 1 ml of each resin, 3 ml of 0.1 mol l⁻¹ hydrochloric acid and 27 ml of ultrapure water. A, inflection point of hydrochloric acid; B, inflection point of each resin; C, half point of the equivalent points.

whereas the -COOH group at the *para* position had a pK_a of about 2.9. When the sample, the CCTS-HPA resin, was titrated, apparently the amount of H⁺ from HCl and H⁺ from -COOH group could not be separated. At the first end point (A), the volume of 0.10 mol l⁻¹ NaOH required to neutralize total acid of HCl and -COOH group was 4.3 ml, which is attributed to neutralization of HCl (3.0 ml of NaOH is needed) and the neutralization of -COOH group at *para* position (1.3 ml of NaOH is required). The most important thing is that the volume of NaOH, which is required to neutralize the -COOH group at the *meta* position, should be the same as that used to neutralize the -COOH group at the *para* position. From the second end point (B), it is clear that the numbers of both the -COOH groups are the same as each other, since 1.3 ml of NaOH is needed to neutralize the -COOH group at the *meta* position. From such results, the HPA moiety attached to CCTS was about 0.13 mmol in 1 ml resin (≈0.19 g dry weight), which corresponds to 0.70 mmol g⁻¹ resin.

The adsorption capacity of both resins for Cr(VI) was examined by equilibrating 0.1 g of CCTS-HPA resin with 100 ml of 150 mg l⁻¹ Cr(VI) at pH 3.5. At an appropriate interval time, 0.1 ml of the solution was taken, and subsequently diluted to 100-fold with 1 mol l⁻¹ HNO₃ before a measurement by ICP-AES. It was found that the adsorption capacity of CCTS-HPA resin was 100.9 mg g⁻¹.

Studies on the speciation of Cr(III) and Cr(VI) using CCTS-HPA and ME-03 resins

As shown in Fig. 4, which was for the first time obtained in this work, the CCTS-HPA resin could adsorb almost completely only two elements, such as chromium (pH 3 – 5) and silver (pH 2 – 6). To clarify the chromium species adsorbed on the resins, the adsorption behavior of Cr(III) and Cr(VI) was investigated in detail.

The speciation studies of Cr(III) and Cr(VI) were performed by examining the adsorption of each chromium species on CCTS-HPA resin and commercially available ME-03 resin. The CCTS-HPA resin could adsorb Cr(VI) quantitatively at the pH range of 3 – 5, whereas Cr(III) could not be retained in the acidic region (pH 1 – 4), and was slightly retained at pH 5 – 9. From such results, it was found that the CCTS-HPA resin exhibits

Table 1 Optimized conditions for the on-line preconcentration and speciation of Cr(III) and Cr(VI)

Parameter	Range examined	Selected condition
pH of sample	pH 1 – 9	pH 3.5
Sample loading flow rate	10 – 50 μl s ⁻¹	30 μl s ⁻¹
Eluent concentration	0.5 – 3 mol l ⁻¹ HNO ₃	2 mol l ⁻¹
Eluent volume (2 mol l ⁻¹ HNO ₃)	0.1 – 2 ml	0.5 ml
Eluent flow rate for Cr(III)	10 – 70 μl s ⁻¹	50 μl s ⁻¹
Eluent flow rate for Cr(VI)	10 – 70 μl s ⁻¹	30 μl s ⁻¹

Table 2 Effect of matrices on the recovery of 1 μg l⁻¹ of each Cr(III) and Cr(VI)

Matrix solution	Recovery, ^a %	
	Cr(III)	Cr(VI)
Na ⁺ (50 mg l ⁻¹), SO ₄ ²⁻ (105 mg l ⁻¹)	104.3	97.5
K ⁺ (50 mg l ⁻¹), Cl ⁻ (45 mg l ⁻¹)	97.6	101.7
Ca ²⁺ (50 mg l ⁻¹), NO ₃ ⁻ (155 mg l ⁻¹)	108.7	95.1
Mg ²⁺ (50 mg l ⁻¹), Cl ⁻ (147 mg l ⁻¹)	102.6	102.6
Na ⁺ (20 mg l ⁻¹), K ⁺ (10 mg l ⁻¹), Ca ²⁺ (50 mg l ⁻¹), Mg ²⁺ (15 mg l ⁻¹), SO ₄ ²⁻ (42 mg l ⁻¹), Cl ⁻ (53 mg l ⁻¹), NO ₃ ⁻ (155 mg l ⁻¹)	101.9	96.1
Na ⁺ (50 mg l ⁻¹), K ⁺ (50 mg l ⁻¹), Ca ²⁺ (50 mg l ⁻¹), Mg ²⁺ (50 mg l ⁻¹), SO ₄ ²⁻ (105 mg l ⁻¹), Cl ⁻ (192 mg l ⁻¹), NO ₃ ⁻ (155 mg l ⁻¹)	108.4	93.3

Sample volume: 5 ml (pH 3.5).

a. Recovery (%) = (peak height with matrices/peak height without matrices) × 100.

remarkable affinity and selectivity towards Cr(VI) in acidic regions. It is well-known that in the pH range from 2 to 8, anionic species of Cr(VI) are present in the form of HCrO₄⁻ and CrO₄²⁻ in the aqueous solution, while CrO₄²⁻ is the predominant species above pH 8. Accordingly, the species of Cr(VI) presents in the form of HCrO₄⁻ may adsorb on the CCTS-HPA resin in the acidic regions. In acidic regions (pH 1 – 4), Cr(III) exists as [Cr(H₂O)₆]³⁺, and it tends to be hydrolyzed at pH > 4, and eventually precipitated as Cr(OH)₃. Therefore, the increased response at pH > 4 was probably due to the formation of insoluble hydroxide,²⁹ which could be slightly retained on the resin without any interaction.

The resin, ME-03, showed good collection efficiency for Cr(III) at pH 3 – 5, whereas Cr(VI) could not be retained on this resin. Therefore, in this study, ME-03 resin was selected for the adsorption/collection of Cr(III).

Optimization of an automated pretreatment system (Auto-Pret System) for the on-line speciation of Cr(III) and Cr(VI)

To provide a highly sensitive method for the speciation of Cr(III) and Cr(VI), some experimental variables for an automated on-line preconcentration system, which involved sample pH, sample flow rate, concentration and a flow rate of the eluent, were thoroughly optimized. The optimized parameters of Auto-Pret System are summarized in Table 1. Under the optimal conditions, the total analysis time for both Cr(III) and Cr(VI) was 7 min 45 s when 5 ml of the sample was used.

Effect of matrices

The effects of various matrices on the recoveries of Cr(III) and Cr(VI) were studied, the results were given in Table 2. In this experiment, the effects of single-matrix and mixed-matrices

Fig. 4 Adsorption behavior of trace elements at various pHs with CCTS-HPA resin. Sample, 5 ml; concentration of each element, $5 \mu\text{g l}^{-1}$; column size, $4 \text{ cm} \times 2 \text{ mm i.d.}$; eluent, 2.5 ml of $2 \text{ mol l}^{-1} \text{ HNO}_3$. Data for the adsorption behavior of Cr was obtained for Cr(VI).

Fig. 5 Flow signals of Cr(III) and Cr(VI) obtained by the proposed method. The sample volume was 5 ml; other conditions were the same as in Table 1.

solutions were studied, and the peak heights of each chromium species ($1 \mu\text{g l}^{-1}$) with and without the addition of matrices were compared. As shown in Table 2, the recovery of Cr(III) was in the range of 97.6 to 108.7%, whereas for Cr(VI) it was in the range of 93.3 to 102.6% at various concentrations of the matrices examined. These results indicate that the proposed method is not interfered by matrices constituents present in water samples.

Analytical merits

The peak profiles of $0 - 5 \mu\text{g l}^{-1}$ of each chromium species (sample volume: 5 ml) obtained under the optimum conditions are shown in Fig. 5. The small negative peak was observed just after switching SV-1 and SV-2 in the elution step of Cr(VI) and Cr(III). This system peak appearing just after switching the valves for several seconds does not interfere with the measurements of Cr. The linear dynamic range of the proposed

method was 0.1 to $5 \mu\text{g l}^{-1}$, and the linear equation of the calibration graphs for Cr(III) and Cr(VI) were $Y = 107.6X + 3.0$ ($R^2 = 0.9948$) and $Y = 151.4X + 8.3$ ($R^2 = 0.9997$), respectively, where X was the Cr concentration ($\mu\text{g l}^{-1}$), and Y was intensity (cps). The limit of detection ($S/N = 3$) was 0.06 and $0.04 \mu\text{g l}^{-1}$ for Cr(III) and Cr(VI), respectively. The relative standard deviations ($n = 6$) of analytes examined at $1 \mu\text{g l}^{-1}$ were less than 2%. The enrichment factors were calculated by comparing the peak height obtained by the preconcentration procedure with those obtained without preconcentration by using $5 \mu\text{g l}^{-1}$ of each chromium species (sample volume: 5 ml), and were 10.3 and 15.4 for Cr(III) and Cr(VI), respectively.

Application to the speciation of chromium in water samples

The applicability of the proposed method was demonstrated by the determinations of Cr(III) and Cr(VI) in water samples,

Table 3 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, %	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Zasu River	0	0	0.31 ± 0.02	0.11 ± 0.00		
	0.2	0.2	0.51 ± 0.02	0.32 ± 0.01	99.9	100.3
Asahi River	0	0	0.30 ± 0.02	0.10 ± 0.00		
	0.2	0.2	0.49 ± 0.02	0.31 ± 0.00	97.0	103.4
Tap water (VBL)	0	0	0.15 ± 0.01	0.10 ± 0.01		
	0.2	0.2	0.36 ± 0.00	0.31 ± 0.01	101.6	106.1
Tap water (Fac. of Science)	0	0	0.12 ± 0.02	0.07 ± 0.01		
	0.1	0.1	0.22 ± 0.01	0.17 ± 0.01	94.1	97.0
Mineral drinking water (Volvic)	0	0	0.23 ± 0.02	0.15 ± 0.00		
	0.2	0.2	0.43 ± 0.02	0.36 ± 0.01	97.9	107.1
Mineral drinking water (Evian)	0	0	0.79 ± 0.04	0.62 ± 0.03		
	0.8	0.8	1.61 ± 0.03	1.41 ± 0.02	102.9	97.8

Sample volume: 5 ml (pH 3.5). Other conditions are the same as in Table 1.

as shown in Table 3. According to the results in Table 3, the concentrations of chromium in these samples were much lower than the regulation limit (WHO, $50 \mu\text{g l}^{-1}$), which indicates good environmental management. It also showed that Cr(III) was the main species of Cr in natural water samples and mineral drinking water. To ensure the accuracy of the analytical results, the samples were spiked by known amounts of both chromium species. The recovery of Cr(VI) was found in the range of 97.0 – 107.1%, whereas for Cr(III), it was 94.1 – 102.9%. Such results indicate that the proposed method showed good accuracy.

Conclusions

The use of CCTS-HPA resin and ME-03 chelating resin, which were packed in mini-columns installed into the Auto-Pret System coupled with ICP-AES, allowed the simultaneous determination of both chromium species without pre-oxidation or pre-reduction procedures. Other advantages of the proposed method are: rapid analysis, good sensitivity and accuracy for the determination of Cr(III) and Cr(VI) at sub- $\mu\text{g l}^{-1}$ levels, and less reagent consumption compared to flow-injection methods.^{6,20,21,24} The Auto-Pret System developed in this work can be used as a versatile technique for the speciation of other toxic elements.

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