

Spectrophotometric Determination of Ultra trace Tri & Hexavalent Chromium by Using on-line Flow Injection Analysis with Dual Pre-concentration Column

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An on-line flow injection analysis with dual pre-concentration method was developed to determine the ultra trace tri and hexavalent chromium in water. In this system, the cation and anion pre-concentration columns were combined with a 10-port injection valve and then used to separate and concentrate Cr (III) and Cr (VI) selectively. The two species of concentrated chromium were sequentially eluted and determined by using HCl-KCl buffer of pH 1.8 as an eluent. Cr (III) was oxidized by hydrogen peroxide to Cr (VI). It was detected spectrophotometrically at 548 nm by complexation with DPC (diphenylcarbazide). Several factors such as concentration of H₂O₂, DPC and coil length in reaction condition were optimized. The linear range for Cr (III) and Cr (VI) was 0.1-50 µg/L. The limit of detections (3σ) of Cr (III) and Cr (VI) were 52 ng/L and 44 ng/L under the optimized FIA system, and their recoveries 98% and 103%, respectively. This method was applied to analyze contamination level of chromium species in tap water, groundwater and bottled water.

Key Words : Tri & hexavalent chromium, Flow injection analysis (FIA), Dual pre-concentration column

Introduction

Discharge of heavy metals has caused serious environmental pollution due to a rapid industrialization and a growth in population. The environmental contamination by toxic heavy metals has become a serious environmental problem. In particular, chromium is one of the major pollutants in environment, which have found in several chemical forms with oxidation numbers.¹ It is reported that chromium is discharged from the industries related to plastic coatings, electroplating, leather tanning and finishing, in pigments and for wood preservative. Both a trivalent Cr (III) and hexavalent Cr (VI) form of chromium are stable enough to be found in wastewater samples. The abundant ratio of Cr (III) and Cr (VI) depends on many factors such as the redox potential, pH, the presence of oxidizing or reducing compounds, the kinetics and the total chromium concentration.² Trace amount of Cr (III) is essential to mammals for the maintenance of glucose, lipid and protein metabolism, while Cr (VI) is known to be extremely toxic to humans because Cr (VI) present in the diet is reduced to Cr (III) in the gastrointestinal tract.³ The toxic nature of the Cr (VI) is attributed to their high oxidation potential and their relatively small size, which enables them to penetrate cell membranes.⁴ Hence, selective and sensitive analytical methods for determining speciation of chromium in environmental samples are demanded. The traditional off-line methods involve separation and pre-concentration of a particular chromium species before manual transport of the treated sample to an instrument for the determination of chromium with colorimetric atomic spectrometric techniques.⁵ Therefore, the off-line speciation methods for chromium species are often needed for prolonged sample manipulation. It has

reported that the on-line column pre-concentration methods using FIA system compared to their off-line batch methods offer a number of significant advantages for ultra trace determinations: greater efficiency, lower consumption of sample and reagents, improved precision, reduced risk of contamination and increased sampling frequency.⁶ Several researchers have proposed the on-line dual column methods for the simultaneous determination of Cr (III) and Cr (VI) by combining atomic absorption spectrophotometry with FIA.^{5,7} The method required two different eluents for elution of the analytes, making the FIA analysis rather complicated. Sequential injection analysis (SIA) coupled with AAS using mini column has been reported for the separation of chromium species.^{4,8} Lee *et al.*⁹ reported the method for the determination of Cr (III) and Cr (VI) in urine using a flow injection on-line sorption separation system coupled with electrothermal atomic absorption spectrophotometry. On-line pre-concentration system coupled with elemental analytical methods such as ICP-MS¹⁰ and ICP-AES,¹¹ X-ray fluorescence¹² was used to determine Cr (III) and Cr (VI). On-line coupling of liquid chromatography with ICP-MS is one of the most powerful techniques for chromium speciation, while the instrumentation is quite expensive.⁸ Some successful attempts for automation of the chromium retention and elution on pre-concentration column have been made using the on-line flow injection procedures. FIA with on-line oxidation of Cr (III) to Cr (VI) has been used to automatic 1,5-diphenyl carbazide (DPC) methods, which is selective for Cr (VI), and so that DPC reacts Cr (VI) in acidic medium to form a red-violet colored complex. Cr (III) in environmental samples is usually calculated by the difference between total chromium and Cr (VI) concentration. Such indirect measuring method for Cr (III) is rather incon-

venient and troublesome, but up to now there was no easy and simple way to determine selectively an ultra trace amount of Cr (III). In this work, a FIA system equipped with two kinds of cation and anion exchange pre-concentration columns on ten port valve has been developed for the speciation of Cr (III) and Cr (VI). The FIA system was devised to comprise simple and distinctive components for the determination of Cr (III) and Cr (VI) by eluting sequentially two chromium species concentrated on the cation and anion pre-concentration column with a common eluent.

Experimental Section

Chemicals. The cation (Oasis WCX Online Column – 30 μm , 2.1×20 mm) and anion (Oasis WAX Online Column – 30 μm , 2.1×20 mm) exchange columns were used for pre-concentration of both Cr (III) and Cr (VI). DPC and NaHCO_3 , NaOH were purchased from Sigma (Steinheim, Germany). Stock standard solution of 1000 mg L^{-1} Cr (III) and Cr (VI) were purchased from Aldrich (Milwaukee, USA). All other reagents used were of the highest purity available but at least of analytical reagent grade. The deionized water of $18 \text{ M}\Omega\text{cm}^{-1}$ resistivity used in this work was prepared using Milli-Q water purification system (Millipore, Paris, France).

Preparation of Standard and Reagent Solution. Cr (III) and Cr (VI) working standard solutions were prepared daily, by step-wise dilution of a 1000 mg L^{-1} stock solution. The standard solution of DPC (25 mM) was prepared by dissolving the appropriate amount of DPC in 50 mL of methanol. This solution was then diluted to 500 mL with 0.1 M H_2SO_4 . The eluent was prepared by mixing of 0.2 M KCl (75 mL) and 0.2 M HCl (51 mL) and then diluting the mixture to 500 mL of ultrapure water. The oxidant was prepared by diluting 0.08 M H_2O_2 in Na_2CO_3 (0.05 M) – NaOH (0.1 M) buffer.

FIA System and Apparatus. The FIA system consists of a manifold with a 10-port injection valve (Supelco) and a peristaltic pump (Minipuls-3, Gilson), UV-Vis spectrophotometer (SPD-10A, Shmadzu). All the tubes and reaction coils used were $1/16''$ OD \times 0.5 mm ID PTFE tubing. The samples passed through the reaction coil were detected by UV-Vis spectrophotometer (SPD-6AV, Shmadzu). An Autochro 2000 (Younglin) software was used for data acquisition. For the on-line pre-concentration and detection of both Cr (III) and Cr (VI), the operating procedures and corresponding schematic diagram of the proposed system were shown in Figure 1 and 2. Cr (III) and Cr (VI) were concentrated on the two types of cation and anion exchange column connected to 10-port injection valve, separately. The two species of concentrated chromium were sequentially eluted and quantified by using eluent solution (HCl-KCl buffer, pH 1.8). Cr (III) eluted from the cation exchange pre-concentration column was reacted with hydrogen peroxide to oxidize to Cr (VI) in the oxidation coil (RC.1). The violet coloured reaction product with DPC was detected at 548 nm by UV-Vis detector.

Application to Real Samples. It is known that Cr (VI) exists in forms of H_2CrO_4 , HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$,

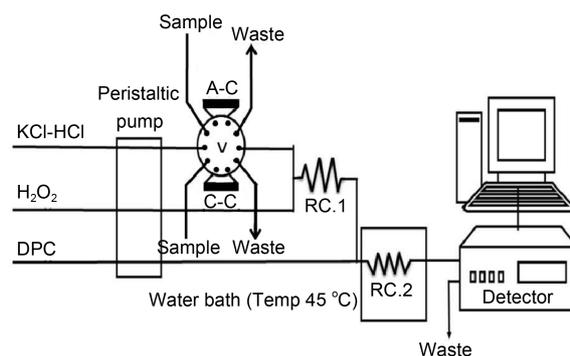


Figure 1. A schematic diagram of the flow injection system to determine Chromium (III and VI) using spectrophotometric detection. A-C, Anion pre-concentration column; C-C, Cation pre-concentration column; RC.1, reaction coil; RC.2, oxidation coil.

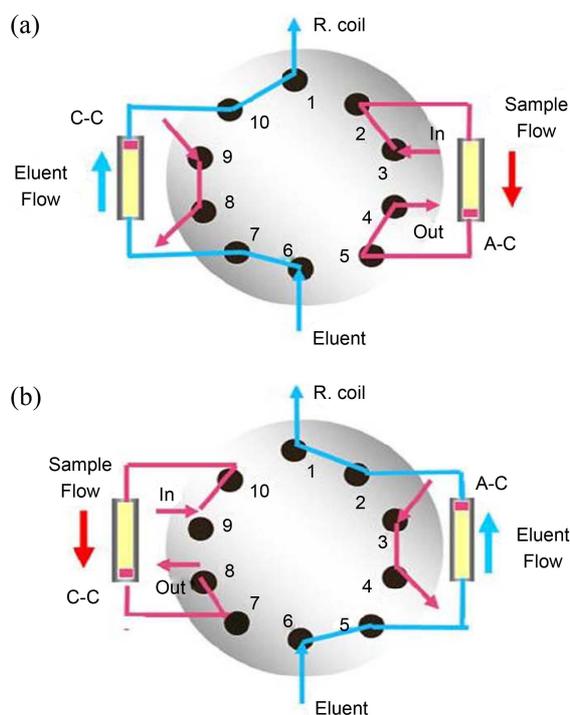


Figure 2. A schematic flow diagram of 10-port injection valve connected with two pre-concentration column. (a) the position for eluting Cr (III) and pre-concentration of Cr (VI); (b) the position for eluting Cr (VI) and pre-concentration of Cr (III); A-C, Anion pre-concentration column; C-C, Cation pre-concentration column.

HCr_2O_7^- in aqueous solution. A change in form of these species is influenced by concentration and acidity of Cr (VI), while Cr (III) exists in a form of Cr^{3+} in acidic solution, and CrOH^{2+} , or $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$, and $\text{Cr}(\text{OH})_4^-$ in basic solution. Han Cui *et al.* reported that Cr (VI) was only partially retained by anion exchange column within the range of $\text{pH} < 4$, attributed to the existence of H_2CrO_4 .¹³ On the other hand, Sun *et al.* represented that the adsorption ability for Cr (VI) was dramatically decreased at below $\text{pH} 4$ on an anion exchange column, while the ability for Cr (III) was rapidly decreased at $\text{pH} > 6$ on cation exchange column. It seemed that the pH range of 5-6 was suitable for pre-concentration

of both Cr (III) and Cr (VI) species.⁷ Thus, the pH of samples should be controlled at a slightly acidic medium to concentrate Cr (III) and Cr (VI) selectively by using a weak anion or a weak cation exchange column. In this work, all the standard solution and interference solution and real sample solution were used by being adjusted close to pH 5 adding acetic acid before they were pre-concentrated.

Results and Discussion

Selection of Eluent. The cation and anion pre-concentration column were combined with a 10-port injection valve and then used to concentrate Cr (III) and Cr (VI), respectively. On-line FIA system which sequentially eluted two different types of Cr (III) and Cr (VI) concentrated on the cation and anion pre-concentration column was established by using a common eluent. An acidic and basic solution as an eluent for desorption of pre-concentration column have been used in the cation and anion pre-concentration column, respectively. Han Cui *et al.*¹³ have reported that Cr (VI) was concentrated on the pre-concentration column packed with strong anion exchange resin and then was eluted with H₂SO₄, NaNO₃, HNO₃, KBr, and NaCl, as the result, the use of NaNO₃ showed the most suitable recovery of Cr (VI). The reason has considered that electrostatic interaction between anion and anion exchange resin varies with ionic strength as well as size of an anion. Sun *et al.* described that satisfactory recovery for Cr (III) and Cr (VI) could be obtained by elution directly to AAS from cation or anion microcolumn for flow injection (FI) on-line pre-concentration with 15% nitric acid or 8% ammonium nitrate solution, respectively.⁷ However, the method was complicated and both of eluents used was too severe. We would like to look for a desorption eluent for eluting commonly Cr (III) and Cr (VI) from cation and anion pre-concentration column under more mild condition for facility and safety of FIA system. Preliminary test for three candidate such as H₂SO₄, HNO₃, and HCl-KCl as a common desorption eluent was carried out. HCl-KCl (pH 1.8) was the most efficient desorbing eluent for both of chromium species, Cr (III) and Cr (VI), concentrated on cation and anion pre-concentration column, respectively. Thus, in this work 0.02 M HCl-0.03 M KCl (pH 1.8) as a common eluent for desorption of Cr (III) and Cr (VI) on pre-concentrated cation and anion column connected to 10-port injection valve was selected in the proposed FIA system.

Oxidation Agent of Cr (III). In this work, Cr (III) and Cr (VI) reacted with DPC in acidic solution and the reaction products were determined by using UV-Vis detector after selective concentration followed by sequential elution. The process is carried out for the determination of a violet colored product which is developed by reaction with Cr (III) reduced after the DPC was converted into 1,5-diphenylcarbazone by the oxidation capability of Cr (VI) as following equation (1) according to the absorption spectroscopy.¹⁴



H₄L : 1,5-Diphenylcarbazide

H₂L : Diphenylcarbazone

Therefore, there is a need to oxidize Cr (III) to Cr (VI) prior to reaction with DPC to determine Cr (III) by UV-Vis spectrophotometric analysis. It was known that oxidants such as K₂S₂O₈, KMnO₄, H₂O₂/NaOH, and KIO₄/NaOH had been often used because of its high oxidation efficiency in many previous studies.^{15,16} KMnO₄ among oxidants mentioned above has a problem in applying to the FIA in this work as it was absorbed same wave length at 548 nm and thus was excluded. K₂S₂O₈, H₂O₂, and KIO₄ were tested by a batch method and, as a result, H₂O₂ showed a little better oxidation efficiency in an basic solution (pH 10) than other oxidants. Therefore, H₂O₂/Na₂CO₃ (0.05 M) – NaOH (0.1 M) buffer (pH 10) was used as an oxidant. The effects of the concentration (0-140 mM) of H₂O₂ on oxidation of Cr (III) were observed when the same amount of Cr (III) and Cr (VI) were injected, respectively (Figure 3). The result was shown the peak area of Cr (VI) was gradually decreased with increasing the concentration of hydrogen peroxide. It appeared because an oxidation reaction of the DPC with Cr (VI) was influenced by hydrogen peroxide. The highest peak area of Cr (III) was achieved at 80 mM in hydrogen peroxide. It can be seen that the peak area of Cr (III) became almost equal to Cr (VI) when the concentration of an oxidant was 80 mM. The peak area of Cr (III) and Cr (VI) were decreased in a similar trend as the concentration of oxidant was increased. The efficiency of oxidation of Cr (III) into Cr (VI) showed more than 99% compared with the peak area of the same amount concentration of Cr (VI) measured by the proposed FIA system. Therefore, H₂O₂ (80 mM)/Na₂CO₃ (0.05 M) – NaOH (0.1 M) buffer (pH 10) was chosen as optimal.

Effect of Oxidation Coil Length. The effect of length of oxidation coil, RC.1, on the determination was examined in the range of 1-5 m to investigate the optimal reaction time for the oxidation reaction Cr (III) eluted from a cation pre-concentration column with oxidant. The result was as shown

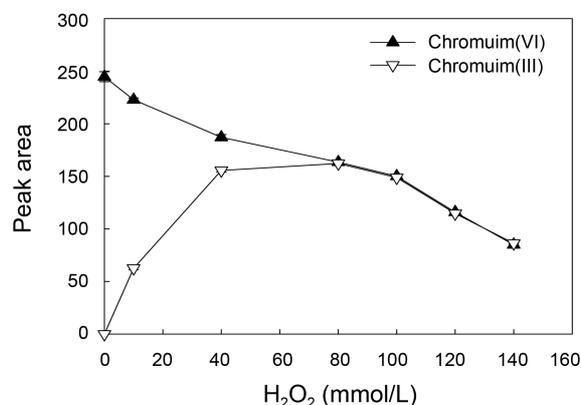


Figure 3. Effect of hydrogen peroxide concentration on peak area. Conditions: eluent, 0.02 M HCl and 0.03 M KCl buffer (pH 1.8); H₂O₂ 80 mM/Na₂CO₃ (0.05 M) – NaOH (0.1 M) buffer; oxidation coil, 2.5 m; DPC 2.5 mM; H₂SO₄ 0.1 M; reaction coil, 1 m; flow rate, 0.5 mL/min; UV-vis detector 548 nm.

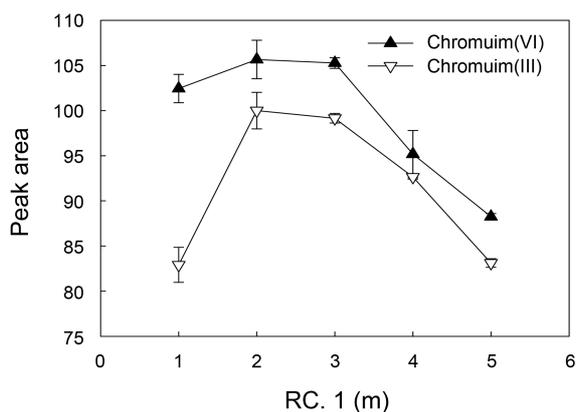


Figure 4. Effect of oxidation coil length on peak area. Experimental conditions are the same as those in Figure 3.

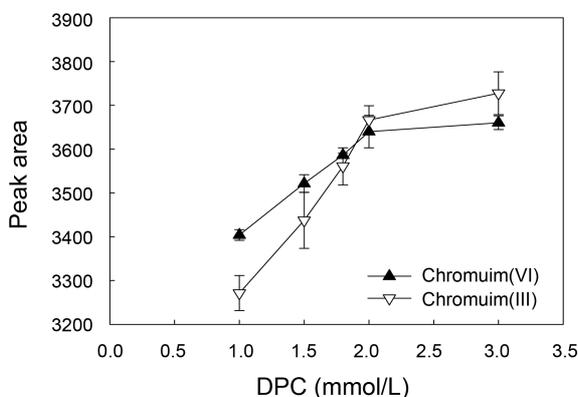


Figure 5. Effect of DPC concentration on peak area. Experimental conditions are the same as those in Figure 3.

in Figure 4. The peak area of Cr (III) increased rapidly up to 2 m with increasing the oxidation coil length, and leveled off over 2-3 m, indicating that the best oxidation efficiency (ca. 95% oxidation) for Cr (III) was achieved in the range 2-3 m. On the other hand, the peak area of Cr (VI) was almost kept constant up to 3 m with increasing the oxidation coil length, and decreased significantly when the length of RC.1 exceeded 3 m where the peak area of Cr (VI) started to be affected by oxidant. Therefore, 2.5 m was selected as optimal length of oxidation coil RC.1.

Effect of Concentration of DPC and Sulfuric Acid. A variation of the absorbance based on the reaction of chromium species with DPC concentration ranged from 1 to 3 mM was examined. The peak area of Cr (III) and Cr (VI) were rapidly increased up to 2 mM, and the peak area of the two chromium species tended to rapidly decrease beyond 2 mM as shown in Figure 5. A decrease in solubility was observed when the concentration of the DPC was more than 3 mM in 10% MeOH. The reaction product of chromium species with DPC was formed well in an acidic condition, and influenced by the pH. Effect of concentration in sulfuric acid was also examined (Figure 6). As a result, it appeared that both of two chromium species got the highest sensitivity at 0.1 M of sulfuric acid solution. Thus, the concentration of DPC and sulfuric acid were selected as 2.5 mM and 0.1 M,

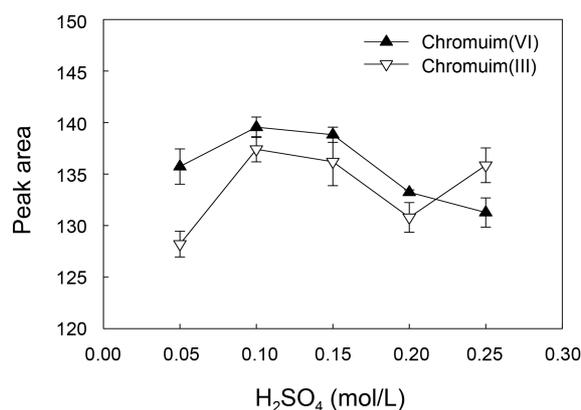


Figure 6. Effect of sulfuric acid concentration on peak area. Experimental conditions are the same as those in Figure 3.

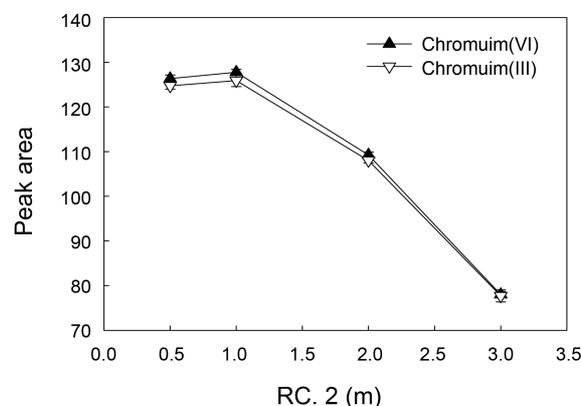


Figure 7. Effect of reaction coil length on peak area. Experimental conditions are the same as those in Figure 3.

respectively.

Effect of Reaction Coil Length. The Cr (III) and Cr (VI) eluted from the two pre-concentration column and then passed through the oxidation coil should react with the DPC in reaction coil, RC.2. The length of a reaction coil was an important factor affecting the result of the FIA system.¹⁷ The effect of length of a reaction coil in the range of 0.5-3 m on absorbance of reaction product between chromium and DPC was investigated after the analytical conditions of the FIA system obtained earlier were fixed (Figure 7). As a result, both Cr (III) and Cr (VI) showed the maximum value of the peak area when the length of a reaction coil was at 1 m, and almost the similar peak area when Cr (III) and Cr (VI) with the same concentration were injected. However, it showed that the peak area of the two chromium species were rapidly decreased when a coil length was exceeded above 1 m. Andersen¹⁶ described that this phenomenon happened because H₂O₂ oxidized Cr (III) into Cr (VI) in an alkaline solution, but reversely reduced Cr (VI) into Cr (III) in acidic solution such as reaction coil (RC.2). Therefore, the length of a reaction coil was selected as 1 m which was not influenced by hydrogen peroxide and seemed to give the highest peak area.

Calibration Curve and Detection Limit. As mentioned above, Cr (III) and Cr (VI) were selectively concentrated

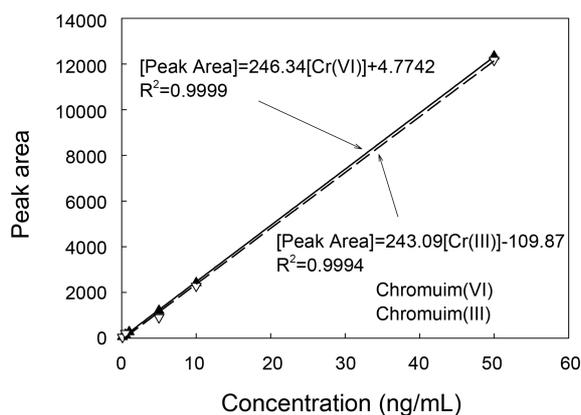


Figure 8. Calibration curves of Chromium (III) and (IV) in the on-line FIA system optimized in this study.

and sequentially detected by reaction with DPC by the proposed FIA system. Cr (III) needs to be oxidized to Cr (VI) followed by reaction with DPC to determine Cr (III) using UV-Vis detector. H_2O_2 was used as an oxidant in basic solution on the present FIA to perform an oxidation process mentioned above. However, the hydrogen peroxide residue influenced partially Cr (VI)-DPC reaction as well as determination of Cr (VI) after addition of oxidant for oxidation of Cr (III) as it can be seen under the proposed FIA system. The reason that a consistent amount of the total chromium was obtained by oxidizing Cr (III) with H_2O_2 could be explained because a consistent data could be achieved if the analytical conditions such as the reagents concentration and flow rate in the proposed FIA system were changed within a specific range. Many studies, which employed the process of oxidizing Cr (III) by using an oxidant in the FIA and SIA system, conformed that the quantitative data could be obtained under constant analytical conditions.^{10,16,18} Calibration curves between 0.1 and 50 $\mu\text{g/L}$ by three replication injection of 5 mL to investigate the determination of Cr (III) and Cr (VI) under the optimum conditions of the proposed FIA system were plotted (Figure 8). Both of calibration curves between Cr (III) and Cr (VI) showed a good agreement and linearity with concentration: Cr (III), regression equation, $PA = 243.09 [Cr(III)] + 109.87$, $R^2 = 0.9994$; Cr (VI), $PA = 246.34 [Cr(VI)] + 4.7742$, $R^2 = 0.9999$. Comparison of both species showed 2% of difference between both of gradients, while around 3.6% of difference between concentrations obtained by two regression equations in a virtual value of peak area,

Table 1. Interference by various ions in Cr (III) and Cr (VI) analysis

Anions	Relative intensity ^a	Cations	Relative intensity
$\text{Cr}_2\text{O}_7^{2-}$ (Cr^{6+})	100	Cr^{3+}	100
Cl^-	ND	Na^+	ND
F^-	ND	K^+	ND
BrO_3^-	4.6	Ca^{2+}	2.5
IO_3^-	3.2	Mg^{2+}	3.5
NO_2^-	ND	Mn^{2+}	5.4
NO_3^-	1.4	Cu^{2+}	3.1
HPO_4^{2-}	ND	Fe^{2+}	8.4
SO_4^{2-}	6.4	Fe^{3+}	33.1
CO_3^{2-}	2.5	Al^{3+}	2.3

^aRelative intensity: Peak area of interference/Peak area of chromium reduced to 100

[PA] = 5000 were represented. Therefore, the sequential analysis of Cr (III) and Cr (VI) was possible under optimal analytical conditions. The limit of detection (3σ) of Cr (III) and Cr(VI) was 52 ng/L and 44 ng/L under the proposed FIA system, respectively.

Interference. The interference of cations and anions were examined which coexisted in a real sample when Cr (III) and Cr (VI) were determined by using the optimized FIA system with dual pre-concentration column. It appeared that interference for counter ions of Cr (III) and Cr (VI) was removed while each Cr (III) and Cr (VI) were concentrated on the cation and anion pre-concentration column and sequentially eluted, respectively. Thus, the interference of 9 anions related to Cr (VI) 5 $\mu\text{g/L}$ (5 mg/L for F^- , Cl^- , BrO_3^- , IO_3^- , NO_2^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} , CO_3^{2-}) and 9 cations related to Cr(III) 5 $\mu\text{g/L}$ (20 mg/L for Na^+ , K^+ , Ca^{2+} , Mg^{2+} and 1 mg/L for Mn^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+}) was examined and the result was shown in Table 1. SO_4^{2-} ion showed the largest interference at 6.4%, while BrO_3^- and IO_3^- ion gave the interference at 4.6 and 3.2% in case of Cr (VI). In addition, anion had the comparatively low sensitivity at below 2.5% compared to the peak of Cr (VI). In the interference of cations to Cr (III), Fe^{3+} ion showed the highest 33.1%, while Fe^{2+} , Mn^{2+} , and Mg^{2+} ions gave the interference of 8.4%, 5.4%, and 3.5%, respectively. Other cations showed the low interference at less than 2.5%. The interference of Fe^{3+} and Fe^{2+} were too strong among interference ions to determine accurately the amount of chromium species in a sample analysis including iron. Thus, the interference of Fe^{3+} ion was

Table 2. Recovery (%) of Cr (III) and Cr (VI) added to water samples (n = 3)

Samples	Cr(VI) added ($\mu\text{g/L}$)	Cr(VI) found ($\mu\text{g/L}$)	Recovery (%)	Cr(III) added ($\mu\text{g/L}$)	Cr(III) found ($\mu\text{g/L}$)	Recovery (%)
Tap Water	0	0.059 ± 0.003	-	0	0.64 ± 0.015	-
Ground Water	0.5	0.57 ± 0.006	101.5	0.5	1.13 ± 0.044	98.1
Bottled Water	0	0.099 ± 0.002	-	0	0.70 ± 0.016	-
Water	0.5	0.61 ± 0.008	103	0.5	1.19 ± 0.013	97.9
Tap Water	0	ND	-	0	ND	-
Ground Water	0.5	0.51 ± 0.008	102.5	0.5	0.49 ± 0.013	98.4

Table 3. Concentrations of Cr (III) and Cr (VI) in real samples (n = 3)

Samples	No	Sampling site	Cr(VI) ($\mu\text{g/L}$)	RSD (%)	Cr(III) ($\mu\text{g/L}$)	RSD (%)
Ground Water	1	C-1	0.29	1.8	1.68	3.3
	2	C-2	0.12	4.1	1.24	2.8
	3	C-3	0.06	3.3	3.33	3.6
Bottled Water	4	C-4	ND	-	0.63	5.1
	5	B-1	ND	-	0.57	2.3
	6	B-2	0.15	1.3	2.15	0.1
	7	B-3	0.08	2.3	0.89	2.8
	8	B-4	ND	-	1.2	0.7

effectively eliminated through the complex and precipitation of Fe^{3+} with phosphate ion by adding 5 times amount of phosphate in solution including Fe^{3+} ion. The interference to Cr (III) were decreased at 11% for Fe^{3+} ion, and 6.5% for Fe^{2+} ion, respectively by adding phosphate(monobasic) to mask the interference of iron. The recovery was investigated by adding an appropriate amount of Cr (III) and Cr (VI) into tap water, groundwater, and bottled water (Table 2). The recoveries of both Cr (VI) and Cr (III) were shown to be ranged of 101-103% and 97.9-98.4%, respectively for 5 mL injection of tap water, groundwater, and bottled water included Cr (III) and Cr (VI) at concentration of 0.5 $\mu\text{g/L}$, respectively. The mean recovery of Cr (VI) was 102%, a little higher than 98% of Cr (III).

Analysis of Real Samples. Four bottled waters were obtained from the market, and four sites of ground waters near Jeonju city were determined. Ground waters and bottled waters were refrigerated at 4 °C after water sampling and then filtering with a 0.45 μm membrane filter, and measured by adjusting to pH 5 with an acetic acid. The results were shown in Table 2. An amount of Cr (VI) was detected in the range of 0.06-0.29 $\mu\text{g/L}$, and Cr (III) was in the ranged 0.63-3.33 $\mu\text{g/L}$, comparatively more than Cr (VI), from samples of three sites except one site among groundwater of four sites. On the other hand, the content of Cr (VI) was distributed in the range of 0.08-0.15 $\mu\text{g/L}$ in bottled water only from two samples. The content of Cr (III) was in the range of 0.57-2.15 $\mu\text{g/L}$, and shown to the similar tendency with the groundwater. It appeared that contamination level for chromium was low due to the absence of contamination source to produce chromium around the four sites.

Conclusion

The study on spectrophotometric determination of ultra trace Cr (III) and Cr (VI) using dual pre-concentration on-line flow injection analysis system was as follows. This work investigated the method for directly determining an ultra trace amount of Cr (III) and Cr (VI) in different way of existing methods which indirectly quantified Cr (III) by subtracting Cr (VI) from total chromium. The FIA system for this work was comprised a cation and anion pre-concentration column installed to a 10-port injection valve, reaction

coils, and UV-Vis detector, and devised to be sequentially injected after pre-concentration of ultra trace amounts of two chromium species. The two chromium species were sequentially eluted and reacted with DPC, and quantified at 548 nm by being desorbed with the mixed solution of 0.02 M HCl and 0.03 M KCl (pH 1.8) after Cr (III) and Cr (VI) were concentrated on a cation and anion-ion exchange column, respectively. Sensitivity of Cr (III) showed almost the same sensitivity with Cr (VI) when 80 mM H_2O_2 was used to oxidize Cr (III) into Cr (VI). The FIA system showed the optimum analytical conditions when the coil length for oxidation of Cr (III) was 2.5 m, the concentration of the DPC was 3 mM, and the coil length for reaction between the DPC and chromium species was 1 m. Under the optimum condition, the interference of cations (9 species) was identified when Cr (III) was quantified, while interference of anions (9 species) was checked when Cr (VI) was quantified. Most ions did not interfere nearly, but phosphate was successfully used to mask Fe^{3+} and Fe^{2+} as Fe^{3+} and Fe^{2+} showed 33.1% and 8.4% of interference for Cr (III), respectively. A calibration curve showed a linear relationship over 0.1-50 $\mu\text{g/L}$, and the detection limits (3σ) of Cr (III) and Cr(VI) showed 52 ng/L and 44 ng/L, respectively. Recoveries of chromium species showed 98.1% for Cr (III) and 102.6% for Cr (VI). The level of Cr (III) was ranged from 0.63 to 3.33 $\mu\text{g/L}$ and Cr (VI) ranged from ND to 0.29 $\mu\text{g/L}$ in groundwater (4 sites), while Cr (III) was ranged from 0.57 to 2.15 $\mu\text{g/L}$ and Cr (VI) ranged from ND to 0.15 $\mu\text{g/L}$ in bottled water (4 samples).

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