

Spectrophotometric Flow Injection Analysis of Chromium(VI) Coupled with On-line Solid-phase Extraction with Anion-exchange Resin Cartridge Column

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Trace amount of CrO_4^{2-} in water sample was collected and concentrated on a cartridge type mini-column (4 cm in length and 2 mm i.d.) packed with anion-exchange resin, Toyopearl QAE-550C. The collection and concentration were carried out automatically using a sequential injection procedure. The handling sequence was the steps of cleaning, washing and conditioning of the resin, collection of CrO_4^{2-} on the resin, and elution of CrO_4^{2-} from the resin to a detection system. The CrO_4^{2-} eluate was introduced into the photometric flow injection analysis system using 1,5-diphenylcarbazide as a derivatizing reagent. When an aliquot of 5.0 mL or 20 mL sample solution was treated, the sensitivity increased by 6.4 and 23 times, respectively. By combining the automated on-line pretreatment system with the photometric flow injection system, CrO_4^{2-} at 10^{-9} mol L⁻¹ level was determined without expensive detectors such as ICP-AES. On the basis of the interference study, the proposed system was applied to the analysis of a river water sample. Concentration of CrO_4^{2-} at 2.5×10^{-9} mol L⁻¹ was determined, and satisfactory results were also obtained with recovery tests.

Keywords Chromium(VI), 1,5-diphenylcarbazide, spectrophotometry, anion-exchange resin, cartridge column, on-line solid-phase extraction

1. Introduction

Concern on the toxicity of metallic elements, such as mercury and lead, leads us to the development of the determination methods at trace levels including chemical speciation. Chromium is one of the notable elements according to the varying toxicity with its oxidation state. While Cr(III) is considered to be essential to living organism, Cr(VI) is suspected to be carcinogenic substance [1,2]. Therefore, WHO provides a provisional guideline level of 0.05 mg L⁻¹ of total chromium for drinking water [1,2].

As determination methods for chromium(VI), photometric reagent of 1,5-diphenylcarbazide (DPC) has widely been used with its specific colorization reaction with Cr(VI) and sensitivity [3]. On the basis of the reaction characteristics, DPC has been used in spectrophotometric flow injection analysis of Cr(VI) [4], as well as speciation analysis of Cr(VI) and Cr(III) [5]. Photometric and chemiluminometric reagents of chromotropic acid [6], lucigenin [7], and $[\text{Ru}(\text{bpy})_3]^{2+}$ complex [8], have also been developed for FIA.

Atomic spectrometry, such as atomic absorption spectrometry (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES), are sensitive detection methods for metallic elements, and chromium has been determined. Since every oxidization state of a certain element is detected at identical sensitivity by the atomic spectrometry, chemical separation should be accompanied with the speciation analysis of dissolved chromium species, *i.e.*, Cr(III) and Cr(VI). Ion-pair solvent extractions of Cr(VI) with DPC and Cl^- to isoamyl alcohol [9] and Cr(VI) with ammonium pyrrolidine dithiocarbamate (APDC) to toluene drop [10] were done prior to electrothermal-AAS determinations. Solid-sorbents were also used for the selective collection of Cr(VI) coupled with off-line pretreatment; Cr(VI)-APDC complex was adsorbed on polymethacrylate resin and was eluted with dilute HNO_3 solution prior to graphite furnace-AAS determination [11]. On-line

pretreatment is convenient for the coupling flow injection analysis with the speciation of Cr(III) and/or Cr(VI). Complex of Cr(VI)-APDC was retained on a cartridge column packed with hydrophobic poly-chlorotrifluoroethylene beads, and was eluted with isobutyl methyl ketone to flame AAS determination [12]. Chelex-100 and anion-exchange resins were used for selective collections of Cr(III) and Cr(VI) species, respectively, and both species were separately determined by flame AAS [13]. Cation-exchange and anion-exchange resin reactors were used to collect and determine Cr(III) and Cr(VI) species, respectively [14]. Oxidation of Cr(III) with Ce(IV) [15], and reduction of Cr(VI) with ascorbic acid [16,17] or hydroxylamine [18] were done prior to the solid-phase extraction of objective species and its determination as total chromium. Solid-sorbents of TiO_2 [19] and Zr modified SiO_2 [20] as packing material were developed for the selective collections of Cr(III) or Cr(VI).

Although atomic spectrometry can determine chromium sensitively, the instrumental and its running costs would be obstacles to establish convenient and inexpensive analysis. Therefore, selective collection and concentration of objective chromium species, that is suitable to the universal detection such as UV-vis spectrophotometry, has intensively been studied to determine the chromium species sensitively. In photometric flow injection manifolds for the determination of Cr(VI), on-line collection and concentration were made with a cartridge column packed with TiO_2 [21] and activated Al_2O_3 [22,23]. A cation-exchange resin was also packed in a photometric flow-through cell [24]. Spectrophotometric sequential injection analysis of Cr(VI) was also studied with reflection spectrophotometry [25], membrane diffusion [26], and lab-on-valve [27] apparatuses.

In this study, we aimed at developing the detection sensitivity toward CrO_4^{2-} by spectrophotometric FIA using DPC as a derivatizing reagent. On-line collection and concentration of CrO_4^{2-} was performed with a cartridge column packed with anion-exchange resin. Chromate ion in sample solution was selectively collected and eluted through a sequential injection procedure, and detected photometrically. Determination of CrO_4^{2-} was achieved at 10^{-9} mol L⁻¹ level.

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2. Experimental

2.1 Reagents

Potassium chromate was purchased from Nacalai Tesque (Kyoto, Japan), and it was used to prepare the standard solution of CrO_4^{2-} . Photometric reagent of 1,5-diphenylcarbazide (DPC), as well as nitric acid, was from Wako Pure Chemical Industries (Osaka, Japan). Toyopearl QAE-550C as strong anion-exchanger (Tosoh, particle size: 50-150 μm) was packed in a cartridge column; the dimensions of the column were 4 cm in length and 2 mm i.d. Both ends of the column were packed with cotton filter. Buffer components of acetic acid and ammonia were from Kanto Chemical (Tokyo, Japan). Water purified with Elix 3/Milli-Q Element (Nihon Millipore, Tokyo, Japan) was used throughout.

2.2 Apparatus

A spectrophotometric FIA system was assembled with a double plunger pump (Sanuki DMX-2000), a switching valve (Hamilton MVP with a valve head of eight-port loop flow path, SW) with a 400 μL injection coil, and a spectrophotometer (Soma Visible detector S3250). An FIA monitor (F.I.A. Instruments) was used to record the absorbance signals. Teflon tubing of 0.8 mm i.d. was used to connect the items.

An automated pretreatment (Auto-Pret) system was also assembled with a syringe pump (Hamilton PSD/2) with a 10 mL glass syringe, a selection valve (Hamilton MVP with a valve head of eight-port distribution flow path, SV). A cartridge column made of acryl-resin block was installed on a switching valve. Anion-exchange resin was packed in the cartridge column and the column was used for the on-line solid-phase extraction. The Auto-Pret FIA system is schematically illustrated in Fig. 1.

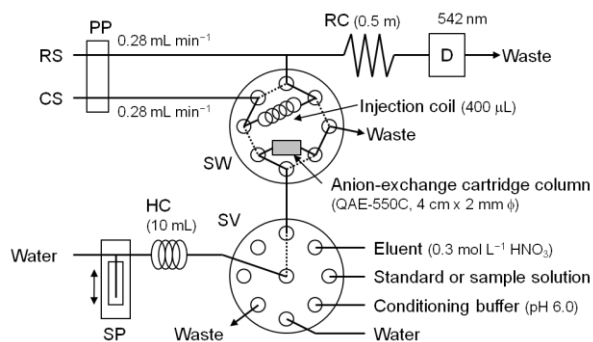


Fig. 1 Schematic diagram of Auto-Pret FIA system.

RS: reagent solution (6×10^{-4} mol L^{-1} DPC dissolved in 0.30 mol L^{-1} HNO_3); CS: carrier solution (0.30 mol L^{-1} HNO_3); PP: double plunger pump; SW: eight-port switching valve; SV: eight-port selection valve; SP: 10 mL syringe pump; RC: reaction coil (0.8 mm i.d. x 50 cm); HC: holding coil (10 mL); D: spectrophotometric detector (542 nm).

2.3 Procedure

Collection/concentration of CrO_4^{2-} was done on an anion-exchange resin cartridge column mounted on an eight-port switching valve (Fig. 1); several solutions were automatically and sequentially passed through the cartridge column by using a syringe pump and an eight-port selection valve. The sequence on collection/concentration from an aliquot of 5.0 mL sample solution to the cartridge column is summarized in Table 1. The

switching valve was kept at an inject position during the collection sequence, as is shown in Fig. 1. After CrO_4^{2-} collected on the cartridge column and washed, the SW was turned to a load position. Chromate ion collected on the cartridge column was eluted with 0.30 mol L^{-1} HNO_3 , and the effluent was passed through the injection coil and held in it, as is written in the last sequence in Table 1. Subsequently, the effluent solution held in the injection coil was propelled to the reaction coil and to the detector by turning the SW to the injection position. Formed complex between CrO_4^{2-} and DPC was detected by a spectrophotometric detector at 542 nm, and the absorbance signal was recorded on an FIA monitor.

Table 1 Operating procedure for the Auto-Pret system

Sequence step	SP	SV port	Flow rate, $\mu\text{L s}^{-1}$	Volume, mL
Cleaning	aspirate	Eluent	100	3.0
	dispense	to SW	85	3.0
Washing	aspirate	Water	100	1.0
	dispense	to SW	85	1.0
Conditioning	aspirate	Buffer	100	3.0
	dispense	to SW	85	3.0
Collection	aspirate	Sample	100	(5.0) ^a
	dispense	to SW	85	(5.0) ^a
Washing	aspirate	Water	100	0.40
	dispense	to SW	85	0.40
Eluting	aspirate	Eluent	100	0.9
	dispense	to SW	45	0.9

a: Sample volume is variable on demand.

3. Results and Discussion

3.1 Physical parameters and its analytical figures of merit for flow injection analysis

Photometric flow injection analysis of chromate ion has been established by using 1,5-diphenylcarbazide as derivatizing reagent detecting Cr(III) complex formed [4,5]. The FIA parameters to realize sensitive detection were also examined in this study with CrO_4^{2-} concentrations at 0 and 1.0×10^{-6} mol L^{-1} ; the results are summarized in Table 2. Calibration graph was drawn at the concentration range of CrO_4^{2-} over $0-1.0 \times 10^{-7}$ mol L^{-1} . Linearity of the calibration graph was $r^2 = 0.993$ with almost zero blank (intercept Abs.: 5×10^{-6}). The limit of detection was calculated to be 5×10^{-9} mol L^{-1} at the signal to noise ratio of 3. Repeatability for 6.0×10^{-8} mol L^{-1} CrO_4^{2-} was 3.1% RSD with 10 measurements. The sample throughput was 12 h⁻¹.

Table 2 Working FIA parameters^a

Parameters	Range examined	Working conditions
Flow rate (single x 2)	0.13 – 0.88 mL min ⁻¹	0.28 mL min ⁻¹
HNO_3 in carrier	0.20 – 0.50 mol L^{-1}	0.30 mol L^{-1}
DPC in RS	4×10^{-5} – 1×10^{-3} mol L^{-1}	6.0×10^{-4} mol L^{-1}
Sample volume	100 – 500 μL	400 μL
RC coil length	0.5 – 3.0 m	0.5 m
Detection wavelength	–	542 nm

a: Examined at $[\text{CrO}_4^{2-}] = 0$ and 1.0×10^{-6} mol L^{-1} .

3.2 Optimization of parameters for the Auto-Pret system

The present study aimed at selective and effective collection/concentration of CrO_4^{2-} and connecting it to the photometric FIA of CrO_4^{2-} . Therefore in this study,

anion-exchange resin, Toyopearl QAE-550C, was packed in the cartridge column to collect CrO_4^{2-} . The sequence of the solution handling was operated as listed in Table 1. The parameters were optimized to achieve efficient collection and sensitive detection of CrO_4^{2-} .

3.2.1 Concentration of HNO_3 in the eluent solution

As a carrier solution in the present FIA, the concentration of HNO_3 was set at 0.30 mol L^{-1} to obtain the highest signal. To meet the Auto-Pret system to the photometric FIA, the concentration of HNO_3 as eluent was examined; the results are shown in Fig. 2. When the concentrations of HNO_3 both in the FIA carrier and in the eluting solution are matched, ghost signal according to the turbulence by mixing two solutions was small, while the signal intensity to CrO_4^{2-} was not changed. Therefore, HNO_3 concentration in the eluent solution was also set at 0.30 mol L^{-1} .

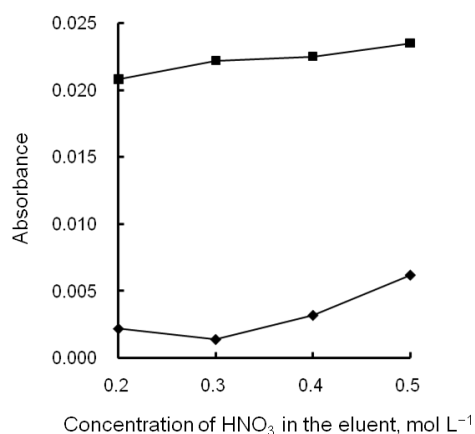


Fig. 2 Effect of concentration of HNO_3 in the eluent. ◆: blank; ■: $[\text{CrO}_4^{2-}] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$.

3.2.2 Eluent volume

The CrO_4^{2-} zone eluted from the cartridge column should efficiently be introduced into the injection coil at the elution step. The sampling volume of the injection loop was $400 \mu\text{L}$, and the eluent volume passing through the cartridge column was examined at the volume range over $400 \mu\text{L}$. The elution was operated in opposite direction of the collection step to reduce the dead volume. The results are shown in Fig. 3. Highest signal was obtained at the eluent volume of $600 \mu\text{L}$. This result indicates that additional volume of $200 \mu\text{L}$ was passed through the

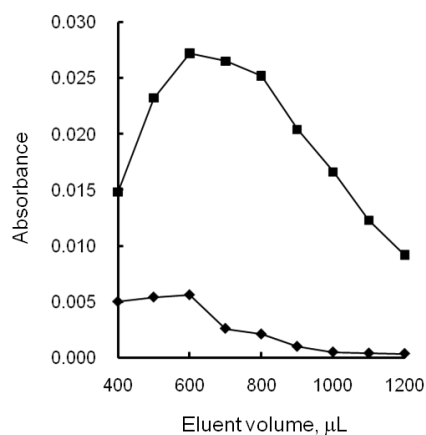


Fig. 3 Effect of eluent volume on FIA signal. ◆: blank; ■: $[\text{CrO}_4^{2-}] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$.

injection coil to collect the most concentrated CrO_4^{2-} zone; the volume would correspond to the dead volume of both of the connection tube and the cartridge column. The blank signal got smaller with increasing volume of the eluent, which would be attributed to the matched solutions between the eluent taken in the injection coil and the carrier solution. Considering the blank level and signal-to-noise ratio, eluent volume of $900 \mu\text{L}$ was selected, *i.e.*, eluent zone from $500 \mu\text{L}$ to $900 \mu\text{L}$ was introduced into the injection coil.

3.2.3 Flow rate of the eluent solution

Flow rate of the eluting solution was examined in the range between $45\text{--}85 \mu\text{L s}^{-1}$; the results are shown in Fig. 4. Highest signal was obtained at the flow rate of $45 \mu\text{L s}^{-1}$, while the blank signal slightly increased with the flow rate. Therefore, the flow rate was set at $45 \mu\text{L s}^{-1}$. The flow rate is the minimum set value with this equipment. Low flow rate would have suppressed the dispersion of the eluted CrO_4^{2-} zone.

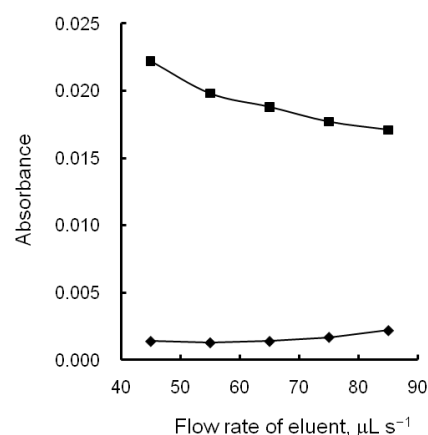


Fig. 4 Effect of flow rate of eluent on FIA signal. ◆: blank; ■: $[\text{CrO}_4^{2-}] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$.

3.2.4 pH of the sample solution

This study adopts anion-exchange mechanism for the collection and concentration of CrO_4^{2-} in an aqueous solution, and pH of the sample solution should be controlled. The pH condition of the sample solution was examined in the range between 1.0 and 9.0. The results are shown in Fig. 5. While the signal intensity for CrO_4^{2-} is smaller at low pH conditions, the intensity was almost plateau at neutral to weakly alkaline pH region. Chromate ion is protonated in acidic pH conditions to form H_2CrO_4 , and adsorption to the anion-exchange resin would be interfered. Considering the hydrolysis of other metal ions, pH of the sample solution was set at 6.0 with 0.50 mol L^{-1} ammonium acetate buffer. The buffer solution was also used as the conditioning solution of the cartridge column.

3.2.5 Flow rate of the sample solution

On handling large amount of sample solution, its flow rate is one of the predominant factors on total analysis time; fast flow rate increases the sample throughput, while quantitative collection is concerned. The flow rate of the sample solution was examined in the range between $45\text{--}85 \mu\text{L s}^{-1}$; the results are shown in Fig. 6. Even at fast flow rate of the sample solution, signal height for CrO_4^{2-} was almost identical. Chromate ion was collected at the entering side of the cartridge column with less dispersion. The flow rate, $85 \mu\text{L s}^{-1}$, was the highest flow rate controllable, and the flow rate was set at $85 \mu\text{L s}^{-1}$.

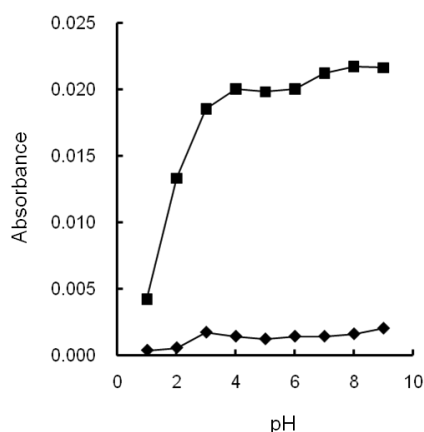


Fig. 5 Effect of sample pH of FIA signal. \blacklozenge : blank; \blacksquare : $[\text{CrO}_4^{2-}] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$.

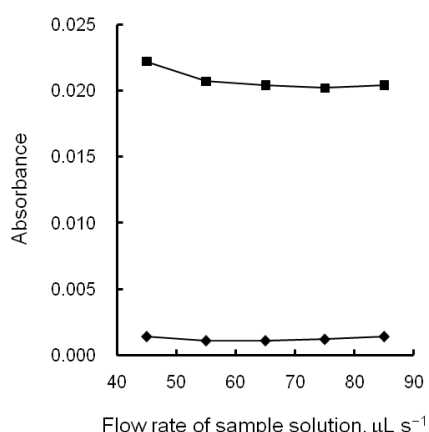


Fig. 6 Effect of flow rate of sample solution. \blacklozenge : blank; \blacksquare : $[\text{CrO}_4^{2-}] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$.

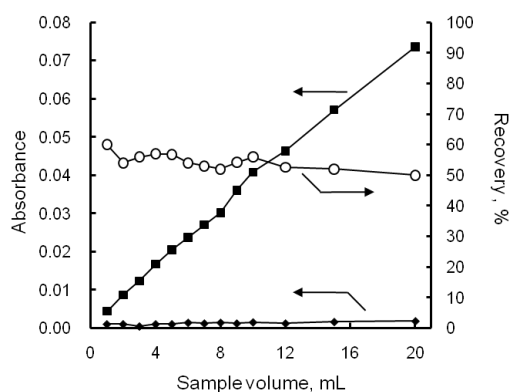


Fig. 7 Effect of sample volume on signal height and recovery. \blacklozenge : blank; \blacksquare : $[\text{CrO}_4^{2-}] = 1 \times 10^{-7} \text{ mol L}^{-1}$.

3.2.6 Effect of sample volume

Treatment of large-volume sample solution was examined to improve both the concentration factor and the detection sensitivity. The sample volume passing through the cartridge column was investigated in the range between 1.0 mL to 20.0 mL. The results are shown in Fig. 7. Signal intensity increased linearly with the sample volume, while the blank signal was almost identical. The results indicate that CrO_4^{2-} was collected on the cartridge column quantitatively. Increases in the sensitivity were 6.4 and 23 times for 5.0 mL and 20 mL sample volumes, respectively.

Recovery of CrO_4^{2-} was calculated by comparing the amount

of CrO_4^{2-} using the maximum absorbance data; the values were around 50%–60% in the volume range examined. The incomplete recovery suggested that CrO_4^{2-} collected on the cartridge column dispersed during the elution, as is discussed in section 3.2.2, and complete introduction to the injection loop was difficult. An aliquot volume of 400 μL among the dispersed zone was reproducibly introduced into the injection coil. Considering the detection sensitivity and analysis time, sample volume of 5 mL was conventionally chosen.

The parameters optimized on Auto-Pret system are summarized in Table 3.

Table 3 Optimized conditions on Auto-Pret system

Parameters	Range examined	Working conditions
Eluent volume	400 – 1200 μL	900 μL
Eluent flow rate	45 – 85 $\mu\text{L s}^{-1}$	45 $\mu\text{L s}^{-1}$
Sample flow rate	45 – 85 $\mu\text{L s}^{-1}$	85 $\mu\text{L s}^{-1}$
pH of sample solution	1.0 – 9.0	6.0
Sample volume	1.0 – 20.0 mL	5.0 mL

3.3 Analytical figures of merit

Calibration graph for CrO_4^{2-} by the photometric FIA coupled with the Auto-Pret system was drawn at the concentrations of $10^{-9} \text{ mol L}^{-1}$ level; the results are shown in Fig. 8, where an aliquot volume of 5.0 mL was treated. Limit of detection on the basis of 3σ of the blank signal was estimated to be $2.2 \times 10^{-9} \text{ mol L}^{-1}$, which corresponded to $0.13 \mu\text{g L}^{-1}$. Reproducibility of the Auto-Pret photometric FIA was examined with 10 replicate measurements of $8.0 \times 10^{-9} \text{ mol L}^{-1} \text{ CrO}_4^{2-}$; the RSD was 8.8 %.

When a sample volume of 5.0 mL was handled by this photometric FIA including Auto-Pret system, the total analysis time was 13 min, while it took 26 min with an aliquot volume of 20.0 mL. The sample volume to be handled would be controlled according to the priority of the analysis, such as rapidity or sensitivity.

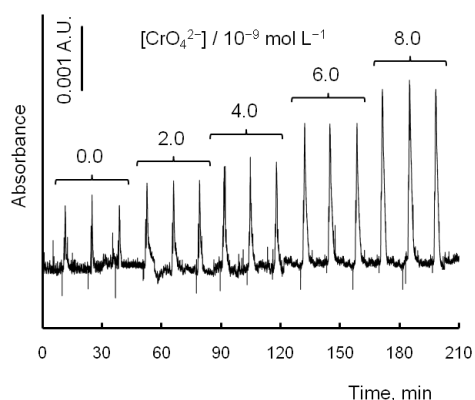


Fig. 8 Calibration graph for CrO_4^{2-} by the Auto-Pret photometric FIA system. Sample volume: 5.0 mL.

3.4 Interferences

Color reaction of 1,5-diphenylcarbazide is specific to Cr(VI), and therefore it is used in photometric FIA. This study adopts anion-exchange mechanism for the on-line concentration of CrO_4^{2-} , and several kinds of inorganic ions as interfering substances were examined; change in the signal height within $\pm 5\%$ was used as a tolerance level. The results are summarized

in Table 4. Interference from most of the cationic species examined is little except for Fe^{2+} ; because Fe^{2+} is a reducing agent. Although CrO_4^{2-} was collected on an anion-exchange cartridge column, most anions did not interfere with the collection and determination of CrO_4^{2-} ; NO_2^- was an interfering substance according to its reducing ability. On the basis of the interfering study, the proposed FIA system is applicable to the practical solutions with low concentrations of salts and ions such as river water and tap water.

3.5 Comparison with reported analysis methods

Various reports have been published for the determination of Cr(VI) in water samples including speciation analysis. The detection method, concentration system, determination range, and limit of detection are summarized in Table 5. Although this study adopts conventional photometric FIA, the limit of detection for Cr(VI) is comparable or close to flame AAS [13,16,20], ET-AAS [19], and ICP-AES [14,18].

Table 4 Effect of coexisting substances

Species	Added as	Conc. / mol L ⁻¹	Recovery, %
Na ⁺	NaF	1.0×10 ⁻¹	98.4
F ⁻	NaF	1.0×10 ⁻¹	98.4
K ⁺	KF	1.0×10 ⁻²	97.9
HCO ₃ ⁻	NaHCO ₃	1.0×10 ⁻²	98.0
H ₃ BO ₃	H ₃ BO ₃	1.0×10 ⁻²	99.1
Cl ⁻	NaCl	1.0×10 ⁻³	95.8
Br ⁻	NaBr	1.0×10 ⁻³	96.3
NO ₃ ⁻	NaNO ₃	1.0×10 ⁻³	95.0
SO ₄ ²⁻	Na ₂ SO ₄	1.0×10 ⁻³	97.5
I ⁻	NaI	1.0×10 ⁻⁴	95.5
Mg ²⁺	MgSO ₄	1.0×10 ⁻⁴	98.4
Ca ²⁺	CaCl ₂ ·2H ₂ O	1.0×10 ⁻⁴	98.9
Fe ³⁺	AAS std. ^a	1.0×10 ⁻⁴	97.8
Al ³⁺	AAS std. ^a	1.0×10 ⁻⁴	96.8
Cu ²⁺	AAS std. ^a	1.0×10 ⁻⁴	96.1
Cr ³⁺	Cr(NO ₃) ₃ ·9H ₂ O	1.0×10 ⁻⁵	97.3
NO ₂ ⁻	NaNO ₂	1.0×10 ⁻⁶	98.9
Fe ²⁺	Mohr salt	1.0×10 ⁻⁷	95.6

a: Standard solution for atomic absorption spectrometry.

Table 5 Comparison of analytical figures of merit

Cr species	Reagents	Detection method	Concentration system	Limit of detection (Determination range)	Ref.
Cr(VI)	DPC	Spectrophotometry	Anion-ex. resin	2.5 nmol L ⁻¹ = 0.13 μg L ⁻¹	This study
Cr(VI)	DPC	Spectrophotometry	–	18 ng mL ⁻¹ (0-2 μg mL ⁻¹)	[5]
Cr(III)	(Ce ^{IV} Ox.)	Spectrophotometry	–	55 ng mL ⁻¹ (0-4 μg mL ⁻¹)	
Cr(VI)	Chromotropic acid	Spectrophotometry	–	1 μg L ⁻¹ (3-4000 μg/L)	[6]
Total Cr	(KIO ₄ Ox)	Spectrophotometry	–	10 μg L ⁻¹ (30-1200 μg/L)	
Cr(VI)	[Ru(bpy) ₃] ²⁺	Fl. quenching	–	33 ng mL ⁻¹ (0.1-20 μg mL ⁻¹)	[8]
Cr(VI)	DPC-Cl ⁻	ET-AAS	Solvent Extraction	0.024 μg L ⁻¹ (0-2 μg L ⁻¹)	[9]
Cr(VI)	APDC	ET-AAS	Solvent Extraction SIA	0.02 μg L ⁻¹ (0.5-6 μg L ⁻¹)	[10]
Cr(VI)	APDC	GF-AAS	Polymethacrylate resin	0.03 μg L ⁻¹	[11]
Total Cr	(Direct)	GF-AAS	–	0.3 μg L ⁻¹	
Cr(VI)	APDC	Flame AAS	PCTFE beads MIBK	0.4 μg L ⁻¹ (1-50 μg L ⁻¹)	[12]
Cr(III)	–	Flame AAS	Chelex-100 resin	2 ng mL ⁻¹ (75-350 ng mL ⁻¹)	[13]
Cr(VI)	–	Flame AAS	anion resin	2 ng mL ⁻¹ (75-350 ng mL ⁻¹)	
Cr(III)	–	ICP-AES	Cation-ex. resin disk	0.02 μg L ⁻¹	[14]
Cr(VI)	–	ICP-AES	Anion-ex. resin disk	0.04 μg L ⁻¹	
Cr(VI)	DPC	Spectrophotometry	C18 sorbent	0.02 μg mL ⁻¹ (1-25 μg mL ⁻¹)	[15]
Total Cr	(Ce ^{IV} Ox.)	Spectrophotometry	C18 sorbent	0.02 μg mL ⁻¹	
Cr(III)	–	Flame AAS	Chelating resin	0.2 μg L ⁻¹	[16]
Total Cr	(Ascorbic acid Red.)	Flame AAS	Chelating resin	0.2 μg L ⁻¹	
Cr(III)	–	ICP-AES	IDA resin	0.08 μg L ⁻¹ (0.2-2.0 μg L ⁻¹)	[18]
Cr(VI)	(NH ₂ OH Red)	ICP-AES	IDA resin	0.15 μg L ⁻¹ (0.2-2.0 μg L ⁻¹)	
Cr(III)	–	ET-AAS	TiO ₂ beads	30 ng L ⁻¹	[19]
Cr(VI)	–	ET-AAS	TiO ₂ beads	24 ng L ⁻¹	
Cr(III)	–	Flame AAS	SiO ₂ - ZrP	1.9 μg L ⁻¹ (0-250 μg L ⁻¹)	[20]
Cr(VI)	–	Flame AAS	SiO ₂ - Zr	2.3 μg L ⁻¹ (0-250 μg L ⁻¹)	
Cr(VI)	DPC	Spectrophotometry	TiO ₂ beads	0.8 ng mL ⁻¹ (2-100 ng mL ⁻¹)	[21]
Cr(VI)	DPC	Spectrophotometry	Al ₂ O ₃	0.2 μg L ⁻¹ (1-5 μg L ⁻¹)	[22]
Cr(VI)	DPC	Spectrophotometry	Al ₂ O ₃	0.7 ng mL ⁻¹ (0-0.03 μg mL ⁻¹)	[23]
Cr(VI)	DPC	Spectrophotometry	Cation-ex. in flow	70 pg in 7.9 cm ³ sample	[24]
Total Cr	(S ₂ O ₈ ²⁻ Ox.)	through cell	through cell	120 pg in 7.9 cm ³ sample	
Cr(VI)	DPC	Spectrophotometry	C ₁₈ beads - SIA	2.4 μg L ⁻¹ (0.02-0.5 mg L ⁻¹)	[25]
Cr(VI)	DPC	Spectrophotometry	Membrane SIA	20 μg L ⁻¹	[26]
Cr(VI)	DPC	Spectrophotometry	SIA-LOV	5.6 μg/L (24-2000 μg/L)	[27]
Total Cr	(bismuthate Ox.)	Spectrophotometry	SIA-LOV	6.8 μg/L (32-2000 μg/L)	

3.6 Application to a practical water sample

The proposed Auto-Pret photometric FIA system was applied to the determination of CrO_4^{2-} in river water sample with an aliquot of 5.0 mL volume. Standard addition was carried out for the analysis of Zasugawa river water. The flow signals are shown in Fig. 9, and the analytical results are summarized in Table 5. It can be seen from the results that CrO_4^{2-} in Zasugawa river water was fairly determined. The recovery of the spiked CrO_4^{2-} was also satisfactory.

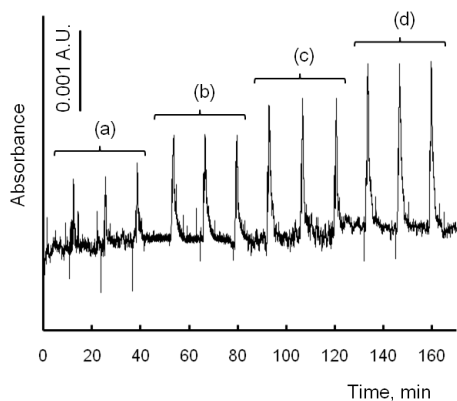


Fig. 9 Flow signals for a river water sample with spike tests. (a), blank; (b), Zasugawa river water; (c), Zasugawa river water spiked with $2.0 \times 10^{-9} \text{ mol L}^{-1} \text{ CrO}_4^{2-}$; (d), Zasugawa river water spiked with $4.0 \times 10^{-9} \text{ mol L}^{-1} \text{ CrO}_4^{2-}$. Sample volume: 5.0 mL. Other conditions are as in Tables 2 and 3. Sampling date: July 22nd, 2010.

Table 6 Analytical results and recovery test for Cr(VI) in river water sample

Sample ^a	CrO_4^{2-} added / $10^{-9} \text{ mol L}^{-1}$	CrO_4^{2-} found / $10^{-9} \text{ mol L}^{-1}$	Recovery, %
Zasugawa	0.0	2.5	–
river	2.0	4.6	105
	4.0	6.4	96

a: Sampled on July 22nd, 2010. Sample volume: 5.0 mL.

4. Conclusion

Chromate ion at $10^{-9} \text{ mol L}^{-1}$ level was determined by spectrophotometric flow injection analysis using DPC as a photometric reagent. On-line collection and concentration were performed on a cartridge column packed with anion-exchange resin through sequential injection procedure. Although CrO_4^{2-} was not introduced to the FIA system completely, the sensitivity increased by the order of 6.4 and 23 times with sample volumes of 5.0 mL or 20 mL, respectively. The proposed system was fairly applied to the analysis of river water sample.

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