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Speciation of V, Cr and Fe by capillary electrophoresis–bandpass reaction cell inductively coupled plasma mass spectrometry

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Abstract

Capillary electrophoresis–dynamic reaction cell inductively coupled plasma mass spectrometry (CE–DRC-ICP-MS) for the speciation of iron(III/II), vanadium(V/IV) and chromium(VI/III) is described. Two different CE migration modes were employed for separating the six metal ions using pre-capillary complexation. One is counter-electroosmotic mode in which iron(III/II) and vanadium(V/IV) ions were well separated using a 60 cm × 75 μm i.d. fused silica capillary. The voltage was set at +22 kV and a 15 mmol l^{-1} tris(hydroxymethyl)aminomethane (Tris) buffer (pH 8.75) containing 0.5 mmol l^{-1} ethylenediaminetetraacetic acid (EDTA) and 0.5 mmol l^{-1} *ortho*-phenanthroline (phen) was used as the electrophoretic buffer. The other is co-electroosmotic mode in which chromium(VI/III) ions were well separated while the applied voltage was set at −22 kV and a 10 mmol l^{-1} ammonium citrate buffer (pH 7.7) containing 0.5 mmol l^{-1} diethylenetriaminepentaacetic acid (DTPA) and 0.01% polybrene was used as the electrophoretic buffer. The mass spectra were measured at *m/z* 51, 52 and 56 for V, Cr and Fe, respectively. The interfering polyatomic ions of $^{35}Cl^{16}O^+$, $^{40}Ar^{12}C^+$ and $^{40}Ar^{16}O^+$ on $^{51}V^+$, $^{52}Cr^+$ and $^{56}Fe^+$ determination were reduced in intensity significantly by using NH_3 as the reaction cell gas in the DRC. The detection limits were in the range of 0.1–0.5, 0.4–1.3 and 1.2–1.7 ng ml^{-1} for V, Cr and Fe, respectively. Applications of the method for the speciation of V, Cr and Fe in wastewater were demonstrated. The recoveries were in the range of 92–120% for various species.

Keywords: Dynamic reaction cell; Complexation; Water analysis; Iron; Vanadium; Chromium; Metal cations

1. Introduction

Metal speciation is important in a variety of environmental, biological, geological and medical applications. The bio-availability, accumulation and toxicological properties of metals are very much dependent on the chemical forms in which they occur in the nature; hence an accurate determination of each species is important to evaluate the potential risk of some metals [1]. Capillary electrophoresis (CE) is being increasingly applied for the determination of metal ions, primarily because of its great flexibility and easy implementation [2]. An overview of the state-of-the-art of capillary electrophoresis (CE) for metal speciation analysis has been presented by Dabek-Zlotorzynska et al. [3]. Separations of metal ions that exist in a free, uncomplexed form are comparatively rare in the practice of CE because the absolute mobility values of most of the metal ions in their free form do not differ enough from one to another to envision electrophoretic separations of practical interest. Obviously, complexation presents the most valuable approach for performing metal speciation and offers a powerful means of manipulation and separation selectivity. Two complexing agents were simultaneously used by several authors reported for the iron speciation by CE with UV-Vis detection [1,3–5]. The redox potential of the Fe^{III}/Fe^{II} system must be maintained at a high level to preserve the stability of samples with respect to oxido-reductive phenomena. This in turn requires a strong complexing agent of Fe^{II}. *ortho*-Phenantroline and ethylenediaminetetraacetic acid (EDTA) or cyclohexanedinitrilotetraacetic acid (CDTA) were selected to complex with Fe^{II} and Fe^{III}, respectively, in previous papers [1,3–5]. On the other hand, a solution of 5 mmol l^{-1} EDTA (pH 4) complexing agent was directly used as a carrier electrolyte for the CE separation of V^V/V^{IV} [1,6]. The CE separation of Cr^{VI}/Cr^{III} was fulfilled by using diethylenetriaminepentaacetic acid (DTPA) [1] and 2,6-pyridinedicarboxylic acid [7] as pre-capillary complexing agent, and the co-electroosmotic mode was used in the papers.

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A variety of CE detectors have been utilized in the metal speciation studies. UV-Vis detection which is available with most commercial instruments has been extensively used in such studied as described above. Photometric schemes are preferred due to ease of set-up (no interface between CE and UV-Vis detector) and minimal loss in separation efficiency [3]. However, derivatization is usually required for UV-Vis detection due to the lack of chromophores in metal ions. The processes might suffer from sensitivity, specificity or productivity limitations. As a detection technique, inductively coupled plasma mass spectrometry (ICP-MS) provides the advantages of low detection limit, multi-element detection, and element- and isotope-specific detection capabilities. CE, a powerful separation technique, has many applications in the field of analytical chemistry when it is coupled with ICP-MS [8,9]. However, a functional interface for coupling of CE and ICP-MS could lead to loss in separation efficiency. The determination of V, Cr and Fe by ICP-MS is known to suffer from the polyatomic isobaric interferences on the vanadium signal at *m*/*z* 51 caused by $^{35}Cl^{16}O^{+}$ and $^{34}S^{16}OH^{+}$, on the chromium signal at *m*/*z* 52 caused by $^{40}Ar^{12}C^{+}$ and $^{35}Cl^{16}OH^{+}$, and on the iron signal at *m*/*z* 56 caused by $^{40}Ar^{16}O^{+}$. Furthermore, ^{50}V (0.25%), ^{53}Cr (9.5%) and other minor isotopes of Cr and Fe will face other isobaric and polyatomic ion interferences. ^{51}V (99.8%), ^{52}Cr (83.8%) and ^{56}Fe (91.7%) were selected in this study. The dynamic reaction cell (DRC) and/or collision cell technique is proved to be an effective method for alleviating such isobaric interferences [10–22]. In order to alleviate such interferences, Jiang and co-workers [18–20] employed DRC-ICP-MS as the detection technique for Cr^{VI}/Cr^{III} and V^{V}/V^{IV} speciation using liquid chromatographic method and determination of total Cr in water and urine samples. Similarly, Deng et al. [21] established DRC-ICP-MS-based immunoassay with ammonia as reaction gas and alleviated argon-based isobaric interference for the Fe determination.

The optimization of the CE–ICP-MS operating conditions and its analytical figures of merit, as well as its applications to V, Cr and Fe speciation in wastewater samples are described in this paper.

2. Experimental

2.1. CE–ICP-MS system

The instrumental setup of the CE–ICP-MS system consists of a laboratory-made capillary electrophoresis unit equipped with a Spellman CZE-1000R high-voltage power supply (Spellman Electronics, Plainview, NY, USA) and an ELAN 6100 DRC-ICP-MS instrument (Perkin-Elmer Sciex, Concord, Canada). Peak areas and peak heights were measured by the Turbochrom Workstation (Perkin-Elmer). Ammonia reaction gas (99.999% purity) was from Air Liquide (Taiwan). The cell gas flow rates were selected as reported by Jiang and co-workers [20,21]. Solution of 5 ng ml^{-1} of test elements in pure water and the electrophoretic buffer (treated as the blank) solution were introduced into the nebulization system successively to evaluate suitable rejection parameter *q* (Rpq) values at the best S/N ratio. The Rpq is the q Mathieu parameter that is used to selectively filter out low mass interference ion in the DRC mode [10]. The experimental conditions of the DRC-ICP-MS system are listed in Table 1.

Table 1
Equipment and operating condition

ICP-MS instrument	Perkin-Elmer Sciex ELAN 6100 DRC
Plasma conditions	
Radiofrequency power	1300 W
Plasma gas flow	15 l min^{-1}
Auxiliary gas flow	1.10 l min^{-1}
Nebulizer gas flow	1.10 l min^{-1}
DRC parameters	
NH_3 reaction gas flow	0.4 ml min^{-1}
Rejection parameter a	0
Rejection parameter q	0.5 for Cr and V; 0.7 for Fe
Autolens	on
Mass spectrometer settings	
Resolution	0.7 amu at 10% peak maximum
Dwell time	100 ms
Sweeps/reading	10
Readings/replicate	500 for Fe and V; 300 for Cr
Isotopes monitored	^{51}V, ^{52}Cr, ^{56}Fe
CE–ICP-MS interface	CETAC CEI-100
Liquid uptake rate	5.5 μl min^{-1}

A detailed description of the CEI-100 capillary electrophoresis interface (CETAC, Omaha, NE, USA) was given in previous papers [22,23]. The nebulizer worked in the self-aspiration mode at a flow rate of around 5.5 μl min^{-1} which was measured according to the operation manual of CEI-100 [24]. A 0.1% (v/v) HNO_3 solution was used as the makeup liquid to provide the electrical connection and to adapt the flow rate of the nebulizer.

2.2. CE separation system and conditions

Two CE migration modes were selected, one mode is counter-electroosmotic for Fe^{II}-phen/Fe^{III}-EDTA and V^{IV}-EDTA/V^{V}-EDTA speciation, and another mode is co-electroosmotic for Cr^{III}-DTPA/Cr^{VI} speciation followed as reported in the previous paper [25]. A fused silica capillary (Alltech) of 60 cm × 75 μm i.d. × 375 μm o.d. was used as electrophoresis capillary. The capillary was conditioned before use as the method described in previous papers [24,25]. Since it is not easy to condition the separation capillary between runs during the CE–ICP-MS analysis, we did not do conditioning between runs. However, from the experiment results, we found that the reproducibility of the separation was quite good. Sample was injected into the CE capillary by the hydrodynamic method by placing inlet

end of the capillary into the sample solution and raising this end 10 cm above the outlet [24]. The injected volume was about 20 nl for 30 s injection. The applied voltage was +22 kV and −22 kV for counter-electroosmotic mode and co-electroosmotic mode, respectively.

2.3. Reagents and solutions

Analytical-reagent grade chemicals were used without further purification. Purified water (18.2 MΩ cm), from a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used to prepare all the solutions. Ammonium citrate, hexadimethrine bromide (polybrene) and tris(hydroxymethyl)aminomethane (Tris) were obtained from Sigma (St. Louis, MO, USA). Ethylenediaminetetraacetic acid disodium salt (EDTA), disodium tetraborate and potassium dichromate were purchased from Merck (Darmstadt, Germany). 3-cyclohexylamino-1-propanesulfonic acid (CAPS), sodium dihydrogenphosphate monohydrate, diethylenetriaminepentaacetic acid (DTPA), chromium(III) ion standard solution, vanadium(IV) ion standard solution, ferrous chloride tetrahydrate and ammonium(meta)vanadate were purchased from Fluka (Buchs, Switzerland). 1,10-Phenanthrolinium chloride monohydrate (phen) was purchased from Riedel-de Haën (Seele, Germany). Stock solutions (100 mmol l^{-1}) of EDTA and DTPA were prepared in 50 mmol l^{-1} sodium hydroxide solution and phen was prepared in pure water. Stock solutions (1000 μg ml^{-1}) of Fe^{II} and Fe^{III} were prepared by dissolving the two iron salts in 0.4 mol l^{-1} hydrochloric acid solution. Stock solutions (1000 μg ml^{-1}) of V^{V} and Cr^{VI} were prepared by dissolving NH_4VO_3 and $K_2Cr_2O_7$ in 0.5% (v/v) sulfuric acid and pure water, respectively. Fe^{II} solution is prone to aerial oxidation at low concentration; it needs to complex with phen to increase the Fe^{II}/Fe^{III} oxidation potential [3]. The electrophoretic buffer solutions were adjusted to the desired pH using 0.1 mol l^{-1} NaOH or 0.1 mol l^{-1} HCl. All solvents and solutions for CE analysis were filtered through a poly(divinylidene difluoride) (PVDF) filter (Millipore) of 0.22 μm porosity.

2.4. Sample preparation

The applicability of the method to real samples was demonstrated by the analysis of two wastewater samples collected from steel-industry and one purified wastewater sample collected from electroplating plant. After collection, the samples were filtered through 0.22 μm membrane filter to eliminate suspended matter. The samples was not acidified as the pH values of all samples were in the range 3–4, which is the optimum pH range for the pre-capillary complexation of iron species as reported by Pozdniakova et al. [4]. They were added in order with appropriate volumes of 50 mmol l^{-1} solution of phen and EDTA for the determination of Fe and V species and then diluted to the adequate concentration with pure water. For the speciation of Cr, the samples were added with appropriate volumes of 50 mmol l^{-1} solution of DTPA and diluted to the adequate concentration with pure water. In all experiments, an appropriate complexing agent was added to give approximately 0.5 mmol l^{-1} concentration in the final injected sample solution. The buffer and the concentration of buffer used in this study were different from those reported in the literatures [1,3–7]. In order to form the metal complexes quantitatively, in this work, a relatively high concentration of complexing agent was used in the complexation reaction. The complexation time of real samples was same as that of the standards (10 min). The concentrations of various metal ions were determined by external calibration method. Since it is difficult to obtain a SRM to certify the concentrations of various V, Cr and Fe species, we did the recovery check on various samples analyzed to demonstrate the accuracy of the analysis. Furthermore, we determined the total concentrations of V, Cr and Fe in the samples analyzed using solution nebulization DRC-ICP-MS.

3. Results and discussion

3.1. Selection of CE conditions

Initially, we tried to separate the six metal ions simultaneously under the same CE conditions. However, in the counter-electroosmotic mode (injection at anode and detection at cathode), Cr^{VI} (as CrO_4^{2-}) could not be seen in the electropherogram possibly due to its higher electrophoretic mobility than the electroosmotic flow (EOF) and migrated toward the inlet. In the co-electroosmotic mode (injection at cathode and detection at anode), migration time of Fe-$phen^{2+}$ was about 20 min that resulted in broad signal. Furthermore, a number of V^{IV} (as VO-$EDTA^{2-}$) peaks were observed which could be attributed to the formation of different V^{IV} anionic complexes under the experimental condition. Hence, we decided to use two different CE migration modes for separating the six metal ions.

3.1.1. Speciation of Fe^{III}/Fe^{II} and V^{V}/V^{IV}

As described in previous papers [1,2], in this work, two different complexing agents namely phen and EDTA have been used for the complexation of Fe^{II}, Fe^{III}, V^{IV} and V^{V}. In the following experiments, buffers were tested for the separation of the four metal-complex ions. All tested electrophoretic buffers were taken in 0.5 mmol l^{-1} phen and 0.5 mmol l^{-1} EDTA to prevent the metal chelates dissociation during CE separation. The effect of the electrophoretic buffer on the CE separation was investigated first. In this study, several buffers, including NaH_2PO_4, Tris, CAPS and $Na_2B_4O_7$, were tested for the best separation of the four metal-complex ions. Each buffer solution was present at 10 mmol l^{-1}. It should be mentioned that it was not the optimum concentration used for real sample analyses. All the buffers were adjusted to pH 8.5 and the test solutions

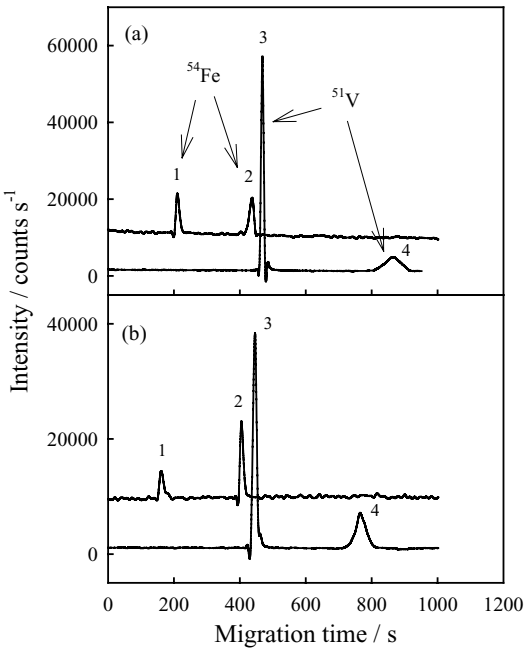

Fig. 1. Effect of electrolytes on CE separation of Fe and V species: (a) Tris and (b) $Na_2B_4O_7$. Each buffer solution was present at 10 mmol l^{-1} (pH 8.5). Test solutions containing 2 μg ml^{-1} of Fe^{II} and Fe^{III} and 0.5 μg ml^{-1} of V^{IV} and V^{V} were analyzed in the standard mode of ICP-MS. Fe was detected at *m/z* 54 while V was detected at *m/z* 51. (1) Fe^{II} (Fe-phen^{2+}); (2) Fe^{III} (Fe-EDTA^{-}); (3) V^{IV} (VO-EDTA^{2-}); and (4) V^{V} (VO_2-EDTA^{3-}).

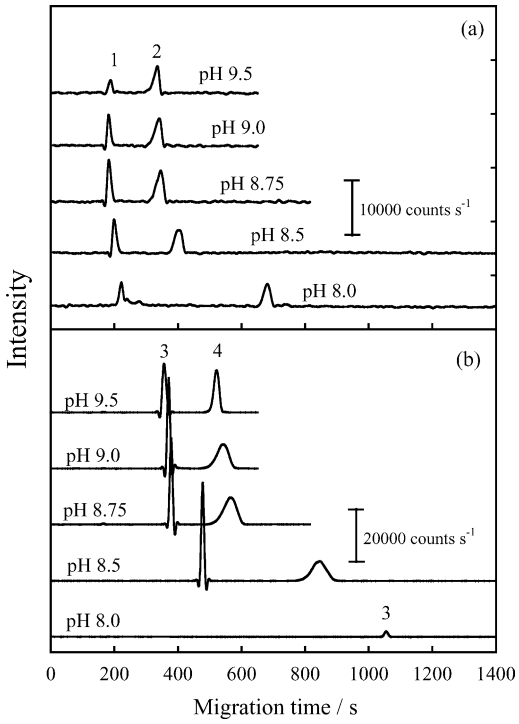

Fig. 2. Effect of the pH of separating electrolyte on CE separation of (a) Fe and (b) V species. Tris buffer solution was present at 10 mmol l^{-1}. The numbered peaks are the same as in Fig. 1.

containing 2 μg ml^{-1} of Fe^{II} and Fe^{III} and 0.5 μg ml^{-1} of V^{IV} and V^{V} were analyzed in the standard mode of ICP-MS analysis. No reaction gas was used in the standard mode. As shown in Fig. 1, good separations were obtained when Tris and $Na_2B_4O_7$ were used as electrophoretic buffers. Tris buffer has been selected for the separation because the separated electropherogram were having similar peak areas when compared to $Na_2B_4O_7$. Although a slight difference in matrix effect in ICP-MS analysis might be detected when different buffers were used for separation, the difference was not significant. Since ICP-MS is an element-selective detection method and the dissolved solid content in the introduced solution was not high, the non-spectroscopic interference of ICP-MS analysis was not significant in this study.

Fig. 2 shows the effect of the pH of separating electrolyte on CE separation in the range of 8.0–9.5. As shown in Fig. 2a, if the pH was more than 9, the Fe-phen^{2+} signal diminished possibly due to the dissociation of Fe-phen^{2+} complex during CE separation. Furthermore, as shown in Fig. 2b, no VO_2-EDTA^{3-} peak was displayed when the pH was less than 8.5. It could be due to low mobility of EOF, which could not surpass the high electrophoretic mobility of VO_2-EDTA^{3-} in the counter-electroosmotic mode. Furthermore we found that the peak areas of two different Fe species were quite different at pH 9.5. pH 8.75 was selected for Fe and V separation, although V could get better peak shape at pH greater than 8.75. The effect of the concentration of separating electrolyte on CE separation was also investigated in the range of 5–25 mmol l^{-1}. The peak height of VO-EDTA^{2-} increased with the increase of electrolyte concentration till it was 15 mmol l^{-1} with no change on further increase. Furthermore we found that the best electropherograms of Fe and V speciation could be obtained when a buffer concentration of 15 mmol l^{-1} was used. Hence, an electrolyte concentration of 15 mmol l^{-1} has been selected. During this study, a little increase in migration time has been observed with the increase of electrolyte concentration.

3.1.2. *Speciation of Cr^{III}/Cr^{VI}*

As described by Pozdniakova and Padarauskas [1], Cr^{III} forms stable complexes with various aminopolycarboxylic acids ($\log\beta$ = 23.4, 25.6, and 28.3 for EDTA, CDTA and DTPA). However, better results were reported with DTPA [1], which is a doubly charged chelate. We used the co-electroosmotic mode reported in our previous paper [25] for the separation of Cr^{VI} (CrO_4^{2-}) and Cr-DTPA^{2-}. In the following experiments, different buffers were tested in the presence of 0.5 mmol l^{-1} DTPA and 0.01% polybrene to prevent Cr-DTPA^{2-} dissociation and hold constant the positive surface charge density on the capillary wall during CE separation. The type of the electrophoretic buffer on the CE separation was investigated first. All the buffers were adjusted to pH 7.5. Test solution containing 0.5 μg ml^{-1} of Cr^{III} and Cr^{VI} was analyzed in the standard mode of ICP-MS. As shown in Fig. 3, good separation was obtained with ammonium citrate buffer. No separation was

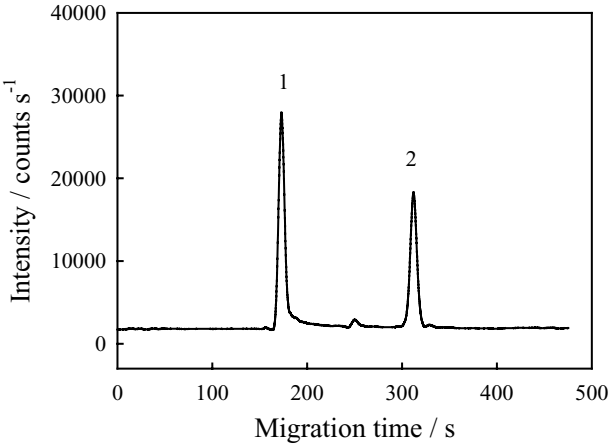

Fig. 3. Electropherogram of Cr^{III} and Cr^{VI}. Ammonium citrate buffer solution was present at 10 mmol l^{-1} (pH 7.5). Test solution containing 0.5 μg ml^{-1} of Cr^{III} and Cr^{VI} was analyzed in the standard mode (detected at *m*/*z* 52) of ICP-MS. (1) Cr^{VI} (CrO_4^{2-}); and (2) Cr^{III} (Cr-$DTPA^{2-}$).

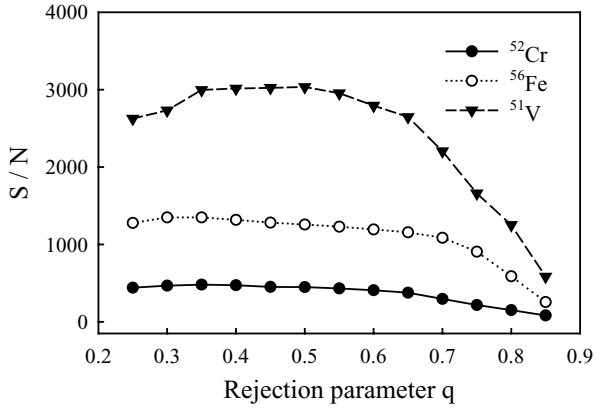

Fig. 4. Ratio of the signal of analyte solution to the noise of electrophoretic buffer vs. Rpq (detected at *m*/*z* 51, 52 and 56). The reaction gas flow rate of NH_3 was set at 0.4 ml min^{-1}. Two different electrophoretic buffers used for separation were treated as the blank.

achieved with ammonium acetate and/or ammonium phosphate buffers. In the following experiments, ammonium citrate buffer was selected.

The effect of the pH of separating electrolyte on CE separation in the range 6.7–8.7 was studied. We found that the Cr-$DTPA^{2-}$ signal diminished and split into two possibly due to the dissociation of Cr-$DTPA^{2-}$ complex during CE separation when the pH was over than 8.0. Therefore, the optimal pH of 7.7 was selected. The effect of the concentration of separating electrolyte on CE separation was also investigated using 5, 10 and 15 mmol l^{-1} of electrophoretic buffer. The Cr-$DTPA^{2-}$ signal was not seen when the concentration of electrolyte was 5 mmol l^{-1} and diminished when the concentration of electrolyte was 15 mmol l^{-1} on the electropherogram. Hence, an electrolyte concentration of 10 mmol l^{-1} has been selected. During this study, a little increase in migration time has been observed with the increase of electrolyte concentration.

3.2. Selection of DRC conditions

As reported in previous papers [18–21,26], the determination of V, Cr and Fe has been carried out using ammonia gas in the reaction cell that alleviated the effect of polyatomic isobaric interferences. Fig. 4 shows S/N versus rejection parameter *q* (Rpq) at *m*/*z* 51, 52 and 56 when the flow rate of ammonia gas was fixed at 0.4 ml min^{-1} [20,21]. A solution of 5 ng ml^{-1} V, Cr and Fe was treated as the test solution, the electrophoretic buffer for counter-electroosmotic mode was treated as the blank for Fe and V, and other hand, the electrophoretic buffer for co-electroosmotic mode was treated as the blank for Cr. As shown in Fig. 4, the S/N values did not change significantly when the Rpq values were in the range of 0.4–0.6. After evaluation, 0.5 was used for V and Cr determinations. On the other hand, in order to reduce the background ion signal at *m*/*z* 56, an Rpq value of 0.7 was selected for Fe determination.

3.3. Optimized electrophoretic separation

Several parameters related to quantification, including detection limit, linearity and repeatability, were examined under the above-optimized conditions. Repeatability was determined using six injections of a test mixture containing 0.2 μg ml^{-1} (as element) of V^{IV}, V^{V}, Cr^{III}, Cr^{VI}, Fe^{II} and Fe^{III} species. As shown in Table 2, the relative standard deviation of the peak heights and peak areas were less than 8.2 and 6.0%, respectively, and the repeatability of migration times was better than 2.1% for all species. Calibration curves based on peak height and peak area were linear with correlation coefficient (r^2) better than 0.997 for each metal ion in the range tested (0.02–1 μg ml^{-1}). The detection limit was estimated from the peak height versus concentration plot and based on the concentration (as element) necessary to yield a net signal equal to three times the standard deviation of the background. The CE–ICP-MS detection limit was about 0.1, 0.5, 1.3, 0.4, 1.2 and 1.7 ng ml^{-1} for V^{IV}, V^{V},

Table 2
Repeatability of migration time, peak area and peak height of the CE elution peaks ($n = 6$)

Compound	Migration time ± S.D.[a] (s)	Repeatability of peak area[b] (%)	Repeatability of peak height[b] (%)
Fe^{II} (Fe-$phen^{2+}$)	198 ± 6	1.9	7.2
Fe^{III} (Fe-$EDTA^{-}$)	380 ± 6	4.0	6.0
V^{IV} (VO-$EDTA^{2-}$)	400 ± 5	5.3	5.8
V^{V} (VO_2-$EDTA^{3-}$)	585 ± 8	4.6	4.6
Cr^{VI} (CrO_4^{2-})	185 ± 6	6.0	7.2
Cr^{III} (Cr-$DTPA^{2-}$)	310 ± 8	4.9	8.0

[a] S.D.: standard deviation.
[b] Relative standard deviation.

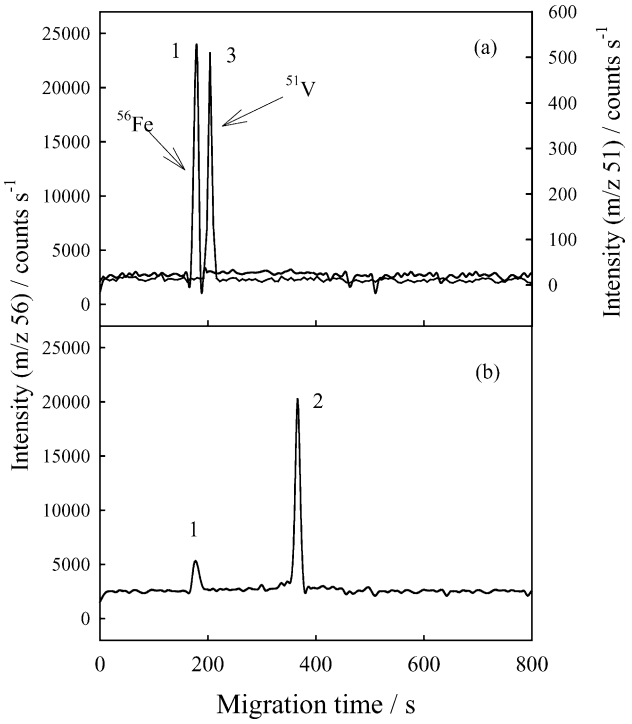

Fig. 5. Typical electropherograms of Fe and V speciation for: (a) wastewater sample collected from steel-industry and (b) wastewater sample collected from electroplating plant. Sample no. 1 was diluted 5000-fold for Fe speciation and diluted five-fold for V speciation study. Sample no. 3 was diluted 10-fold for Fe speciation study. The numbered peaks are the same as in Fig. 1.

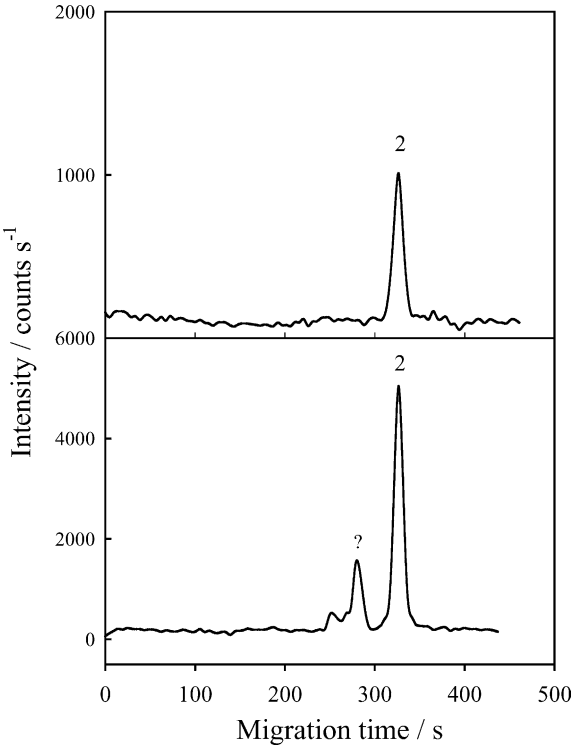

Fig. 6. Typical electropherograms of Cr speciation for (a) wastewater sample collected from steel-industry (b) purified wastewater sample collected from electroplating plant. Sample nos. 1 and 3 were diluted 10- and 50-fold, respectively. The numbered peaks are the same as in Fig. 3.

Cr^{III}, Cr^{VI}, Fe^{II} and Fe^{III}, respectively. The detection limits reported for CE with UV-Vis detection were in the range of 0.1–0.4, 0.02–0.16 and 0.06–2.8 μg ml^{-1} for various V, Cr and Fe species, respectively [1,3–5,7]. The CE–ICP-MS results are superior to those reported for CE with UV-Vis detection.

3.4. Sample analysis

In order to prove that the system works for practical analysis, two wastewater samples collected from steel-industry and a purified wastewater sample collected from electroplating plant were analyzed. Typical electropherograms of Fe and V speciation obtained for one sample (no. 1) collected from steel-industry and other (no. 3) from electroplating

Table 3
Concentrations and recoveries of metal ions in water samples measured by DRC-ICP-MS and CE–DRC-ICP-Ms[a] ($n = 3$)

Metal ions	No. 1[b]		No. 2[b]		No. 3[c]	
	Concentration found (μg ml^{-1})	Recovery[d] (%)	Concentration found (μg ml^{-1})	Recovery[d] (%)	Concentration found (μg ml^{-1})	Recovery[d] (%)
Fe^{II}	1360 ± 30	104 ± 9	29.3 ± 1.5	101 ± 5	0.82 ± 0.04	102 ± 4
Fe^{III}	–[e]	120 ± 3	4.3 ± 0.4	98 ± 6	2.48 ± 0.06	103 ± 7
Fe_{total}	1410 ± 50		40.3 ± 2.6		3.42 ± 0.07	
V^{IV}	0.047 ± 0.003	92 ± 6	0.009 ± 0.002	92 ± 3	–	99 ± 4
V^{V}	–	93 ± 5	–	98 ± 6	–	94 ± 4
V_{total}	0.051 ± 0.004		0.010 ± 0.001		–	
Cr^{VI}	–	–	–	–	–	102 ± 5
Cr^{III}	0.66 ± 0.05	188 ± 8	0.018 ± 0.002	200 ± 6	5.90 ± 0.08	118 ± 9
Cr_{total}	0.62 ± 0.08		0.013 ± 0.001		6.11 ± 0.07	

[a] Values are means of three measurements ± standard deviation.
[b] The wastewater samples were collected from steel industry.
[c] The purified wastewater sample was collected from electroplating plant.
[d] The recovery was determined by spiking the diluted sample with 0.1 μg ml^{-1} of various metal ions.
[e] Not detected.

plant were shown in Fig. 5a and b. As expected, Fe^{II} was found to be the major species in wastewater sample from steel-industry. However individual species of vanadium could not be quantified in sample No. 3 as the levels were below the method detection limits. From the experiment, we found that there was a large difference in the migration times between the standard solution and the sample solution for various vanadium species. We think that the pH and composition of injected sample solution could be quite different from the standard solutions that resulted in the difference in the migration time. We did spike different vanadium species into sample solution to identify the species present in the sample. Typical electropherograms obtained for Cr speciation were shown in Fig. 6a and b. In all the samples, recoveries of analytes were studied by spiking 0.1 $\mu g\,ml^{-1}$ of each metal ion in water sample. As the recoveries were nearly quantitative for all the species, quantification has been carried out with external calibration method. Peak area was used for quantification work. The results are shown in Table 3. As shown, the recoveries were in the range of 92–120% for all metal ions except Cr in the wastewater samples from steel-industry. Recovery of Cr^{VI} in these samples was poor with an enhanced recovery of Cr^{III}, possibly due to the reduction of Cr^{VI} to Cr^{III} in the presence of excess of Fe^{II}. The CE–DRC-ICP-MS results were also compared with the total concentrations of Fe, V and Cr in these samples. The total concentration was determined by DRC-ICP-MS with solution nebulization. As shown, a satisfactory agreement was obtained between these two methods. However, little discrepancy in the values of Cr^{III} and total Cr of sample no. 2 was due to improper integration of the signal in peak area mode as the levels were very low.

4. Conclusion

The merits of coupling CE and DRC-ICP-MS with commercially modified micro-concentric nebulization for speciation of V, Cr and Fe have been demonstrated. Two CE migration modes were employed for separating the six metal ions using pre-capillary complexation. The system could provide an excellent, rapid and sensitive separation technique for speciation of V, Cr and Fe. Detection limits of different species of V, Cr and Fe obtained with this system are low enough for many applications. Therefore, the potential applications of CE–DRC-ICP-MS to biological compounds other than environmental samples for metal speciation are under investigation in our laboratory.

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