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Simultaneous determination of chromium(III) and chromium(VI) by ion chromatography with inductively coupled plasma mass spectrometry

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Abstract

A combined system of inductively coupled plasma mass spectrometry (ICP-MS) with ion chromatography (IC) was used for the speciation of the chromium (Cr) species. After chelation with ethylenediaminetetraacetic acid (EDTA), Cr(III) and Cr(VI) were separated by anion-exchange chromatography. Subsequently, eluates from a separation column were directly introduced into the ICP-MS and detected at m/z 52 and 53. Separation parameters were optimized for the chromium species. Excelpak ICS-A23 (75 × 4.6 mm I.D.) packed with hydrophilic polymer based anion-exchange resin (ion-exchange capacity: 0.05 mequiv. g^{-1} dry weight) was used as separation column and $1.0 \cdot 10^{-3}$ *M* EDTA-2NH_4–0.01 *M* oxalic acid (pH 7.0) was used as a mobile phase. Cr(III) and Cr(VI) were completely separated within 8 min without any interference of ArC^+ and ClO^+. Detection limits ($S/N = 3$) for Cr(III) and Cr(VI) were $8.1 \cdot 10^{-5}$ and $8.8 \cdot 10^{-5}$ mg Cr/l, respectively. The linear range was 4 orders of magnitude, from $0.5 \cdot 10^{-3}$ to 5 mg Cr/l. With regard to reproducibility, R.S.D. ($n = 5$) was better than 2.5%. The developed IC–ICP-MS method was applied to the determination of the chromium species and metal elements in water.

1. Introduction

Chromium (Cr) can occur in at least three different valences, viz., Cr(VI), Cr(III) and Cr(II). In general, most of the chromium species are either Cr(III) or Cr(VI), with far fewer existing as Cr(II). In water samples, chromium exists as chromic [Cr^{3+}] or chromate [CrO_4^{2-} = Cr(VI)]. Cr(III) is an essential element for humans and animals and plays an important role as the glucose-tolerance factor (GTF) in insulin metabolism [1,2]. On the other hand, Cr(VI) is very toxic for humans and causes chronic adverse effects [1]. Therefore, to evaluate the toxicity of chromium in environmental and biological samples, speciation of the chromium species is required.

High-performance liquid chromatography (HPLC) and ion chromatography (IC) are good separation methods for such a speciation study. Separation procedures utilizing chelating reagents have been described for the speciation of the chromium species [3–13]. When using the chelation technique, both chromium species are

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retained on the separation column and not affected by a solvent front peak (water dip). Dithizone [3], β-diketones [4], 8-quinolinol [5] and dithiocarbamate derivatives [6,7] were applied to the speciation of the chromium species by reversed-phase HPLC. Ethylenediaminetetraacetic acid (EDTA) [8–13] has also been used for the speciation chromium. The EDTA chelates are retained on anion-exchange resins because EDTA easily forms stable negatively charged chelates with many metal elements, regardless of the metal ion charge. Although the EDTA chelating method is an effective separation procedure for metal elements, lack of sensitivity and selectivity causes a problem in the determination of trace amounts of elements in samples containing complicated matrices.

In order to improve its sensitivity and selectivity, an atomic emission spectrometric method, such as direct current plasma emission spectrometry (DCP) or inductively coupled plasma atomic emission spectrometry (ICP-AES), has been combined with HPLC or IC as an element-selective detector [14–18]. However, these methods cannot perform simultaneous multi-elemental detection. Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive, accurate and precise analytical tool for ultra-trace multi-elemental and isotopic analysis. Although ICP-MS cannot give any information on speciation, several researchers have applied ICP-MS as an element-selective and multi-elemental detector because it combines well with HPLC or IC [19–26].

In this paper, simultaneous determination of the chromium species by IC with ICP-MS as the element-selective and multi-elemental detector is described. The chromium species were separated by an anion-exchange chromatograph after chelating with EDTA. The eluate was directly introduced into the ICP-MS system for the detection of the chromium species. The conditions for separation and complex formation were optimized for the chromium species. The developed IC–ICP-MS method was applied to the determination of chromium species and metal elements in water.

2. Experimental

2.1. Reagents

Chromium nitrate and potassium chromate used in this study were purchased from Wako Pure Chemical Industries (Osaka, Japan). Pure water was obtained from a Milli-Q/SP system (Nihon Millipore, Tokyo, Japan). Stock solutions (0.01 mol Cr/l) of both chromium species were prepared by dissolving each reagent in pure water and were stored in a refrigerator. Analytical solutions were prepared by diluting the stock solutions to obtain an adequate chromium concentration.

Analytical reagent grade oxalic acid, ultrapure acetic acid and ammonium hydroxide (25%) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Ethylenediaminetetraacetic acid diammonium salt (EDTA-2NH_4) and metal–EDTA chelates were purchased from Dojindo Laboratories (Kumamoto, Japan).

2.2. Ion chromatography

The ion chromatograph used in this experiment was a Model IC7000S (Yokogawa Analytical Systems, Tokyo, Japan). Excelpak ICS-A23 and Excelpak ICS-A2G (Yokogawa Analytical Systems, Tokyo, Japan) were chosen as separation columns. The ICS-A23 column is 75 × 4.6 mm I.D., packed with hydrophilic polymer-based anion-exchange resin (particle diameter, 6 μm) with 0.05 mequiv./g dry weight. ICS-A2G (25 × 2.7 mm I.D., packed with the same packing) is used as a guard column for the ICS-A23. For separation of the chromium species, EDTA-2NH_4 and oxalic acid were used as the mobile phase, the pH being adjusted with 25% ammonium hydroxide. Ammonium salt was selected as the mobile phase in this study, because sodium salt might clog the ICP torch and decrease the sensitivity of the ICP-MS [25].

Poly[ethylenetetrafluoroethylene] (ETFE) tubing (800 × 0.3 mm I.D.) was used for the connection between the column and the nebulizer of the ICP-MS system. Unless otherwise

stated, the ion chromatograph was operated under the following conditions: mobile phase flow-rate, 1.0 ml/min; column temperature, 40°C; and injection volume, 0.05 ml.

2.3. ICP-MS

The ICP-MS instrument used in this experiment was a Model HP 4500 (Hewlett-Packard, Wilmington, DE, USA). The operating parameters are described in Table 1. A Scott-type spray chamber, maintained at 0°C by means of a Peltier-type thermoelectric module, a Fassel-type torch and a concentric glass nebulizer (Precision Glassblowing, CO, USA) were used in the experiments. For data acquisition of the IC–ICP-MS, a selected-ion monitoring (SIM) mode was used. A quantitative analysis mode (QTM) was used for data acquisition of the conventional introduction system. For the QTM, an atomic mass unit (amu) was divided into 20 points and the middle three points were used for data acquisition. An adequate dwell time of the amu was chosen for each metal element and the scan was repeated three times. A pulse-counting mode was used. For data acquisition of calcium (Ca), an analog detection mode was used, because a large amount of Ca was generally present in the water samples, i.e. tap water, ground water and river water. For tuning of the ICP-MS system, a standard solution of 0.01 mg/l yttrium (Y) was analyzed. The system was tuned to get a maximum signal for Y by monitoring m/z 89 and changing a bias of lenses.

Table 1
ICP-MS operating conditions

Instrument	Model HP 4500
Radiofrequency forward power	1.3 kW
Radiofrequency reflected power	<5 W
Plasma gas flow	Ar, 16 l/min
Auxiliary gas flow	Ar, 1.0 l/min
Carrier gas flow	Ar, 1.03 l/min
Sampling depth	5 mm from load coil
Monitoring mass	m/z 52 and 53
Dwell time	0.1 s
Number of scans	1

2.4. Other procedures

In order to determine the water hardness, the concentrations of magnesium and calcium were determined by both a titration method and by IC with conductometric detection. The titration method was operated according to the JIS (Japanese Industrial Standard) K0102-1993, "The Testing Method for Industrial Waste Water". The IC operating parameters were as follows: Excelpak ICS-C25 column (Yokogawa Analytical Systems, Tokyo, Japan) packed with silica-based weak cation-exchange resin; mobile phase, $1 \cdot 10^{-3}$ *M* 2,6-pyridinedicalcoxylic acid–$5 \cdot 10^{-3}$ *M* tartaric acid; flow-rate, 1.0 ml/min; column temperature, 40°C; injection volume, 0.05 ml.

3. Results and discussions

3.1. Formation of complex

The formation rate of the complex between Cr(III) and EDTA is very slow [27]. With regard to the toxic compound analysis, it is essential to increase the complex formation rate to shorten the analysis time. The formation rate of the complex is affected by reaction temperature and pH. Complex formation was performed according to previous reports [11–13] with slight modifications. In the present study, the effects of temperature and pH on the complex-forming reaction were confirmed.

A mixed solution of Cr(III) and EDTA (molar ratio 1:50) was incubated at 20, 40 and 60°C. A 0.05-ml volume of the reactant solution was analyzed by IC–ICP-MS, using 0.01 *M* of EDTA-2NH_4 (pH 7.0) as the mobile phase. The time required for complete complex formation at 20, 40 and 60°C was 350, 30 and 15 min, respectively. Complex formation was favoured by higher temperatures. It should be noted that higher temperatures might also provoke oxidation of Cr(III) by chromate, because the oxidation ability of chromate is enhanced at higher temperatures. As a consequence of this result

and the results of previous reports [11–13], a reaction temperature of 40°C was chosen.

The rate of complex formation is also affected by the pH of the reaction medium. The pH was varied from 3 to 10. pH adjustment was made by adding acetic acid or ammonium hydroxide. Fig. 1a shows the relationship between pH and the peak area of the Cr(III)–EDTA complex formed in a mixed solution of $1 \cdot 10^{-5}$ *M* of Cr(III) and EDTA (molar ratio 1:100) during an incubation time of 30 min at 40°C. While the peak area of Cr(III)–EDTA remained constant at pH 3–6, it decreased above pH 6, due to ionization of EDTA above pH 6, resulting in less complex formation. At pH 10, the peak of free Cr(III) (chromic ion, Cr^{3+}) was observed at the solvent front and the sum of both peak areas was the same as that of the Cr(III)–EDTA peak at pH 6.

The oxidation ability of chromate is enhanced at higher pH. Fig. 1b shows that the relationship between the reaction pH and the peak area of the Cr(III)–EDTA complex formed in the mixed solution was correlated with the chromate peak (chromate concentration was $1 \cdot 10^{-5}$ *M*) under the same conditions. The peak area of Cr(III)–EDTA decreased above pH 6 as shown in Fig. 1a, but that of Cr(VI) increased above pH 6. The sum of the peak areas of both chromium species at pH 10 was the same as that at pH 6, which means that part of the Cr(III) was oxidized to Cr(VI) by chromate during the complex-forming reaction at higher pH.

As a consequence of these results, the following reaction conditions were chosen for the complex formation: pH for the complex-forming reaction, 6.0; reaction temperature, 40°C; incubation time, 30 min. These optimized conditions were almost the same as those described in previous reports [11–13].

3.2. Optimization of separation conditions

The effect of the mobile-phase pH was examined in order to optimize the IC operating conditions. EDTA-2NH_4 was used as the mobile phase and the mobile-phase pH was varied from 6 to 10 at a fixed EDTA-2NH_4 concentration of $3 \cdot 10^{-3}$ *M*. A sample of Cr(III)–EDTA and Cr(VI) ($1 \cdot 10^{-5}$ *M*) was used of which 0.05 ml was injected. Detection on the ICP-MS system was performed at *m/z* 52 and 53.

Fig. 2 shows the relationship between the retention time of the chromium species and the

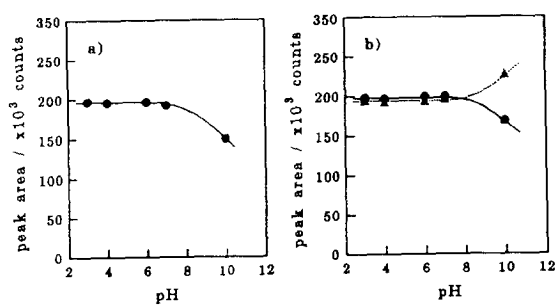

Fig. 1. Relationship between the pH used for the complex forming reaction and the peak areas of the Cr(III)–EDTA complex and Cr(VI). (a) The peak area of the Cr(III)–EDTA complex formed in a mixed solution of Cr(III) and EDTA. (b) The peak area of the Cr(III)–EDTA complex formed in the mixed solution coexisting with chromate. Column, Excelpak ICS-A2G/ICS-A23; mobile phase, 0.01 *M* EDTA-2NH_4 (pH 7.0); flow-rate, 1.0 ml/min; column temperature, 40°C. Detection is performed at *m/z* 53. Sample is $1 \cdot 10^{-5}$ mol Cr/l each and the injection volume is 0.05 ml. (●) Cr(III), (▲) Cr(VI).

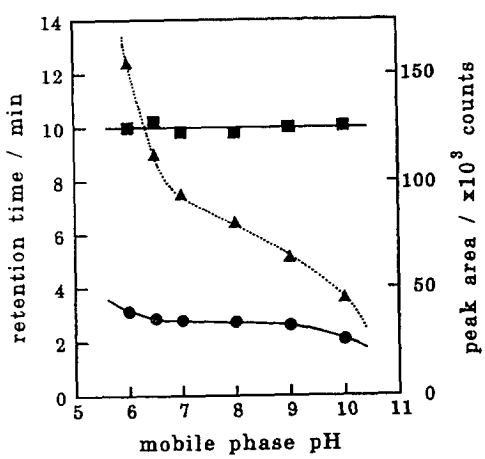

Fig. 2. Relationship between the retention times of the chromium species, the Cr(III)–EDTA peak area and the mobile phase pH. Conditions and sample as in Fig. 1 except for the mobile phase. The mobile phase is $3 \cdot 10^{-3}$ *M* EDTA-2NH_4. (●) Cr(III), (▲) Cr(VI), (■) peak area of Cr(III)–EDTA.

mobile-phase pH. In the range of this experiment, Cr(III)–EDTA and Cr(VI) were clearly retained and Cr(III)–EDTA was completely separated from the solvent front. Below pH 6, the peak of Cr(VI) was not eluted within 30 min. Although the retention time of Cr(VI) decreased as the mobile-phase pH increased, a peculiar elution behaviour was observed, as shown in Fig. 2. This behaviour was due to ionization of EDTA and chromate. Because EDTA has four acidic dissociation constants (pKa), viz., 1.99, 2.67, 6.16 and 10.26, and chromate has two, viz., 0.74 and 6.49, two inflection points were observed in the vicinity of pH 6.5 and 10. It should be noted that a higher pH of the mobile phase might provoke oxidation of Cr(III) by chromate and decomposition of the Cr(III)–EDTA complex, as well as complex-forming reaction. As indicated by the constant Cr(III)–EDTA peak area, no oxidation and no degradation were observed at pH 6–10 (Fig. 2).

However, the peak shape of Cr(VI) showed severe tailing and the peak height was about one-half that of Cr(III)–EDTA under these elution conditions. This means that the ionic strength of EDTA was essentially low at neutral pH. Furthermore, the background counts of the ICP-MS detection were very high at m/z 52. Therefore, the mobile phase was changed from EDTA to oxalic acid which is a strongly ionic and low-carbon compound. The effect of the oxalic acid concentration in the mobile phase was examined. The oxalic acid concentration was varied from 0.005 to 0.012 M at a fixed mobile-phase pH of 7.0 and an EDTA-2NH$_4$ concentration of $2 \cdot 10^{-3}$ M. EDTA-2NH$_4$ was added to the mobile phase to stabilize the complex. In order to determine the void volume (V_0), a sample containing 1 mg Li/l (Li) was analyzed at m/z 7 under the same conditions. Fig. 3 shows the relationship between the capacity factors (k') of the chromium species and the concentration of oxalic acid. The capacity factors of both chromium species decreased as the oxalic acid concentration increased. A linear relationship was obtained between the k' values of the chromium species and the oxalic acid concentration. When using oxalic acid as the mobile phase, symmetrical peaks of the chromium species were observed and the peak height of Cr(VI) was higher than when EDTA was used as the mobile phase.

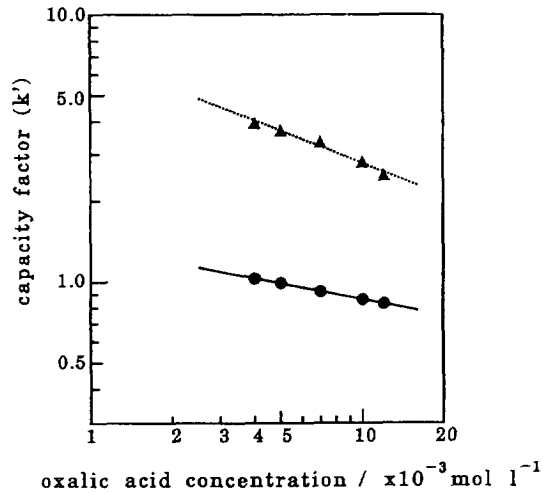

Fig. 3. Relationship between the capacity factors of the chromium species and the concentration of oxalic acid. Conditions and sample as in Fig. 1 except for the mobile phase. The mobile phase is $2 \cdot 10^{-3}$ M EDTA-2NH$_4$–oxalic acid (pH 7.0). (●) Cr(III), (▲) Cr(VI).

An adequate addition of EDTA to the mobile phase is required to stabilize the EDTA complex. Since the background counts and the baseline noise of the ICP-MS detection depended on the EDTA concentration, the effect of the concentration of EDTA added to the mobile phase was examined. The EDTA-2NH$_4$ concentration was varied from 0 to $3 \cdot 10^{-3}$ M at a fixed mobile-phase pH of 7.0 and a fixed oxalic acid concentration of 0.01 M. Fig. 4 shows the relationship between the k' values of the chromium species and the EDTA-2NH$_4$ concentration. The capacity factors of the chromium species decreased as the EDTA-2NH$_4$ concentration increased. Fig. 5 shows the effect of the EDTA-2NH$_4$ concentration on the background counts, the baseline noise and S/N ratio of the ICP-MS system. The background counts and the baseline noise at both m/z 52 and 53 increased with increasing EDTA-2NH$_4$ concentration. Although the S/N ratio at m/z 52 decreased with increasing EDTA-2NH$_4$ concentration, m/z 53 revealed a maximum at $1 \cdot 10^{-3}$ M EDTA-2NH$_4$.

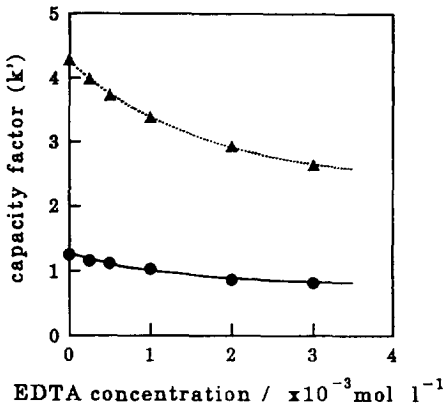

Fig. 4. Relationship between the capacity factors of the chromium species and the EDTA-2NH_4 concentration. Conditions and sample as in Fig. 1 except for the mobile phase. The mobile phase is EDTA-2NH_4–0.01 *M* oxalic acid (pH 7.0). (●) Cr(III), (▲) Cr(VI).

The reason of the conflicting *S/N* ratio has still to be solved.

The optimized operational conditions are described in Table 2. To determine low-level concentrations of the chromium species, the injection volume was increased from 0.05 ml to 0.5 ml and the dwell time was increased from 0.1 to 1.0 s. A chromatogram of Cr(III) and Cr(VI) is shown in Fig. 6. The chromium species were completely separated and detected within 8 min without interference of the water dip.

In this study two buffer modifiers (EDTA and oxalic acid) were used as the mobile phase. These modifiers may form a complex with Cr(III). At pH 7.0, EDTA can form a very stable complex with Cr(III), whereas oxalic acid can not because of its acidity. With EDTA as modifier Cr(III) mainly exists as the complex Cr(III)–EDTA (though the existence of a hydroxo complex should be considered because the logarithm of the stability constant of the hydroxo complex is very low compared with that of the complex Cr(III)–EDTA). Of the two buffer modifiers, oxalic acid only functions as an eluent of the Cr species, while EDTA functions both as

Table 2
Optimized operating conditions

Instrument	Model IC7000S
Column	Excelpak ICS-A2G/ICS-A23 (25 × 2.7 mm I.D./75 × 4.6 mm I.D.)
Mobile phase	$1.0 \cdot 10^{-3}$ *M* EDTA-2NH_4–0.01 *M* oxalic acid (pH 7.0)
Flow-rate	1.0 ml/min
Column temperature	40°C
Detector	ICP-MS
Monitoring mass	*m/z* 52
Dwell time	1.0 s
Injection volume	0.5 ml

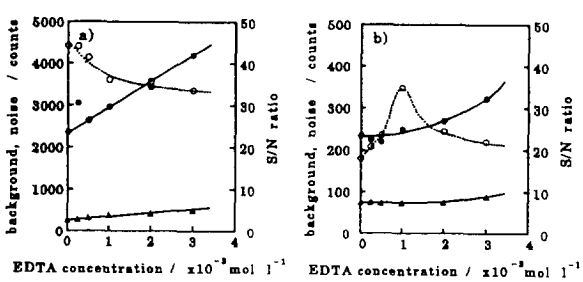

Fig. 5. Effect of the EDTA-2NH_4 concentration on background counts, baseline noise and *S/N* ratio of ICP-MS at *m/z* 52 (a) and 53 (b). Conditions and sample as in Fig. 4. (●) Background counts, (▲) baseline noise, (○) *S/N* ratio.

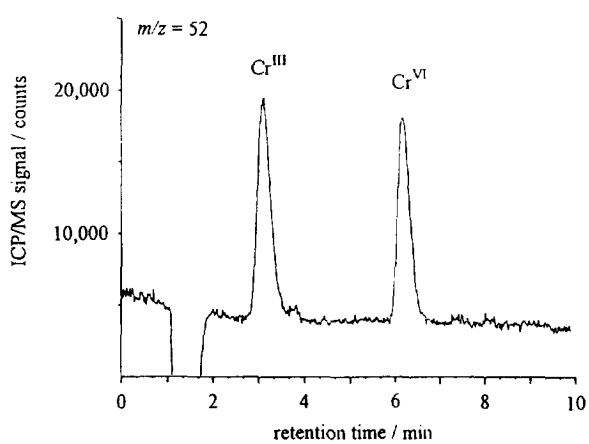

Fig. 6. Chromatogram of chromium species obtained by IC–ICP-MS. Conditions as in Table 2. Sample is $0.5 \cdot 10^{-3}$ mg Cr/l each. Injection volume is 0.5 ml.

an eluent of the Cr species and as a stabilizer of the Cr(III) complex.

3.3. Linearity, detection limits, reproducibility and interferences

Linearity, detection limits and reproducibility were determined for both chromium species. The linear range was 4 orders of magnitude, from $0.5 \cdot 10^{-3}$ to 5 mg Cr/l. The detection limits and the reproducibility were calculated for a $1 \cdot 10^{-3}$ mg Cr/l solution by injection of a 0.5-ml sample. The detection limits ($S/N = 3$) for Cr(III) and Cr(VI) at m/z 52 were $8.1 \cdot 10^{-5}$ and $8.8 \cdot 10^{-5}$ mg Cr/l, respectively. The relative standard deviations ($n = 5$) for $1 \cdot 10^{-3}$ mg Cr/l of both chromium species were 2.35% and 1.79%, respectively. Furthermore, the recoveries of added chromium species were examined. An amount of $1 \cdot 10^{-3}$ mg Cr/l of both chromium species was added to ground water and analyzed under the same conditions. The recoveries of Cr(III) and Cr(VI) by IC–ICP-MS ranged from 102 to 115% with averages of about 103.9 and 110.4%, respectively ($n = 5$).

Since the chromium species are decomposed and turned into Cr, O, H and C ions in plasma, the sensitivity of the determination of the chromium species as chromium does not depend on its structure. When the concentration as chromium is the same, each species must give the same peak area on the chromatogram. In this study, good agreement was obtained for the different chromium species.

It must be taken into consideration that polyatomic ion (molecular ion) interference may occur in ICP-MS [28,29]. The $^{40}Ar^{12}C^+$ ion can be generated from carbon in the mobile phase and the argon gas used as the plasma gas. This ion interferes with the determination of chromium at m/z 52, which is the most abundant chromium isotope. Interference by the $^{37}Cl^{16}O^+$ ion at m/z 53, due to high contents of chlorine in the sample ion, also occurred. Although the background count at m/z 52 was relatively high due to the use of organic acid as the mobile phase, interference from carbon in the sample was not observed. When a 100 mg/l chloride solution was analyzed under the same conditions, the ClO^+ ion at m/z 53 was detected before and separated from the Cr(III)–EDTA complex.

3.4. Simultaneous separation of other metal elements

As described above, EDTA can form stable chelates with many metal elements. The IC–ICP-MS system with EDTA as the chelating compound was applied to the determination of metal elements. Several metal EDTA chelates were determined by the IC–ICP-MS system under the same conditions. The retention times of the metal–EDTA chelates and their detection limits as metal element are given in Table 3. Although metal–EDTA chelates could not be completely separated with the IC column, qualitative and quantitative analysis of metal elements can easily be carried out by using ICP-MS because of its element selectivity (Fig. 7).

3.5. Determination of the chromium species and metal elements in water

The developed IC–ICP-MS method was applied to the determination of chromium species and metal elements in water. Each sample was analyzed by both IC–ICP-MS and ICP-MS with the conventional introduction system. For the determination of magnesium and calcium, the same samples were also analyzed by the titration method and IC with conductometric detection. Hardness, as calcium carbonate ($CaCO_3$), was calculated from the concentrations of magnesium and calcium. The concentrations of the metal elements as determined by each procedure are given in Table 4.

Although 2 μg Cr/l (total Cr) or less was determined in each sample, Cr(VI) was not detected in samples A and B. The concentration of Cr as determined by IC–ICP-MS agreed with the ICP-MS results which were relatively higher than those obtained with IC–ICP-MS. This means that the ICP-MS results obtained with the conventional introduction method suffered from

Table 3
Retention times and detection limits of the chromium species and metal elements

Element	m/z	Dwell time (s)	Counting mode	Retention time (min)	Detection limit (μg/l)[a]
Cr(III)	52	0.50	pulse	3.08	0.14
Cr(VI)	52	0.50	pulse	6.13	0.16
Mg	24	0.01	pulse	3.17	0.16
Ca	44	0.01	analog	2.78	27.78
Mn	55	0.20	pulse	3.05	0.02
Fe	57	0.20	pulse	2.62	1.82
Co	59	0.10	pulse	3.46	0.007
Ni	60	0.10	pulse	3.43	0.18
Cu	63	0.10	pulse	3.60	0.01
Zn	66	0.10	pulse	3.50	0.27
Pb	208	0.10	pulse	3.17	0.05

[a] As metal element.

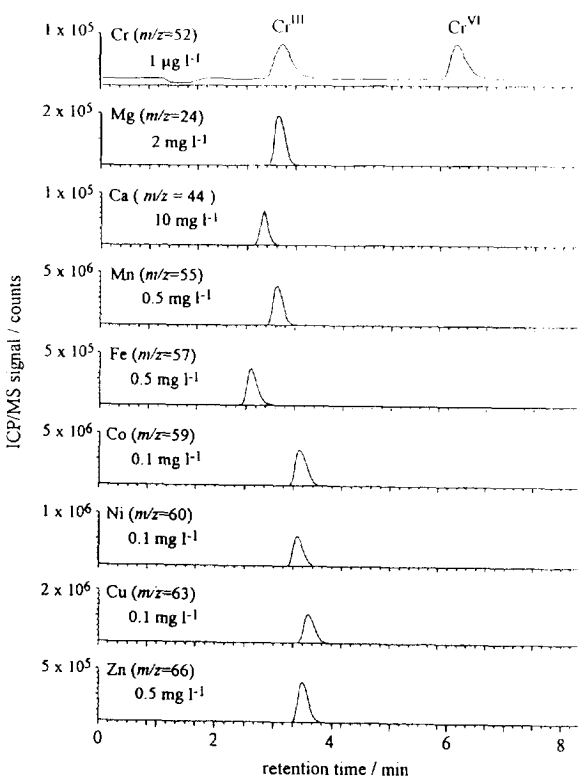

Fig. 7. Chromatograms of chromium species and metal elements by IC–ICP-MS. Conditions as in Tables 2 and 3.

interference by some matrices components, such as carbon and chlorine. The concentrations of the metal elements as determined by both methods correlated rather well, except for Fe. The concentration of Fe as determined by ICP-MS may appear higher than that determined by IC–ICP-MS, because m/z 57 shows interference from the ions $^{40}Ar^{16}O^{1}H$ and $^{40}Ca^{16}O^{1}H$. With respect to hardness, good agreement was observed for all methods.

4. Conclusions

An analytical method for the speciation of chromium species utilizing chelation is presented. Cr(III) and Cr(VI) were completely separated and detected within 8 min by the IC–ICP-MS method without any interference by ArC^{+} and ClO^{+}. The IC–ICP-MS chelation method not only presents a useful procedure for the speciation of chromium species, but can also be used for a multi-element analysis. Moreover, the IC–ICP-MS system facilitates the sample preparation process. The combination of IC–ICP-MS and chelation will be very useful for environmental monitoring of chromium species and many other metal elements in water. Further experiments will be required on the precision

Table 4
Determination of the chromium species and metal elements in water

Element	Procedures	m/z	Dwell time (s)	Concentration (μg/l)[a]				
				A	B	C	D	E
Cr^{III}	IC–ICP-MS	52	0.50	0.81	1.01	0.17	0.41	0.75
Cr^{VI}	IC–ICP-MS	52	0.50	N.D.	N.D.	0.23	0.13	1.19
Total Cr	IC–ICP-MS	–	–	0.81	1.01	0.40	0.54	1.94
	ICP-MS	52	1.00	0.71	0.75	0.68	0.93	2.21
Mn	IC–ICP-MS	55	0.20	2.53	1.97	0.37	0.09	0.01
	ICP-MS	55	0.50	2.79	2.78	0.25	0.09	0.01
Fe	IC–ICP-MS	57	0.20	57.70	60.53	88.02	126.80	45.86
	ICP-MS	57	0.10	84.32	106.90	114.70	156.00	77.42
Ni	IC–ICP-MS	60	0.10	1.53	8.02	1.10	0.42	0.91
	ICP-MS	60	0.50	1.47	11.00	1.57	0.57	0.92
Cu	IC–ICP-MS	63	0.10	3.39	7.81	1.78	0.48	0.88
	ICP-MS	63	0.10	2.84	12.69	3.14	0.32	1.04
Mg (mg/l)	IC–ICP-MS	24	0.01	3.75	3.64	4.80	3.52	3.77
	ICP-MS	24	0.10	4.71	4.71	6.64	3.57	4.39
	IC	–	–	4.00	3.80	5.90	3.50	4.00
	Titration	–	–	4.20	4.20	5.60	4.30	1.90
Ca (mg/l)	IC–ICP-MS	44	0.01	24.22	25.86	37.31	48.89	23.48
	ICP-MS	44	0.10	20.65	22.70	31.90	39.57	20.09
	IC	–	–	18.20	19.70	28.90	38.50	18.80
	Titration	–	–	18.80	20.40	30.80	38.60	19.50
Hardness as $CaCO_3$[b] (mg/l)	IC–ICP-MS	–	–	76	79	112	136	74
	ICP-MS	–	–	70	76	107	114	68
	IC	–	–	62	65	96	110	52
	Titration	–	–	64	68	100	112	57

The conditions of IC–ICP-MS were the same as those given in Table 2 except for the dwell times of ICP-MS.
[a] Unit is μg/l except for the concentrations of Mg, Ca and hardness.
[b] Calculated from the concentration of Mg and Ca.
N.D. = not detected. A–C = tap-water samples; D, E = ground-water samples.

and the accuracy of the determination of metal elements by IC–ICP-MS.

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