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Technical Report

Simple and Rapid HPLC-ICP-MS Method for the Simultaneous Determination of Cr(III) and Cr(VI) by Combining a 2,6-Pyridinedicarboxylic Acid Pre-Complexation Treatment

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A simple and rapid analytical method was developed for the simultaneous determination of two chromium species, Cr(III) and Cr(VI), in the environmental waters by high-performance liquid chromatography–inductively coupled plasma-mass spectrometry (HPLC-ICP-MS). This study incorporated a chelating pretreatment with 2,6-pyridinedicarboxylic acid (PDCA) to convert Cr(III) species into a stable Cr(III)-PDCA anion complex, which was then separated from Cr(VI) oxyanion using an anion exchange column. Building on the fundamental analytical approach proposed by Shigeta *et al*. (doi: 10.2116/analsci.18P012), the mobile phase was optimized to ensure stability for ICP-MS detection, avoiding nonvolatile salts. Chromium species and chloride ions were effectively separated within 6 minutes at a flow rate of 0.6 mL min^{-1} with the optimized mobile phase, which consisted of 50 mmol L^{-1} ammonium acetate (pH 6.80) and 2 mmol L^{-1} PDCA. The detection limits were 0.18 μg L^{-1} and 0.09 μg L^{-1} for Cr(III) and Cr(VI), respectively, at *m/z* 52 under He collision mode.

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1. INTRODUCTION

The oxidation state of an element varies from species to species, which can influence how it behaves in the environment. It is also recognized that the toxicity of some heavy metals depends on specific species rather than total amounts. Therefore, the demand for techniques to accurately determine heavy metal speciation has increased.[1)] For chromium (Cr), the most stable oxidation states in the surface environment are trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. Cr(III) is toxic only at high concentrations and even essential for humans at trace levels, whereas Cr(VI) is highly toxic and more soluble in water.[2)] Cr(VI) has been used in various industries, such as electroplating, paint manufacture, and metallurgy. These industries are the main contamination sources of chromium in the surface waters, except in the ultramafic lithology, where some cases exceed drinking water regulations (0.70–245 μg L^{-1} Cr).[3–5)] Because chromium toxicity is species-specific, the determination of total chromium in surface waters is not sufficient for environmental risk assessment. Thus, numerous analytical methods for chromium speciation have been developed in the last decades.[6–8)] Among the various methods, the combination of high-performance liquid chromatography (HPLC) with inductively coupled plasma–mass spectrometry (ICP-MS) is one of the most powerful and sensitive analytical tools in chromium speciation analysis.[9,10)]

Determination of chromium by ICP-MS detection provides comprehensive information on the presence of chromium species but has some limitations. Chromium has four stable isotopes (^{50}Cr, ^{52}Cr, ^{53}Cr, and ^{54}Cr), with the most abundant isotope being ^{52}Cr, representing approximately 83.8% of the total. The introduction of matrices containing high levels of chlorine (Cl) or carbon (C) into an ICP source will result in the production of polyatomic ions, including $^{35}Cl^{16}OH^+$, $^{40}Ar^{12}C^+$, and $^{37}Cl^{14}NH^+$, within the plasma.

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The presence of these polyatomic ions may interfere with the ability to detect ^{52}Cr isotope, given that they exhibit the same integer *m/z*. One effective strategy for reducing polyatomic interferences is to separate chlorine- and carbon-based interferences from chromium species by chromatography prior to ICP ionization. An alternative approach is the utilization of a collision/reaction cell (CRC) with He and/or H_2 gas,[11,12] though this approach also reduces the chromium ion signal.[11]

The simultaneous separation of chromium species and interfering compounds has been achieved through the utilization of a variety of HPLC methods. These include reversed-phase chromatography (RPC),[13] ion-exchange chromatography (IC),[14–18] ion-pairing chromatography (IPC),[19,20] and hydrophilic interaction liquid chromatography (HILIC).[21] Currently, IC-ICP-MS using an aqueous mobile phase is commonly used for chromium speciation analysis in most applications. Simultaneous retention of Cr(III) and Cr(VI) on a single ion exchange column is impossible due to their opposite valences (*e.g.,* $Cr(H_2O)_6^{3+}$, $HCrO_4^-/CrO_4^{2-}$). Previous studies have proposed the use of chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and 2,6-pyridinedicarboxylic acid (PDCA), to unify Cr(III) into anionic species ($[Cr(EDTA)]^-$, $[Cr(PDCA)_2]^-$) and separate it from Cr(VI) in an anion exchange column.[11,14,17,22–25] However, when EDTA is used as the ligand, a substantial amount of chloride may impede the quantification of Cr(III) at *m/z* 52 due to the molecular ion interference. This is because the retention time of the chloride ion (Cl^-) is nearly identical to that of the Cr(III)-EDTA complex.[11]

Shigeta *et al.*[25] proposed a technique for separating and determining chromium species that involved the combination of HPLC-ICP-MS and a chelating pretreatment with PDCA under near-neutral pH conditions. The principal benefit of this approach is that it enables the separation of the Cr(III)-PDCA from Cl^- while maintaining the original oxidation states of chromium species during analysis. For a more tolerant and simplified approach, a mobile phase without nonvolatile salts is typically preferred to avoid salt deposition on the ICP interface during long-term analysis. This study aims to develop a simple and rapid method for simultaneously determining chromium species by HPLC-ICP-MS. Based on the analytical concept of Shigeta *et al.*,[25] a mixture of ammonium acetate buffer and PDCA was used as a mobile phase suitable for ICP-MS detection, and HPLC separation conditions were optimized by varying buffer pH and flow rate.

2. EXPERIMENTAL

2.1. Reagents and solutions

The mobile phase stock solutions of 500 mmol L^{-1} ammonium acetate (CH_3COONH_4) and 20 mmol L^{-1} PDCA were prepared by diluting CH_3COONH_4 (>97.0%, conforms to RoHS2, Kanto Chemical, Tokyo, Japan) and PDCA (99%, Acros Organics, Geel, Belgium) with ultrapure water. A diluted ammonia solution (25.0–27.9%, for metal analysis, Kanto Chemical) and a diluted acetic acid (>99.7%, conforms to RoHS2, Kanto Chemical) were used to adjust pH for the subsequent experiments.

The 100 µg L^{-1} Cr(III) standard stock solution was prepared by diluting 1000 mg L^{-1} Cr(III) standard solution (for Atomic absorption spectrometry (AAS) analysis, in 0.1 mol L^{-1} HNO_3, Kanto Chemical). For Cr(VI) standard stock, two different reagents were used. One was 100 mg L^{-1} Cr(VI) standard solution (for AAS analysis, in 0.01 mol L^{-1} HNO_3, Kanto Chemical), and the other was potassium dichromate ($K_2Cr_2O_7$) (Reagent Plus grade, >99.5%, Sigma Aldrich, St. Louis, MO, USA). In the former case, the 100 µg L^{-1} Cr(VI) standard stock solution was prepared by diluting 100 mg L^{-1} Cr(VI) standard solution with ultrapure water. In the latter case, the 100 mg L^{-1} Cr(VI) standard stock was prepared by dissolution of $K_2Cr_2O_7$ in ultrapure water. This stock solution was diluted to 100 µg L^{-1} on the day of analysis. The Cr(VI) standard solution, prepared from $K_2Cr_2O_7$, was the primary solution utilized in the experiments conducted in this study, except for the optimization of the mobile phase pH. This was due to the observation from preliminary experiments that the Cr(VI) standard solution, prepared by dilution of the liquid phase Cr(VI) standard, may contain colloidal phase chromium, which could potentially affect the signal intensity per unit concentration of Cr(VI). The initially dissolved Cr(VI) may undergo precipitation when reduced to Cr(III) via photo-reduction or other processes under acidic pH conditions during the storage period.

In addition, a solution of 210 mg L^{-1} hydrochloric acid (HCl) was prepared by diluting HCl (35%, Ultrapur-100, Kanto Chemical) to confirm the separation of Cl^- from chromium species in retention time. Ultrapure water (18.2 MΩ·cm, Milli-Q Advantage System, Millipore, Billerica, MA, USA) was used for the preparation of all solutions and standards.

2.2. Chelating pretreatment

For preparing the Cr(III)–Cr(VI) mixed standard solutions, the two mobile phase stock solutions, Cr(III) standard stock solution, Cr(VI) standard stock solution, and ultrapure water, were simultaneously transferred to 15 mL polypropylene tubes. The solutions were then heated in a water bath at 80°C for 30 minutes to achieve complexing of Cr(III) with PDCA to obtain 0.5, 1, 2.5, 5, and 10 µg L^{-1} Cr(III)–Cr(VI) mixed standard solutions. The pH of the chelating solution was fixed at 6.80.[25,26] All prepared solutions were analyzed within a few hours.

2.3. Instrumentation

The separation of chromium species was performed by a bio-inert HPLC system Agilent 1260 II infinity (Agilent Technologies, Santa Clara, CA, USA) equipped with an Agilent Bio WAX anion exchange column (5190–2488, 5 µm particle size, Agilent Technologies) packed in a metal-free PEEK hardware (4.6 mm i.d.×50 mm). The column temperature was maintained at room temperature using a column oven (G7116A). A bio-inert high-performance autosampler (G5668A) was employed for the sample injection, with an injection volume of 10 µL. The mobile phase was delivered at a flow rate of 0.3–0.7 mL min^{-1} with a bioinert quaternary pump (G5611A). The outlet of the column was connected directly to the nebulizer of the ICP-MS (Agilent 8800 ICP-MS/MS, Agilent Technologies).

The ICP-MS was operated at a moderate plasma condition (1200 W) with a lower carrier gas flow to reduce the formation of polyatomic ions, primarily derived from Ar gas, which interfere with chromium isotopes. For the chromium isotope, *m/z* 52 was acquired, and the amount of chlorine at

Table 1. Optimized parameters for HPLC and ICP-MS conditions.

HPLC	
Column	Agilent Bio WAX (4.6 mm i.d. × 50 mm)
Mobile phase	50 mmol L^{-1} CH_3COONH_4, 2 mmol L^{-1} PDCA (pH 6.80)
Flow rate	0.6 mL min^{-1}
Column temperature	Room temperature
Injection volume	10 μL
ICP-MS	
RF power	1200 W
Plasma gas	15 L min^{-1}
Auxiliary gas	1.0 L min^{-1}
Carrier gas	1.0 L min^{-1}
Sampling depth	5.5 mm
Spray chamber temperature	2°C
Injector	2.5 mm i.d.
CRC gas	He 4.3 mL min^{-1}
KED	+3 V
Monitored isotope (*m/z*)	^{52}Cr, ^{35}Cl
Integration time	1 s for ^{52}Cr, 0.001 s for ^{35}Cl

CRC, collision/reaction cell; HPLC, high-performance liquid chromatography; ICP-MS, inductively coupled plasma-mass spectrometry; KED, kinetic energy discrimination; PDCA, 2,6-pyridinedicarboxylic acid.

m/z 35 was also monitored to investigate the interference of $^{35}Cl^{16}OH^+$ on $^{52}Cr^+$. Polyatomic interferences of ArC^+ and ClO^+ produced in Ar plasma were reduced by adding He gas into the CRC. Detailed analytical conditions of HPLC-ICP-MS are shown in Table 1.

3. RESULTS AND DISCUSSION

3.1. Optimization of HPLC condition

At elevated pH values, the complexation rate between Cr(III) and PDCA is relatively slow,[27] whereas Cr(VI) is reduced to Cr(III) at acidic pH.[9] For these reasons, an eluent with a pH of 6–7, close to neutral, was employed to optimize the separation of chromium species. To investigate the impact of pH on chromatographic behavior, the mobile phase pH was adjusted to four discrete values (6.22, 6.41, 6.71, and 7.03) at a flow rate of 0.3 mL min^{-1}, and Cr(III) and Cr(VI) were introduced at a 1:1 ratio. Subsequent experiments were performed to determine the optimal flow rate for the separation of chromium species and Cl^- using the mobile phase with a pH of 6.80. The flow rate was varied between 0.3 mL min^{-1} and 0.7 mL min^{-1}.

Figure 1 shows that Cr(III)-PDCA and Cr(VI) are successfully separated, although the retention times of Cr(III)-PDCA and Cr(VI) are not significantly different at all pH values. The acid dissociation equilibrium of CH_3COOH shifts toward a more dissociated form with increasing pH when CH_3COONH_4 buffer is used as the eluent. This reaction can typically increase the elution strength of the eluent and reduce the retention time of the anions. However, the retention time of Cr(VI) showed the opposite tendency, with a slight increase at higher pH values. Below pH 6.5, the hydrogen chromate ($HCrO_4^-$) is likely predominant, while the chromate (CrO_4^{2-}) is predominant above pH 6.5.[9] The longer retention times at higher pH (6.71 and 7.03) can be attributed to the prevalence of CrO_4^{2-}, which has a relatively strong electrostatic interaction with the column stationary group than $HCrO_4^-$.

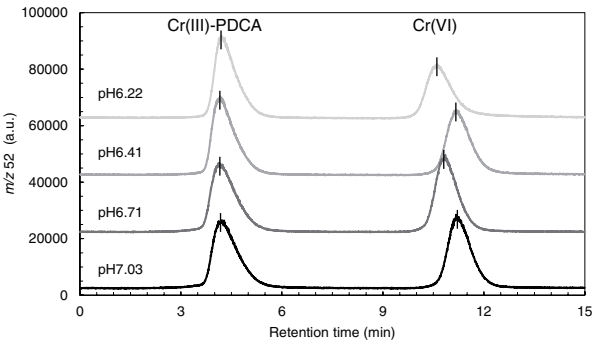

Fig. 1. Chromatograms of 100 μg L^{-1} Cr(III)-PDCA and Cr(VI) for *m/z* 52 at pH 6.22 (light gray), 6.41 (gray), 6.71 (dark gray), and 7.03 (black) under the flow rate of 0.3 mL min^{-1}. PDCA, 2,6-pyridinedicarboxylic acid.

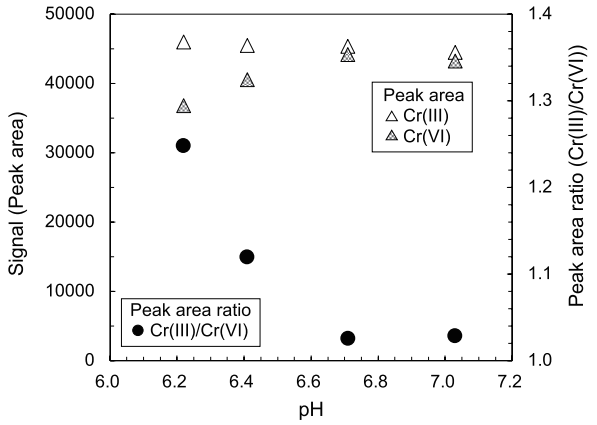

Fig. 2. Signals (peak area) of Cr(III) (open triangle) and Cr(VI) (mesh triangle) and peak area ratio of Cr(III)/Cr(VI) (closed circle) at pH 6.22, 6.41, 6.71, and 7.03.

Furthermore, at lower pH (6.22 and 6.41), the Cr(VI) peak area decreased and the Cr(III) peak area increased. The calculated peak area ratios for Cr(III) to Cr(VI) as Cr(III)/Cr(VI) are 1.2 and 1.1, respectively, for pH 6.22 and 6.41 (Fig. 2). The Cr(III)/Cr(VI) ratio tends to increase, particularly in conditions with lower pH. Given that chemical speciation analysis by ICP-MS dissociates to the atomic level for detection, it is expected that the peak area will be consistent across different chemical species when the same molar concentration of analyte is introduced. These findings suggest that Cr(VI) species are undergoing reduction to Cr(III) species in the lower pH conditions. Conversely, no Cr(VI) reduction was observed at pH values above 6.71, and the Cr(III)/Cr(VI) ratio exhibited a value of approximately 1.0 (Fig. 2). Therefore, the optimal pH range for the mobile phase is between 6.71 and 7.03, which allows for complete separation and preservation of the original chromium species.

Both chromium species were determined within approximately 13 minutes under a flow rate of 0.3 mL min^{-1}, almost twice the time of the method reported by Shigeta *et al.*[25] The maximum flow rate that maintained the separation between Cl^- and Cr(III)-PDCA was verified for a high sample throughput. The fastest separation was achieved within 5 minutes at a flow rate of 0.7 mL min^{-1}, but the Cl^- and Cr(III)-PDCA peaks were not completely separated at high

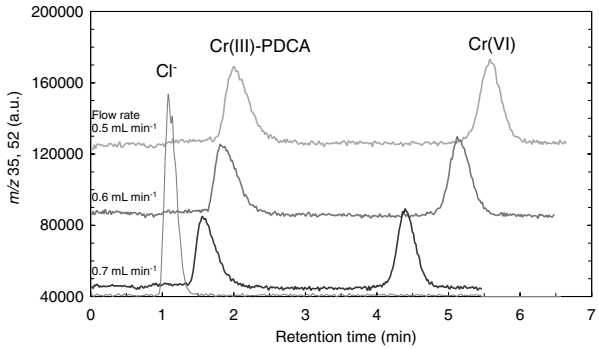

Fig. 3. Chromatograms of 10 μg L^{-1} Cr(III)-PDCA and Cr(VI) for *m/z* 52, using a pH 6.80 mobile phase and a flow rate of 0.5 mL min^{-1} (light gray), 0.6 mL min^{-1} (gray), and 0.7 mL min^{-1} (black) with the chromatogram of 210 mg L^{-1} Cl for *m/z* 35 at a flow rate of 0.6 mL min^{-1} (gray). PDCA, 2,6-pyridinedicarboxylic acid.

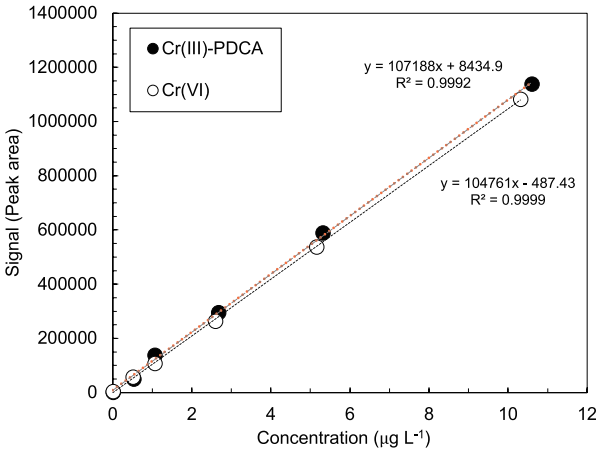

Fig. 4. Calibration curves for Cr(III) (closed circle) and Cr(VI) (open circle) under optimized HPLC and ICP-MS conditions.

Cl contents (210 mg L^{-1}) (Fig. 3). Therefore, 0.6 mL min^{-1} was designated as the optimal flow rate at which Cl^- and Cr(III)-PDCA can be completely separated even in water samples with high concentrations of Cl, such as industrial wastewater and brackish water. Under the optimal conditions, chromium species can be analyzed within 6 minutes (Fig. 3).

3.2. Calibration curve and detection limits

The linear dynamic range was determined by analyzing five calibration standards (0.5, 1, 2.5, 5, and 10 μg L^{-1}) for both Cr(III) and Cr(VI). The correlation coefficients for these calibration curves exceeded 0.999, indicating strong linearity across the tested range (Fig. 4). Subsequently, the 0.5 μg L^{-1} standard was subjected to five replicate measurements with a 10 μL injection to determine the detection limits. The standard deviation of the replicate analyses was calculated, multiplied by 3.29, and divided by the slope of the calibration curve. The resulting detection limits were 0.18 μg L^{-1} and 0.09 μg L^{-1} for Cr(III) and Cr(VI) at *m/z* 52, respectively. These values are comparable to or better than those reported in earlier studies utilizing chromatographic techniques (IC-ICP-MS or IPC-ICP-MS) considering the injection volume.[11,15,17,20,23–25] Furthermore, the detection limit of Cr(VI) achieved in this study is sufficiently low to satisfy Japan's environmental quality standard for Cr(VI) in water (0.02 mg L^{-1}).[28]

4. CONCLUSIONS

This study developed a simple and rapid method for the simultaneous determination of Cr(III) and Cr(VI) by combining chelating pretreatment with PDCA and IC coupled to ICP-MS. The mobile phase, a mixture of ammonium acetate buffer and PDCA devoid of nonvolatile salts, effectively separated the chromium species from chloride ions under near-neutral pH conditions (6.71–7.03). Although a flow rate of 0.7 mL min^{-1} provided the quickest analysis time, a rate of 0.6 mL min^{-1} is recommended for samples with high chloride ion (>210 mg L^{-1}) to ensure complete separation of Cr(III)-PDCA from chloride ion peak. Under the optimized condition, the analysis time for both species is less than 6 minutes, with detection limits of 0.18 μg L^{-1} for Cr(III) and 0.09 μg L^{-1} for Cr(VI) at *m/z* 52, which are comparable to or better than those reported in previous studies using HPLC-ICP-MS. These advantages make this method well-suited for analyzing environmental water and industrial wastewater samples, where rapid determination of chromium chemical species with high sample throughput is essential.

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We confirm that this work is original and has not been published elsewhere, nor is it currently under consideration for publication elsewhere.

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The authors have no relevant financial or non-financial interests to disclose.

DATA AVAILABILITY STATEMENT

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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