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Application News

ICP Mass Spectrometer ICPMS-2040 Series, ICPMS-2050 Series

Speciation Analysis of Chromium by LC-ICP-MS Based on ISO 24384

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User Benefits
◆ Enables Cr(III) and Cr(VI) to be measured simultaneously in accordance with ISO 24384.
◆ Suffers less interference from coexisting substances than the conventional method for measuring Cr(VI) and can be analyzed with a simple pretreatment.
◆ Easy to connect instruments simply by attaching the LC column outlet piping to the ICP-MS nebulizer.

■ Introduction

There are two types of chromium, Cr(III) and Cr(VI), and Cr(VI) is highly toxic. Conventionally, to selectively measure harmful Cr(VI), diphenylcarbazide absorptiometry was used, or Cr(III) was removed beforehand by the iron coprecipitation method and then measured by elemental analysis. However, problems were caused due to interference from coexisting substances and the need for complicated pretreatment operations.

In recent years, the speciation analysis method for Cr using LC-ICP-MS has been attracting attention as a solution to such issues. In February 2024, ISO 24384[1] Determination of chromium(VI) and chromium(III) in water was published as a method applicable to the analysis of wastewater, surface water, groundwater and drinking water.

In this method, Cr(III) is chelated using 2,6-pyridinedicarboxylic acid (PDCA) or ethylenediaminetetraacetic acid (EDTA) and then separated and quantified by LC-ICP-MS. This method is less prone to interference, is simple to use , and allows simultaneous determination of Cr(III) and Cr(VI). In this application, EDTA was used as a chelating agent, and the results of performing chromium speciation using a Prominence Inert Analysis System connected to an ICPMS-2050 are reported.

■ Sample

Mineral water A (soft water), B (hard water), C (hard water), Tap water, river water and wastewater

■ Sample Pretreatment

(1) Filter sample through a syringe filter with a pore size of 0.45 μm.
(2) Adjust the pH of 10 mL of the filtrate to about 6.9 with nitric acid.
(3) Add 2 mL of 0.025 mol/L EDTA solution adjusted to around pH 6.9, and adjust to 20 mL with pure water.
    Note: At this point, the spiked samples for the spike recovery test were spiked with 10 μg/L of Cr(III) and Cr(VI).
(4) Heat at 70 ± 3 °C for 60 minutes.
(5) Cool and filter through a syringe filter with a pore size of 0.2 μm.

■ Standard Solution/Calibration Curve Sample

• Cr(III) Standard Solution:　Cr(III) 1000 mg/L from chromium(III) nitrate nonahydrate
• Cr(VI) Standard Solution:　Cr(VI) 1000 mg/L from potassium dichromate

Calibration curve samples were prepared using the above standard solutions to obtain the concentrations shown in Table 1. At this time, sample pretreatment (3) and subsequent steps were performed, and the samples were chelated in the same method.

Table 1 Calibration Curve Samples Concentration (μg/L)

Element	STD1	STD2	STD3	STD4	STD5	STD6	STD7
Cr(III)	0.05	0.2	0.5	2	5	10	20
Cr(VI)	0.05	0.2	0.5	2	5	10	20

■ Instrument Configurations and Analysis Conditions

LC and ICP-MS instrument configurations and analysis conditions are shown in Tables 2 to 4.

Table 2 LC Configuration and Analysis Conditions

System:	Prominence Inert
Column:	Shodex SI-35-4D (150 mm × 4.0 mm I.D., 3.5 μm)
Guard Column:	Shodex SI-95(G) (10 mm × 4.6 mm I.D., 9 μm)
Column Type:	Anion exchange column
Base Material:	Spherical porous particles of polyvinyl alcohol modified with quaternary ammonium
Column Housing:	PEEK
Mobile Phase:	100 mmol/L HNO$_3$ pH7.0 (pH adjusted with NH$_4$OH)
Mobile Phase Flowrate:	0.45 mL/min
Column Temp.:	25 °C
Injection Volume:	200 μL
Vial:	Polypropylene

Table 3 ICP-MS Configuration

Instrument:	ICPMS-2050
Nebulizer:	Nebulizer DC04
Torch:	Mini Torch
Chamber:	Cyclone Chamber
Sampling Cone:	Nickel
Skimmer Cone:	Nickel

Table 4 ICP-MS Analysis Conditions

RF Power:	1.2 kW
Sampling Depth:	5 mm
Plasma Gas Flowrate:	9.0 L/min
Auxiliary Gas Flowrate:	1.1 L/min
Carrier Gas Flowrate:	0.45 L/min
Dilution Gas Flowrate:	0.40 L/min
Cell Gas:	He
Cell Gas Flowrate:	3.5 mL/min
Cell Voltage:	-15 V
Energy Filter:	7 V
Element • m/z:	Cr • m/z = 52

■ Retention Times of Cr(III) and Cr(VI)

The changes in the retention times of Cr(III) and Cr(VI) with and without EDTA chelation treatment are shown in Fig. 1.
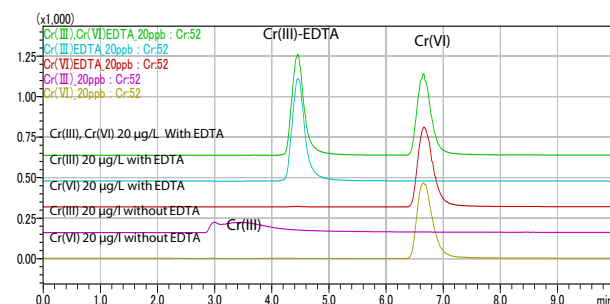

Fig. 1 Effect of EDTA Chelation Treatment on Chromatograms

Generally, Cr(III) exists as Cr^{3+} and Cr(VI) exists as a chromate ion (CrO_4^{2-}) or dichromate ion ($Cr_2O_7^{2-}$) in solution. Without EDTA chelation, Cr(III) is present as a cation, is not retained in the anion exchange column and appears as a broad peak at first. When chelation treatment with EDTA is performed, Cr(III) forms a chelate complex and is retained in the column. On the other hand, since Cr(VI) does not react with EDTA and always exists as an anion, it has the same retention time regardless of the presence or absence of EDTA.

■ Resolution and Linearity of Calibration Curve

Fig. 2 shows the chromatograms obtained when the calibration curve samples for 0.05 to 20 µg/L of each component were measured. The resolution of Cr(III) and Cr(VI) is 4.4, achieving complete separation. Fig. 3 shows the calibration curves for each component. The calibration curve showed good linearity.
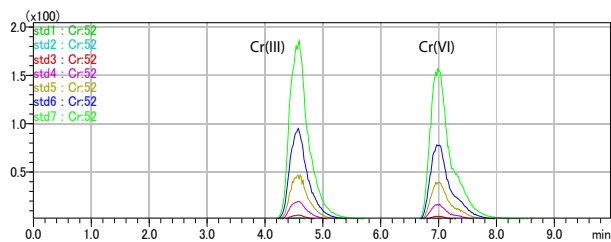
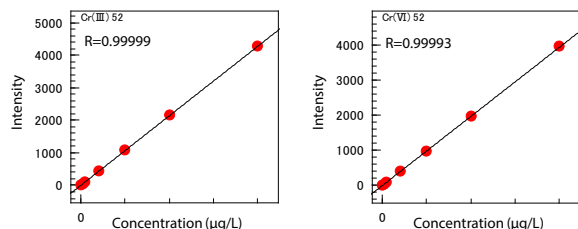Fig. 2 Chromatograms of Calibration Curve Samples

Fig. 3 Calibration Curve (Left: Cr(III) Right: Cr(VI))

■ Measurement Sensitivity

Fig. 4 shows the results of five repeated measurements of STD1 (0.050 µg/L). The detection limit was calculated by converting three standard deviations of the peak area value obtained by repeated measurement of STD1 into concentration. The detection limits obtained are shown in Table 5.
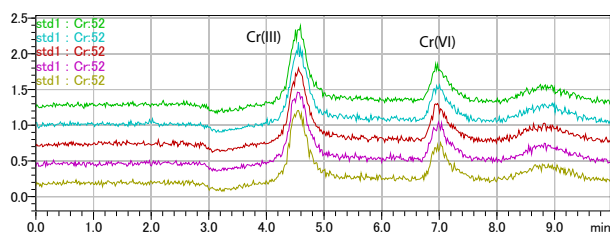
Fig. 4 Repeated Measurement of STD1 (0.05 µg/L)

■ Results of Sample Analysis

The results of the sample analysis are shown in Table 5. In spike recovery tests conducted on each sample, the recovery rate was 97 to 109 %, well within the 80 to 120 % range recommended by ISO. In addition, the total concentrations of Cr(III) and Cr(VI) were comparable to those of total Cr measured only by ICP-MS, and the difference between the quantitative values was less than 30 %, which is the criterion for determining the presence of interference.

■ Conclusion

In this study, a Prominence inert analysis system was connected to an ICPMS-2050 and various samples were measured.

The measurement sensitivity and resolution were good, and the spike recovery rate for each sample met the criteria required by ISO 24384 well.

The LC-ICP-MS method can simultaneously quantify Cr(III) and Cr(VI) using only simple pretreatment and is less prone to the effects of coexisting substances than the conventional method. The LC-ICP-MS analysis system is easily constructed by simply attaching the LC column outlet piping to the ICP-MS nebulizer.

This analysis was performed on an ICPMS-2050 equipped with a collision/reaction cell, but it can also be performed on the ICPMS-2040, a model dedicated to the collision mode.

<References>

1) ISO 24384:2024 "Water quality — Determination of chromium(VI) and chromium(III) in water — Method using liquid chromatography with inductively coupled plasma mass spectrometry (LC-ICP-MS) after chelating pretreatment" (Edition 1, 2024)

Table 5 Sample Analysis Results (µg/L)

	Cr(III) Undiluted Concentration	Cr(VI) Undiluted Concentration	Cr(III) Spike Recovery Rate	Cr(VI) Spike Recovery Rate	Cr(III), (VI) Total Concentration	Total Cr Concentration (Measured by ICP-MS only)
Limit of Detection 3σ (In the Measurement Solution)	0.015	0.006	-	-	-	0.007
Limit of Detection 3σ (In the Undiluted Solution)	0.031	0.011	-	-	-	0.014
Blank Test Solution	<	<	-	-	<	<
Mineral Water A (Soft Water)	<	0.12	99 %	101 %	0.12	0.13
Mineral Water B (Hard Water)	<	0.17	108 %	109 %	0.17	0.19
Mineral Water C (Hard Water)	<	<	102 %	107 %	<	<
Tap Water	<	0.21	98 %	98 %	0.21	0.20
River Water	0.11	<	104 %	97 %	0.11	0.14
Wastewater	<	0.17	101 %	99 %	0.17	0.19

<: Below Limit of Detection

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