

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

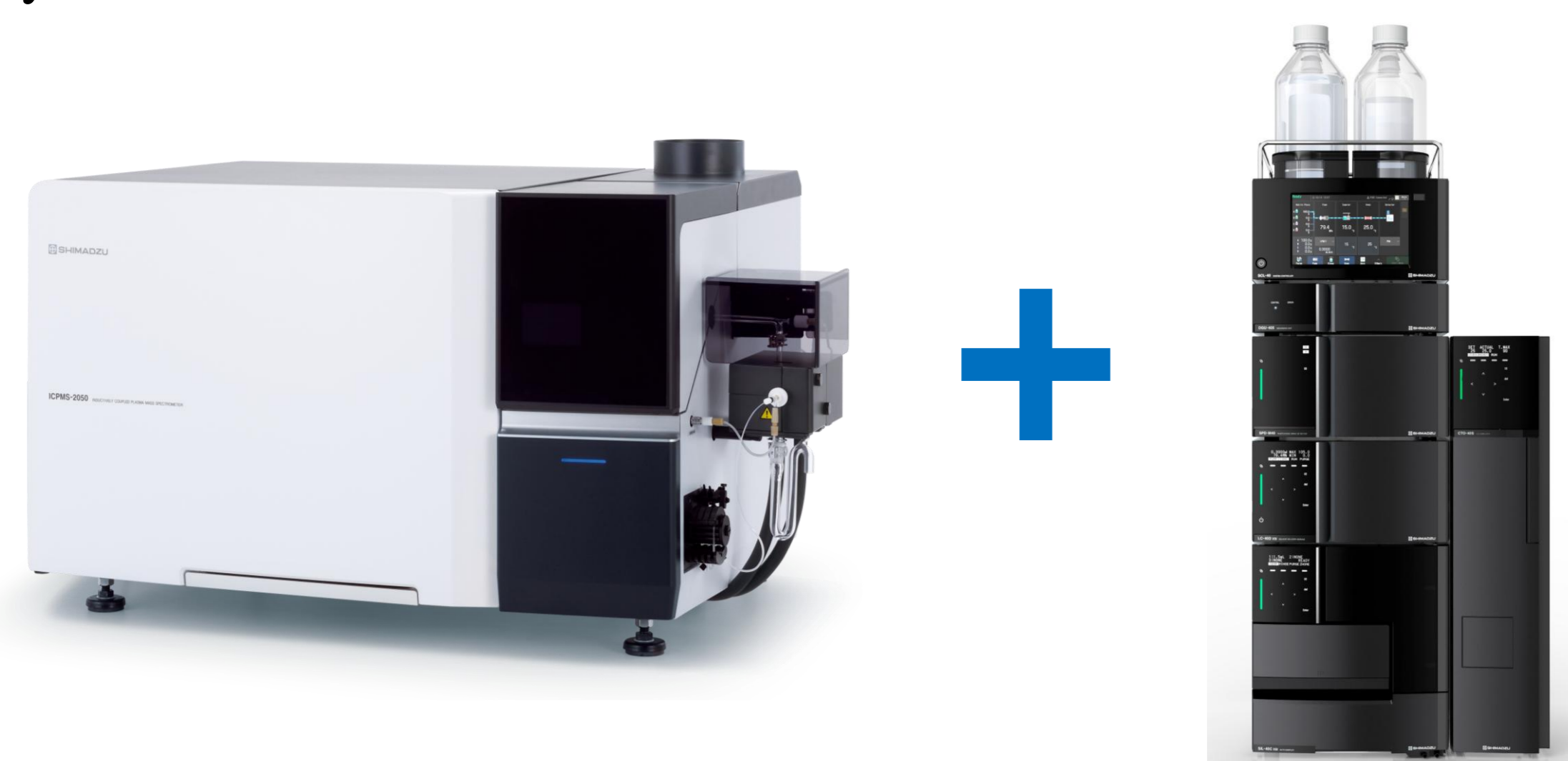
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1. Introduction

As a method for the analysis of hazardous Cr (VI) in environmental water, diphenylcarbazide spectrophotometry is widely used; however, there are also issues such as interference from coexisting substances and complicated pretreatment. In February 2024, ISO 24384¹⁾ Determination of chromium(VI) and chromium(III) 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).

Here, 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 shown.



2. Sample & Pretreatment

Sample:

6 sample types were analyzed: mineral water A (soft water), B (hard water), C (hard water), tap water, river water and wastewater.

Pretreatment:

- Filter sample through a syringe filter with a pore size of 0.45 μm .
- Adjust the pH of 10 mL of the filtrate to about 6.9 with nitric acid.
- 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 $\mu\text{g/L}$ of Cr(III) and Cr(VI).

- Heat at 70 ± 3 °C for 60 minutes.
- Cool and filter through a syringe filter with a pore size of 0.2 μm .

3. Instrument Configurations and Analysis Conditions

Table 1. ICP-MS Configuration

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

Table 2. ICP-MS Analysis Conditions

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

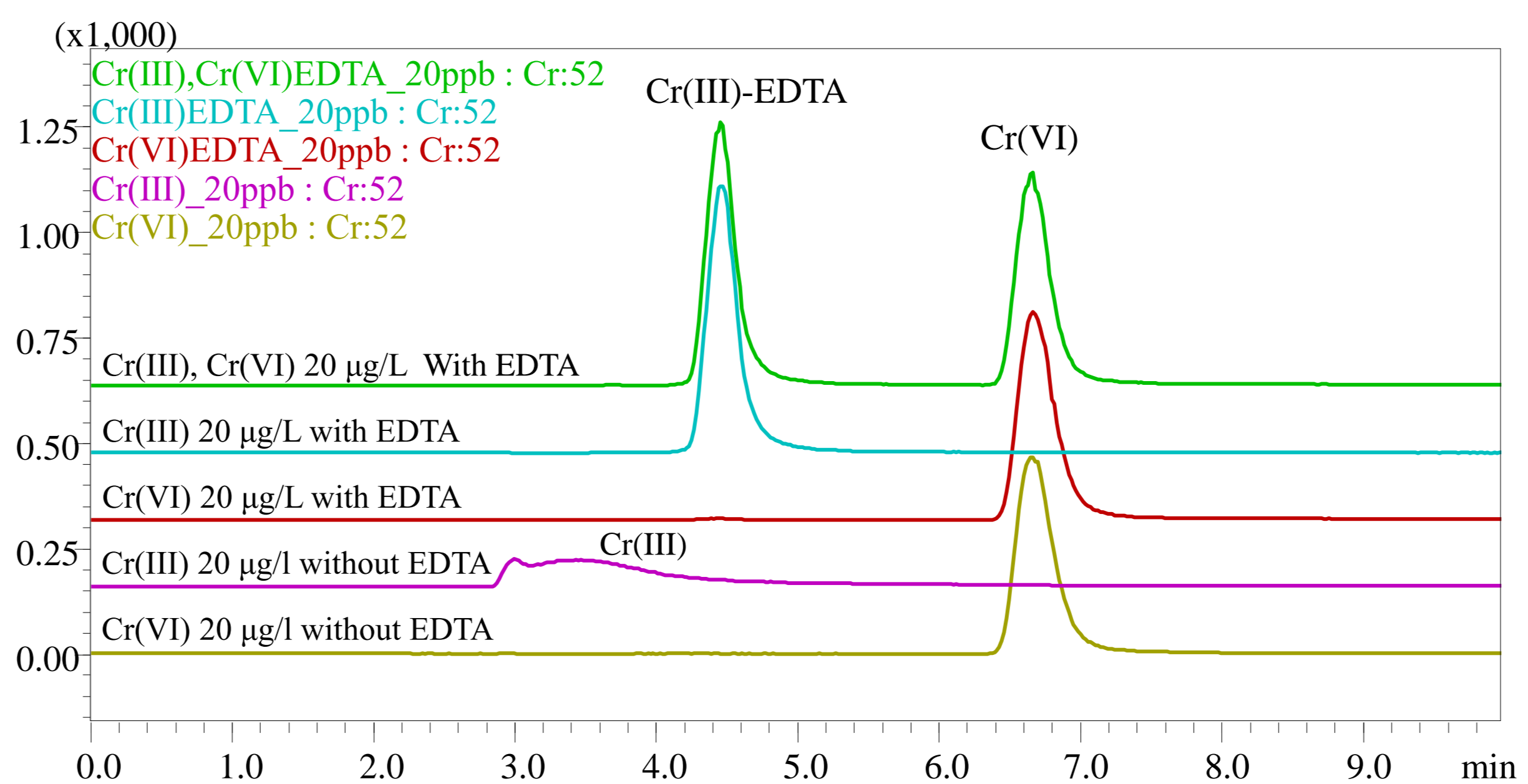
Table 3. LC Configuration and Analysis Conditions

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
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

4. Retention Time of Cr(III) and Cr(VI)

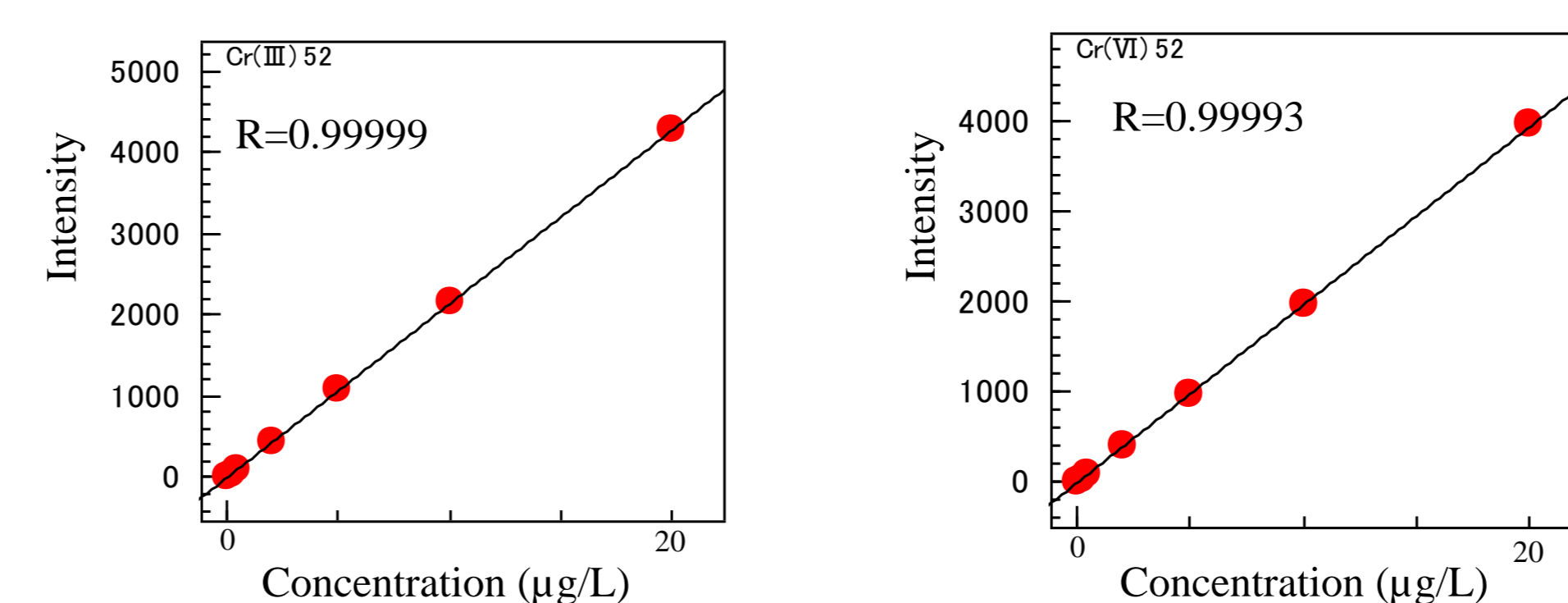
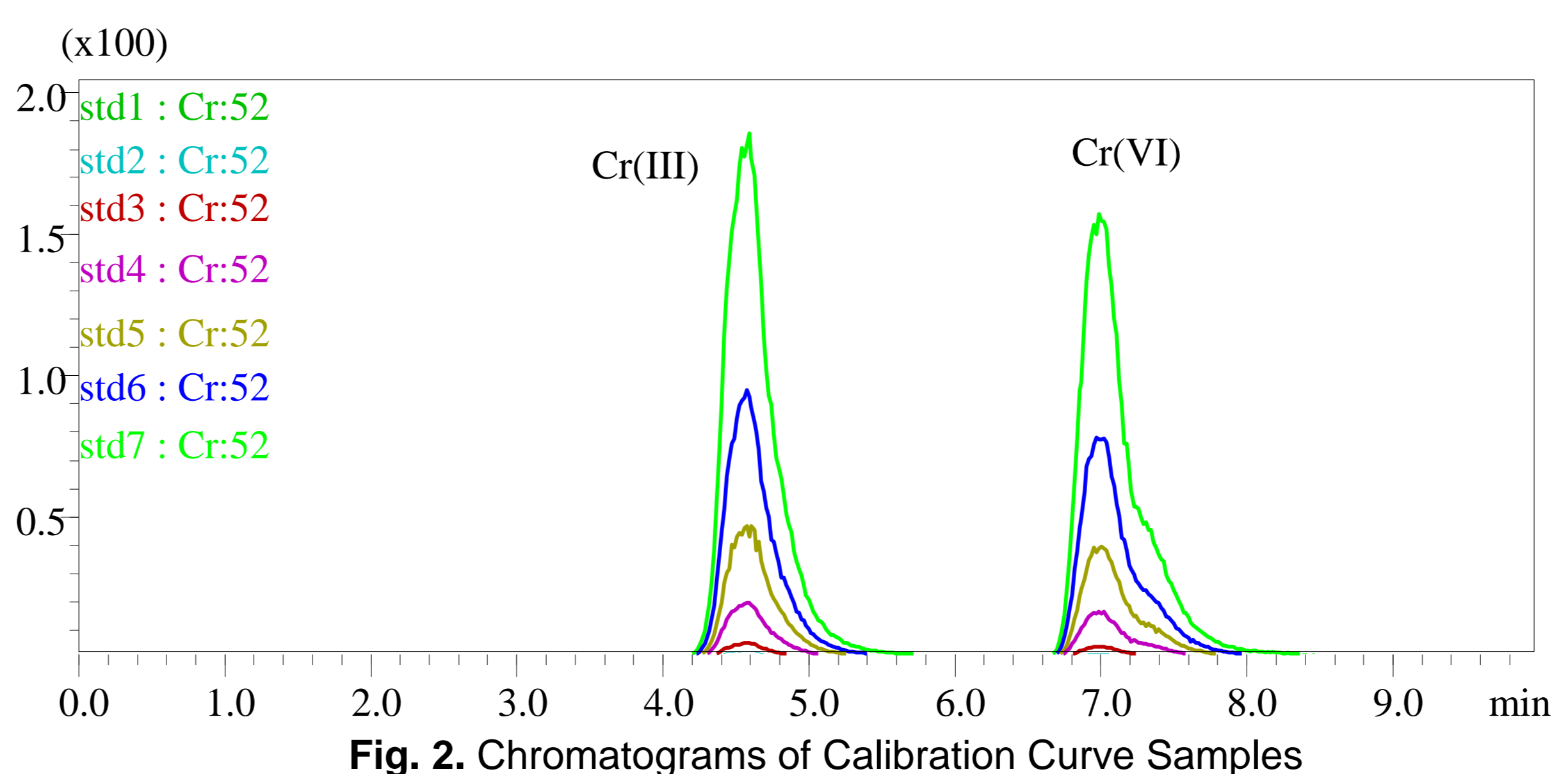
The changes in the retention times of Cr(III) and Cr(VI) with and without EDTA chelation treatment are shown in Fig. 1.

Generally, Cr(III) exists as Cr³⁺ and Cr(VI) exists as a chromate ion (CrO₄²⁻) or dichromate ion (Cr₂O₇²⁻) in solution. Without EDTA chelation, Cr³⁺ 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.



5. Resolution and Linearity of Calibration

Fig. 2 shows the chromatograms when the calibration standards from 0.05 to 20 $\mu\text{g/L}$ of each component were measured. The resolution of Cr(III) and Cr(VI) is 4.4, achieving complete separation. Fig. 3 shows the calibration for each component which shows good linearity.



6. Sensitivity

The detection limit was calculated as three standard deviations of the peak area value obtained from the repeated measurement of STD1 by its concentration ($3\sigma \times \text{conc}$), which are shown in Table 4.

Table 4. Sample Analysis Results ($\mu\text{g/L}$)

	Cr(III) Undiluted Concentration	Cr(VI) Undiluted Concentration	Cr(III) Spike Recovery	Cr(VI) Spike Recovery	Cr(III), (VI) Total Concentration	Total Cr Concentration (Measured by ICP-MS)
Limit of Detection 3σ (In the solution)	0.015	0.006	-	-	-	0.007
Limit of Detection 3σ (Before dilution)	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

7. Results of Sample Analysis

The results of the sample analysis are shown in Table 4. 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 24384. In addition, the total concentrations of Cr(III) and Cr(VI) were comparable to those of total Cr measured only by ICP-MS, which is the criterion for determining the presence of interference.

8. Summary

Six types of water samples were measured using a Prominence inert analysis system which connected to an ICPMS-2050.

The 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.

<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)