

Chromium VI Analysis Revisited to Respond to Evolving Environmental Regulations

August 2024

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Background

 Introduction of chromium analysis and United States Environmental Protection Agency (EPA) methods

• Experimental Conditions

● Instruments (NexeraTM lite inert) and analytical conditions

• Results

• Quality control (QC) requirements in EPA method and experimental data

Today's presentation

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Why Chromium analysis is important?



- Cr is widely used in steelmaking, paints, etc.
- The most common forms of chromium: trivalent chromium (Cr III), hexavalent chromium (Cr VI) and metallic chromium.
- The toxicity of Cr varies greatly depending on its valence.

While Cr III is non-toxic and essential for human health, Cr VI is highly toxic.

• Most of countries has established regulations and laws for public water.

Regulatory drivers for Cr VI analysis

- Total Cr is regulated in drinking water since 1942.
- In 1991, EPA set the maximum Contaminant Level (MCL) for total Cr at 100 μg/L.
- In July 2014, California adopted the first national standard for Cr VI in drinking water, setting MCL at 0.010 mg/L (invalidated in 2017).
- In April 2024, California added the MCL at 10 μg/L for Cr VI into the current regulation (MCL at 50 ug/L for Total Cr).

EPA method 218.7 outline

In EPA Method 218.7, Cr VI is separated by anion exchange column.

The colored complex formed between Cr VI and 1,5diphenylcarbazide in the post column derivation is detected at 530 nm.

EPA 218.7 requires

- Low detection limit (DL) of Cr VI \rightarrow from 0.0044 to 0.015 µg/L
- Large injection volume
 - \rightarrow usually 1 mL

METHOD 218.7

DETERMINATION OF HEXAVALENT CHROMIUM IN DRINKING WATER BY ION CHROMATOGRAPHY WITH POST-COLUMN DERIVATIZATION AND UV-VISIBLE SPECTROSCOPIC DETECTION

1. SCOPE AND APPLICATION

1.1 METHOD – Method 218.7 provides procedures for the determination of hexavalent chromium Cr(VI) as the chromate anion CrO₄² in finished drinking water using ion chromatography. Samples are analyzed by direct injection. This method is intended for use by analysts skilled in the operation of ion chromatographic instrumentation and in the interpretation of the associated data.

	Chemical Abstracts Services
Analyte	Registry Number (CASRN)
Hexavalent chromium (as CrO ₄ ²⁻)	13907-45-4

1.2 SUPPORTING DATA

- 1.2.1 Single-laboratory method performance data, presented in Section 17, were collected using 4-mm i.d. anion exchange chromatographic columns designed for use with ammonium hydroxide/ammonium sulfate eluent systems and 4-mm i.d. columns designed for use with carbonate/bicarbonate eluent systems.
- 1.2.2 Precision and accuracy data have been generated for the analysis of Cr(VI) in reagent water and finished drinking water from both ground water and surface water sources (Sect. 17, Tables 4, 5 and 6).
- 1.2.3 Single laboratory Lowest Concentration Minimum Reporting Levels (LCMRLs) for Cr(VI) ranged from 0.012 to 0.036 microgram per liter (µg/L) (Section 17, Table 3). The LCMRL is the lowest spiking concentration such that the probability of spike recovery in the 50% to 150% range is at least 99%. The procedure used to determine the LCMRL is described elsewhere.¹ Laboratories using this method are not required to determine LCMRLs, but they must demonstrate that the Minimum Reporting Level (MRL) for Cr(VI) meets the requirements described in Section 9.2.4.
- 1.2.4 Determining a detection limit (DL) for Cr(VI) is optional (Sect. 9.2.6). The DL is defined as the statistically calculated minimum concentration that can be measured with 99% confidence that the reported value is greater than zero.² DLs for Cr(VI) fortified into reagent water ranged from 0.0044 to 0.015 µg/L (Table 3).
- 1.3 METHOD FLEXIBILITY The laboratory is permitted to modify chromatographic conditions including IC columns and eluent compositions different from those utilized in the method. Changes may not be made to sample collection and preservation (Sect. 8) or to the quality control (QC) requirements (Sect. 9). Method modifications should be considered

218.7-2

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Instruments for Cr Analysis

PARAMETER	INSTRUMENT	PROS	CONS
Total Chromium	Atomic Absorption	Low price Short analysis time	Other components cannot be analyzed simultaneously
	ICP-OES	Simultaneous analysis	High price
	ICP-MS	Simultaneous analysis High sensitivity	High price
Cr VI	UV-vis	Short analysis time	Complicated pretreatment
	IC	Low price	Other components cannot be analyzed simultaneously





Instrument configuration



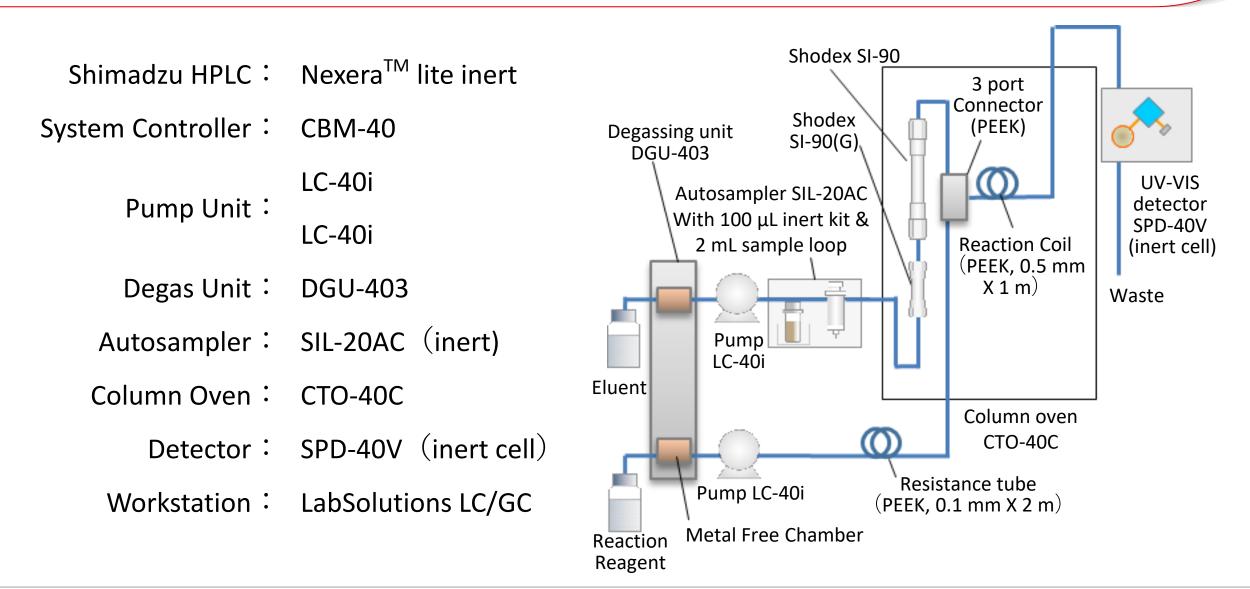
Ion Chromatograph is same as an inert LC without a suppressor Suppressor is not required in EPA 218.7

6.5 ION CHROMATOGRAPHY SYSTEM WITH POST-COLUMN REACTOR

- 6.5.1 IC SYSTEM An analytical system consisting of an autosampler, pump module with vacuum degassing option, sample loop, guard column, anion separator column, post-column reagent addition capability, post-column reaction coil, UV–Vis absorbance detector set to monitor a wavelength of 530 nm, and a data acquisition and management system. The system must not contain any metal parts in the sample, eluent and reagent flow paths.
- 1.3 METHOD FLEXIBILITY The laboratory is permitted to modify chromatographic conditions including IC columns and eluent compositions different from those utilized in the method. Changes may not be made to sample collection and preservation (Sect. 8) or to the quality control (QC) requirements (Sect. 9). Method modifications should be considered

https://www.shimadzu.com/an/products/liquid-chromatography/hplc-system/nexera-lite-inert/index.html

Instrument configuration and flow path diagram



Analytical conditions

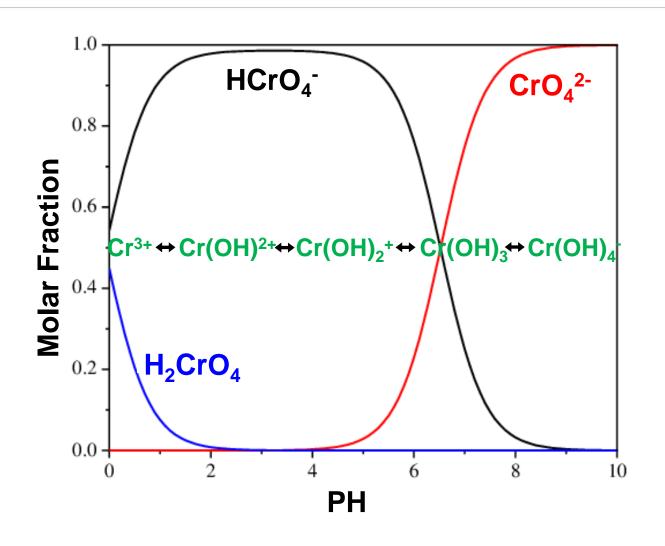
Column	•	Shodex SI-90 (250 mm $ imes$ 4.0 mm I.D., 9 μ m)
Guard Column	:	Shodex SI-90(G) (10 mm $ imes$ 4.6 mm I.D., 9 μ m)
Eluent	:	50 mmol/L Ammonium sulfate 20 mmol/L Ammonium hydroxide
Eluent Flow Rate	•	
Post Column Reagents	:	
Post Column Reagents Flow rate	:	1 N Sulfuric acid 0.3 mL/min
Column temp.	:	45 °C
Injection volume	:	1000 μL
Vial	:	Shimadzu Vial, LC, 4 mL, Polypropylene
Detection	:	UV-VIS (530 nm, inert cell)
Reaction Coil	:	250 μL (1 m $ imes$ 0.5 mm I.D.,(PEEK))

Analytical conditions

Column	•	Shodex SI-90 (250 mm $ imes$ 4.0 mm I.D., 9 μ m)
Guard Column	:	Shodex SI-90(G) (10 mm $ imes$ 4.6 mm I.D., 9 μ m)
Eluent	:	50 mmol/L Ammonium sulfate 20 mmol/L Ammonium hydroxide
Eluent Flow Rate	:	0.8 mL/min
Post Column Reagents	:	2 mmol/L 1,5-diphenylcarbazide 10% Methanol 1 N Sulfurio poid
Post Column Reagents Flow rate	:	1 N Sulfuric acid <mark>0.3 mL/min</mark>
Column temp.	:	45 °C
Injection volume	:	1000 μL
Vial	:	Shimadzu Vial, LC, 4 mL, Polypropylene
Detection	:	UV-VIS (530 nm, inert cell)
Reaction Coil	:	250 μL (1 m $ imes$ 0.5 mm I.D.,(PEEK))

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Chromium speciation as f(pH)



- Cr(III) typically exists as cationic aqua-hydroxo complexes
- Cr(VI) exists typically as an anionic chromate species
- Interconversion of Cr(III) & Cr(VI) depending on sample conditions (pH)

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QC requirements of EPA method 218.7

_	TABLE 8.	INITIAL DEMONSTRA	TION OF CAPABILITY (IDC) QUALITY CONTROL REQUIREMENTS	

Method Reference	Requirement	Specification and Frequency Acceptance Criteria	
Section 9.2.1	Demonstration of low system background	Analyze an LRB after the high calibration standard during the IDC calibration.	Cr(VI) concentration is <1/3 of the MRL.
Section 9.2.2	Demonstration of precision	Analyze seven replicate Laboratory Fortified Blanks (LFBs) fortified near the midrange of the calibration curve.	Percent relative standard deviation must be $\leq 15\%$.
Section 9.2.3	Demonstration of accuracy	Calculate average recovery for replicates used in Section 9.2.2.	Mean recovery within $\pm 15\%$ of the true value.
Section 9.2.4	MRL confirmation	Fortify and analyze seven replicate LFBs at the chosen MRL concentration. Confirm that the Upper Prediction Interval of Results (PIR) and Lower PIR (Sect. 9.2.4.2) meet the recovery criteria.	Upper PIR $\leq 150\%$ Lower PIR $\geq 50\%$
Section 9.2.5	Quality Control Sample (QCS)	Analyze mid-level QCS.	Cr(VI) must be within $\pm 15\%$ of the true value.

QC requirements of EPA method 218.7

	TABLE 9. ONGOING QUALITY CONTROL REQUIREMENTS				
Method Reference Requirement		Requirement	Specification and Frequency	Acceptance Criteria	
•	Section 10.2	Initial calibration	Use the external standard calibration technique to generate a linear or quadratic calibration curve. Use at least six standard concentrations. Validate the calibration curve as described in Section 10.2.3.	When each calibration standard is calculated as an unknown using the regression equations, the lowest level standard should be within $\pm 50\%$ of the true value. All other points should be within $\pm 15\%$ of the true value.	
	Section 9.3.1	Laboratory Reagent Blank (LRB)	Analyze one LRB with each Analysis Batch.	Demonstrate that Cr(VI) is below ¹ / ₃ the Minimum Reporting Level (MRL), and that other sources of interference do not prevent identification and quantitation.	
	Section 10.3	Continuing Calibration Check (CCC)	Verify initial calibration by analyzing a low-level CCC at the beginning of each Analysis Batch. Subsequent CCCs are required after every 10 field samples and after the last field sample in a batch.	The lowest level CCC must be within $\pm 50\%$ of the true value. All other points must be within $\pm 15\%$ of the true value. Results for field samples that are not bracketed by acceptable CCCs are invalid.	
	Section 9.3.4	Laboratory Fortified Sample Matrix (LFSM)	Analyze one LFSM per Analysis Batch. Fortify the LFSM with Cr(VI) at a concentration greater than the native concentrations. Calculate LFSM recovery.	For LFSMs fortified at concentrations $\leq 2 \times MRL$, the result must be within $\pm 50\%$ of the true value. At concentrations greater than the 2 x MRL, the result must be within $\pm 15\%$ of the true value.	
•	Section 9.3.5	Laboratory Fortified Sample Matrix Duplicate (LFSMD) or Laboratory Duplicate (LD)	Analyze at least one LFSMD or LD with each Analysis Batch.	For LFSMDs or LDs, relative percent differences must be $\leq 15\%$. ($\leq 50\%$ if concentration $\leq 2 \times MRL$.)	
	Section 9.3.6	Quality Control Sample (QCS)	Analyze mid-level QCS with each new calibration curve.	Cr(VI) must be $\pm 15\%$ of the true value.	

TABLE 9. ONGOING QUALITY CONTROL REQUIREMENTS

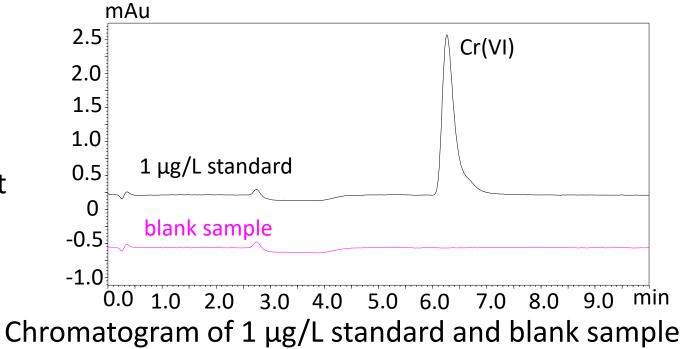
Sample preparation and elution time

Preparation of standard samples

- Diluting sodium chromate tetrahydrate with pure water (Analyte PDS).
- Prepare a series of calibration standards (6 levels) by diluting the Analyte PDS.
- To prevent reduction to Cr II, pH control solution added to all samples, and pH was adjusted to greater than 8 with
 mAu
 2.5
 Cr(VI)

Elution time

The elution time for Cr VI was about 6 min.



Initial calibration

- The calibration curve was created with 6 points between 0.02-1 μ g/L.
- The coefficient of correlation (r²) was 0.99997.

Results of calibrations Peak Area 40000-Setting conc. Conc. 35000 **STD** Peak area $(\mu g/L)$ $(\mu g/L)$ 30000 25000 STD-1 0.02 529 0.0197 20000 0.05 STD-2 1615 0.0472 15000 10000 STD-3 0.10 0.1035 3845 r²: 0.99997 5000 0.25 STD-4 9606 0.2491 0.00 0.25 1.00 0.50 0.75 0.50 STD-5 19571 0.5010 Concentration ($\mu g/L$) STD-6 1.00 39296 0.9995 Calibration curve

Laboratory duplicate

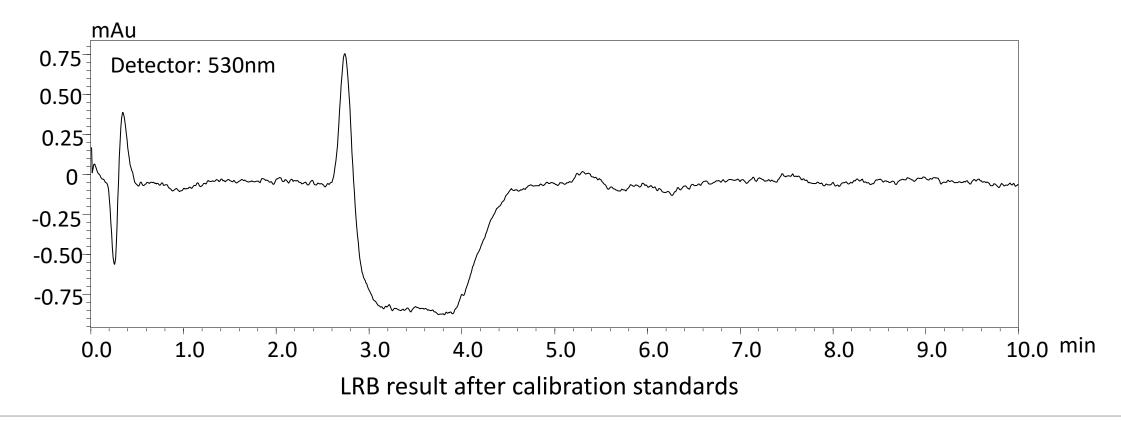
- Calculate the relative percent difference (RPD) for duplicate measurements (LD1 and LD2) using the equation: $_{RPD} = \frac{|LD_1 - LD_2|}{(LD_1 + LD_2)/2} \times 100$
- EPA requirement: RPD must be $\leq 15\%$. ($\leq 50\%$ if concentration $< 2 \times MRL$.)

Laboratory duplicate measurements

STD	Setting conc. (µg/L)	Peak area 1	Peak area 2	Mean area	%RPD
STD-1	0.02	529	550	539.5	3.89
STD-2	0.05	1615	1565	1590	3.14
STD-3	0.1	3845	3718	3781.5	3.36
STD-4	0.25	9606	9821	9713.5	2.21
STD-5	0.5	19571	19380	19475.5	0.98
STD-6	1	39296	39738	39517	1.12

Demonstration of low system background

- A laboratory reagent blank (LRB) after the high calibration standard during the IDC calibration was analyzed
- Cr VI was N.D.



Demonstration of precision and accuracy

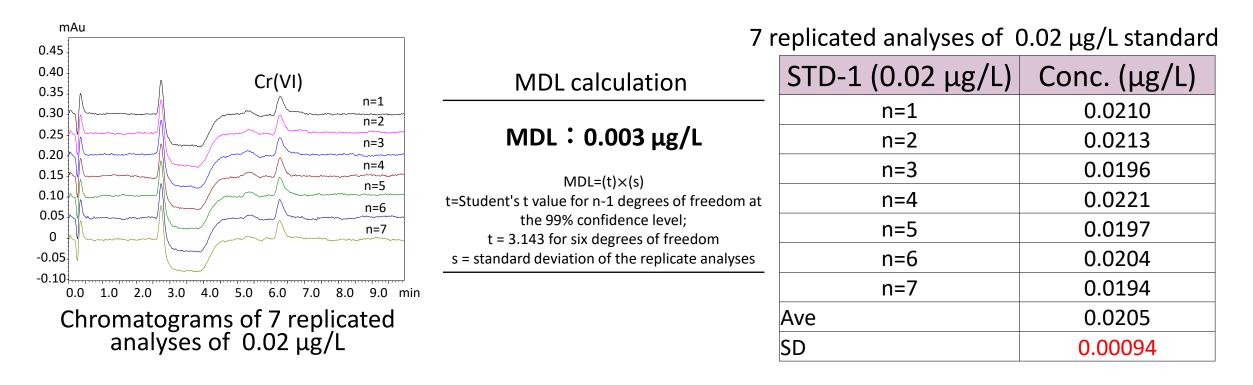
- Prepared 3 laboratory fortified blank (LFB) samples (0.02, 0.1, 1 μg/L) and analyzed 7 replicate LFBs
- EPA 218.7 requirements: Percent relative standard deviation (%RSD) must be $\leq 15\%$, mean recovery within $\pm 15\%$ of the true value

Concentration of standards	0.02 μg/L	0.1 μg/L	1 μg/L
Mean measured value (µg/L)	0.0205	0.102	1.01
Mean recoveries of true value(%)	102.5	102.2	101.4
Area precision (%RSD)	4.93	2.66	0.51

Recoveries and precision of area

Method detection limit (MDL) and quantitation limit

- MDL calculated as (t) x (S) after 7 replicated analyses of 0.02 μ g/L Cr VI.
- MDL of 0.003 μg/L enables a LOQ of 0.009 μg/L for Cr VI, which is adequate for routine analysis at the California PHG of 0.02 μg/L.



Analysis examples of mineral water and tap water

• Following the procedure described in EPA method 218.7, 3 kinds of commercially available mineral water and tap water were analyzed.

Sample	Mineral water A	Mineral water C	Mineral water S	Tap water
Mean measured value (µg/L)	<mdl< td=""><td>0.80</td><td>0.0095</td><td>0.021</td></mdl<>	0.80	0.0095	0.021
Relative standard deviation (%RSD)		0.37	3.74	6.14

Analytical results of samples

Fortified sample matrix test

- Low and high concentrations of Cr VI standard were added to samples, and 7 replicated analyses were measured.
- Mean recovery calculation followed by EPA Method 218.7.

$$\%R = \frac{(A - B)}{C} \times 100$$

where

- A = measured concentration in the fortified sample,
- B = measured concentration in the unfortified sample, and

C = fortification concentration.

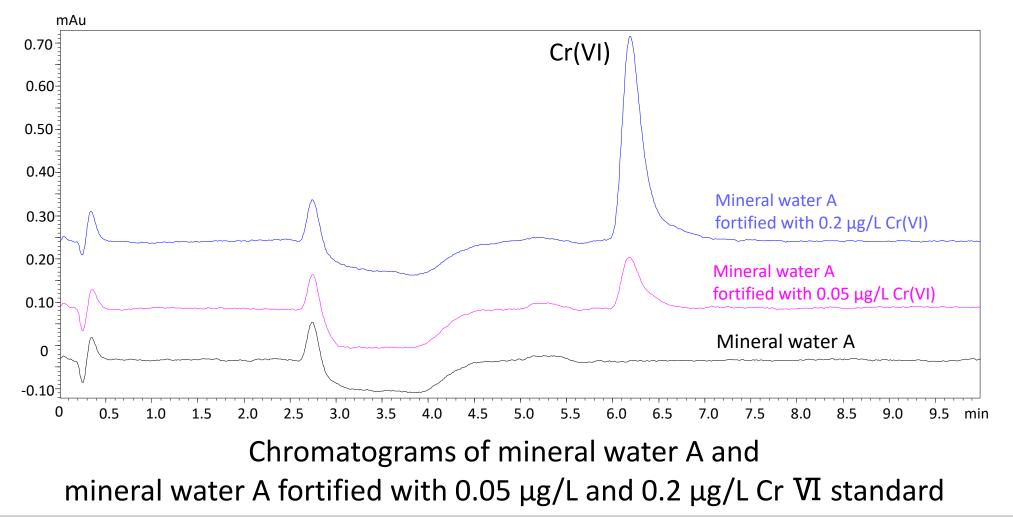
 EPA 218.7 requirement: %RSD must be ≦15%, mean recovery within ±15% of the true value)

Analytical results of fortified sample matrix test

Sample	Fortification (µg/L)	Concentration of unfortified sample (µg/L)	Mean measured value (µg/L)	Mean recovery (%)	%RSD
Mineral	0.05	<mdl< td=""><td>0.051</td><td>101.9</td><td>4.79</td></mdl<>	0.051	101.9	4.79
water A	er A 0.2	SIMIDL	0.20	101.5	0.95
Mineral water C	0.2	0.80	0.99	97.2	0.46
Mineral	0.05	0.0095	0.058	97.5	3.89
water S	0.2		0.21	97.9	4.68
Тар	0.05	0.021	0.071	99.4	3.55
water	0.2	0.021	0.22	101.7	0.85

Chromatograms of analysis and fortified sample

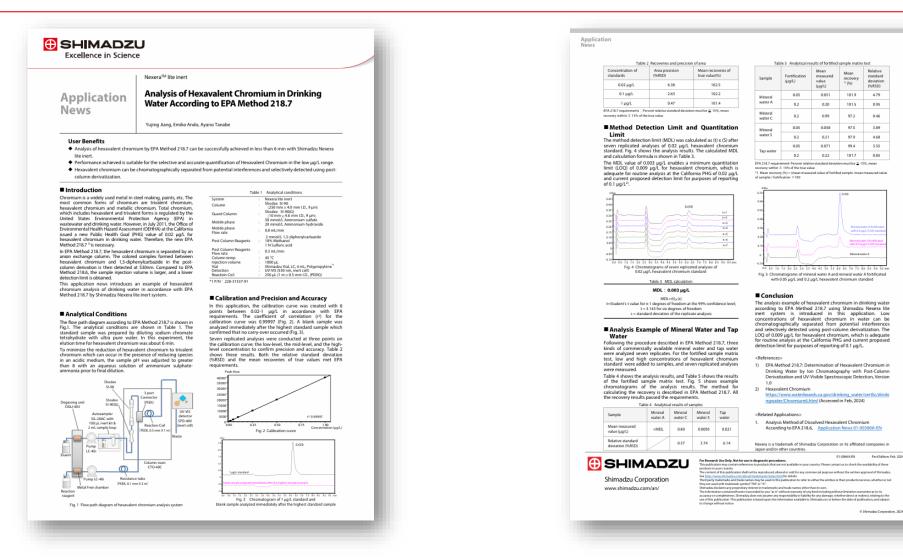
• Example chromatograms of the analysis results.



Summary

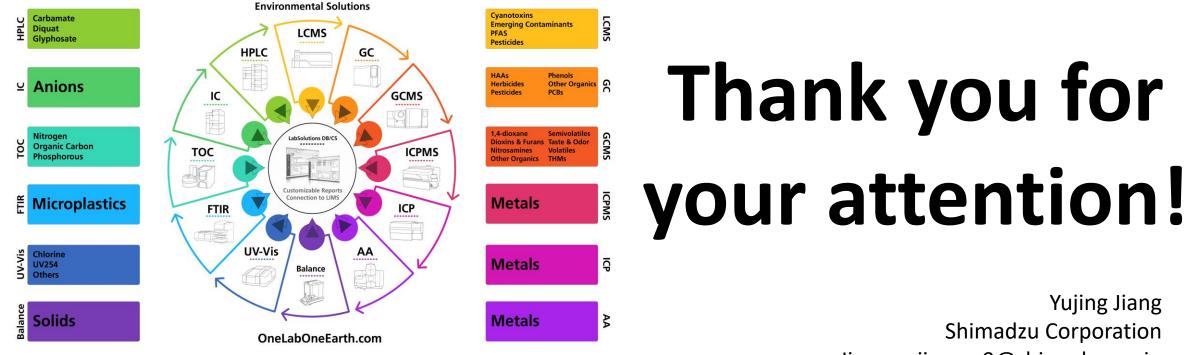
Requirement	Acceptance criteria	Results	
Demonstration of low system background	Cr VI concentration after high calibration standard <1/3 MRL	Cr VI was N.D	PASSED!
Demonstration of precision	Percent relative standard deviation must be ≦15% (seven replicated)	3 LFB samples (0.02, 0.1, 1 μg/L) were analyzed. Percent relative standard deviation no more than 5%.	PASSED!
Demonstration of accuracy	Mean recovery within \pm 15% of the true value	3 LFB samples were analyzed. Recoveries were within 100~103%.	PASSED!
Quality Control Sample (QCS)	Concentration of mid-level QCS must be within \pm 15% of the true value	The recovery of mid-level QCS was 102.2%	PASSED!
Laboratory Fortified Sample Matrix (LFSM)	The recovery of LFSM must be within \pm 15% of the true value	All the recoveries of LFSM were within 97%~102%.	PASSED!
Laboratory Duplicate (LD)	For LDs, relative percent differences must be $\leq 15\%$	Each sample's relative percent differences no more than 4%.	PASSED!

Application news 01-00669



https://www.shimadzu.com/an/sites/shimadzu.com.an/files/pim/pim_document_file/applications/application_note/22616/an_01-00669-en.pdf





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