SHIMADZU
Excellence in Science

Ion Chromatography Solutions for

Environmental Analysis

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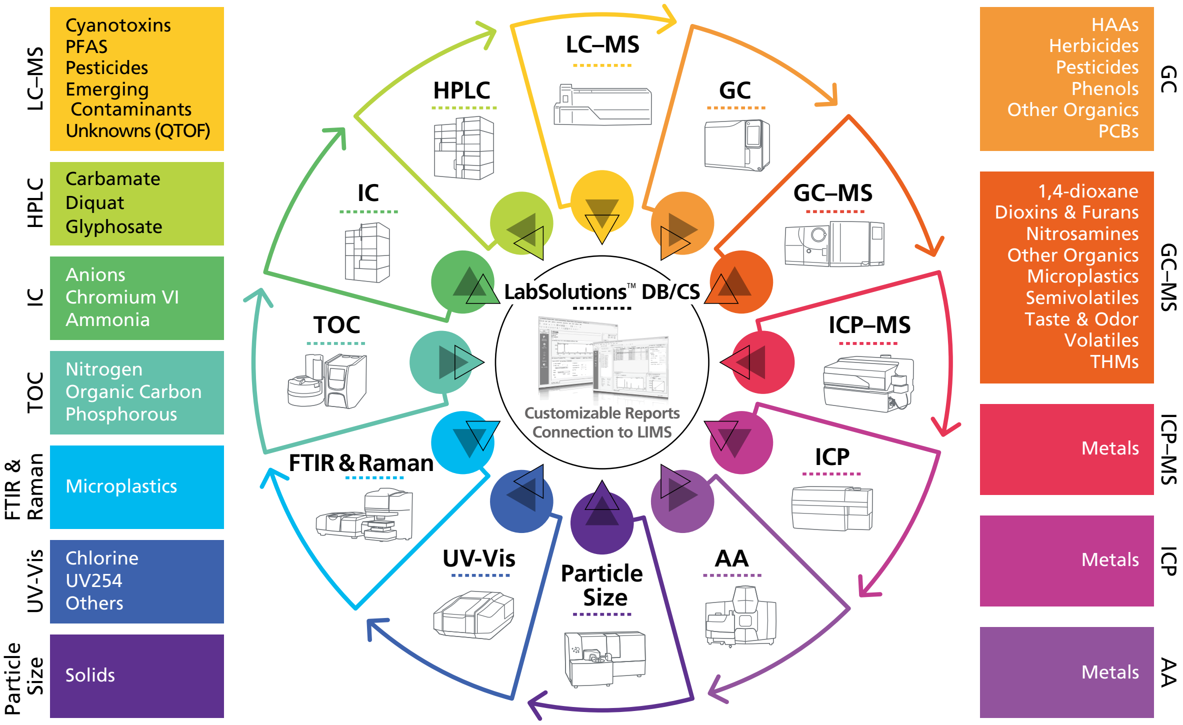
Overview of Environmental Analysis

Shimadzu has focused on the development of instruments for environmental analysis for decades, helping scientists to detect, identify and quantify trace-level pollutants and meet environmental testing demands, for both regulatory purposes and to advance Research & Development. We offer total solutions to support your environmental monitoring of air, water (drinking, wastewater, surface…), and soil, from regulated contaminants (pesticides, anions, disinfection by-products, dioxins…) to emerging ones, such as microplastics and PFAS, as well as greenhouse gases (GHG, including CO_2, CH_4, and N_2O) and carbon dioxide capture and storage (CCUS). These solutions include a wide range of analytical and measuring technologies/instruments including chromatography (GC, LC, and SFC), mass spectrometry (GC–MS, LC–MS, and MALDI), sum parameter (TOC), and spectroscopy (UV-Vis, FTIR, AAS, and ICP–OES).

Analytical Instruments for Environmental Analysis

Shimadzu offers the most comprehensive portfolio of solutions for the analysis of regulated and emerging contaminants in all types of environmental samples.

	Water	Air	Soil & Sediments	Solid Waste	PFAS	Microplastics	Carbon dioxide Capture, Utilization and Storage (CCUS)
UV-Vis	✓					✓	
FTIR, Raman				✓		✓	
TOC	✓	✓	✓			✓	
IC	✓	✓	✓				
HPLC	✓	✓	✓	✓			
LC–MS	✓		✓	✓	✓		
GC	✓	✓	✓	✓	✓		✓
GC–MS	✓	✓	✓	✓	✓	✓	✓
ICP–MS	✓	✓	✓	✓			
ICP–OES	✓	✓	✓	✓			
AA	✓	✓	✓	✓			
Particle size				✓			



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Relevance of Ion Chromatography in Environmental Analysis: Regulations and Analytical Methods

Ion chromatography is widely used for water quality monitoring. Anions and cations in a wide variety of water samples, including drinking water, ground water, wastewater and sea water, can be analyzed. Most countries have established regulations and standards for these contaminants. Below is a summary of the standards for contaminants that are routinely analyzed by ion chromatography.

Table 1 List of water quality standards using ion chromatography

Components	WHO	US EPA	EU		Japan	China
	Standard value	National Primary Drinking Water Regulations MCL*1	Standard value	Notes	Standard value	Standard value
Inorganics						
Chloride (Cl^-)	—	250 mg/L	250 mg/L (indicator parameters)		200 mg/L	250 mg/L
Fluoride (F^-)	1500 µg/L	2.0 mg/L	1.5 mg/L	[nitrate]/50 + [nitrite]/3 ≤ 1	0.8 mg/L	1.0 mg/L
Nitrate (NO_3^-)	50 mg/L	10 mg/L	50 mg/L		10 mg/L (Total amount of NO_3–N and NO_2–N)	10 mg/L (as N)
Nitrite (NO_2^-)	3 mg/L	1 mg/L	0.5 mg/L		0.04 mg/L (as NO_2–N)	—
Sodium (Na^+)	—	—	200 mg/L		200 mg/L	200 mg/L
Sulfate (SO_4^{2-})	—	250 mg/L	250 mg/L (indicator parameters)		—	250 mg/L
Hexavalent chromium (Cr_6^+)	—	0.1 mg/L (Total chromium)	—		0.02 mg/L	0.05 mg/L
Disinfectants and disinfectant by-products						
Bromate (BrO_3^-)	10 µg/L	0.01 mg/L	10 µg/L		0.01 mg/L	0.01 mg/L
Chlorate (ClO_3^-)	700 µg/L	—	0.25 mg/L	Max concentration of 0.70 mg/L if chlorine dioxide, or other disinfectants that generate chlorate, is used for potable water.	0.6 mg/L	0.7 mg/L
Chlorite (ClO_2^-)	700 µg/L	0.8 mg/L (Chlorine Dioxide as ClO_2^-)	0.25 mg/L		0.6 mg/L (target value)	0.7 mg/L
<Reference>	https://www.who.int/publications/i/item/9789241549950	https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations	https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32020L2184		https://www.env.go.jp/water/water_supply/kijun/kijunchi.html#01 (Japanese only)	GB/T 5749-2022 Standard for drinking water quality (Chinese only)

*1 MCL: Maximum Contaminant Level.

Relevance of Ion Chromatography in Environmental Analysis: Analytical Methods

Table 2 List of EPA methods and ASTM standards of water quality using ion chromatography

Regulations			Target Components
EPA	218.6	Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography	Hexavalent chromium
	218.7	Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-column Derivatization and UV-Visible Spectroscopic Detection	
	300.0	Determination of Inorganic Anions by Ion Chromatography	Part A: Bromide Chloride Fluoride Nitrate Nitrite Phosphate-P Sulfate Part B: Bromate Chlorate Chlorite
	300.1	Determination of Inorganic Anions in Drinking Water by Ion Chromatography	
	302	Determination of Bromate in Drinking Water Using Two-Dimensional Ion Chromatography with Suppressed Conductivity Detection	Bromate
	314.0	Determination of Perchlorate in Drinking Water Using Ion Chromatography	Perchlorate
	314.1	Determination of Perchlorate in Drinking Water Using Inline Column Concentration/ Matrix Elimination Ion Chromatography With Suppressed Conductivity Detection	
	314.2	Determination of Perchlorate in Drinking Water Using Two-Dimensional Ion Chromatography with Suppressed Conductivity Detection	
	317	Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography With the Addition of A Post-column Reagent for Trace Bromate Analysis	Bromate, Bromide, Chlorite, Chlorate
	326	Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography Incorporating the Addition of A Suppressor Acidified Post-column Reagent for Trace Bromate Analysis	Bromate, Bromide, Chlorite, Chlorate
ASTM	D2036A	Standard Test Methods for Cyanides in Water	Cyanides
	D4327-03	Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography	Fluoride, Chloride, Nitrite, Phosphate, Bromide, Nitrate, Sulfate
	D5257	Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography	Hexavalent chromium
	D6850-18	Standard Guide for QC of Screening Methods in Water	—
	D6581	Standard Test Methods for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Suppressed Ion Chromatography	Bromate, Bromide, Chlorate, Chlorite
	D6919-03	Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography	Lithium, Sodium, Potassium, Magnesium, Calcium, Ammonium
	D8001	Standard Test Method for Determination of Total Nitrogen, Total Kjeldahl Nitrogen by Calculation, and Total Phosphorus in Water, Wastewater by Ion Chromatography	Nitrogen, Phosphorus

<References> https://www.epa.gov https://www.astm.org

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Overview of Ion Chromatography

Ion chromatography (IC) is a type of liquid chromatography technique that measures ionic compounds. These chemicals, when present in solution, are separated and quantified in a packed column with an ion exchange resin as a stationary phase and using electrolyte solution as eluent. The most common detector is the electrical conductivity detector, which has high sensitivity, selectivity, and relatively low cost of operation. Other detectors, such as an electrical conductivity detector and a UV-visible absorption photometric detector, can be used. The detector chosen is based on the physico-chemical properties of the analytes of interest. In some cases, a post column derivatization step may be used to enhance sensitivity and selectivity of the analytical method.

IC is a reliable measurement method that has been widely adopted in standardized analytical methods for analysis of environmental samples, foods and other materials. In 1986, Shimadzu developed its first ion chromatograph. Shimadzu has since become a world-leading ion chromatograph manufacturer, developing both suppressor and non-suppressor systems.

Introduction of Ion Exchange Chromatography

Ion exchange chromatography (IEX) is a separation method using the difference of charge states between the eluent and analytes from the stationary phase in the column. It is mainly used for the analysis of ionic compounds.

There are two types of IEX methods: anion exchange chromatography and cation exchange chromatography.

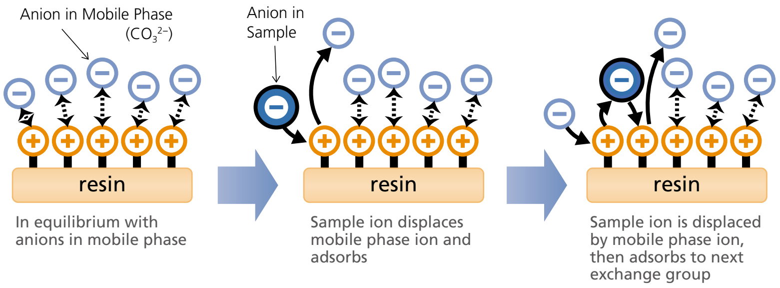


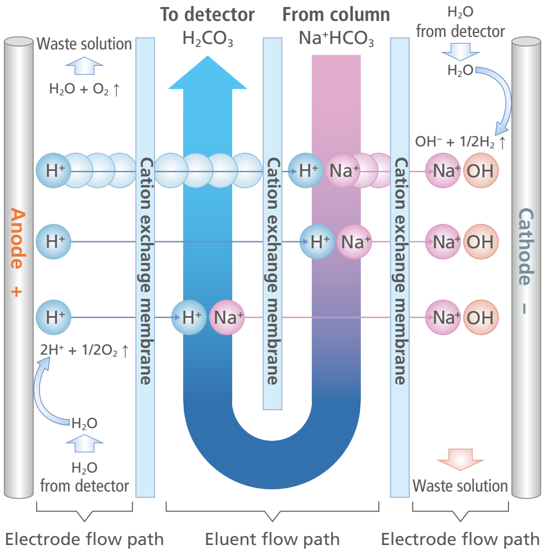
Figure shows how anion exchange chromatography.

In the stationary phase of anion exchange chromatography, packing materials modified with positively charged ion-exchange groups are used. When the eluent enters the column, it adsorbs onto the ion exchange groups of the stationary phase due to electrostatic attraction.

The eluent continuously introduces anions into the column, resulting in a repeated adsorption and desorption of anions between the stationary and eluents, i.e. a state of equilibrium.

When a sample containing anions is introduced into the column during this state, the anions in the sample are adsorbed through electrostatic interactions with the functional groups of the stationary phase. At the same time, the anions from the eluent that were previously adsorbed on the stationary phase are desorbed. The sample anions adsorbed on the stationary phase are then desorbed and adsorbed onto the next ion exchange group.

This exchange phenomenon is repeated until the sample anions completely move through the column and are eluted.



Structure and principles behind the ICDS™-40A anion suppressor unit

The suppressor method of electric conductivity detection changes the eluent composition to a composition with lower electrical conductivity. When anions are separated, the presence of sodium ions generates eluted carbonate ions. Eliminating the sodium ions just before the detector changes the eluent to a slightly acidic aqueous carbonate solution, with lower electric conductivity. Meanwhile, in the regions where the inorganic anions in the sample elute, the carbon dissociation equilibrium shifts toward creating more H^+ ions that become pair ions in order to maintain balanced charges. Because hydrogen ions have a higher equivalent electric conductivity than other ions, this increases the peak response.

* For more details:
https://www.shimadzu.com/an/service-support/technical-support/analysis-basics/liquid-chromatography/ion/64intro/

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Shimadzu's Ion Chromatography Solutions

Anion Suppressor Ion Chromatograph: HIC-ESP

The HIC-ESP is an anion suppressor ion chromatograph with a built-in electrodialytic suppressor, boasting the same low carryover and excellent injection precision characteristic of Shimadzu HPLCs to bring you highly reliable results. The newly developed anion suppressor prevents peak spreading and achieves high sensitivity, providing stable functionality even over long periods of use.

Conductivity Detector

CDD-10A*VP*

A temperature-regulating device in the detection cell and the placement of the detection cell in the column oven ensure precise temperature control. This enables analysis with low noise conditions and a stable baseline even when using electrical conductivity detection, which is sensitive to temperature fluctuations.

Degassing Unit

DGU-403

Because the unit adopts an online degassing system with high performance and low internal volume, it is easy to replace the eluent and more stable analysis is achieved. Offline degassing of the eluent with ultrasonic waves or decompression is not necessary.

Solvent Delivery Pump

LC-40i

Although it is a metal-free pump that uses a series double plunger system, it has stable liquid delivery performance with suppressed pulsation.

Anion Suppressor Unit

ICDS™-40A

This is an electrodialytic suppressor unit built into the top part of the column oven. It achieves high performance even with low internal volume.

Column Oven

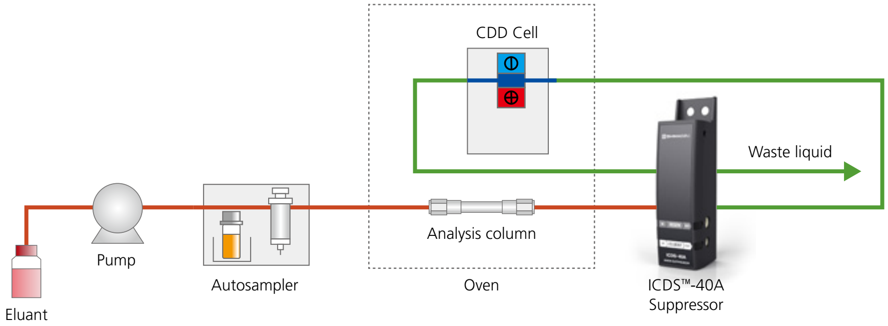
CTO-40S

The forced air circulation oven has extremely precise temperature regulation, and can be used with a variety of column lengths up to 300 mm.

Autosampler

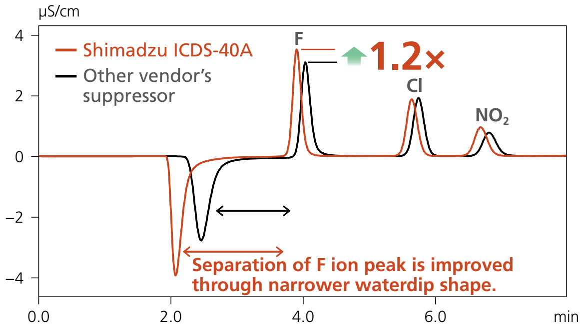
SIL-20A/20AC (Inert kit)

The SIL-20A/20AC is a full-volume autosampler with very low carryover, which allows high accuracy, high-speed injection of volumes from 0.1 µL up. The wetted parts are made inert using the inert kit.



Anion Suppressor Unit ICDS™-40A

With a unique design in which the eluent flow path bends back around, combined with dialytic membrane the new ICDS-40A anion suppressor unit achieves higher efficiency and stable suppression while maintaining a small internal volume (patent pending).



Separation of F ion peak is improved through narrower waterdip shape.

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Shimadzu's Ion Chromatography Solutions

Non-suppressed Anion Ion Chromatograph: HIC-NS

The mobile phase conductivity is affected by temperature changes and solvent delivery pump pressure variations, which can lead to baseline noise and drift. With suppressors, noise is reduced by reducing mobile phase conductivity, the source of these problems. With non-suppressor systems, however, this problem must be dealt with by improving basic hardware performance. Shimadzu accomplishes this using its proprietary high basic performance. This includes pulse-free solvent delivery, which suppresses pressure variations during solvent delivery to a bare minimum, and double temperature control, featuring detector cells equipped with thermal control functionality arranged within the column oven.

Solvent Delivery Pump

LC-40i

With the pulse-free solvent delivery pump, which is capable of solvent delivery at 100 nL/min to 5 mL/min, conductivity detection, which does not require suppressors, can be performed.

Autosampler

SIL-20A/20AC (Inert kit)

The SIL-20A/20AC is a full-volume autosampler with very low carryover, which allows high accuracy, high-speed injection of volumes from 0.1 µL up. The wetted parts are made inert using the inert kit.

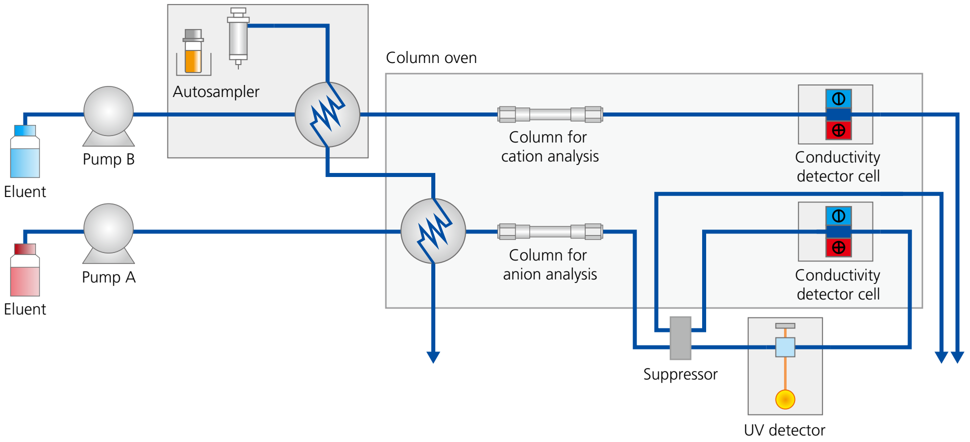
Column Oven

CTO-40C

The column oven features forced air-circulation, which has an established reputation for HPLC column temperature control. Furthermore, thanks to the electronic cooling function, column temperature can be controlled from an ambient temperature of −15 °C. In addition to columns, this large-capacity oven can simultaneously accommodate a suppressor/non-suppressor conductivity detector cell assembly.

Dual Flow-Line Analysis System: HIC-ESP/NS

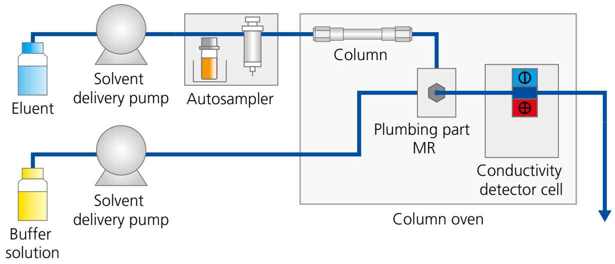
With automatic switching of the sample injection valves, a sample loop with two flow lines is consolidated into one. Simultaneous analysis is performed by adding sample to the two sample loops with a single sample injection. This system is ideal for routine analysis of anions and cations as in tap water quality analysis. A UV detector can also be used when the anion suppressor system is used.



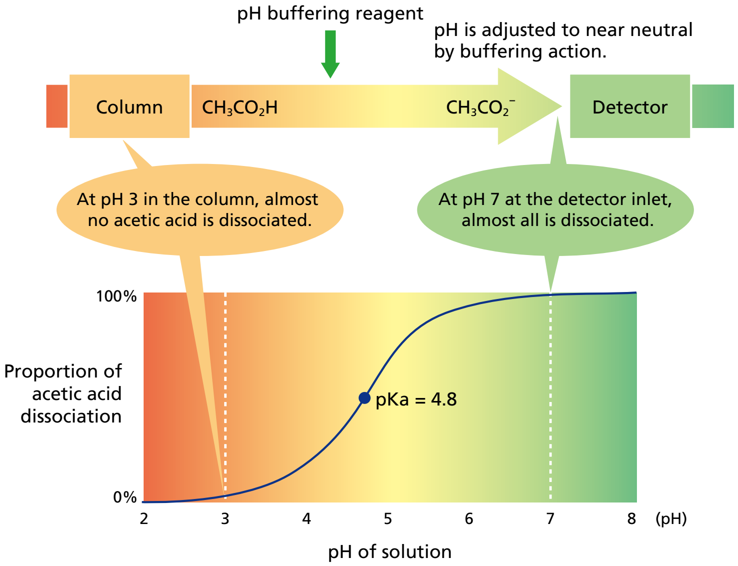
Flow-line diagram for the dual flow-line analysis system

Nexera™ Organic Acid Analysis System

This system is ideal for organic acid analysis of samples with matrices. Combining ion-exclusion chromatography with Shimadzu's unique detection technique (pH buffered electric conductivity detection), the system excels in both selectivity and sensitivity.



Flow-line diagram for the Nexera organic acid analysis system

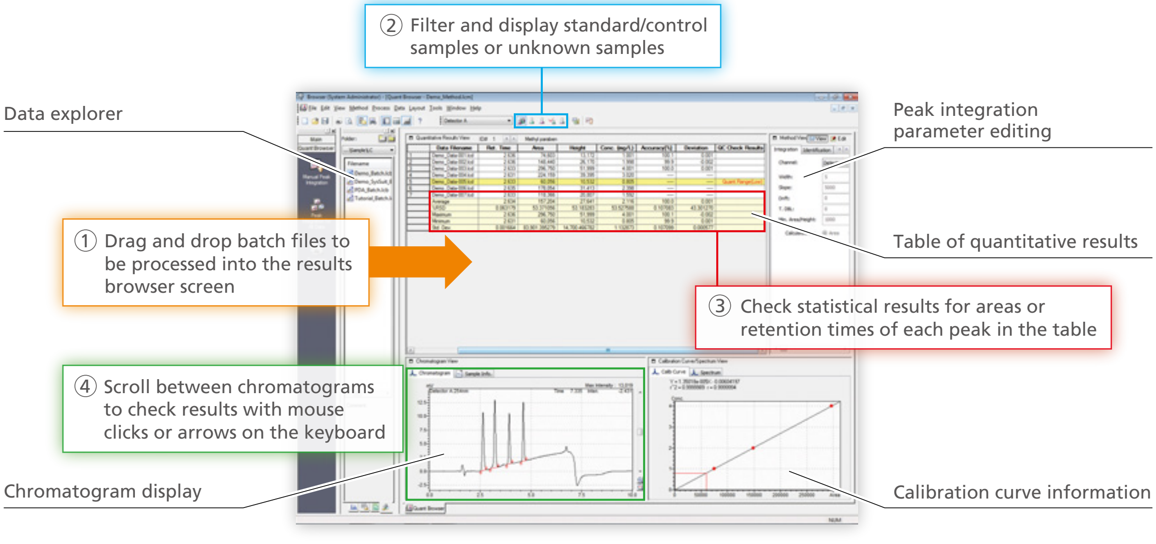


Condition of organic acid in pH buffering method

LabSolutions Software

Settings for analysis parameters, continuous analysis, auto-shutdown, data processing, and report creation can all be managed from LabSolutions analysis software. Data integrity can be handled with the addition of LabSolutions DB and LabSolutions CS.

- Start-up
- Analysis preparations
- Analysis method settings
- Analysis sequence settings
- Auto-shutdown
- Data analysis
- Report creation



② Filter and display standard/control samples or unknown samples

Data explorer

Peak integration parameter editing

① Drag and drop batch files to be processed into the results browser screen

Table of quantitative results

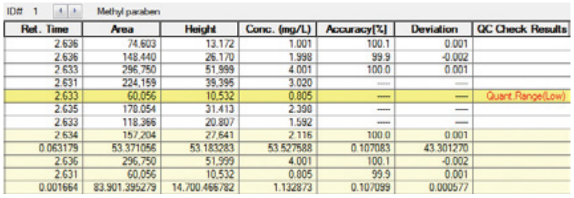
③ Check statistical results for areas or retention times of each peak in the table

④ Scroll between chromatograms to check results with mouse clicks or arrows on the keyboard

Chromatogram display

Calibration curve information

Quantitative results browser



ID# 1 Methyl paraben

Ret. Time	Area	Height	Conc. (mg/L)	Accuracy[%]	Deviation	QC Check Results
2.636	74.603	13.172	1.001	100.1	0.001	
2.636	148.440	26.170	1.998	99.9	-0.002	
2.633	296,750	51,999	4.001	100.0	0.001	
2.631	224,159	39,395	3.020	-----	-----	
2.633	60,056	10.532	0.805	-----	-----	Quant.Range(Low)
2.635	178.054	31.413	2.398	-----	-----	
2.633	118.366	20.807	1.592	-----	-----	
2.634	157,204	27,641	2.116	100.0	0.001	
0.063179	53.371056	53.183283	53.527588	0.107083	43.301270	
2.636	296,750	51,999	4.001	100.1	-0.002	
2.631	60,056	10.532	0.805	99.9	0.001	
0.001664	83.901.395279	14.700.466782	1.132873	0.107099	0.000577	

Automatic judgments on analytical results

Results can be checked and errors or outliers detected much more quickly, with the software automatically judging calibration curve validity, maximum and minimum limits for sample values, etc.

Lineup of Columns

The column type used for ion chromatography differs depending on whether suppressors are used and whether they are used for anion or cation analysis. Below are the characteristics of each column.

Non-Suppressor Type	Anion Analysis	Shim-pack™ IC-A1	Capable of analyzing inorganic anions. Compatible with acid or basic mobile phases of wide pH range.
		Shim-pack IC-A3	Provides outstanding separation efficiency in the analysis of inorganic anions and acid ions, especially when weakly acid mobile phase is used.
	Cation Analysis	Shim-pack IC-C1	Capable of analyzing cations such as alkaline metal ions, alkali earth metal ions, transition metal ions, rare earth metal ions, and alkyl amines.
		Shim-pack IC-C4	Capable of simultaneous analysis of alkali metal ions and alkaline earth metal ions. Enhances the separation of sodium and ammonium ions.
Suppressor Type	Anion Analysis	Shim-pack IC-SA2	Capable of determining fluoride ions, chloride ions, nitrite ions, bromide ions, nitrate ions, phosphate ions and sulfuric acid ions.
		Shim-pack IC-SA3	Provides high-resolution performance when analyzing fluoride ions, chloride ions, nitrous acid ions, bromide ions, nitric acid ions, phosphate ions and sulfuric acid ions as well as chlorous acid ions, chloric acid ions and bromic acid ions.

<Reference>: https://www.shimadzu.com/an/service-support/technical-support/analysis-basics/liquid-chromatography/ion/ic-wash/

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Analysis of Anions

Analysis of Inorganic Anions in Tap Water According to EPA Method 300.1 Using Ion Chromatography

Application >

Keywords: **EPA 300, tap water**

Many countries have standards for environmental and drinking water. In the United States, the Environmental Protection Agency (EPA) provides methods for the analysis of inorganic anions in water by ion chromatography (EPA Method 300.1).

In this article, we introduce examples of the analysis of 10 inorganic anions in accordance with EPA Method 300.1 using the HIC-ESP.

Benefits

- Suppressed ion chromatography can be used for analysis of tap water according to EPA Method 300.1.
- It can measure 10 anions including disinfection byproducts with high sensitivity in about 22 minutes.
- The ICDS-40 reuses the waste liquid from the detector into reclaimed liquid, allowing environmentally conscious analysis.

Flow Path Diagram

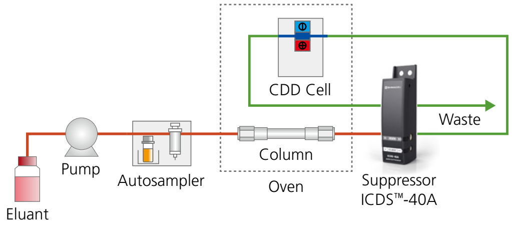

Fig. 1 The HIC-ESP Suppressor Ion Chromatograph Flow Chart for Anion Analysis

Analytical Conditions

Table 1 Analytical Conditions

Column	Shodex SI-52 4E (250 mm × 4.0 mm I.D., 5 µm)
Guard column	Shodex SI-92G (10 mm × 4.6 mm I.D., 9 µm)
Mobile phase	5.4 mmol/L sodium carbonate
Flow rate	0.8 mL/min
Column temp.	45 °C
Injection volume	50 µL (Part A), 200 µL (Part B)
Vial	Shimadzu Vial, LC, 4 mL, Polypropylene*1
Detection	Conductivity

*1 P/N: 228-31537-91

Analysis of Standard Solutions and MDL

Fig. 2 shows the results of injecting 50 µL of a mixed standard solution of Part A. Fig. 3 shows the results of injecting 200 µL of a mixed standard solution of Part B.

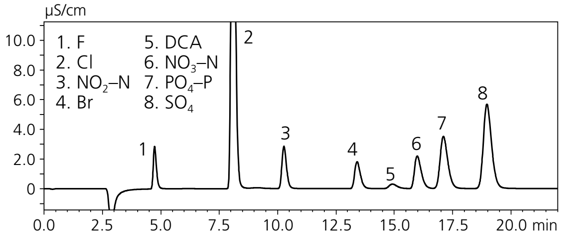

Fig. 2 Chromatogram of Standard Solution (Part A)
(1: 0.5 mg/L 2: 10 mg/L 3: 0.5 mg/L 4: 2 mg/L
5: 1 mg/L 6: 0.5 mg/L 7: 2.5 mg/L 8: 5 mg/L)

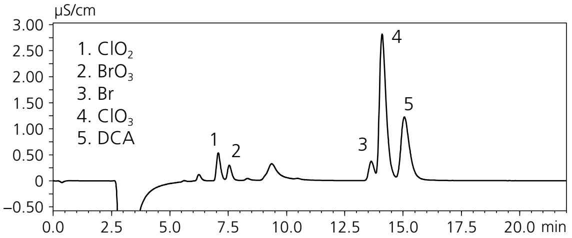

Fig. 3 Chromatogram of Standard Solution (Part B)
(1, 2, 3: 100 µg/L 4, 5: 1000 µg/L)

Sample Analysis of Tap Water

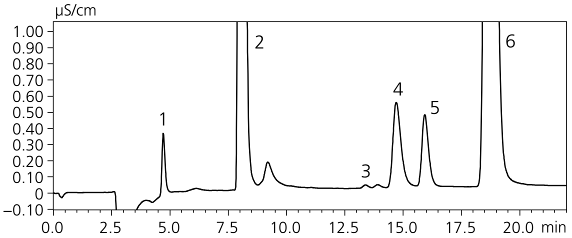

Fig. 4 Chromatogram of Tap Water (Part A)
(Peak: 1. F, 2. Cl, 3. Br, 4. DCA, 5. NO_3–N, 6. SO_4)

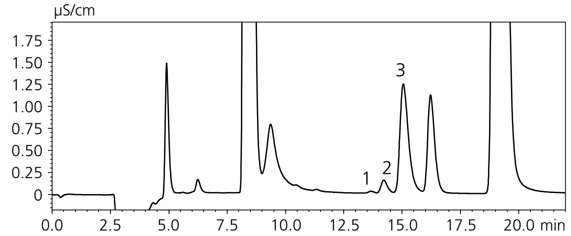

Fig. 5 Chromatogram of Tap Water (Part B)
(Peak: 1. Br, 2. ClO_3, 3. DCA)

Conclusion

This article introduced inorganic anion analysis in accordance with EPA Method 300.1 using the Shimadzu HIC-ESP with suppressed ion chromatography.

Analysis of Anions

US EPA 300 Method-Compliant Environmental and Water Analysis

Keywords: **EPA 300**

Application >

In this article, an EPA 300-compliant quantitative analysis of 7 general inorganic anions in various types of water samples was conducted using an HIC-ESP, an ion chromatograph equipped with an electrodialytic suppressor.

Benefits

- EPA 300-compliant analysis of inorganic anions with high sensitivity and high reliability is possible by using the Shimadzu HIC-ESP ion chromatograph system.

Analysis of Standard Solution

Fig. 6 shows the results when a 50 µL mixed standard sample of the 7 anions prescribed in EPA 300 was injected.

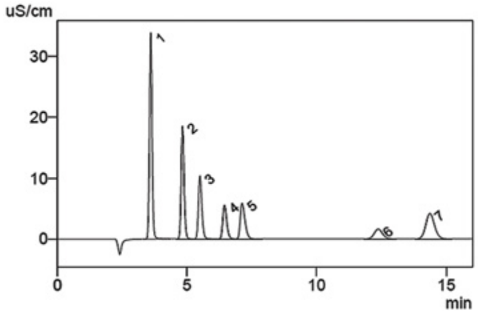

Fig. 6 Chromatogram of Mixed Standard Sample of Anions
Peaks: 1. F (5 mg/L), 2. Cl (5 mg/L), 3. NO_2 (5 mg/L), 4. Br (5 mg/L), 5. NO_3 (5 mg/L), 6. PO_4 (5 mg/L), 7. SO_4 (5 mg/L)

Linearity and Detection Limit

For the detection limit, in accordance with the procedure described in Method 300, an MDL (Method Detection Limit) standard sample was prepared, 7 continuous analyses were carried out, and the MDL was calculated as (t) × (S). Here, *t* means the t value for the 99% confidence level (Student's t-value in t-test; in 7 continuous analyses, t = 3.14), and *S* means the standard deviation of 7 continuous analyses.

Table 2 shows the calibration curve range, linearity, MDL standard concentration, and calculated MDL.

Table 2 Linear Calibration Region, Linearity, MDL Standard, and MDL

Component	Calibration curve range (mg/L)	Coefficient of correlation (r^2)	MDL standard concentration (µg/L)	MDL (µg/L)
F	0.05–20	0.9999	10	3.31
Cl	0.1–100	0.9992	5	2.05
NO_2	0.05–20	0.9995	20	1.49
Br	0.05–20	0.9989	20	3.3
NO_3	0.05–20	0.9991	20	2.69
PO_4	0.05–20	0.9995	50	14.38
SO_4	0.05–20	0.9992	20	3.63

Analysis Conditions

Table 3 shows the analytical conditions.

Table 3 Analytical Conditions

Column:	Shim-pack IC-SA2 (250 mm L. × 4.0 mm I.D.)
Mobile phase:	1.8 mmol/L Sodium Carbonate 1.7 mmol/L Sodium Hydrogen Carbonate
Flow rate:	1.0 mL/min
Column temp.:	40 °C
Injection volume:	50 µL
Detection:	Electro conductivity detector

Repeatability and Accuracy

The repeatability of the retention time and peak area was verified by using a mixed standard sample with 10 mg/L of each ion.

The repeatability of the retention time and peak area was verified from the results of 5 continuous analyses each day. Table 4 shows the results for the 1st and 4th days. The results showed excellent repeatability of the retention times and peak areas of all components during the test period.

Table 4 Repeatability of Retention Time and Peak Area (One Day, Day-to-Day Repeatability)

Component	1st day		4th day	
	Retention time (%RSD)	Peak area (%RSD)	Retention time (%RSD)	Peak area (%RSD)
F	0.06	0.07	0.12	0.72
Cl	0.06	0.07	0.15	0.78
NO_2	0.06	0.14	0.18	0.70
Br	0.07	0.24	0.20	0.75
NO_3	0.08	0.20	0.22	0.97
PO_4	0.15	0.25	0.24	0.64
SO_4	0.13	0.18	0.30	0.63

Table 5 Recovery Rates of Blank and Tap Water

Component	Spiked concentration (mg/L)	Recovery rate (%)	
		Ultrapure water	Tap water
F	2.0	93.9	99.4
Cl	2.0	94.0	96.2
NO_2	2.0	96.1	95.2
Br	2.0	97.1	91.2
NO_3	2.0	98.0	106.0
PO_4	2.0	98.4	103.0
SO_4	2.0	98.3	92.6

Conclusion

EPA 300-compliant analysis of inorganic anions with high sensitivity and high reliability is possible by using the Shimadzu HIC-ESP ion chromatograph.

index

Analysis of Anions

ASTM D4327-03 Compliant Analysis of Anions in Drinking Water

Application >

Keywords: **drinking water**

An ion chromatograph is widely used in detection and quantitative analysis of ion components in aqueous solutions. ASTM D4327-03 issued by ASTM International (the United States) specifies the test methods for analysis of 7 species of anions in drinking water or wastewater by suppressed ion chromatography.

This article introduces an ASTM D4327-03 compliant analysis of anions in drinking water using a Shimadzu HIC-ESP anion suppressor ion chromatograph.

Benefits

- Enables acquisition of data compliant with ASTM D4327-03.
- Applicable to anion analyses of not only drinking water, but also tap water.

Analysis of Drinking Water

Two types of commercially-available drinking water (A, B) were filtered with a 0.2 µm filter prior to the analysis. Fig. 7 shows the analysis results for the two drinking water samples.

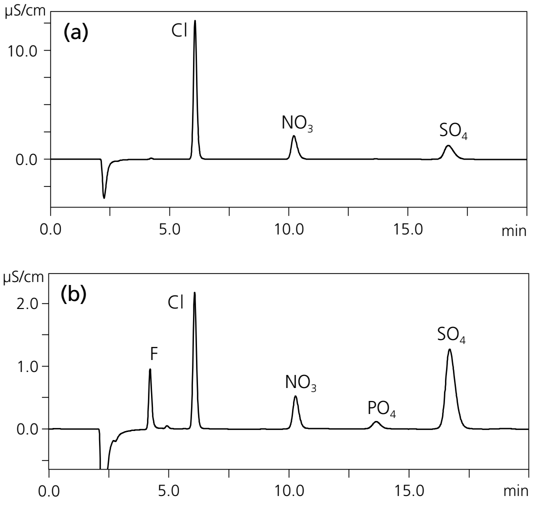

Fig. 7 Chromatograms of Commercial Drinking Water Samples (a) Drinking Water A, (b) Drinking Water B

Analysis of Tap Water

Using this method, a sample of tap water was analyzed after filtration with a 0.2 µm filter. Fig. 8 shows the analysis results.

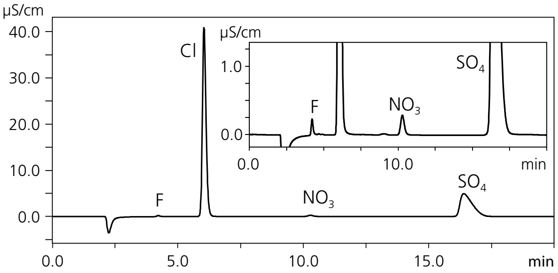

Fig. 8 Chromatogram of Tap Water and Enlarged Figure

Analysis Conditions

Table 6 Analytical Conditions

Column:	Shim-pack IC-SA2*1 (250 mm × 4.0 mm I.D., 9 µm)
Guard column:	Shim-pack IC-SA2(G)*2 (10 mm × 4.6 mm I.D., 9 µm)
Mobile phase:	0.6 mmol/L Sodium Carbonate 12.0 mmol/L Sodium Hydrogen Carbonate
Flow rate:	1.0 mL/min
Column temp.:	30 °C
Injection volume:	50 µL
Vial:	Shimadzu Vial, LC, 4 mL, Polypropylene*3
Detection:	Conductivity (CDD-10AVP)

*1 P/N: 228-38983-91 *2 P/N: 228-38983-92 *3 P/N: 228-31537-91

Spike and Recovery Test

Table 7 shows the results of a spike-and-recovery test of the tap water conforming to ASTM D4327-03. The test was conducted by spiking the sample with standard solution. The recovery rate was calculated using the equation shown below the table, as specified in ASTM D4327-03.

Table 7 Percent recovery of the spike

F	Cl	PO_4	SO_4	NO_2	Br	NO_3
97.5	100.9	106.3	99.5	106.8	107.9	98.6

Unit: %

$$P = 100\,[A(V_S + V) - BV_S] / CV$$

P : Percent recovery of the spike
A : Analyte concentration (mg/L) in spiked sample
B : Analyte concentration (mg/L) in unspiked sample
C : Concentration (mg/L) of analyte in spiking solution
V_S : Volume (mL) of sample used, and
V : Volume (mL) added with spike

Conclusion

This article introduced analyses of anions contained in drinking water and tap water based on ASTM D4327-03 using a Shimadzu HIC-ESP suppressor ion chromatograph.

Reference

1) ASTM D4327-03, Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography, ASTM International, West Conshohocken, PA, 2003, www.astm.org

Analysis of Anions

ASTM D4327-03 Compliant Analysis of Anions in Wastewater

Application >

Keywords: **wastewater**

The ion chromatograph is widely used in detection and quantitative analysis of ion components in aqueous solutions. ASTM D4327-03 [1)] issued by ASTM International in the United States specifies the test methods for analysis of seven anions (fluoride ion, chloride ion, nitrite ion, bromide ion, nitrate ion, phosphate ion, sulfate ion) in drinking water or wastewater by suppressed ion chromatograph.

This article introduces an ASTM D4327-03 compliant analysis of anions in industrial wastewater using a Shimadzu HIC-ESP anion suppressor ion chromatograph. A high-resolution column, Shim-pack IC-SA3, was used because industrial wastewater has a high content of contaminants.

Benefits

- Enables acquisition of data with excellent linearity and repeatability.
- Separation of contaminant components and target anions in wastewater is possible by using the Shim-pack IC-SA3.
- This test method is also applicable to anion analyses of drinking water.

Analysis of Industrial Wastewater

Using this technique, industrial wastewater was filtered with a 0.2 µm filter and then diluted 10 times with ultrapure water prior to the analysis. Fig. 9 shows the analysis results. Although contaminant peaks appeared in close proximity to some components, such as the fluoride ion and phosphate ion, satisfactory separation of those components was also possible by using a Shim-pack IC-SA3 as the analysis column.

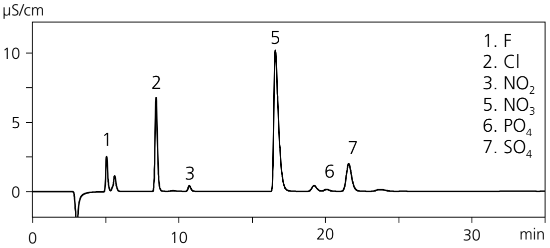

Fig. 9 Chromatogram of Industrial Wastewater

Analysis Conditions

Table 8 shows the analysis conditions of the standard solution of the seven anions.

Table 8 Analytical Conditions

Column:	Shim-pack IC-SA3*[1] (250 mm × 4.0 mm I.D., 5 µm)
Guard column:	Shim-pack IC-SA3(G)*[2] (10 mm × 4.6 mm I.D., 5 µm)
Mobile phase:	3.6 mmol/L Sodium Carbonate
Flow rate:	0.8 mL/min
Column temp.:	40 °C*[3]
Suppressor:	Electrodialytic suppressor ICDS-40A
Injection volume:	50 µL
Vial:	Shimadzu Vial, LC, 4 mL, Polypropylene*[4]
Detection:	Conductivity

*1 P/N: 228-41600-91
*2 P/N: 228-41600-92
*3 The temperature can be changed according to the separation pattern of the components in the analysis sample. In the analysis of the industrial wastewater used in this experiment, satisfactory separation of contaminants and phosphate ions was possible at 40 °C.
*4 P/N: 228-31537-91

Linearity and Repeatability

A 4-level calibration curve was created for the seven anions that are the targets of analysis in ASTM D4327-03 in a concentration range conforming to the ASTM standard. All the coefficients of determination (r^2) of the calibration curves showed 0.990 or greater, as specified in ASTM D4327-03. Table 9 shows the employed calibration levels.

Table 9 Calibration Levels of Seven Anions

	F	Cl	PO_4	SO_4	NO_2	Br	NO_3
STD 1	0.20	0.20	1.00	2.00	0.40	0.20	0.60
STD 2	1.00	1.00	5.00	10.00	2.00	1.00	3.00
STD 3	5.00	5.00	25.00	50.00	10.00	5.00	15.00
STD 4	10.00	10.00	50.00	100.00	20.00	10.00	30.00

Unit: mg/L

Table 10 Repeatability of Retention Times and Peak Areas at Lowest Calibration Levels

	F	Cl	PO_4	SO_4	NO_2	Br	NO_3
Concentration (mg/L)	0.20	0.20	1.00	2.00	0.40	0.20	0.60
Retention time %RSD	0.01	0.01	0.03	0.03	0.02	0.03	0.04
Area %RSD	0.33	0.35	0.39	0.19	0.18	0.59	0.21

Conclusion

This article introduced analyses of anions based on ASTM D4327-03 using a Shimadzu HIC-ESP anion suppressor ion chromatograph. Satisfactory separation of contaminants contained in industrial wastewater was possible by using this instrument in combination with a high-resolution Shim-pack IC-SA3 column. This analysis technique is applicable not only to industrial wastewater, but also to anion analysis of drinking water.

Reference

1) ASTM D4327-03, Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography, ASTM International, West Conshohocken, PA, 2003, www.astm.org

index

Analysis of Anions

Analysis of Total Nitrogen and Total Phosphorus in Environmental Water According to ASTM D8001 by Ion Chromatography

Keywords: **ASTM D8001, total nitrogen, total phosphorus**

Application >

In recent years, the issue of eutrophication of water quality has attracted attention. Measures against eutrophication are included in Goal 14 of the SDGs, "Life below water." The major causes of eutrophication are thought to be phosphorus and nitrogen, which nourish phytoplankton in water. Industrial and domestic wastewater produced by human activities contains a large amount of nitrogen and phosphorus, which are discharged into rivers, leading to eutrophication. Therefore, it is essential to control the concentration of phosphorus and nitrogen in wastewater.

Benefits

- Total Nitrogen (TN) and Total Phosphorus (TP) in environmental water can be analyzed in accordance with ASTM D8001.
- TN and TP can be measured simultaneously in a single alkaline persulfate digestion.

Analytical Conditions

Table 11 shows the analytical conditions.

Table 11 Analytical Conditions

Column	Shodex SI-52 4E (250 mm × 4.0 mm I.D., 5 μm)
Guard column	Shodex SI-92G (10 mm × 4.6 mm I.D., 9 μm)
Mobile phase	3.6 mmol/L Sodium carbonate
Flow rate	0.8 mL/min
Column temp.	45 °C
Injection volume	200 μL
Vial	Shimadzu Vial, LC, 4 mL, Polypropylene*1
Detection	Conductivity

*1 P/N: 228-31537-91

Analysis of Standard Solution

Figure 10 shows the chromatogram (100 μg/L each).

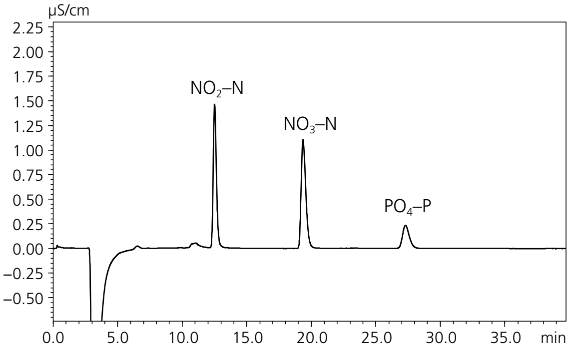

Fig. 10 Chromatogram of Mixed Standard Solutions (100 μg/L each)

Digestion and Analysis of Mixed Digest-check Sample

Table 12 Spike Recoveries of Mixed Digest-check Sample (*n*=7)

		TN	TP
Digestion blank	Average of measured concentration (mg/L)	0.012	N.D.
	Concentration of stock solution (mg/L)	0.55	N.D.
Mixed digest-check sample	**Compounds**	**Glycine** (FW: 111.5)	**Glycerol phosphate** (FW: 306.1)
	Average of measured concentration (mg/L)	0.11	0.039
	Concentration of stock solution (mg/L)	4.97	1.74
	Found concentration (mg/L)	4.42	1.74
	Weight (g)	0.42	0.50
	Expected concentration (mg/L)	4.22	1.62
Spike recovery (%)		**105.8**	**107.8**

Analysis of Environmental Water

Table 13 Analytical Results (*n*=3)

	Nitrogen (μg/L)		Phosphorus (μg/L)
Undigested sample	**NO$_2$–N**	**NO$_3$–N**	**PO$_4$–P**
Average of measured concentration	N.D. *2	N.D.	N.D.
Digested sample	**NO$_3$–N**		**PO$_4$–P**
Concentration of stock solution *3	0		0
TKN *4	0		—

*2 Below MDL.
*3 (Average of measured concentration of digested sample – average of measured concentration of digested blank) × dilution ratio
*4 Concentrations of NO$_3$–N and NO$_2$–N in the undigested sample – Actual concentration of NO$_3$–N in the digested sample

Conclusion

This article introduces the analysis of total nitrogen and total phosphorus in environmental water according to ASTM D8001. The HIC-ESP was used for measurement in accordance with the standard. Furthermore, stable analysis is possible by using the electrodialytic suppressor ICDS-40A.

Reference

1) ASTM D8001, Standard Test Method for Determination of Total Nitrogen, Total Kjeldahl Nitrogen by Calculation, and Total Phosphorus in Water, Wastewater by Ion Chromatography, ASTM International, West Conshohocken, PA, www.astm.org

Analysis Using a Dual System

Simultaneous Analysis of Anions and Cations Using Ion Chromatograph Dual Channel System

Keywords: **dual channel system, simultaneous analysis**

Application >

This dual channel system enables simultaneous analysis of anions and cations. For anions, suppressor and non-suppressor methods can be selected, and a UV-VIS detector can be used for the suppressor method. This article introduces applications obtained by a combination of anion analysis with the electrodialytic suppressor system HIC-ESP and cation analysis with a non-suppressor system.

Benefits

- Various kinds of samples can be analyzed.
- Both anion and cation analytical results were obtained in a single run, resulting in improved work efficiency, and good repeatability was obtained.

Flow Path Diagram

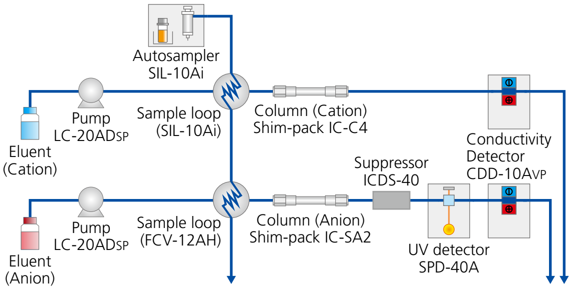

Fig. 11 HIC-ESP/NS Ion Chromatograph Dual Channel System Flow Path Diagram

Analytical Conditions

Analysis was carried out using a Shim-pack IC-SA2 column for anions and a Shim-pack IC-C4 column for cations. Mobile phase composition and flow rate can be changed according to the analytical purpose, but since the column oven is shared with anion analysis and cation analysis channels, the temperature condition must be set to the same value. Here, the sampling volume is set to 1600 µL to completely displace the two sample loops with standard solution, but the actual injection volume is determined by the sample loop volume (50 µL each, here).

Table 14 Analytical Conditions

Anion
Column: Shim-pack IC-SA2 (250 mm × 4.0 mm I.D., 9 µm)*1
Shim-pack IC-SA2(G) (10 mm × 4.6 mm I.D., 9 µm)*2
Mobile phase: 12 mmol/L sodium hydrogen carbonate,
0.6 mmol/L sodium carbonate
Flow rate: 1.0 mL/min
Cation
Column: Shim-pack IC-C4 (150 mm × 4.6 mm I.D., 7 µm)*3
Shim-pack IC-GC4 (10 mm × 4.6 mm I.D., 7µm)*4
Mobile phase: 2.5 mmol/L oxalic acid
Flow rate: 1.0mL/min
Column temp.: 40°C
Injection vol.: 50 µL ea. (Setting: 1600 µL)
Vial: Shimadzu Vial, LC, 4 mL, Polypropylene*5
Detection: Conductivity, UV-VIS (210 nm)

*1 P/N: 228-38983-91
*2 P/N: 228-38983-92
*3 P/N: 228-41616-91
*4 P/N: 228-59900-91
*5 P/N: 228-31537-91

Analysis of Standard Solutions

Table 15 Composition of Anion Standard Mixture

F^-	Fluoride ion	0.025 mg/L
Cl^-	Chloride ion	0.025 mg/L
NO_2^-	Nitrite ion	0.1 mg/L
Br^-	Bromide ion	0.1 mg/L
NO_3^-	Nitrate ion	0.1 mg/L
PO_4^{3-}	Phosphate ion	0.25 mg/L
SO_4^{2-}	Sulfate ion	0.1 mg/L

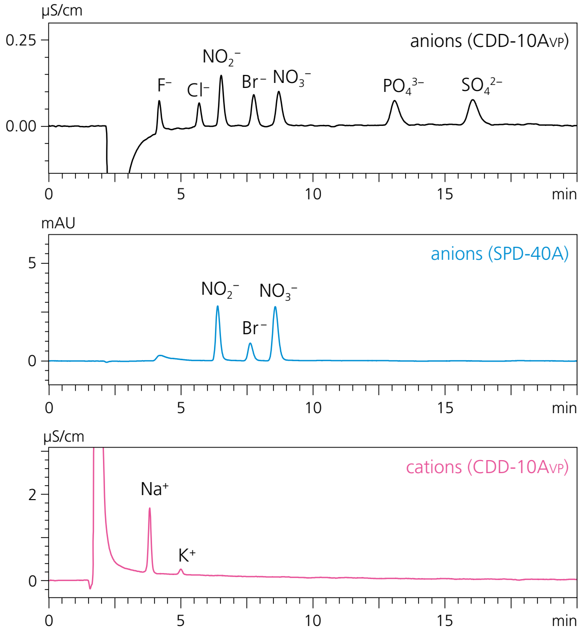

Fig. 12 Chromatograms of Anion Standard Mixture

Table 16 Composition of Cation Standard Mixture

Li^+	Lithium ion	0.01 mg/L
Na^+	Sodium ion	0.04 mg/L
NH_4^+	Ammonium ion	0.04 mg/L
K^+	Potassium ion	0.1 mg/L
Mg^{2+}	Magnesium ion	0.1 mg/L
Ca^{2+}	Calcium ion	0.1 mg/L

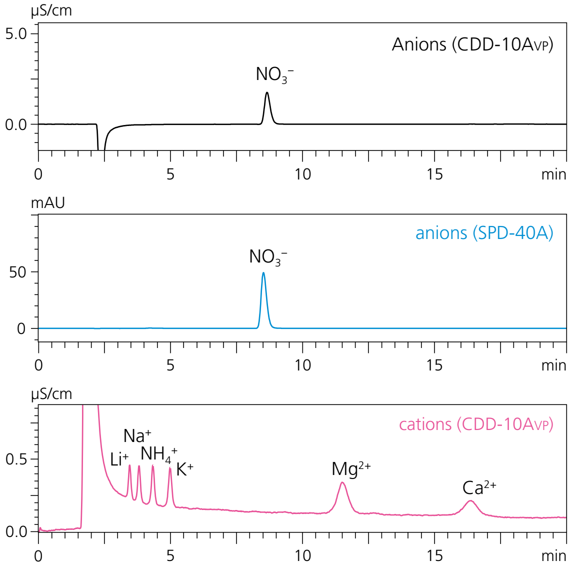

Fig. 13 Chromatograms of Cation Standard Mixture

Area Repeatability and Lower Limit of Quantification

Each lower limit of quantification (LOQ, mg/L) was calculated as the concentration at which the S/N ratio was 10.

Table 17 Area repeatability (*n* = 6) and lower limit of quantification

	concentration (mg/L)	area repeatability (%RSD)	LOQ (mg/L)
F^-	0.025	2.45	0.008
Cl^-	0.025	2.30	0.011
NO_2^-	0.1	2.20	0.021
Br^-	0.1	1.34	0.034
NO_3^-	0.1	2.88	0.031
PO_4^{3-}	0.25	2.48	0.11
SO_4^{2-}	0.1	3.53	0.042
NO_2^- (UV-VIS)	0.1	0.35	0.003
Br^- (UV-VIS)	0.1	0.52	0.009
NO_3^- (UV-VIS)	0.1	0.41	0.003
Li^+	0.01	1.26	0.003
Na^+	0.04	1.89	0.010
NH_4^+	0.04	2.65	0.009
K^+	0.1	1.82	0.022
Mg^{2+}	0.1	3.05	0.028
Ca^{2+}	0.1	3.78	0.062

Analysis of Mineral Water

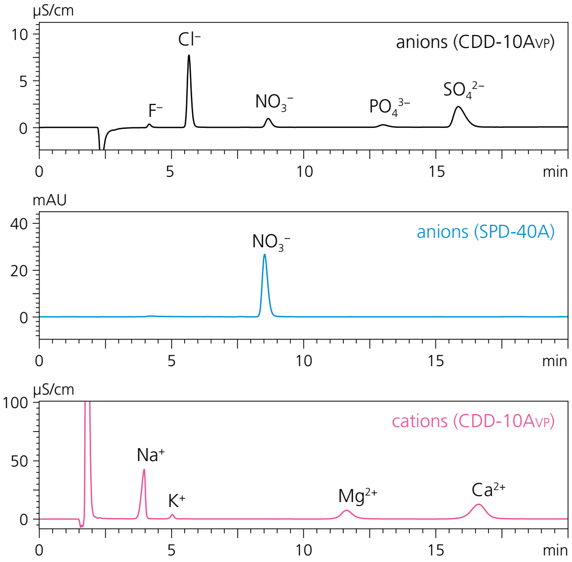

Fig. 14 Chromatograms of Mineral Water

Analysis of Soil Extracted Water

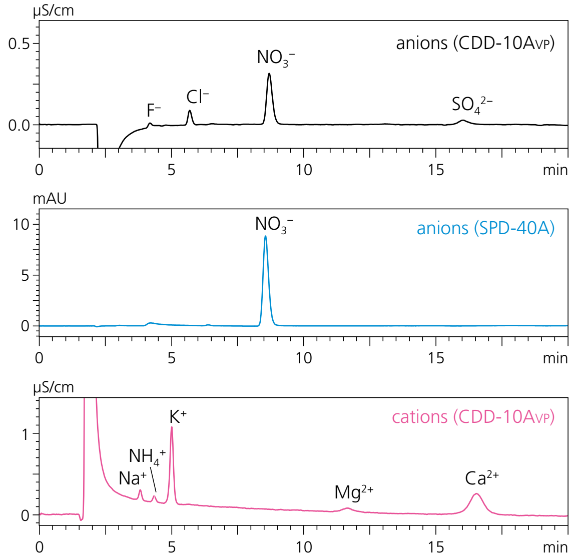

Fig. 15 Chromatograms of Soil Extracted Water

Conclusion

This article introduces applications obtained by a combination of anion analysis with the electrodialytic suppressor system HIC-ESP and cation analysis with a non-suppressor system. Both anion and cation analytical results were obtained in a single run, resulting in improved work efficiency, and good repeatability was obtained.

Analysis of Cations

Analysis of Cations in Drinking Water and Wastewater, Conforming to ASTM D6919-03

Keywords: **ion chromatograph, wastewater**

Application >

Ion chromatography can be widely employed for the detection and quantification of ionic components in aqueous solutions. ASTM D6919-03 1), published by ASTM International, USA, specifies an ion chromatographic method for analyzing the six cations (lithium, sodium, ammonium, potassium, magnesium, and calcium) in drinking water and wastewater. This article introduces analysis of the six cations in drinking water and wastewater using a non-suppressor ion chromatograph that conforms to ASTM D6919-03.

Benefits

- Data with good linearity and repeatability can be obtained in analysis conforming to ASTM D6919-03.
- Cations in drinking water and wastewater can be quantified.
- Separation of sodium and ammonium ions can be improved by adding 18-crown-6 ether to the mobile phase.

Analysis of Standard Solution

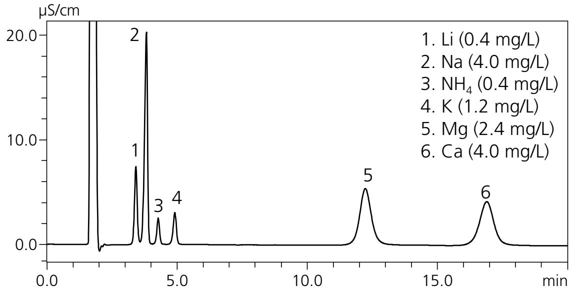

Fig. 16 Chromatogram of Six Cations

Analysis of Drinking Water and Tap Water

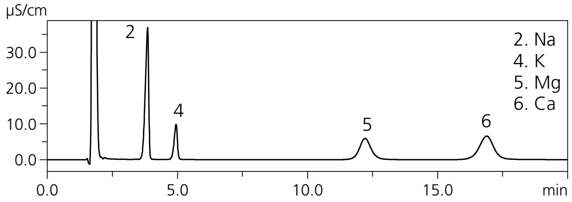

Fig. 17-1 Chromatogram of Commercial Drinking Water A

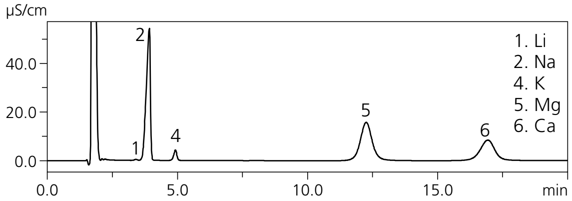

Fig. 17-2 Chromatogram of Commercial Drinking Water B

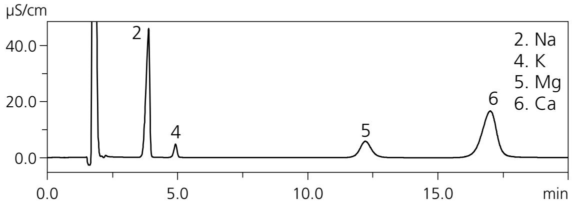

Fig. 17-3 Chromatogram of Tap Water

Analysis Conditions

Table 18 Analytical Conditions

Column:	Shim-pack IC-C4*1 (150 mm × 4.6 mm I.D., 7 µm)
Guard column:	Shim-pack IC-GC4*2 (8 mm × 3 mm I.D., 7 µm)
Mobile phase:	2.5 mmol/L Methanesulfonic Acid
Flow rate:	1.0 mL/min
Column temp.:	40°C
Injection volume:	50 µL
Vial:	Shimadzu Vial, LC, 4 mL, Polypropylene*3
Detection:	Conductivity

*1 P/N: 228-41616-91 *2 P/N: 228-59900-91 *3 P/N: 228-31537-91

Analysis of Factory Wastewater

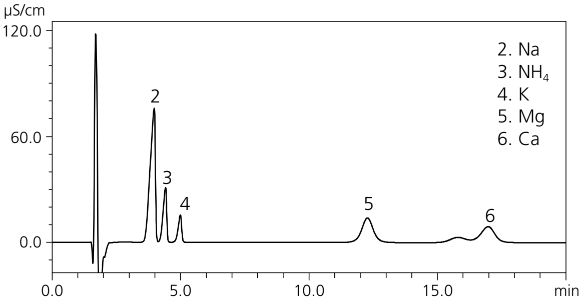

Fig. 18 Chromatogram of Factory Wastewater

Conclusion

This article introduced the cation analysis of drinking water and wastewater using a non-suppressor ion chromatograph conforming to ASTM D6919-03.

Reference

1) ASTM D6919-03, Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography, ASTM International, West Conshohocken, PA, 2003, www.astm.org

index

Analysis of Cations

Quantifying NH_4^+ in Industrial Wastewater Using Ion Chromatography (Non-Suppressor System)

Keywords: **wastewater, non-suppressor**

Application

Plating solution and wastewater from plating plants contain multiple ions including those of sodium and ammonium. Ion chromatography is used to quantify these types of ions. Ion chromatography employs a conductivity detector to selectively detect only ions. However, since the eluent contains ions that cause an increased background level, a suppressor which is located between the column and detector is sometimes used to convert the eluent into pure water by means of ion exchange.

This article compares calibration curves created using suppressor and non-suppressor systems and introduces an example of measuring cations contained in industrial wastewater using the non-suppressor system.

Benefits

- NH_4^+ can be analyzed by ion chromatography (non-suppressor system).
- The signal strength is not much different from suppressors, although there is no background noise reduction effect.

Suppressor and Non-Suppressor System

The curvature occurs due to the use of a suppressor system in which the eluent is converted into water that doesn't have any pH buffering capacity. Consequently, the dissociations of target ions are suppressed due to the increasing pH value of the eluent flowing into the conductivity detector along with the increase of ammonium ions. In other words, the equilibrium relationship expressed by the following formula shifts to the left-hand side.

$$NH_3 + H_2O\ NH_4 \leftrightarrows OH$$

This leads to a reduction in responsiveness to conductivity as the concentration of ammonium ions increases, and a curved line is obtained for the calibration curve.

Analysis Conditions

Column:	Shim-pack IC-C4 (150 mm L. × 4.6 mm I.D.)
Mobile phase:	3 mmol/L methanesulfonic acid
Flow rate:	1.0 mL/min
Column temp.:	40 °C
Detection:	Conductivity detector (CDD-10AVP)
Injection vol.:	50 µL

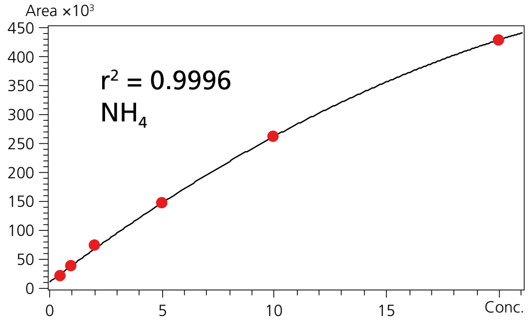

Fig. 19 NH_4 Calibration Curve Obtained Using the Suppressor System (Second-order approximation)

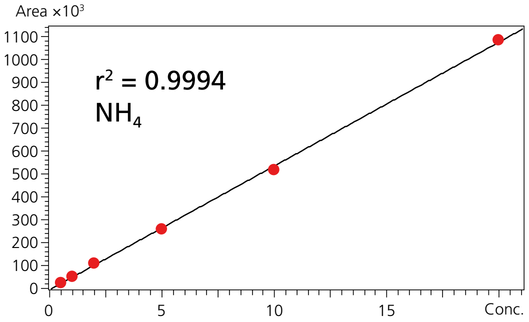

Fig. 20 NH_4 Calibration Curve Obtained Using the Non-Suppressor System (First-order approximation)

Chromatogram of Industrial Wastewater

Industrial wastewater was filtered through a membrane filter with a pore size of 0.2 µm dedicated to ion chromatography, and then analyzed using a non-suppressor system.

Fig. 21 shows the corresponding chromatogram. Favorable separation is achieved even for samples that contain significantly more sodium ions than ammonium ions and the high linearity of the calibration curve enables accurate quantitation.

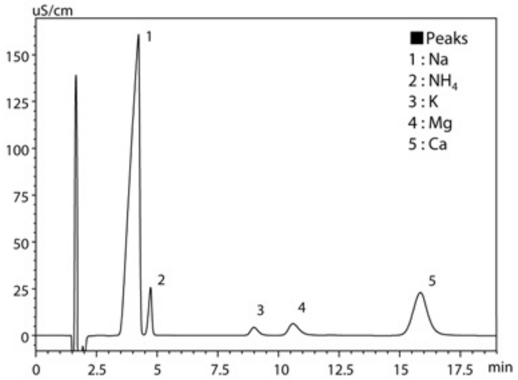

Fig. 21 Chromatogram of Industrial Wastewater

Analysis of Cations

Analysis Method of Dissolved Hexavalent Chromium According to EPA 218.6

Application >

Keywords: **hexavalent chromium, EPA 218.6**

The method for analyzing dissolved Cr (VI) in drinking water, ground water, and industrial wastewater is described in EPA 218.6. This article demonstrates analysis of Cr (VI) with the Shimadzu Prominence™ Inert System. Dissolved Cr (VI) is separated by an anion exchange column. The colored complex formed between Cr (VI) and diphenyl carbazide in the post-column derivatization is then detected at 530 nm.

Benefits

- Hexavalent chromium Cr (VI) could chromatographically be separated from potential interferences and selectively detected using post-column derivatization.
- Trace concentrations of Cr (VI) can be analyzed according to EPA 218.6

Flow Path Diagram

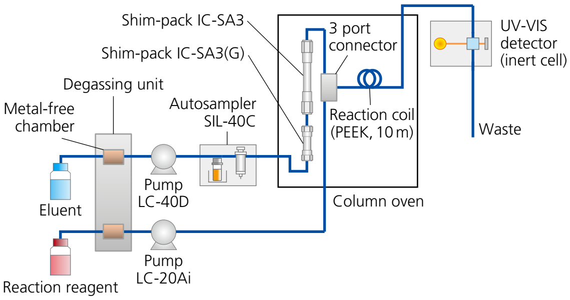

Fig. 22 Flow Path Diagram of Cr (VI) Analysis System

Analytical Conditions

Table 19 Analytical Conditions

Column:	Shim-pack IC-SA2*1 (250 mm × 4.0 mm I.D., 9 µm)
Guard column:	Shim-pack IC-SA2(G)*2 (10 mm × 4.6 mm I.D., 9 µm)
Mobile phase:	25 mmol/L Ammonium sulphate, 10 mmol/L Ammonium hydroxide
Mobile phase flow rate:	1.5 mL/min
Post column reagents:	2 mmol/L Diphenylcarbohydrazide 10 %(*v/v*) Methanol 0.5 mmol/L Sulfuric acid
Post column reagents flow rate:	0.5 mL/min
Column temp.:	40 °C
Injection volume:	250 µL
Vial:	Shimadzu Vial, LC, 4 mL, Polypropylene*3
Detection:	UV-VIS (530 nm, Inert cell)
Reaction coil:	10 m × 0.5 mm I.D. (PEEK)

*1 P/N: 228-38983-91 *2 P/N: 228-38983-92 *3 P/N: 228-31537-91

Analysis of Repeatability

Table 20 shows the repeatability of area and retention time for seven repeated analyses of each standard sample.

Table 20 Repeatability of Area and Retention Time

concentration (mg/L)	Retention time repeatability (%RSD)	Area repeatability (%RSD)
5 µg/L	0.04	2.16
20 µg/L	0.02	0.56
50 µg/L	0.04	0.16

Calculation of Method Detection Limit

The MDL was calculated from the results of the seven repeated analyses of a 1 µg/L Cr (VI) standard sample.

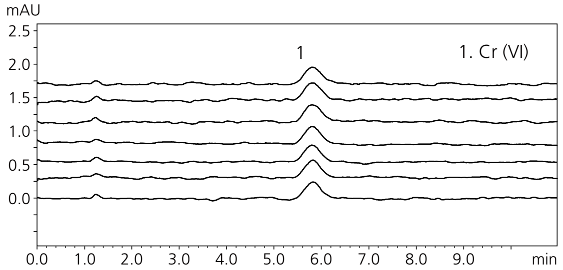

Fig. 23 Seven Repeated Analyses of a 1 µg/L Standard Sample

Analysis of Sample

Simulated wastewater and the sample obtained by adding a 1 µg/L Cr (VI) standard to the simulated wastewater were analyzed according to the procedure described in EPA 218.6. The percent recovery calculation method was in accordance with EPA 218.6.

Table 21 Percent Recovery

R: 106.7 %

$$R = \frac{C_F - C}{F} \times 100$$

R = percent recovery
C_F = fortified sample concentration
C = sample background concentration
F = concentration equivalent of Cr (VI) added to sample

Conclusion

The analysis of Cr (VI) according to EPA method 218.6 is introduced in this article. Cr (VI) can be selectively analyzed with the post-column reaction.

Reference

1) EPA Method 218.6: Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography, Rev. 3.3

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Analysis of Cations

Analysis of Hexavalent Chromium in Drinking Water According to EPA 218.7

Keywords: **hexavalent chromium, EPA 218.7**

Application >

In EPA Method 218.7, the hexavalent chromium is separated by an anion exchange column. The colored complex formed between hexavalent chromium and 1,5-diphenylcarbazide in the post-column derivatization is then detected at 530 nm. Compared to EPA Method 218.6, the sample injection volume is larger, and a lower detection limit is required.

This article introduces an example of hexavalent chromium analysis for several types of drinking water in accordance with EPA Method 218.7 using the Shimadzu Nexera lite inert system.

Benefits

- Hexavalent chromium in drinking water can be analyzed according to EPA Method 218.7.
- Hexavalent chromium can be chromatographically separated from potential interferences and selectively detected using post-column derivatization.

Flow Path Diagram

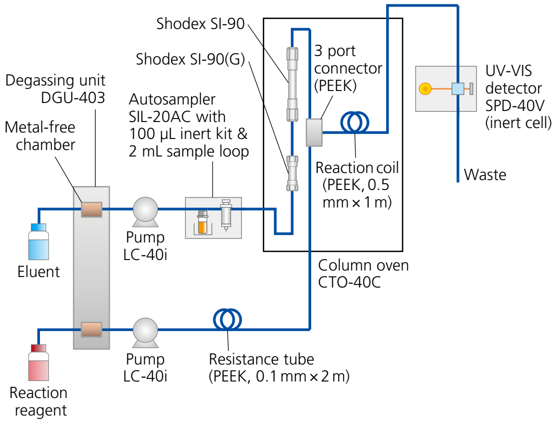


Fig. 24 Flow Path Diagram of Cr (VI) Analysis System

Analytical Conditions

Table 22 Measurement Conditions

Column:	Shodex SI-90 (250 mm × 4.0 mm I.D., 9 µm)
Guard column:	Shodex SI-90(G) (10 mm × 4.6 mm I.D., 9 µm)
Mobile phase:	50 mmol/L Ammonium sulfate 20 mmol/L Ammonium hydroxide
Mobile phase flow rate:	0.8 mL/min
Post column reagents:	2 mmol/L 1,5-diphenylcarbazide 10 % (*v/v*) Methanol 0.5 mol/L Sulfuric acid
Post column reagents flow rate:	0.3 mL/min
Column temp.:	45 °C
Injection volume:	1000 µL
Vial:	Shimadzu Vial, LC, 4 mL, Polypropylene*1
Detection:	UV-VIS (530 nm, inert cell)
Reaction coil:	1 m × 0.5 mm I.D., (PEEK)

*1 P/N: 228-31537-91

Method Detection Limit

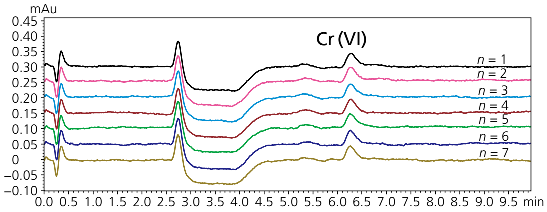


Fig. 25 Chromatograms of Seven Replicated Analyses of a 0.02 µg/L Hexavalent Chromium Standard

Table 23 MDL calculation

MDL: 0.003 µg/L

$$\mathrm{MDL} = (t) \times (s)$$

t = Student's t value for n−1 degrees of freedom at the 99% confidence level;
t = 3.143 for seven degrees of freedom
s = standard deviation of the replicate analyses

Analysis of Sample

Table 24 Analytical Result of Samples

Sample	Mineral water A	Mineral water C	Mineral water S	Tap water
Mean measured value (µg/L)	N.D.*1	0.80	0.0095	0.021
Relative standard deviation (%RSD)		0.37	3.74	6.14

*1 Not Detected (< MDL)

Conclusion

Hexavalent chromium in water can be chromatographically separated from potential interferences and selectively detected using post-column derivatization.

Reference

1) EPA Method 218.7: Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatization and UV-Visible Spectroscopic Detection, Version 1.0 Public Health Goal for Hexavalent Chromium in Drinking Water. https://oehha.ca.gov/water/public-health-goals-phgs

Analysis of Cations

Measuring Hexavalent Chromium Compounds in Atmospheric Dust

— Ion Chromatography Post-Column Absorption Spectroscopy Method —

Application >

Keywords: **hexavalent chromium, post-column method**

In March 2018, Japan's Ministry of the Environment issued the "Manual of measurement methods for hazardous air pollutants—Measurement method for hexavalent chromium compounds in atmospheric dust". In this manual, hexavalent chromium compounds are measured using the alkali impregnated filter collection – ion chromatography post-column derivatization spectroscopic absorption method. Diphenyl carbonohydrazide, which specifically reacts with hexavalent chromium, is used as the post-column derivatization reagent.

Benefits

- It is possible to analyze according to the "Manual of measurement methods for hazardous air pollutants—Measurement method for hexavalent chromium compounds in atmospheric dust".
- Hexavalent chromium can be measured in accordance with EPA 218.6 with the same instrument configuration.

Analytical Conditions

Table 25 Measurement Conditions

■ Separation	
Column:	Shim-pack IC-SA2 (250 mm L., 4.0 mm I.D.)
Guard column:	Shim-pack IC-SA2G (10 mm L., 4.6 mm I.D.)
Eluent:	10 mmol/L Sodium Carbonate / 10 mmol/L Sodium Bicarbonate
Flow rate:	1.0 mL/min
Column temp.:	40 °C
■ Injection vol.:	0.25 mL
■ Post Column Derivatization	
Reaction reagent:	2 mmol/L Diphenyl carbonohydrazide – 10 %-Methanol – 0.5 mol/L Sulfate
Flow rate:	0.2 mL/min
Reaction temp.:	40 °C
Reaction coil:	0.5 mm I.D. × 8 mL. (PTFE)
■ Detection:	UV-VIS detector at 540 nm (SPD-20AV, W lamp, Inert Cell)

Analysis of Standard Samples

Fig. 26 shows the chromatograms of potassium dichromate standard solutions diluted to between 0.1 and 5.0 ng/mL using ultra-pure water.

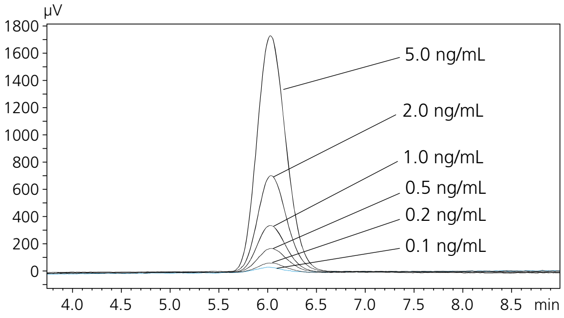


Fig. 26 Chromatograms of Standard Solutions

Repeatability of the Standard Solutions

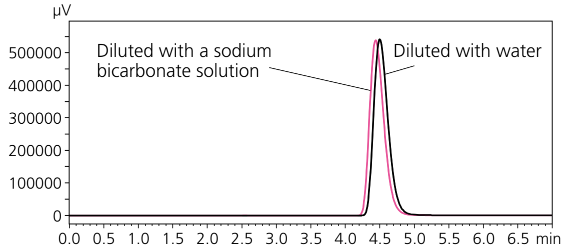
Table 26 lists the peak area, quantitation value (concentration), and accuracy of each measurement.

Table 26 Repeatability of Area and Retention Time

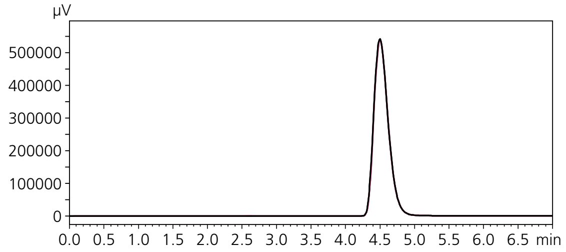
Measurement	Area	Concentration (ng/mL)	Accuracy (%)
1	724	0.099	99.1
2	719	0.098	98.5
3	743	0.102	101.7
4	731	0.100	100.0
5	736	0.101	100.8
Average	731	0.100	
%RSD	1.3	1.6	

Influence of Sample Matrix

Fig. 27 compares the chromatograms of the standard solution when diluted, respectively, with water and with sodium bicarbonate solution, which is used to prepare the alkali impregnated filter. Sodium carbonate released from the alkali-impregnated filter is a matrix and the elution strength becomes slightly stronger, causing a change in the elution time by a few seconds. However, we can see that the peak shapes are the same.



(a) Before retention time alignment



(b) After retention time alignment

Fig. 27 Comparison of Dilution Solvents with a 1000 ng/mL Standard Solution

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Lineup of Liquid Chromatography Systems

Liquid chromatography (LC) is a separation technique used to separate and analyze each component in a mixture.

Shimadzu provides a range of liquid chromatography systems from HPLC (High Performance Liquid Chromatography) to UHPLC, preparative systems, and more. We also offer solutions for supercritical fluid chromatography and ion chromatography. LabSolutions dedicated software simplifies method development and routine workflows for quantitative and qualitative analysis. Shimadzu's Shim-pack columns ensure high-quality analysis data over for a multitude applications.

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The Nexera series is a family of HPLC systems that marries AI and IoT enhancements to set new industry standards.

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Nexera™ lite inert

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HPLC/UHPLC/SFC System

LC-2030C NT

The LC-2030C NT is an integrated high-performance liquid chromatography system. The intuitive touch-screen interface and stable column performance over many continuous injections ensure reliable data every time, whether you are an HPLC beginner or an expert.

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