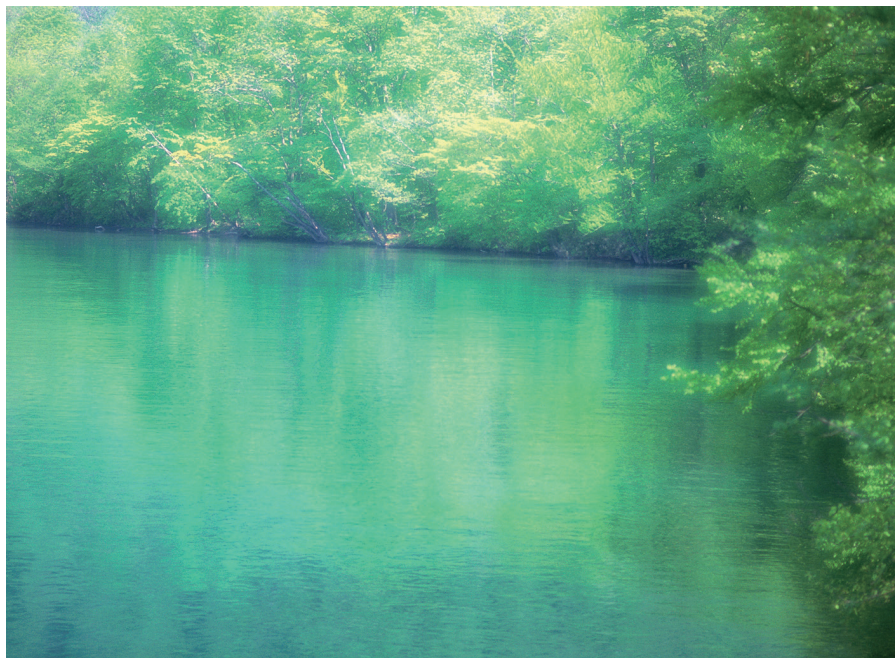


# Application Note

## Application Note No.9 (Environment)



Environment

## Data on Tap Water Quality Standards

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### 1. Tap Water Quality Standard

Water quality standards for tap water are established to protect water quality so that people can lead healthy and productive lives. In 2003, the water quality standard was greatly revised in Japan. These standards are constantly revised to keep up with changing technology. As a result we can better assemble the right know-how and technology, and sequentially consider them.

The water quality standard based on Ordinance 4 of Japan's Water Supply Act is provided by the "Ministerial Ordinance Concerning Water Quality Standards" (Ministry of Health, Labour and Welfare Ordinance No. 101, May 30, 2003 [Final revision, Ministry of Health, Labour and Welfare Ordinance 18, February 17, 2010]). Tap water must pass all water quality standards. As a consequence, companies

and other entities whose business is to supply water must have their tap water inspected in accordance with the Water Supply Act.

Items outside of water quality standards should be considered for water quality control. These items include target settings for water quality control, items where the actual detection conditions are unclear for tap water, and materials with unclear toxicity assessments. Adequate information and knowledge of these items should also be available.

Tap water companies should develop plans for water quality tests and provide customers with information on the tests for water quality standard and related matters.

## 1-1 Water Quality Standard

Rolling revisions to 50 items in the water quality standard published in 2003 were conducted. Chloric acid was added in April 2008. The water quality standard regarding "1,1-dichloroethylene" was removed in April 2009 (Shall be a water quality control target setting item, "cis-1,2-dichloroethylene" was changed to "cis-1,2-dichloroethylene and trans-1,2-dichloroethylene," and the "amount of total organic carbon (TOC)" was increased to 3 mg/L max.

The water quality criterion value for "cadmium and its compounds" was increased to 0.003 mg/L max. in April, 2010. Table 1 lists all of the items.

The coefficient of variations listed in the table below are

based on "Exhibit 5 Setting Accuracy for Water Quality Standard Items" of the "Ministry of Health, Labour and Welfare; Health Service Bureau, Water Supply Div. Ordinance No. 1010001, October 10, 2003." This Ordinance states that "the standard value for the water quality test should be measured up to 10 % (However, nonionic surfactants are 1/4 the reference value). For this, the variations of values in the vicinity of 10 % of the standard value should be retained so that the values shown are less than the coefficient of variation (however, nonionic surfactants are 1/4 the reference value)."

**Table 1 Water Quality Standard List (Effective April 1, 2010)**

No.	Item	Criteria	Test Method	Coefficient of Variation
1	Common bacteria	Number of colonies in 1 mL of test water must be 100 or less.	Standard agar medium	—
2	Escherichia coli	None detected	Specific enzyme-substrate method	—
3	Cadmium and its compounds	0.003 mg/L or less cadmium	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %
4	Mercury and its compounds	0.0005 mg/L or less mercury	Reduction vaporization-atomic absorption	10 %
5	Selenium and its compounds	0.01 mg/L or less selenium	Flameless atomic absorption ICP-MS Hydride generation-atomic absorption Hydride generation-ICP-AES	10 % 10 % 10 % 10 %
6	Lead and its compounds	0.01 mg/L or less lead	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %
7	Arsenic and its compounds	0.01 mg/L or less arsenic	Flameless atomic absorption ICP-MS Hydride generation-atomic absorption Hydride generation-ICP-AES	10 % 10 % 10 % 10 %
8	Hexavalent chromium compounds	0.05 mg/L or less hexavalent chromium	Flameless atomic absorption Flame atomic absorption ICP-AES ICP-MS	10 % 10 % 10 % 10 %
9	Cyanide ion and cyanogen chloride	0.01 mg/L or less cyanide	Ion chromatography-post-column absorption photometry	10 %
10	Nitrate nitrogen and nitrite nitrogen	10 mg/L max.	Ion chromatography (anion)	10 %
11	Fluorine and its compounds	0.8 mg/L or less fluorine	Ion chromatography (anion)	10 %
12	Boron and its compounds	1.0 mg/L or less boron	ICP-AES ICP-MS	10 % 10 %
13	Carbon tetrachloride	0.002 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
14	1,4-dioxane	0.05 mg/L max.	PT-GC/MS HS-GC/MS Solid-phase extraction-GC/MS	20 % 20 % 20 %
15	cis-1,2-dichloroethylene and trans-1,2-dichloroethylene	0.04 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
16	Dichloromethane	0.02 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
17	Tetrachloroethylene	0.01 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
18	Trichloroethylene	0.03 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
19	Benzene	0.01 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
20	Chloric acid	0.6 mg/L max.	Ion chromatography	10 %
21	Chloroacetic acid	0.02 mg/L max.	Solvent extraction-GC/MS	20 %
22	Chloroform	0.06 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
23	Dichloroacetic acid	0.04 mg/L max.	Solvent extraction-GC/MS	20 %
24	Dibromochloromethane	0.1 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
25	Bromic acid	0.01 mg/L max.	Ion chromatography-post-column absorption photometry	10 %

No.	Item	Criteria	Test Method	Coefficient of Variation
26	Total trihalomethane(s)	0.1 mg/L max.	Same method as indicated for chloroform, dibromochloromethane, bromodichloromethane, and bromoform (item 22, 24, 28, and 29, respectively.)	—
27	Trichloroacetic acid	0.2 mg/L max.	Solvent extraction-GC/MS	20 %
28	Bromodichloromethane	0.03 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
29	Bromoform	0.09 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
30	Formaldehyde	0.08 mg/L max.	Solvent extraction-derivatization-GC/MS	20 %
31	Zinc and its compounds	1.0 mg/L or less zinc	Flameless atomic absorption Flame atomic absorption ICP-AES ICP-MS	10 % 10 % 10 % 10 %
32	Aluminum and its compounds	0.2 mg/L or less aluminum	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %
33	Iron and its compounds	0.3 mg/L or less iron	Flameless atomic absorption Flame atomic absorption ICP-AES ICP-MS	10 % 10 % 10 % 10 %
34	Copper and its compounds	1.0 mg/L or less copper	Flameless atomic absorption Flame atomic absorption ICP-AES ICP-MS	10 % 10 % 10 % 10 %
35	Sodium and its compounds	200 mg/L or less sodium	Flameless atomic absorption Flame atomic absorption ICP-AES ICP-MS Ion chromatography (cation)	10 % 10 % 10 % 10 % 10 %
36	Manganese and its compounds	0.05 mg/L or less manganese	Flameless atomic absorption Flame atomic absorption ICP-AES ICP-MS	10 % 10 % 10 % 10 %
37	Chloride ion	200 mg/L max.	Ion chromatography (cation) Titration method	10 % 10 %
38	Calcium, magnesium, etc. (hardness)	300 mg/L max.	Flame atomic absorption ICP-AES ICP-MS Ion chromatography (cation) Titration method	10 % 10 % 10 % 10 % 10 %
39	Post-evaporation residue	500 mg/L max.	Weight measurement	—
40	Anionic surfactants	0.2 mg/L max.	Solid-phase extraction-HPLC	10 %
41	(4S,4aS,8aR)octahydro-4,8a-dimethylnaphthalen-4a(2H)-ol (also known as Geosmin)	0.00001 mg/L max.	PT-GC/MS HS-GC/MS Solid phase microextraction-GC/MS	20 % 20 % 20 %
42	1,2,7,7-tetramethylbicyclo[2,2,1]heptan-2-ol (also known as 2-methylisoborneol)	0.00001 mg/L max.	PT-GC/MS HS-GC/MS Solid phase microextraction-GC/MS	20 % 20 % 20 %
43	Nonionic surfactants	0.02 mg/L max.	Solid-phase extraction-absorption photometry	20 %
44	Phenols	0.005 mg/L max. converted to phenol	Solid-phase extraction-derivatization-GC/MS	20 %
45	Organic substances (total organic carbon (TOC))	3 mg/L max.	Total organic carbon measurement (TOC) method	10 %
46	pH value	Between 5.8 and 8.6	Glass electrode method Glass electrode method by continuous automated measurement device	— —
47	Taste	No abnormal taste	By taste sense	—
48	Odor	No abnormal odor	By olfactory sense	—
49	Chromaticity	5 degrees max.	Colorimetric method Transmittance photometry Transmittance photometry by continuous automated spectrophotometer	— 10 % 10 %
50	Turbidity	2 degrees max.	Turbidimetric method Transmittance photometry Transmittance photometry by continuous automated spectrophotometer Integrating sphere photometry Integrating sphere photometry by continuous automated measurement device Scattered light measurement Transmission and scattered light measurement	— 10 % 10 % 10 % 10 % 10 % 10 %

## References

- 1) Water Quality Standards under Ministry of Health, Labour and Welfare: <http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/kijun/index.html>
- 2) Ministerial Ordinance for Revision of Water Quality Standard under Ministry of Health, Labour and Welfare: <http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/kijun/suishitsu22.html>

## 1-2 Water Quality Control Target Setting Items

Heterotrophic bacteria and fipronil (as one of the agricultural chemicals) were added as water quality control target setting items in April 2008.

In April 2009, "Aluminum and its compounds" and "1,1-dichloroethylene" were added, the target values of "dichloroacetonitrile" and "chloral hydrate" were changed, the target values of agricultural chemicals "EPN (pesticide)" and "chlorpyrifos (pesticide)" were readjusted, and "trans-1,2-dichloroethylene" was removed. In April 2010, "1,1,2-trichloroethane" was removed, and the target values of agricultural chemicals "isoprothiolane," "dithiopyr," "mefenaset," "bromobutide," "esprocarb," "pyriproxyfen"

were readjusted. Table 2 lists all of the items.

The coefficient of variations listed in the table below are based on "Exhibit 1 Setting Accuracy for Water Quality Control Target Setting Items" of the "Ministry of Health, Labour and Welfare; Health Service Bureau, Water Supply Div. Ordinance No. 1010001, October 10, 2003." This Ordinance states that "the standard value for the water quality test should be measured up to 10 % . For this, the variations of values in the vicinity of 10 % of the standard value should be retained so that the values shown are less than the coefficient of variation."

**Table 2 Water Quality Control Target Item List (Effective April 1, 2010)**

No.	Item	Criteria	Test Method	Coefficient of Variation
1	Antimony and its compounds	0.015 mg/L or less antimony	Hydride generation-atomic absorption Hydride generation-ICP-AES ICP-MS	10 % 10 % 10 %
2	Uranium and its compounds	0.002 mg/L or less uranium (provisional)	ICP-MS Solid-phase extraction-ICP-AES	10 % 10 %
3	Nickel and its compounds	0.01 mg/L or less nickel (provisional)	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %
4	Nitrite nitrogen	0.05 mg/L max. (provisional)	Ion chromatography	10 %
5	1,2-dichloroethane	0.004 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
6	Deleted	Deleted	Deleted	Deleted
7	Deleted	Deleted	Deleted	Deleted
8	Toluene	0.2 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
9	Di-(2-ethylhexyl) phthalate	0.1 mg/L max.	Solvent extraction-GC/MS	20 %
10	Chlorite	0.6 mg/L max.	Ion chromatography Ion chromatography-post-column absorption photometry	10 % 10 %
11	Deleted	Deleted	Deleted	Deleted
12	Chlorine dioxide	0.6 mg/L max.	Ion chromatography Ion chromatography-post-column absorption photometry	10 % 10 %
13	Dichloroacetonitrile	0.01 mg/L max. (provisional)	Solvent extraction – GC/MS	20 %
14	Chloral hydrate	0.02 mg/L max. (provisional)	Solvent extraction – GC/MS	20 %
15	Agricultural chemicals <sup>*1</sup>	1 or less detected index values	Method specified for each individual pesticide	—
16	Residual chlorine	1 mg/L max.	Diethyl-p-phenylene diamine (DPD) method Electrical current Absorption photometry Absorption photometry by continuous automated measurement device Polarography	10 % 10 % 10 % 10 % 10 %
17	Calcium, magnesium, etc. (hardness)	10 mg/L max. 100 mg/L max.	Flame atomic absorption ICP-AES ICP-MS Ion chromatography Titration method	10 % 10 % 10 % 10 % 10 %
18	Manganese and its compounds	0.01 mg/L or less manganese (provisional)	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %
19	Free carbon dioxide	20 mg/L max.	Titration method	10 %
20	1,1,1-trichloroethane	0.3 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
21	Methyl t-butyl ether	0.02 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
22	Organic substances, etc. (potassium permanganate consumption)	3 mg/L max.	Titration method	10 %
23	odor intensity (Threshold Odor Number (TON))	3 max.	By olfactory sense	—
24	Post-evaporation residue	30 mg/L max. 200 mg/L max.	Weight measurement	—
25	Turbidity	1 degree max.	Turbidimetric method Transmittance photometry Transmittance photometry by continuous automated spectrophotometer Integrating sphere photometry Integrating sphere photometry by continuous automated measurement device Scattered light measurement Transmission and scattered light measurement	— 10 % 10 % 10 % 10 % 10 % 10 %
26	pH value	About 7.5	Glass electrode method Glass electrode method by continuous automated measurement device	— —
27	Causticity (Langlier saturation index)	-1 or greater, as close to 0 as possible	Calculation method	—
28	Heterotrophic bacteria	2000 or fewer colonies in 1 mL of test water (provisional)	R2A agar medium method	—
29	1,1-dichloroethylene	0.1 mg/L max.	PT-GC/MS HS-GC/MS	20 % 20 %
30	Aluminum and its compounds	0.1 mg/L or less aluminum	Flameless atomic absorption ICP-AES ICP-MS	10 % 10 % 10 %

\*1: Details of agricultural chemicals are shown in Table 36 on page 39.

## 2. Test Methods

This section describes the various test methods used for the water quality standards and water quality control target setting items.

Metals are analyzed using atomic absorption spectrometry (AAS), inductively coupled plasma emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) testing methods.

Anion/cation, cyanide compounds, cyanogen chloride, bromate ions and anionic surfactants are analyzed using ion chromatography (IC) and high-performance liquid

chromatography (HPLC) testing methods.

Volatile organic compounds, haloacetic acids, formaldehyde, geosmin, and phenols are analyzed using gas chromatography-mass spectrometry (GC/MS).

Nonionic surfactants are analyzed using the ultraviolet-visible spectrophotometer (UV), and organic matter is analyzed using the total organic carbon analyzer (TOC).

Table 3 shows each of the items, analytical instruments, and references to the respective pages in this Application Note.

**Table 3 Analytical Instruments List**

Item	Instrument	Product Name	Features	Page
Metals	Atomic absorption spectrophotometer (AAS)	AA-7000	High sensitivity	p.6-10
	Inductively coupled plasma emission spectrometer (ICP-AES)	ICPE-9000	High sensitivity, multi-element simultaneous analysis	
	Inductively coupled plasma mass spectrometer (ICP-MS)	ICPM-8500	Ultra-high sensitivity, multi-element simultaneous analysis	
Cations Anions Cyanide and cyanogen chloride Bromate ion Anionic surfactants	Ion chromatograph (IC) High-performance liquid chromatograph (HPLC)	Prominence Prominence UFLC	High quantitation accuracy Separation analysis possible High expandability	p.11-18
Volatile organic compounds Haloacetic acids Formaldehyde 2-methylisoborneol/geosmin Phenols	Gas chromatograph - mass spectrometer (GCMS)	GCMS-QP2010 Plus	High sensitivity High stability System support including pretreatment accessories	p.19-34
Nonionic surfactants	Ultraviolet-visible spectrophotometer (UV)	UV-1800	Easy operation Rapid measurement Space saving	p.35-36
Organic substances	Total organic carbon analyzer (TOC)	TOC-V	Powerful oxidation High sensitivity, high accuracy Rapid measurement	p.37-38

### References

- 1) Regulation pertaining to Water Supply Act: <http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/hourei/suidouhou/index.html>
- 2) Information related to tap water quality: <http://www.mhlw.go.jp/topics/bukyoku/kenkou/suido/suishitsu/06.html>



## 2-1 Metals (Atomic Absorption Spectrometry, Inductively Coupled Plasma Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry)

Atomic absorption spectrometry (referred to hereinafter as AAS), inductively coupled plasma emission spectrometry (referred to hereinafter as ICP-AES) and inductively coupled plasma mass spectrometry (referred to hereinafter as ICP-MS) are methods of analyzing metals in tap water.

Many test items include high concentration components that are greater than ppm level, such as sodium and calcium, and trace elements that are less than ppb level, such as lead and cadmium.

Therefore, analysis techniques must be set up as simply and as efficiently as possible. This Application Note introduces analysis examples of river water using multi-type ICP-AES (ICPE-9000) and ICP-MS (ICPM-8500) spectrometers.

### [Separation Testing Methods]

Table 4 shows tap water quality test items and testing methods.

When analyzing many of the items in the water quality standard or target settings, standard analysis can be efficiently done using ICP-AES or ICP-MS, or by combining AAS and other testing methods.

### Simultaneous Analysis Using ICP-MS

Simultaneous analysis can be conducted using ICP-MS for all items except for mercury. Iron (Fe) analysis must be effective at reducing polyatomic ion (collision cell/reaction cell, etc.) formation by using reactions or collisions between gas molecules. If the equipment used does not have this reduction function, iron analysis should be done using a combination of AAS or ICP-AES.

### Simultaneous Analysis Using ICP-AES

High sensitivity analysis of trace elements such as lead and cadmium using the ultrasonic nebulizer is possible with the ICP-AES. A standard nebulizer is used for high concentration elements such as boron (B) and sodium (Na), and a hydride vapor generator for analysis of arsenic (As), selenium (Se), and antimony (Sb).

Analysis must be conducted using a hydride vapor generator to prepare and measure each element. Since simultaneous element analysis is not possible with the hydride vapor generator, a more efficient form of analysis would be the hydride generation-AAS method.

**Table 4 Water Quality Test Items and Test Methods for Tap Water**

Test Method			AAS				ICP-AES		ICP-MS	IC	Titration
Test Item		Standard (Criteria Value) mg/L	Flame	Flameless	Hydride Generation	Reduction Vaporization	Hydride Generation	Solid Phase Extraction			
Cd	Water quality standard item	0.003		○			○		○		
Hg	Water quality standard item	0.0005				○					
Se	Water quality standard item	0.01		○	○		○		○		
Pb	Water quality standard item	0.01		○			○		○		
As	Water quality standard item	0.01		○	○		○		○		
Cr <sup>6</sup>	Water quality standard item	0.05	○	○			○		○		
B	Water quality standard item	1					○		○		
Zn	Water quality standard item	1	○	○			○		○		
Al	Water quality standard item	0.2		○			○		○		
	Target setting item	0.1		○			○		○		
Fe	Water quality standard item	0.3	○	○			○		◎		
Cu	Water quality standard item	1	○	○			○		○		
Na	Water quality standard item	200	○	○			○		○	○	○
Mn	Water quality standard item	0.05	○	○			○		○		
	Target setting item	0.01	○	○			○		○		
Hardness	Water quality standard item	300	○				○		○	○	○
	Target setting item	10-100	○				○		○	○	○
Sb	Target setting item	0.015			○		○		○		
U	Target setting item	0.002						○	○		
Ni	Target setting item	0.01		○			○		○		
Mo	Required test item	0.07		○			○		○		
Ba	Required test item	0.7		○			○		○		
Ag	Required test item			○			○		○		

◎ : Method for reducing polyatomic ions due to collision of gas molecules or other reactions (collision cell/reaction cell)

**Table 5 ICP-AES Analytical Conditions**

Instrument	: ICPE-9000
Radio frequency power	: 1.2 (kW)
	: 1.0 (kW) UAG-1, HVG-ICP
Plasma gas flow rate (Ar)	: 10 (L/min)
Auxiliary gas flow rate (Ar)	: 0.6 (L/min)
Carrier gas flow rate (Ar)	: 0.7 (L/min)
Sample introduction	
Nebulizer	: Coaxial nebulizer
	: Ultrasonic nebulizer (UAG-1)
	: Hydride vapor generator (HVG-ICP)
Spray chamber	: Cyclone chamber
Torch	: Mini torch
View method	: Axial/Radial

**Table 6 ICP-MS Analytical Conditions**

Instrument	: ICPM-8500
Radio frequency power	: 1.2 (kW)
Plasma gas flow rate (Ar)	: 7 (L/min)
Auxiliary gas flow rate (Ar)	: 1.5 (L/min)
Carrier gas flow rate (Ar)	: 0.62 (L/min)
Sample Introduction	
Nebulizer	: Coaxial nebulizer
Spray chamber	: Cooled type Scott spray chamber
Torch	: Mini torch
Sampling depth	: 5 (mm)
Sampling interface	: Copper type

**Table 7 Electrically Heated (Flameless) AAS Analytical Conditions**

Instrument	: AA-7000				
Measurement wavelength	: Pb 283.3 nm				
Matrix modifier	: Palladium nitrate				
Temperature Program (Tube Used: High Density Tube)					
	Stage	Temperature (°C)	Time (sec)	Heating Mode	Ar Gas Flowrate (L/min)
1	Drying	150	20	RAMP	0.10
2	Drying	250	10	RAMP	0.10
3	Ashing	800	10	RAMP	1.00
4	Ashing	800	10	STEP	1.00
5	Atomization	2200	3	STEP	0.00
6	Cleaning	2500	2	STEP	1.00

**[Pretreatment]**

Add 1 mL of nitric acid to 100 mL of test water, and heat on a hot plate without boiling. When the test sample evaporates down to 90 mL or less, stop heating. Let the test sample cool to room temperature, and then add the internal standards (ICP-AES: yttrium, ICP-MS: beryllium, cobalt, gallium, yttrium, indium, and thallium). Adjust the volume to 100 mL using distilled water, and use this as the analytical sample.

**Pretreatment Using the Hydride Generation Method (Selenium)**

Add 4 mL of hydrochloric acid (1 + 1) to 20 mL of test water, and heat gently on a hot plate. When the test sample evaporates down to 20 mL or less, stop heating and let the test sample cool to room temperature. Adjust the volume to 20 mL using distilled water, and use this as the analytical sample.

**Pretreatment Using the Hydride Generation Method (Arsenic)**

Add 4 mL of nitric acid to 20 mL of test water, and then add 2 mL of sulfuric acid (1 + 1) and one drop of potassium permanganate solution (3 w/v %) respectively. Cover with a watch glass and heat on a hot plate. When the color of the potassium permanganate disappears during heating, add another drop of potassium permanganate solution (3 w/v %). Check for cloudiness caused by sulfuric acid, and continue to heat the test solution without allowing it to dry and harden. Allow the test sample cool to room temperature. Add 4 mL of hydrochloric acid (1 + 1) and 2 mL of potassium iodide solution (20 w/v %), and adjust the volume to 20 mL using distilled water, and use this as the analytical sample.

**[Analytical Sample]**

Certified River Water Standard JSAC 0301-1 (unspiked), 0302 (spiked) (The Japan Society for Analytical Chemistry Certification)

**[Conditions]**

Tables 5, 6 and 7 show the measurement parameters.

**[Analysis]****Analysis Using ICP-AES**

The coaxial nebulizer was used for simultaneous analysis of boron, sodium, potassium, calcium, and magnesium, and the remaining trace elements were measured using the ultrasonic nebulizer (UAG-1). The hydride vapor generator (HVG-ICP) was used to analyze arsenic and selenium.

**Analysis Using ICP-MS**

Simultaneous analysis was performed on all elements, and iron (Fe) was analyzed for reference.

**Analysis Using AAS**

The hydride vapor generator was used to analyze arsenic and selenium, and the flameless method was used to analyze lead.

**[Results]**

Table 8 shows the quantitative results and detection limits of ICP-AES, ICP-MS and AAS. Good quantitative results were obtained for all the elements, and matched the certified standard values. The spectral profiles of ICP-AES are shown in Fig. 1 and 2.

**Table 8 River Water Quantitation Results Using ICP-AES, ICP-MS, and AAS**

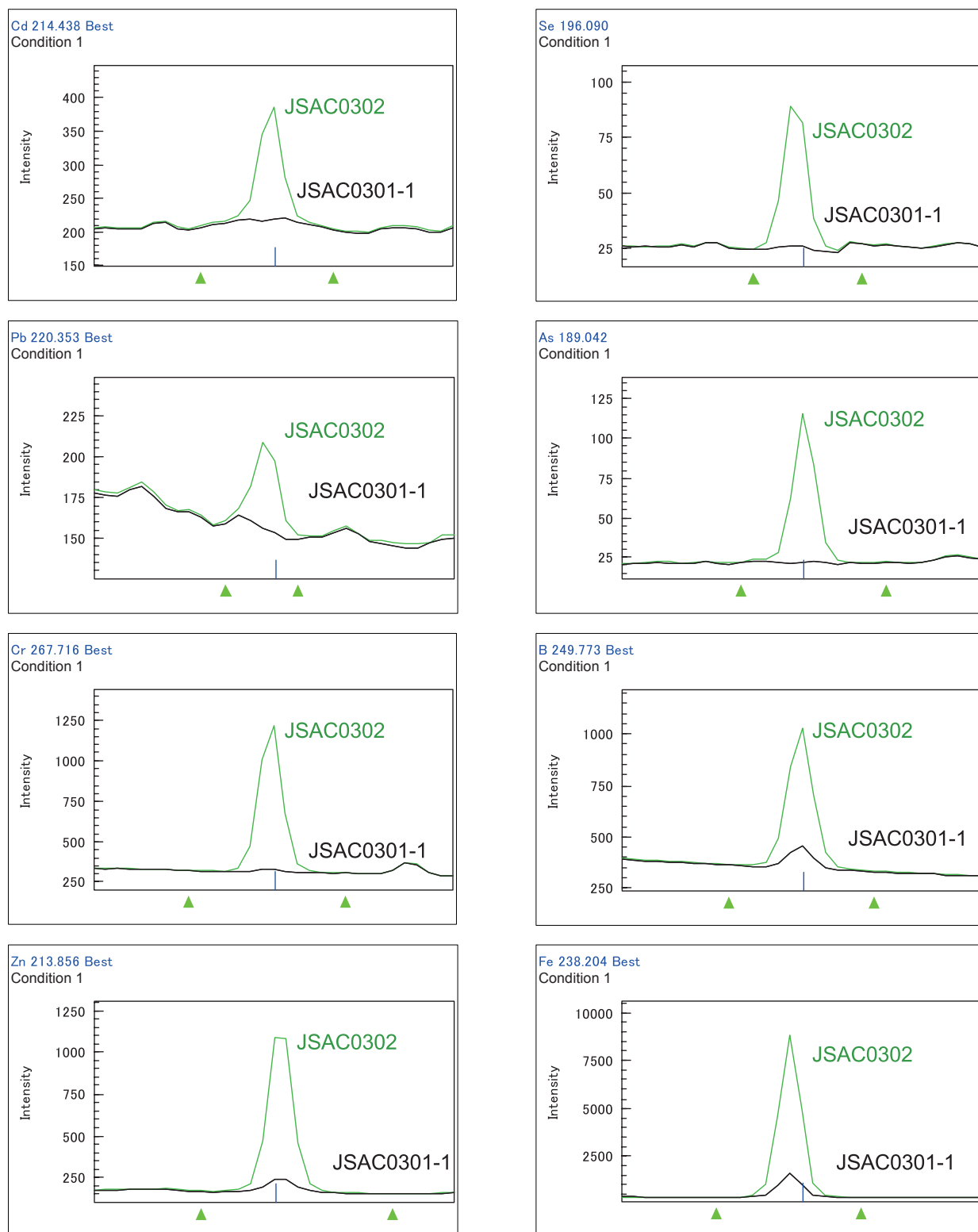
Test Method Sample Name Element	ICP-AES (ICPE-9000)				ICP-MS (ICPM-8500)			Certified Value	
	JSAC 0301-1	JSAC 0302	Detection Limit		JSAC 0301-1	JSAC 0302	Detection Limit	JSAC0301-1	JSAC0302
Unit: µg/L									
Cd	N.D	1.02	0.01	UAG	0.002	1.00	0.001	0.0023 ± 0.0007	1.01 ± 0.01
Se	N.D	4.9	0.1	HVG	0.2	5.1	0.05	*0.13	5.0 ± 0.1
	(N.D)	(5.1)	(0.2)	(HVG-AAS)					
Pb	N.D	10.3	0.2	UAG	0.007	9.98	0.0005	*0.005	10.1 ± 0.2
	(N.D)	(10.2)	(0.1)	(FLS-AAS)					
As	0.2	5.4	0.05	HVG	0.24	5.27	0.01	0.24 ± 0.03	5.3 ± 0.2
	(0.2)	(5.1)	(0.1)	(HVG-AAS)					
Cr	0.2	10.0	0.04	UAG	0.15	10.2	0.03	0.15 ± 0.01	10.1 ± 0.2
B	8.7	59.5	0.2		8.80	58.0	0.02	8.6 ± 0.3	59 ± 1
Zn	0.2	9.9	0.05	UAG	0.21	10.0	0.005	0.19 ± 0.03	10.2 ± 0.3
Al	20	66.1	0.4	UAG	18.5	66.4	0.02	19.0 ± 0.9	67 ± 1
Fe	5.0	56.5	0.02	UAG	5	55	0.6	4.7 ± 0.3	56 ± 1
Cu	0.6	10.2	0.1	UAG	0.57	10.3	0.01	0.57 ± 0.07	10.3 ± 0.2
Mn	0.13	5.0	0.006	UAG	0.13	5.06	0.007	0.125 ± 0.007	5.0 ± 0.1
U					0.0028	0.0029	0.0002	0.0029 ± 0.0002	0.0029 ± 0.0001
Ni	N.D	9.8	0.05	UAG	0.07	9.84	0.01		9.9 ± 0.2
Mo	0.4	0.4	0.1	UAG	0.38	0.37	0.003	0.38 ± 0.01	0.38 ± 0.01
Be	N.D	0.97	0.004	UAG	ND	0.98	0.006		0.99 ± 0.04
Ba	0.61	0.61	0.002	UAG	0.597	0.596	0.0007	0.60 ± 0.02	0.60 ± 0.01
Unit: mg/L									
K	0.58	0.57	0.01		0.58	0.58		0.57 ± 0.02	0.57 ± 0.01
Na	4.34	4.36	0.004		4.37	4.35	0.001	4.4 ± 0.1	4.33 ± 0.07
Mg	2.86	2.85	0.0005		2.81	2.85	0.00005	2.85 ± 0.04	2.83 ± 0.03
Ca	12.1	12.2	0.0001		12.0	12.1	0.001	12.0 ± 0.2	12.2 ± 0.2

UAG: Ultrasonic nebulizer, HVG: Hydride vapor generator

Detection Limit : Three times the concentration of the standard deviation obtained from repeat measurements of calibration curve blank  
( ) : AAS results

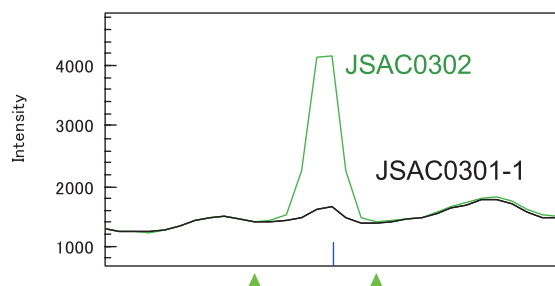
\* : Reference value





**Fig. 1 Spectral Profiles Using ICP-AES**

Cu 324.754 Best  
Condition 1



Mn 257.610 Best  
Condition 1

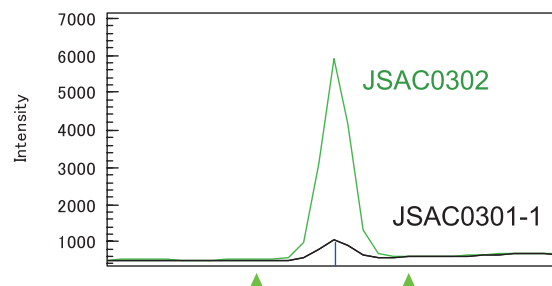


Fig. 2 Spectral Profiles Using ICP-AES

## 2-2 Cation (Ion Chromatography)

Ion Chromatography, AAS, ICP-AES, ICP-MS as well as other testing methods can be utilized for simultaneous analysis of sodium, magnesium and calcium (hardness) prescribed in the water quality standard.

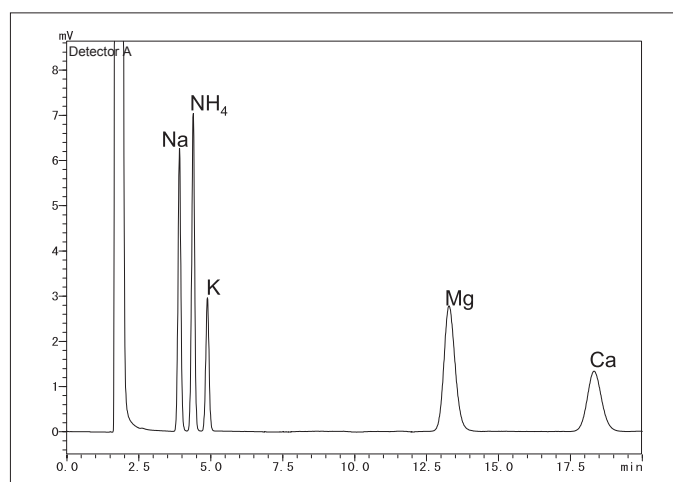
### 2-2-1 Simultaneous Analysis of Cations for Five Compounds

Fig. 3 shows simultaneous analysis examples for 5 inorganic cations using the Shim-pack IC-C4 analytical column, and Table 9 shows their analytical conditions. The ammonium ions in these examples are not among the water quality standard items. However, they are a key indicator

in water quality control. The ammonium ion can also be analyzed under the conditions shown in Table 9. In this case, the ammonium ion elutes after the sodium ion, clearly providing sufficient separation between the two ions.

**Table 9 Analytical Conditions**

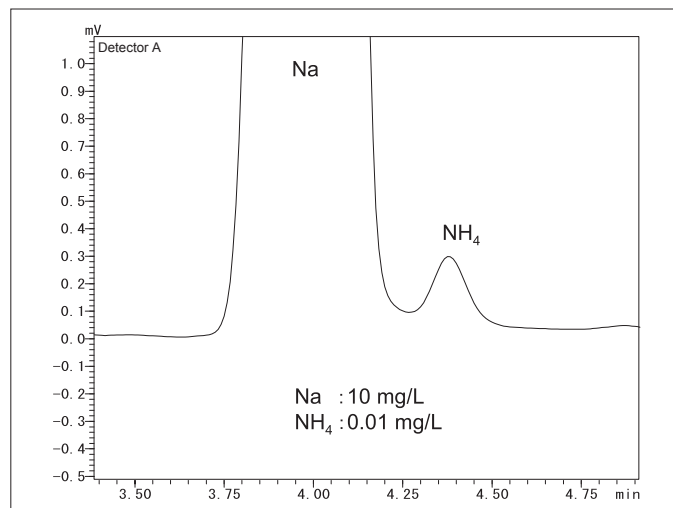
Column	: Shim-pack IC-C4 (150 mm L. × 4.6 mm I.D.)
Guard column	: Shim-pack IC-GC4 (8 mm L. × 3 mm I.D.)
Mobile phase	: 2.5 mmol/L aqueous oxalic acid solution
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Detector	: CDD-10A <sub>VP</sub> (non-suppressor method)
Injection vol.	: 50 µL



**Fig. 3 Chromatogram of Cation Mixture Standard Solution (1.0 mg/L each)**

### 2-2-2 Separation of Sodium and Ammonium Ions

Fig. 4 shows a chromatogram of sodium and ammonium ions in which the ratio of their concentrations in the standard solution is "1000:1," respectively (Table 9 shows the analytical conditions). Even with this high concentration ratio of sodium to ammonium ions, it is clear that there is sufficient separation to conduct quantitation of these analytes.



**Fig. 4 Chromatogram of Sodium and Ammonium Ions**

2-3 Anion (Ion Chromatography)

Ion chromatography can be utilized as a testing method for the simultaneous analysis of 3 items; fluorine and its compounds, total nitrogen (nitrite and nitrate) (at 10 mg/L or less), and the chloride ion.  
For the analysis of chloric acid, first add 1 mL of ethylenediamine solution (50 mg/mL) to 1 L of test water

as a pretreatment step. Here we introduce an example of analysis using the Shimadzu Prominence HIC-SP (suppressor method) Ion Chromatograph and the special Shim-pack IC-SA3 column for simultaneous analysis of the above anions including chloric acid.

2-3-1 Simultaneous Analysis of Chloric Acid and Anions

Table 10 shows the analytical conditions for the analysis of a mixture of anion standards.  
Fig. 5 shows the results of simultaneous analysis of 10 inorganic anions including chloric acid using the Shim-pack IC-SA3 analytical column.  
Both chlorous acid (standard concentration 0.6 mg/L) and

nitrite nitrogen (standard concentration 0.05 mg/L) are target analytes for water quality control. Chlorous acid is analyzed using a conductivity detector, and nitrite nitrogen is analyzed using a conductivity detector or UV absorption detector.

Table 10 Analytical Conditions

Column	: Shim-pack IC-SA3 (250 mm L. × 4.0 mm I.D.)
Mobile phase	: 3.6 mmol/L sodium carbonate solution
Flow rate	: 0.8 mL/min
Column temp.	: 45 °C
Detector	: CDD-10A <sub>SP</sub> (suppressor method)
Injection vol.	: 50 µL

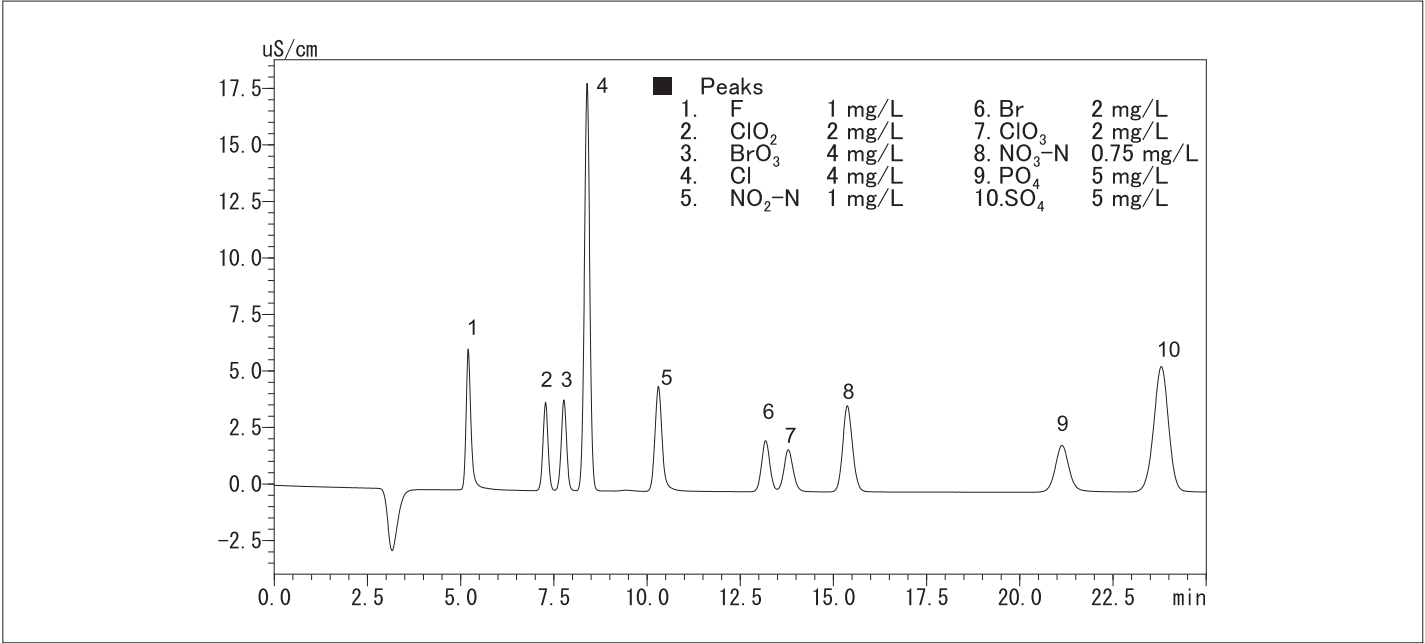


Fig. 5 Chromatogram of Anion Mixture Standard Solution

### 2-3-2 Effect of Ethylenediamine on Chloric Acid Analysis

In the test method for chloric acid, pretreatment specifies that 1 mL of ethylenediamine solution (50 mg/mL) be added to 1 L of test water. The pretreatment is confirmed to have no influences on the analysis of fluorine and the chloride ion, nitrite nitrogen and nitrate nitrogen, before simultaneous analysis of chloric acid and these anions is conducted.

Fig. 6 shows the chromatogram obtained from analysis of ethylenediamine solution (50 mg/L) using the analytical conditions shown in Table 10. It is clear that there are no interference peaks eluted due to the ethylenediamine.

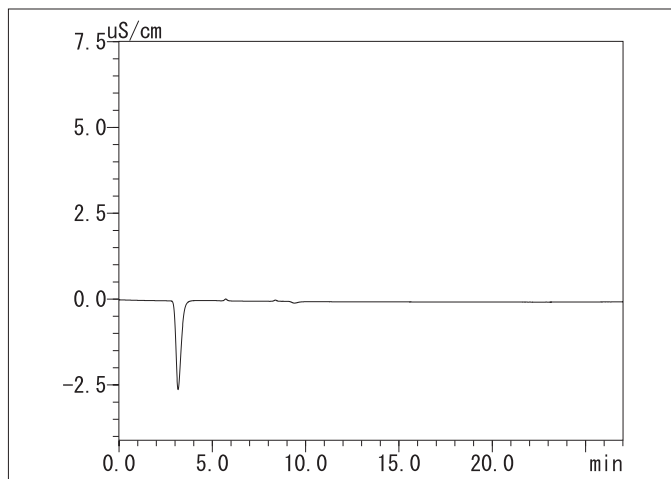


Fig. 6 Chromatogram of Ethylenediamine Solution (50 mg/L)

### 2-3-3 UV Absorption Detection of Nitrite Nitrogen

In the water quality standard, the standard criteria value for total nitrate nitrogen and nitrite nitrogen is 10 mg/L or less. However, the target value for nitrite nitrogen listed as a water quality control target item is 0.05 mg/L. For the quantitation range lower limit (LOQ) concentration of 0.005 mg/L, the standard value may be effected by the chloride ion, etc. eluted just before it, resulting in an incorrect quantitation value. Therefore, nitrite nitrogen analysis

can be conducted with an absorption detector using UV absorption to detect nitrite nitrogen.

Using an absorption detector allows for selective detection of nitrite nitrogen without the effect of chloride ions that exhibit almost no UV absorption. Fig. 7 shows a chromatogram obtained from analysis of river water using a conductivity detector, and Fig. 8 shows a chromatogram obtained using an absorption detector.

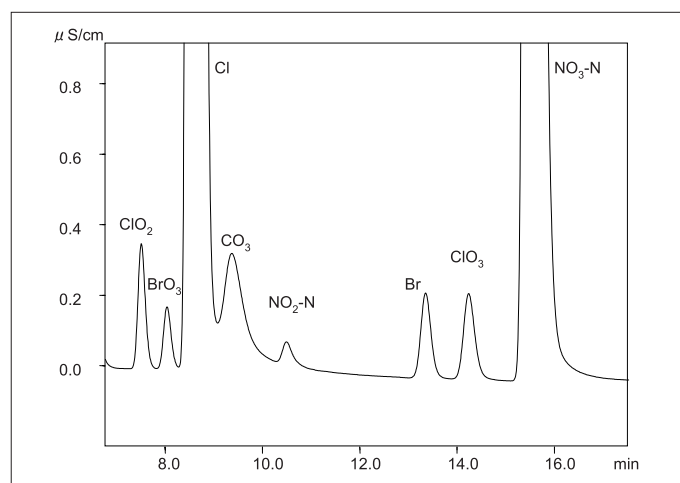


Fig. 7 Conductivity Detection of Tap Water

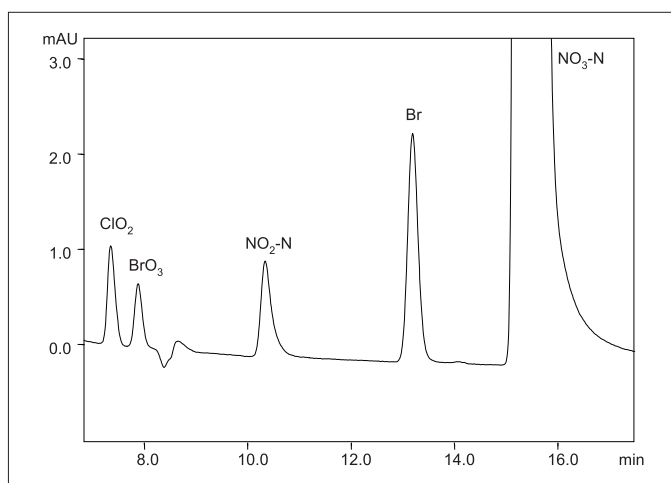


Fig. 8 UV Absorption Detection of Tap Water



## 2-4 Cyanide Ion and Cyanogen Chloride

Ion chromatography with post-column derivatization is used as the test method. The total content of the cyanide ion and the cyanogen chloride is converted to the cyanide ion, and the cyanide ion has a water quality standard value of 0.01 mg/L. A 1/10 concentration (0.001 mg/L) of the

standard value should be within CV 10 % at an injection volume of 50 to 250  $\mu\text{L}$ . Here we introduce the Shimadzu Prominence Cyanogen Analysis System using examples of analysis of cyanide and cyanogen chloride.

### 2-4-1 Analysis Method

In the notification law, detection at 638 nm, with the following analysis method is prescribed.

First, the cyanide ion and cyanogen chloride are separated using an ion exchange column. Then post-column derivatization is conducted using the 4-pyridinecarboxylic acid-pyrazolone method. With the post-column method, reactions occur in two stages. In the first stage chloramine

T solution is used, and in the second stage 1-phenyl-3-methyl-5-pyrazolone / 4-pyridinecarboxylic acid is used. Fig. 9 shows the principle of detection using the above two-stage reaction, and Fig. 10 shows the flow diagram of the Shimadzu cyanogen analysis system in accordance with the notification law.

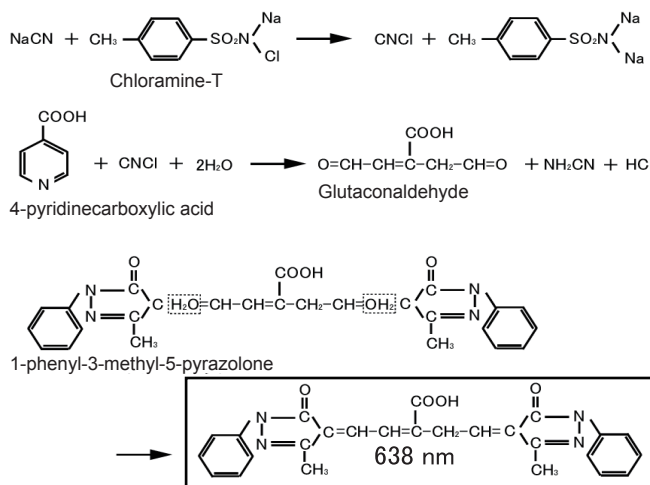


Fig. 9 Reaction Formulas

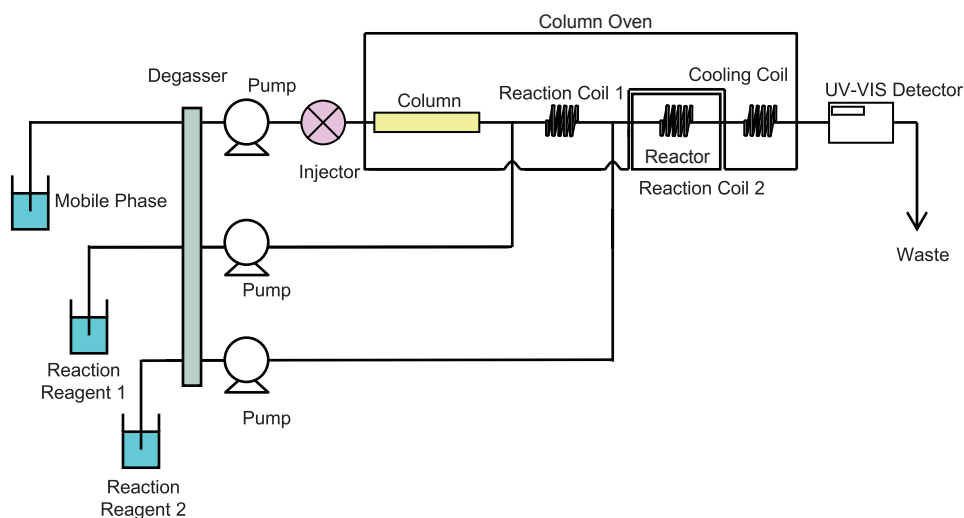


Fig. 10 Flow Diagram

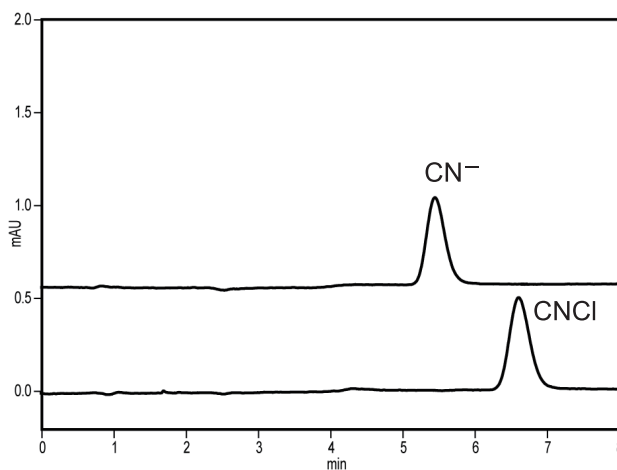
### 2-4-2 Analysis of Standard Sample

Table 11 shows the analytical conditions, and Fig. 11 shows the analysis results for the standard solution of cyanide ion and cyanogen chloride. Standard solutions are prepared due to the low stability of cyanogen chloride. Also, the

sample must be cooled because the cyanogen chloride evaporates if kept at room temperature during analysis.

**Table 11 Analytical Conditions**

<Separation>	
Column	: Shim-pack Amino-Na (100 mm L. × 6.0 mm I.D.)
Mobile phase	: 10 mmol/L tartrate (sodium) buffer solution (pH = 4.2)
Flow rate	: 0.6 mL/min
Column temp.	: 40 °C
Injection vol.	: 100 µL
<Post-Column Reaction>	
Primary Reaction	
Reagent	: 1.8 mM including chloramine-T 100 mmol/L phosphate buffer solution
Flow rate	: 0.5 mL/min
Reaction temp.	: 40 °C
Secondary Reaction	
Reagent	: 14.4 mmol/L 1-phenyl-3-methyl-5-pyrazolone + 48.3 mmol/L 4-pyridinecarboxylic acid (sodium)
Flow rate	: 0.5 mL/min
Reaction temp.	: 100 °C
Detector	: SPD-20AV at 638 nm (W lamp)



**Fig. 11 Chromatograms of Cyanide Ion and Cyanogen Chloride Standard Solutions (0.001 mg/L each)**

## 2-5 Bromate Ion

A water quality standard value for bromic acid is 0.01 mg/L. A 1/10 concentration (0.001 mg/L) of the standard value should be within CV 10 % using an injection volume of 50 to 250 µL.

### 2-5-1 Analysis of Bromic Acid

In the notification law, detection at 268 nm, with the following analysis method is prescribed. First, after separation of the bromate ion using an ion exchange column, post-column derivatization using the tribromide ion method is conducted. With the post-column method,

Here we introduce the Shimadzu Prominence Bromic Acid Analysis System using the Shim-pack IC-Bromate column for analysis of bromic acid.

reactions occur in two stages. In the first stage potassium bromide and sulfuric acid is used, and in the second stage a sodium nitrite solution is used. Fig. 12 shows the reaction for the tribromide ion method using the above two-stage reaction, and Fig. 13 shows the flow diagram.

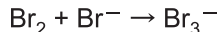
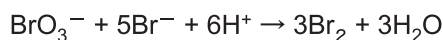


Fig. 12 Reaction Formulas

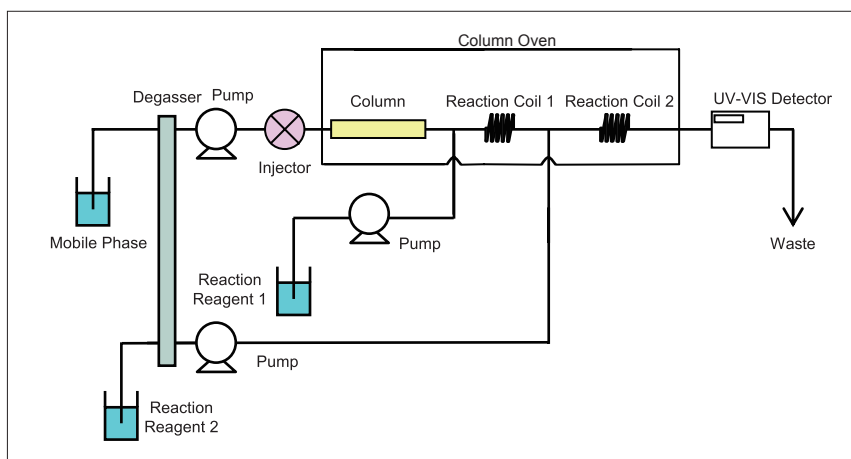


Fig. 13 Flow Diagram

### 2-5-2 Analysis of Standard Samples

Table 12 shows the analytical conditions. For the analysis of bromic acid in tap water, chlorous acid derived from a sodium hypochlorite solution, which is used as a tap water treatment chemical, may interfere with the analysis of

bromic acid. However, Fig. 14 shows that good separation of chlorous acid and bromate ion can be obtained using the conditions shown in Table 12.

Table 12 Analytical Conditions

<Separation>	
Column	: Shim-pack IC-Bromate (150 mm L. × 4.0 mm I.D.)
Mobile phase	: 1.7 mmol/L sodium hydrogen carbonate / 1.8 mmol/L sodium carbonate
Flow rate	: 1.0 mL/min
Column temp.	: 40 °C
Injection vol.	: 200 µL
<Post-Column Reaction>	
Primary Reaction	
Reagent	: 1.5 mol/L potassium bromide + 1.0 mol/L sulfuric acid
Flow rate	: 0.4 mL/min
Reaction temp.	: 40 °C
Secondary Reaction	
Reagent	: 1.2 mmol/L sodium nitrite (Na)
Flow rate	: 0.2 mL/min
Reaction temp.	: 40 °C
Detector	: SPD-20AV at 268 nm (D2 lamp)

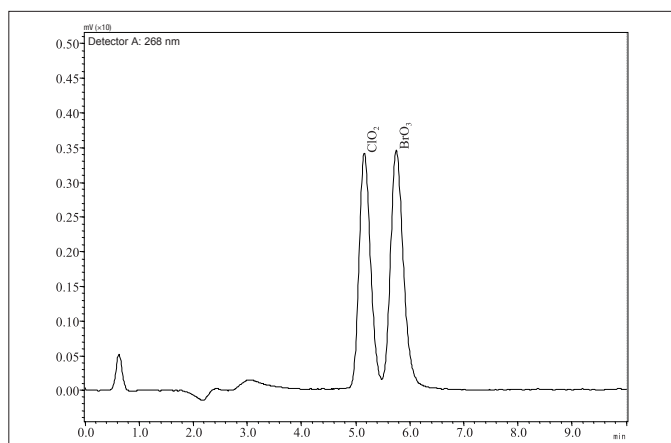


Fig. 14 Chromatogram of Bromate Ion and Chlorous Acid in Standard Solution (0.01 mg/L each)

## 2-6 Anionic Surfactants

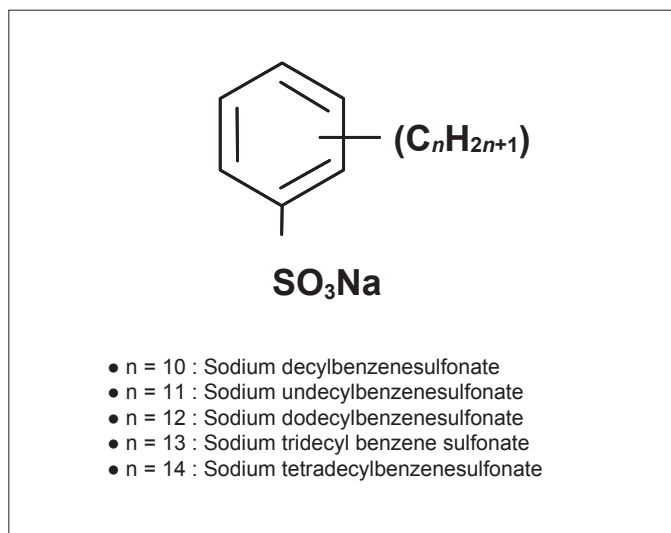
The water quality standard value for anionic surfactants is set at 0.2 mg/L or less for a total of five constituents. The test method specifies use of HPLC with fluorescence detection.

### 2-6-1 Analysis of Anionic Surfactants

Fig. 15 shows the structural formulas of five anionic surfactant analytes (sodium decylbenzenesulfonate, sodium undecylbenzenesulfonate, sodium dodecylbenzenesulfonate, sodium tridecyl benzene sulfonate, and sodium tetradecylbenzenesulfonate).

Also, isomers that have different alkyl chains for each component are included.

Here, we introduce analysis examples using the Shimadzu Prominence Anionic Surfactant Analysis System.



**Fig. 15 Structural Formulas of Anionic Surfactants**

Following is the prescribed pretreatment procedure for this method:

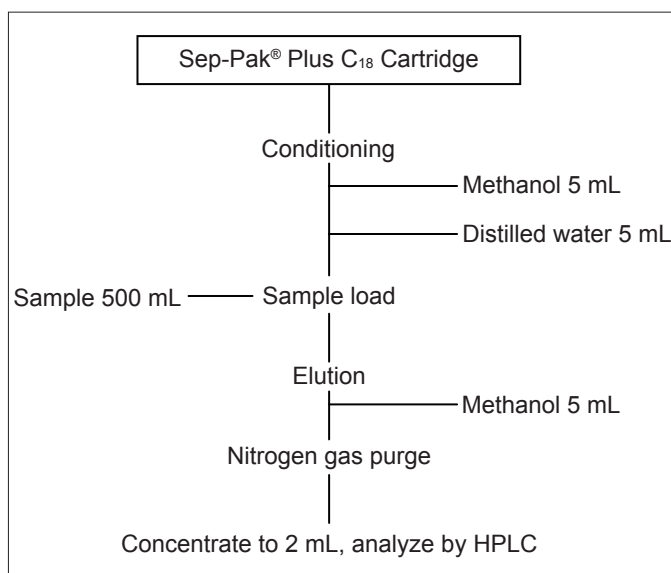
(1) Inject 5 mL methanol, then 5 mL of distilled water into the solid-phase extraction (SPE) cartridge.

(2) Pass 500 mL of test water (if the concentration of each anionic surfactant contained in the test water exceeds 0.5 mg/L, adjust the test solution to 500 mL by adding in 0.02 to 0.5 mg/L of distilled water) through the SPE cartridge at a flow rate of 30 mL per minute.

(3) Elute 5 mL of methanol slowly from the top of SPE cartridge into a test tube.

(4) Evaporate all but 2 mL of the solution from step 3 using nitrogen gas.

Fig. 16 shows a flow chart of the pretreatment procedure.



**Fig. 16 Sample Pretreatment**

## 2-6-2 Analytical Conditions and Results

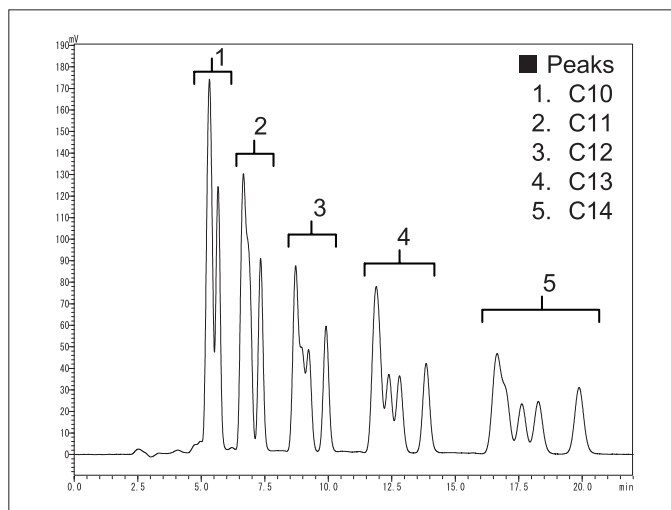
Fig. 17 shows the results obtained from analysis of a standard mixture of five anionic surfactants (0.04 mg/L each, total 0.2 mg/L) using a 20  $\mu$ L injection volume. Table 13 shows the analytical conditions used.

According to the official test method, the test sample is

**Table 13 Analytical Conditions**

Column	: Shim-pack VP-ODS (250 mm L. $\times$ 4.6 mm I.D.)
Mobile phase	: Water / acetonitrile = 35 / 65 (v/v)
Flow rate	: 1.0 mL/min
Column temp.	: 40 $^{\circ}$ C
Detector	: RF-20Axs Ex at 221 nm, Em at 284 nm
Injection vol.	: 20 $\mu$ L

to be concentrated by a factor of 250 to 1 before injecting into the HPLC, as indicated in Fig. 16. However, using the Prominence RF-20Axs high-sensitivity fluorescence detector, analysis can be conducted using direct injection, without concentrating the sample.



**Fig. 17 Chromatogram of Anionic Surfactant Standard Mixture**



## 2-7 Volatile Organic Compounds

The volatile organic compounds listed in Table 14 are restricted in tap water as either water quality standard items or water quality control target items. Volatile organic compounds are analyzed using the purge and trap-GC/

MS or the headspace-GC/MS method. In this Application Note, we introduce analysis examples using these two measurement methods.

**Table 14 Water Quality Standard Items and Water Quality Control Target Items**

Item		Standard and Target Values
Carbon tetrachloride	Standard item	0.002 mg/L max.
1,4-dioxane	Standard item	0.05 mg/L max.
Cis-1,2-dichloroethylene Trans-1,2-dichloroethylene	Standard item	0.04 mg/L max.
Dichloromethane	Standard item	0.02 mg/L max.
Tetrachloroethylene	Standard item	0.01 mg/L max.
Trichloroethylene	Standard item	0.03 mg/L max.
Benzene	Standard item	0.01 mg/L max.
Chloroform	Standard item	0.06 mg/L max.
Dibromochloromethane	Standard item	0.1 mg/L max.
Total trihalomethane	Standard item	0.1 mg/L max.
Bromodichloromethane	Standard item	0.03 mg/L max.
Bromoform	Standard item	0.09 mg/L max.
1,2-dichloroethane	Quality control target item	0.004 mg/L max.
Toluene	Quality control target item	0.2 mg/L max.
1,1,1-trichloroethane	Quality control target item	0.3 mg/L max.
Methyl t-butyl ether	Quality control target item	0.02 mg/L max.
1,1-dichloroethylene	Quality control target item	0.1 mg/L max.
1,3-dichloropropene (pesticide)	Quality control target item	0.002 mg/L max.

## 2-7-1 Purge and Trap-GC/MS Method

### 2-7-1-1 Analytical Conditions

Table 15 shows the purge and trap and the GC/MS analytical conditions.

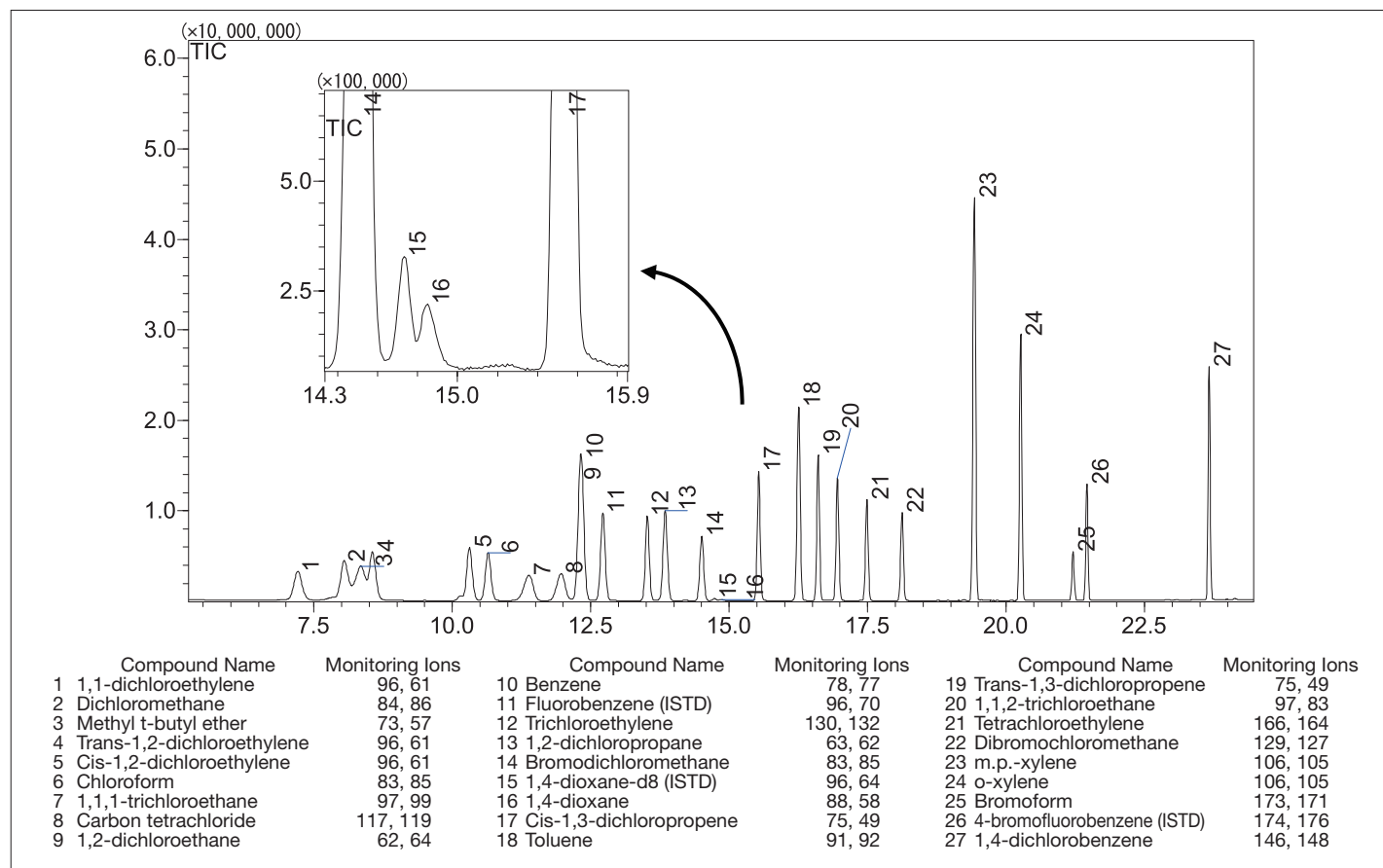
**Table 15 Analytical Conditions**

Analytical instrument : GCMS-QP2010 Plus / AQUA PT 5000J Plus + AQUAauto70			
Column : AQUATIC (60 m × 0.32 mm I.D., df = 1.4 μm) GL Science			
Purge and trap			
Sample vol.	: 5 mL	Trap tube	: GL Trap 1
Transfer line temp.	: 150 °C	Sample mount temp.	: 60 °C
Sample heater	: OFF	Purge time	: 8 min
Dry purge time	: 3 min	Dry purge flow rate	: 40 mL/min
Desorb temp.	: 220 °C	Desorb flow rate	: 300 mL/min
Bake temp.	: 230 °C	MCS bake temp.	: 230 °C
-GC-			
Injection port temp.	: 150 °C	Carrier gas P&T	: Helium (90 kPa)
Oven temp.*1)	: 35 °C (5 min) → (6 °C/min) → 90 °C → (10 °C/min) → 220 °C (3 min)		
-MS-			
Ion source temp.	: 200 °C	Ionization mode	: EI
Interface temp.	: 200 °C	Ionization current	: 60 μA
-Scan mode-			
Event time	: 0.5 sec	Start <i>m/z</i> -end <i>m/z</i>	: <i>m/z</i> 35-280
-SIM mode-			
Event time	: 0.2 sec	Monitoring ion	: See Fig. 18.
Valve oven temp. : 150 °C			
MCS temp. : 40 °C			
Purge flow rate : 40 mL/min			
Desorb time : 6 min			
Bake time : 15 min			
Bake flow rate : 80 mL/min			

\*1) It may be necessary to set the initial temperature to 40 °C, depending upon the ambient temperature.

### 2-7-1-2 Results

Fig. 18 shows the total ion chromatogram of the standard sample solution.



**Fig. 18 Total Ion Chromatogram**

Fig. 19 shows the SIM chromatograms of the restricted standard items obtained from measurement of 0.0001 mg/L

standard samples (1,4-dioxane, 0.005 mg/L).

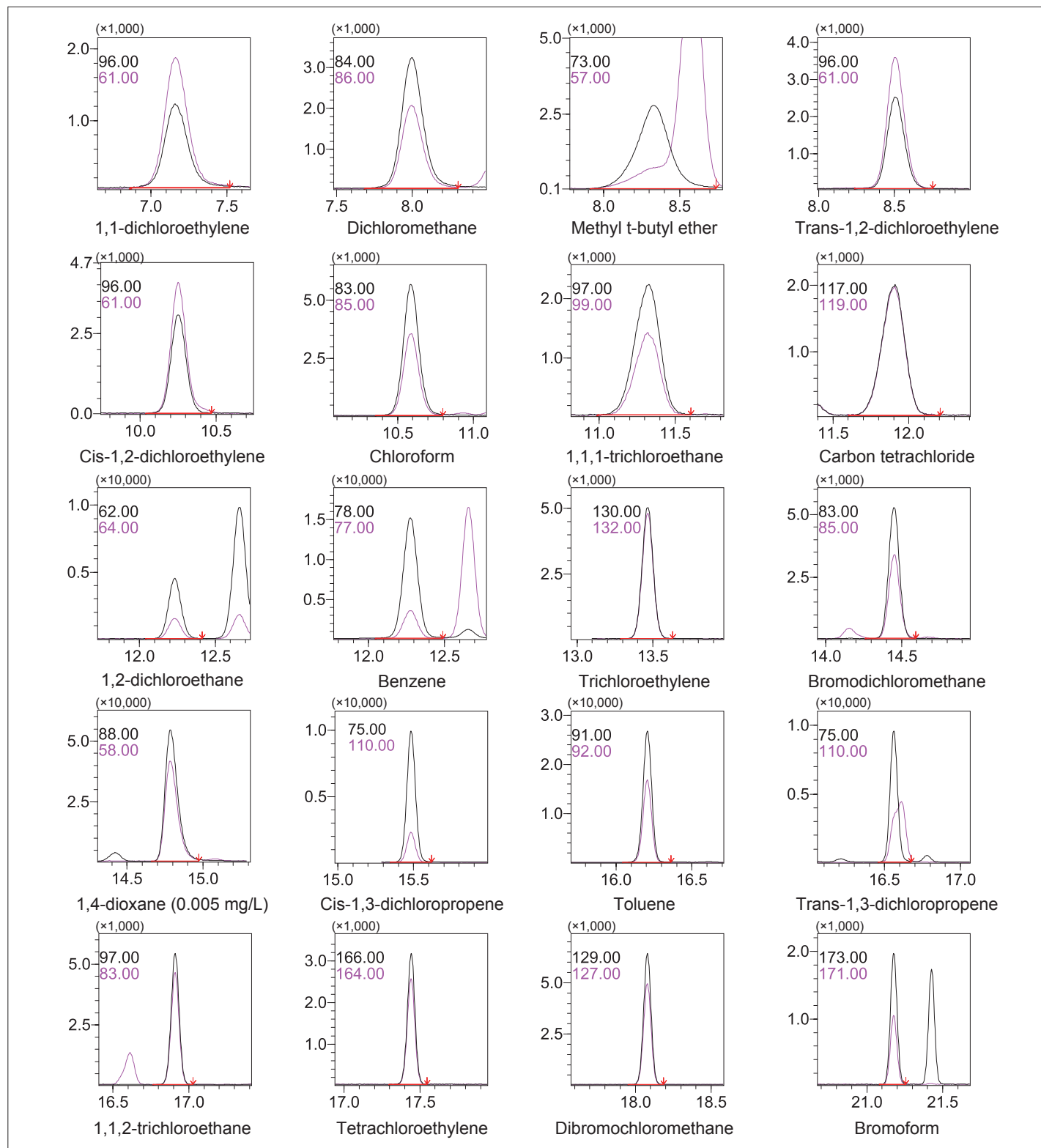


Fig. 19 SIM Chromatograms (0.0001 mg/L, except for 1,4-dioxane at 0.005 mg/L)

Table 16 shows the repeatability accuracy obtained from repeat analysis of 0.0001 mg/L standard samples. Acceptable repeatability may not be obtained for 1,4-dioxane depending on the instrumental conditions.

At 1/10 the specified concentration for 1,4-dioxane, however, it should not be a problem obtaining acceptable repeatability.

**Table 16 Repeatability (0.0001 mg/L)**

	IS Group	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
1,1-dichloroethylene	1	0.00209	0.00219	0.00209	0.00196	0.00182	7.03
Dichloromethane	1	0.00525	0.00543	0.00512	0.00486	0.00465	6.15
Methyl t-butyl ether	1	0.00685	0.00711	0.00674	0.00651	0.00627	4.82
Trans-1,2-dichloroethylene	1	0.00329	0.00341	0.00324	0.00320	0.00312	3.29
Cis-1,2-dichloroethylene	1	0.00355	0.00364	0.00348	0.00345	0.00335	3.11
Chloroform	1	0.00671	0.00696	0.00658	0.00658	0.00640	3.08
1,1,1-trichloroethane	1	0.00417	0.00428	0.00408	0.00404	0.00391	3.44
Carbon tetrachloride	1	0.00352	0.00356	0.00340	0.00332	0.00323	4.04
1,2-dichloroethane	1	0.00438	0.00453	0.00431	0.00427	0.00418	3.01
Benzene	1	0.01660	0.01726	0.01646	0.01646	0.01599	2.75
Fluorobenzene	1	-	-	-	-	-	-
Trichloroethylene	1	0.00428	0.00445	0.00422	0.00419	0.00409	3.22
1,2-dichloropropane	1	0.00400	0.00408	0.00396	0.00386	0.00377	3.06
Bromodichloromethane	1	0.00439	0.00453	0.00429	0.00428	0.00416	3.15
1,4-dioxane-d8	2	-	-	-	-	-	-
1,4-dioxane	2	0.04640	0.04442	0.04183	0.04665	0.04619	4.50
Cis-1,3-dichloropropene	1	0.00661	0.00681	0.00652	0.00642	0.00620	3.47
Toluene	1	0.01797	0.01866	0.01780	0.01773	0.01721	2.93
Trans-1,3-dichloropropene	1	0.00557	0.00574	0.00547	0.00534	0.00517	4.00
1,1,2-trichloroethane	1	0.00337	0.00346	0.00333	0.00330	0.00320	2.89
Tetrachloroethylene	1	0.00185	0.00190	0.00180	0.00179	0.00172	3.83
Dibromochloromethane	3	0.02470	0.02635	0.02475	0.02481	0.02419	3.27
m.p.-xylene	3	0.09776	0.10588	0.09859	0.09921	0.09716	3.54
o-xylene	3	0.04485	0.04848	0.04540	0.04545	0.04448	3.47
Bromoform	3	0.00664	0.00711	0.00661	0.00667	0.00646	3.65
4-bromofluorobenzene	3	-	-	-	-	-	-
1,4-dichlorobenzene	3	0.04961	0.05291	0.04909	0.04911	0.04783	3.84

## 2-7-2 Headspace-GC/MS Method

### 2-7-2-1 Analytical Conditions

Table 17 shows the analytical conditions for the headspace and GC/MS.

**Table 17 Analytical Conditions**

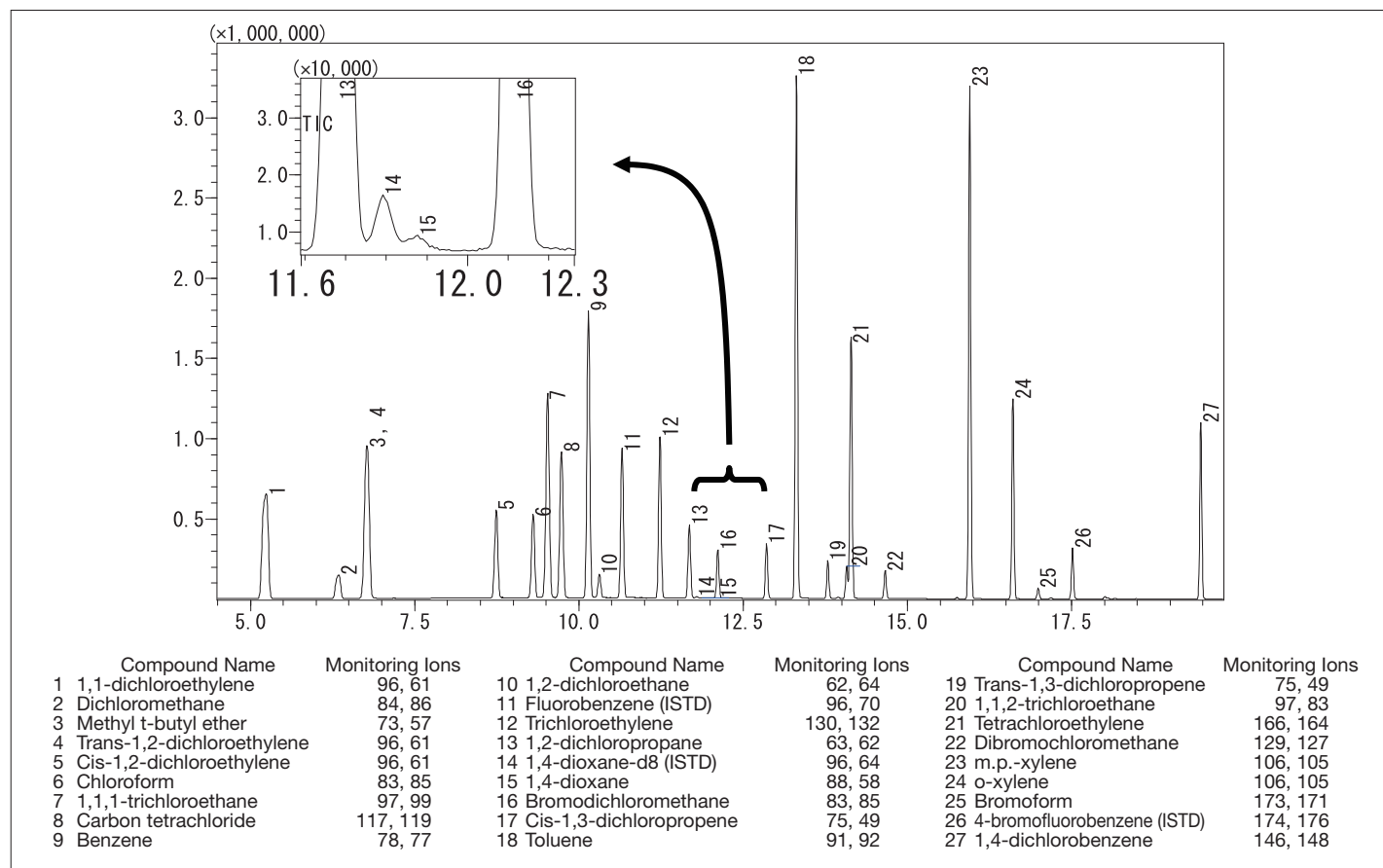
Analytical instrument : GCMS-QP2010 Plus / TurboMatrix HS		
Column : Rtx-624 (60 m × 0.32 mm I.D., df = 1.8 µm) Restek		
Headspace		
Sample vol.	: 15 mL + 4.5 g NaCl	Pressurization time : 1 min
Aspiration time	: 0 min	Oven temp. : 70 °C
Needle temp.	: 100 °C	HS carrier gas pressure : 150 kPa
Vial septum	: Butyl / PTFE <sup>(*)</sup>	Vial venting : OFF
Injection port temp. : 200 °C		
Column oven temp. <sup>(*)</sup> : 35 °C (5 min) - (10 °C/min) - 230 °C (5 min)		
Injection time : 0.2 min		
Heating time : 30 min		
Transfer temp. : 150 °C		
Ion source temp. : 200 °C		
Interface temp. : 230 °C		
Ionization mode : EI		
Ionization current : 60 µA		
Start m/z-end m/z : m/z 35-280		
Monitoring ion : See Fig. 20.		

\*1) Conditioning might be necessary for the blank.

\*2) It may be necessary to set the initial temperature to 40 °C, depending upon the ambient temperature.

### 2-7-2-2 Results

Fig. 20 shows the total ion chromatogram obtained from analysis of the standard sample.



**Fig. 20 Total Ion Chromatogram**



Fig. 21 shows the SIM chromatograms of the restricted standard items obtained from measurement of 0.0001 mg/L

L standard samples (1,4-dioxane, 0.005 mg/L).

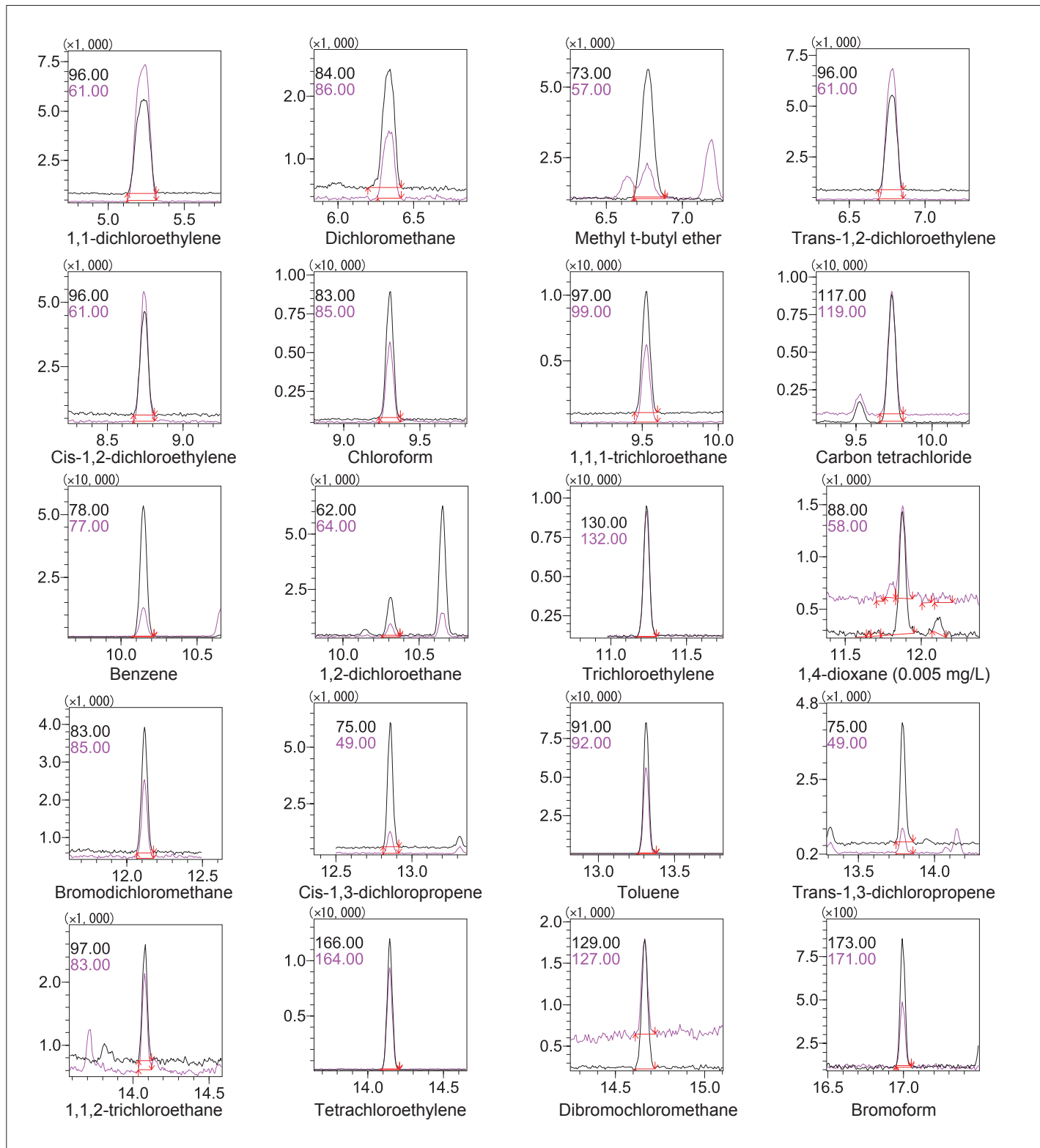


Fig. 21 SIM Chromatograms (0.0001 mg/L, except for 1,4-dioxane at 0.005 mg/L)

Table 18 shows the repeatability accuracy obtained from repeat analysis of 0.0001 mg/L standard samples. The

concentration of 1,4-dioxane was 0.005 mg/L.

**Table 18 Repeatability (0.0001 mg/L, except for 1,4-dioxane at 0.005 mg/L)**

	IS Group	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
1,1-dichloroethylene	1	0.0155	0.0157	0.0158	0.0155	0.0160	1.31
Dichloromethane	1	0.0051	0.0051	0.0051	0.0050	0.0049	1.70
Methyl t-butyl ether	1	0.0126	0.0128	0.0129	0.0136	0.0132	2.95
Trans-1,2-dichloroethylene	1	0.0117	0.0119	0.0120	0.0120	0.0121	1.29
Cis-1,2-dichloroethylene	1	0.0076	0.0075	0.0078	0.0074	0.0075	2.06
Chloroform	1	0.0139	0.0144	0.0139	0.0139	0.0139	1.53
1,1,1-trichloroethane	1	0.0170	0.0179	0.0175	0.0172	0.0177	2.12
Carbon tetrachloride	1	0.0152	0.0159	0.0156	0.0154	0.0156	1.73
Benzene	1	0.0837	0.0811	0.0816	0.0806	0.0834	1.68
1,2-dichloroethane	1	0.0027	0.0026	0.0027	0.0027	0.0027	1.31
Fluorobenzene (ISTD)	1	-	-	-	-	-	-
Trichloroethylene	1	0.0120	0.0121	0.0119	0.0117	0.0119	1.40
1,2-dichloropropane	1	0.0057	0.0058	0.0059	0.0058	0.0058	1.31
Bromodichloromethane	1	0.0046	0.0045	0.0046	0.0046	0.0044	2.04
Cis-1,3-dichloropropene	1	0.0069	0.0067	0.0069	0.0069	0.0067	1.51
Toluene	1	0.1075	0.1042	0.1041	0.1035	0.1078	1.96
Trans-1,3-dichloropropene	1	0.0044	0.0044	0.0045	0.0044	0.0043	1.43
1,1,2-trichloroethane	1	0.0022	0.0021	0.0022	0.0022	0.0022	1.67
Tetrachloroethylene	1	0.0149	0.0148	0.0151	0.0148	0.0150	0.94
Dibromochloromethane	3	0.0114	0.0109	0.0109	0.0110	0.0109	2.06
m.p.-xylene	3	0.4109	0.4050	0.3915	0.3896	0.4009	2.26
o-xylene	3	0.1515	0.1507	0.1448	0.1456	0.1485	2.02
Bromoform	3	0.0050	0.0051	0.0055	0.0052	0.0053	3.30
4-bromofluorobenzene (ISTD)	3	-	-	-	-	-	-
1,4-dichlorobenzene	3	0.080494	0.078151	0.07807	0.078726	0.077725	1.40

0.005 mg/L

	ISTD	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
1,4-dioxane-d8 (ISTD)	2	-	-	-	-	-	-
1,4-dioxane	2	0.31946	0.324768	0.319279	0.31674	0.307274	2.02

## 2-8 Haloacetic Acids

For haloacetic acids in tap water, the three components shown in Table 19 are restricted as water quality standard items. Haloacetic acids are analyzed using the solvent

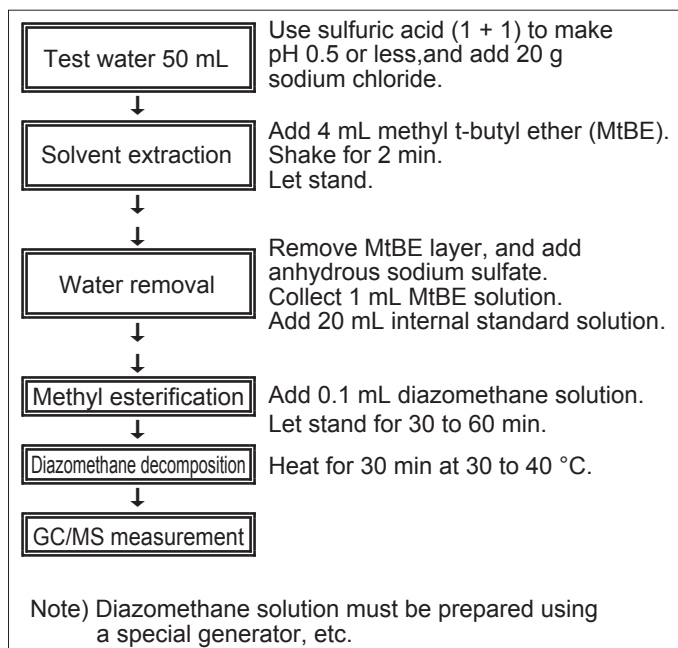
extraction-derivatization-GC/MS method. In this Application Note, we introduce analysis examples using this measurement method.

**Table 19 Water Quality Standard Items**

Item		Standard
Chloroacetic acid	Standard Item	0.02 mg/L
Dichloroacetic acid		0.04 mg/L
Trichloroacetic acid		0.2 mg/L

### 2-8-1 Pretreatment and Analytical Conditions

Fig. 22 shows the pretreatment flow chart for haloacetic acids, and Table 20 shows the analytical conditions for GC/MS.



**Fig. 22 Pretreatment Procedure for Haloacetic Acids**

**Table 20 Analytical Conditions for Haloacetic Acids**

Analytical instrument	: GCMS-QP2010 Plus		
Column	: Rtx-5MS (30 m × 0.25 mm I.D., df = 1.0 μm) Restek		
-GC-			
Injection port temp.	: 230 °C	Injection vol.	: 1 μL
Injection mode	: Splitless	Sampling time	: 1 min
Oven temp.	: 35 °C (5 min) <sup>*)</sup> → (10 °C/min) → 230 °C (3 min)		
Carrier gas	: Helium		
Control mode	: Constant linear velocity (48.6 cm/sec)		
-MS-			
Interface temp.	: 230 °C	Ion source temp.	: 200 °C
Ionization mode	: EI	Ionization current	: 150 μA
-Scan mode-			
Event time	: 0.5 sec		
Start <i>m/z</i> -end <i>m/z</i>	: <i>m/z</i> 50-200		
-SIM mode-			
Event time	: 0.2 sec		
Monitoring ions:			
Chloroacetic acid	: <i>m/z</i> 108, 77	Dichloroacetic acid	: <i>m/z</i> 83, 85
Trichloroacetic acid	: <i>m/z</i> 117, 119		
1,2,3-trichloropropane	: <i>m/z</i> 110, 75		

\*1) It may be necessary to set the initial temperature to 40 °C, depending upon the ambient temperature.

## 2-8-2 Results

Fig. 23 shows the total ion chromatogram.

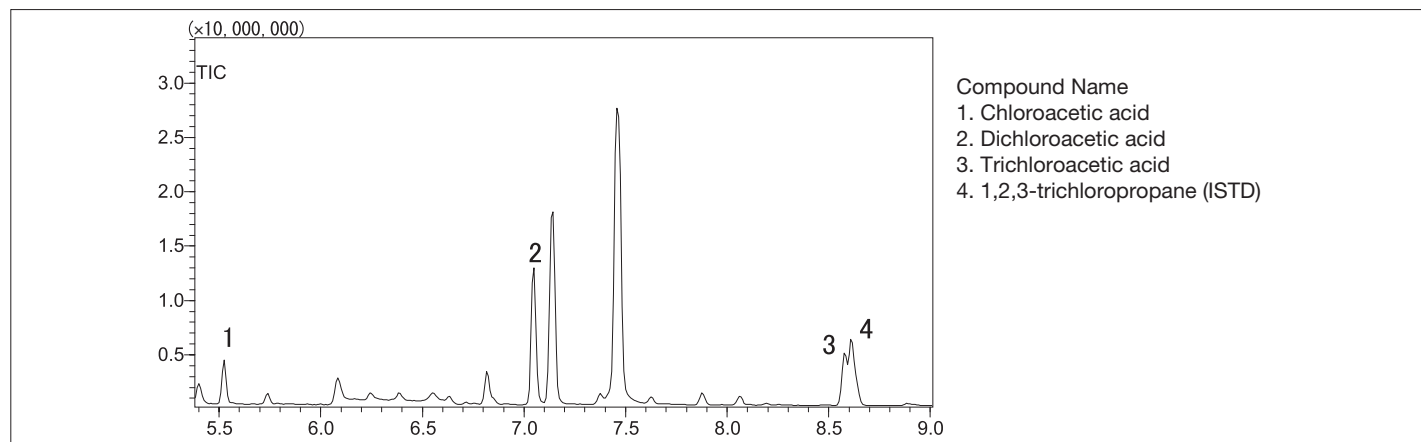


Fig. 23 Total Ion Chromatogram

Fig. 24 shows SIM chromatograms of standard samples (chloroacetic acid and dichloroacetic acid: 0.0018 mg/L, trichloroacetic acid: 0.0006 mg/L, respectively converted to

concentration in water). Table 21 shows the repeatability of five consecutive measurements of this sample.

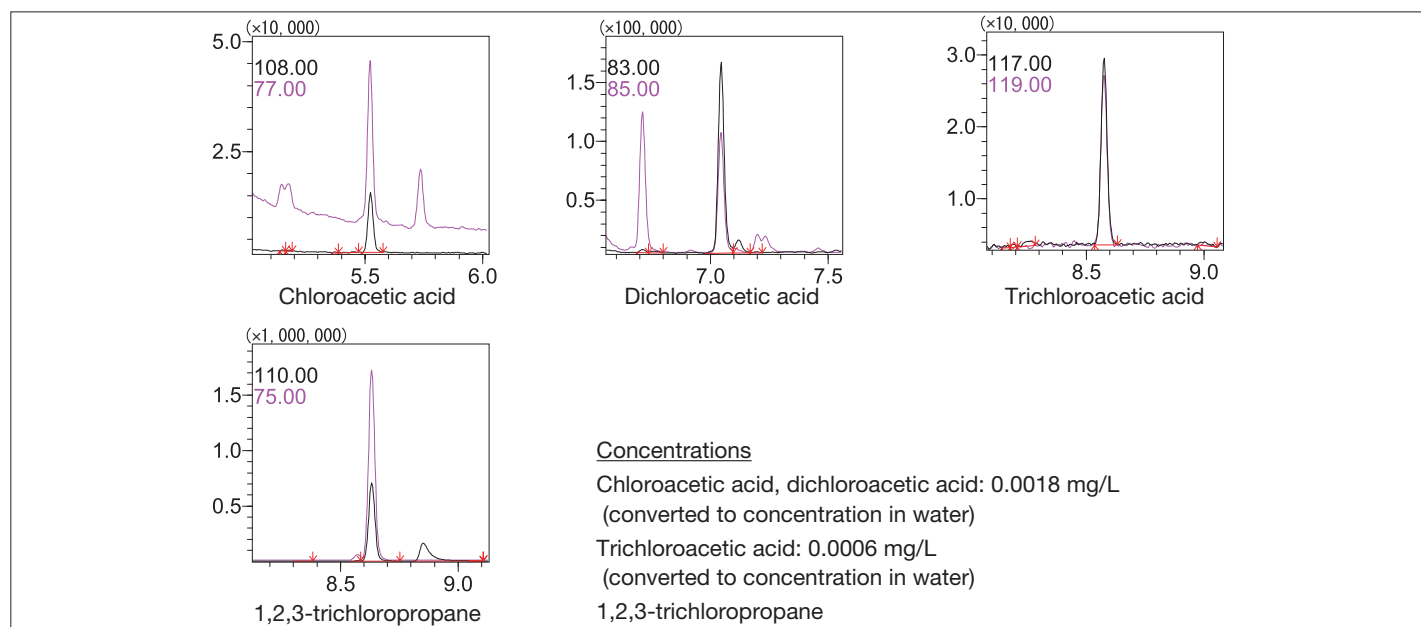


Fig. 24 SIM Chromatograms

Table 21 Repeatability

Compound Name (Concentration in Water)	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
Chloroacetic acid (0.0018 mg/L)	0.01607	0.016283	0.016615	0.015616	0.016395	2.34
Dichloroacetic acid (0.0018 mg/L)	0.220397	0.215898	0.219021	0.216379	0.224642	1.61
Trichloroacetic acid (0.0006 mg/L)	0.035835	0.037137	0.03473	0.035689	0.0362	2.43
1,2,3-trichloropropane	1	1	1	1	1	-

## 2-9 Formaldehyde

Formaldehyde in tap water is restricted as a water quality standard item. The standard value is 0.08 mg/L. The formaldehydes are analyzed using the solvent extraction-

derivatization-GC/MS method. In this Application Note, we introduce analysis examples using this measurement method.

### 2-9-1 Pretreatment and Analytical Conditions

Fig. 25 shows the flow chart for pretreatment of formaldehyde, and Table 22 shows the analytical conditions for GC/MS.

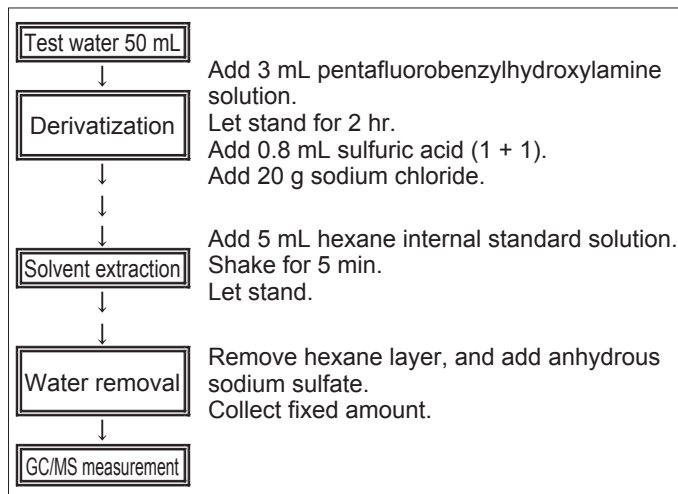


Fig. 25 Pretreatment Procedure for Formaldehyde

Table 22 Analytical Conditions for Formaldehyde

Analytical instrument	: GCMS-QP2010 Plus
Column	: Rtx-5MS (30 m L. × 0.25 mm I.D., df = 1.0 μm) Restek
-GC-	
Injection port temp.	: 250 °C
Injection vol.	: 1 μL
Injection mode	: Splitless
Sampling time	: 1 min
Oven temp.	: 40 °C (2 min) → (10 °C/min) → 250 °C (3 min)
Carrier gas	: Helium
Control mode	: Constant linear velocity (47.6 cm/sec)
-MS-	
Interface temp.	: 250 °C
Ion source temp.	: 200 °C
Ionization mode	: EI
Ionization current	: 150 μA
-Scan Mode-	
Event time	: 0.5 sec
Start m/z-end m/z	: m/z 45-250

### 2-9-2 Results

Fig. 26 shows the total ion chromatogram, Fig. 27 shows the mass chromatogram, and Table 23 shows the

repeatability in analysis of a standard sample (0.001 mg/L, converted to concentration in water).

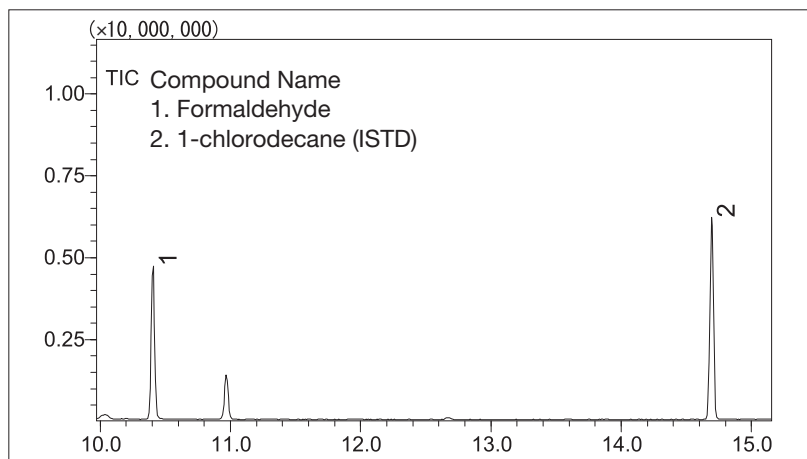


Fig. 26 Total Ion Chromatogram

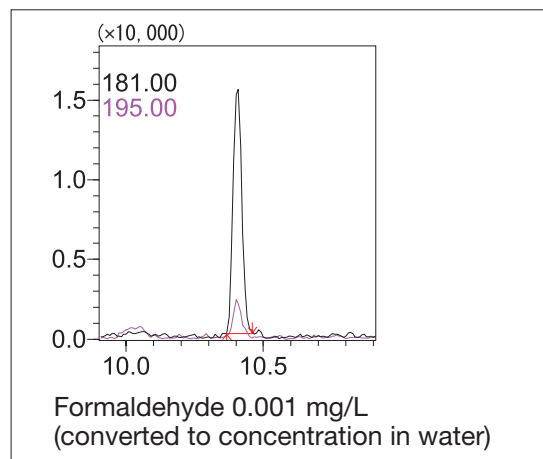


Fig. 27 Mass Chromatogram

Table 23 Repeatability

	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
Formaldehyde	0.012672	0.013101	0.012099	0.012058	0.012561	3.47
1-chlorodecane	1	1	1	1	1	-

## 2-10 Methylisoborneol and Geosmin

Musty odor substances (2-methylisoborneol and geosmin) are restricted as water quality standard items (standard value: 0.00001 mg/L).

Three analytical methods are specified for measurement of 2-methylisoborneol and geosmin: solid-phase extraction-GC/MS, purge and trap-GC/MS and headspace-GC/MS. In this Application Note, we introduce analysis examples using the purge and trap-GC/MS and headspace-GC/MS

methods. The standard values for 2-methylisoborneol and geosmin are low. Therefore, it is important to separate these two from their impurities when conducting measurement.

As there are cases where separation is difficult under the analytical conditions introduced below, the column type and oven temperature must be selected according to the separation conditions.

### 2-10-1 Purge and Trap-GC/MS Method

#### 2-10-1-1 Analytical Conditions

Table 24 shows the analytical conditions using the purge and trap, and GC/MS.

**Table 24 Analytical Conditions**

Analytical instrument : GCMS-QP2010 Plus / AQUA PT 5000J Plus + AQUAauto70			
Column : InertCap 1 (30 m L. × 0.32 mm I.D., df = 0.4 μm) GL Science			
-Purge and Trap-			
Sample vol.	: 20 mL <sup>*1)</sup>	Trap tube	: GL Trap 1
Transfer line temp.	: 150 °C	Sample mount temp.	: 60 ° C
Sample heater	: OFF	Purge time	: 12 min
Dry purge time	: 3 min	Dry purge flow rate	: 40 mL/min
Desorb temp.	: 220 °C	Desorb flow rate	: 300 mL/min
Bake temp.	: 230 °C	Bake flow rate	: 80 mL/min
-GC-			
Injection port temp.	: 200 °C	Carrier gas P&T	: Helium (120 kPa)
Oven temp. <sup>*2)</sup>	: 35 °C (6 min) → (10 °C/min) → 220 °C (3 min)		
-MS-			
Ion source temp.	: 200 °C	Ionization mode	: EI
Interface temp.	: 220 °C	Ionization current	: 150 μA
-Scan Mode-			
Event time	: 0.5 sec	Start <i>m/z</i> -end <i>m/z</i>	: <i>m/z</i> 50-200
-SIM Mode-			
Event time	: 0.2 sec		
Monitoring ions:			
2-methylisoborneol : <i>m/z</i> 95, 107, 135		Geosmin : <i>m/z</i> 112, 111, 125	

\*1) The addition of sodium chloride (salting) is obligatory according the Water Supply Act. Although salting is not used in this Application Note, it is by no means a recommendation that salting not be conducted.

\*2) It may be necessary to set the initial temperature to 40 °C, depending upon the ambient temperature.

## 2-10-1-2 Results

Fig. 28 shows the total ion chromatogram and mass chromatogram of the standard sample (2-methylisoborneol:  $m/z$  95, geosmin:  $m/z$  112). Fig. 29 shows the SIM

chromatograms of the standard sample (0.000001 mg/L), and Table 25 shows the repeatability.

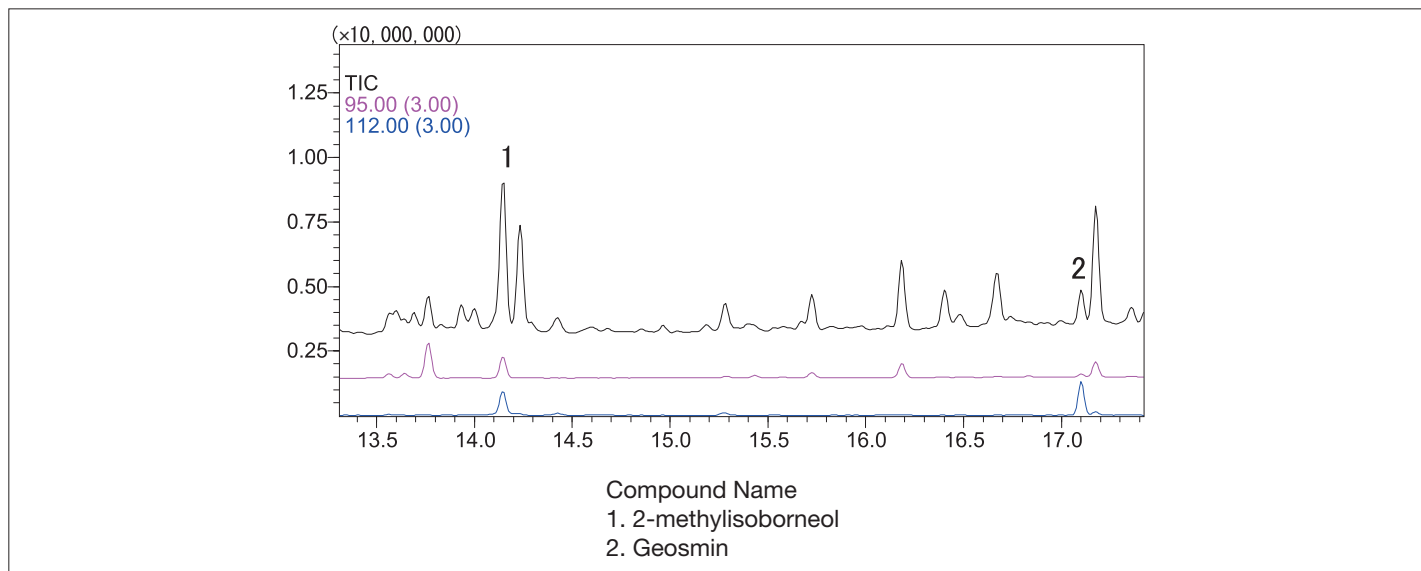


Fig. 28 Total Ion Chromatogram and Mass Chromatogram

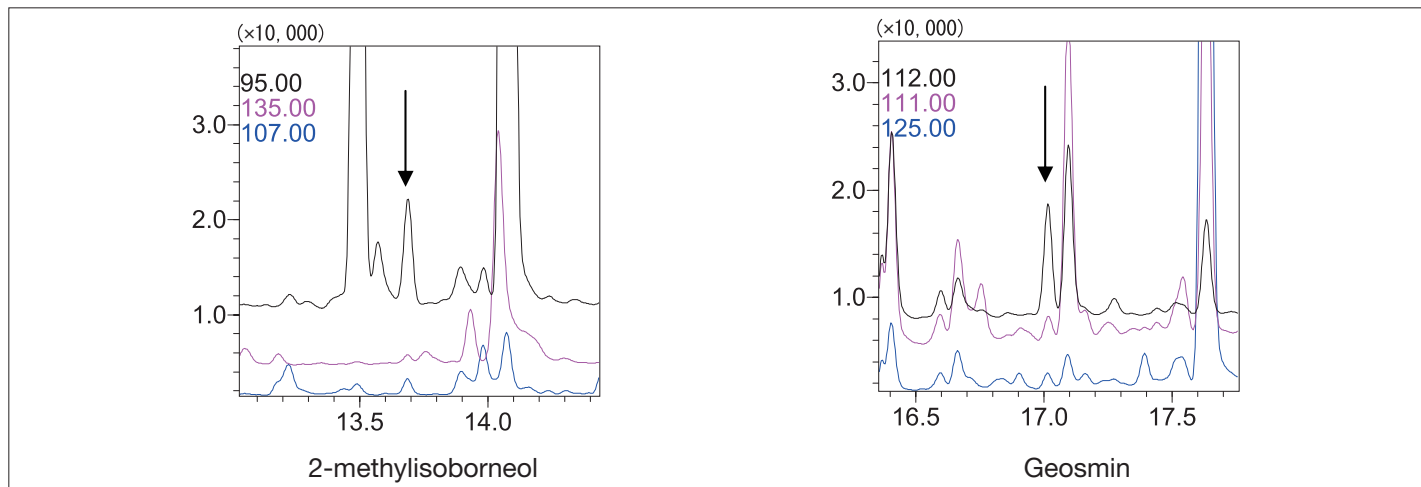


Fig. 29 SIM Chromatograms (0.000001 mg/L)

Table 25 Repeatability (0.000001 mg/L, n = 5)

	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
2-methylisoborneol	26489	27738	28093	27464	28448	2.70
Geosmin	22324	20201	22105	22402	22390	4.33



## 2-10-2 Headspace-GC/MS Method

### 2-10-2-1 Analytical Conditions

Table 26 shows the analytical conditions for the headspace and GC/MS.

**Table 26 Analytical Conditions**

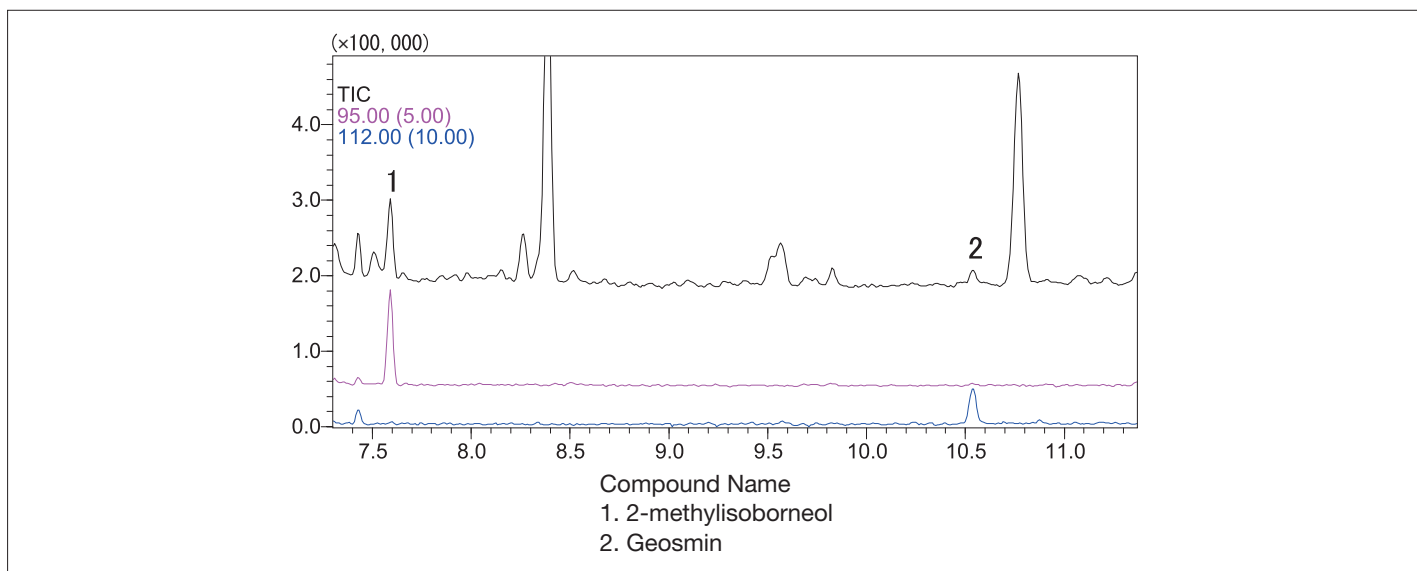
Analytical instrument	: GCMS-QP2010 Plus / TurboMatrix HS with PPC and Vial Shaker (Option)		
Column	: Rtx-5MS (30 m L. × 0.25 mm I.D., df = 1.0 μm) Restek		
-Headspace-			
Sample vol.	: 10 mL + 3.5 g NaCl		
Pressurization time	: 1 min	Injection time	: 1 min
Oven temp.	: 80 °C	Heating time	: 30 min
HS carrier gas pressure	: 120 kPa	Transfer temp.	: 180 °C
Vial venting	: OFF	Sample shaker	: ON
-GC-			
Injection port temp.	: 200 °C		
Column oven temp.*1)	: 35 °C (1 min) → (30 °C/min) → 170 °C → (5 °C/min) → 230 °C (5 min)		
-MS-			
Ion source temp.	: 200 °C	Ionization mode	: EI
Interface temp.	: 220 °C	Ionization current	: 150 μA
-Scan Mode-			
Event time	: 0.5 sec	Start <i>m/z</i> -end <i>m/z</i> : <i>m/z</i> 50-200	
-SIM Mode-			
Event time	: 0.2 sec		
Monitoring ions:			
2-methylisoborneol	: <i>m/z</i> 95, 107, 135	Geosmin	: <i>m/z</i> 112, 111, 125
*1) It may be necessary to set the initial temperature to 40 °C, depending upon the ambient temperature.			

\*1) It may be necessary to set the initial temperature to 40 °C, depending upon the ambient temperature.

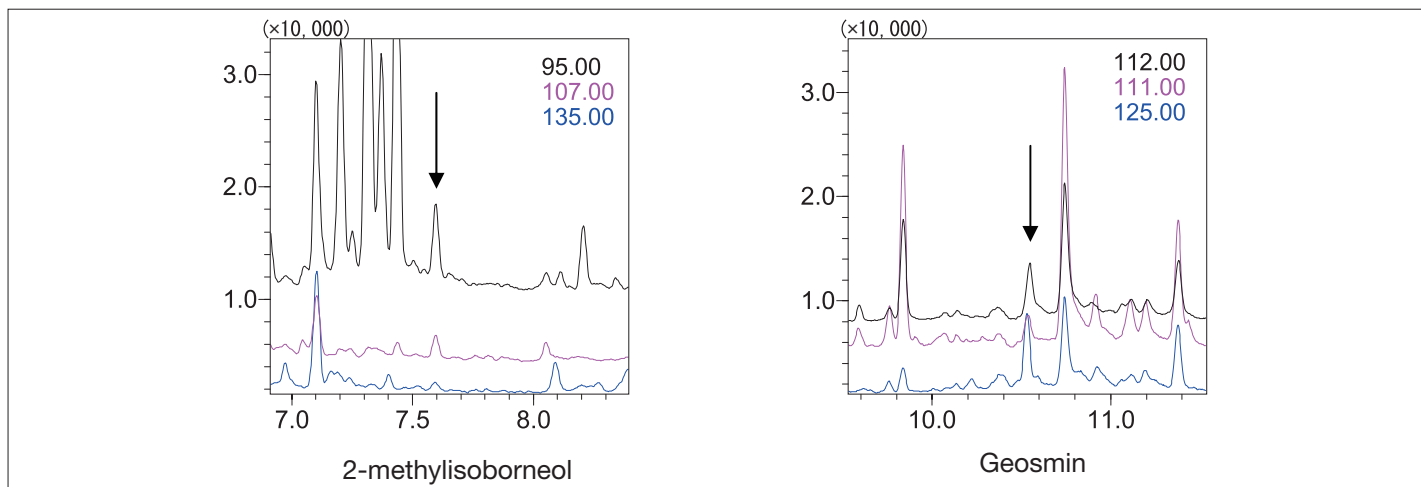
### 2-10-2-2 Results

Fig. 30 shows the total ion chromatogram and mass chromatogram of the standard sample (2-methylisoborneol: *m/z* 95, geosmin: *m/z* 112). Fig. 31 shows the SIM

chromatograms of the standard sample (0.000001 mg/L), and Table 27 shows the repeatability obtained in analysis with a concentration of 0.000001 mg/L.



**Fig. 30 Total Ion Chromatogram and Mass Chromatogram**



**Fig. 31 SIM Chromatograms (0.000001 mg/L)**

**Table 27 Repeatability (0.000001 mg/L, n = 5)**

	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
2-methylisoborneol	10883	11304	10499	11185	11141	2.91
Geosmin	11043	11577	11262	11191	11463	1.89

## 2-11 Phenols

Table 28 shows the six target phenol compounds in tap water. The phenols are analyzed using the solid-phase extraction-derivatization-GC/MS method. In this

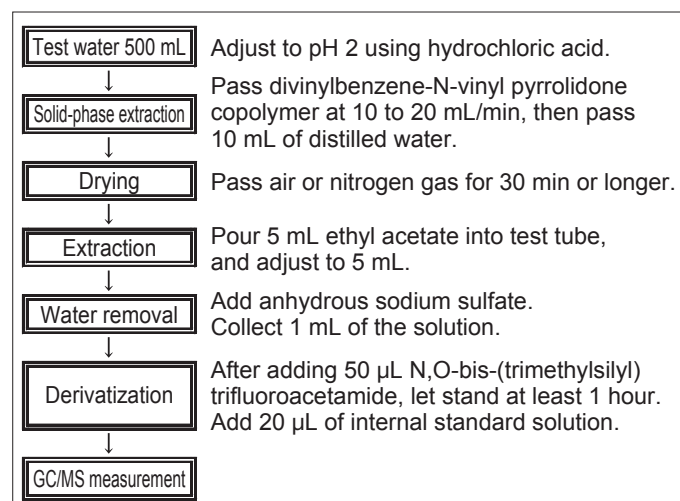
Application Note, we introduce analysis examples using this measurement method.

**Table 28 Water Quality Standard Items**

Item	Standard
Phenol	0.005 mg/L by phenol conversion calculation
2-chlorophenol	
4-chlorophenol	
2,6-dichlorophenol	
2,4-dichlorophenol	
2,4,6-trichlorophenol	

### 2-11-1 Pretreatment and Analytical Conditions

Fig. 32 shows the pretreatment flow chart for phenols, and Table 29 shows the analytical conditions for GC/MS.



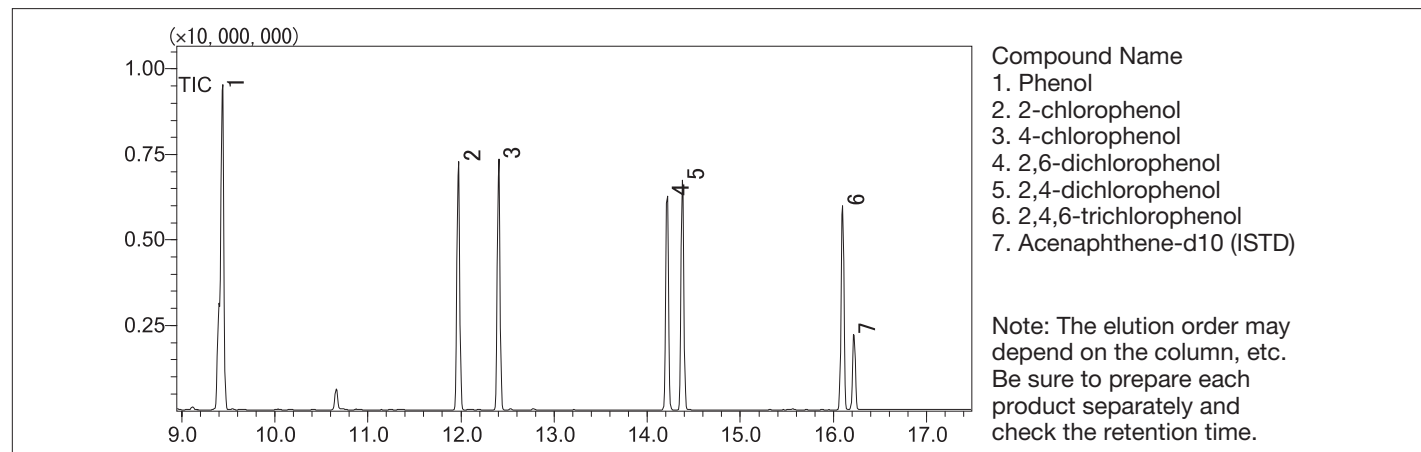
**Fig. 32 Pretreatment Procedure for Phenols**

**Table 29 Analytical Conditions for Phenols**

Analytical instrument	: GCMS-QP2010 Plus
Column	: Rtx-5MS (30 m L. × 0.25 mm I.D., df = 1.0 µm) Restek
-GC-	
Injection port temp.	: 250 °C
Injection vol.	: 1 µL
Injection mode	: Splitless
Sampling time	: 1 min
Oven temp.	: 50 °C (1 min) → (10 °C/min) → 250 °C (3 min)
Carrier gas	: Helium
Control mode	: Constant linear velocity (46.6 cm/sec)
-MS-	
Interface temp.	: 250 °C
Ion source temp.	: 200 °C
Ionization mode	: EI
Ionization current	: 150 µA
-Scan Mode-	
Event time	: 0.5 sec
Start m/z-end m/z	: m/z 60-300

### 2-11-2 Results

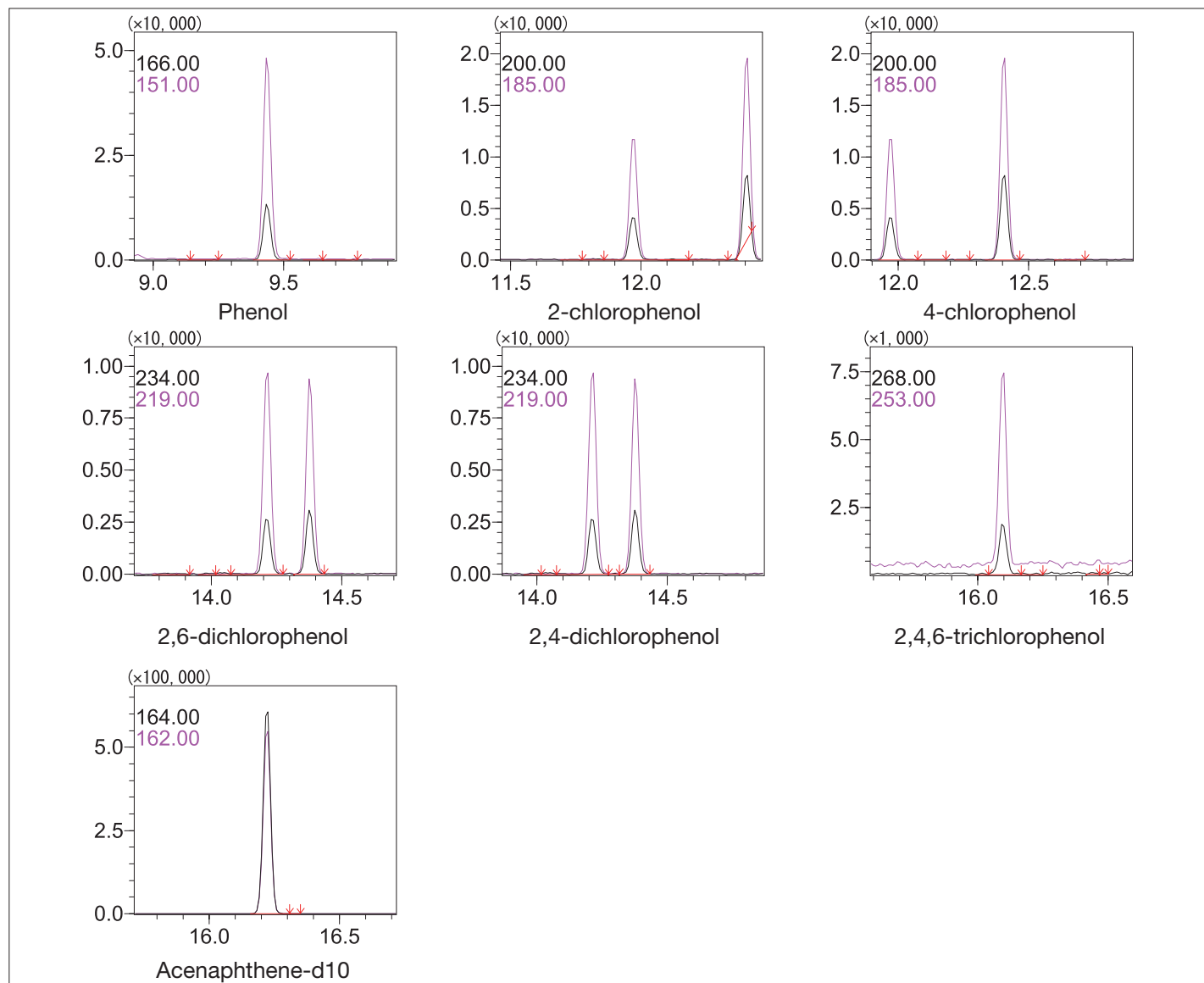
Fig. 33 shows the total ion chromatogram.



**Fig. 33 Total Ion Chromatogram for Phenols**

Fig. 34 shows the mass chromatogram obtained from analysis of a 0.05 mg/L standard sample (0.0005 mg/L, converted to concentration in water). Table 30 shows the

repeatability obtained in five consecutive measurements of this sample.



**Fig. 34 Mass Chromatograms (0.05 mg/L: Converted to concentration in water – 0.0005 mg/L)**

**Table 30 Repeatability (0.0001 mg/L)**

	Area Ratio 1	Area Ratio 2	Area Ratio 3	Area Ratio 4	Area Ratio 5	CV Value (%)
Phenol	0.021718	0.022297	0.021617	0.022024	0.022094	1.27
2-chlorophenol	0.007015	0.006976	0.006674	0.006951	0.006858	1.98
4-chlorophenol	0.013490	0.013586	0.012648	0.012716	0.012692	3.6
2,6-dichlorophenol	0.004454	0.004376	0.004491	0.004589	0.004196	3.34
2,4-dichlorophenol	0.005000	0.005075	0.005150	0.005400	0.005033	3.12
2,4,6-trichlorophenol	0.003208	0.003459	0.003282	0.003145	0.003399	3.96
Acenaphthene-d10	1	1	1	1	1	-

## 2-12 Nonionic Surfactants

Nonionic surfactants are one of several new water quality standard items in revisions to the Water Supply Act. Solid-phase extraction-absorption spectroscopy is prescribed

as the official method for water quality test of nonionic surfactants. Here we measure nonionic surfactants in water using the UV-VIS spectrophotometer.

### 2-12-1 Pretreatment Procedure by Solid-Phase Extraction

Solid-phase extraction-absorption spectrophotometry is prescribed as the method (Method established by the Japanese Minister of Health, Labour and Welfare Based on Regulations of Ministerial Ordinance Concerning Water Quality Standards (Ministry of Health, Labour and Welfare Notification No. 261, July 22, 2003)) for analyzing nonionic surfactants, and solid-phase extraction is used as the pretreatment technique. Solid-phase extraction is an extremely common pretreatment method that is used before liquid chromatography or GC/MS. It is used to remove interfering components and to concentrate components present at low concentrations.

To analyze the nonionic surfactant, solid-phase extraction was conducted using a commercial solid-phase column that has an octadecyl group chemically bonded to silica gel.

Fig. 35 shows the pretreatment procedure for solid-phase extraction in the analysis of nonionic surfactants. The first step in analyzing nonionic surfactants using solid-phase extraction is to perform column conditioning by injecting methanol and purified water into the solid-phase column.

Next, a water sample is passed through the solid-phase column, and purified water is added. The water is removed from the solid-phase column. Upon removal of the water, the nonionic surfactant is extracted from the solid-phase column using toluene. The extracted material is then used as the test solution for analysis.

- (1) Inject 5 mL methanol and 5 mL purified water.  
↓
- (2) Pass 1000 mL of test water (containing 0.005 to 0.04 mg/L nonionic surfactant, adjusted to pH 9 with sodium hydroxide solution (4 w/v %)) through the solid-phase column at a flowrate of 10 to 20 mL per minute.  
↓
- (3) Pass 10 mL of purified water through the solid-phase column.  
↓
- (4) Remove the water from the solid-phase column (vacuum or nitrogen gas purge).  
↓
- (5) Pass toluene slowly through the solid-phase column in the reverse direction of the water flow. Collect exactly 5 mL of toluene in a 10 mL centrifuge tube with a stopper, and use this as the sample solution.

Note: Refer to the details outlined in the "Method established by the Japanese Minister of Health, Labour and Welfare Based on Regulations of Ministerial Ordinance Concerning Water Quality Standard (Ministry of Health, Labour and Welfare Notification No. 261, July 22, 2003)"

**Fig. 35 Pretreatment Procedure**

## 2-12-2 Analysis of Nonionic Surfactants in Water and Results

Analysis of nonionic surfactants in the test solution extracted from the solid-phase column is conducted based on the procedure of Fig. 36.

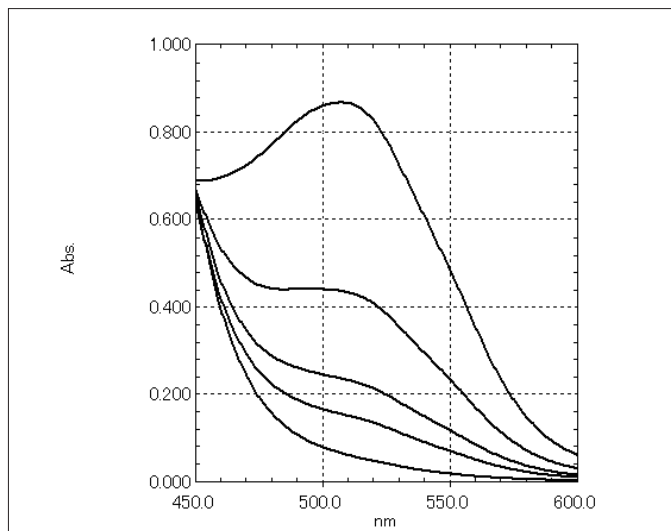
It is first necessary to prepare the standard samples to be used for generating the calibration curve. Transfer staged volumes of the nonionic surfactant standard solution into volumetric flasks, and then add 1000 mL of distilled water to each flask, respectively (0.005 to 0.04 mg/L).

These standard samples are used to generate a calibration curve by solid-phase extraction and analysis using the same solid-phase column as that used for the actual sample. Fig. 37 shows the spectral profiles of the standard samples. Fig. 38 shows the calibration curve of nonionic surfactants and the results of analysis of nonionic surfactants in tap water.

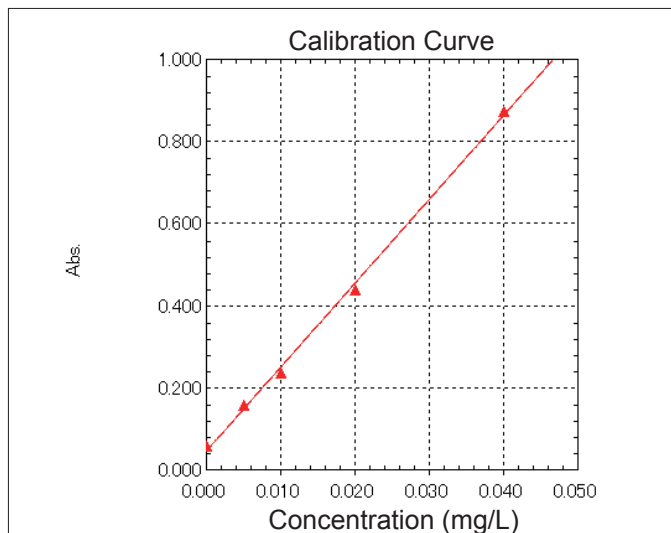
- (1) Add 2.5 mL ammonium thiocyanate cobalt (II) solution and 1.5 g potassium chloride to 5 mL of the test solution and shake for 5 min to mix.
- ↓
- (2) Centrifuge at 2,500 rpm for 10 min to separate.
- ↓
- (3) Using a Pasteur pipette, transfer 4 mL of the toluene layer to a separate 10 mL centrifugal separation tube with a stopper.
- ↓
- (4) Add 1.5 mL PAR solution and gently shake for 3 min to mix.
- ↓
- (5) Centrifuge at 2,500 rpm for 10 min to separate.
- ↓
- (6) Remove the toluene layer.
- ↓
- (7) Transfer a portion of the liquid to a detector cell.
- ↓
- (8) Measure the absorbance at wavelength of 510 nm.
- ↓
- (9) Calculate the concentration of the nonionic surfactant in the test solution using the generated calibration curve.

Note: Refer to the details outlined in the "Method established by the Japanese Minister of Health, Labour and Welfare Based on Regulations of Ministerial Ordinance Concerning Water Quality Standard (Ministry of Health, Labour and Welfare Notification No. 261, July 22, 2003)"

**Fig. 36 Analysis Operations**



**Fig. 37 Absorption Spectra of Nonionic Surfactant Standard Solutions**



Calibration Curve Function  $\text{Conc.} = 0.04892 \times \text{Abs.} - 0.00225$   
Correlation Coefficient 0.99852

### Tap Water Analysis Results

Sample ID	Concentration	Absorbance
sample	0.002	0.081

**Fig. 38 Calibration Curve and Results of Analysis of Nonionic Surfactant in Tap Water**

## 2-13 Organic Substances (Total Organic Carbon Amount)

On April 1, 2009 the standard for organic substances (total organic carbon (TOC)) was strengthened from 5 mg/L to 3 mg/L. As a result, the quantitation lower limit of the TOC analyzer used in the measurements (within 10 % coefficient of variation) must be 1/10 (0.3 mg/L) of the standard value.

### 2-13-1 Analysis of TOC Samples with Quantitation Lower Limit Value Up to 0.3 mg/L

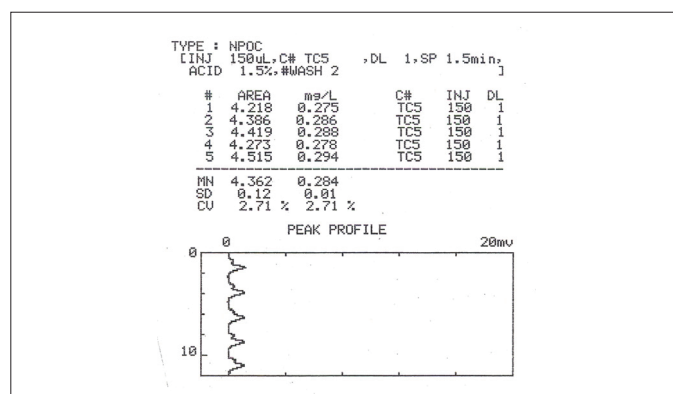
Analyses of a potassium hydrogen phthalate aqueous solution adjusted to a TOC concentration of 0.25 mg/L were conducted using the standard catalyst and the high-sensitivity catalyst, respectively. Tables 31 and 32 show the analytical conditions, and Fig. 39 and 40 show the analysis data.

Since the pure water used for preparing the sample

contained approximately 0.02 to 0.03 mgC/L TOC as impurities, the analysis results value for the 0.25 mgC/L potassium hydrogen phthalate aqueous solution (Table 33) is approximately 0.27 to 0.28 mgC/L. However, the respective coefficients of variation (CV) are within 10 %, so it is clear that quantitation of 0.3 mgC/L is possible.

**Table 31 Analytical Conditions**

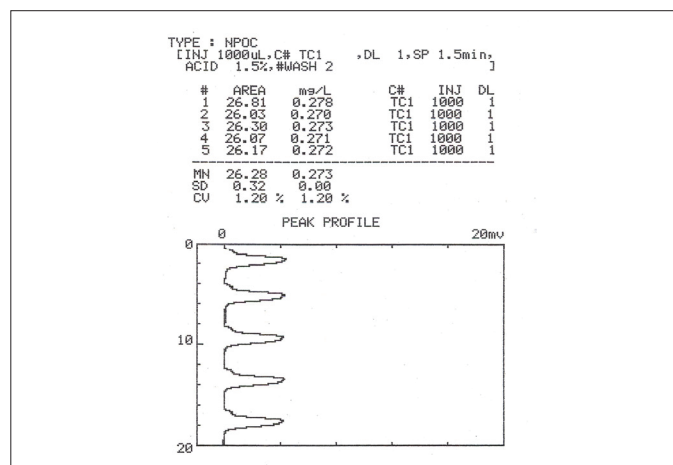
Instrument	: TOC-V <sub>CSH</sub>
Catalyst	: Standard catalyst
Injection vol.	: 150 µL
Measurement item	: TOC (TOC by acidification and sparging)
Calibration curve	: 2-point calibration curve using 0 to 3 mgC/L potassium hydrogen phthalate aqueous solution
Sample	: 0.25 mgC/L potassium hydrogen phthalate aqueous solution



**Fig. 39 Analysis Data**

**Table 32 Analytical Conditions**

Instrument	: TOC-V <sub>CSH</sub>
Catalyst	: High-sensitivity catalyst
Injection vol.	: 1000 µL
Measurement item	: TOC (TOC by acidification and sparging)
Calibration curve	: 2-point calibration curve using 0 to 3 mgC/L potassium hydrogen phthalate aqueous solution
Sample	: 0.25 mgC/L potassium hydrogen phthalate aqueous solution



**Fig. 40 Analysis Data**

**Table 33 Analytical Results**

Sample Name	Catalyst	TOC Concentration (mgC/L)	Coefficient of Variation
0.25 mgC/L potassium hydrogen phthalate aqueous solution	Standard	0.284	2.71 %
	High-sensitivity	0.273	1.20 %

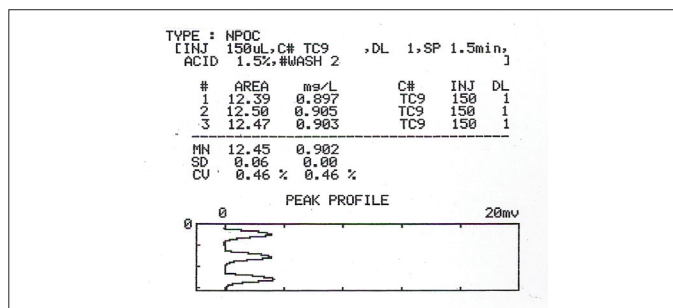
### 2-13-2 TOC Measurements of Tap Water

Shown below is an example of tap water analyzed using a standard catalyst. Table 34 shows the analytical conditions, Fig. 41 shows the analysis data, and Table 35 shows

analysis results. The TOC concentration was 0.902 mgC/L and the coefficient of variation was 0.46 %.

**Table 34 Analytical Conditions**

Instrument	: TOC-V <sub>CSH</sub>
Catalyst	: Standard catalyst
Injection vol.	: 150 µL
Measurement item	: TOC (TOC by acidification and sparging)
Calibration curve	: 2-point calibration curve using 0 to 3 mgC/L potassium hydrogen phthalate aqueous solution
Sample	: Tap water at Shimadzu Corp. Sanjo Works



**Fig. 41 Analysis Data**

**Table 35 Analytical Results**

Sample Name	TOC Concentration (mgC/L)	Coefficient of Variation
Tap water at Shimadzu Corp. Sanjo Works	0.902	0.46 %



### 3. [Reference Material] Water Quality Control Target Setting Items for Agricultural Chemicals (102 Substances)

Table 36 shows the target values of agricultural chemicals for the water quality control target items, test methods, quantitation lower limits, and the coefficients of variation.

The target values listed in the table are based on "Exhibit 2 Water Quality Testing and Measurement Accuracy of Agricultural Chemicals (Water Quality Control Target Items 15) of the "Ministry of Health, Labour and Welfare; Health Service Bureau, Water Supply Div. Ordinance No. 1010001," October 10, 2003. This Ordinance states that "as a rule, measurement of agricultural chemicals should be conducted at a concentration up to 1/100 of the target value, should be accurate and within the set criteria values listed for coefficients of variation.

The quantitation lower limit value (when adopting a

general measurement instrument and a commonly used test) should be listed in conjunction with the agricultural chemical and test methods in a table below."

The detection index value (DI) shown in the formula below should be less than one for all 102 agricultural chemicals in the water quality control target setting items. In the formula, DI is the detection index value, DVi is the detection value for agricultural chemical i, and GVi is the target value for agricultural chemical i.

$$DI = \sum_i DVi / GVi$$

The test methods for agricultural chemicals are expected to be issued in a separate Application Note.

**Table 36 Agricultural Chemicals**

No.	Agricultural Chemical	Target Value (mg/L)	Test Method	Quantitation Lower Limit	Coefficient of Variation
1	Thiuram	0.02	Solid-phase extraction-LC/MS (P)	0.0002	20 %
2	Simazine (CAT)	0.003	Solid-phase extraction-GC/MS	0.00001	20 %
3	Thiobencarb	0.02	Solid-phase extraction-GC/MS	0.00002	20 %
4	1,3-dichloropropene (D-D)	0.002	PT-GC/MS HS-GC/MS	0.0001 0.0001	20 % 20 %
5	Isoxathion	0.008	Solid-phase extraction-GC/MS	0.00001	20 %
6	Diazinon	0.005	Solid-phase extraction-GC/MS	0.00002	20 %
7	Fenitrothion (MEP)	0.003	Solid-phase extraction-GC/MS	0.00001	20 %
8	Isoprothiolane (IPT)	0.3	Solid-phase extraction-GC/MS	0.00001	20 %
9	Chlorothalonil (TPN)	0.05	Solid-phase extraction-GC/MS	0.00001	20 %
10	Propyzamide	0.05	Solid-phase extraction-GC/MS	0.00001	20 %
11	Dichlorvos (DDVP)	0.008	Solid-phase extraction-GC/MS	0.00005	20 %
12	Fenobucarb (BPMC)	0.03	Solid-phase extraction-GC/MS	0.00001	20 %
13	Chlornitrophen (CNP): outdated pesticide	0.0001	Solid-phase extraction-GC/MS	0.0001	20 %
14	CNP-amino metabolite	-	Solid-phase extraction-GC/MS	0.0001	20 %
15	Iprobenfos (IBP)	0.008	Solid-phase extraction-GC/MS	0.00005	20 %
16	EPN	0.004	Solid-phase extraction-GC/MS	0.00005	20 %
17	Bentazon: outdated herbicide	0.2	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00001 0.00005 0.000002	20 % 20 % 20 %
18	Carbofuran (metabolite of carbosulfan)	0.005	HPLC-post-column Solid-phase extraction-LC/MS (P)	0.00005 0.000005	20 % 20 %
19	2,4-dichlorophenoxyacetic acid (2,4-D)	0.03	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (N)	0.00001 0.00005	20 % 20 %
20	Trichlopyr	0.006	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (N)	0.00001 0.00002	20 % 20 %
21	Acephate	0.08	LC/MS (P)	0.0008	20 %
22	Isofenphos: outdated pesticide	0.001	Solid-phase extraction-GC/MS	0.00003	20 %
23	Chlorpyrifos	0.003	Solid-phase extraction-GC/MS	0.00005	20 %
24	Trichlorfon (DEP)	0.03	Solid-phase extraction-GC/MS	0.0002	20 %

No.	Agricultural Chemical	Target Value (mg/L)	Test Method	Quantitation Lower Limit	Coefficient of Variation
25	Pyridaphenthion: outdated pesticide	0.002	Solid-phase extraction-GC/MS	0.00005	20 %
26	Iprodione	0.3	Solid-phase extraction-GC/MS Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P)	0.00002 0.001 0.0001	20 % 20 % 20 %
27	Etridiazole (Echloomezole)	0.004	Solid-phase extraction-GC/MS	0.00001	20 %
28	Oxine copper	0.04	Solid-phase extraction-LC/MS (P) LC/MS (P)	0.00005 0.0004	20 % 20 %
29	Captan	0.3	Solid-phase extraction-GC/MS	0.0001	20 %
30	Chloroneb	0.05	Solid-phase extraction-GC/MS	0.00002	20 %
31	Tolclophos-methyl	0.2	Solid-phase extraction-GC/MS	0.00001	20 %
32	Flutolanil	0.2	Solid-phase extraction-GC/MS	0.00001	20 %
33	Pencycuron	0.04	Solid-phase extraction-GC/MS	0.0001	20 %
34	Metalaxyl	0.05	Solid-phase extraction-GC/MS	0.00005	20 %
35	Mepronil	0.1	Solid-phase extraction-GC/MS	0.00001	20 %
36	Ashram	0.2	Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.001 0.0001 0.0005	20 % 20 % 20 %
37	Dithiopyr	0.009	Solid-phase extraction-GC/MS	0.00001	20 %
38	Terbucarb (MBPMC): outdated herbicide	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
39	Napropamide	0.03	Solid-phase extraction-GC/MS	0.00001	20 %
40	Pyributicarb	0.02	Solid-phase extraction-GC/MS	0.00002	20 %
41	Butamifos	0.01	Solid-phase extraction-GC/MS	0.0001	20 %
42	Bensulide (SAP): outdated herbicide	0.1	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00001 0.00001	20 % 20 %
43	Benfluralin (Bethrodine)	0.08	Solid-phase extraction-GC/MS	0.00001	20 %
44	Pendimethalin	0.1	Solid-phase extraction-GC/MS	0.00001	20 %
45	Mecoprop (MCP)	0.005	Solid-phase extraction-derivatization-GC/MS Solid-phase extraction-LC/MS (N)	0.00005 0.00002	20 % 20 %
46	Methyldymron: outdated pesticide	0.03	Solid-phase extraction-GC/MS	0.00005	20 %
47	Alachlor	0.01	Solid-phase extraction-GC/MS	0.00002	20 %
48	Carbaryl (NAC)	0.05	Solid-phase extraction-HPLC HPLC-post column Solid-phase extraction-LC/MS (P)	0.0005 0.0001 0.00002	20 % 20 % 20 %
49	Edifenphos (EDDP)	0.006	Solid-phase extraction-GC/MS	0.00005	20 %
50	Pyroquilon	0.04	Solid-phase extraction-GC/MS	0.00001	20 %
51	Fthalide	0.1	Solid-phase extraction-GC/MS	0.00001	20 %
52	Mefenacet	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
53	Pretilachlor	0.04	Solid-phase extraction-GC/MS	0.00001	20 %
54	Isoprocab (MIPC)	0.01	Solid-phase extraction-GC/MS	0.00005	20 %
55	Thiophanate-methyl	0.3	Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P)	0.002 0.00005	20 % 20 %
56	Thenylchlor	0.2	Solid-phase extraction-GC/MS	0.00002	20 %
57	Methidathion (DMTP)	0.004	Solid-phase extraction-GC/MS	0.00001	20 %
58	Carpropamid	0.04	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00002 0.00005	20 % 20 %
59	Bromobutide	0.1	Solid-phase extraction-GC/MS	0.0001	20 %
60	Molinat	0.005	Solid-phase extraction-GC/MS	0.00001	20 %
61	Procymidone	0.09	Solid-phase extraction-GC/MS	0.0001	20 %
62	Anilofos	0.003	Solid-phase extraction-GC/MS	0.00005	20 %
63	Atrazine	0.01	Solid-phase extraction-GC/MS	0.00005	20 %
64	Dalapon	0.08	LC/MS (N)	0.001	20 %

No.	Agricultural Chemical	Target Value (mg/L)	Test Method	Quantitation Lower Limit	Coefficient of Variation
65	Dichlobenil (DBN)	0.01	Solid-phase extraction-GC/MS	0.00001	20 %
66	Dimethoate	0.05	Solid-phase extraction-GC/MS	0.00005	20 %
67	Diquat	0.005	Solid-phase extraction-HPLC	0.001	20 %
68	Diuron (DCMU)	0.02	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.0001 0.0001	20 % 20 %
69	Endosulfan (Benzoepin)	0.01	Solid-phase extraction-GC/MS	0.00005	20 %
70	Etofenprox	0.08	Solid-phase extraction-GC/MS	0.00005	20 %
71	Fenthion (MPP)	0.001	Solid-phase extraction-GC/MS Solid-phase extraction-LC/MS (P)	0.00001 0.00002	20 % 20 %
72	Glyphosate	2	Derivatization-HPLC HPLC-post-column	0.0005 0.002	20 % 20 %
73	Malathion (Malathion)	0.05	Solid-phase extraction-GC/MS	0.00005	20 %
74	Methomyl	0.03	HPLC-post-column Solid-phase extraction-LC/MS (P)	0.0001 0.00002	20 % 20 %
75	Benomyl	0.02	Solid-phase extraction-LC/MS (P)	0.00002	20 %
76	Benfuracarb	0.04	Solid-phase extraction-LC/MS (P)	0.000004	20 %
77	Simetryne	0.03	Solid-phase extraction-GC/MS	0.00002	20 %
78	Dimepiperate: outdated pesticide	0.003	Solid-phase extraction-GC/MS	0.00002	20 %
79	Phenthoate (PAP)	0.004	Solid-phase extraction-GC/MS	0.00004	20 %
80	Buprofezin	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
81	Ethylthiomethone	0.004	Solid-phase extraction-GC/MS	0.00004	20 %
82	Probenazole	0.05	Solid-phase extraction-LC/MS (P)	0.0001	20 %
83	Esprocarb	0.03	Solid-phase extraction-GC/MS	0.0001	20 %
84	Daimuron	0.8	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00005 0.00005	20 % 20 %
85	Bifenox: outdated pesticide	0.2	Solid-phase extraction-GC/MS	0.0001	20 %
86	Bensulfuron methyl	0.4	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00001 0.00001	20 % 20 %
87	Tricyclazole	0.08	Solid-phase extraction-LC/MS (P)	0.000002	20 %
88	Piperophos: outdated pesticide	0.0009	Solid-phase extraction-GC/MS	0.00005	20 %
89	Dimethametryn	0.02	Solid-phase extraction-GC/MS	0.00001	20 %
90	Azoxystrobin	0.5	Solid-phase extraction-LC/MS (P)	0.00002	20 %
91	Iminoctadine acetate	0.006	Solid-phase extraction-HPLC-post-column Solvent extraction-HPLC-post-column	0.005 0.005	20 % 20 %
92	Fosetyl	2	LC/MS (N)	0.02	20 %
93	Polycarbamate	0.03	Derivatization-HPLC	0.002	20 %
94	Halosulfuron methyl	0.3	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.00005 0.00005	20 % 20 %
95	Flazasulfuron	0.03	Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.000002 0.000002	20 % 20 %
96	Thiodicarb	0.08	Solid-phase extraction-LC/MS (P)	0.00005	20 %
97	Propiconazole	0.05	Solid-phase extraction-GC/MS	0.0002	20 %
98	Siduron	0.3	Solid-phase extraction-HPLC Solid-phase extraction-LC/MS (P) Solid-phase extraction-LC/MS (N)	0.002 0.00002 0.00002	20 % 20 % 20 %
99	Pyriproxyfen	0.3	Solid-phase extraction-GC/MS	0.00001	20 %
100	Trifluralin	0.06	Solid-phase extraction-GC/MS	0.00001	20 %
101	Cafenstrole	0.008	Solid-phase extraction-GC/MS	0.00001	20 %
102	Fipronil	0.0005	Solid-phase extraction-LC/MS (N)	0.000005	20 %

Note: In the test method column, P: positive mode, and N: negative mode

## 5. Summary

The safety in use of tap water depends on the water quality tests that are required to be conducted by companies that supply water. The water quality standards established by the Water Supply Act dates back to 1958. Since then, it has gone through several revisions, the most comprehensive of which was in 2003. This revision served to greatly strengthen water quality control for tap water. Since 2003, revisions have been conducted when necessary.

Test items include items that relate to health and the water-related characteristics of tap water. Also, target items are wide-ranging, and include bacteria, organic and inorganic materials, and metals. As a manufacturer of analytical

instruments, we offer a range of measuring instruments for water quality control for laboratories to conduct water quality tests. Shimadzu's analytical instrument was used for the tap water quality tests conducted in this Application Note in order to provide the latest measurement results and summaries of analytical conditions. Our efforts would be rewarded if the information offered in the Application Note proves useful and interesting to those working in companies that supply water, and to people with an interest in testing the quality of tap water.

October, 2009

From everyone in the Environmental Project

## Liability Release

The content described in this Application Note is current as of April 2010. Be sure to check the latest regulations, etc. prior to performing the measurements described in this Application Note.

Furthermore, Shimadzu cannot guarantee that the information or contents obtained for this Application Note are correct or useful for any specific purpose.

Shimadzu shall not assume responsibility for direct or indirect damage to equipment or property caused by using this Application Note. Any results or phenomenon that may occur as a result of using this material will be the sole responsibility of the customer.

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