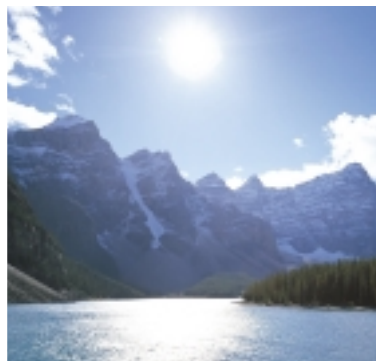# SHIMADZU
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Analysis Guidebook

Environmental Analyses

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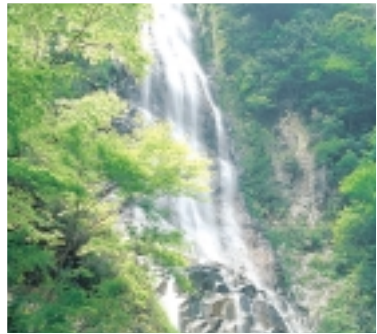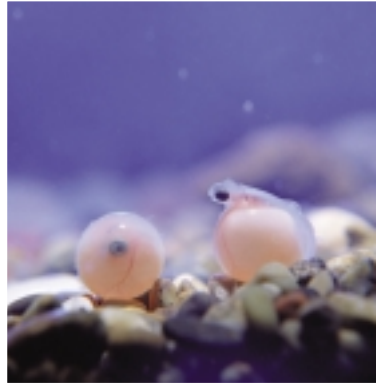
1. Drinking Water

1.1 Analysis of Anions in Tap Water — *Ion Chromatograph*
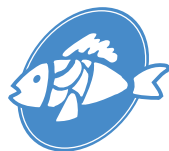
■Explanation

In December 1992 amendments were made to the Ministerial ordinance related to water quality standard, the ion chromatograph (IC) method was adopted as the negative ion analysis method. The following three items are the items in which IC is used as the test method.

Standard Item (Item Relating to Health)

♦ Fluorine

♦ Nitrate nitrogen and nitrite nitrogen

Standard Item (Item relating to properties that tap water should have)

♦ Chlorine ion

With regard to these items, the use of the IC enables simultaneous analysis of subject ions without any special pretreatment. Furthermore, simultaneous analysis can be performed on sulfuric acid ions and phosphate anions not raised as issues in the water standard.

References

Drinking Water Test Method & Explanation (Fiscal 1993 Volume) 164 – 198

Ministry of Health and Welfare, Environ. Health Bureau, Water Supply & Environ, Sanitation Dept. Edition

Japan Water Works Association

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : Ion chromatograph
Column : Shim-pack IC-A3 (150mm ✕ 4.6mm I.D.)
Mobile phase : 8.0mM p-hydroxybenzoic acid
Flow rate : 1.5mL/min
Temperature : 40˚C
Detection : Electric conductivity detector
*Bis-Tris : Bis (2-hydroxyethyl) iminotris (hydroxymethyl) methane

■Peaks
1 CO_3^{2-} (35mg/L)
2 F^- (0.071mg/L)
3 Cl^- (10.1mg/L)
4 NO_3^- (1.2mg/L)
5 SO_4^{2-} (17.8mg/L)
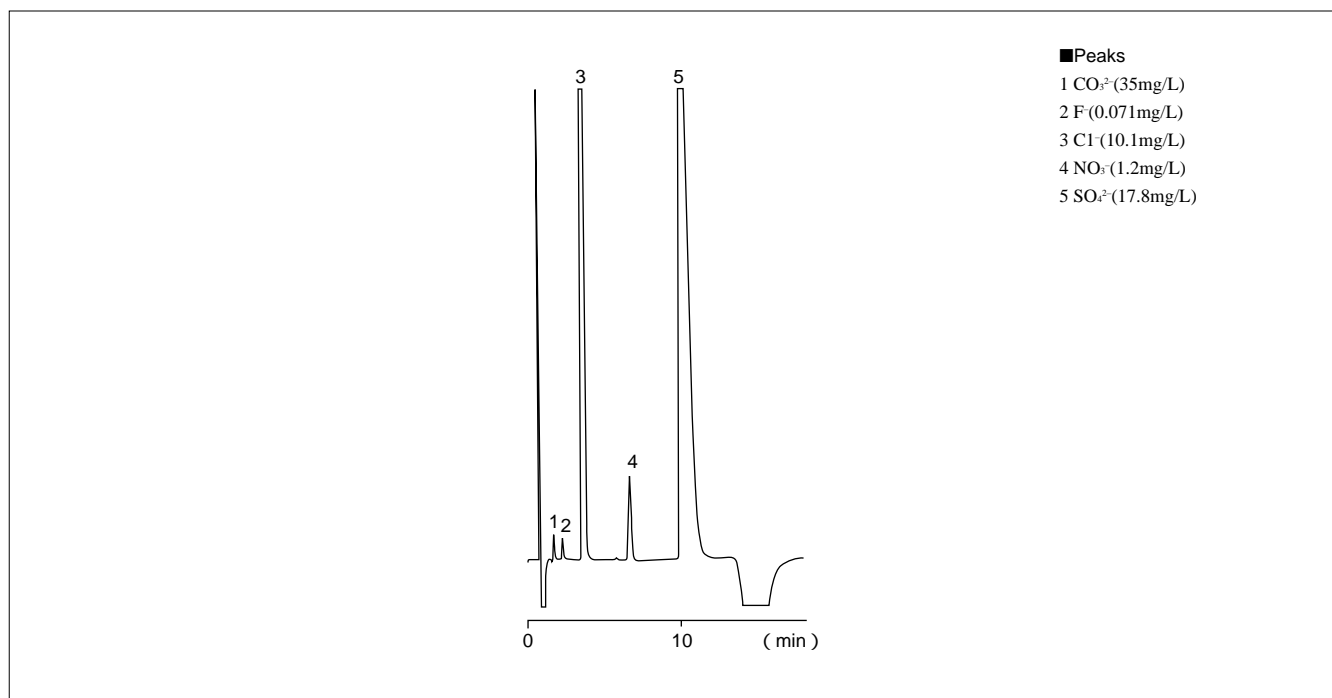
Fig. 1 Analysis Example of Tap Water

1.2 Analysis of Cations in Tap Water — *Ion Chromatograph*

■Explanation

Sodium, and calcium and magnesium, etc., as items related to properties that tap water should have are defined as test subjects for hardness. Currently, the ion chromatograph method (IC) is not used as a test method for these elements, but it could be used to measure such items. Furthermore, in addition to the above, the IC can also simultaneously measure lithium ions, potassium ions, and ammonium ions.

In particular, ammonia is an element targeted for measuring from the point of view of comprehending pollution levels. Here, the IC method is an excellent way of being able to simultaneously analyze elements.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : Ion chromatograph
Column   : Shim-pack IC-C3 (100mm ✕ 4.6mm I.D.)
Mobile phase : 2.0mM oxalic acid
Flow rate   : 1.2mL/min
Temperature : 40°C
Detection   : Electric conductivity detector

■Peaks
1 Na^+ 8.25ppm
2 NH_4^+ 0.01ppm
3 K^+ 1.66ppm
4 Mg^{2+} 2.22ppm
5 Ca^{2+} 11.85ppm
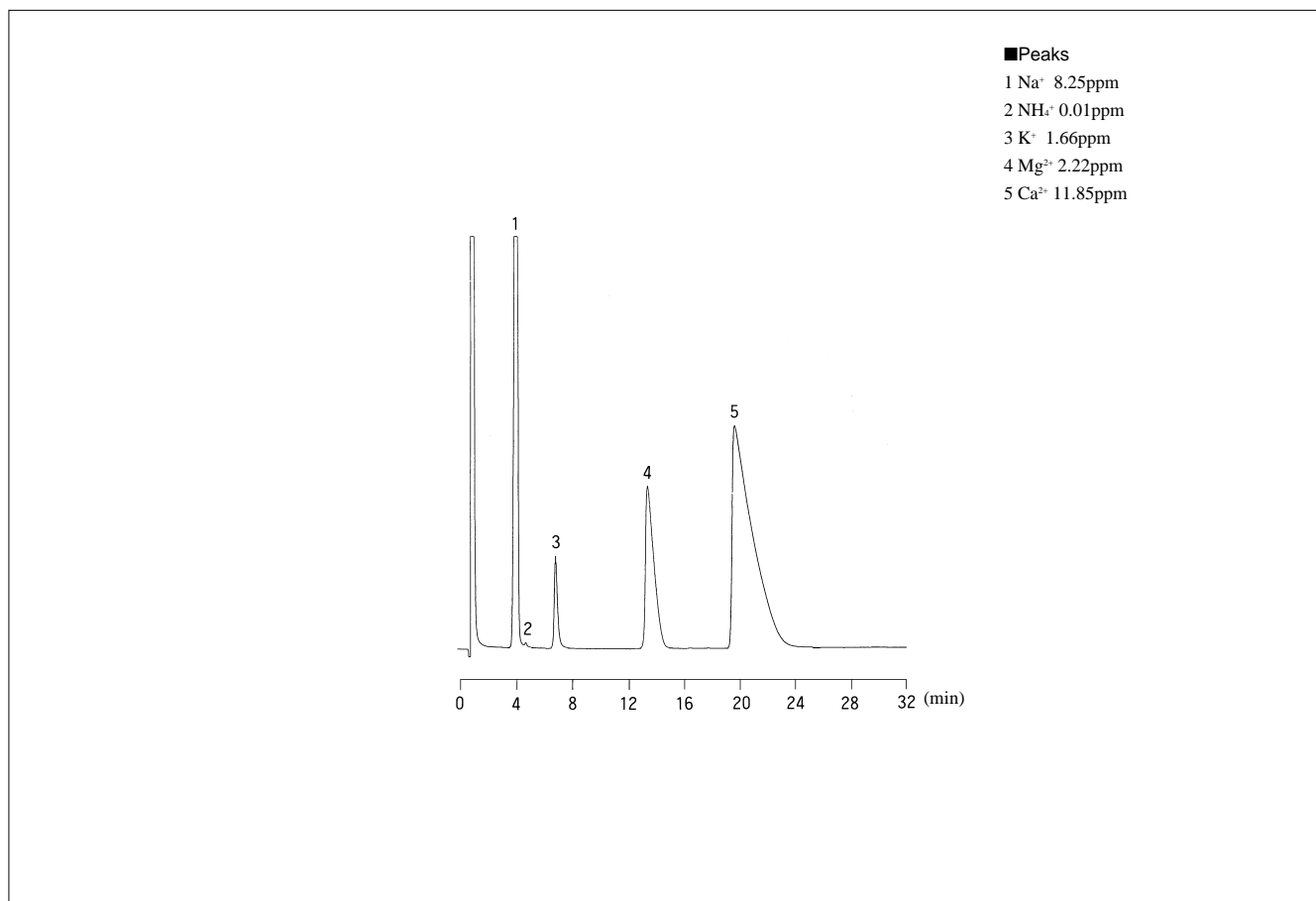
Fig. 2 Analysis example of sample with addition of 10 ppb of NH_4^+ in tap water

Drinking Water
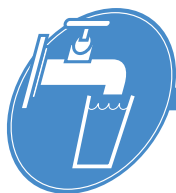
1.3 Analysis of Anions in Tap Water — PIA-1000

■Explanation

This is a tap-water analysis example using the personal ion analyzer PIA-1000. Not only is the PIA-1000 useful because of its portability but it also proves effective as a sub-device in the laboratory. Although a compact model, the accuracy of the PIA-1000 is on a par with conventional models, which makes it a potent force in everyday analysis work.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : PIA-1000
Column : Shim-pack IC-A3(S)
Mobile phase : PIA-1000 dedicated anion
analysis mobile phase, IC-MA3-1
Flow rate : 0.2mL/min

■Peaks
1 HCO_3^- (32.83mg/L)
2 F^- (0.130mg/L)
3 $C\ell^-$ (12.62mg/L)
4 NO_3^- (0.158mg/L)
5 SO_4^{2-} (16.49mg/L)
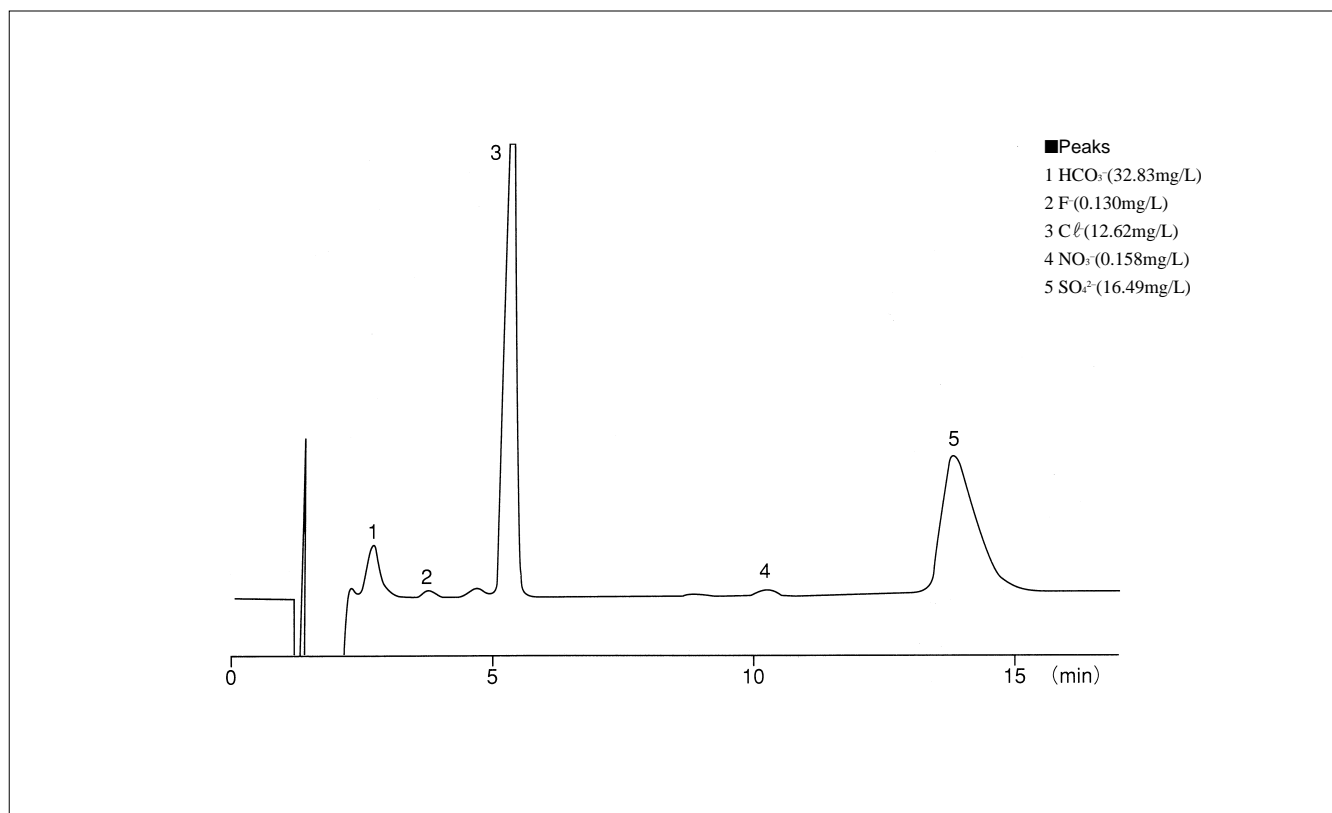
Fig. 3 Analysis Example of Tap Water (PIA-1000)

1.4 Analysis of Volatile Organic Compound (VOC) in Tap Water (1) — *Purge & Trap GC/MS*

■Explanation

The purge trap method involves purging volatile organic compound that exists in water using helium or nitrogen gas, holding it in a trap tube, then quickly heating it to induct it into a GC/MS column. Nearly all the volatile constituents included in a 5mL sample are concentrated in the trap tube to enable highly sensitive analysis.

Figure 4 is a SIM chromatograph of the 23 constituent compounds targeted and individual 0.1µg/L concentrations of p-bromofluorbenzene (IS). The chart 1 shows the names of the targeted compounds and the SIM selected ions.

References

(1) Drinking Water Test Method & Explanation,
    Japan Water Works Association volume
(2) Environmental Water Analysis Manual,
    Environmental Science Research Group volume
(3) New Wastewater Standards and Other Analysis
    Methods,
    Environmental Science Research Group volume

■Analytical Conditions

P&T: Tekmer-Dohrmann LSC3000J (No cryofocus)
    Trap tube   : GI (TENAX)
    Sample purge time : 6min
    Desorption   : 225˚C, 2min

Shimadzu GCMS-QP5050A

    Column   : DB-624 60m ✕ 0.32mm I.D.,
                       1.8µm(df)
    Column temperature : 40˚C(1min)-10˚C/min
    Carrier gas   200˚C(5min)
                     : He 100kPa

Ion set number:1 SIM=1205609							
61.00	96.00	84.00	86.00	83.00	85.00	117.00	119.00
78.00	62.00	64.00	97.00				
Ion set number:2 SIM=746888							
130.00	132.00	63.00	65.00	83.00	85.00	110.00	112.00
91.00	92.00	97.00	166.00	164.00	129.00	127.00	
Ion set number:3 SIM=5754303							
91.00	106.00	173.00	175.00	95.00	174.00	146.00	148.00
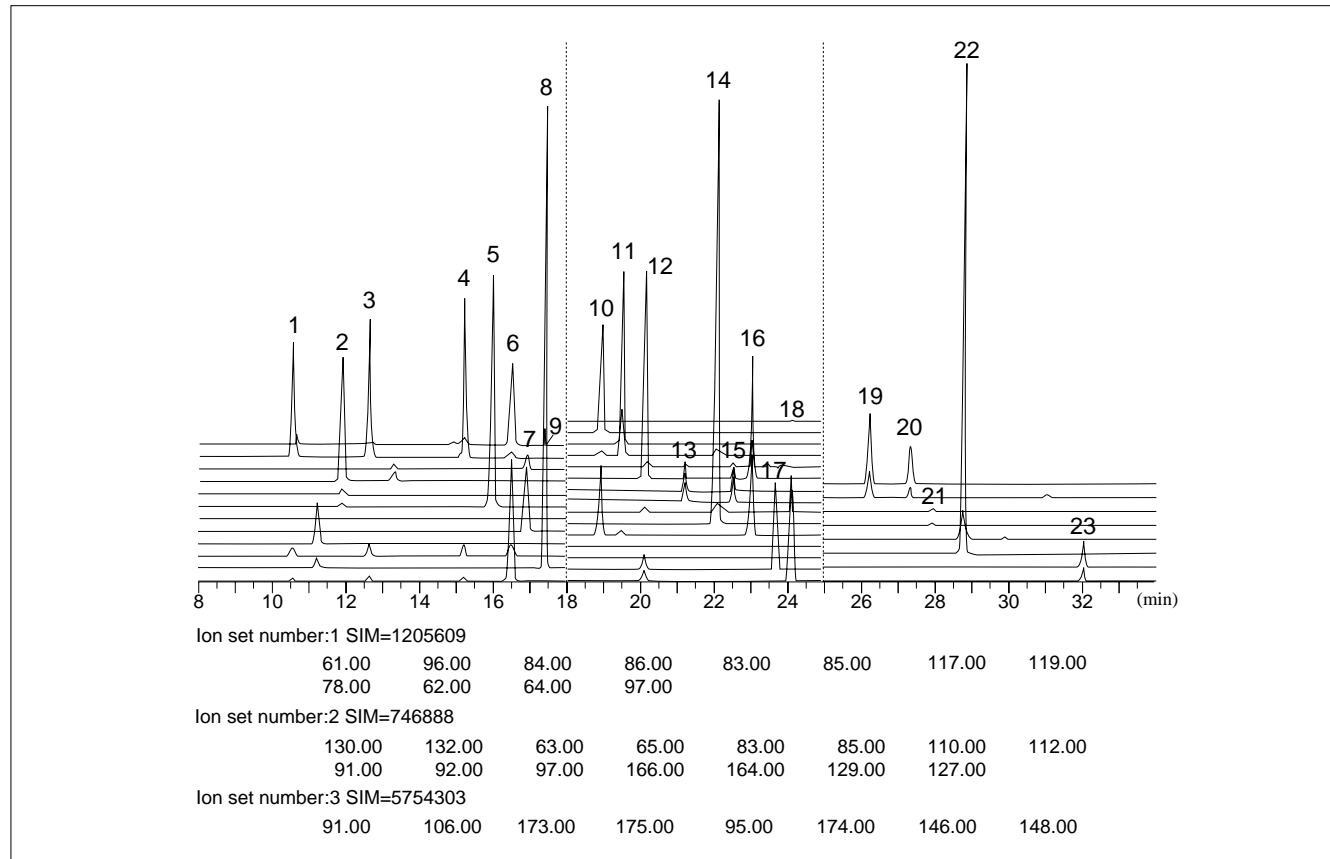
Fig. 4 Measuring example of 0.1 µg/L added water

Drinking Water
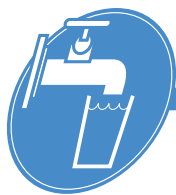
1.4 Analysis of Volatile Organic Compound (VOC) in Tap Water (2) — Purge & Trap GC/MS

ID	Name	SIM Selected Ions	ID	Name	SIM Selected Ions
1	1,1-dichloroethene	96,61	13	cis-1,3-dichloroproene	75,110
2	Dichloromethane	84,86	14	Toluene	92,91
3	trans-1,2-dichloroethane	96,61	15	trans-1,3-dichloropropene	75,110
4	cis-1,2-dichloroethane	96,61	16	1,1,2-trichloroethene	97,99
5	Chloroform	83,85	17	Tetrachloroethene	166,164
6	1,1,1-trichloroethane	97,99	18	Dibromochloromethane	129,127
7	Tetrachloromethane	117,119	19	m,p-xylene	106,91
8	Benzene	78,77	20	o-xylene	106,91
9	1,2-dichloroethane	62,64	21	Bromoform	173,175
10	Trichloroethene	130,132	22	p-bromofluorbenzene(IS)	174,176
11	1,2-dichloropropane	63,62	23	p-dichlorobenzene	146,148
12	Bromodichloromethane	83,85			

Chart 1 SIM selected ions
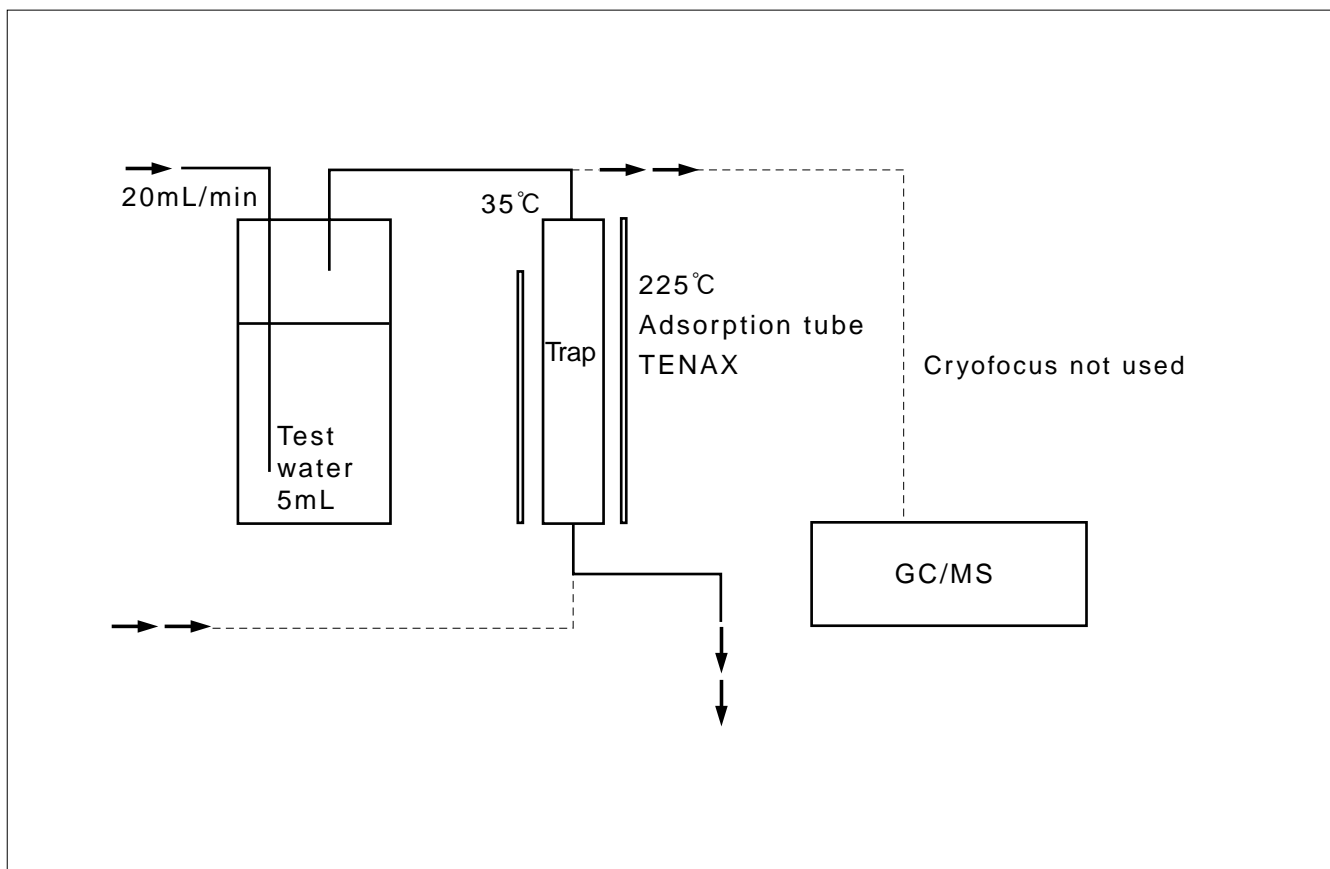
Fig. 5 Purge & trap GC/MS system

1.5 Analysis of Musty Smelling Components in Tap Water (1) — *Purge & Trap GC/MS*

■Explanation

Japanese tap water has an established reputation in the area of quality as drinking water; however, in recent years, it has a musty odor depending on the season. And the substances that cause this musty odor are known to be 2-methylisoborneol and geosmin. The threshold value for the odors of these compounds is approximately 10ppt, which is low, and cannot be detected in source state by GC/MS analysis, so the purge trap method, as shown in the drinking water test method, is used to concentrate the compounds for analysis by GC/MS. This purge trap method involves forcing the targeted compound into a gas phase using aeration, holding this gas phase in a concentration tube filled with TENAX TA, then forcing out of the concentration tube by heating.

References

(1) Drinking Water Test Method & Explanation,
    Japan Water Works Association volume
(2) Environmental Water Analysis Manual,
    Environmental Science Research Group volume

■Analytical Conditions

P&T: Tekmer-Dohrmann LSC3000J

Trap tube   : G1 (TENAX TA)
Sample purge time : 11min
Force out   : 225°C, 8min

Shimadzu GCMS-QP5050A

Column   : DB-1701 30m ✕ 0.32mm
                          I.D. 1μm(df)
Column temperature : 60°C(3min)-10°C(min)
                          240°C(10min)
Carrier gas   : He 40kPa
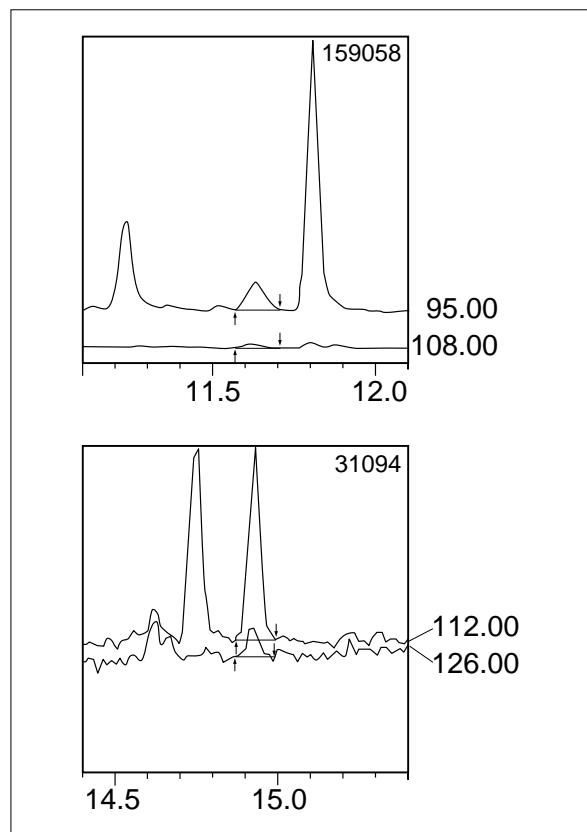
Fig. 6 Analysis example of musty odor 3.0ppt
(Upper: 2-MIB, lower: geosmin)

ID #1   Mass No.: 95.00 Element name: 2-MIB
Surface area = 11829.5 *Concentration + 16926
Contribution ratio = 0.997846

	Concentration (ppt)
1	0.500
2	1.000
3	3.000
4	5.000

ID #2 Mass No.: 112.00 Element name: geosmin
Surface area = 14468.8 *Concentration + 5982.67

	Concentration (ppt)
1	0.500
2	1.000
3	3.000
4	5.000
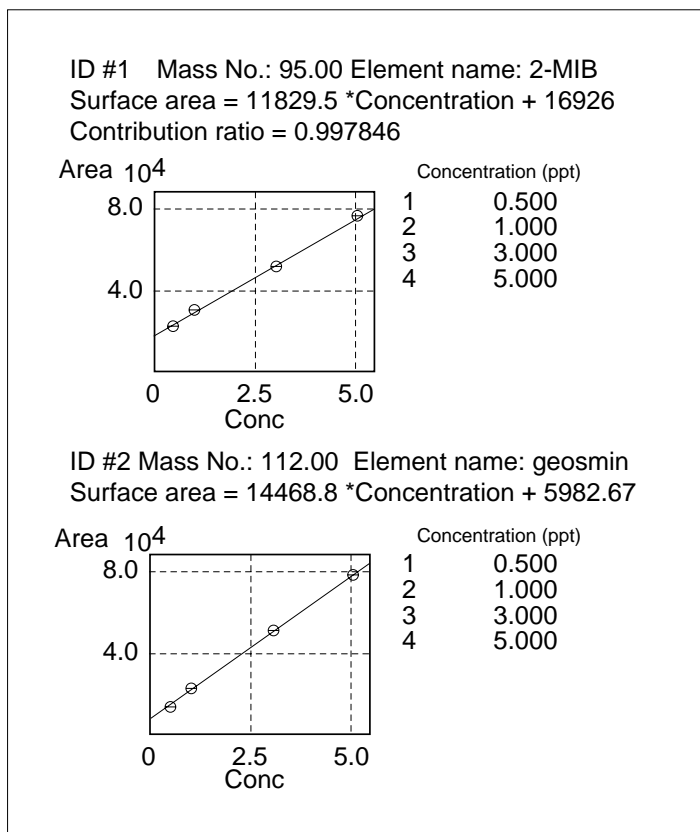
Fig. 7 Calibration curve
(Upper: 2-MIB, lower: geosmin)

1.5 Analysis of Musty Smelling Components in Tap Water (2) — *Purge & Trap GC/MS*

Reference Example 1

2-Methylisoborneol:m/z 95,108   Geosmin:m/z 112.126
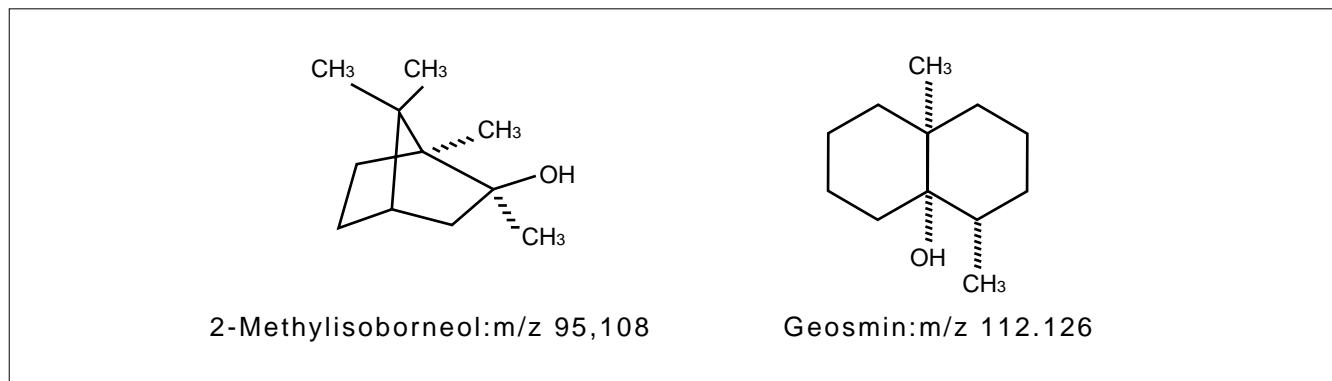
Fig. 8 Structures of 2-MIB and geosmin
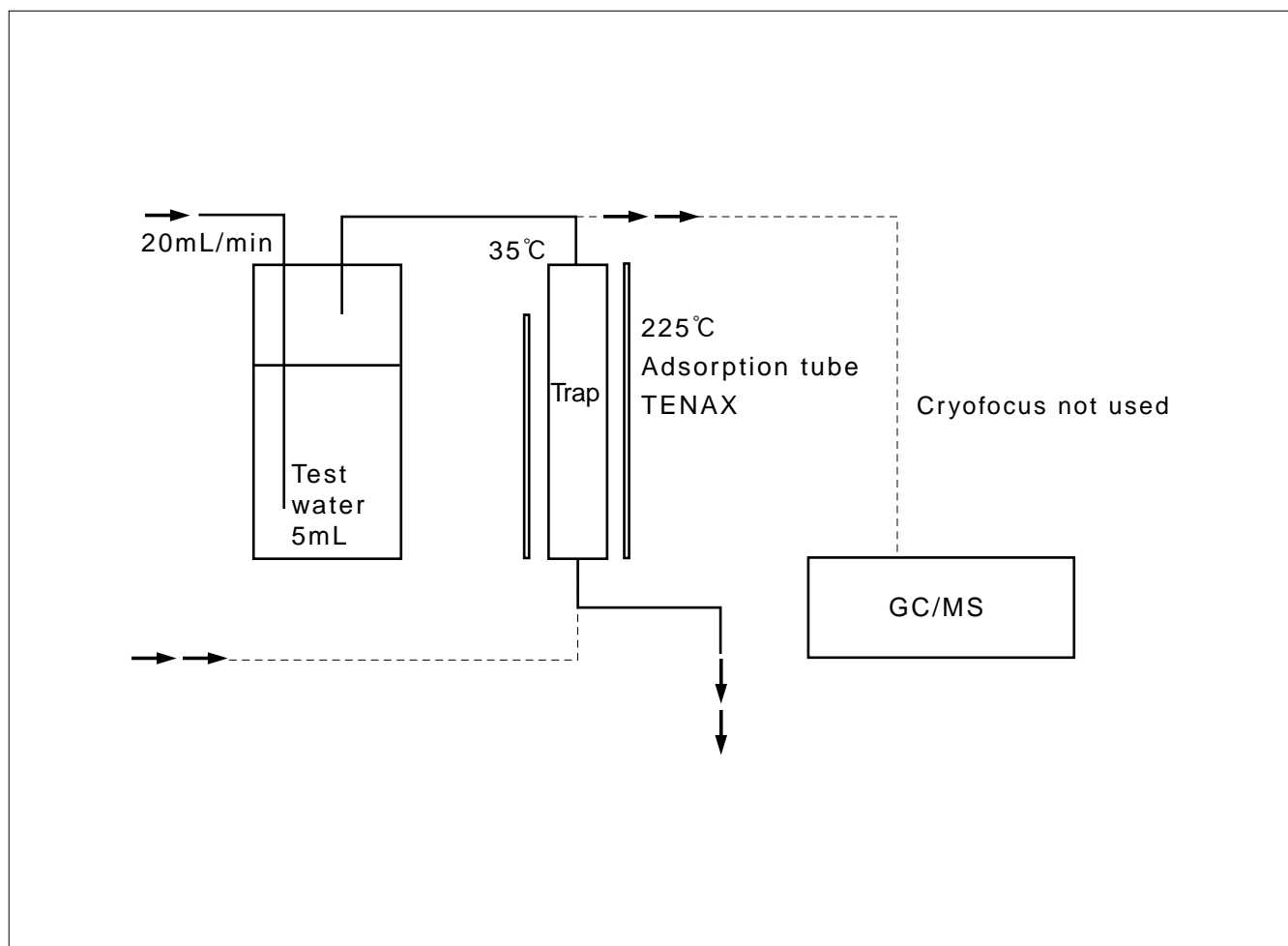
Fig. 9 Principle diagram of purge & trap method

1.6 Analysis of Non-organic Components in Tap Water (1) — *ICP-AES*

■Explanation

With regard to the testing method for metals in tap water, there are an analysis method using ICP emission spectroscopic method or atomic absorption method, and an absorptiometric analysis as colorimetric method. Here, an ICP emission spectroscopic analysis method as a simultaneous analysis method will be introduced.

Tap water was qualified and quantified using the ultrasonic nebulizer in the ICP-AES. The results of the qualitative analysis revealed Al, B, Ba, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, S, Si, Sr, and Zn. Quantitative analysis was performed for the elements detected by qualitative analysis and the elements laid down in the water quality standard.

References

(1) Partial amendment of Ministerial ordinance related to water quality standard for drinking water and Water Supply Law Operation Regulations, etc., introduced on December 21, 1992

(2) Drinking Water Test Method & Explanation, Japan Water Works Association volume

■Pretreatment

A water sample of 100mL was prepared, 1mL of nitric acid added, and thermally concentrated without quite boiling. Heating was stopped once solution volume dropped below 100mL, cooled, and measured up with purified water to create a 100mL sample for analysis.

■Analytical Conditions

Instrument   : ICPS-7500
                          Ultrasonic nebulizer UAG-1
High-frequency   : 27.12MHz
High-frequency output   : 0.8kW
Cooling gas   : Ar 14.0L/min
Plasma gas   : Ar 1.2L/min
Carrier gas   : Ar 0.7L/min
Purge gas   : Ar 3.5L/min
Sample suction rate   : 2.0mL/min
Observation method   : longitudinal

Element	Analytical Value (mg/L)	Element	Analytical Value (mg/L)	Element	Analytical Value (mg/L)
Ar	0.0048	Cr	<0.0005	Na	8.76
As	<0.005	Cu	0.0005	Pb	<0.002
B	0.025	Fe	0.0034	S	4.45
Ba	0.0052	K	1.36	Si	0.77
Ca	9.84	Mg	1.72	Sr	0.056
Cd	0.0003	Mn	0.0002	Zn	0.0022

Chart 2 Tap water analysis results (µg/mL)

1.6 Analysis of Non-organic Components in Tap Water (2) — *ICP-AES*
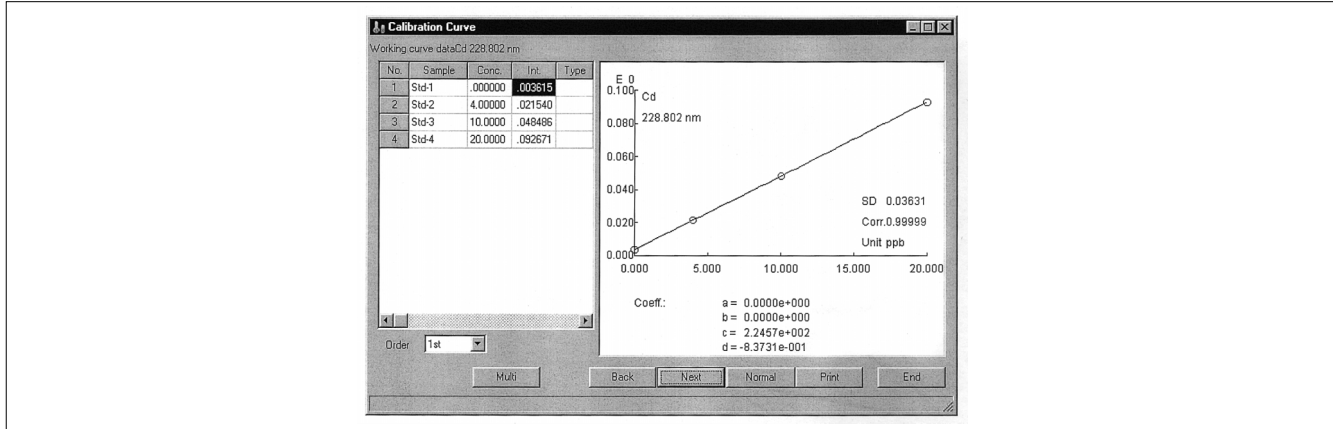
Fig. 10 Cd calibration curve
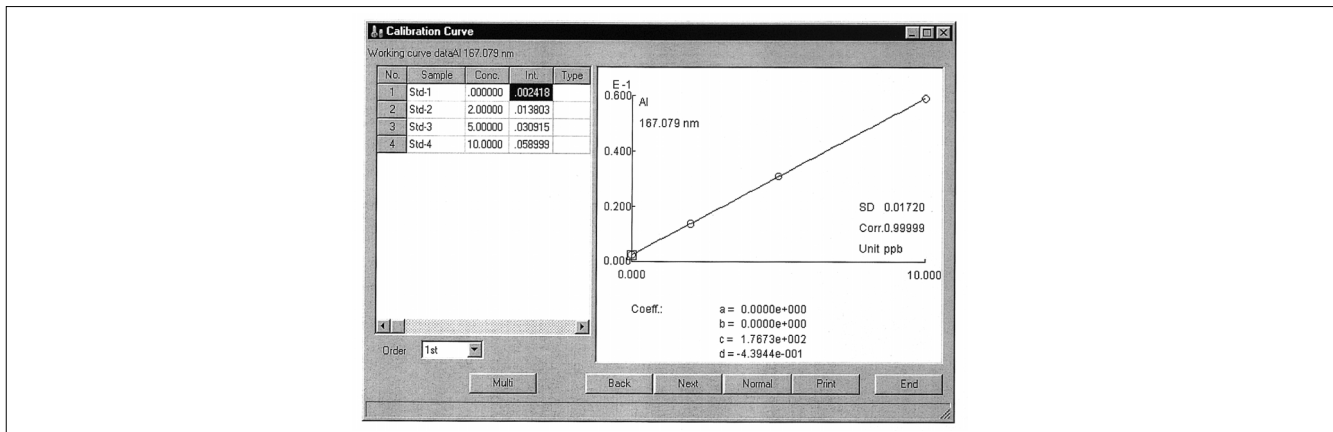
Fig. 11 Al calibration curve
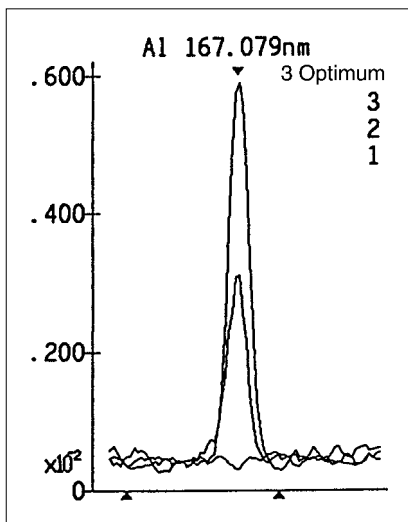
Fig. 12 Profile of Al 167.079nm
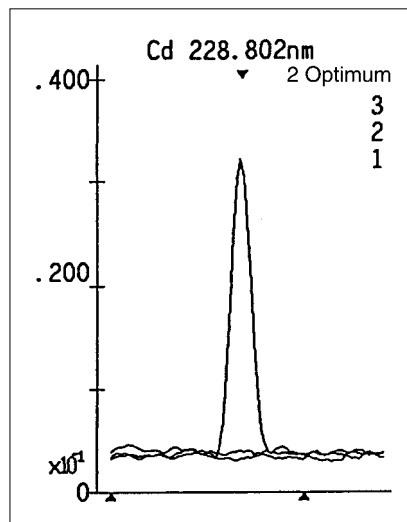
Fig. 13 Profile of Cd 228.802nm
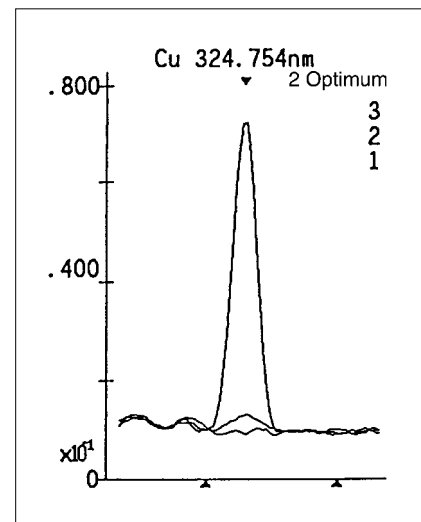
Fig. 14 Profile of Cu 324.754nm

1.7 Analysis of Non-organic Components in Mineral Water (1) — *ICP-AES*

■Explanation

Mineral water brands are forms of drinking water just like tap water, and large quantities of domestic and import brands are consumed, which has led to calls for amendments of the regulations governing this type of water. The following is explanation of some highly sensitive analysis performed to find traces of metal elements in mineral water using an ICP emission spectrometer and a Ultrasonic nebulizer.

One method of performing highly sensitive analysis involves longitudinal observation of plasma. By using this method, background spectrum is reduced by argon lighting, which enables highly sensitive measuring. As a result, sensitivity can be improved by about 5 fold in comparison with conventional lateral observation. Traces of metal elements (Al, Cr, Mn, Fe, Mi, Cu, Zn, As, Se, Mo, Cd, Pb) were quantified using the ICP emission spectrometer and the Ultrasonic nebulizer.

Some imported mineral water contain a large amounts of Ca (60 to 100 μ/mL) in comparison to domestic products. For this reason, background compensation is necessary for certain elements.

References

(1) Partial amendment of Ministerial ordinance related to water quality standard for drinking water and Water Supply Law Operation Regulations, etc., introduced on December 21, 1992

(2) Partial amendment of operation ordinance for water pollution prevention related to environment standards, introduced on March 8, 1993

■Pretreatment

Promptly transfer 50mL of sample to plastic beaker after breaking seal on mineral water bottle, add 1mL of nitric acid, and stir sufficiently.

■Analytical Conditions

Instrument	: ICPS-7500
	Ultrasonic nebulizer UAG-1
High-frequency	: 27.12MHz
High-frequency output	: 1.0kW
Cooling gas	: Ar 14.0L/min
Plasma gas	: Ar 1.2L/min
Carrier gas	: Ar 0.8L/min
Purge gas	: Ar 3.5L/min
Sample suction rate	: 2.0mL/min
Observation method	: longitudinal

	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F	Sample G	Sample H	Sample I	Qualitative Lower Limit
Al	0.46	0.04	1.32	3.22	0.08	3.56	0.80	0.04	0.04	0.04
Cr	0.1	0.26	0.67	0.54	0.1	0.1	0.21	0.19	0.1	0.1
Mn	0.10	0.19	0.07	0.01	0.76	1.61	0.04	0.69	0.05	0.01
Fe	0.08	0.20	0.91	0.19	0.08	0.08	0.12	0.09	0.08	0.08
Ni	0.37	0.31	0.93	0.18	0.36	0.60	0.57	0.34	0.1	0.1
Cu	0.52	0.26	0.19	0.1	0.1	0.31	0.41	0.26	0.21	0.1
Zn	0.64	0.58	2.14	0.26	6.30	1.67	0.61	0.15	0.10	0.01
As	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Se	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Mo	0.1	0.1	0.1	0.1	1.52	3.22	2.02	0.46	0.1	0.1
Cd	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Pb	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4

Chart 3 Analysis Results for Mineral Water (ng/mL)

1.7 Analysis of Non-organic Components in Mineral Water (2) — *ICP-AES*
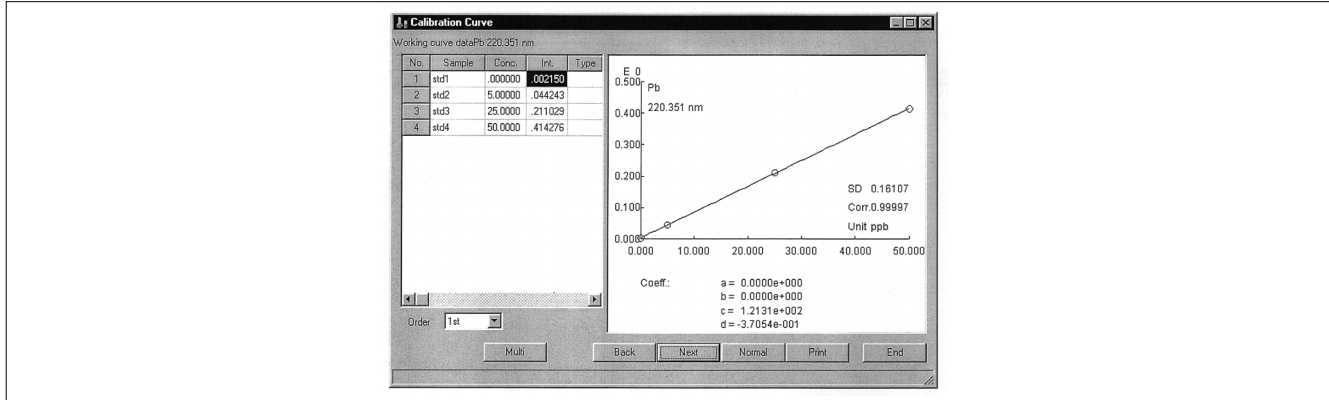
Fig. 15 Pb calibration curve
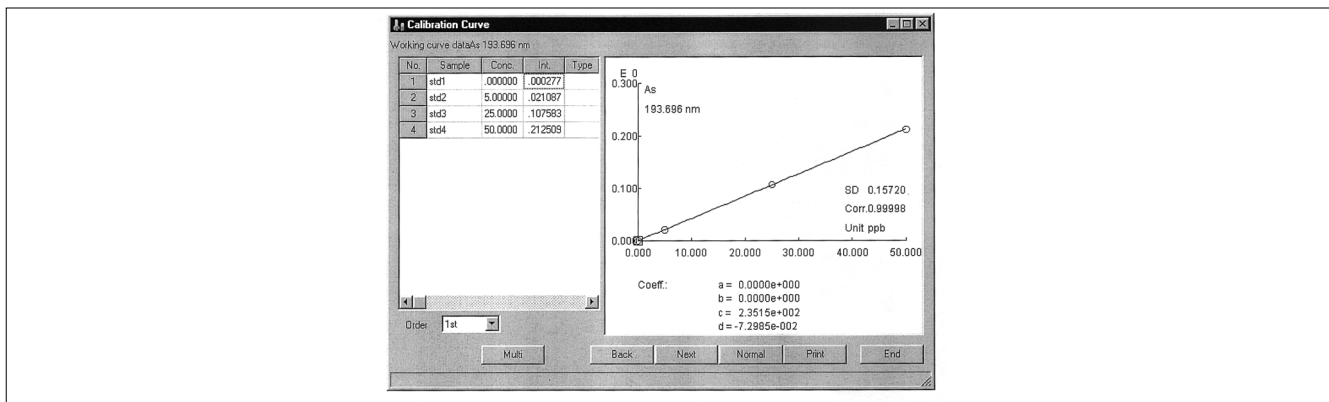
Fig. 16 As calibration curve
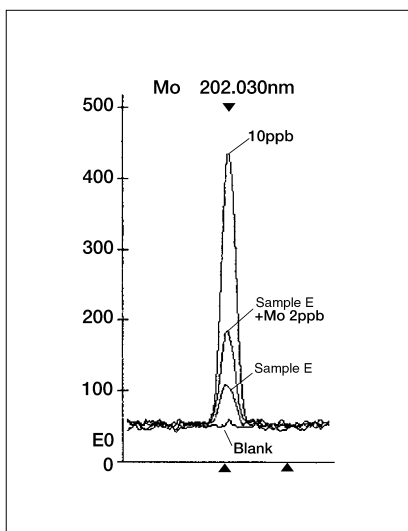
Fig. 17 Peak profile of Mo
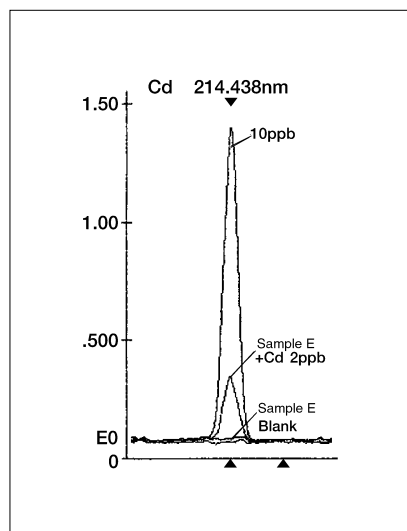
Fig. 18 Peak profile of Cd
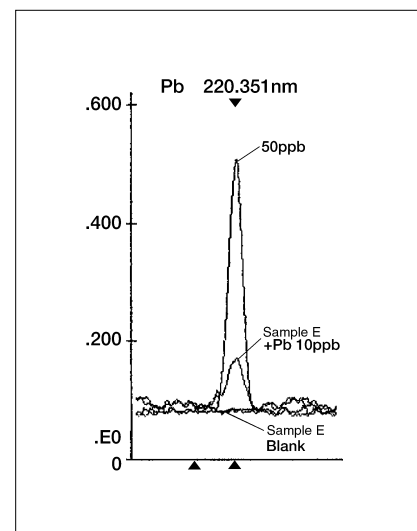
Fig. 19 Peak profile of Pb
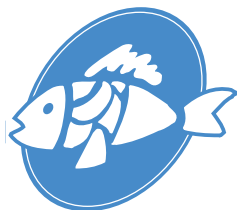
2. Environment Water

2.1 Analysis of Anions in River Water – *Ion Chromatograph*

■Explanation

The river and lake water – which is the source of our daily tap water – needs to be constantly analyzed and monitored as any change in the water quality can directly affect human health. Furthermore, the non-organic negative ion components in river and lake water reflect the nature of the water source and soil, so that each variation in ion concentration can be used to indicate change in the environment. Also, in recent years, eutrophication problems are occurring in rivers and lakes due to the inflow of domestic wastewater. And, once again, the analysis of non-organic ions is important for research work on the causes and levels of pollution.

References

Drinking Water Test Method & Explanation (Fiscal 1993 Volume) 164 – 198
Ministry of Health and Welfare Environ. Health Bureau, Water Supply & Environ. Sanitation Dept. Edition
Japan Water Works Association

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument	: Ion chromatograph
Column	: Shim-pack IC-A3 (150mm ✕ 4.6mm I.D.)
Mobile phase	: 8.0mM p-hydroxybenzoic acid, 3.2mM Bis-Tris*
	: 1.5mL/min
Flow rate	: 40˚C
Temperature	: Electric conductivity detector
Detection	: Bis (2-hydroxyethyl) iminotris
*Bis-Tris	(hydroxymethyl) methane

■Peaks
1 CO_3^{2-}
2 F^- (0.088mg/L)
3 Cl^- (6.10mg/L)
4 NO_2^- (0.048mg/L)
5 Br^- (0.21mg/L)
6 NO_3^- (1.28mg/L)
7 SO_4^{2-} (7.78mg/L)

Fig. 20 Analysis of River Water A

■Peaks
1 CO_3^{2-}
2 PO_4^{3-} (0.106mg/L)
3 F^- (0.148mg/L)
4 Cl^- (10.19mg/L)
5 NO_2^- (0.138mg/L)
6 Br^- (0.019mg/L)
7 NO_3^- (2.55mg/L)
8 SO_4^{2-} (15.73mg/L)

Fig. 21 Analysis of River Water B

2.2 Analysis of Cations in River Water — *Ion Chromatograph*

■Pretreatment

Filtering through a membrane filter (0.45 μm) for ion chromatography

■Analytical Conditions(Fig. 22)

Instruement : Ion chromatograph
Column   : Shim-pack IC-C3 (100mm ✕ 4.6mm I.D.)
Mobile phase: 3.0mM oxalic acid
Flow rate   : 1.2mL/min
Temperature : 40℃
Detection   : Electric conductivity detector

■Analytical Conditions(Fig. 23)

Instruement : Ion chromatograph
Column   : Shim-pack IC-C3 (100mm ✕ 4.6mm I.D.)
Mobile phase: 1.0mM Dipicolinic acid
                    1.0mM oxalic acid
Flow rate   : 1.2mL/min
Temperature : 40℃
Detection   : Electric conductivity detector

■Peaks
1 Na^+(12.42mg/L)
2 K^+(2.73mg/L)
3 Mg^{2+}(4.38mg/L)
4 $Ca2^+$(16.93mg/L)

Fig. 22 Analysis of River Water A

■Peaks
1 Li^+(0.007mg/L)
2 Na^+(19.63mg/L)
3 NH_4^+(0.106mg/L)
4 K^+(4.09mg/L)
5 Ca^{2+}(21.63mg/L)
6 Mg^{2+}(4.13mg/L)
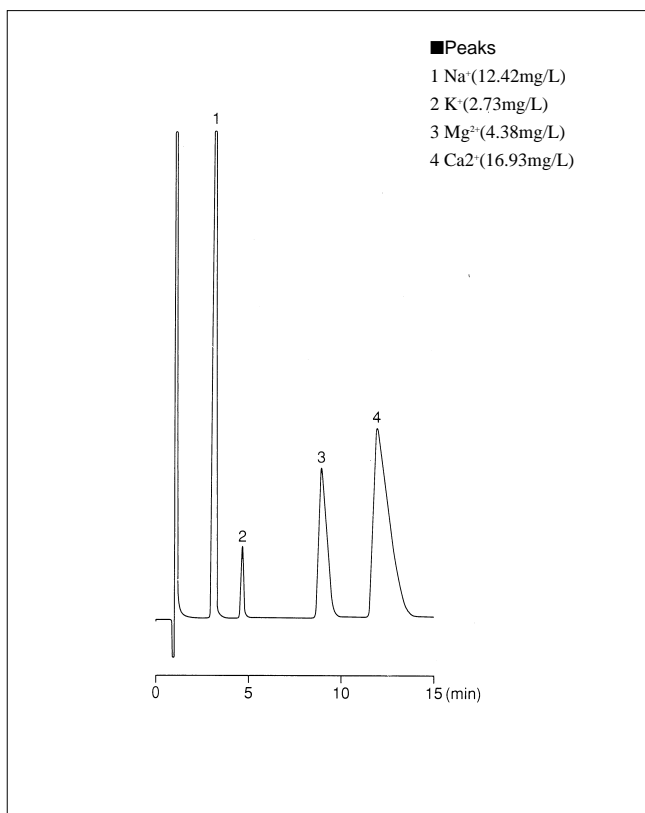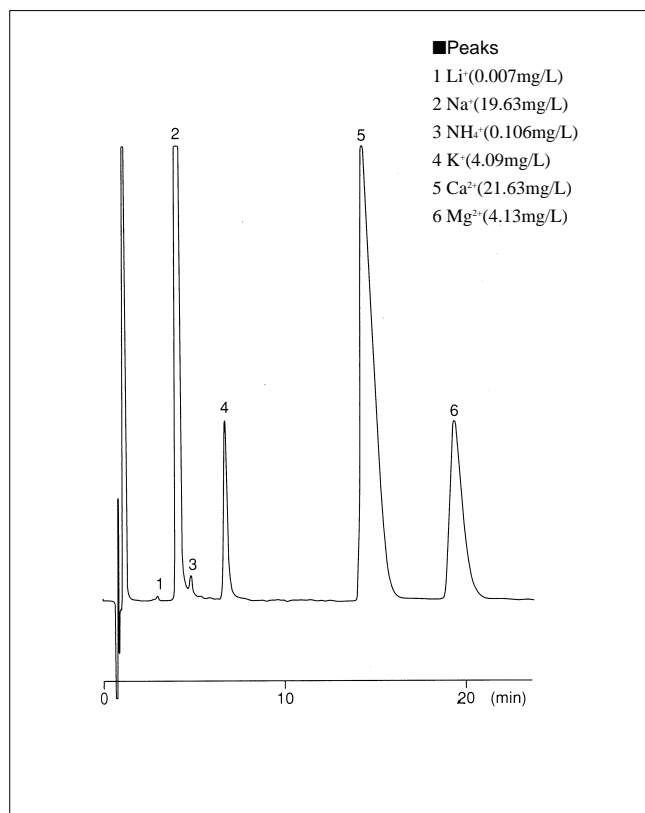
Fig. 23 Analysis of River Water B

2.3 Analysis of Anions in Lake Water – *Ion Chromatograph*

■Explanation

The river and lake water – which is the source of our daily tap water – needs to be constantly analyzed and monitored as any change in the water quality can directly affect human health. Furthermore, the non-organic negative ion components in river and lake water reflect the nature of the water source and soil, so that each variation in ion concentration can be used to indicate change in the environment. Also, in recent years, eutrophication problems are occurring in rivers and lakes due to the inflow of domestic wastewater, which makes the analysis of non-organic ions even more important for research work on the causes and levels of pollution.

References

Drinking Water Test Method & Explanation (Fiscal 1993 Volume) 164 – 198
Ministry of Health and Welfare, Environ. Health Bureau, Water Supply & Environ. Sanitation Dept. Edition
Japan Water Works Association

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : Ion chromatograph
Column   : Shim-pack IC-A3 (150mm ✕ 4.6mm I.D.)
Mobile phase : 8.0mM p-hydroxybenzoic acid, 3.2mM Bis-Tris*
Flow rate   : 1.5mL/min
Temperature : 40˚C
Detection   : Electric conductivity detector
*Bis-Tris   : Bis (2-hydroxyethyl) iminotris (hydroxymethyl) methane

■Peaks
1 CO_3^{2-}
2 F^- (0.147mg/L)
3 Cl^- (9.65mg/L)
4 NO_2^- (0.059mg/L)
5 Br^- (0.030mg/L)
6 NO_3^- (0.309mg/L)
7 SO_4^{2-} (12.38mg/L)
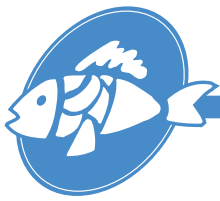
Fig. 24 Analysis of Lake Water A

Environment Water

2.4 Analysis of Cations in Lake Water – *Ion Chromatograph*

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : Ion chromatograph
Column : Shim-pack IC-C3 (100mm ✕ 4.6mm I.D.)
Mobile phase : 3.0mM oxalic acid
Flow rate : 1.2mL/min
Temperature : 40°C
Detection : Electric conductivity detector

■Peaks
1 Na$^+$(12.42mg/L)
2 K$^+$(2.73mg/L)
3 Mg^{2+}(4.38mg/L)
4 Ca^{2+}(16.93mg/L)
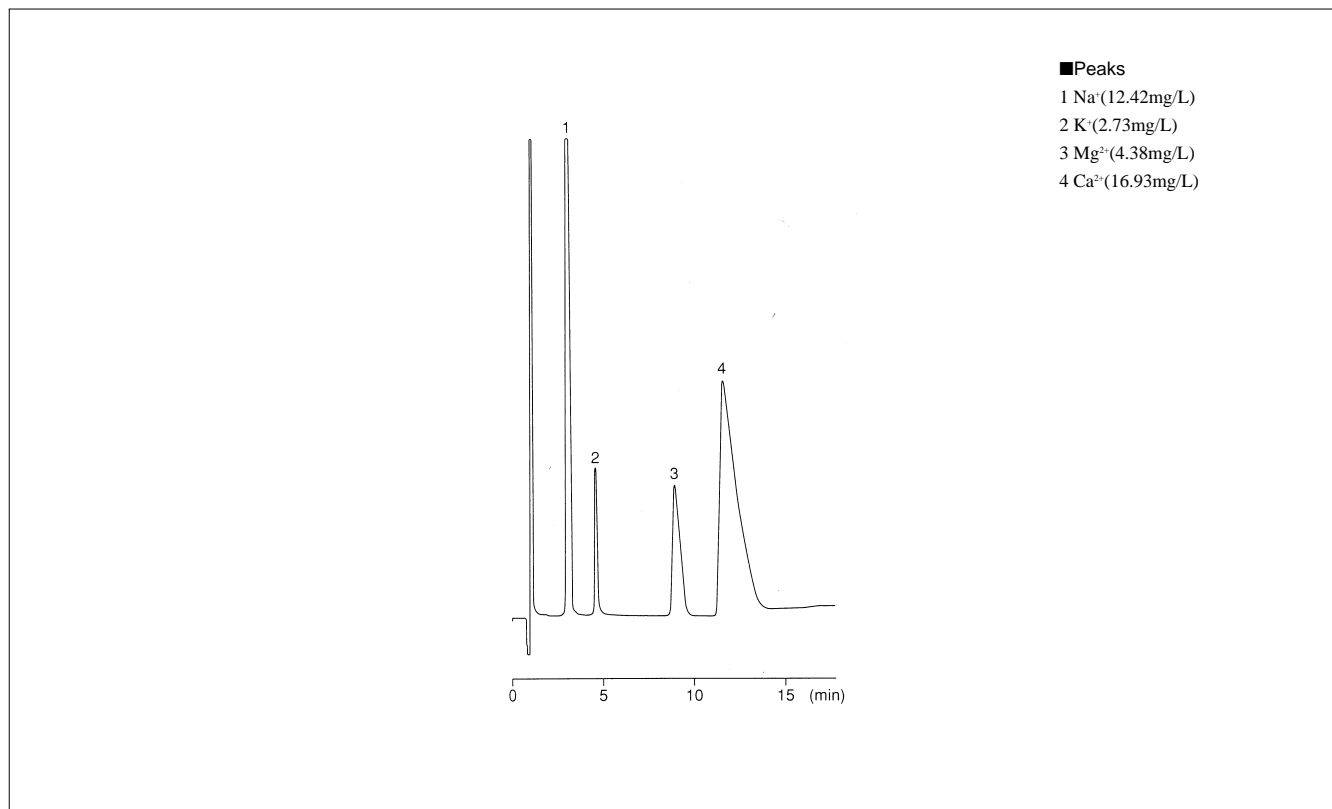
Fig. 25 Analysis of Lake Water B

2.5 Analysis of Anions in River Water — PIA-1000

■Explanation

This is a river-water analysis example using the personal ion analyzer PIA-1000. In this kind of example, the PIA-1000 is a potent force as it can be taken directly to an analyzing site.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : PIA-1000
Column   : Shim-pack IC-A3(S)
Mobile phase : PIA-1000 dedicated anion analysis mobile phase, IC-MA3-1
Flow rate   : 0.2mL/min
Temperature : 35˚C

■Peaks
1 HCO_3^-(52.77mg/L)
2 PO_4^{3-}(0.235mg/L)
3 F^-(0.076mg/L)
4 Cl^-(15.72mg/L)
5 NO_3^-(7.44mg/L)
6 SO_4^{2-}(15.04mg/L)
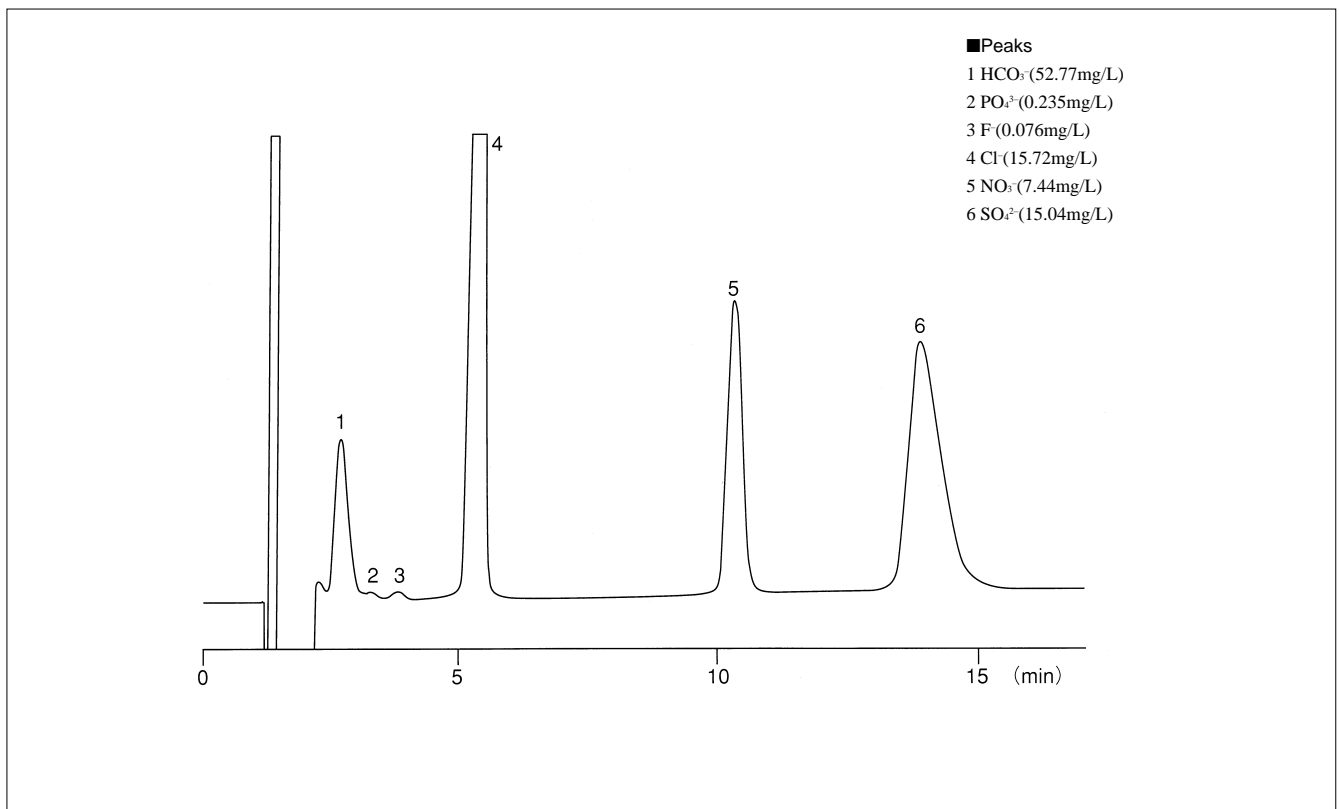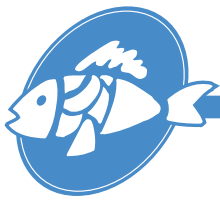
Fig. 26 Analysis example of river water (PIA-1000)

Environment Water

2.6 Analysis of Cations in River Water — PIA-1000

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : PIA-1000
Column : Shim-pack IC-C3(S)
Mobile phase : PIA-1000 dedicated cation analysis mobile phase, IC-MC3-1
Flow rate : 0.2mL/min
Temperature : 35°C

■Peaks
1 Na$^+$(13.33mg/L)
2 NH$_4$$^+$(0.396mg/L)
3 K(2.786mg/L)
4 Mg^{2+}(4.336mg/L)
5 Ca^{2+}(17.07mg/L)
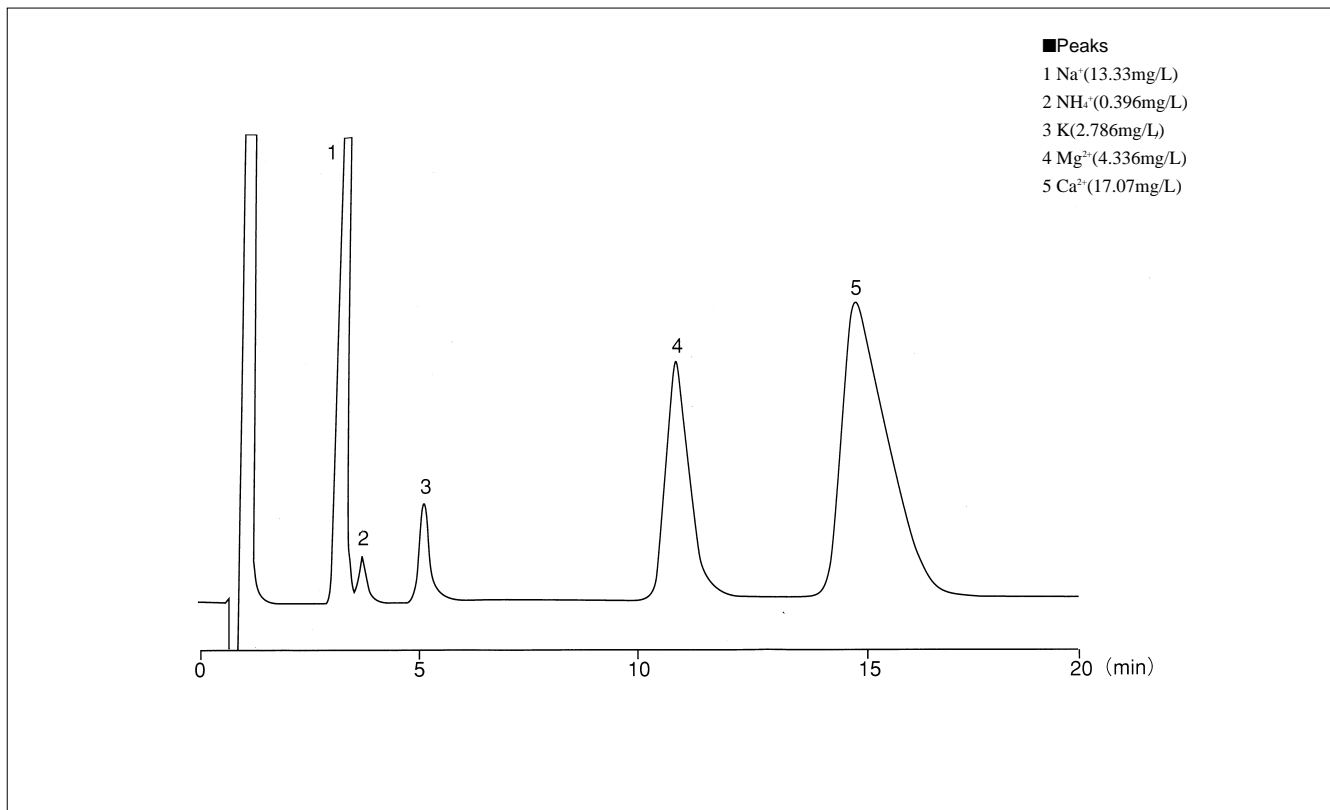
Fig. 27 Analysis Example of River Water (PIA-1000)

2.7 Analysis of Calcium and Magnesium in River Water – *AA*

■Explanation

The atomic absorption method is one of the widely used analysis methods for analyzing chemical elements in solutions because of its simplicity and speed. Here is an analysis example for Ca and Mg in standard substances in river water currently on the market.

References

Water test method for factories (JIS K0101)

Quantitative lower limit value (target)

Ca : 0.09mg/L
Mg: 0.004mg/L

■Sample Adjustments

Sample adjusting is shown on the next page. In the case of calcium and magnesium analysis, an equal amount of lanthanum is added to the total sample including the standard solution to mask interference by coexisting elements.

■Analytical Conditions

Instrument	: AA-6200
Analysis wavelength	: Ca 422.7nm
	: Mg 285.2nm
Flame type	: air acetylene
Background compensation	: D2 method
Interference control agent	: La 0.2W/V %
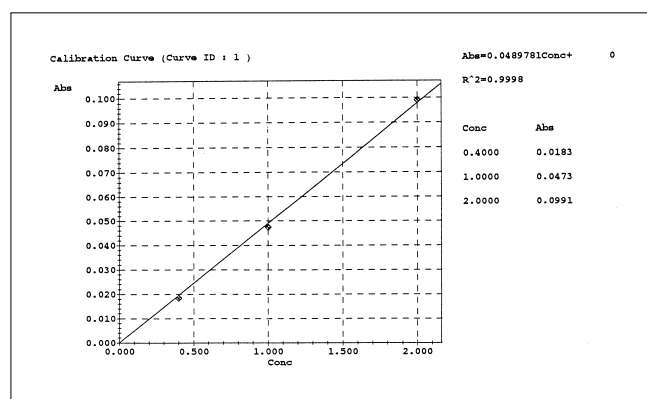
Fig. 28 Ca calibration curve A
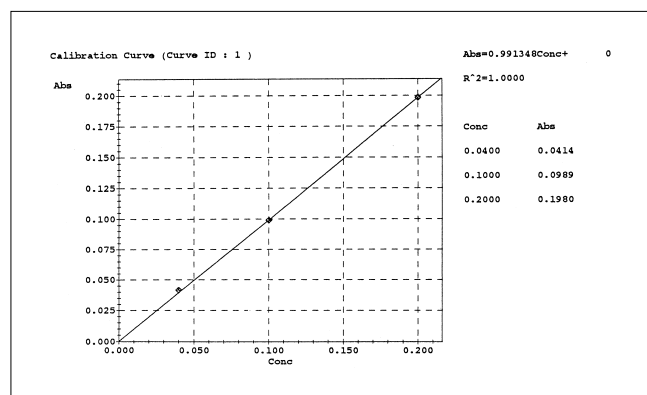
Fig. 29 Mg calibration curve

Fig. 29 Mg signal profile

Fig. 30 Sample Adjustment

	Ca	Mg
SLRS-3	6.02 (6.0± 0.4)	1.60 (1.6± 0.2)
NIST1643d	31.2 (31.04± 0.50)	7.97 (7.989± 0.035)

Chart 4 Measuring results   Unit : mg/L
Certified value in parenthesis
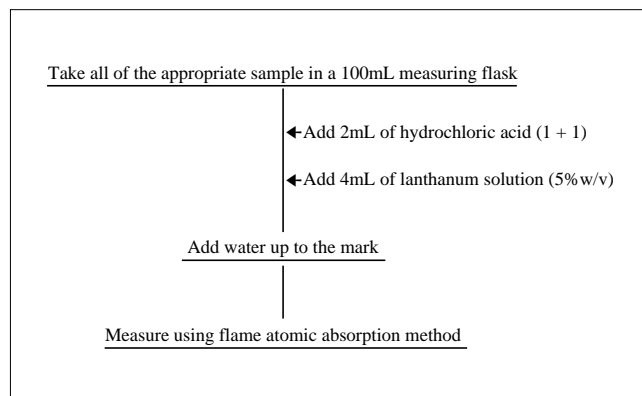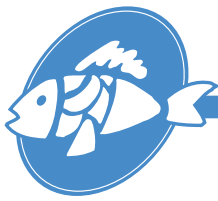
Remarks

If there is suspended matter in the sample, remove it by filtering or use of a centrifuge. Calcium coexists with orthophosphate, sulfate and aluminum, etc., while magnesium coexists with aluminum, so both are impeded. This interference can be removed by adding lanthanum to mask out the coexisting elements. Add lanthanum to sample in equal amounts to the standard solution.

Environment Water

2.8 Analysis of Total Nitrogen and Total phosphorus in River Water — UV

■Explanation

The remarkable overgrowth of plant plankton in sea areas and rivers known as red water or red tide is said to be linked to concentrations of nitrogen and phosphorus. Due to rises in the concentration (eutrophication) of these, environment standards and effluent standards have been laid down by the Environment Agency. Here, the total nitrogen and total phosphorus in the water of a river were measured using the method laid down in the factory wastewater test method (JIS K0102).

References
JIS K0102 Factory wastewater test method

■Measuring Instrument
High pressure boiling instrument sterilizer : KT2-2322
Spectrophotometer:　　　　　　　　　: UV-1600 PC

Standard Sample	Concentration (ppm)	Absorbance
1	0.0000	0.000
2	1.0000	0.205
3	5.0000	1.023

Chart 5 Standard sample measuring results A for total nitrogen

Standard Sample	Concentration (ppm)	Absorbance
1	0.0000	0.000
2	0.5000	0.340
3	1.0000	0.696

Chart 6 Standard sample measuring results B for total phosphorus
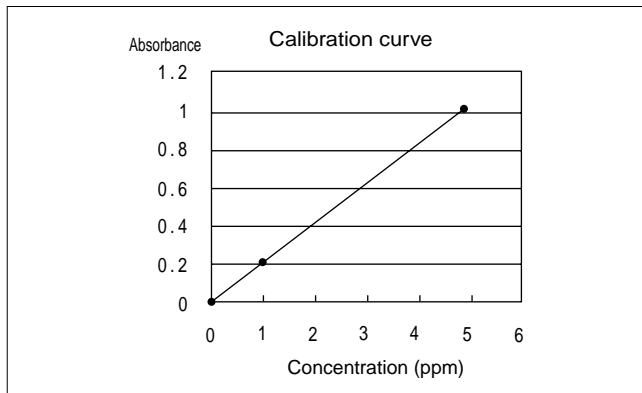
Fig. 31 Calibration curve for total nitrogen
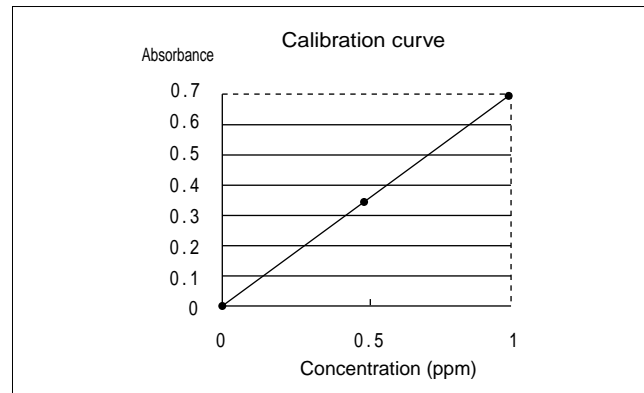
Fig. 32 Calibration curve for total phosphorus

Sample No.	Concentration (ppm)	Absorbance
1	0.431	0.088
2	0.563	0.115
3	0.504	0.103
4	1.042	0.213
5	0.884	0.181
6	0.892	0.183
7	0.892	0.183
8	5.115	1.047

Chart 7 Total nitrogen measuring results A

Sample No.	Concentration (ppm)	Absorbance
1	0.0138	0.007
2	0.0167	0.009
3	0.181	0.124
4	0.179	0.122
5	0.671	0.465
6	0.692	0.479
7	0.177	0.121
8	0.179	0.122

Chart 8 Total phosphorus measuring results B

2.9 Analysis of Non-organic Components in River Water (1) — *ICP-MS*

■Explanation

The testing methods of the Environment Standard item have been amended, so that the ICP mass spectrometry (ICP-MS) method has been adopted for analysis of non-organic metal elements. ICP-MS is noted for the feature of being able to handle many of the chemical elements with a technique that simultaneously analyzes with high sensitivity. Here, an example of river water analysis using the inductively coupled plasma mass spectrometer ICPM-8500 will be introduced. As river water is a source of tap water, it is one of the most commonly tested and important samples among environment samples. In this test, quantitative analysis of standard substances in river water JAC0031 and JAC0032 (Japan Society for Analytical Chemistry Approval) was performed.

References

(1) Partial amendment of Ministerial ordinance related to water quality standard for drinking water and Water Supply Law Operation Regulations, etc., introduced on December 21, 1992
(2) Revision of Water Quality Pollution Prevention Law, etc, introduced on March 8, 1993

■Pretreatment

Nitric acid was added to 50mL of sample, boiled for approximately 10 minutes over a hot plate, cooled, measured up to 50mL with ultra purified water, and stirred thoroughly.

■Analytical Conditions

Instrument : ICPM-8500
High-frequency : 27.12MHz
High-frequency output : 1.2kW
Cooling gas : Ar 7.0L/min
Plasma gas : Ar 1.5L/min
Carrier gas : Ar 0.7L/min
Sample induction unit : Coaxial nebulizer/water cooling chamber (5˚C)
Sample suction rate : 0.4mL/min
Ion induction system : Pt type sampling cone
: Pt type skimmer cone

Element	Mass Number	River Water Standards JAC 0031 (without addition)			River Water Standards JAC 0032 (added)			Detection Limits
		Measured Value	Guaranteed Value	Recovery (%)	Measured Value	Guaranteed Value	Recovery (%)	
B	11	8.6	9.1 ± 0.5	95	57.8	59 ± 2	98	0.004
Al	27	13.4	13.4 ± 0.7	100	62.7	61 ± 2	103	0.002
Cr	52	0.16	0.14 ± 0.02	111	10.1	10.1 ± 0.2	100	0.006
Mn	55	0.43	0.46 ± 0.02	93	5.4	5.4 ± 0.1	100	0.003
Ni	60	0.2	—	—	10.1	10.2 ± 0.3	99	0.003
Cu	63	0.86	0.88 ± 0.03	98	10.2	10.5 ± 0.2	97	0.003
Zn	66	0.74	0.79 ± 0.05	94	10.9	11.3 ± 0.4	96	0.001
As	75	0.27	0.28 ± 0.04	98	5.7	5.5 ± 0.3	104	0.005
Se	77	0.13	(0.1)	—	5.2	5.2 ± 0.3	100	0.03
Cd	114	0.005	(0.003)	—	1.06	1.0 ± 0.02	106	0.001
Pb	208	0.029	0.026 ± 0.003	112	10.3	9.9 ± 0.2	104	0.001

Chart 9 River water analysis results (ng/mL)

Unit: ng/mL
( ): Referencial value
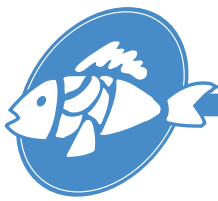
2.9 Analysis of Non-organic Components in River Water (2) — *ICP-MS*
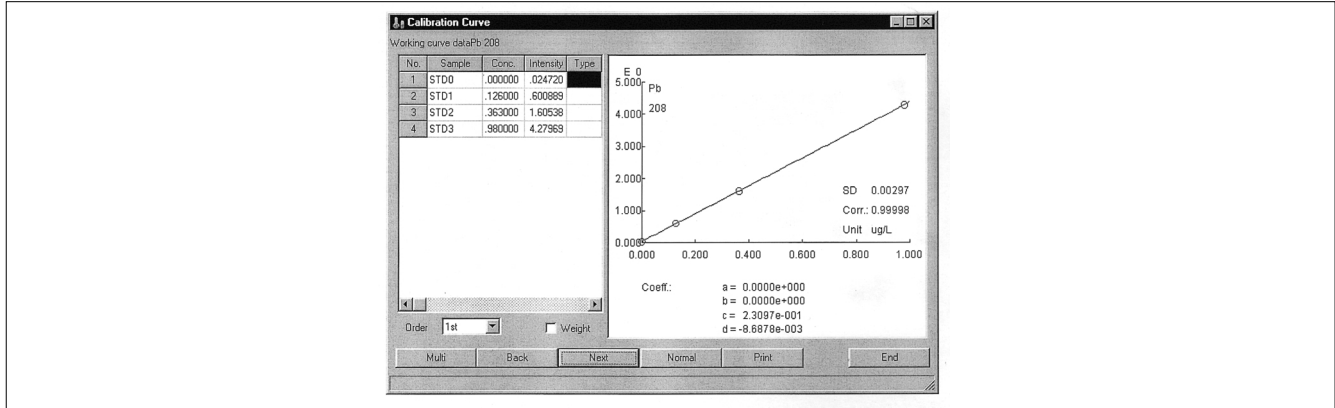
Fig. 33 Pb calibration curve
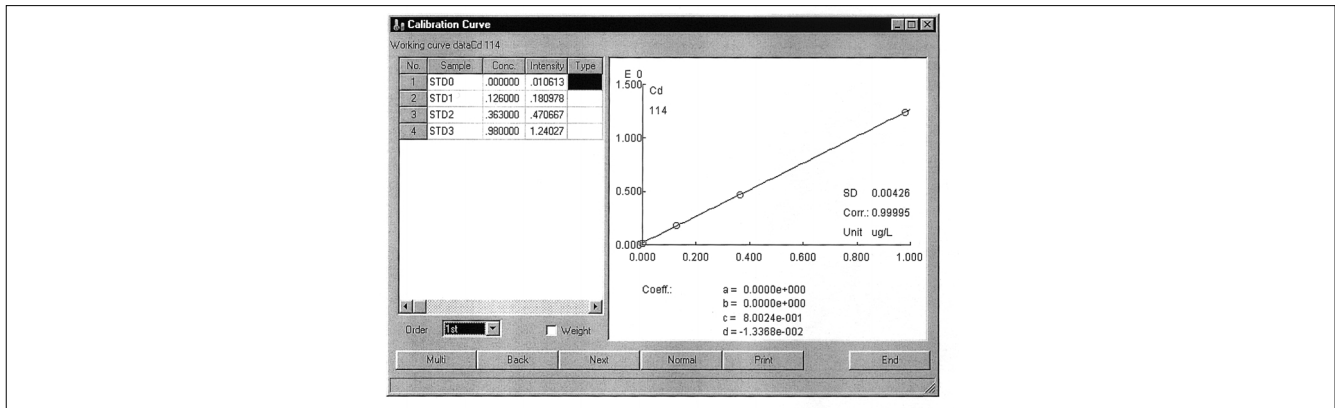
Fig. 34 Cd calibration curve
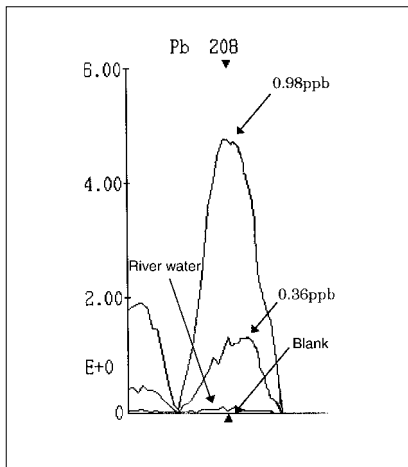
Fig. 35 Pb 208 mass spectra
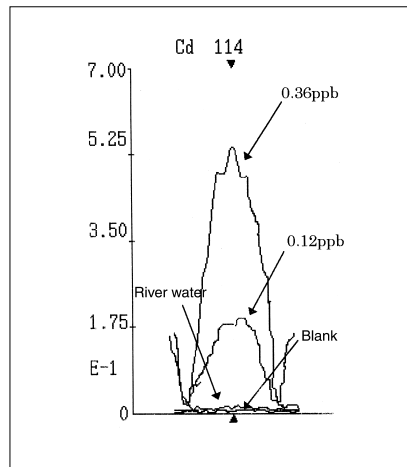
Fig. 36 Cd 114 mass spectra
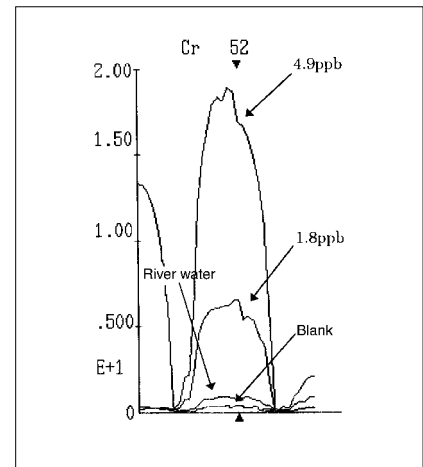
Fig. 37 Cr 52 mass spectra

2.10 Analysis of Anions in Hot Spring Water — *Ion Chromatograph*

■Explanation

This shows an analysis example for non-organic anions and cations in hot spring water.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Column : Shim-pack IC-A1
Mobile phase : 6.0mM boric acid
      1.8mM mannitol
      7. 5mM Tris (hydroxymethyl)
      aminomethane (pH 7.9)
Flow rate : 1.5mL/min
Temperature : 40°C
Detector : Electric conductivity detector

■Peaks
1 HCO_3^-
2 Cl^-
3 NO_3^-
4 SO_4^{2-}
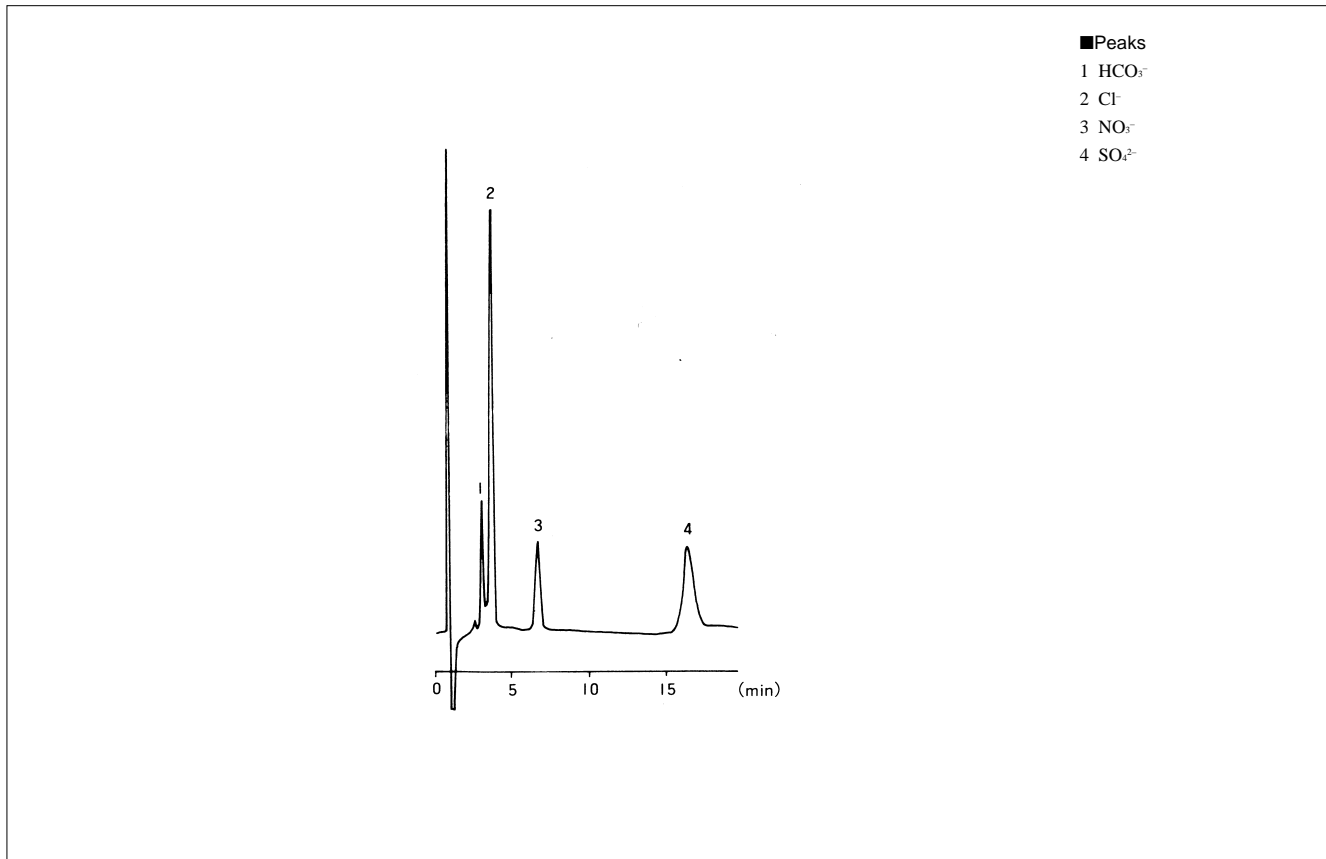
Fig. 38 Analysis of hot spring water

Environment Water

2.11 Analysis of Cations in Hot Spring Water (1) — *Ion Chromatograph*

■Pretreatment
Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions
Column   : Shim-pack IC-C1
Mobile phase : 5mM of nitric acid
Flow rate   : 1.5mL/min
Temperature : 40˚C
Detector   : Electric conductivity detector

■Peaks
1 Na^+
2 NH_4^+
3 K^+
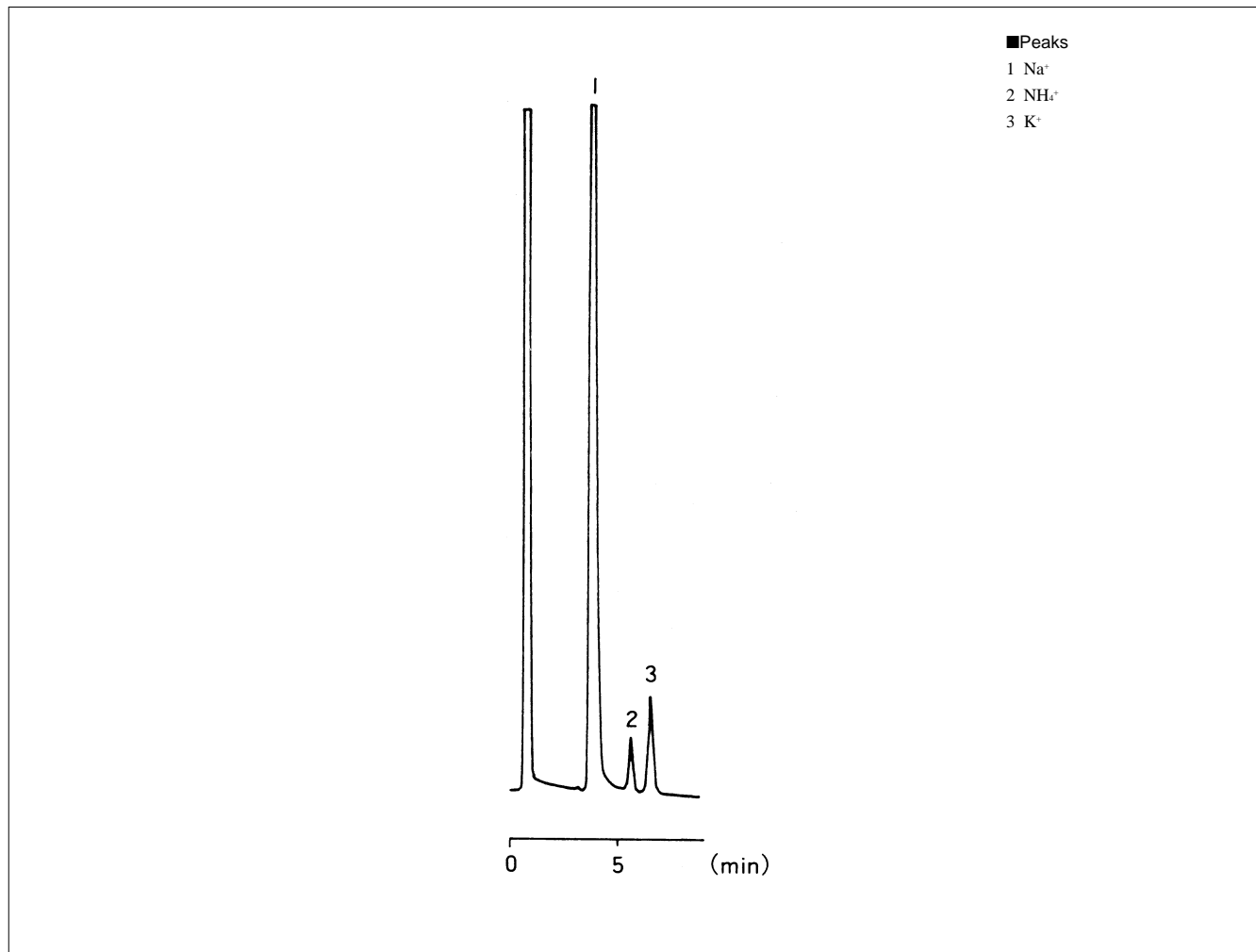
Fig. 39 Hot spring water

2.11 Analysis of Cations in Hot Spring Water (2) — *Ion Chromatograph*

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Column   : Shim-pack IC-C1
Mobile phase : 4mM of tartaric acid, 2mM ethylenediamine
Flow rate   : 1.5mL/min
Temperature : 40°C
Detector   : Electric conductivity detector

■Peaks
1 Mg^{2+}
2 Ca^{2+}
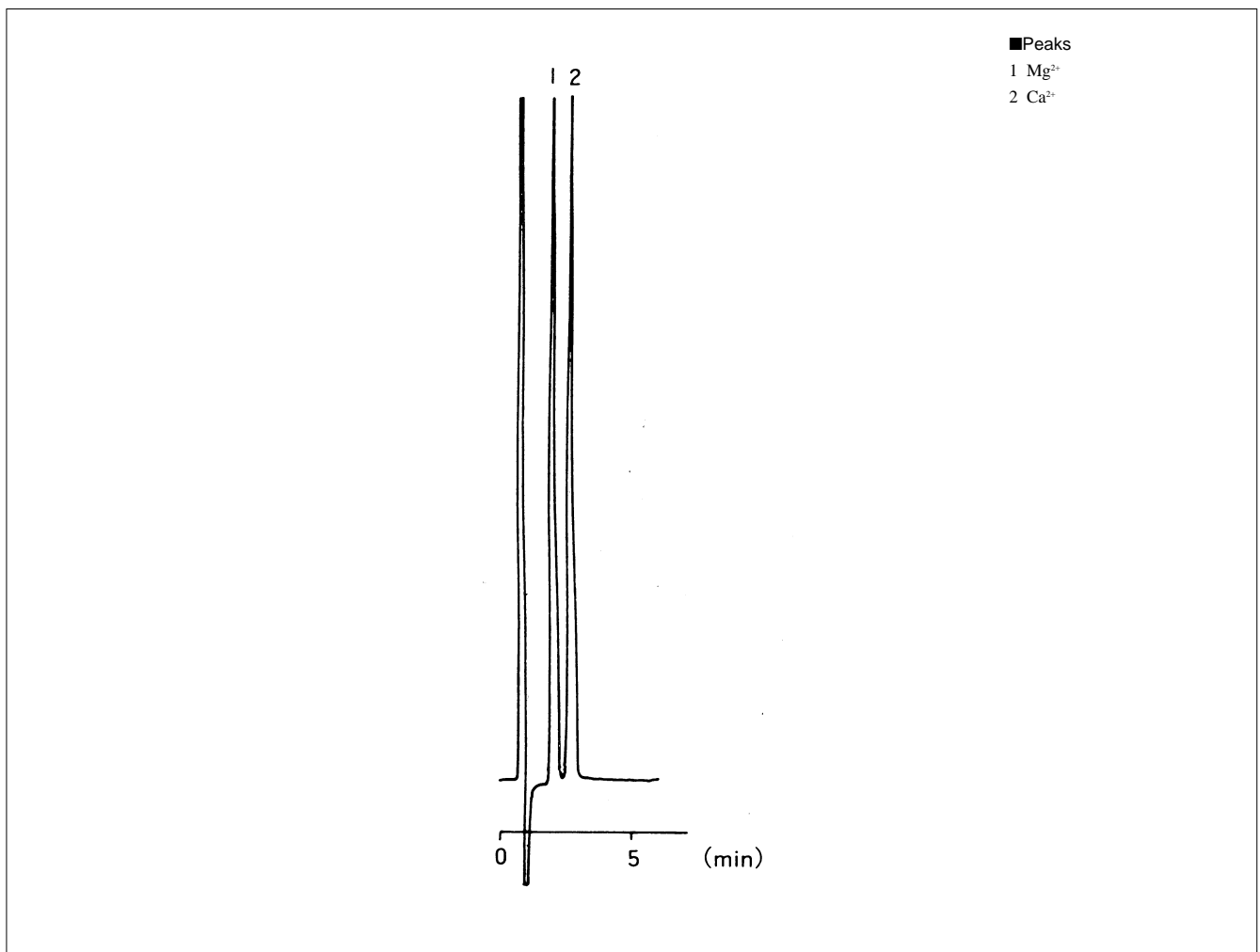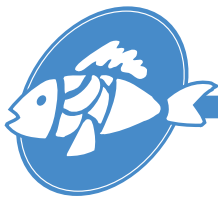
Fig. 40 Hot spring water

2.12 Analysis of Anions in Rainwater – *Ion Chromatograph*

■Explanation

In recent years, the acidification of rainfall has progressed, and is adversely affecting ecosystems. The main cause of acid rain is thought to be that SOx and Nox converts to H_2SO_4, HNO_3, etc., in Rainwater. The pH level in Rainwater is set as the criteria for acid rain; however, as pH is standardized from the equivalent weight relationship of acidic elements and alkali elements, the detailed causes and affects of acid rain cannot be fully determined from the pH value alone. As shown in chart 10, the Environment Agency have designated 8 elements as analysis items. An ion chromatograph – which can handle simultaneous multiple ion analysis - is suitable for the analysis of these items.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument	: Ion chromatograph
Column	: Shim-pack IC-A3 (150mm ✕ 4.6mm I.D.)
	: 8.0mM p-hydroxybenzoic acid,
Mobile phase	3.2mM Bis-Tris*
	: 1.5mL/min
Flow rate	: 40˚C
Temperature	: Electric conductivity detector
Detection	: Bis (2-hydroxyethyl) iminotris
*Bis-Tris	(hydroxymethyl) methane

Ion	Sample Amt mℓ	Conc Allowed µg∕mℓ
SO_4^{2-}	2	0.06
NO_3^-	2	0.05
Cl^-	2	0.01
Na^+	2	0.03
NH_4^+	2	0.02
K^+	2	0.02
Mg^{2+}	2	0.01
Ca^{2+}	2	0.02

Chart 10 Rainwater element analysis items in Environment Agency Studies

■Peaks
1 Cl^- (64.1µg/L)
2 NO_2^- (21.1µg/L)
3 NO_3^- (827.8µg/L)
4 SO_4^{2-} (739.6µg/L)
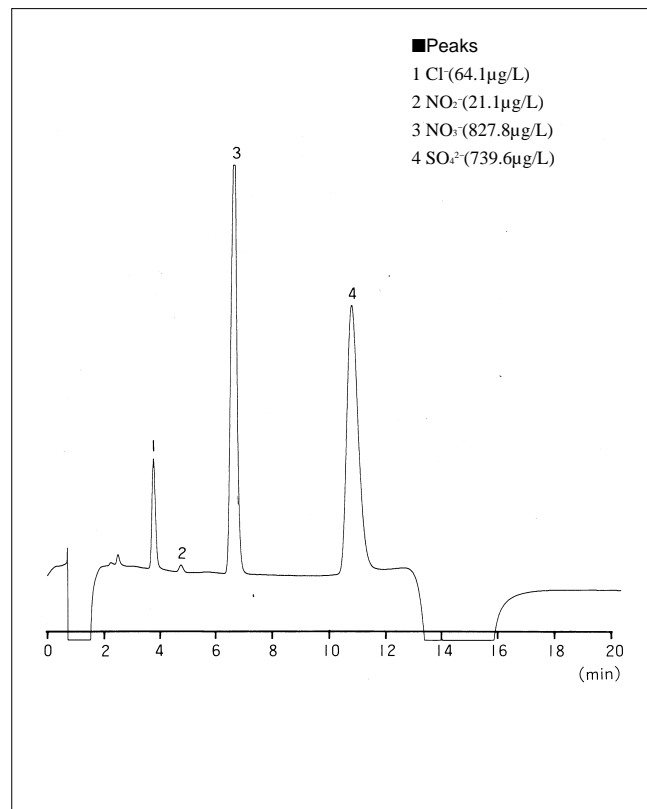
Fig. 41 Rainwater

2.13 Analysis of Cations in Rainwater — *Ion Chromatograph*

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : Ion chromatograph
Column   : Shim-pack IC-C3 (100mm ✕ 4.6mm I.D.)
Mobile phase : 2.5mM oxalic acid
Flow rate   : 1.0mL/min
Temperature : 40˚C
Detection   : Electric conductivity detector

■Peaks
1 Na^+(420µg/L)
2 NH_4^+(139µg/L)
3 K^+(554µg/L)
4 Mg^{2+}(158µg/L)
5 Ca^{2+}(178µg/L)
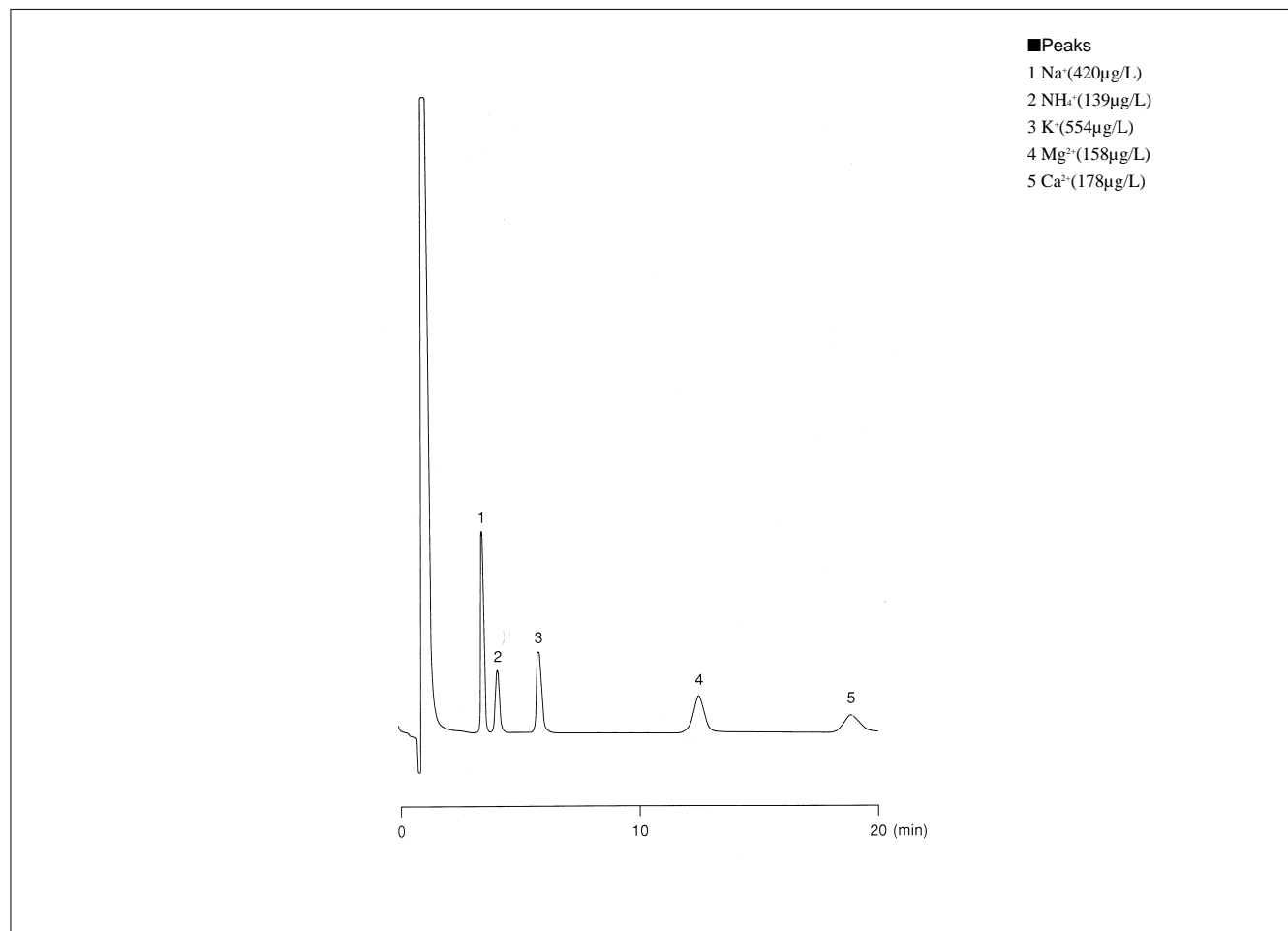
Fig. 42 Analysis of Rainwater

2.14 Analysis of Anions in Rainwater — *PIA-1000*

■Explanation

This is an example of Rainwater analysis using the personal ion analyzer PIA-1000.

■Pretreatment

Filtering through a membrane filter (0.45 μm) for ion chromatography

■Analytical Conditions

Instrument   : PIA-1000
Column   : Shim-pack IC-A3(S)
Mobile phase : PIA-1000 dedicated negative ion analysis
                 mobile phase, IC-MA3-1
Flow rate   : 0.2mL/min

■Peaks
1 F^-(0.043mg/L)
2 Cl^-(17.93mg/L)
3 Br^-(0.067mg/L)
4 NO_3^-(2.440mg/L)
5 SO_4^{2-}(7.715mg/L)
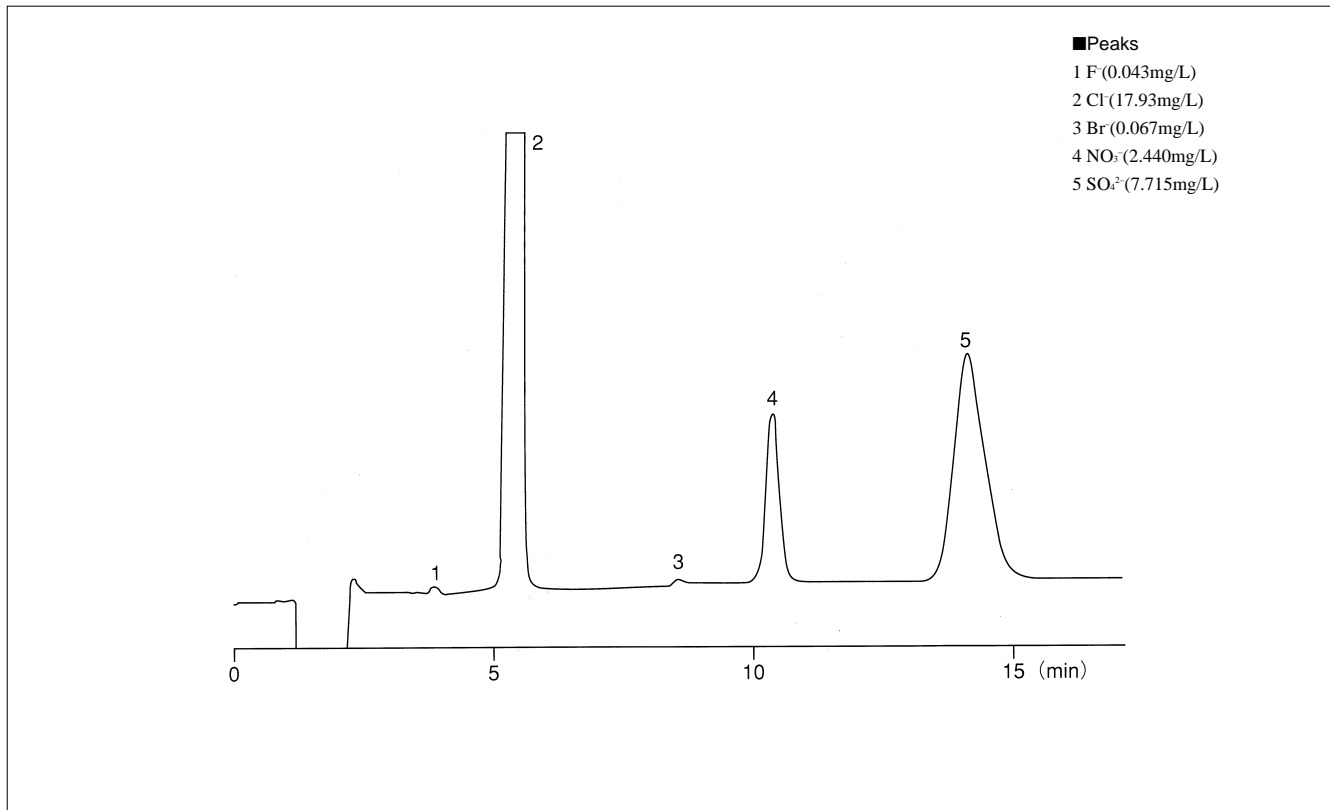
Fig. 43 Rainwater

2.15 Analysis of Cations in Rainwater — *PIA-1000*

■Explanation
This is an example of rainwater analysis using the personal ion analyzer PIA-1000.

■Pretreatment
Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions
Instrument : PIA-1000
Column : Shim-pack IC-C3(S)
Mobile phase : PIA-1000 dedicated positive ion analysis mobile phase, IC-MC3-1
Flow rate : 0.2mL/min
Temperature : 35°C

■Peaks
1 Na^+(9.673mg/L)
2 NH_4^+(0.607mg/L)
3 K^+(0.638mg/L)
4 Mg^+(1.196mg/L)
5 Ca^{2+}(1.294mg/L)
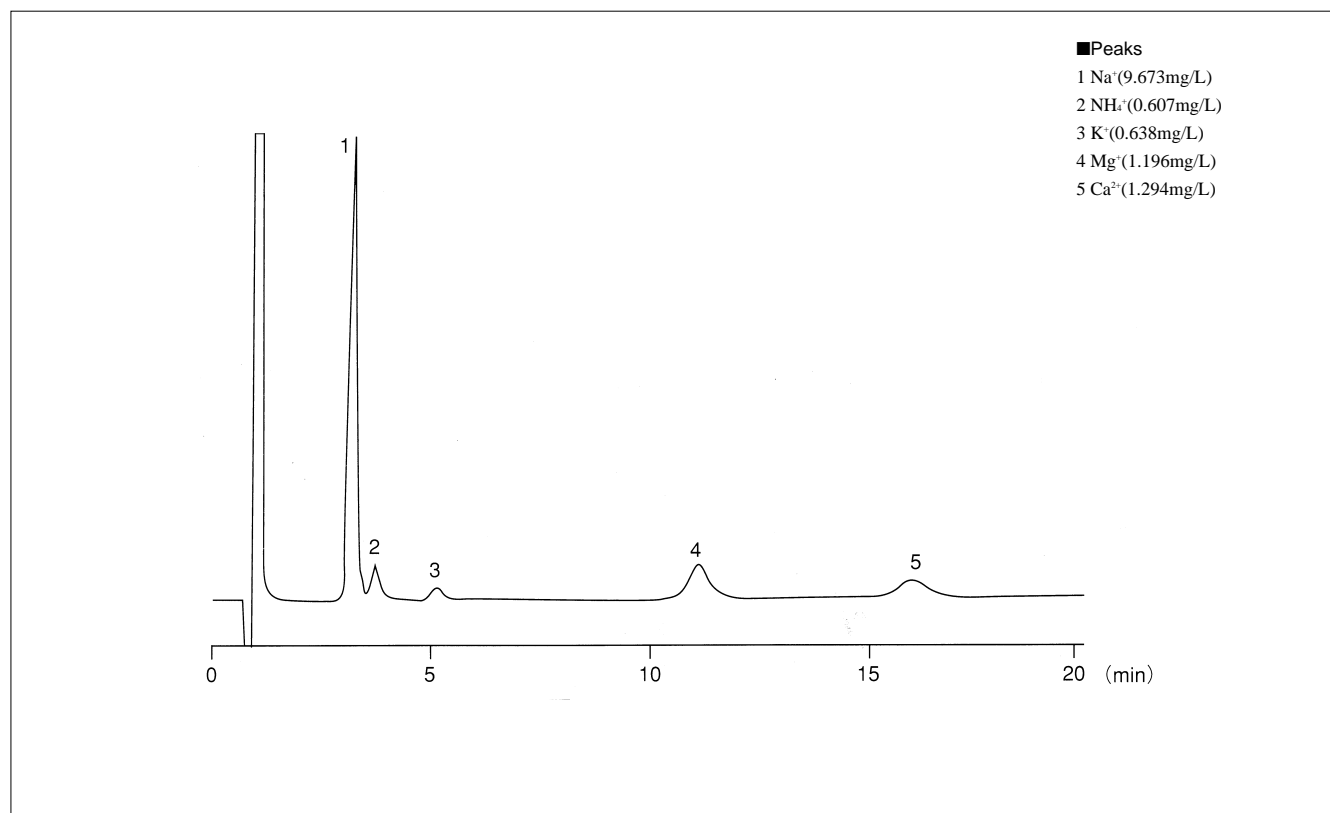
Fig. 44 Rainwater

Environment Water

2.16 Analysis of Sulfurous Acid Ions in Rainwater — HPLC

■Explanation

Sulfurous acid is contained in factory exhaust and vehicle exhaust, and is one of the substances that cause acid rain. The Rankine method and ion chromatograph method are known as quantitative analysis methods for sulfurous acid; however, from the point of view of operability, sensitivity and measuring accuracy, both methods have problems. Here, a newly developed derivatizing fluorometric detector is introduced as an alternative.

With this method, the sulfurous acid is made to react with formaldehyde, induced into a stable hydroxy methansulfonic acid, and decomposition controlled through the sample processing time and separation process. After separation, the sample is made to react with the existing orthophthalaldehyde (OPA) and primary amine, induced into an isoindole derivative, and the target element fluorescently detected. As a result, unstable sulfurous acid compounds can be quantitatively analyzed at a high level of accuracy and high sensitivity.

■Pretreatment

Add citric acid (sodium) (10 mM) containing formaldehyde (10 mM) buffer solution (pH 4.4) to an equal amount of rainwater sample immediately after it has been collected, stir well, let it stand for a minute, then inject.

Reference

Masatoshi Takahashi, Masayuki Nishimura, Morimasa Hayashi, Shimadzu Review Vol. 54, No. 4 (1997)

■Analytical Conditions

Instrument : LC-VP system

(Separation Conditions)
Column : Shim-pack IC-A1 (100mm ✕ 4.6mm I.D.)
Mobile phase : 10mM of citric acid (ammonium) buffer solution (pH 3.2)
Flow speed : 1.0mL/min
Temperature : 50°C

Reaction reagent : (A) 10mM of methanol containing orthophthalaldehyde
(B) 500mM boric acid (sodium) buffer solution (pH 9.2)
(A)/(B) = 1/4 (v/v)
Reaction reagent flow rate : 0.5mL/min
Temperature : 50°C
Detection : fluorometric detector Ex = 320nm Em = 390nm

1,2: pumps,3: injector, 4: column oven,
5: fluorescence detector, 6: data processor, 7: reactor,
8: column, 9:mobile phase, 10: reagent.
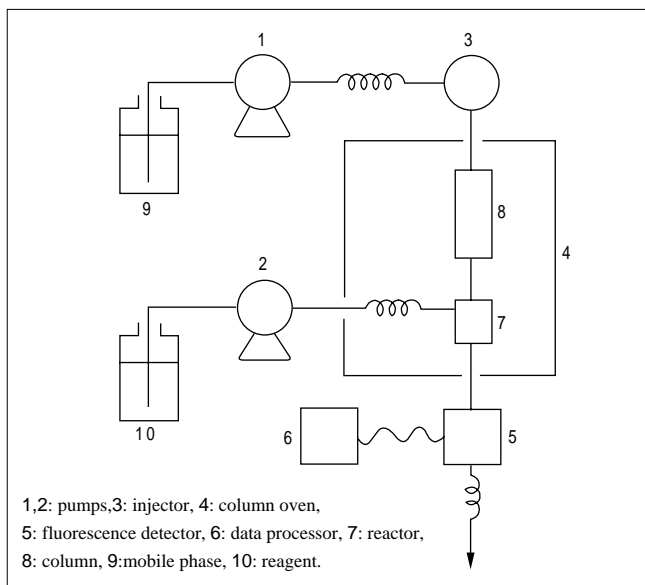
Fig. 45 Instrument configuration

■Peaks
1 SO₃²⁻(210pmol/ml)
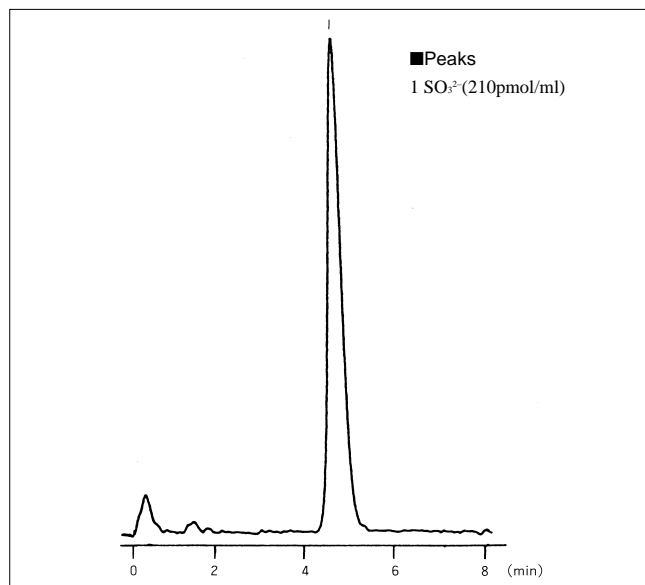
Fig. 46 Rainwater

2.17 Analysis of Anions in Snow Water — *Ion Chromatograph*

■Explanation

Snow water shows acidification tendencies similar to Rainwater, and is having an adverse affect on ecosystems. In recent years, there have been reports stating that snow crystals have deformed into T-shaped and bar-shaped crystals due to sulfur oxide in exhaust smoke and exhaust gas. This comes about from foreign matter in the atmosphere acidifying snow, which hinders the formation of snow crystals causing them to become deformed. This phenomenon has tended to increase from 1993 onward.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : Ion chromatograph
Column : Shim-pack IC-A1 (100mm ✕ 4.6mm I.D.)
Mobile phase : 2.5mM of phthalic acid, 2.4mM of Tris (hydroxymethyl) aminomethane (pH 4.0)
Flow rate : 1.5mL/min
Temperature : 40°C
Detection : Electric conductivity detector

■Peaks
1 Cl^-
2 NO_3^-
3 SO_4^{2-}
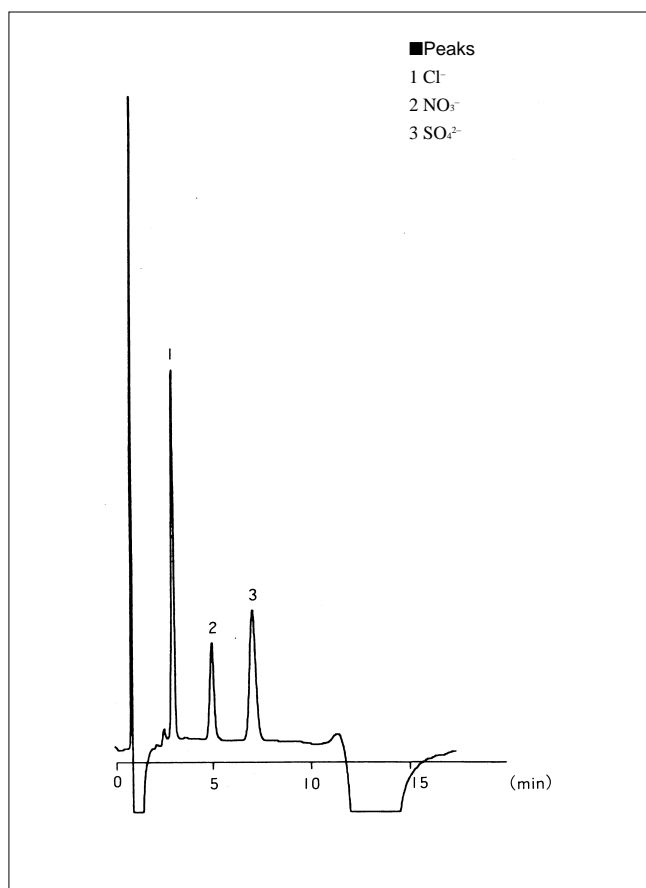
Fig. 47 Analysis of snow water

■Peaks
1 Cl^-
2 NO_3^-
3 SO_4^{2-}
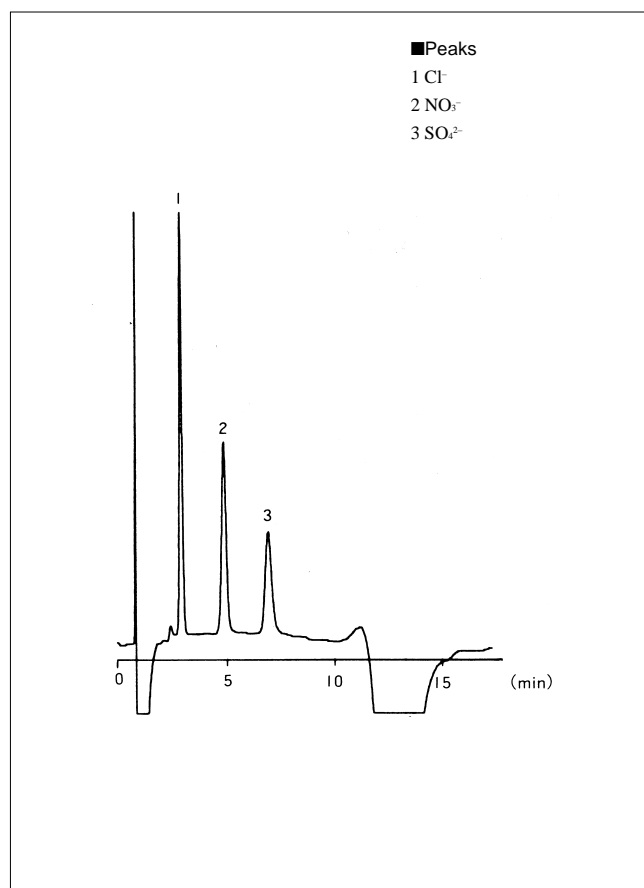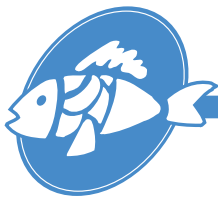
Fig. 48 Analysis of snow water

2.18 Analysis of Anions in Sea Water — *HPLC*

■Explanation

Nitrogen atoms in seawater are said to exist as ions of which nearly all are composed from either NO_2^-, NO_3^-, or NH_4^+. Ion chromatography is well configured as identification analysis method for nitrogen in seawater as it is able to quantify each of the above ions separately. However, conventional ion chromatography using electric conductivity detection has problems accurately quantifying these ions because of the influence of sodium and chloride ions, which exists in vast amounts in seawater. NO_2^- and NO_3^- absorb comparatively well in the ultraviolet region, whereas the ions of Cl^- and SO_4^{2-}, etc., are hardly able to absorb any ultraviolet, so an ultraviolet absorption detection method is a well-suited method for analyzing NO_2^- and NO_3^-. In this case, phosphoric acid buffer solution, which has little ultraviolet absorption is used as the mobile phase for analysis, and detection is conducted at the 210nm level. Also, under these conditions, bromide ions can be analyzed at high accuracy.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : LC-VP system
Column : Asahipak NH2P-50 (250mm ✕ 4.6mm I.D.)
Mobile phase : 10mM of phosphoric acid (sodium) buffer solution (pH 6.9) containing 150mM of sodium perchlorate
Flow rate : 0.8mL/min
Temperature : 35°C
Detection : UV-VIS detector 214nm

■Peaks
1 NO_2^-
2 Br^-
3 NO_3^-
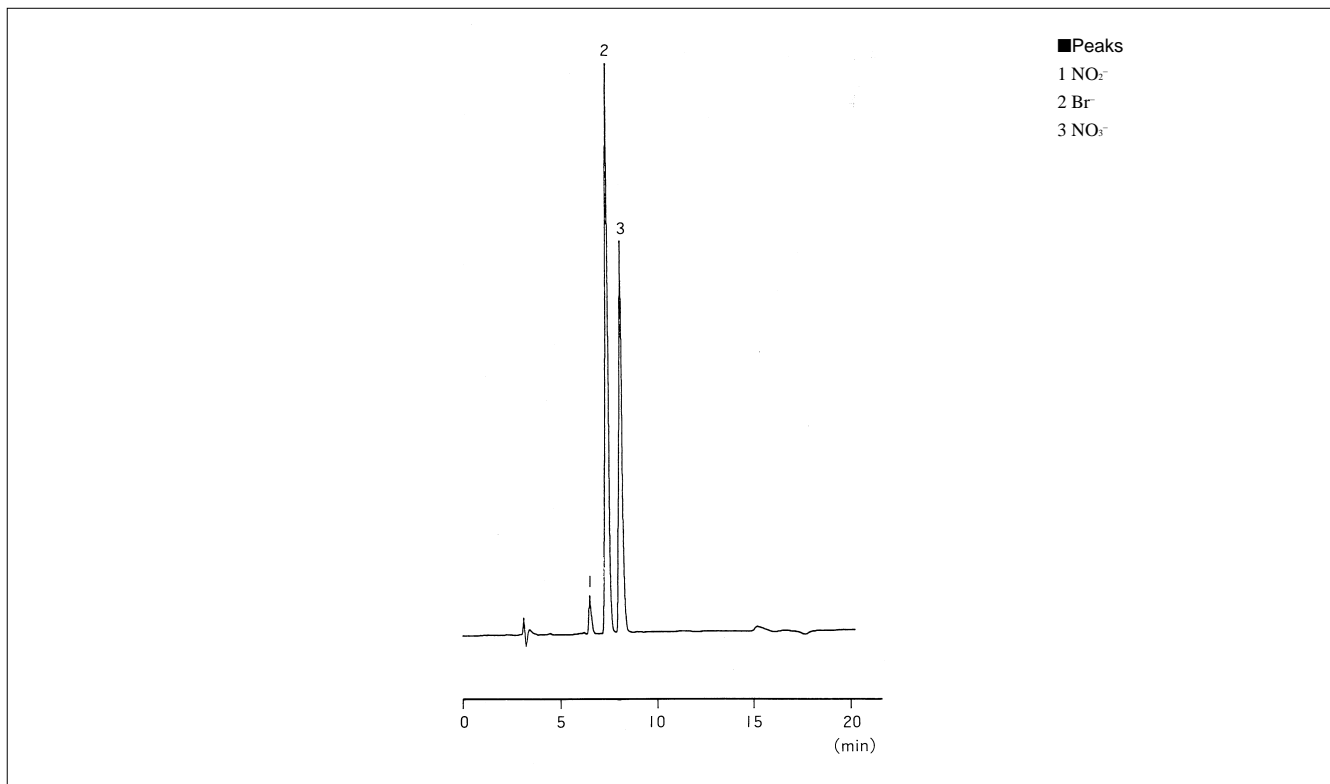
Fig. 49 Seawater

2.19 Analysis of Ammonia Ions in Sea Water — *HPLC*

■Explanation

NH$_4^+$ reacts with orthophthalaldehyde (OPA) to form fluorescent chromaphore. When this reaction is applied to analysis of seawater, the various ions that coexist do not influence analysis, thus enabling highly accurate quantifying of NH$_4^+$. The following is an example of NH$_4^+$ analyzed in seawater using an amino acid analysis system.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument	: LC-VP system
Column	: Shim-pack ISC-07/S1504Na
Trap column	: Shim-pack ISC-30/S1504Na
Mobile phase	: 0.60 N of sodium citrate, 0.20 M of boric acid (pH 10.0, adjusted with NaOH solution)
Flow rate	: 0.3mL/min
Temperature	: 55˚C
Reaction reagent	: OPA solution
Reaction reagent flow rate	: 0.3mL/min
Detection	: Fluorometric detector Ex = 348nm Em = 450nm

■Peaks
1 NH$_4^+$
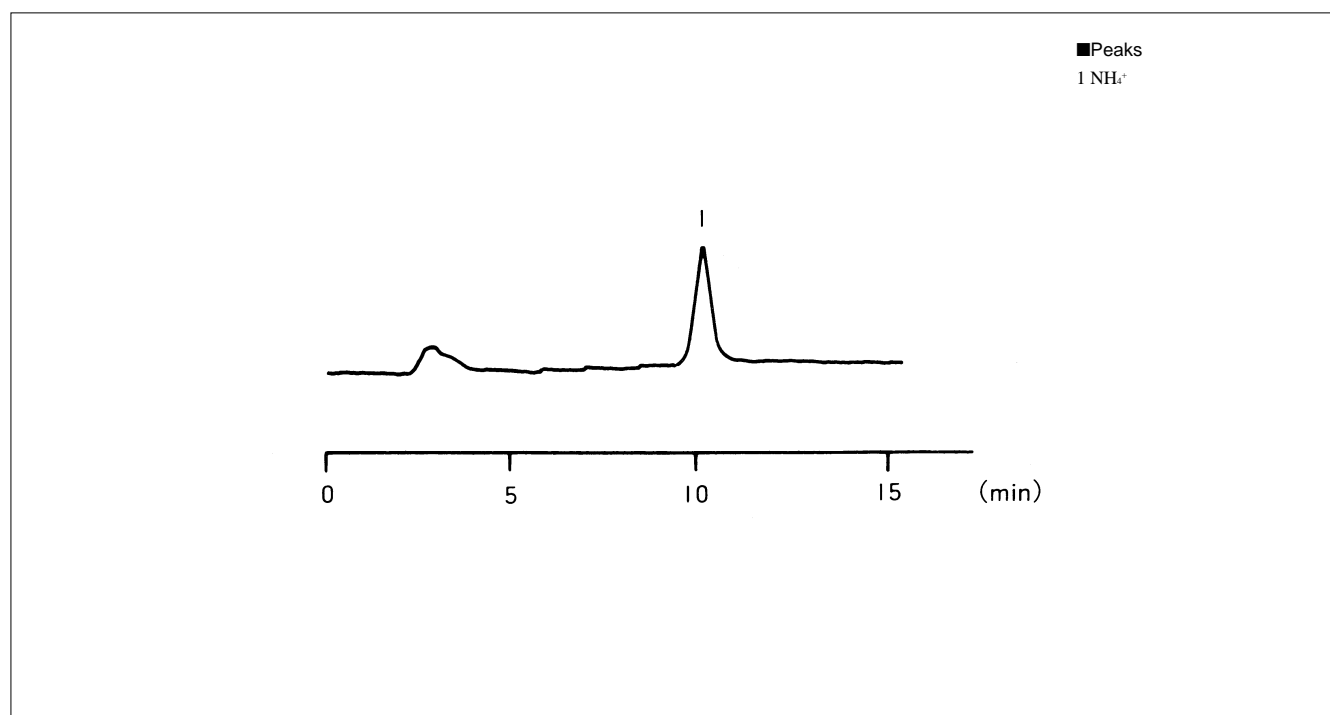
Fig. 50 Seawater

2.20 Analysis of Fluoride Ions in Sea Water (1) — *Ion Chromatograph*

■Explanation

When analyzing fluoride ions with an ion chromatograph, chloride ions - that are amply contained in seawater - interfere with analysis, and prior selective removal of these chlorine ions is required using a silver-type cation replacement cartridge. However, this method causes a drop in the collection rate, and accurate analysis cannot be performed. Here, the diffusive separation method is effective in resolving this problem. A combination of the diffusive separation method and ion chromatography was investigated by professor Okutani et al of the Nihon University, and it was found that Shim-pack IC-A3 column has the most suitable features for this method, so now fluorine ions of 1 ppm or less in seawater can be measured with high accuracy.

■Pretreatment

See next item for details.

■Analytical Conditions

Instrument : Ion chromatograph
Column : Shim-pack IC-A3 (150mm ✕ 4.6mm I.D.)
Guard column : Shim-pack IC-GA3 (10mm ✕ 4.6mm I.D.)
Mobile phase : 8.0mM p-hydroxybenzoic acid, 3.2mM Bis-Tris*
Flow rate : 1.5mL/min
Temperature : 40°C
Detection : Electric conductivity detector
*Bis-Tris : Bis (2-hydroxyethyl) iminotris (hydroxymethyl) methane

■Peaks
1 F⁻(1.15mg/L)

Fig. 51 Fluoride ions in seawater

2.20 Analysis of Fluoride Ions in Sea Water (2) — *Ion Chromatograph*

Reference Example 1
(Diffusive Separation Method)

Diffusive separation uses an acrylic resin diffusion container configured of a box within a box, with the inner box being able to divide the outer box when the whole container is tilted on its side. The diagrams on the right depict the diffusion container from overhead and side view. When diffusion is actually performed, first the outer box compartments (A and B) divided by the inner box are separately filled with 10mL of sample and 10mL of reaction solution (hexamethyldisiloxane saturated 2.7NHClO$_4$), the inner box (C compartment) is filled with 10mL of absorption solution (0.1N NaOH). After sealing the lid on the container, the sample and reaction solution of the outer box are mixed, and left to stand for a night so that the fluoride ions will be quantitatively absorbed into the absorption solution. As the absorption solution has strong alkalinity, it is neutralized in H type ion replacement cartridge column before being injected into the ion chromatograph.

Seawater
Absorption solution   Reaction solution
(0.1N NaOH)
[hexamethyljishirokisan saturated 2.7NHCℓO$_4$]

A

C

B

Mixture of seawater and reaction solution
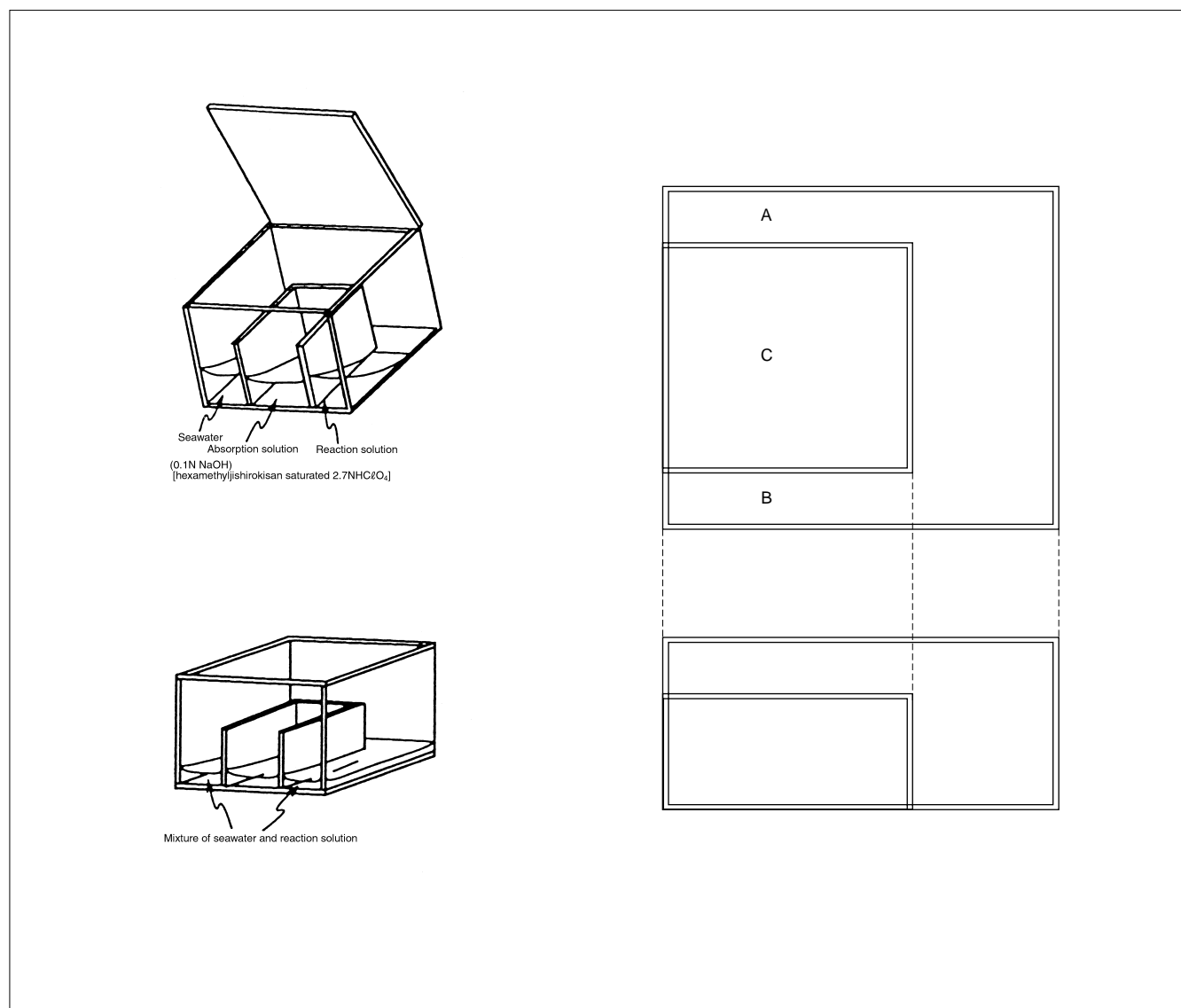
Fig. 52 Diffusive separation container

34
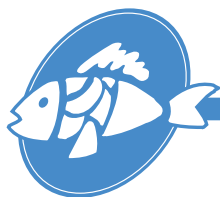
2.21 Analysis of Microcystin in Blue-green Algae (1) — *HPLC*

■Explanation

In recent years, social problems are developing as eutrophication takes a stronger grip in lakes such as Lake Biwa and Lake Kasumigaura along with the phenomenon know as blue-green algae. Toxins are manufactured in some of the blue-green algae, which form blue-green algae, and there have been examples overseas of cattle dying after drinking lake water affected by blue-green algae. Microcystin is a typical toxin (liver toxin) contained in blue-green algae, and there are said to be more than 50 kinds of microcystins in the circular peptides made from the 7 amino acids. The representative types found in Japanese lakes are microcystin LR, YR, and RR.

References
(1) K.I.Harada, et al.: Toxicon, 26(5), 433-439, 1988
(2) K.I.Harada, et al.: J. Chromatogr., 448, 275-283, 1988

■Pretreatment

Microcystin is extracted from blue-green algae using acetic acid (5%). This is stirred and centrifugally separated in 3 repeated operations, then this is cleaned up in accordance with the supernatant. The cleanup operation involves passing the supernatant through an ODS cartridge for solid-phase extraction to adsorb the elements, washing it, then solve it out using methanol.

■Analytical Conditions

Instrument   : LC-VP system
Column   : STR ODS-II (150mm ✕ 6.0mm I.D.)
Mobile phase : 50mM of sodium phosphate buffer
                   solution (pH 3.0)/methanol = 4/6 (v/v)
Flow rate   : 1.0mL/min
Temperature : 40℃
Detection   : UV-VIS Detector 240nm

	R1	R2	R3	R4
Microcystin LR	Leu	Arg	CH3	CH3
Microcystin YR	Tyr	Arg	CH3	CH3
Microcystin RR	Arg	Arg	CH3	CH3
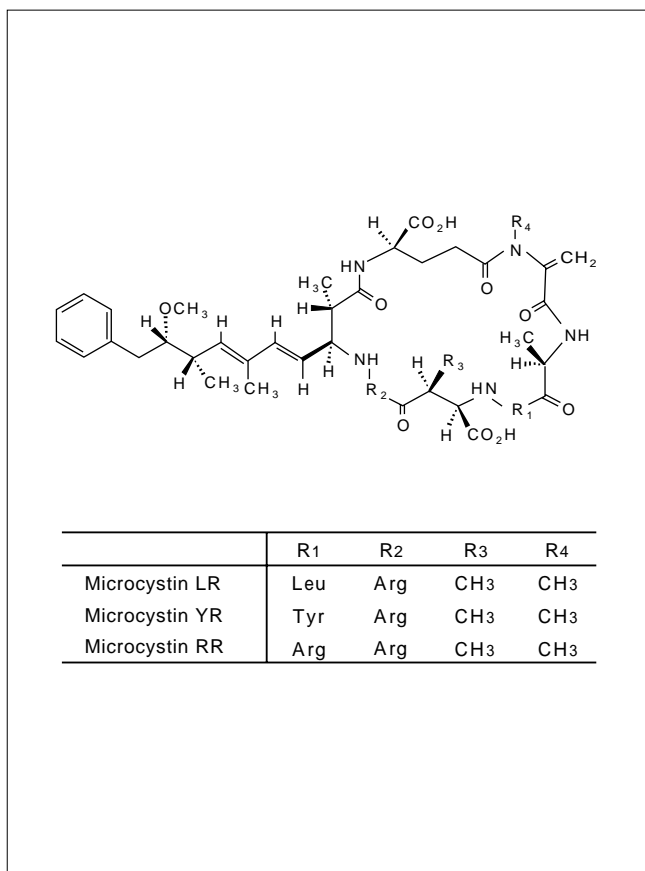
Fig. 53 Microcystin structure

Peaks
1. Microcystin RR
2. Microcystin YR
3. Microcystin LR
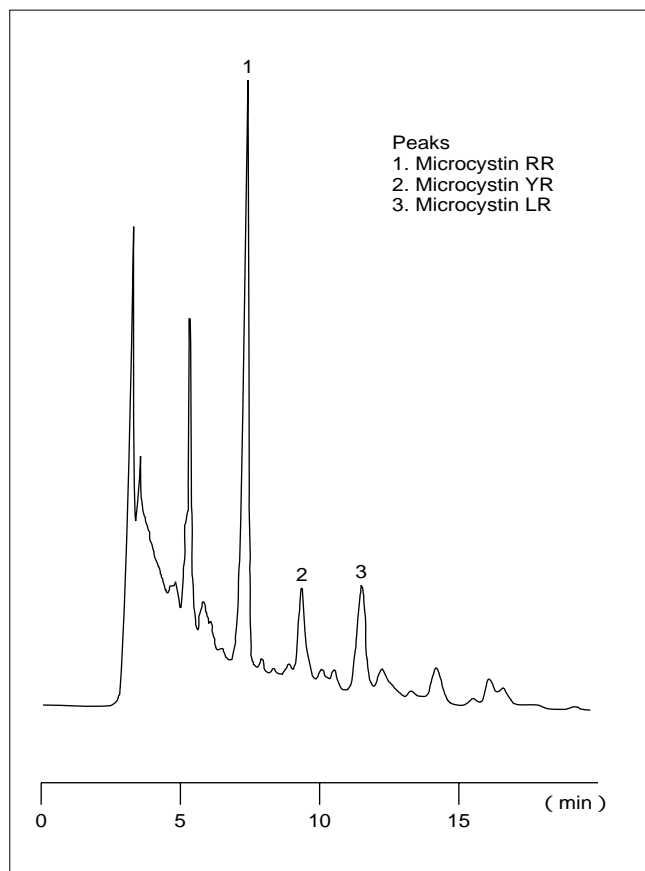
Fig. 54 Analysis of blue-green algae

2.21 Analysis of Microcystin in Blue-green Algae (2) — *HPLC*

Reference Example 1   **Pretreatment Method Flow Chart**

Blue-green algae
> Extraction of microcystin
> 1) 50mL of 5% acetic acid
> 2) Stir for 30 min
> 3) Centrifuge
> <Repeat operations 1) to 3) three times>

Supernatant
> Cleanup with solid-phase extraction method
> (Use Sep-Pak Plus tC18)
> 1) Wash cartridge with 20mL of methanol and 20mL of water
> 2) Liquid permeation of supernatant in cartridge at 10 to 20mL/min flow speed
>   (adsorb the microcystin)
> 3) Wash cartridge with 20mL washing liquid (water/methanol = 9/1)
> 4) Pour 2mL of methanol into cartridge to solve out microcystin

Solving out (2mL)

HPLC

Sample was provided by Mr. Kunimitsu Hitani of the Environmental Chemistry Division of the National Institute of Environmental Studies
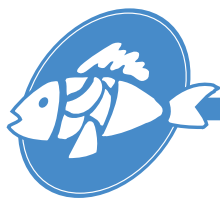
2.22 Analysis of Cyanogen Compounds by Chemical Classification (1) — HPLC

■Explanation

The Ministry of Health and Welfare changed the cyanogens item from a conventional "not to be detected" item to an item "to be detected" at "0.01mg/L or less" in accordance with new water quality standards being implemented in 1993. Also, targeted elements now include cyanogen chloride in addition to cyanogen ions. For quantifying these cyanogens, the conventionally regulated methods have been the colorimetric method and the ion electrode method using the pyridine pyrazolone method and the 4-pyridinecarboxylic acid pyrazolone method, but in the amended drinking water testing method (1993 version), high-speed liquid chromatography was newly added. This measuring method is easier than conventional methods, and has the merits of being highly sensitive and not easily affected by coexisting substances, and more than anything, the major feature of this method is that it can be used in analysis of chemical configuration identification. The high-speed liquid chromatography method listed in the drinking water testing method is a post column derivative method employing the 4-pyridinecarboxylic acid pyrazolone method to enable simultaneous analysis of three elements of cyanogen compounds (cyanogen ion, cyanogen chloride, and thiocyanic acid).

Quantitative Range:
0.001 or less to 0.2mg/L
Measuring accuracy is within CV 10% at the lower limit vicinity of quantification

References

Drinking Water Test Method & Explanation (Fiscal 1993 Volume) 239 - 245
Ministry of Health and Welfare, Environ. Health Bureau, Water Supply & Environ, Sanitation Dept. edition
Japan Water Works Association

■Peaks
1 Thiocyanic acid
2 Cyanogen
3 Cyanogen chloride
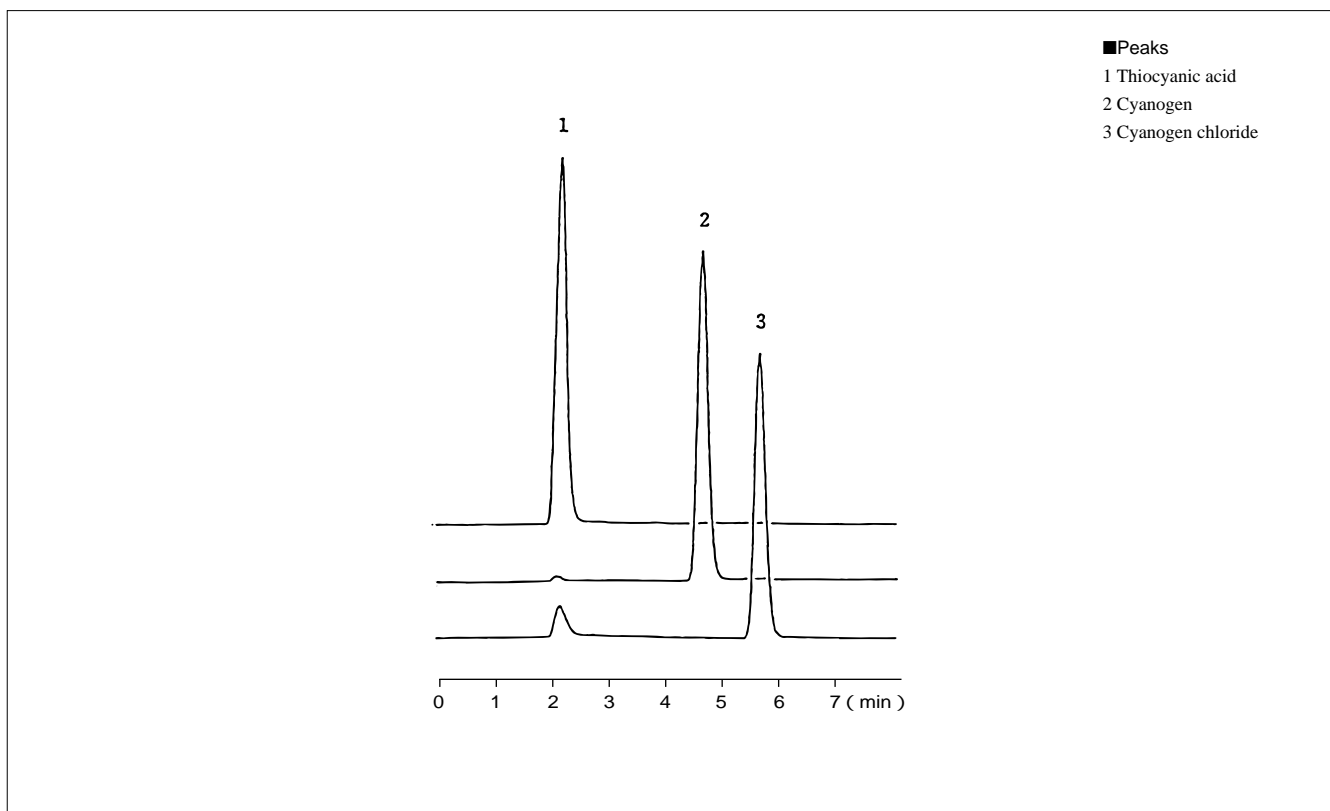
Fig. 55 Chromatogram of cyanogen compound standard samples

2.22 Analysis of Cyanogen Compounds by Chemical Classification (2) — HPLC

■Analytical Conditions

Instrument : LC-VP system
  (Separation Conditions)
Column : Shim-pack AMINO-Na (100mm ✕ 6.0mm I.D.)
Mobile phase : 10mM of tartaric acid (sodium) buffer solution (pH 4.2)
Flow rate : 0.6mL/min
Temperature : 50˚C

(Detection Conditions) Post column derivative method
[Chlorination]
Reagent solution : 200mM of phosphoric acid (sodium) buffer solution containing 2mM of chloramine T (pH 6.8)
Flow rate : 0.3mL/min
Reaction unit : SUS coil (2m ✕ 0.3mm I.D.)
Temperature : 100˚C
[Coloring]
Reagent solution : a mixed solution of ethanol solution of 100mM of 1-phenyl 7-3-methyl-5-pyarozolone and water solution of 20mM of pyridine-4-carboxylic acid (1/3, V/V)
Flow rate : 0.3mL/min
Reaction unit : SUS coil (2m ✕ 0.5mm I.D.)
Temperature : 100˚C
Cooling unit : SUS coil (2m ✕ 0.3mm I.D.)
Detector : UV-VIS detector 638nm

Apparatus;
 1 : Pump for mobile phase
 2 : Sample injector
 3 : Column oven
 4 : Column
 5 : Pump for reagent
 6 : Reaction chamber
 7 : Reactor (0.3mm ✕ 2m)
 8 : Pump for reagent 2
 9 : Reactor (0.5mm ✕ 2m)
10 : Cooling coil (0.3 mm ✕ 2m)
11 : Absorption detector
12 : Data processor
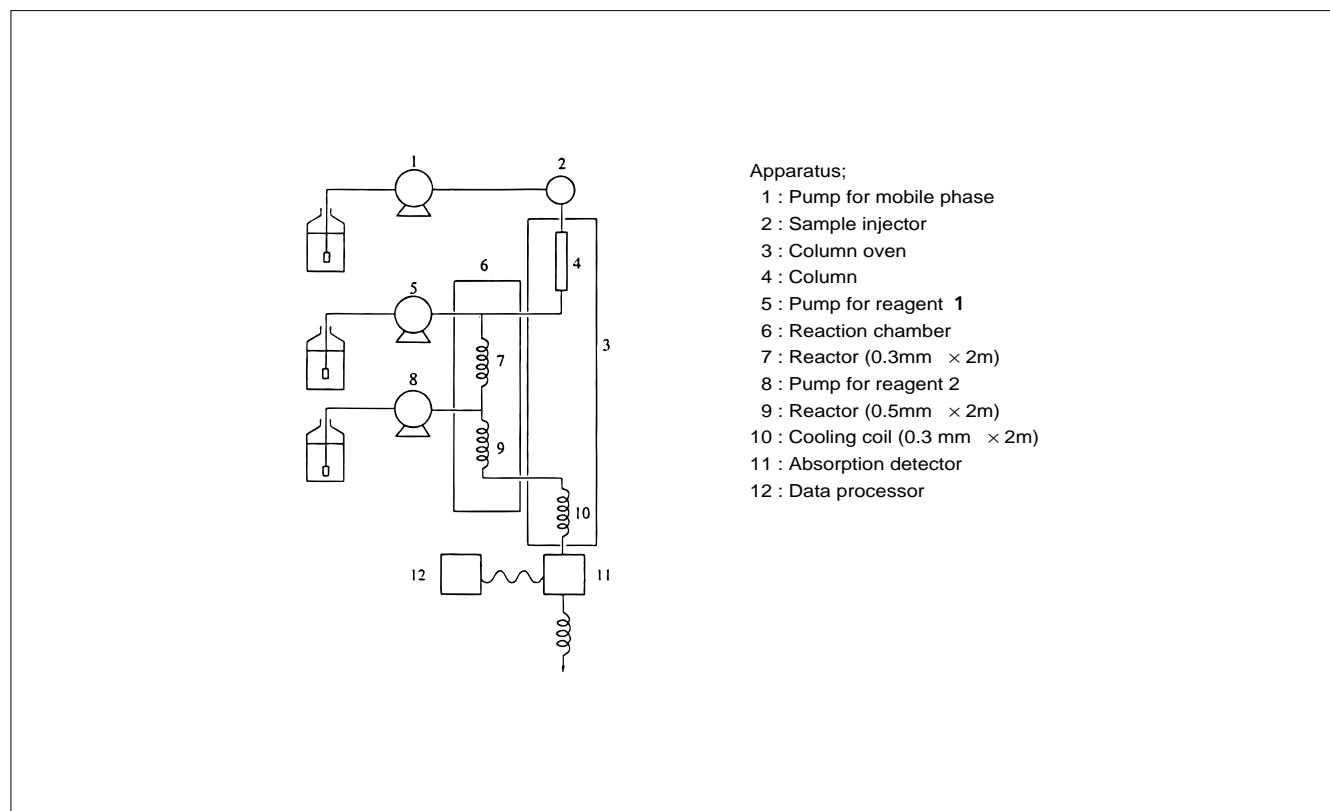
Fig. 56 Analysis system flow route

Environment Water

2.23 Analysis of Alkyl Mercury Compound (1) – *GC*

■Explanation

There are two methods for measuring mercury in the environment – one is the total mercury measuring method employing ultraviolet absorption and atomic absorption and the other is the organic mercury measuring method employing gas chromatography (GC). The GC orientated measuring method is known as the effective analysis method for organic mercury, which was the cause of Minamata disease. As most organic mercury exists in the environment as methyl mercury and ethyl mercury, GC enables highly sensitive and selective detection with ECD using chlorination.

References

Environment Water Quality Analysis Method Manual 411 – 416
Environment Chemical Research Association volume

Quantitative Lower Limit Value (according to above reference material)

0.5µg/L (for analysis of 200mL sample)

■Analytical Conditions

Instrument   : GC-14BPFE
Column   : Thermon-HG 10% Chromosorb
                       W (AW-DMCS)
                       80-100 mesh 0.5m ✕ 3.0mm I.D.
Column temperature : 150°C
Injection inlet temperature : 250°C
Detector temperature : 280°C (ECD)
Carrier gas   : N_2 40mL/min
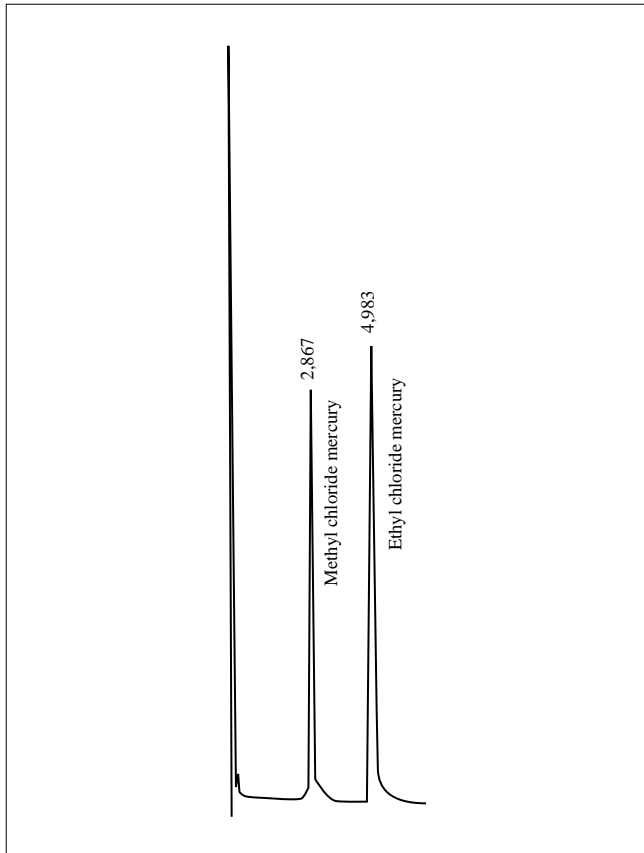
Fig. 57 Standard products (100ppb each)
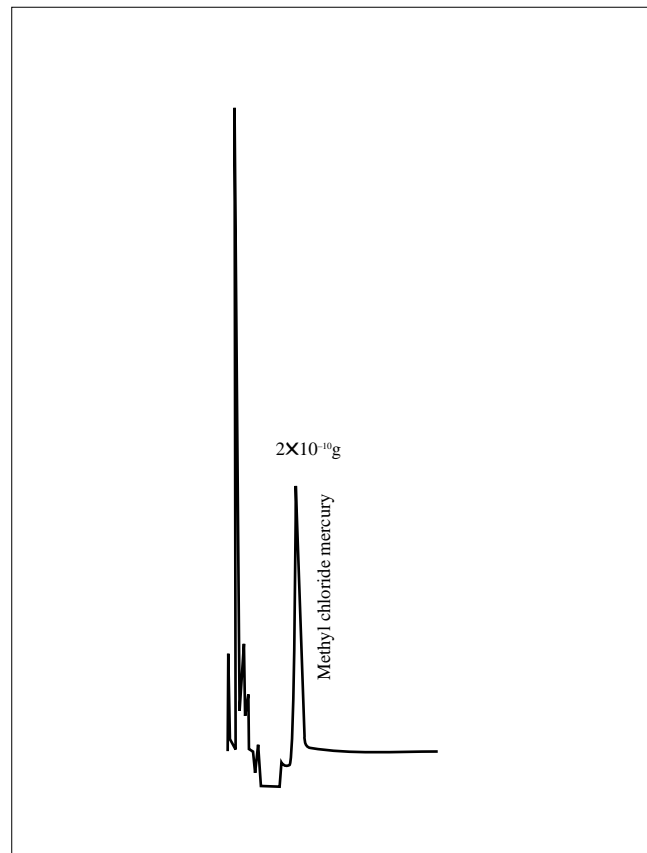
Fig. 58 Methyl mercury in snakehead mullet conserved in river A

2.23 Analysis of Alkyl Mercury Compound (2) – *GC*

Reference Example 1   **Pretreatment Method Flowchart**

200mL sample (500mL separatory funnel used)
> When not neutral, ammonia water or hydrochloric acid are used to neutralize before adding
> hydrochloric acid to provide approximately 2N.

Extraction
> Add 50mL of benzene, shake well for 2 min, transfer water chamber to separatory funnel, and store benzene layer. Once again add 50mL of benzene to the water chamber, stir well for 2 min, and throw away water layer.

Washing the Benzene Layer
> Combine benzene layers, add 20mL of sodium chloride solution (200g/L), stir for approximately 1 min to wash benzene layer, and throw away water layer.

Stripping
> Add 8mL of (1) L-cystine and sodium acetate solution to the benzene layer, stir well for approximately 2 min, allow to stand, then transfer water layer to separatory funnel (20-30 mL).

Extraction
> Add 2mL of hydrochloric acid and 5mL of benzene, shake well for 2 min, allow to stand, then transfer benzene layer to test tube with joint valve.

GC Analysis

> (1) L-cystine and sodium acetate solution
> Dissolve hydrochloric acid L-cystine hydrate 1g, sodium acetate trihydrate 0.8g, and sodium sulphate (anhydrous) 12.8g into water to make 100mL solution.

Reference Example 2   Example of Recommended Instrument Configuration
Main unit : GC-17AAFwE (with WBI) or GC-14BPFE
Detector : ECD
Column : Thermon-HG 10% Chromosorb W (AW-DMCS) 80-100 mesh, 0.5m ✕ 3mm I.D. glass column,
HR-Thermon-HG 15m ✕ 0.53mm I.D.
Auto injector : AOC-20i/s
Data processing system : CLASS-GC10 or Chromatopac C-R7A plus

2.24 Analysis of PCB in Water (1) – *GC*

■Explanation

The polychlorinated biphenyl (PCB) analysis method using gas chromatography (GC) is performed using the method announced by the PCB analytical research group of the Environmental Health Bureau of the Ministry of Health and Welfare. This method is configured from (1) extraction, (2) cleanup, (3) separation from agricultural chemicals, (4) confirmation of PCB, and (5) quantifying of total PCB by means of GC with ECD.

References

Environmental Water Quality Analysis Method Manual 417 – 428
Environment Chemical Research Association volume

Quantitative Lower Limit Value (according to above reference material) 1μg/L

■Analytical Conditions

Instrument	: GC-14BPFE
Column	: OV-1 2% Chromosorb W (AW-DMCS) 80-100 mesh 2.1m ✕ 3.2mm I.D.
	: 210˚C
Column temperature	: 240˚C
Injector inlet temperature	: 280˚C (ECD)
Detector temperature	: N₂ 40mL/min
Carrier gas	
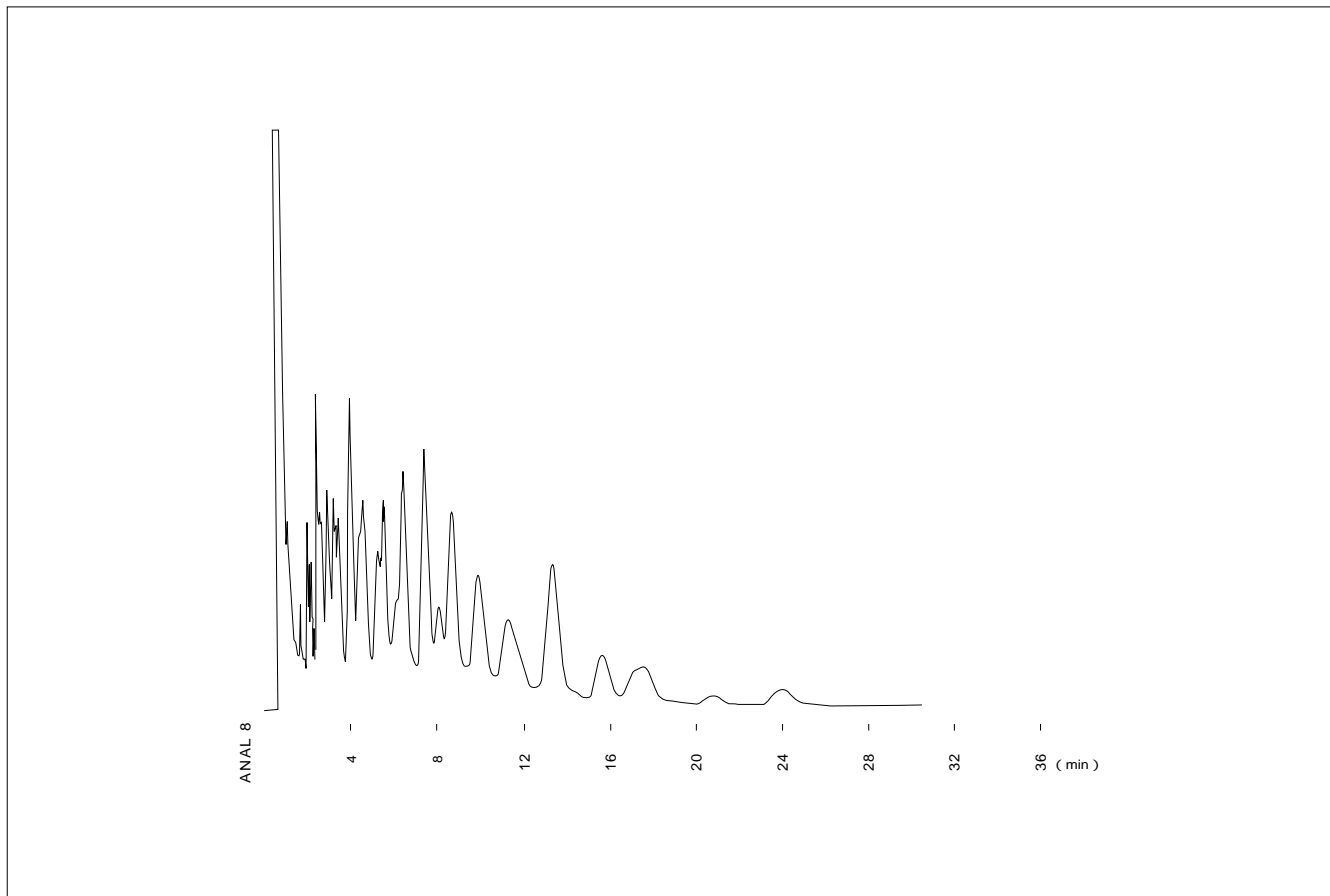
Fig. 59 Standard Products (KC-300/400/500/600 = 1/1/1/1) 1ppm chromatogram

2.24 Analysis of PCB in Water (2) – GC

Reference Example 1   Pretreatment Flowchart

Sample 1L (2L separatory funnel used)

> 50mL of acetone
> 50mL of n-hexane

Extraction

> 2nd measure of 50mL of n-hexane (throw away water layer)

Concentration (K-D concentrator used) 5mL

Silica gel column chromate tube elution test
1. Activation 30min cooling at 130℃ 18 hr by desiccator
2. Mixture (2:1) of KC-300, KC-600, 10ppm n-hexane
3. Chromate tube 10mm *30cm

> Washing with absorbent cotton or glass wool
> permeated with 10mL of n-hexane

Filling   Place 4g of silica gel and 10mL of n-hexane in beaker.
> Flow down n-hexane... stabilize silica gel layer.
> Place 1g of Sodium sulphate (anhydrous) on top of silica gel.

2mL of separate screen test solution
 (dropping as far as the sodium sulphate surface)
> Wash inside of chromate tube twice (1mL each time)
> Attach 300mL separatory funnel, divide 200ml of n-hexane
> effluent into 10mL batches in 20 test tubes.

GC Analysis 5 μm injection
(Confirm stability and collection rate of run-off range 2 or 3 times.)

Reference example)
1. Silica gel column (Wakogel S-1)
10mm internal diameter of glass, silica weight 4g, height 220mm
Runoff n-hexane with valve fully open, runoff speed 2.6mL/min.
2. Florisil PR
10mm internal diameter of glass, florisil weight 4g, height 120mm
Runoff n-hexane with valve fully open, runoff speed 10.5mL/min.

Reference Example 2 Example of Recommended Instrument Configuration

Main unit   : GC-17AAFwE (with WBI) or GC-14BPFE
Detector   : ECD
Column   : OV-1 2% Chromosorb W (AW-DMCS) 80-100 mesh,
                        2.1m ✕ 3.2mm I.D. glass column
Auto injector   : AOC-20i/s
Data processing system: CLASS-GC10 or Chromatopac C-R7A plus

Environment Water

2.25 Analysis of Residual Organic Phosphorus Compounds (1) – *GC*

■Explanation

In order to prevent water pollution in Japanese water catchments for public use, the organic phosphate compounds - parathion, methylparathion, EPN, and methyldimeton – are regulated in the standard items concerning water discharged from factories into water catchments for public use.

References

New discharge standards and their analysis methods 161 – 165
Environment Chemical Research Association Volume (Water Quality Standards Section edition of the Water Quality Bureau of the Environment Agency)

Quantifying Lower Limit Value(according to above reference material) : 0.1mg/L

■Analytical Conditions

Instrument	: GC-17AAFwFp
Column	: DB-1 30m ✕ 0.25mm I.D., 0.25µm(df)
Column temperature	: 50˚C(2min)-270˚C(10min) (10˚C/min)
Injection inlet temperature	: 250˚C
Detector temperature	: 270˚C (FPD P mode)
Carrier gas	: He 1.5mL/min, H2 95mL/min, Air 65mL/min
Injection method	: Splitless
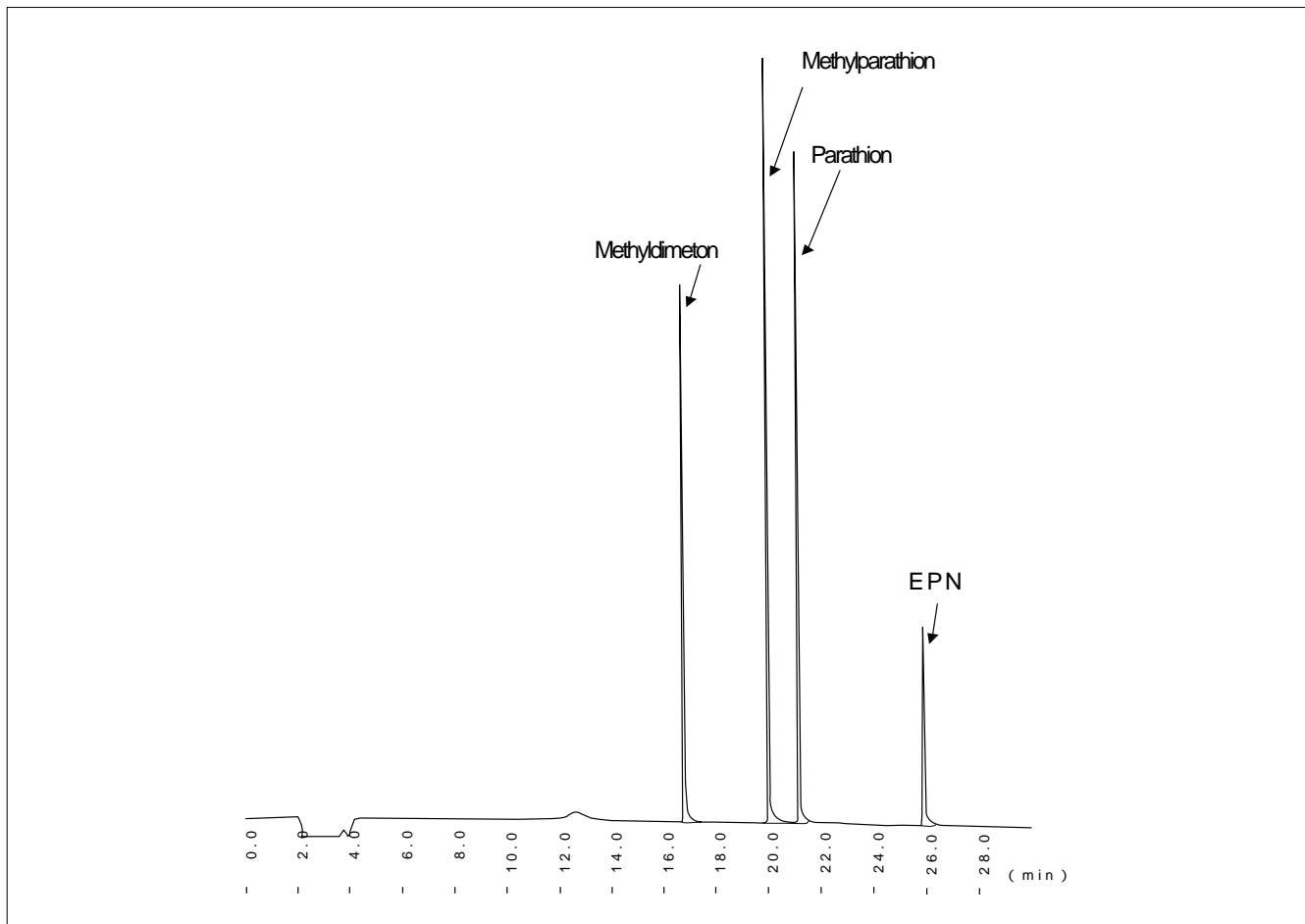
Fig. 60 Standard products (1ppm each) chromatogram

2.25 Analysis of Residual Organic Phosphorus Compounds (2) − *GC*

Reference Example 1   **Pretreatment Method Flowchart**
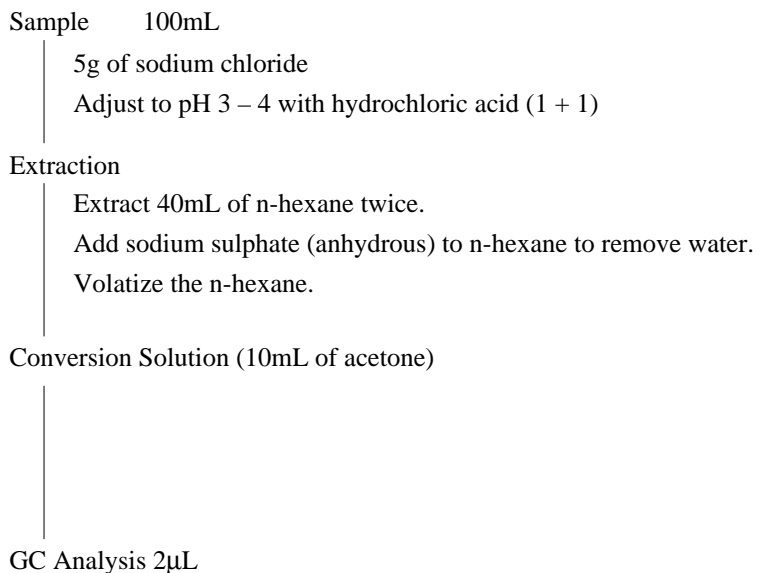
Sample   100mL

  5g of sodium chloride

  Adjust to pH 3 – 4 with hydrochloric acid (1 + 1)

Extraction

  Extract 40mL of n-hexane twice.

  Add sodium sulphate (anhydrous) to n-hexane to remove water.

  Volatize the n-hexane.

Conversion Solution (10mL of acetone)

GC Analysis 2µL

Reference Example 2 Example of Recommended Instrument Configuration

Main unit   : GC-17AAFwFp or GC-14BPFFp
Detector   : FPD
Column   : DB-1 30m ✕ 0.25mm I.D., 0.25µm(df)
Auto injector   : AOC-20i/s
Data processing system : CLASS-GC10 or Chromatopac C-R7A plus
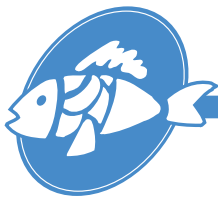
Environment Water

2.26 Analysis of Volatile Organic Compound (VOC) in Wastewater and Environment Water using Head Space Method (1) — *GC/MS*

■Explanation

In addition to the amendments to the water quality standard in tap water in December 1992 and the environment standard for environment water suitable as a source of drinking water in March 1993, a further amendment was also implemented for the wastewater standard in February 1994. The analysis of the compounds itemized in these amendments is performed using the head space method, the solvent extraction method, and the purge trap method. Here, the head space method has the features of being easy to operate, has good reproducibility, an auto sampler can be used, and carry over (pollution levels of conventional analytical instruments caused by components with high concentration levels) is minimal.

References

Drinking Water Test Method & Explanation Japan Water Works Association volume
Environment Water Quality Analysis Manual
Environment Chemical Research Association volume
New wastewater standards and their analysis methods

■Analytical Conditions

Sample : 10ml+NaCl3g

Perkin Elmer HS-40
Sample temp.	: 60˚C
Condition time	: 30min
Needle temp.	: 120˚C
Transfer temp.	: 150˚C
Pressueriz. time	: 2min
Injection time	: 0.20min

Shimadzu GCMS-QP5050A
Carrier gas	: He120kPa
Column	: DB624 60m ✕ 0.32mm I.D. 1.8µm(df)
Column temp.	: 40˚C(2min)-10˚C/min-200˚C(2min)
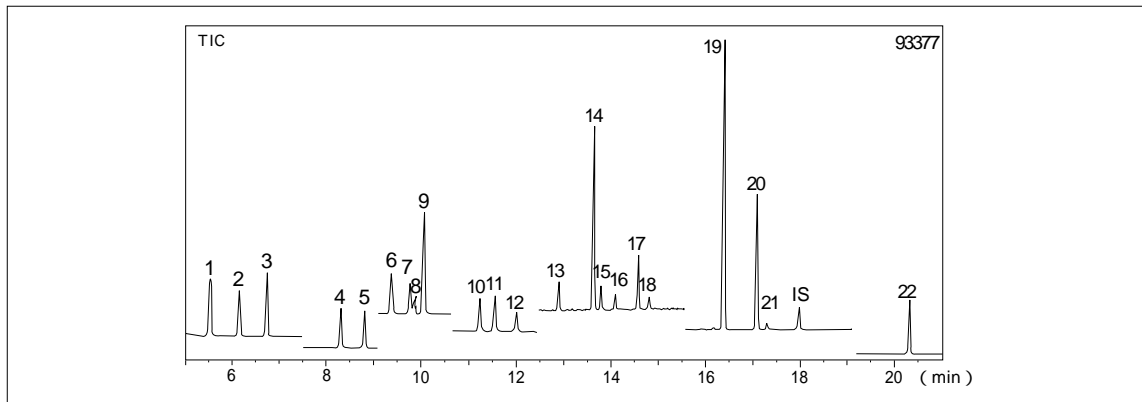
Fig. 61 Analysis example of standard sample (VOC 2ug/L)
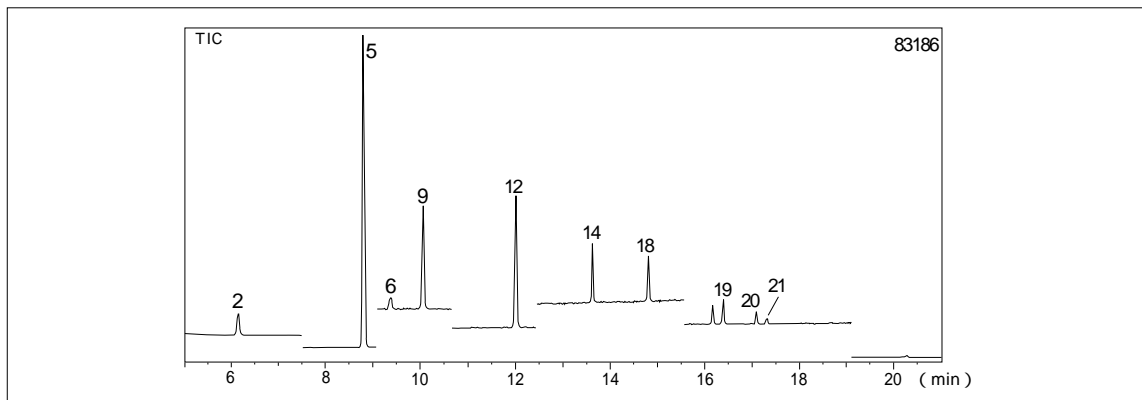
Fig. 62 Analysis example of tap water

2.26 Analysis of Volatile Organic Compound (VOC) in Wastewater and Environment Water using Head Space Method (2) — *GC/MS*
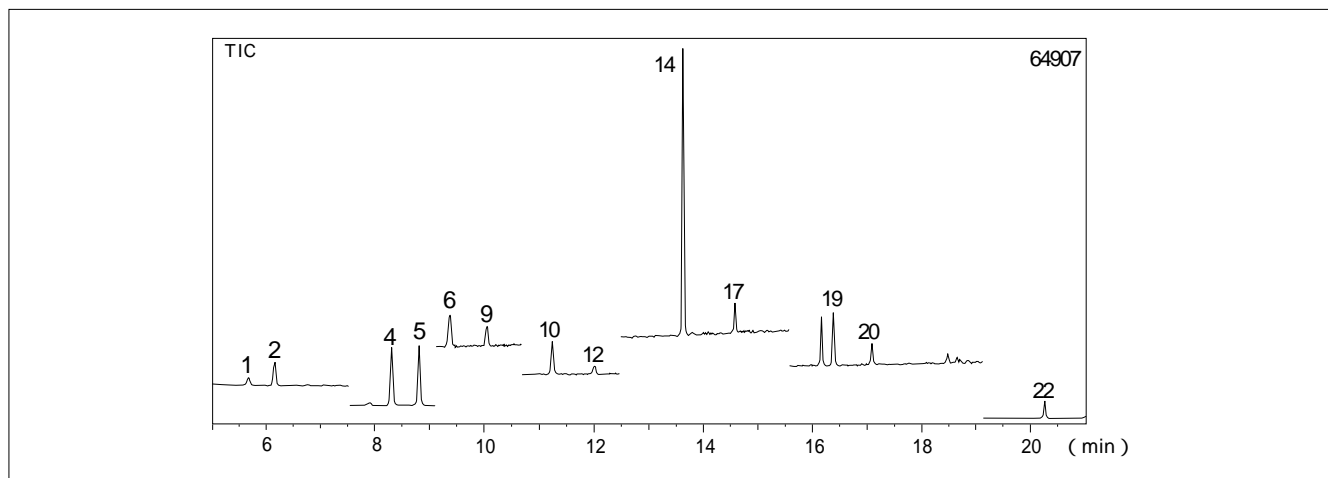
Fig. 63 Analysis example of wastewater

ID	Name	Tap Water (mg/L)	Environment Water (mg/L)	Soil (mg/L)	Wastewater, Sewage, Industrial waste (mg/L)
1	1,1-dichloroethene	0.02	Same as left	Same as left	0.2
2	Dichloromethane	0.02	Same as left	Same as left	0.2
3	trans-1,2-dichloroethane	0.04	Same as left		
4	cis-1,2-dichloroethane	0.04	Same as left	Same as left	0.4
5	Chloroform	0.06	Same as left		
6	1,1,1-trichloroethane	0.3	1.0	1.0	3.0
7	Tetrachloromethane	0.002	Same as left	Same as left	0.02
8	1,2-dichloroethane	0.004	Same as left	Same as left	0.04
9	Benzene	0.01	Same as left	Same as left	0.1
10	Trichloroethene	0.03	Same as left	Same as left	0.3
11	1,2-dichloropropane	0.06	Same as left		
12	Bromodichloromethane	0.03	Same as left		
13	cis-1,3-dichloropropene	*1	Same as left	Same as left	*3
14	Toluene	0.6	Same as left		
15	trans-1,3-dichloropropene	*1	Same as left	Same as left	*3
16	1,1,2-trichloroethene	0.006	Same as left	Same as left	0.06
17	Tetrachloroethene	0.01	Same as left	Same as left	0.1
18	Dibromochloromethane	0.1	Same as left		
19	m,p-xylene	*2	Same as left		
20	o-xylene	*2	Same as left		
21	Bromoform	0.09	Same as left		
22	p-dichlorobenzene	0.3	Same as left		
IS	p-bromofluorobenzene				

Chart 11 Names of measured target compounds together with standard values and indicator values

*1: Total 0.002mg/L
*2: Total 0.4mg/L
*3: Total 0.02mg/L
  : Not regulated

3. Wastewater

3.1 Analysis of Anions in Wastewater — *Ion Chromatograph*

■Explanation

Fluoride, nitrate nitrogen and nitrite nitrogen are raised as necessary monitoring items in the water environment standards, and the ion chromatography method is one of the monitoring methods employed. Non-organic ions in wastewater are one of the causes of pollution and eutrophication in rivers and lakes, and pollution is approaching a critical stage due to abnormal drought in recent years and neglect in the area of sewage facility provision. Thus, the importance of monitoring non-organic ions in wastewater has increased.

References

(1) Drinking Water Test Method & Explanation (Fiscal 1993 Volume) 164 – 198
Ministry of Health and Welfare, Environ. Health Bureau, Water Supply & Environ, Sanitation Dept. edition
Japan Water Works Association
(2) New wastewater standards and their analysis methods 400 – 406
Water Quality Standards Section edition of the Water Quality Bureau of the Environment Agency
Environment Chemical Research Association

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : Ion chromatograph
Column : Shim-pack IC-A1 (100mm ✕ 4.6mm I.D.)
Mobile phase : 2.5mM of phthalic acid, 2.4mM Tris (hydroxymethyl) aminomethane
Flow rate : 1.5mL/min
Temperature : 40°C
Detector : Electric conductivity detector

■Peaks
1 PO_4^{3-}
2 Cl^-
3 NO_3^-
4 SO_4^{2-}
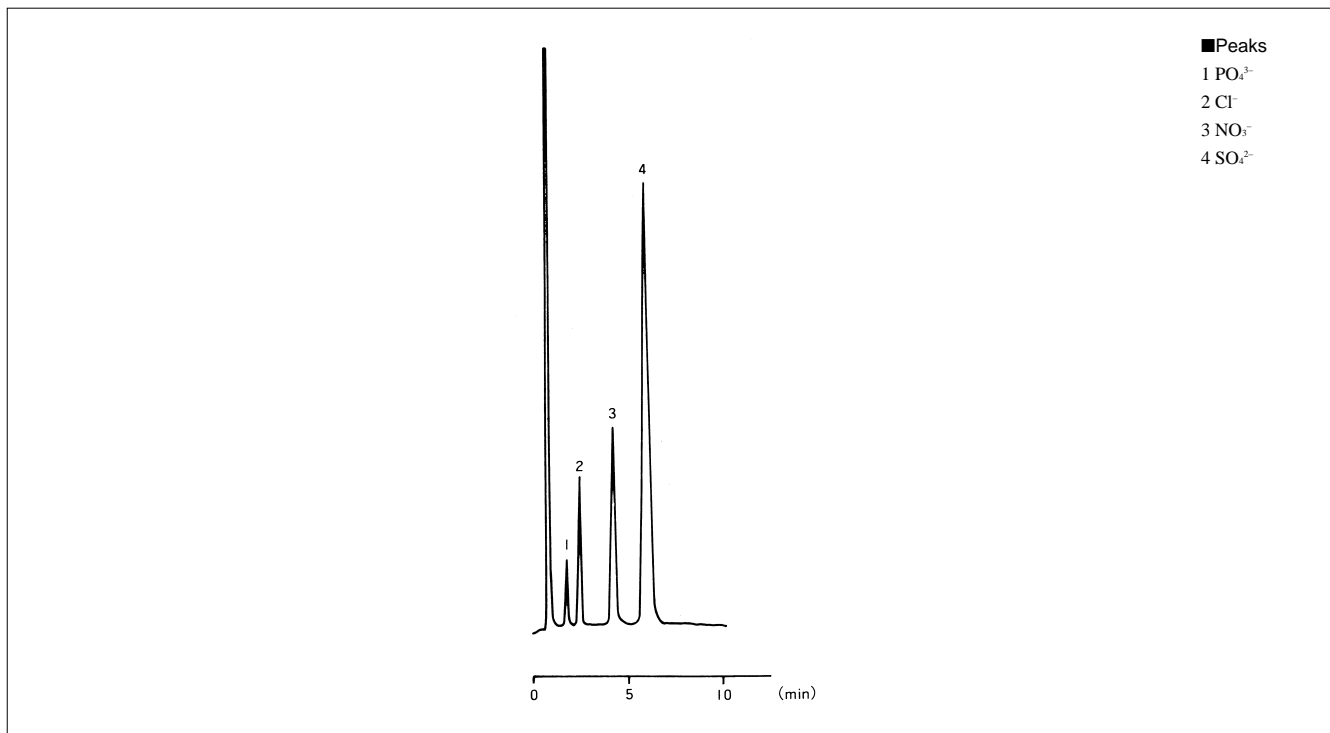
Fig. 64 Analysis of Wastewater

3.2 Analysis of Cations in Wastewater – *Ion Chromatograph*

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : Ion chromatograph
Column   : Shim-pack IC-C1 (100mm ✕ 4.6mm I.D.)
Mobile phase   : 5mM of nitric acid
Flow rate   : 1.5mL/min
Temperature   : 40˚C
Detector   : Electric conductivity detector

■Peaks
1 Na^+
2 NH_4^+
3 K^+
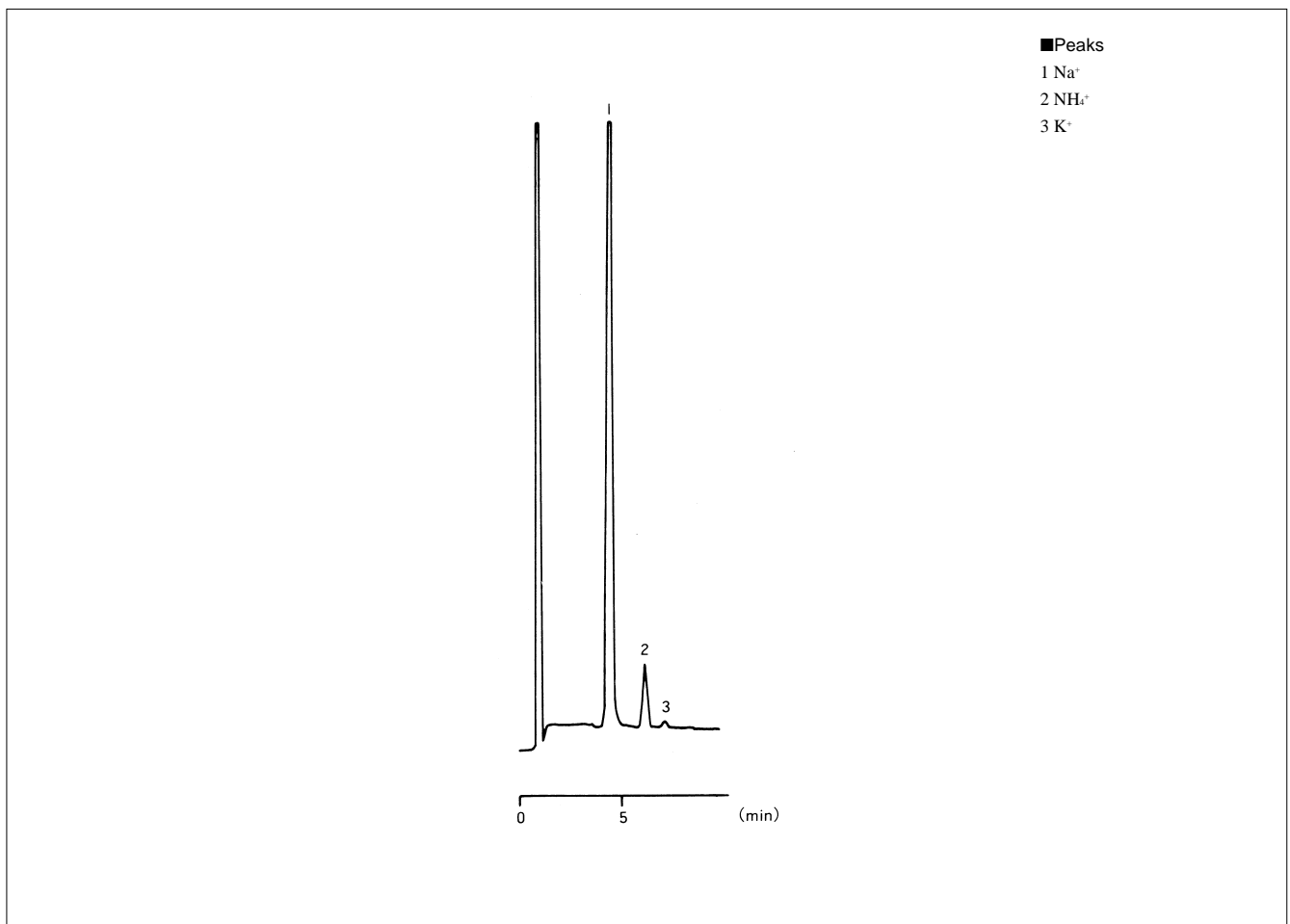
Fig. 65 Analysis of wastewater

Wastewater

3.3 Analysis of Anions in Wastewater — *PIA-1000*

■Explanation

This is an analysis example where the personal ion analyzer PIA-1000 was used to analyze anions contained in processed water at a sewage works.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : PIA-1000
Column   : Shim-pack IC-A3(S)
Mobile phase : PIA-1000 dedicated anion analysis mobile phase, IC-MA3-1
Flow rate   : 0.2mL/min
Temperature : 35°C

■Peaks
1 HCO_3^- (31.01mg/L)
2 PO_4^{3-} (3.245mg/L)
3 F^- (0.169mg/L)
4 Cl^- (60.59mg/L)
5 NO_3^- (47.47mg/L)
6 SO_4^{2-} (56.54mg/L)

Fig. 66 Analysis of wastewater (PIA-1000)

3.4 Analysis of Cations in Wastewater — *PIA-1000*

■Explanation

This is an analysis example where the personal ion analyzer PIA-1000 was used to analyze cations contained in processed water at a sewage works.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : PIA-1000
Column   : Shim-pack IC-C3(S)
Mobile phase : PIA-1000 dedicated cation analysis
                   mobile phase, IC-MC3-1
Flow rate   : 0.2mL/min
Temperature : 35˚C

■Peaks
1 Na^+(58.20mg/L)
2 NH_4^+(0.558mg/L)
3 K^+(10.55mg/L)
4 Mg^{2+}(5.814mg/L)
5 Ca^{2+}(29.29mg/L)
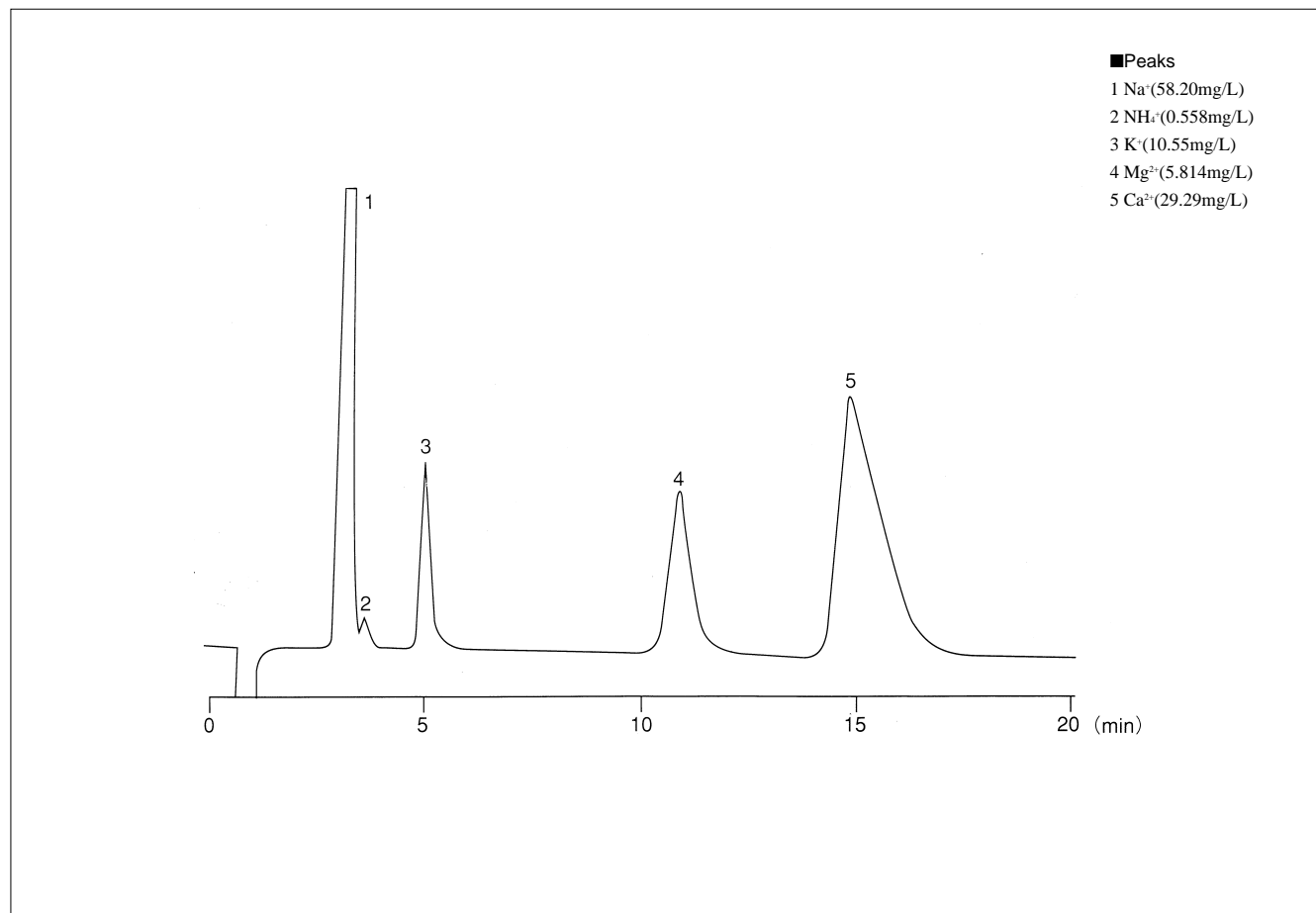
Fig. 67 Analysis of wastewater (PIA-1000)

3.5 Analysis of Volatile Organic Compound (VOC) in Wastewater – GC

■Explanation

In 1993, the environment standard for environment water was greatly amended, and the wastewater standard items became 24 items. And among these, VOC occupies 11 items. Environment water analysis is mostly conducted using GC/MS, but GC can be used for analyzing just those samples that have small amounts of impurities in them. This data is an example of analysis for water with VOC component using head space GC. This method can be used to analyze 10 of the items in the items of the wastewater standard. Benzene needs to be analyzed using FID as it cannot be detected by ECD.
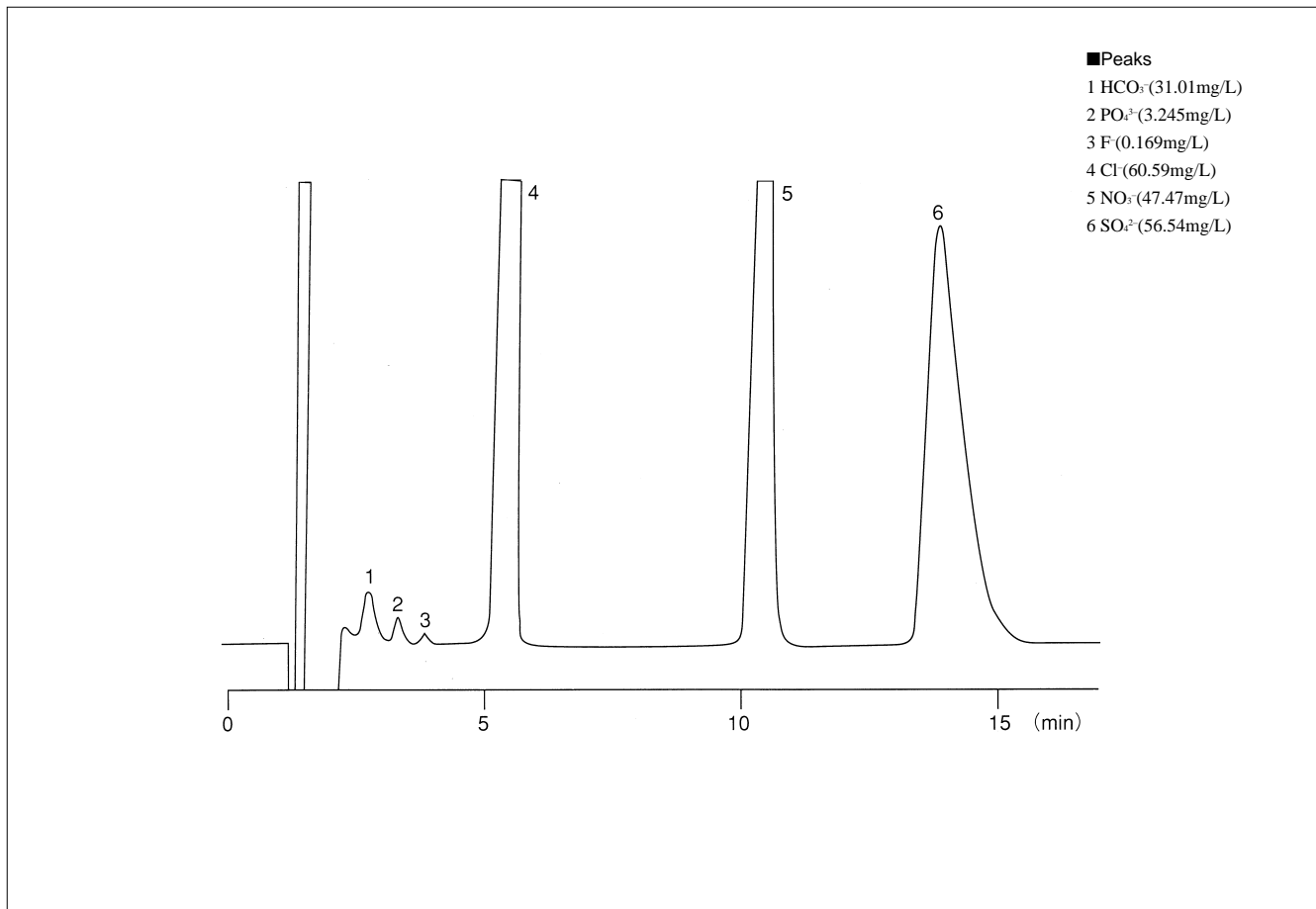
Quantifying Lower Limit Value (target): This greatly differs depending on the element.

■Analytical Conditions

Instrument	: HSS-4A + GC-17AAE
Column	: DB-VRX 75m ✕ 0.45mm I.D., 2.55µm(df)
Column temperature	: 35˚C(5min)-180˚C(5˚C/min)
Injection inlet temperature	: 200˚C
Detector	: ECD 210˚C
Carrier gas	: He 6.0mL/min
Head space heat-reserving conditions	: 50˚C, 60min
Head space injection volume	: 0.2mL (inject total volume)
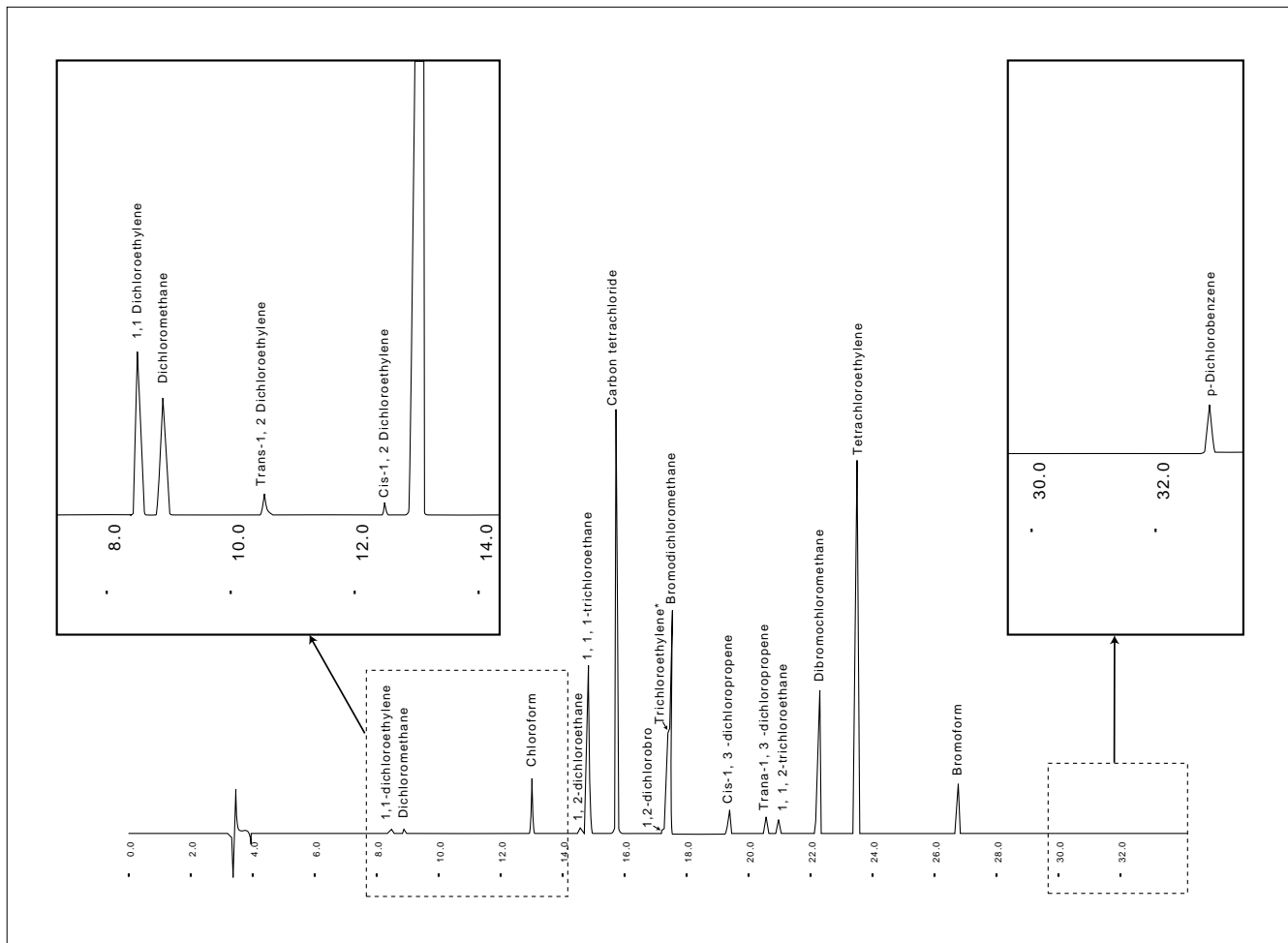
Fig. 68 Analysis example of VOC in environment water using head space GC-ECD (* signifies regulated item of wastewater standard)

4. Atmosphere

4.1 Analysis of Acidic Substances in Exhaust Gas — Ion Chromatograph

■Explanation

Analysis of acidic gas existing in exhaust gas was performed. The analysis targets, HC1, NOx, and SOx, were individually absorbed into absorption solutions, then analyzed by an ion chromatograph. Figure 69 shows the results for analysis of a solution obtained by absorbing HC1 from exhaust gas into 0.4% NaOH. Figure 70 shows the results for analysis of NO_3^- created by absorbing NOx from exhaust gas into a mixed solution $H_2O_2^-$ and Sulfuric acid. Figure 71 shows the results for analysis of SO_4^{2-} created by absorbing SOx from exhaust gas into H_2O_2. All three samples can be measured at high sensitivity without any special pretreatment.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument : Ion chromatograph
Column : Shim-pack IC-A3 (150mm ✕ 4.6mm I.D.)
Guard column : Shim-pack IC-GA3 (10mm ✕ 4.6mm I.D.)
Mobile phase : 5.0mM p-hydroxybenzoic acid, 3.0mM Bis-Tris*
Flow rate : 1.5mL/min
Temperature : 40˚C
Detection : Electric conductivity detector
*Bis-Tris : Bis (2-hydroxyethyl) iminotris (hydroxymethyl) methane

■Peaks
1 Cl⁻(95.6ppm)
2 SO₄²⁻(66.1ppm)

Fig. 69 Analysis of HC1 in exhaust gas

■Peaks
1 Cl⁻(0.42ppm)
2 NO₃⁻(1.98ppm)
3 SO₄²⁻(9.14ppm)
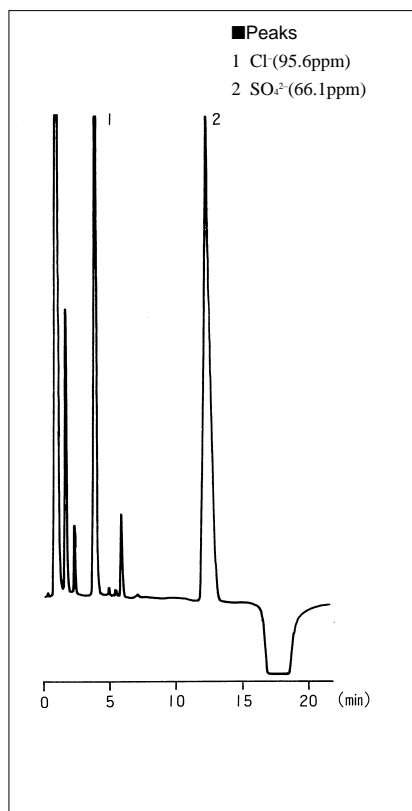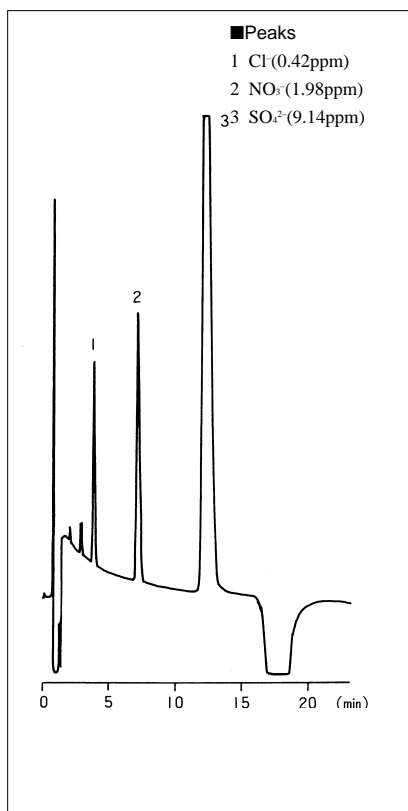
Fig. 70 Analysis of NOx in exhaust gas

■Peaks
1 Cl⁻(49.0ppm)
2 SO₄²⁻(7.94ppm)
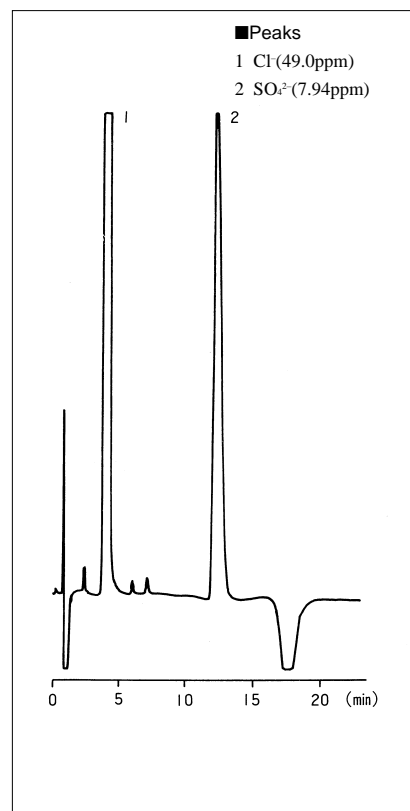
Fig. 71 Analysis of SOx in exhaust gas

Atmosphere

4.2 Analysis of Exhaust Gas Absorption Solution – PIA-1000

■Explanation

Analysis examples using the personal ion analyzer PIA-1000 are shown in figure 72 with absorption solution for exhaust gas of supply water boiler (vacuum flask method) and figure 73 with absorption solution for exhaust gas of a garbage and sewage plant (vacuum flask method). The PIA-1000 enables highly sensitive analysis.

■Pretreatment

Filtering through a membrane filter (0.45 µm) for ion chromatography

■Analytical Conditions

Instrument   : PIA-1000
Column   : Shim-pack IC-A3(S)
Mobile phase : PIA-1000 designated ion analysis mobile
Flow rate   phase, IC-MA3-1
Temperature   : 0.2mL/min
              : 35˚C

■Peaks
1 Cl⁻(0.263mg/L)
2 NO₃⁻(1.969mg/L)
3 SO₄²⁻(4.172mg/L)
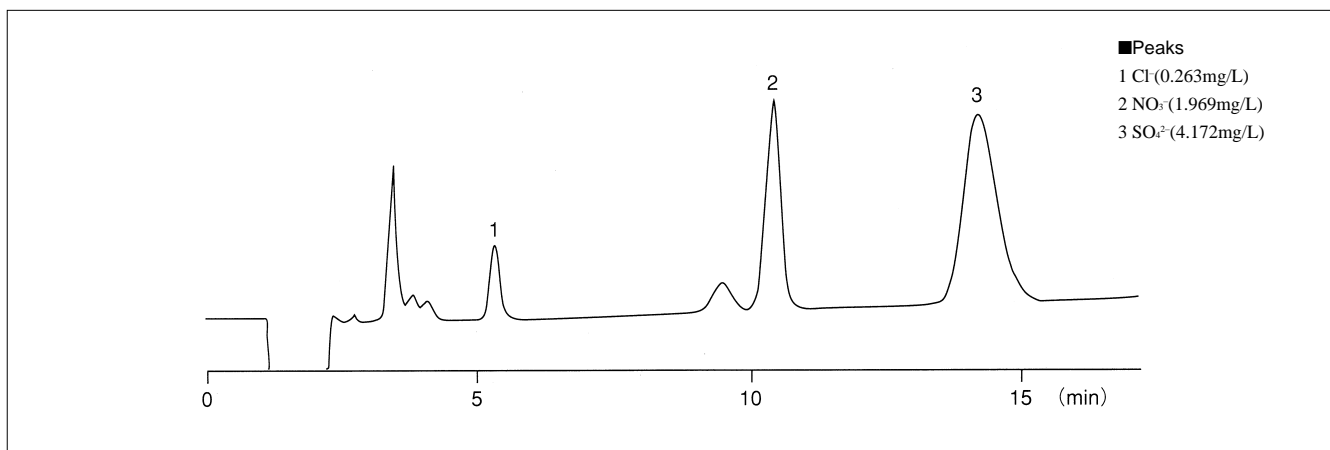
Fig. 72 Analysis of supply water boiler exhaust gas absorption solution

■Peaks
1 Cl(6.332mg/L)
2 NO₃⁻(2.394mg/L)
3 SO₄²⁻(1.029mg/L)

Fig. 73 Analysis of garbage and sewage plant exhaust gas absorption solution

4.3 Analysis of Tolylenediisocyanate (TDI) in Work Environment Monitoring (1) — *HPLC*

■Explanation

In 1995, partial amendments were made to the work environment evaluation standard and the work environment monitoring standard. High-speed liquid chromatography was added to the analysis methods currently being used for ethyleneimine, 3, 3'-dichloro-4, 4'-diaminodithanylmethane, and tolylenediisocyanate (TDI). Among these TDI is greatly used in materials such as the raw material of polyurethane foam, polymerization of cross linked agents, foaming agent, paints, and glues, and is strongly toxic to the human body, which, in cases of acute poisoning, can cause pneumonia and tuberculosis, that can lead to fatalities due to weakening of the heart if the illness becomes serious. Currently, the value for the work environment standard has been amended to 5 ppb, and a measurement level of one tenth of this, 0.5 ppb, is requested. Here, a suitable testing method is the high-speed liquid chromatograph method, which is highly sensitive in comparison to conventional diazotization coupling absorptiometry, and has many features such as the capability of being able to separately quantify isomers.

Reference
Kenji Nakaaki, Shinya Koike, Yuriko Takada: Labor Science, 63 (1), 1-13, 1987

■Pretreatment

After collecting a sample for 10 min in 1-(2-pyridyl) piperazine impregnated filter paper at a gas suction flow rate of 1L/min, remove sampling filter paper, and extract sample using a shaker with 4mL of methanol containing acetic acid. Filter the extracted solution through a 0.45μm membrane filter to make a test solution.
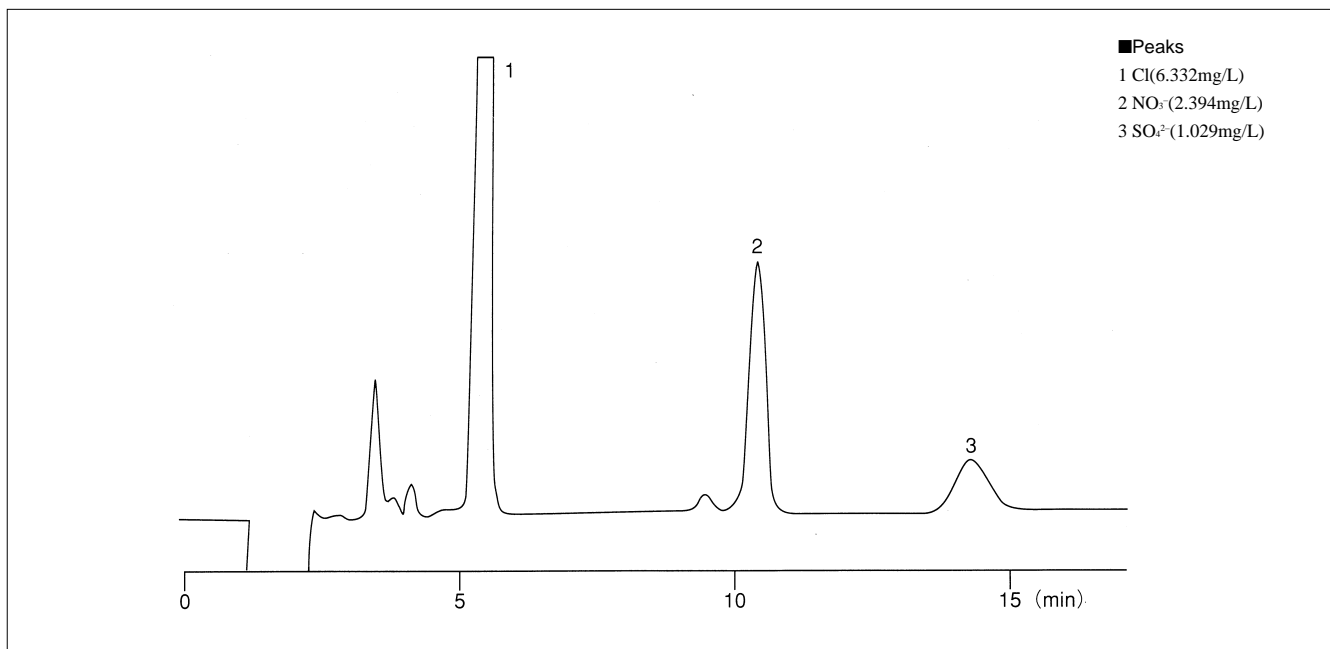
■Analytical Conditions

Device   : LC-VP system
Column   : STR ODS-II (150mm ✕ 4.6mm I.D.)
Mobile phase : 50mM of sodium acetate buffer solution
                 (pH 6.2)/acetonitrile = 68/32 (v/v)
Flow speed   : 1.5mL/min
Temperature : 40˚C
Detector   : UV-VIS detector 247nm
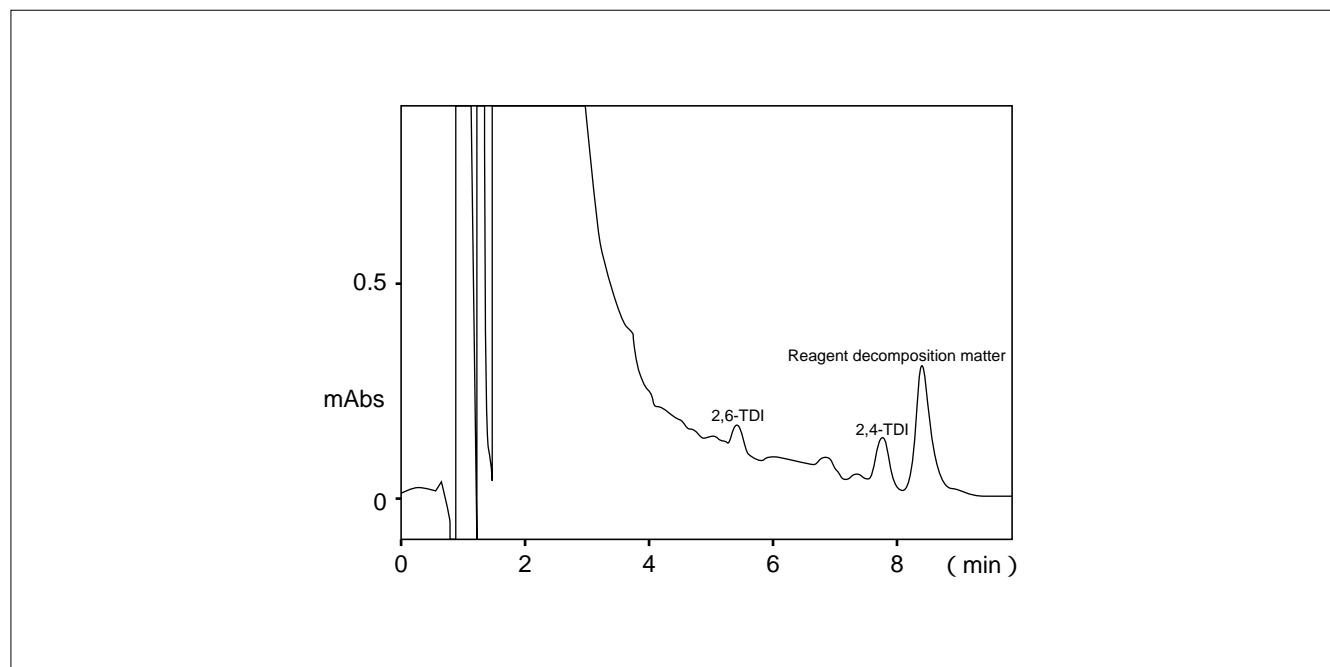
Fig. 74 Analysis of TDI gas sample (0.5 ppb suitable for each)

4.3 Analysis of Tolylenediisocyanate (TDI) in Work Environment Monitoring (2) — HPLC

Reference Example 1   **Sampling and Pretreatment Method**

Sample 10L

Sampling

Collect sample for 10 min in 1-(2-pyridyl) piperazine impregnated filter paper at a gas suction flow rate of 1L/min.

Extraction

Add 4mL of methanol (containing acetic acid of 0.05v/v%) and shake for 30 min.

Filtration

Use a 0.45 μm membrane filter.

HPLC 20 μL Injection
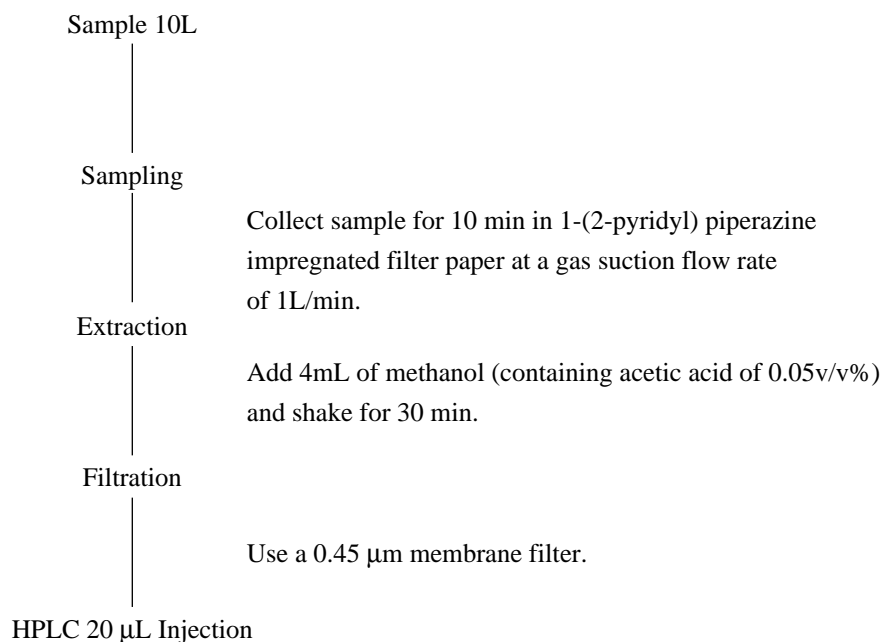
Reference Example 2   **Flow Diagram for TDI Generation Device**

Nitrogen cylinder — Humidification device

Nitrogen cylinder — Standard gas generator

Trap

Glass board for sampling

Solid-phase collecting

Humidity sensor
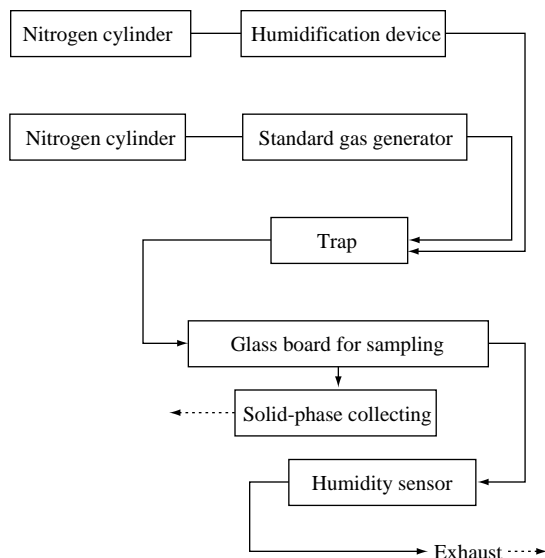
Exhaust

Sample provided by Japan Work Environment Monitoring Association.

4.4 Analysis of Aldehyde/Ketonic products in Exhaust Gas — *HPLC*

■Explanation

This shows an example of analysis performed on aldehyde/ketonic products found in vehicle exhaust gas. In cases where exhaust gas is set as the sample, and negative-phase chromatography is used to separate and detect absorbance, the type of impurities and the amount of content often lead to difficulties in analysis. In particular, impurity peaks are sometimes observed as peak overlay and warping for formaldehyde peaks that solve out quickly. In such cases, these affects can be avoided by adding methanol to mobile phase A solution.

■Pretreatment

Conforming to JIS Law (K0303)
Sample kindly lent by Traffic Safety and Nuisance Research Institute of the Ministry of Transport.

■Analytical Conditions

Device	: LC-VP system
Column	: STR ODS-II (150mm ✕ 6.0mm I.D.)
Mobile phase	: A → B gradient elution method
	A: Water/THF/methanol = 70/10/20 (v/v/v)
	B: Water/acetonitrile, = 30/70 (v/v)
Flow rate	: 1.0mL/min
Temperature	: 45˚C
Detector	: UV-VIS detector 365nm
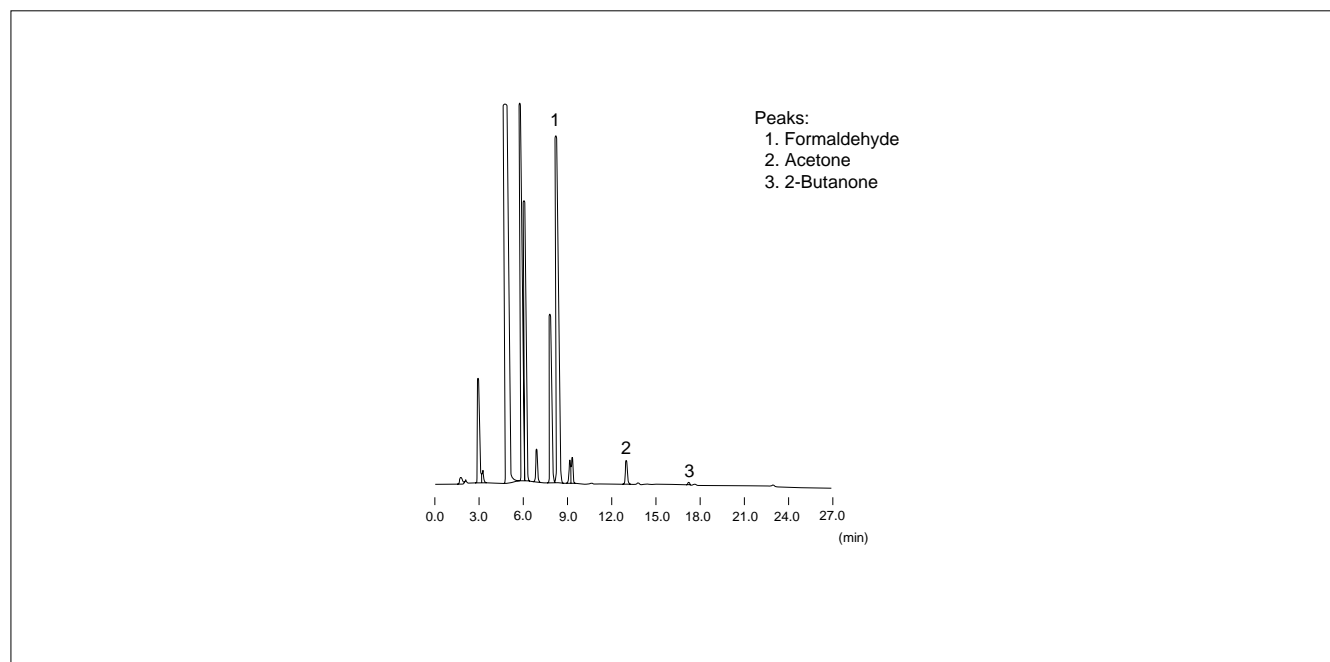
Fig. 75 Analysis of aldehyde/ketonic products in exhaust gas

Atmosphere

4.5 Analysis of Aldehyde/Ketonic products in Room Atmosphere — *HPLC*

■Explanation

With regard to the monitoring regulations and analysis methods for harmful pollutants in the air, the American Environmental Protection Agency (EPA) has already listed recommended analysis methods for 189 compounds with the Clean Air Law. Here, an example of analysis of general residential room air in accordance with the aldehyde analysis method recommended by the EPA is introduced.

■Pretreatment

Sample air was made to pass through silica gel cartridge coated with dinitrophenylhydrazine (DNPH) in acidified state, after trapping each aldehyde/ketonic product as DNHP derivatives, they were extracted by solving out with an organic solvent. This enables high-scale concentration. In the case of this sample, the DNPH cartridge was attached directly to an on-site sampling pump (SHIMADZU VPC-10), the sample concentrated, and solved out with acetonitrite to make the test solution.

■Analytical Conditions

Device   : LC-VP system
Column   : STR ODS-II (150mm ✕ 6.0mm I.D.)
Mobile phase : A → B gradient solving out method
                A: Water/THF/methanol = 70/10/20
                  (v/v/v)
                B: Water/acetonitrite = 30/70 (v/v)
Flow rate   : 1.0mL/min
Temperature : 45˚C
Detector   : UV-VIS detector 365nm

Peaks:
 1. Formaldehyde
 2. Acetaldehyde
 3. Acrolein
 4. Propionaldehyde
 5. Methacrolein
 6. n-Butyraldehyde
 7. Benzaldehyde
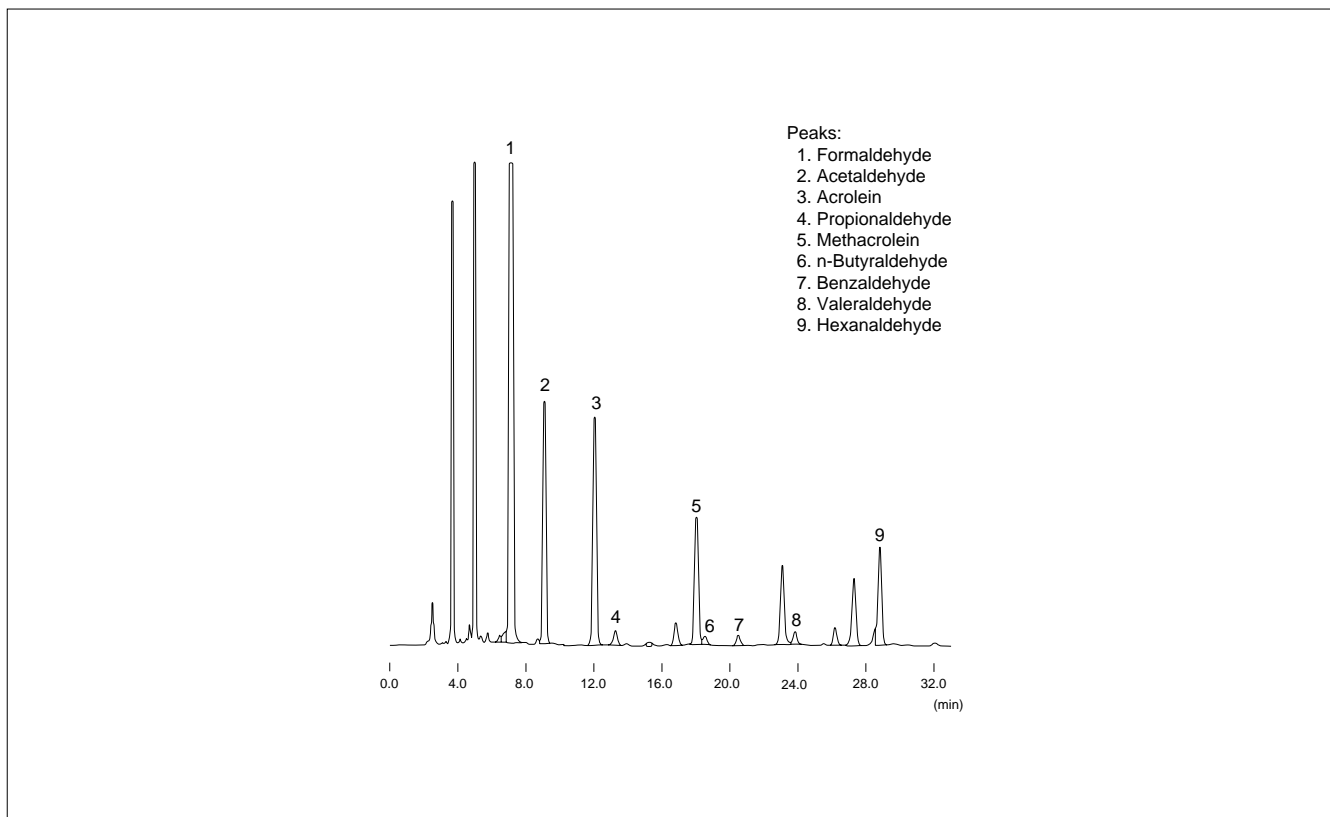 8. Valeraldehyde
 9. Hexanaldehyde

Fig. 76 Analysis of aldehyde/ketonic products in a child's room

4.6 Analysis of Aldehyde Types in Atmosphere (1) – *GC*

■Explanation

There are 13 kinds of harmful air pollutants (substances that can be harmful to human health if in imbibed on a regular basis and cause actual air pollution), and this section introduces the air-borne aldehyde type. Under the Offensive Odor Control Law, factories are obligated to monitor aldehydes at their site perimeters.

References

Actual Monitoring of Harmful Air Pollutants 157 – 200 (1997) Environment Agency, Air Quality Bureau, Air Regulation Section Edition

Quantitative Lower Limit Value (target quantitative lower limit value according to above reference material)

Formaldehyde 0.8µg/µm³ (provisional value)
Acetaldehyde 0.5µg/m³

■Pretreatment

Air-borne aldehyde is changed to a derivative (aldehyde DNPH) using 2, 4-dinitrophenylhydrazine when concentrated and collected, and is measured against a nitrogen compound using a highly sensitive and selective FTD (thermal ionization detector).

■Analytical Conditions

Device	: GC-17AAFwFt
Column	: DB-1 30m ✕ 0.25mm I.D., 0.25µm(df)
Column temperature	: 80˚C(2min)-20˚C/min-90˚C-
Injector inlet temperature	3˚C/min-230˚C
	: 250˚C
Detector temperature	: 280˚C(w-FTD)
Carrier gas	: He 2.9mL/min
Injection method	: Splitless (1min)
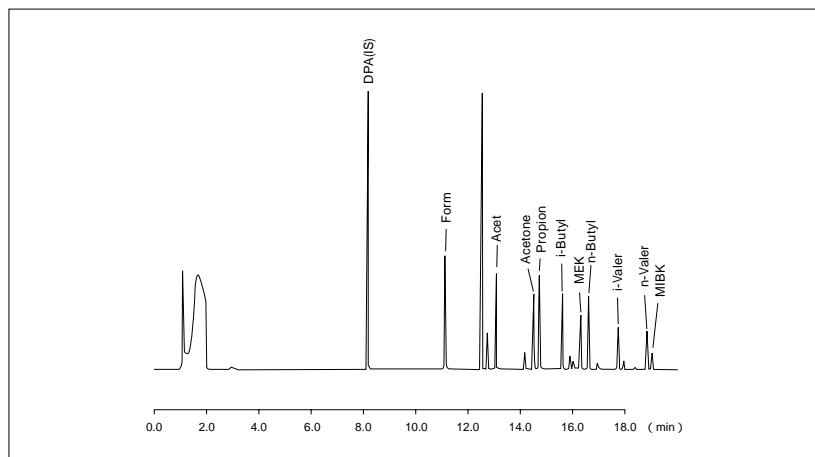
Fig. 77 Analysis example of aldehyde DNPH types

This is an example of analysis of formaldehyde, acetaldehyde together with elements (propionaldehyde, butylaldehyde, and valeraldehyde) targeted by the Offensive Odor Control Law, as well as ketonic substances that reacts with DNPH. Diphenylamine (DPA) was used as the internal standard substance (Fig. 77).
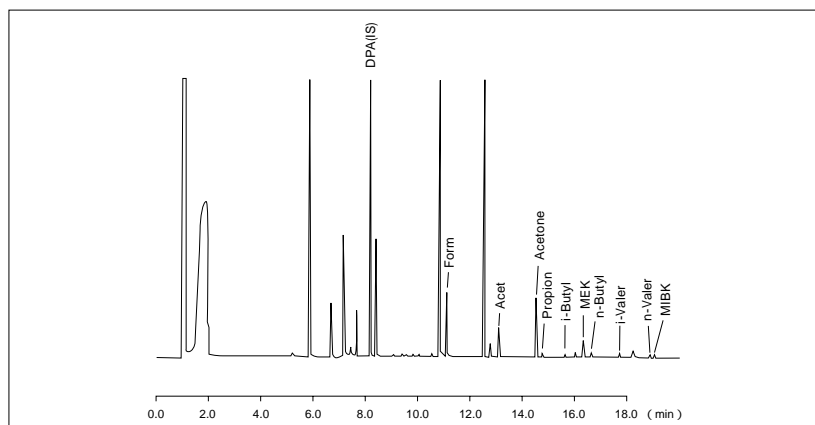
Fig. 78 Analysis example of aldehyde types in the environment

This shows an example of actual air collected and analyzed (Fig. 78).

4.6 Analysis of Aldehyde Types in Atmosphere (2) – *GC*

Reference Example 1   Pretreatment Method

■Sample Collection Method

Two marketed cartridges impregnated with 2, 4-dinitrohydrazine are used in tandem. Pump flow rate is set to be about 0.1 L per minute, and collection is performed continuously for 24 hours. The used air volume is measured with a flowmeter. To prevent the breakup of aldehyde DNPH by air-borne ozone, an ozone scrubber cartridge is attached to the front of the collection cartridge system (Fig. 79).
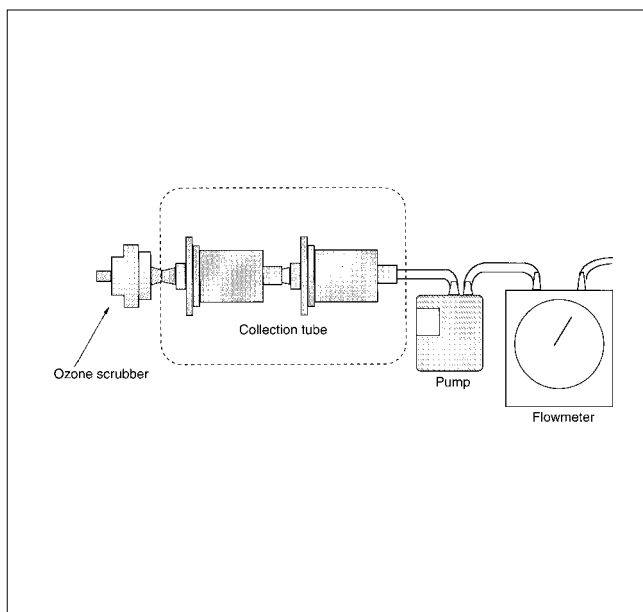
■Cartridge Solving Out Method

Aldehydes react in the cartridges to form aldehyde-DNPHs, and are solved out using acetonitrile. DNPH is also solved out at this time using a positive ion replacement resin as it can interfere with analysis. As the solving out solvent acetonitrile is sensitive to FTD, it is solved into ethyl acetate to make a sample solution (Fig. 80).

Fig. 79 Sample collection method
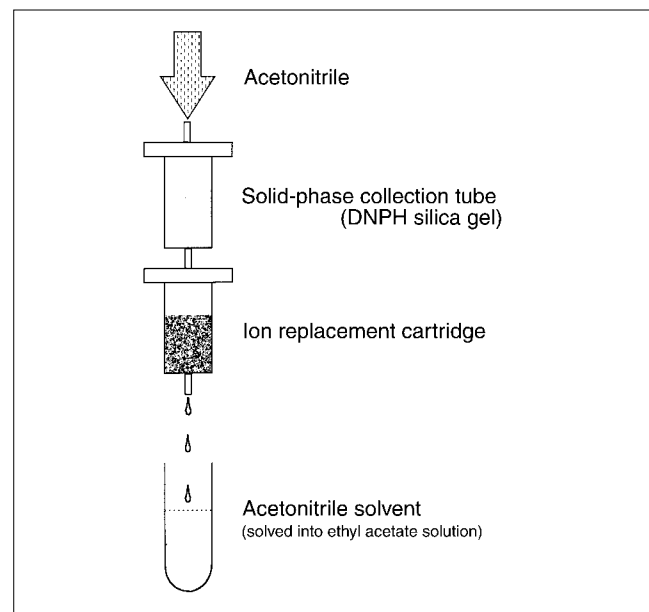
Fig. 80 Solving out method from cartridge

Reference Example 2   Recommended Instrument Configuration

Main unit   : GC-17AAFwFt or GC-14BPFFt+SPL-14
Detector   : FTD
Column   : DB-1 30m ✕ 0.25mm I.D., 0.25μm(df)
Auto injector   : AOC-20i/s
Data processing device   : CLASS-GC10 or Chromatopac C-R7A plus
Solid-phase extraction cartridge : 1 set

4.7 Analysis of Formaldehyde in Room Atmosphere – *UV*

■Explanation

Formaldehyde residue sometimes exists in wall materials and flooring of homes, and this residue is dispersed as a vapor in house air. Consequently, monitoring the concentration of such formaldehyde has become an important task. Here, experimental monitoring was performed in the rooms of a new house using a combination of a solution collection method with water and an acetylacetone colorimetric method.

Reference Material
JIS K0303 Monitoring of HCHO in exhaust gas

Quantitative lower Limit (target): several 10ppb

■Monitoring Device
Concentrated collection device : VPC-10
Spectrophotometer : UV-1600 standard glass cell
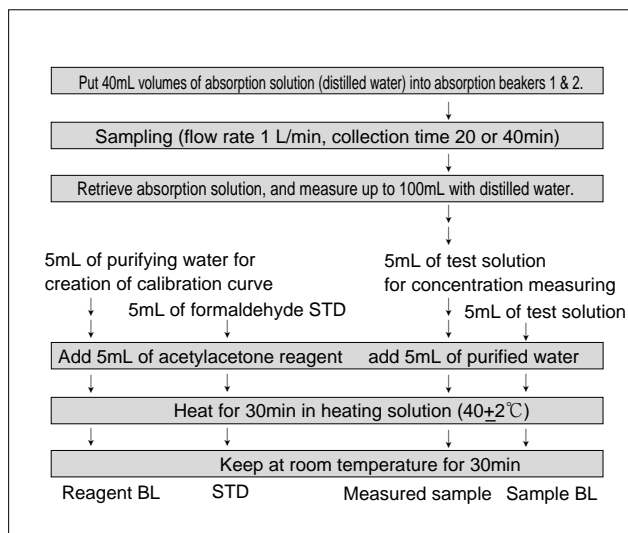
Fig. 81 Measuring flowchart for formaldehyde in air

Wavelength : 412.0
Slit amplitude: 2.0

Multi-point calibration curve
Conc=K1 A+K0
K1=3.762 k0=0.00526

Chi-Square : -0.00118
Data points : 6

ID	Concentration		Absorbance	
1	0.08126	0.020		
1	0.08051	0.020		
Average :	0.08088	0.020	→Room 1 results	(in absorption solution)
Standard deflection :				
2	0.1452	0.037		
2	0.1459	0.037		
Average :	0.1456	0.037	→Room 2 results	(in absorption solution)
Standard deflection :				
3	0.06170	0.015		
3	0.05793	0.014		
Average :	0.05981	0.014	→Room 3 results	(in absorption solution)
Standard deflection :				

Measurement results for formaldehyde in air

Room 1: 0.302ppm(20min)
Room 2: 0.272ppm(40min)
Room 3: 0.223ppm(20min)
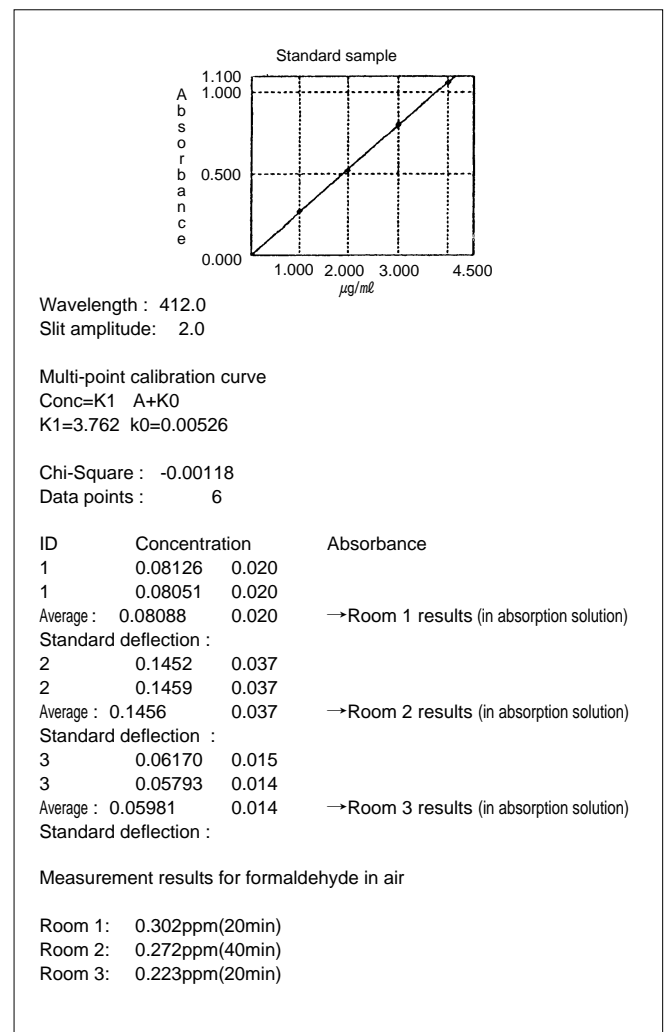
Fig. 82 Measuring example of formaldehyde in air

Atmosphere

4.8 Analysis of Volatile Organic Components (VOC) in Atmosphere(1)
— Solid-phase Adsorption & Thermal Desorption GC/MS

■Explanation

Various substances that are harmful to human health are being found in ambient air, and though the concentrations may not be enough to harm human health directly, there are fears that exposure over time can lead to cancer, etc. With this as a background consideration, a law partially amending the Air Pollution Control Law was introduced in May 1996, and put into practice from April 1st, 1997. The Central Council for Environmental Pollution Control published via the second verdict in October 1996 a list of 234 substances that are potentially harmful air pollutants (HAPs), among which 22 types are listed as being substances that require priority action. In February 1997, an environment standard for annual average of benzene 0.003mg/m³, trichloroethene 0.2mg/m³, tetrachloroethene 0.2mg/m³ was announced to cover air pollution. The analysis method for monitoring this standard involves solid-phase adsorption and thermal desorption. The analysis in this method involves sampling VOC in the atmosphere for 24 hours using a tube.

— Tube —

This is comprised of a glass or stainless tube filled with adsorption material. The adsorption material is graphite carbon black, carbon molecular sieves. These are used in multiple bed form to match targeted sample.

References

(1) Actual Measuring of Harmful Air Pollutants
    Publisher: Editing Committee for Actual Measuring of Harmful Air Pollutants
(2) Manual of Measuring of Harmful Air Pollutants
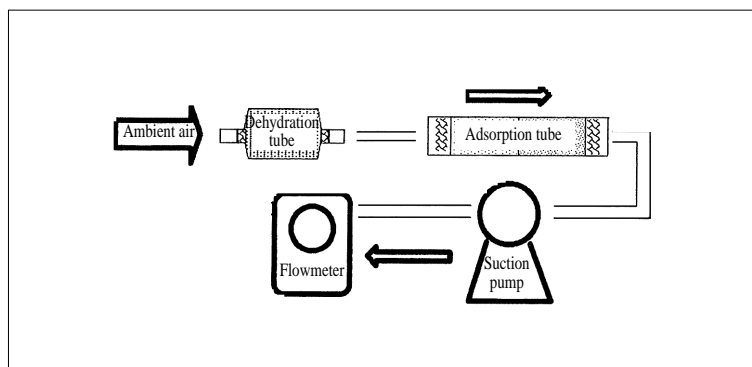   Environment Agency, Air Quality Bureau, Air Regulation Section Edition

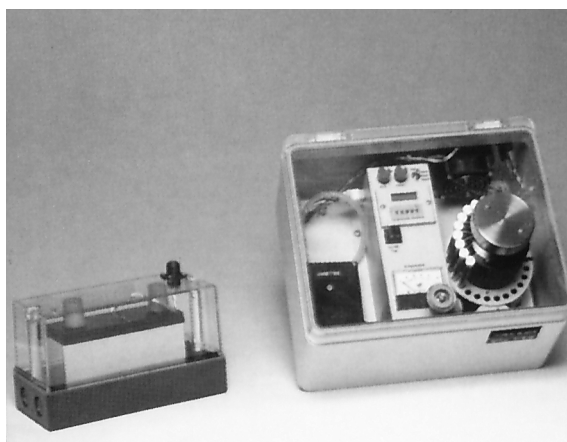Fig. 83 Sampling with tube collection method

Fig. 84 Continuous air sampler

4.8 Analysis of Volatile Organic Components (VOC) in Atmosphere (2)
– Solid-phase Adsorption & Thermal Desorption GC/MS

■**Analytical Conditions**

Thermal desorption ATD-400

Collection tube separation	: 280˚C(5miin)
Separation flow speed	: 50mL/min
Second trap separation	: 280˚C(2min)
Outlet split	: 8mL/min

Shimadzu GCMS-QP5050A

Column	: DB-1 60m ✕ 0.32mm I.D., 5µm(df)
Column temperature	: 40˚C(5min)-5˚C/min-150˚C - 10˚C/min-250˚C(5min)
Carrier gas	: He 100kPa

Fig. 85 ATD-400 system principle

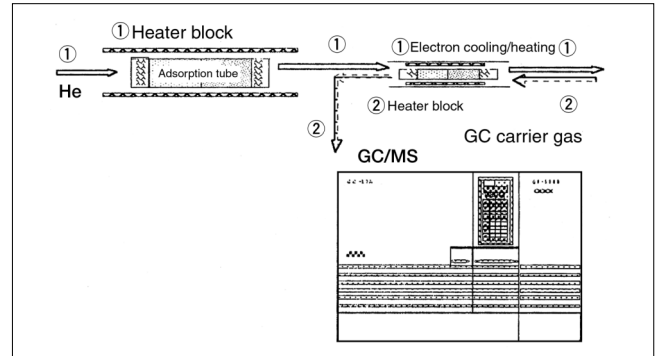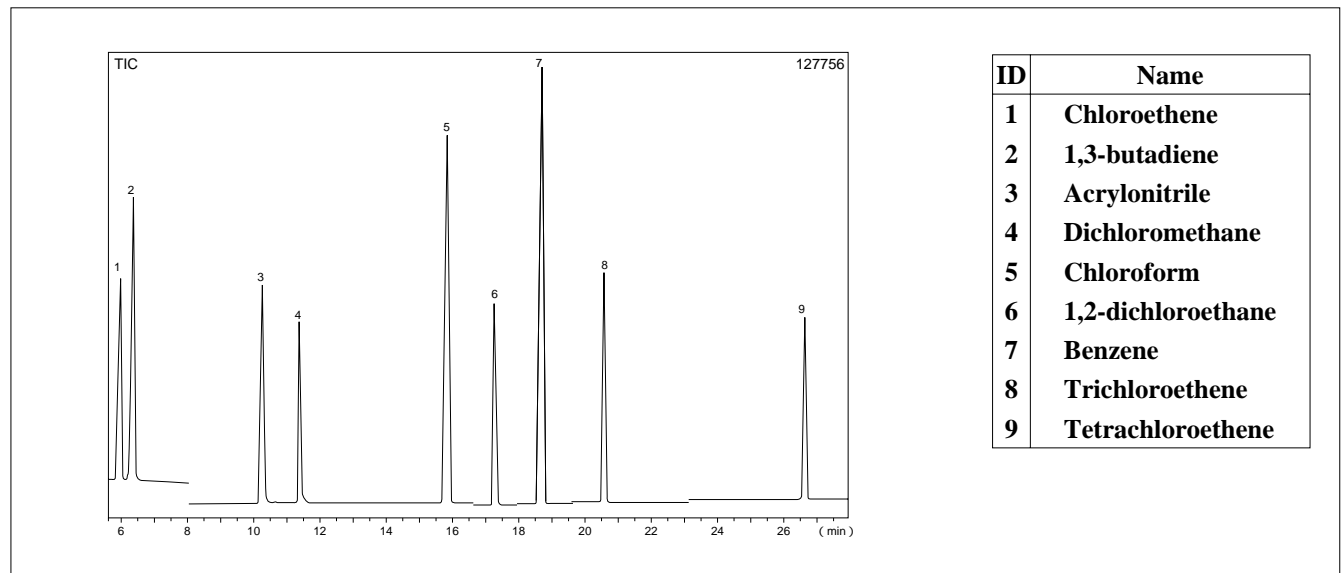| ID	Name
1	Chloroethene
2	1,3-butadiene
3	Acrylonitrile
4	Dichloromethane
5	Chloroform
6	1,2-dichloroethane
7	Benzene
8	Trichloroethene
9	Tetrachloroethene

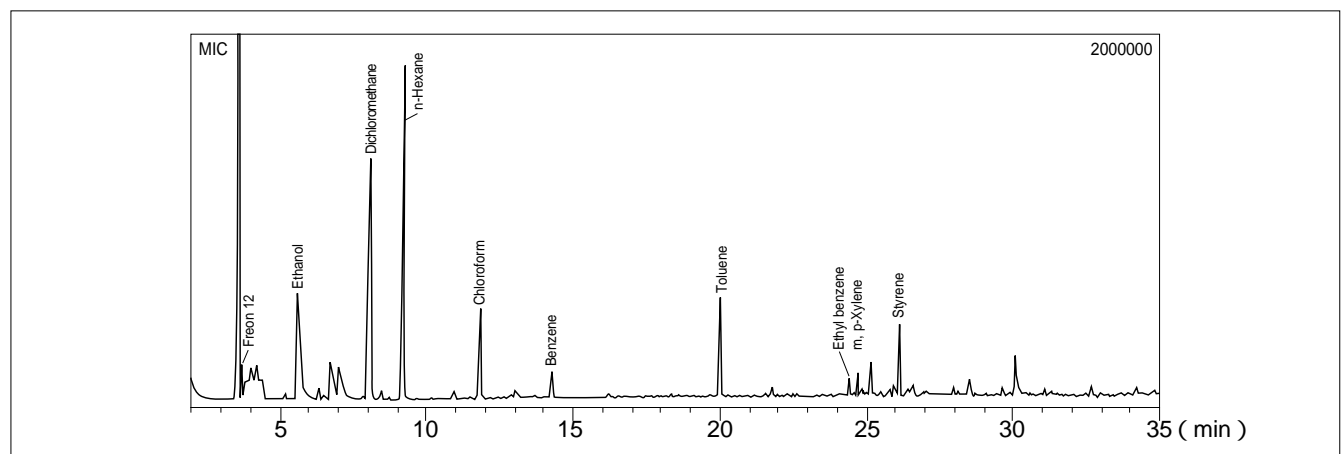Fig. 86 Analysis example (SIM method) of Nine HAPs elements (1ppm ✕ 10mL)

Fig. 87 Measuring example (SCAN method) of lab air

4.9 Analysis of Volatile Organic Components (VOC) in Atmosphere (1)
— Container Collection Method GC/MS

■Explanation

Various substances that are harmful to human health are being found in ambient air, and though the concentration may not be enough to harm human health directly, there are fears that exposure over time can lead to cancer, etc. With this as a background consideration, a law partially revising the Air Pollution Control Law was introduced in May 1996, and put into implementation from April 1st, 1997. The Central Council for Environmental Pollution Control published via the second verdict in October 1996 a list of 234 substances that are potentially harmful air pollutants (HAPs), among which 22 types are listed as being substances that require priority action. In February 1997, an environment standard for annual average of benzene 0.003mg/m³, trichloroethene 0.2mg/m³, tetrachloroethene 0.2mg/m³ was announced to cover air pollution. The analysis method called container collection involves the use of a collection canister (inert processed metal airtight sealing) used to sample the VOC in the atmosphere for 24 hours.

— Canister —

The canister is an airtight, spherical container, which is specially processed to be inert by being formed from a metal construction with electro polished inner surface and pure chrome-nickel oxide thin film (SUMMA®).

References

(1) Actual Measuring of Harmful Air Pollutants
   Publisher: Editing Committee for Actual Measuring of Harmful Air Pollutants
(2) Manual of Measuring of Harmful Air Pollutants
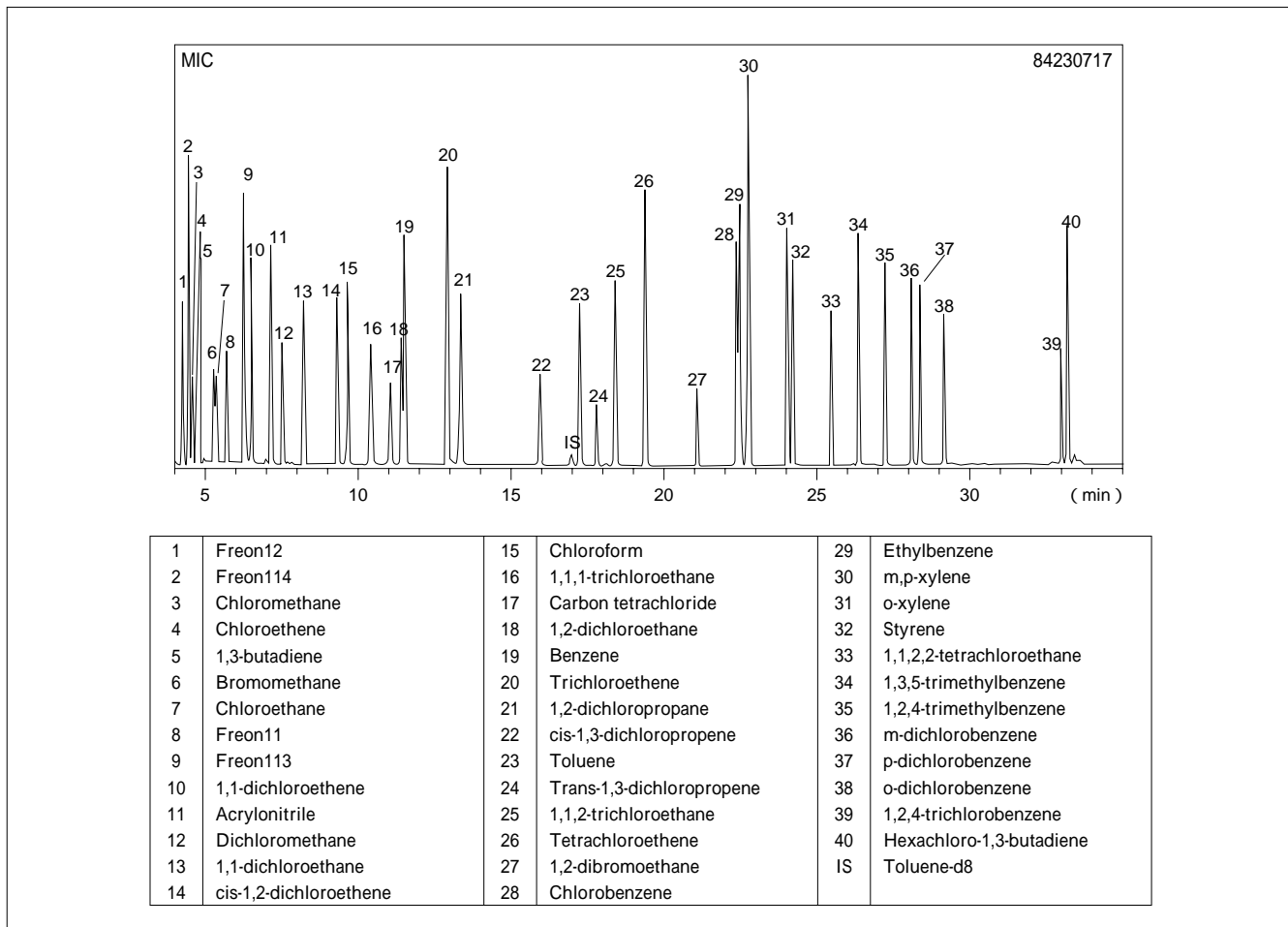   Environment Agency, Air Quality Bureau, Air Pollution Control Edition

#	Compound	#	Compound	#	Compound
1	Freon12	15	Chloroform	29	Ethylbenzene
2	Freon114	16	1,1,1-trichloroethane	30	m,p-xylene
3	Chloromethane	17	Carbon tetrachloride	31	o-xylene
4	Chloroethene	18	1,2-dichloroethane	32	Styrene
5	1,3-butadiene	19	Benzene	33	1,1,2,2-tetrachloroethane
6	Bromomethane	20	Trichloroethene	34	1,3,5-trimethylbenzene
7	Chloroethane	21	1,2-dichloropropane	35	1,2,4-trimethylbenzene
8	Freon11	22	cis-1,3-dichloropropene	36	m-dichlorobenzene
9	Freon113	23	Toluene	37	p-dichlorobenzene
10	1,1-dichloroethene	24	Trans-1,3-dichloropropene	38	o-dichlorobenzene
11	Acrylonitrile	25	1,1,2-trichloroethane	39	1,2,4-trichlorobenzene
12	Dichloromethane	26	Tetrachloroethene	40	Hexachloro-1,3-butadiene
13	1,1-dichloroethane	27	1,2-dibromoethane	IS	Toluene-d8
14	cis-1,2-dichloroethene	28	Chlorobenzene		

Fig. 88 EPA TO14+2 elements (1, 3-butadiene, acrylonitrile) 10ppbv

4.9 Analysis of Volatile Organic Components (VOC) in Atmosphere (2)
– *Container Collection Method GC/MS*

Reference Example 1

Ambient Air Collection Method using Canister

The canister is cleaned before being used for sampling, and set to vacuum state ready for sampling. The following two methods are used for long-period collection of ambient air.

♦ Passive sampling method

The difference in pressure between the atmosphere and canister are used, and the passive sampler adjusted to take samples.

♦ Pressurization collection method

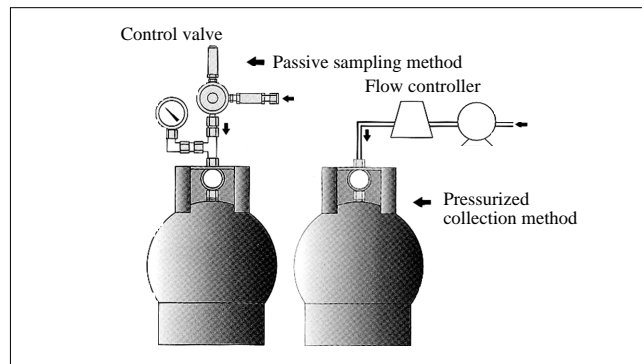Ambient air is sent in by metal bellows pump, and the passive sampler adjusted to take samples.

■Analytical Conditions

Tekmar-Dohrmann AUTOCan™

Concentration temperature	: -100˚C
Sample volume	: 400mL
Desorption temperature	: 220˚C
Desorption time	: 2min
Cryofocus	: -185˚C
	: 2min

Shimadzu GCMS-QP5050A

Carrier gas	: He 110kPa
Column	: AQUATIC 60m ✕ 0.25mm I.D., 1µm(df)
Column temperature	: 40˚C-3.5˚C/min-120˚C-6˚C/min -180˚C-20˚C/min-220˚C(6min)

Fig. 89 Ambient air collection method using canister

Fig. 90 AUTOCan™ analysis flowchart

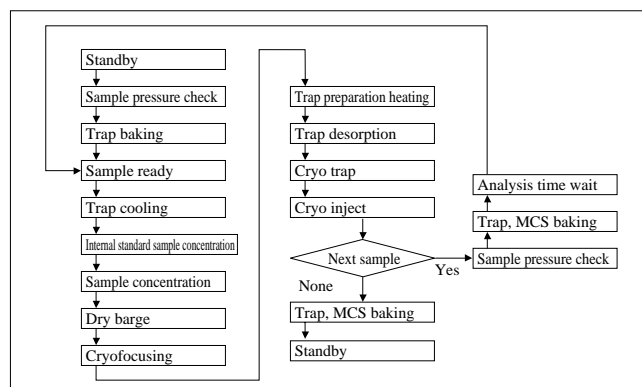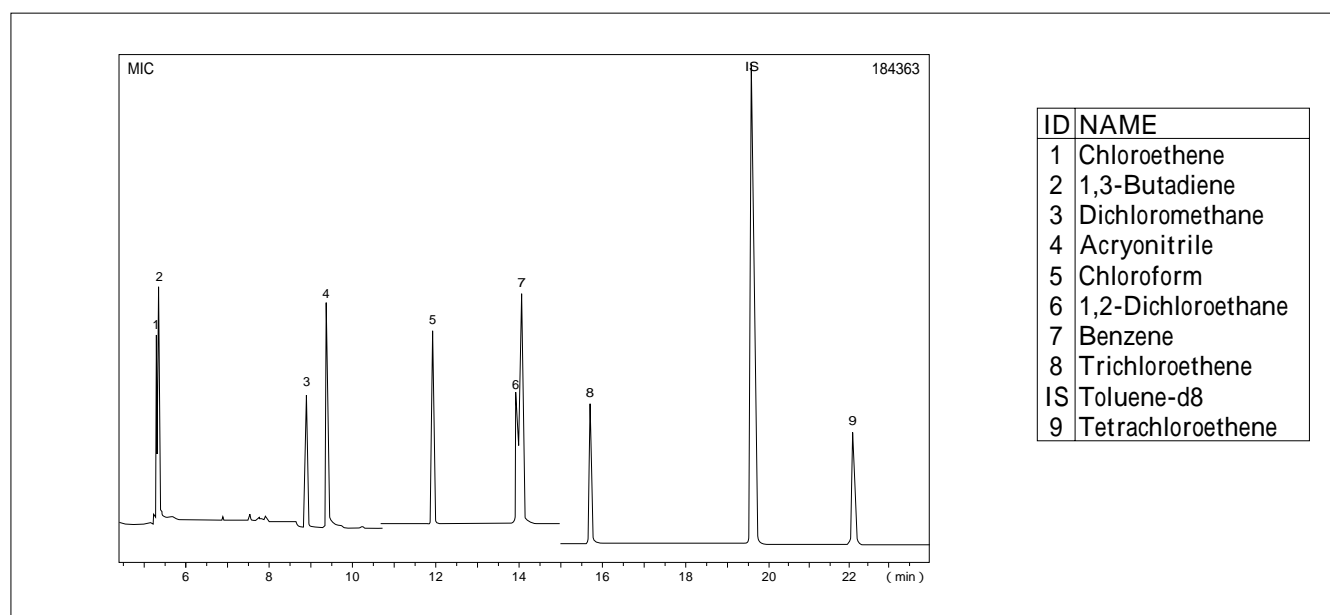| ID	NAME
1	Chloroethene
2	1,3-Butadiene
3	Dichloromethane
4	Acryonitrile
5	Chloroform
6	1,2-Dichloroethane
7	Benzene
8	Trichloroethene
IS	Toluene-d8
9	Tetrachloroethene

Fig. 91 Nine HAPs elements (elements from the 22 priority substances that can be simultaneously analyzed) 0.1ppbv

4.10 Analysis of Non-organic Elements in Atmosphere Dust (1) — *ICP-AES*

■Explanation

Normally, an air sampler is used as an atmosphere sample collection with a quartz filter or membrane filter used for collection. Collected atmosphere dust is put through a separation process with the filter, and harmful elements analyzed using ICP-AES. A highly sensitive analyzer is needed as the atmosphere dust volume is extremely minute. Here, this section introduces the inductively coupled plasma mass spectrometer ICPS-7500, which was used for analysis of urban atmosphere dust standard substances (NIST SRM1648). The solution for the decomposition process was inducted to the ICP, and qualitative analysis performed. The qualitative analysis results show the approximate concentration in the sample solution and the spectral profile. As, Ni, Mn, Cr, and Be from the priority substances and Pb and Cd from the regulated substances were qualitatively analyzed. Measuring was performed by calibration curve, and background compensation was used when necessary.

■Pretreatment

Add 10mL of nitric acid, 3mL of hydrogen peroxide, 5mL of hydrofluoric acid to 0.2g of sample, and decomposition using a microwave high-speed sample decomposition device. Evaporate until dry over a hotplate, then dissolve (1 + 1) with 5mL of nitric acid, and measure up to 100mL with purified water to make analysis sample.

■Analytical Conditions

Instrument	: ICPS-7500
High-frequency	: 27.12MHz
High-frequency output	: 1.2kW
Cooling gas	: Ar 14.0L/min
Plasma gas	: Ar 1.2L/min
Carrier gas	: Ar 0.8L/min
Purge gas	: Ar 3.5L/min
Sample suction volume	: 0.6mL/min
Observation method	: Side view
Observation height	: 11mm

Analysis name: Atmosphere dust　　　Sample name: NIST 1/500

Measuring results

100ppm or more	Ca	180								
10ppm or more	Mg	11	Al	69	P	12	S	30	K	21	Fe	80
	Pb	13								
1ppm or more	Na	8.9	Ti	6.0	Mn	1.5	Cu	1.1	Zn	9.1	Ba	2.3
1ppm or less	Li	.033	Be	.0026	B	.54	Si	.073	Sc	.0087	V	.22
	Cr	.76	Co	.033	Ni	.15	Ga	.053	Ge	.028	As	.14
	Se	.025	Sr	.31	Y	.019	Zr	.20	Nb	.052	Mo	.025
	Ru	.052	Rh	.032	Pd	.015	Ag	.0095	Cd	.13	In	.049
	Sn	.18	Sb	.057	Te	.076	La	.049	Ce	.14	Pr	.091
	Nd	.033	Sm	.017	Eu	.0016	Gd	.012	Tb	.010	Dy	.0069
	Ho	.0036	Tm	.0015	Yb	.0028	Lu	.0011	Hf	.036	Ta	.045
	W	.13	Re	.016	Ir	.0056	Au	.0075	Hg	.016	Tl	.0095
	Bi	.019	Er	.0055	Os	.016	Pt	.10			

Fig. 92 Estimated concentration using qualitative analysis

Analysis name: Atmosphere dust　　　Sample name: NIST 1/500

Li 670.785　Be 313.107　B 208.959　Na 589.592　Mg 279.553　Al 396.153

Si 251.612　P 178.287　S 180.731　K 766.491　Ca 317.933　Sc 361.384

Ti 334.941　V 311.071　Cr 267.716　Mn 257.610　Fe 259.940　Co 228.616

分析名称：大気粉塵　　　試料名：NIST 1/500

Ni 231.604　Cu 327.396　Zn 213.856　Ga 294.364　Ge 209.423　As 189.042

Se 196.026　Sr 407.771　Y 371.029　Zr 343.823　Nb 309.418　Mo 202.030

Ru 269.207　Rh 343.489　Pd 340.458　Ag 328.068　Cd 226.502　In 230.606
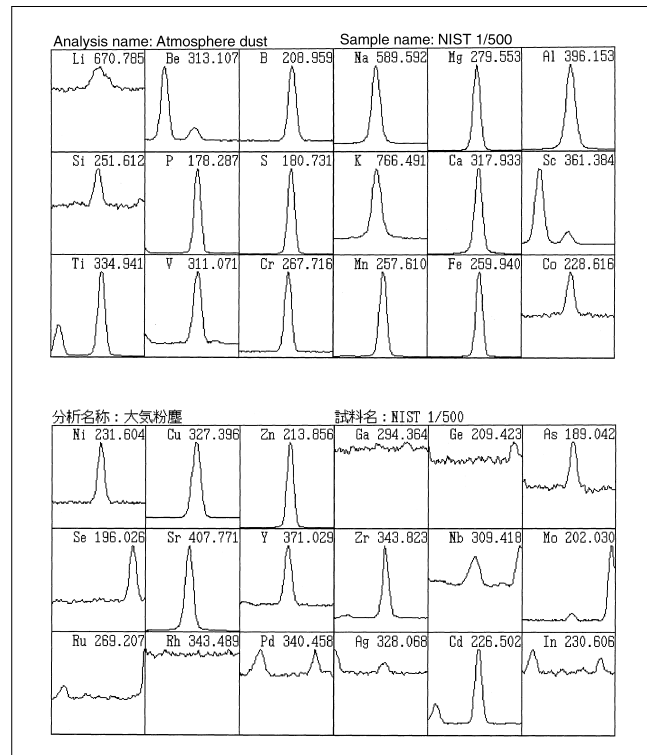
Fig. 93 Spectral line profile for qualitative analysis

4.10 Analysis of Non-organic Elements in Atmosphere Dust (2) — ICP-AES

Element	Measuring Wavelength (nm)	Analytical Value (µg/g)	Guaranteed Performance (µg/g)
Ni	231.604	85.0	82±3
As	189.042	123	115±10
Be	313.107	2.45	
Mn	257.610	815	(860)
Cr	267.716	402	403±12
Pb	220.351	6500	6550±80
Cd	226.502	77.0	75±7

Parenthesis ( ) denote reference value.

Chart 12 Analysis results of atmosphere dust
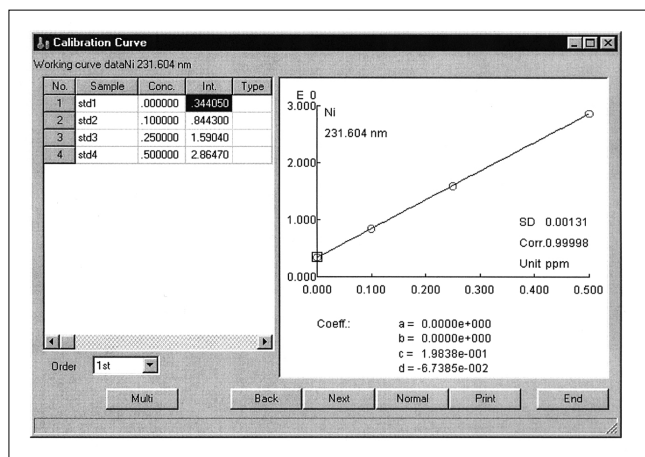
Fig. 94 Ni calibration curve
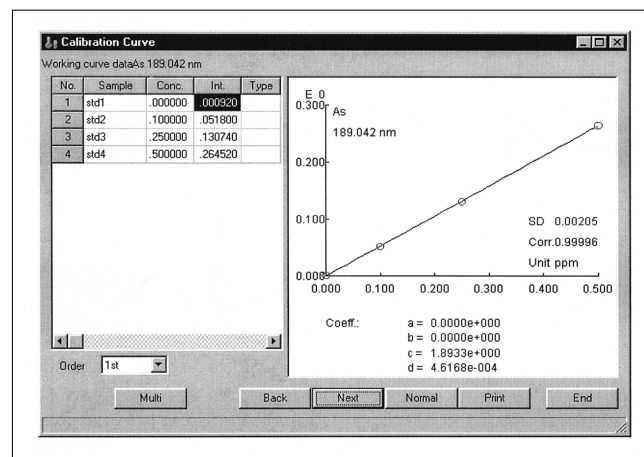
Fig. 95 As calibration curve
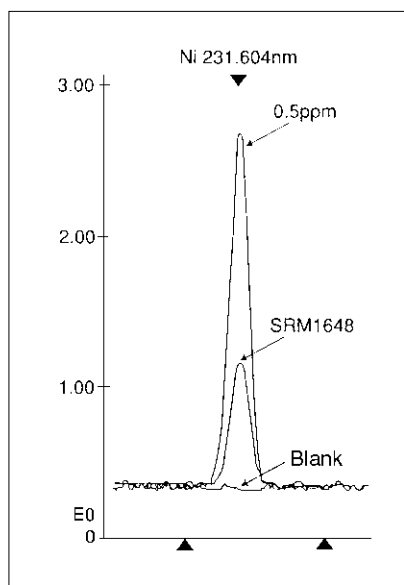
Fig. 96 Ni Spectral line profile
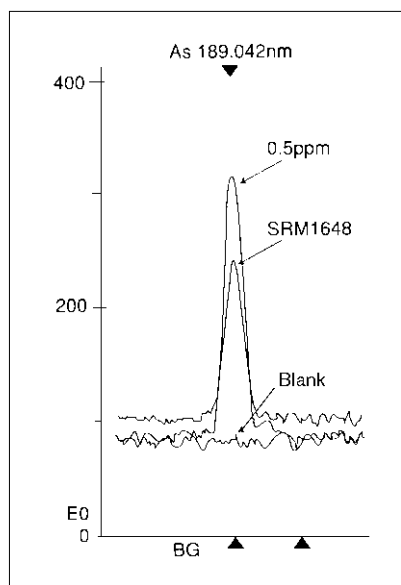
Fig. 97 As Spectral line profile
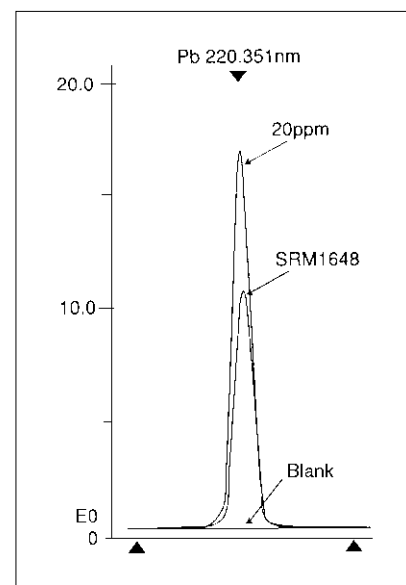
Fig. 98 Pb Spectral line profile

5. Industrial Waste

5.1 Screening of Waste Plastic Material using Horizontal ATR (1) — *FTIR*

■Explanation

A wide range of plastic materials is used in automobiles, household appliances and different kinds of containers to the extent that we have arrived at an era where recycling should become compulsory. The first important step in recycling plastics is the task of screening for separation purposes of the different types of plastics that have been collected. Here, the requirements are (1) instantaneous distinction, (2) measuring regardless of shape, and (3) measuring online. At the moment, the FTIR has trouble fulfilling all three requirements, however this section introduces a horizontal ATR method using diamond prism with which the FTIR measures objects regardless of shape comparatively well – especially solid objects.

■Device Outline

Figure 99 shows a diagram of the Instrument. On the top section of the Instrument there is a stainless steel plate secured with a diamond prism implanted its central section. There are two types of plate available, one with a single-reflector (diameter of 1mm) prism and the other with a multi-reflector (diameter of 3mm) prism, and sample holding by pressure adjustment can also be installed. Furthermore, on the left and right sides of the Instrument there are purge pipe fittings that can be fitted into the sample chamber wall, so that even if the sample chamber lid is open, measuring can still be performed without any affect on the atmosphere in the chamber.

■Measuring Conditions

Decomposition   : $8cm^{-1}$
Estimation   : 100
Apodaizu function : Happ-Genzel
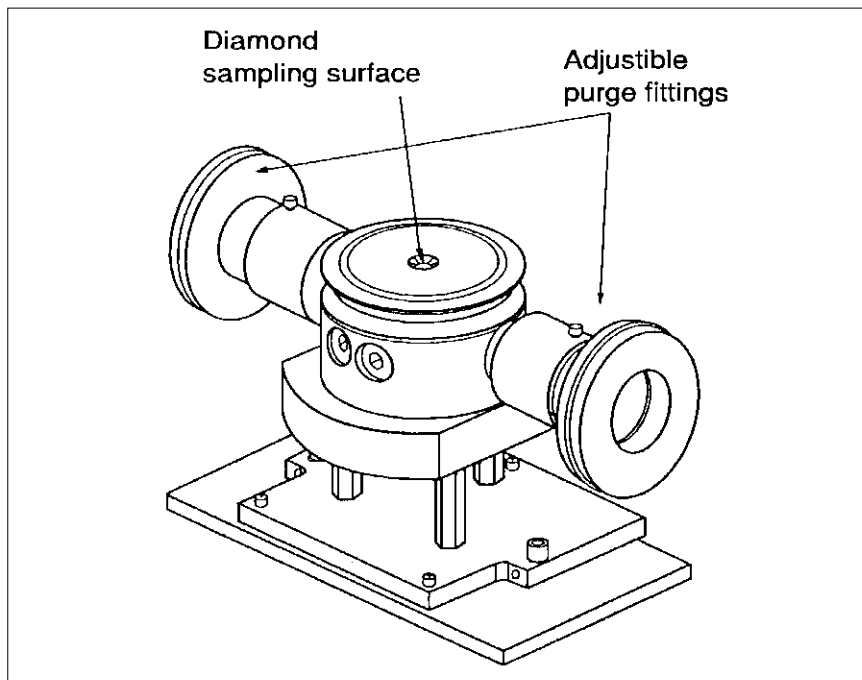   : DLATGS

Fig. 99 External view of instrument

5.1 Screening of Waste Plastic Material using Horizontal ATR (2) — *FTIR*

■Measuring Examples

Figures 100 to 103 show the spectral profiles of polystyrene (PS), polyethylene (PE), polyproplyene (PP), and acrylonitrile butadiene styrene resin. All of these figures show results for plate-shaped samples, but the FTIR can be used to measure quite hard objects like pellets and powder samples.
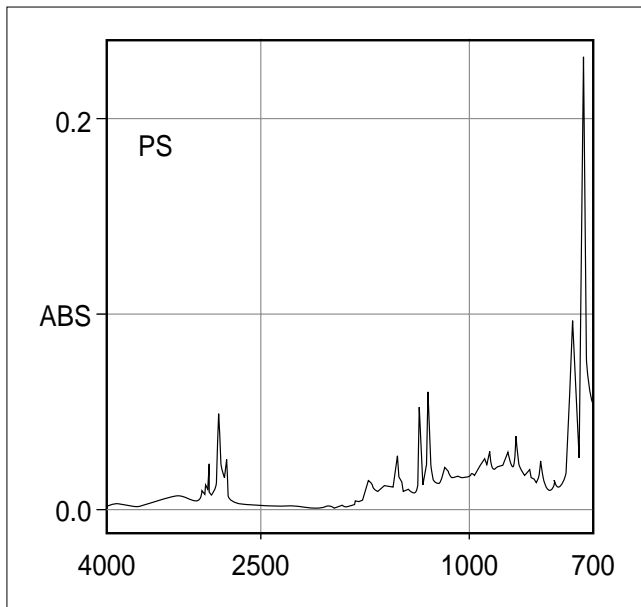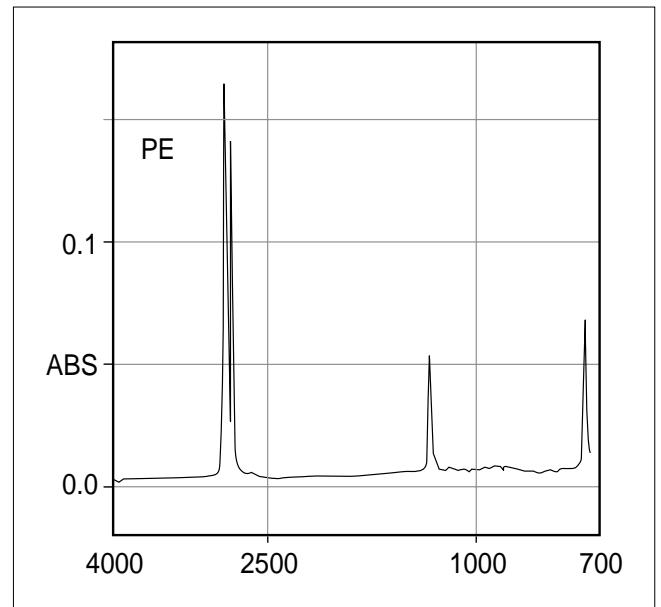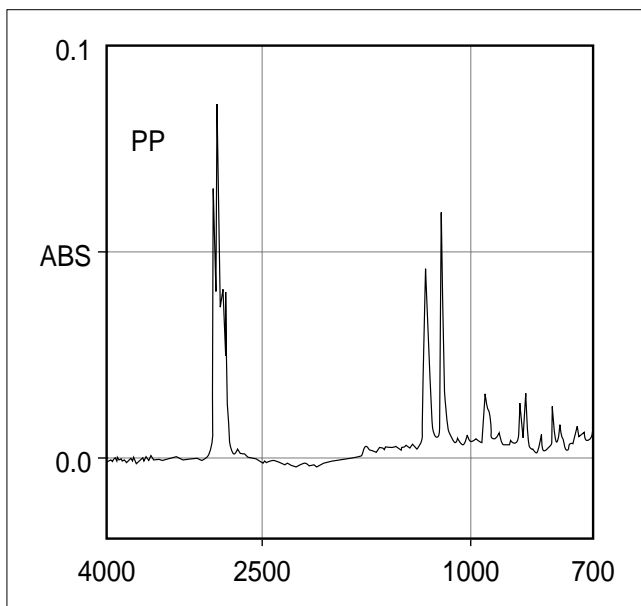
Fig. 100 PS spectra (1/cm)

Fig. 101 PE spectra (1/cm)

Fig. 102 PP spectra (1/cm)
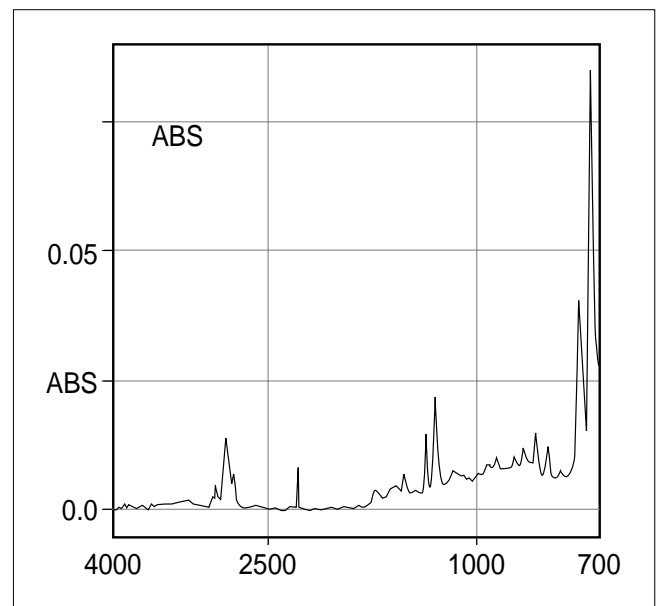
Fig. 103 ABS spectra (1/cm)

Industrial Waste

5.2 Analysis of Non-organic Elements in eluate of incineration ash (1) — *ICP-AES*

■Explanation

Industrial waste is usually buried after being incinerated or compacted. The amount of elution from this type of waste is governed by law, with elements like Cd, Hg, Pb, Cr^{6+}, As, Cu and Zn. Unlike tap water, wastewater and industrial waste have high concentrations of coexisting elements, which makes analysis difficult. Here, the ICP spectrometry analysis method can measure samples with minimal affect from coexisting elements at higher sensitivity with the aid of an ultrasound nebulizer.

References

(1) Verification method for metals, etc., contained in industrial waste
(2) Japanese Industrial Standard (JIS) K0102

■Pretreatment

Under the conditions of the verification method for metals, etc., contained in industrial waste, an elution operation was performed. Next, 100mL of sample was taken from the test solution, 5mL of nitric acid added, boiled over a hotplate for approximately 10 minutes, cooled, measured up to 100mL with purified water, and stirred sufficiently.

■Analtytical Conditions

Device	: ICPS-7500	
	: Ultrasonic nebulizer UAG-1	
High frequency	: 27.12MHz	
Nebulizer	: Coaxial type	UAG-1
High-frequency output	: 1.2kW	0.8kW
Cooling gas	: Ar 14.0L/min	14.0L/min
Plasma gas	: Ar 1.2L/min	1.2L/min
Carrier gas	: Ar 1.0L/min	0.9L/min
Purge gas	: Ar 3.5L/min	3.5L/min
Sample suction volume	: 2.0mL/min	2.0mL/min
Observation method	: Side view	Side view
Observation height	: 15mm	15mm

Element	Analytical Value (mg/L)	
Cd	<0.0005	*
Pb	0.38	*
Cr	<0.0005	*
As	0.010	*
Cu	0.025	
Zn	0.22	
Fe	0.085	
Mn	0.005	
Mo	0.015	
Sb	0.21	*

*: Use of ultrasonic nebulizer UAG-1

Chart 13 Incinerated ash analysis results (mg/L)

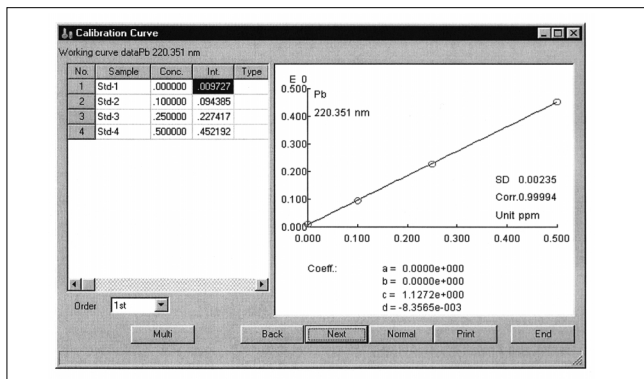# 5.2 Analysis of Non-organic Elements in eluate of incineration ash (2) — ICP-AES
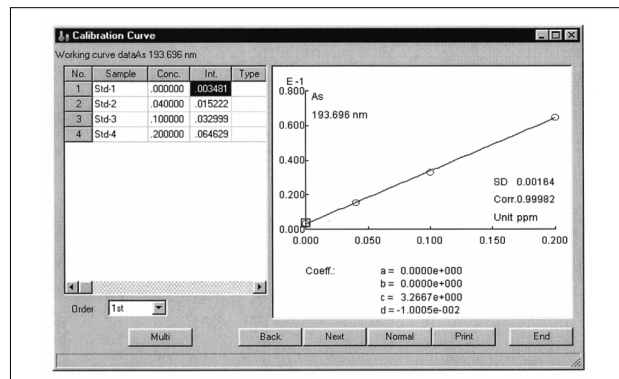

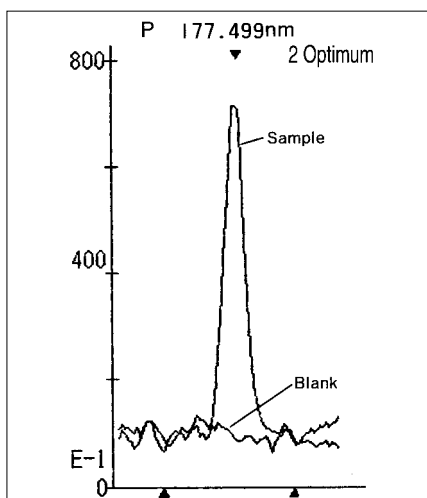Fig. 104 Pb calibration curve

Fig. 105 As calibration curve

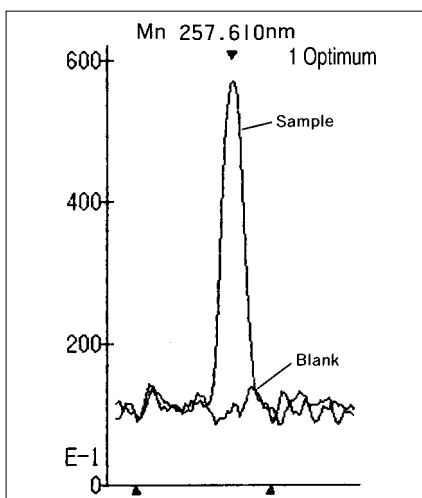Fig. 106 P177.499nm profile

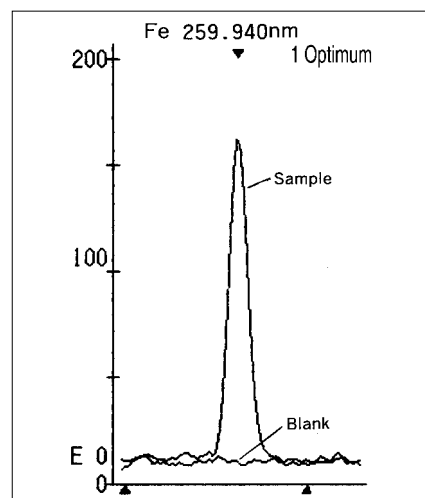Fig. 107 Mn 257.610nm profile

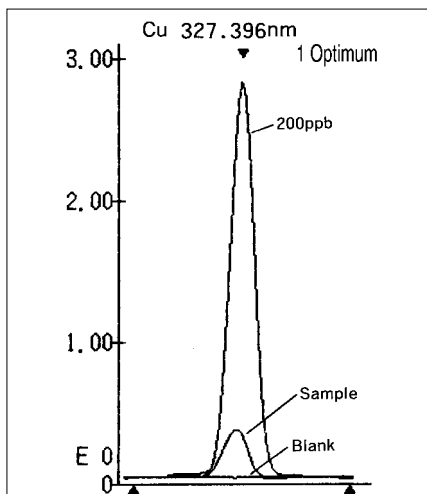Fig. 108 Fe 259.940nm profile
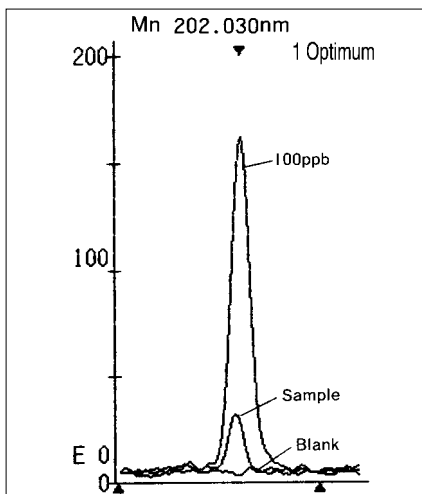

Fig. 109 Cu 327.396nm profile

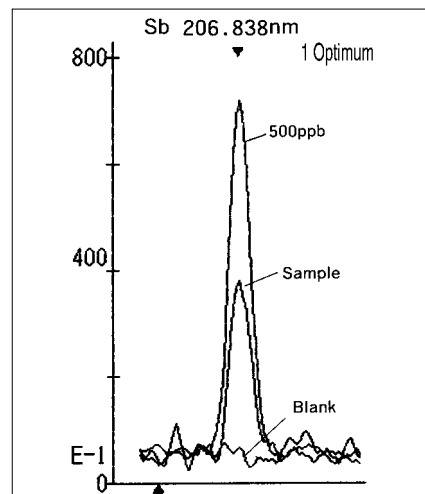Fig. 110 Mo 202.030nm profile

Fig. 111 Sb 206.838nm profile

Industrial Waste

5.3 X-ray Fluorescence Spectrometric Analysis of Industrial Waste (Sludge) — *XRF*

■Explanation

Industrial wastes like sludge and mud have their elements analyzed so that they can be classified for burial, management or reuse. Easy, fast and thorough fluorescent x-raying is the optimum form of analysis for this work. The measuring method employed is qualitative and quantitative analysis. With this method, qualitative analysis is conducted, followed by quantitative analysis of the detected elements or the intensity of that fluorescent x-ray with FP method. Standard samples are not necessary, so this method is extremely useful when the types of analysis samples are numerous and the marketed standard samples are few. The following figure and chart show qualitative and quantitative analysis results as analysis examples of industrial waste.

Quantitative Lower Limit Value (target)

1 to 5ppm (this differs according to element)

■Pretreatment

Grinding Conditions
Instrument : Shaker mill T1-100
Container : Tungsten carbide
Time   : 3min

Pressurized Design Conditions
Device   : Briquet machine MP-35
Pressure : 30t
Time   : 30 sec
Ring   : Vinyl chloride

■Analtytical Conditions

Device   : Sequential x-ray fluorescence
                       spectrometer XRF-1700
X-ray tube   : 4kW, Be thin window, Rh target
Tube voltage   : 40kV
Tube ampere   : 95mA
Spectrometer crystals : LiF, Ge, PET, TAP, SX-48, -58N,
                       -76, -14
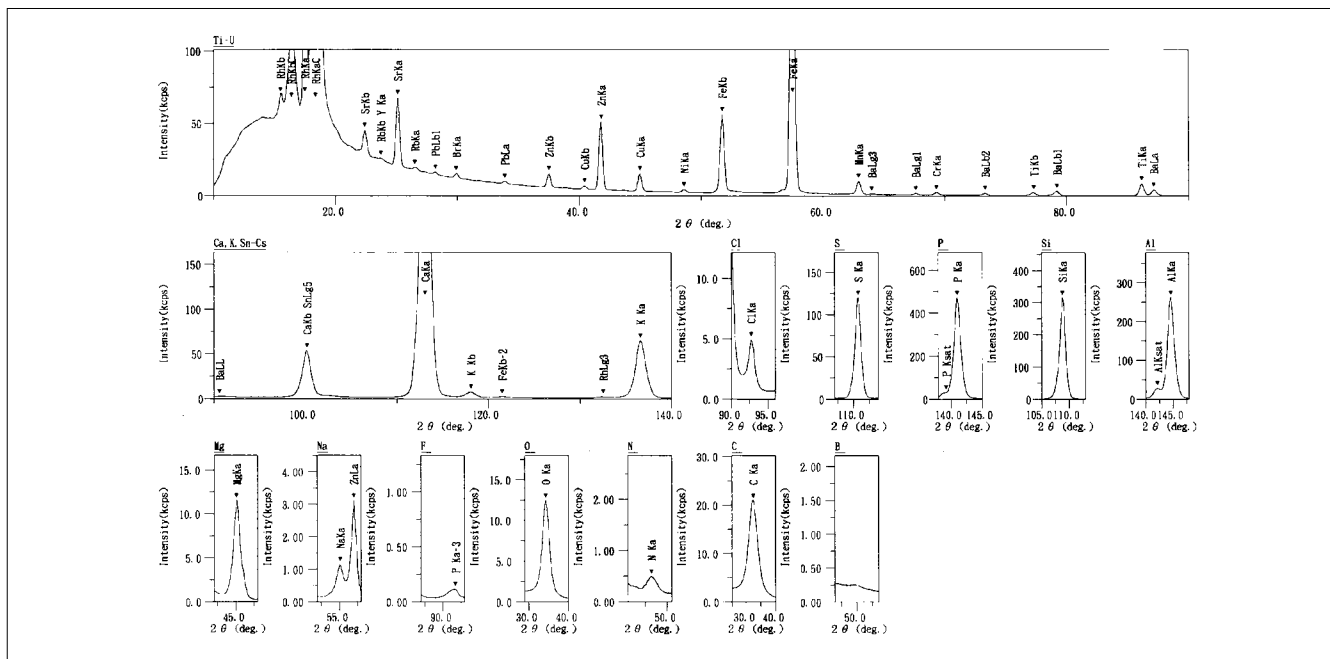Scanning speed   : 8 degree, 4 degree, 2 degree/min

Fig. 112 Qualitative analysis of sludge

CO$_2$	N$_2$O$_5$	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	SO$_3$	Cl	K$_2$O	CaO	TiO$_2$	Cr$_2$O$_3$	MnO	Fe$_2$O$_3$	NiO	CuO	ZnO	Br	Rb$_2$O	SrO	Y$_2$O$_3$	BaO	PbO
60.73	9.99	0.17	0.85	6.97	8.89	5.72	2.12	0.064	0.31	2.81	0.16	0.012	0.038	0.90	0.004	0.018	0.055	0.002	0.001	0.019	0.000	0.18	0.002

Chart 14 Qualitative analysis value (%) of sludge

6. Others

6.1 Analysis of Non-agitated Soil Core Sample using Microscopic FTIR (1) — *FTIR*

■Explanation

To understand the existing form and distribution status of non-organic compounds and organic compounds contained in soil, important information - such as knowledge of the features attributable to the quality and formation of the soil in question - is needed. There are almost no examples of direct soil sampling using FTIR, but sampling of soil hardened with resin is possible. As a soil analysis method, the resin hardening method(1) is actively used to observe and analyze micro structures and surface analysis, because soil samples can be taken by core sampler and kept in a non-agitated state. Here, this section introduces a measuring example of a sample prepared using this method.

Reference

(1) Kenji Tamura, Sadao Nagatsuka, Hiroshi Ohba
    Japan Soil Nutrient Society Magazine: 166-176 (1993)

■Pretreatment

The sample used consisted of the A layer of black soil taken from an eulalia plain, and the pretreatment consisted of the method depicted in reference material (1), which was performed in the following way. The sample provided by core sampler was wind dried, then hardened by impregnation of a polyester-based resin. The sample was then cut to a suitable size, the surface polished, and used for measuring. The prepared sample was set on the stage of an infrared microscope, and measured by mapping employing a reflective method for 5✕5 mm range with aperture size 200 µm square.

■Results

Figures 113 and 114 show the silicic acid compound from the spectra obtained in the measuring results. Both figures show absorption peculiarities for silicic acid compound in the vicinity of 1100 cm^{-1}.

■Measuring Conditions

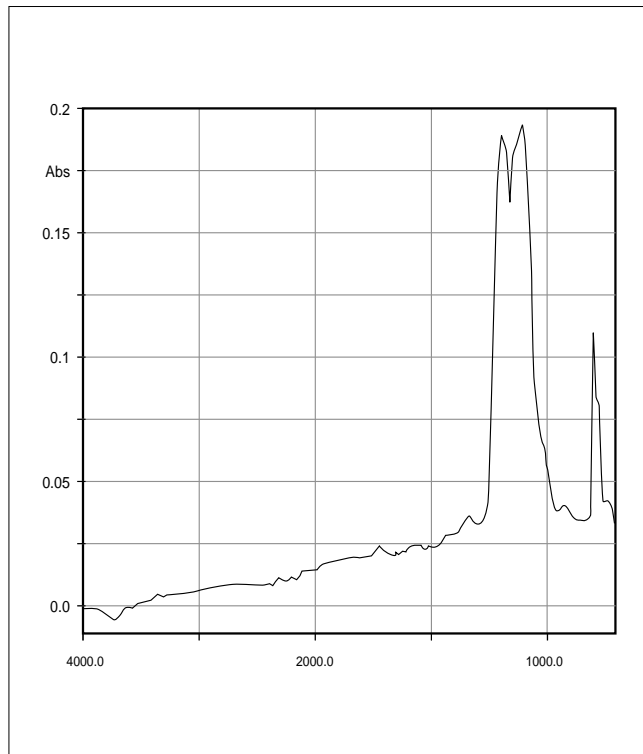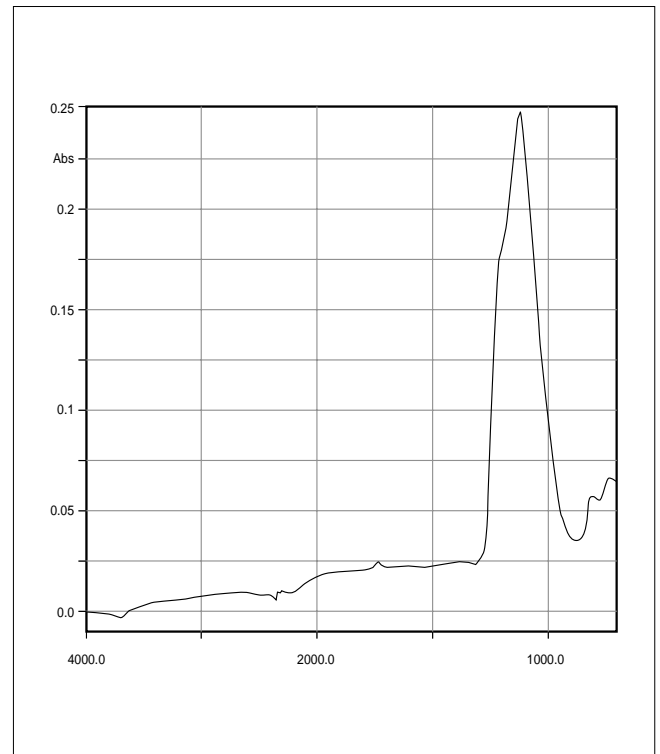|	
Mode	: Reflection
Decomposition	: 8cm^{-1}
Estimate	: 40
Apodaizu function	: Happ-Genzel
Detector	: MCT
Data processing device	: Kramers-Kronig conv.

Fig. 113 Non-organic compound spectrum (1)

Fig. 114 Non-organic compound spectrum (2)

Others

6.1 Analysis of Non-agitated Soil Core Sample using Microscopic FTIR (2) — *FTIR*

If the peak is targeted, and a three-dimensional measuring surface is created from vertical axis values for the peak height in a range of 800 to 1250 cm^{-1}, the diagram in figure 115 can be achieved. The protruding sections show the distribution of silicic acid compound.
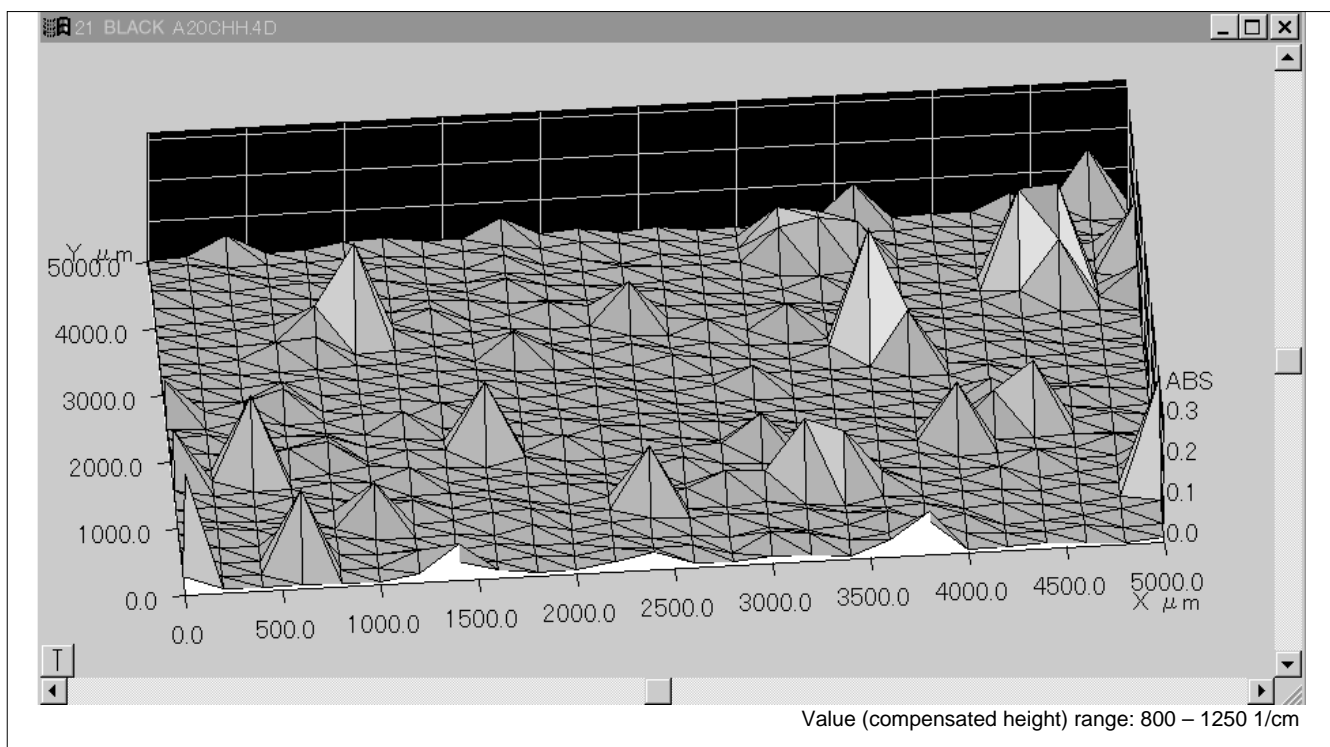

Fig. 115 Mapping diagram of soil core sample

6.2 Analysis of Volatile Organic Compounds (VOC) in Soil (1) — *GC/MS*

■Explanation

Following on from the amendments to the water quality standard in tap water in December 1992 and the environment standard for environment water in March 1993, a further amendment was also implemented for the wastewater standard in February 1994. Next, based on these water standards, the environment standard related to pollution of soil was amended in February 1994. The head space method and purge trap method are used for analysis of the compounds concerned. The head space method features ease of use, provides good reproducibility, can accommodate an auto sampler, and carry over (conforming pollutant level of device caused by concentration level of elements) is minimal. The purge trap method allows analysis of low-concentrate samples at high sensitivity as samples can be concentrated using a collecting agent, which provides excellent sensitivity of 10 to 100 times more than that of the head space method.

References

(1) Drinking Water Test Method & Explanation, Japan Water Works Association volume
(2) Environmental Water Analysis Manual, Environmental Science Research Group volume
(3) New Wastewater Standards and Other Analysis Methods, Environmental Science Research Group volume
(4) Concerning additional items for environment standard related to soil pollution
(Verdict) Central Environment Think Tank January 14th, 1994

■Pretreatment

Creation of Sample

Gravel and pieces of wood exceeding a granular diameter of 5 mm are removed from collected soil.

Sample Solution Preparation

50g of sample and 500mL of solvent (purified water: water without VOC) are placed in a 500mL conical flask with threaded inlet and agitator placed inside, and the flask sealed immediately.

Solving Out

The prepared sample is kept at room temperature and atmosphere (20˚C and 1 atmosphere) while being continually stirred for 4 hours using a magnetic stirrer.

Creation of Test Solution

When the above operations are completed, let the sample solution stand for 10 to 30 minutes, then pass it through a membrane filter with perforation diameter of 0.45 µm to make the measuring sample **solution.**

■Analtytical Conditions

Head Space Method

Head Space Sampler HS-40

Sample volume	: 10mL+NaCl 3g
Sample temperature	: 60˚C
Heat retaining time	: 30min
Needle temperature	: 120˚C
Line temperature	: 150˚C
Pressurization time	: 2min
Injection time	: 0.20min

Shimadzu GCMS-QP5050A

Carrier gas	: He 120kPa
Column	: DB-624 60m ✕ 0.32mm I.D., 1.8µm(df)
	: 40˚C(2min)-10˚C/min -200˚C(2min)

Purge Trap Method

Tekmar-Dohmann LSC3000

Sample volume	: 5mL
Adsorption tube	: G-2(Tenax-Silica gel)
Purge time	: 5min (room temp)
Dry purge time	: 2min
Purge flow rate	: 30mL/min
Desorption time	: 3min(200˚C)
Injection	: 2min(200˚C)
Baking	: 220˚C(30min)
Transfer	: 150˚C

Shimadzu GCMS-QP5050A

Carrier gas	: He 120kPa
Column	: DB-624 60m ✕ 0.32mm I.D., 1.8µm(df)
Column temperature	: 40˚C(5min)-4˚C/min-80˚C -6˚C/min-140˚C-8˚C/min-180˚C -40˚C/min-200˚C(2min)

6.2 Analysis of Volatile Organic Compounds (VOC) in Soil (2) — *GC/MS*
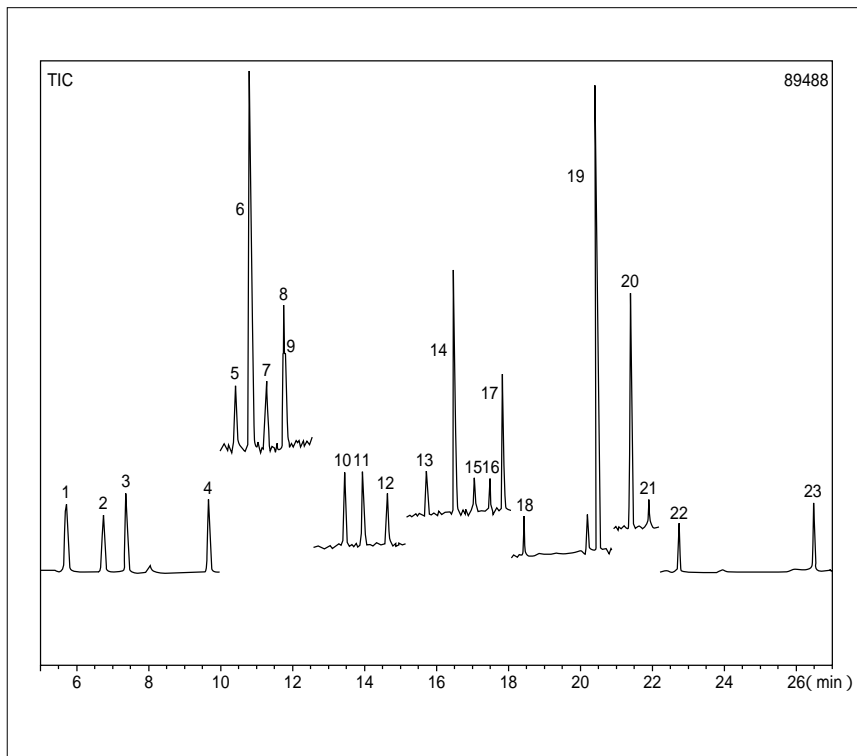

Fig. 116 SIM chromatogram (head space method) for sample with 23
standard elements (1µg/L) added to soil

ID	Name	SIM Selected Ions
1	1,1-dichloroethene	96,61
2	Dichloromethane	84,86
3	trans-1,2-dichloroethene	96,61
4	cis-1,2-dichloroethene	96,61
5	Chloroform	83,85
6	1,1,1-trichloroethane	97,99
7	Tetrachloromethane	117,119
8	Benzene	78,77
9	1,2-dichloroethane	62,64
10	Trichloroethene	130,132
11	1,2-dichloropropane	63,62
12	Bromodichloromethane	83,85
13	cis-1,3-dichloropropene	75,110
14	Toluene	92,91
15	trans-1,3-dichloropropene	75,110
16	1,1,2-trichloroethene	97,99
17	Tetrachloroethene	166,164
18	Dibromochloromethane	129,127
19	m,p-xylene	106,91
20	o-xylene	106,91
21	Bromoform	173,175
22	p-bromofluorobenzene(IS)	174,176
23	p-dichlorobenzene	146,148

Chart 15 SIM selected ions
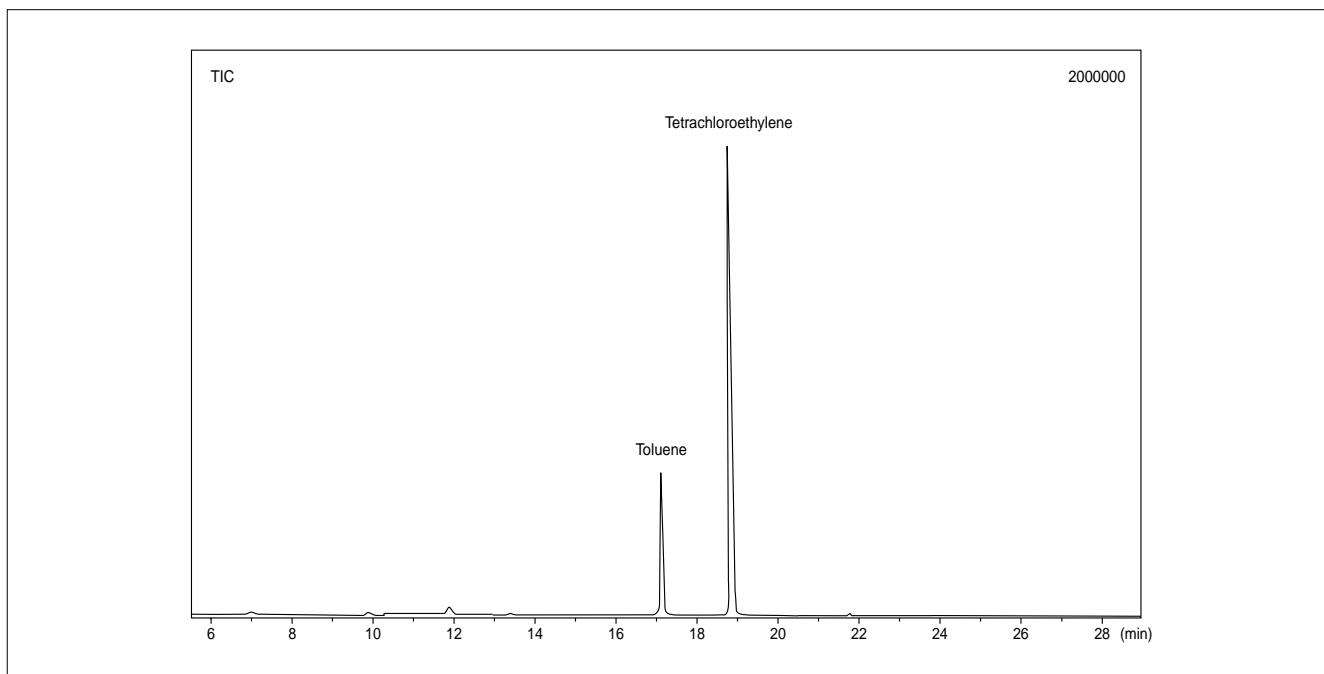
Fig. 117 SIM chromatogram of soil (purge trap method)

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SHIMADZU