

Analysis Guidebook

Electronic and Semiconductor
Industry

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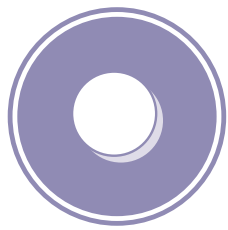
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1. Materials

1.1 Analysis of the Hardening Process of Epoxy Adhesive (1) - FTIR

■ Explanation

The molecular structure of some polymeric materials will change over time when heated, exposed to light or mixed. FTIR is one of the effective analysis methods for tracking this change and has the added feature of being able to simultaneously track multiple absorption peaks. The following introduces an analysis example for the hardening process in epoxy-based adhesive.

Epoxy adhesive hardens upon mixing of the main ingredient and a hardener following the process shown in Fig. 1.1.1. This process was measured over a fixed time interval and the nature of the changes in the functional groups investigated.

■ Pretreatment

A two-agent mixture type epoxy adhesive was mixed and then smeared on a KBr aperture plate of a high-temperature heating cell (special order item). Measuring was performed at five minute intervals over 60 minutes at 80°C.

■ Results

From the spectrum in Fig. 1.1.2 it can be seen that there are hardly any changes in the absorption peculiar to the alkyl groups, carbonyl groups and benzene rings. Conversely, it can be seen that the peaks of the epoxide, amino and hydroxyl groups are gradually changing. In Figs. 1.1.3 and 1.1.4 the peak regions of the epoxide and hydroxyl groups are magnified. Shown in Fig. 1.1.5 are the time course curves of the peak area values of 3,650 to 3,140 cm^{-1} (hydroxyl group) and 925 to 899 cm^{-1} (epoxide group). In addition, shown in Fig. 1.1.6 are the time course curves of the epoxide group measured at cell temperatures of 60°C, 80°C and 100°C.

■ Analytical Conditions

Instrument : FTIR-8200
High-temperature Heating Cell
(special order item)
Resolution : 8 cm^{-1}
Accumulation : 1min
Apodization : Rectangular
Detector : DLATGS

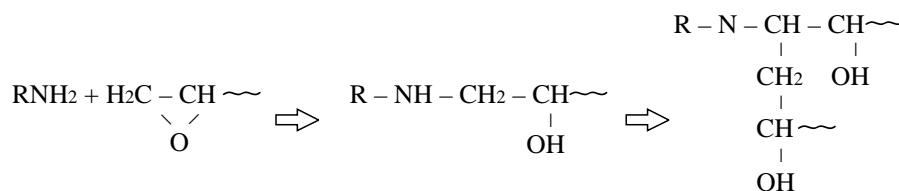


Fig. 1.1.1 Epoxy resin hardening process

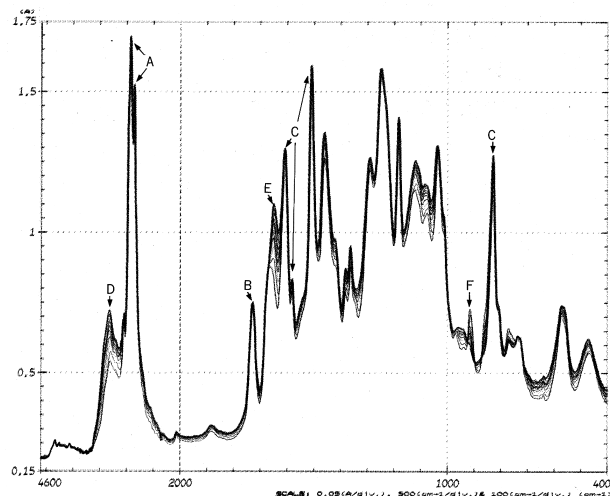


Fig. 1.1.2 Epoxy adhesive infrared spectrum

[A: alkyl group, B: carbonyl group, C: benzene group, D: hydroxyl group, E: amino group, F: epoxide group]

1.1 Analysis of the Hardening Process of Epoxy Adhesive (2) - FTIR

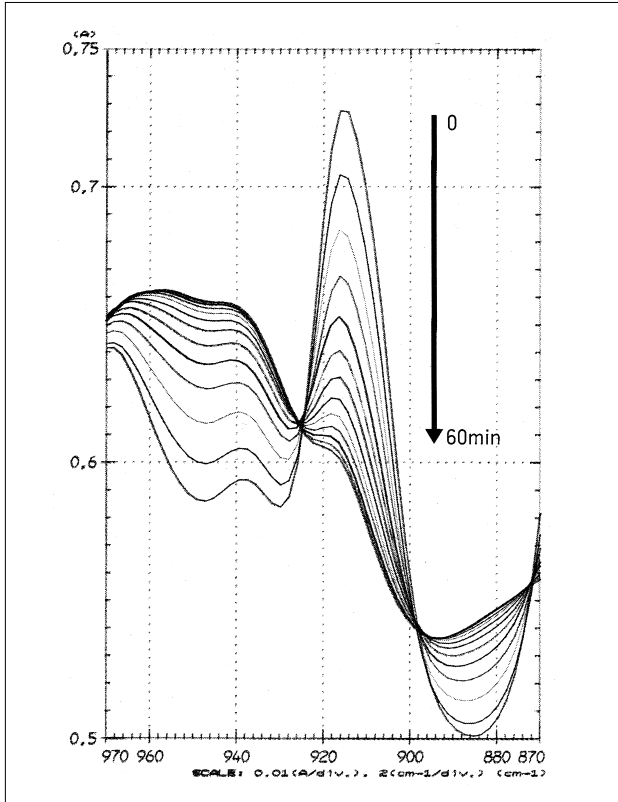


Fig. 1.1.3 Epoxide group infrared spectrum

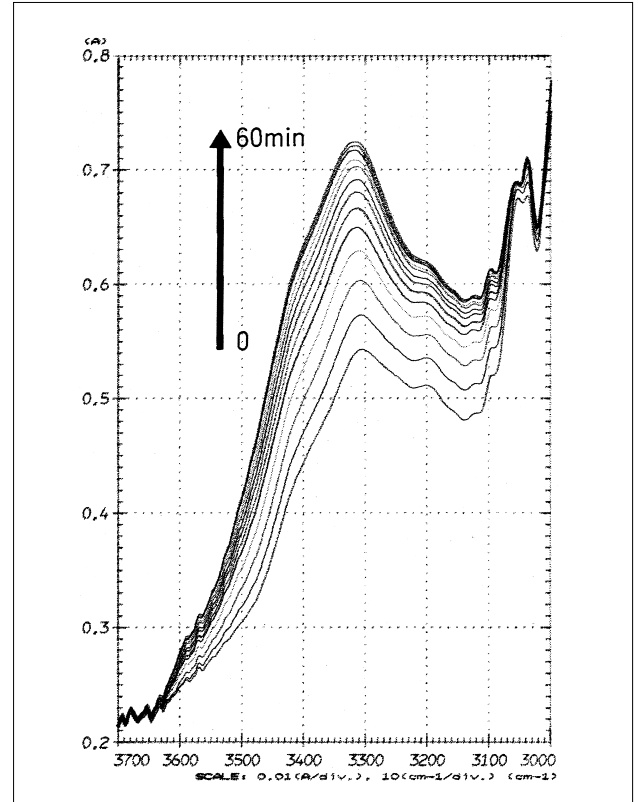


Fig. 1.1.4 Hydroxyl group infrared spectrum

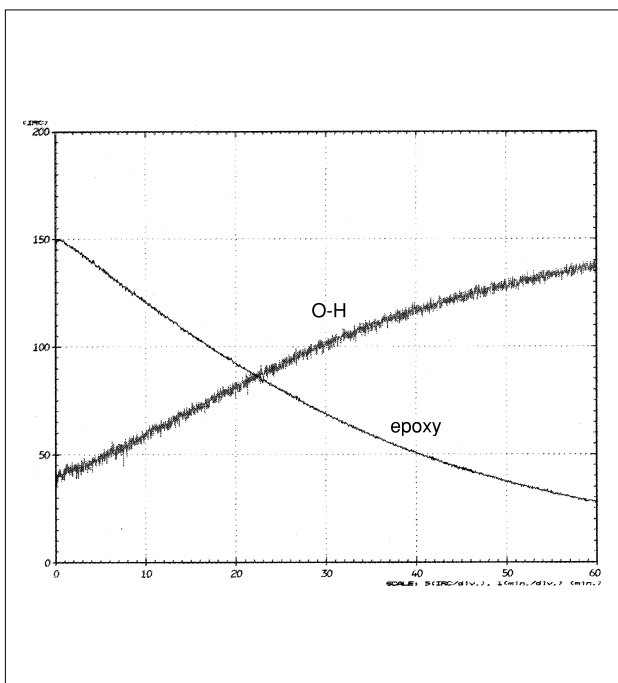


Fig. 1.1.5 Time course curves of hydroxyl group and epoxide group

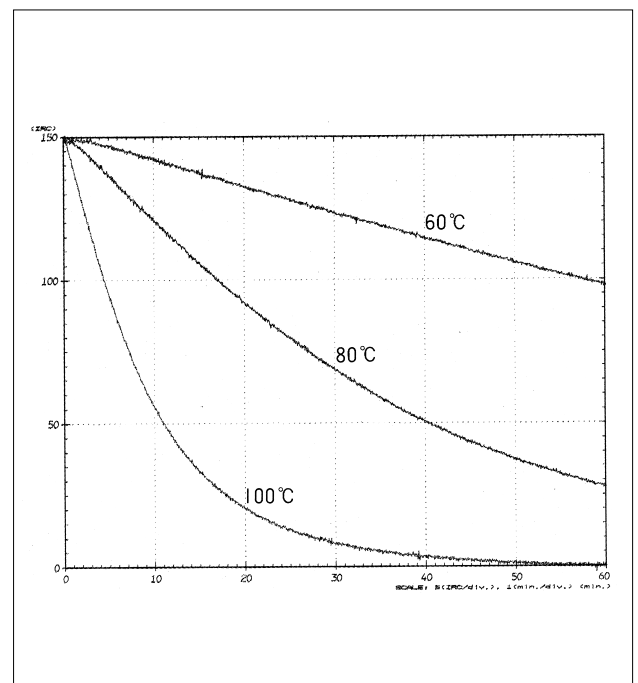
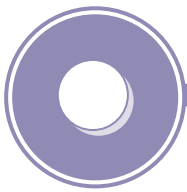


Fig. 1.1.6 Time course curves of epoxide group at each temperature



1.2 Measuring the Transmittance and Reflection Spectra of Optical Materials - UV

■ Explanation

By combining the Shimadzu UV-Vis-NIR Spectrophotometer UV-3101 and the Multipurpose Large-sample Compartment MPC-3100 with built-in integrating sphere, the transmittance and reflection spectra can be measured with a high degree of precision over a wide range of wavelengths from the near infrared to the ultraviolet. Large samples may be measured with no further processing. Introduced here are measurements of samples such as semiconductors, optical discs, thin films and optical elements employing the MPC-3100.

■ Analytical Conditions

Measuring Mode : Reflectance
Slit Width : 20nm
Attachment : Multipurpose Large-sample Compartment MPC-3100

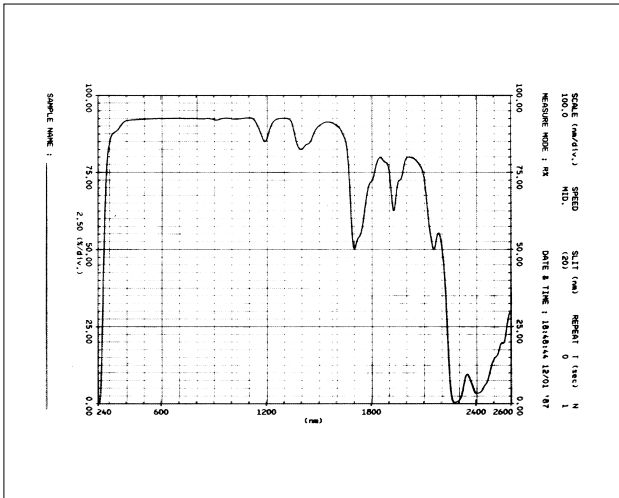


Fig. 1.2.1 Transmittance spectrum of Compact Disc substrate

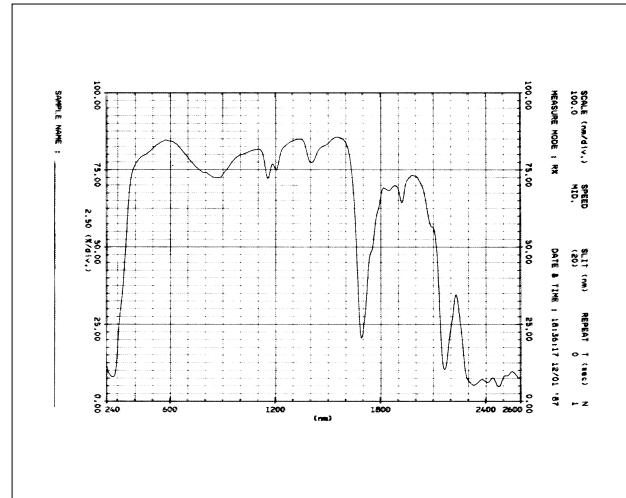


Fig. 1.2.2 Reflection spectrum of Compact Disc

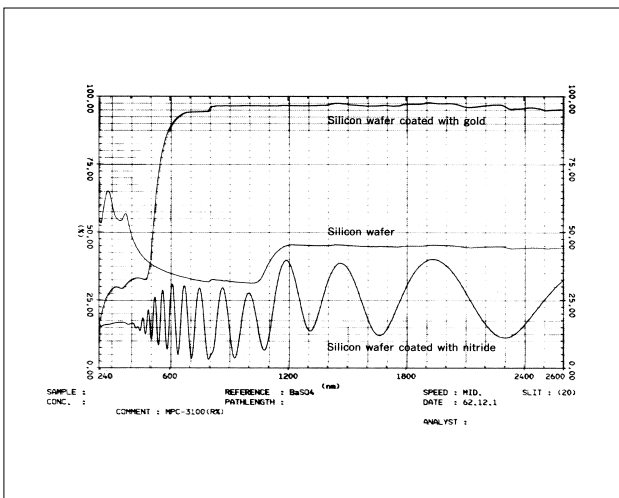


Fig. 1.2.3 Reflection spectrum of silicon wafer

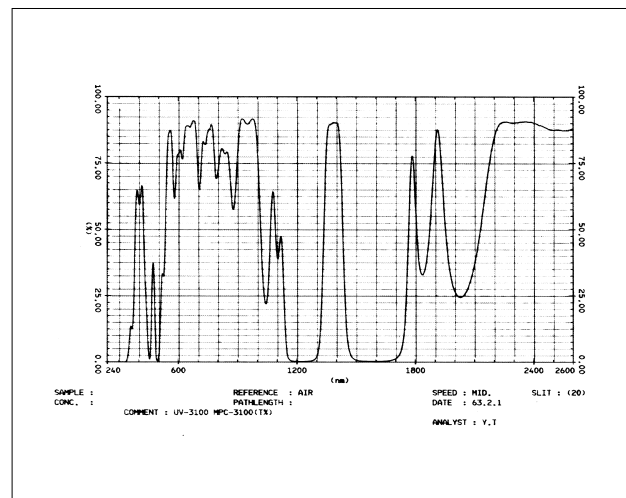


Fig. 1.2.4 Transmittance spectrum of an optical band pass filter

1.3 Analysis of Calcium (Ca) in Electronic Materials - AA

■ Explanation

The measurement of impurities in electronic materials is important. High sensitivity analysis is demanded. With the electro-thermal atomization method, trace amounts can be directly measured by a quick and easy pretreatment of dissolving the sample in an organic solvent. Introduced here is an example of analysis of Ca in an electronic material dissolved in electronic industrial purpose 2-propanol.

■ Lower Limit of Quantitation

Approximately 1.0ppb (Varies depending on throughput. In this instance the throughput is 1g/10g).

■ Pretreatment

(1) 1.0g of the sample was dissolved in electronic industrial purpose 2-propanol. The total weight was made 10.0g and used as the stock solution for the sample.

(2) The standard solution was also prepared with electronic industrial purpose 2-propanol.

■ Analytical Conditions

Wavelength : 422.7 nm
 Lamp Current : 10 mA
 Slit Width : 1.0 nm
 Measuring Mode : BGC-D2

Furnace program:

(Tube type: Pyro-coated tube)

Stage	Temp (°C)	Time (sec)	Heat Mode	Ar Flow Rate (L/min)
HI	50	5	STEP	0.10
1	70	20	RAMP	0.10
2	150	10	RAMP	0.10
3	250	10	RAMP	0.10
4	800	10	RAMP	1.00
5	800	10	STEP	1.00
6	800	3	STEP	0.00
7	2200	3	STEP	0.00
8	2500	2	STEP	1.00

HI: Sample injection stage with graphite tube maintained at set temperature of 50 °C.

7 : Atomizing

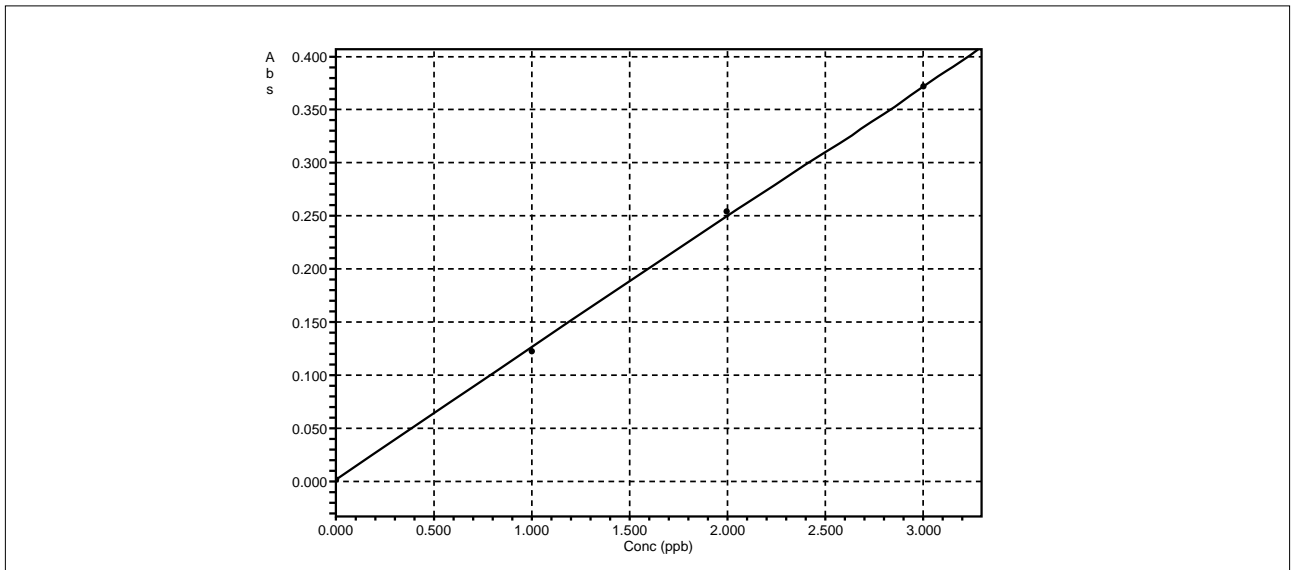
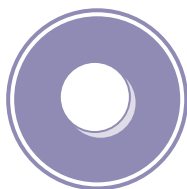


Fig. 1.3.1 Calibration curve

Concentration within solution	Amount of sample collected	Amount of sample made up	Concentration within solid
2.41 ppb	1.00g	10.0 g	24.1 ppb

Table 1.3.1 Measuring results



1.4 Rapid Analysis of Cyclic Siloxane - GC

■ Explanation

Here, cyclic siloxane (contained in silicon products) was analyzed using GC. A direct injection method using a 0.53mm × 30m column and a split injection analysis method using a 0.32mm × 5m column were employed and compared. Split injection analysis with a short column enabled analysis time to be reduced by approximately half.

n-tetradecane was added as the internal standard substance.

■ Analysis Conditions (Total Volume Introduction Method)

- Instrument : GC-17AAFw + WBI-17
- Column : DB1701(0.53mm × 30m df=1.0μm)
- Col.Temp. : 50°C (0min)-300°C (20°C/min)
- Inj.Temp. : 300°C
- Det.Temp. : 300 °C (w-FID)
- Carrier Gas : He (20 mL/min)
- Injection : Direct Injection

■ Pretreatment

- 1g of sample
- ↓ Add 10mL of acetone containing n-tetradecane (20μg/mL)
- Leave for 16hrs at room temp for extraction
- ↓
- GC analysis

■ Analysis Conditions (Total Volume Introduction Method)

- Instrument : GC-17AAFw
- Column : CBP10(0.32mm × 5m df=0.5μm)
- Col.Temp. : 35°C(3min)-300°C (20°C/min)
- Inj.Temp. : 300°C
- Det.Temp. : 300 °C (w-FID)
- Carrier Gas : He 50kPa(9 mL/min)
- Injection : Split 1:5

Note: To elute siloxane (it has a high boiling point), the final rise in temperature is set as being higher than the maximum heat resistance temperature of the column, which means the column will deteriorate rapidly. Keeping the final temperature at 280 °C. will prolong the life of the column but will lengthen analysis time.

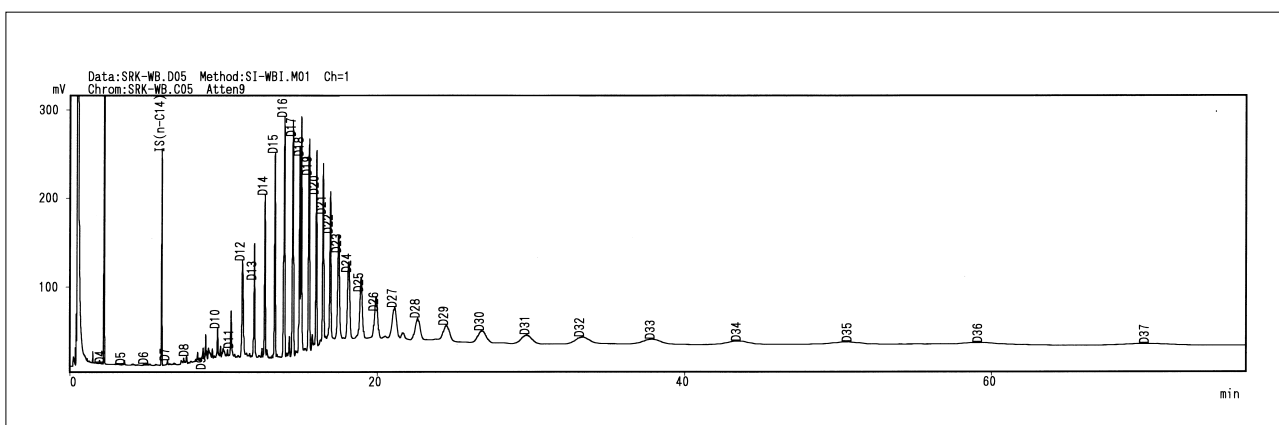


Fig. 1.4.1 Analysis of low molecular weight cyclic siloxane (total volume introduction using 0.53mm × 30m column)

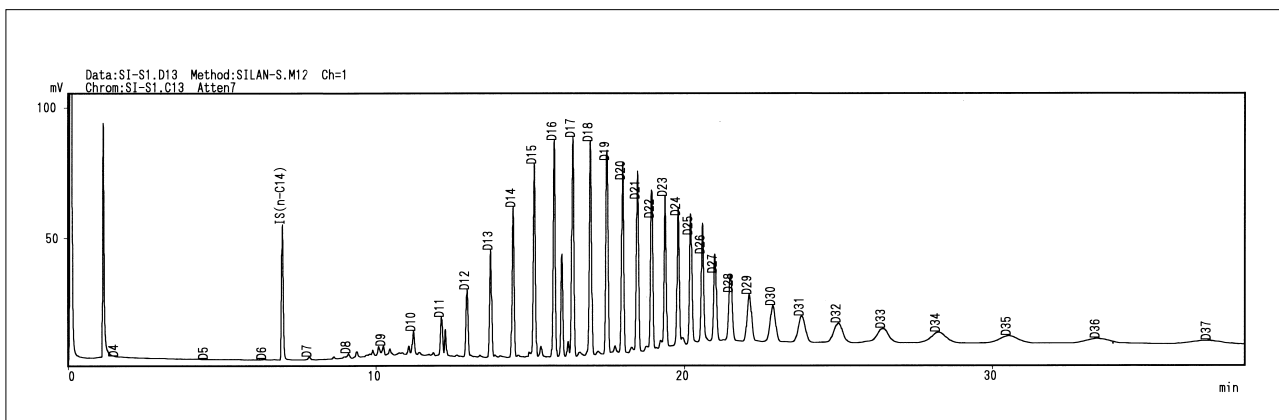


Fig. 1.4.2 Analysis of low molecular weight cyclic siloxane (split method using 0.32mm × 5m column)

1.5 Analysis of Polystyrene - GCMS

■ Explanation

Generally, a polymer such as polystyrene is thermally decomposed and the generated gas analyzed. Introduced here is an example of polystyrene analysis by GC/MS with a direct insertion probe (DI). Such devices are equipped as furnace types or Curie point heating types. The temperature required for thermal decomposition differs but is generally in the region of 500 °C (polystyrene will not be decomposed at 400 °C or lower). The data provided here was measured using QP2000 but the QP5050A also could accomplish the same analysis.

■ Analytical Conditions

Instrument : GCMS-QP2000 JDI800

Pyrolysis Temp : 590 °C

Pyrolysis Time : 1Sec

References

Application News No. M157

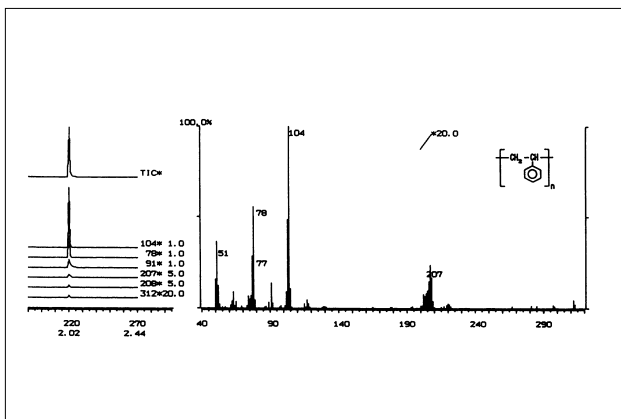


Fig. 1.5.1 Polystyrene mass spectrum (40ng)

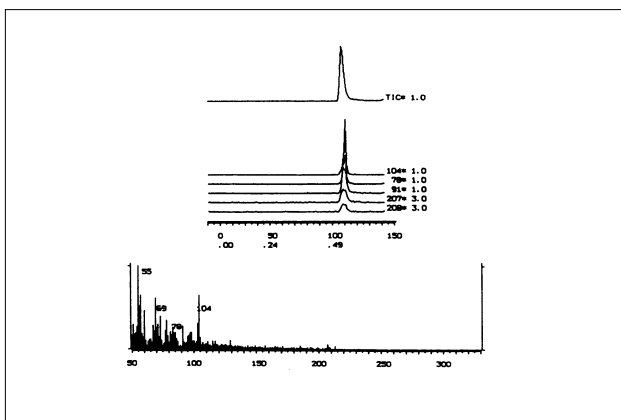


Fig. 1.5.2 Polystyrene mass spectrum (100pg)

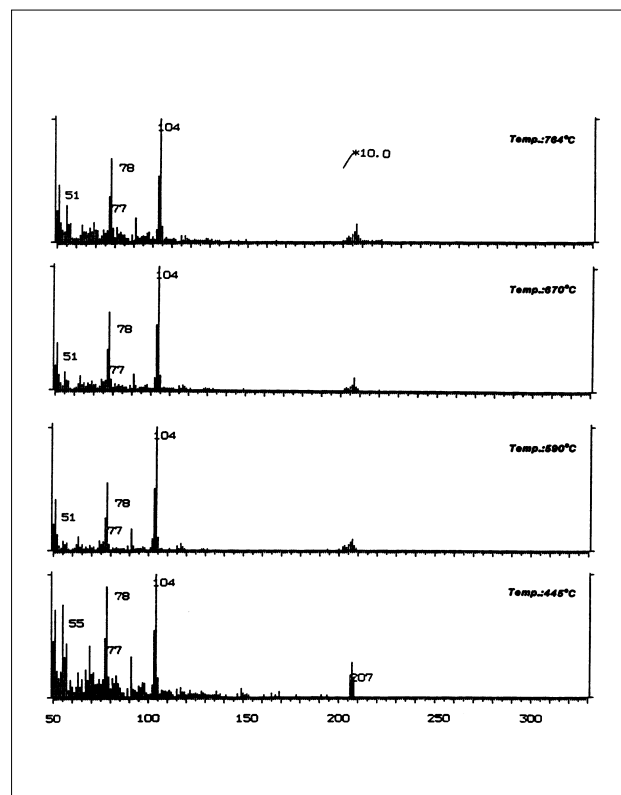
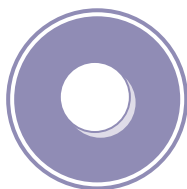


Fig. 1.5.3 Polystyrene mass spectrum using each decomposition temperature



1.6 Analysis of Ethylene - Vinyl Acetate Copolymer (1) - GCMS

■ Explanation

Polymers of increasing complexity are rapidly being developed for various applications. This analysis introduces an ethylene - vinyl acetate copolymer (EVA). Here, two types of analysis are possible through the use of a double-shot pyrolyzer (PY-2020D).

1) Evolved gas analysis method (EGA)

This involves constantly heating the sample and directly inducting the generated gas into a mass spectrometer (MS) to obtain data similar to TG-MS data.

2) Thermal decomposition (momentary thermal decomposition method and multi-stage thermal decomposition method)

This involves using two types of thermal decomposition (both differing from conventional thermal decomposition) applied to the same sample.

Fig. 1.6.1 shows EVA generated data using the evolved gas analysis method described in item 1). The initial peak is the detected acetic acid generated from the vinyl acetate. The m/z 57 peak showing hydrocarbon appears from around the 260 °C, denoting the decomposition of polyethylene. Figs. 1.6.2 and 1.6.3 show thermal decomposition chromatograms (400 °C and 550 °C) for the multi-stage thermal decomposition method.

■ Analytical Conditions

Instrument	: GCMS-QP5050A PY-2020D (FRONTIER LAB.)
Column	: Ultra ALLOY + 5 0.25mm × 30m df 0.25 μm
Col.Temp.	: 50 °C (5min) - 320 °C (10°C/min)
Inj. Temp.	: 300 °C
I/F Temp.	: 280 °C
Carrier Gas	: 100kPa
Split	: 1:50

References

Application News No. M196

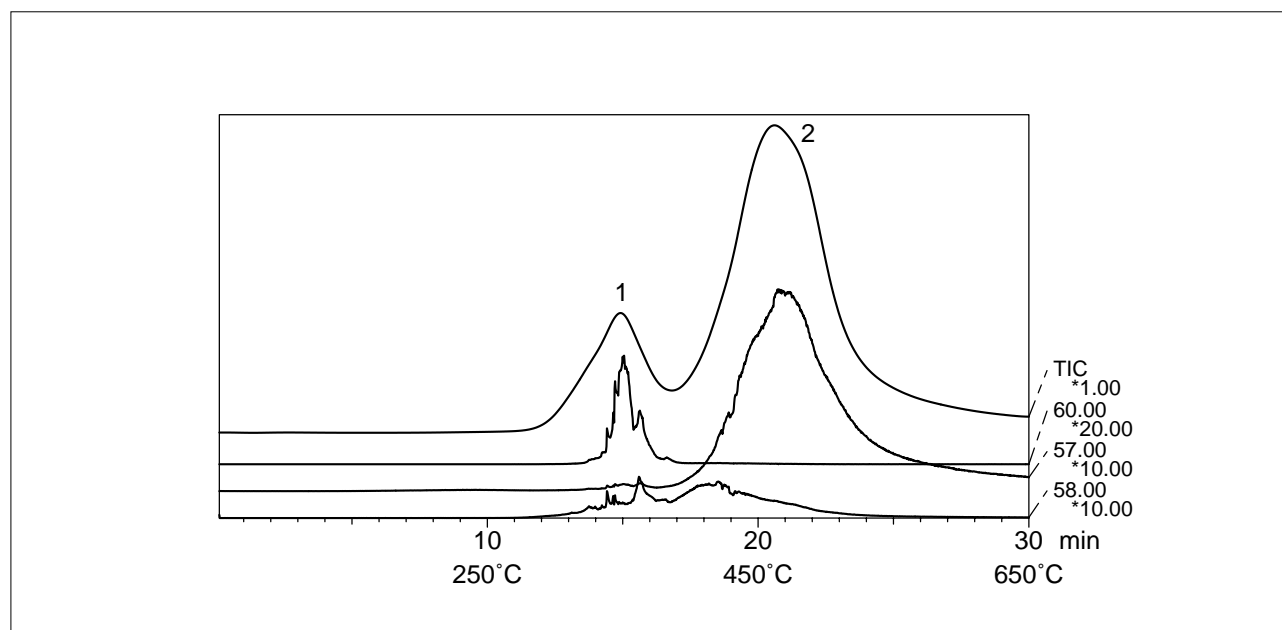


Fig. 1.6.1 EGA curve for EVA

1.6 Analysis of Ethylene - Vinyl Acetate Copolymer (2) - GCMS

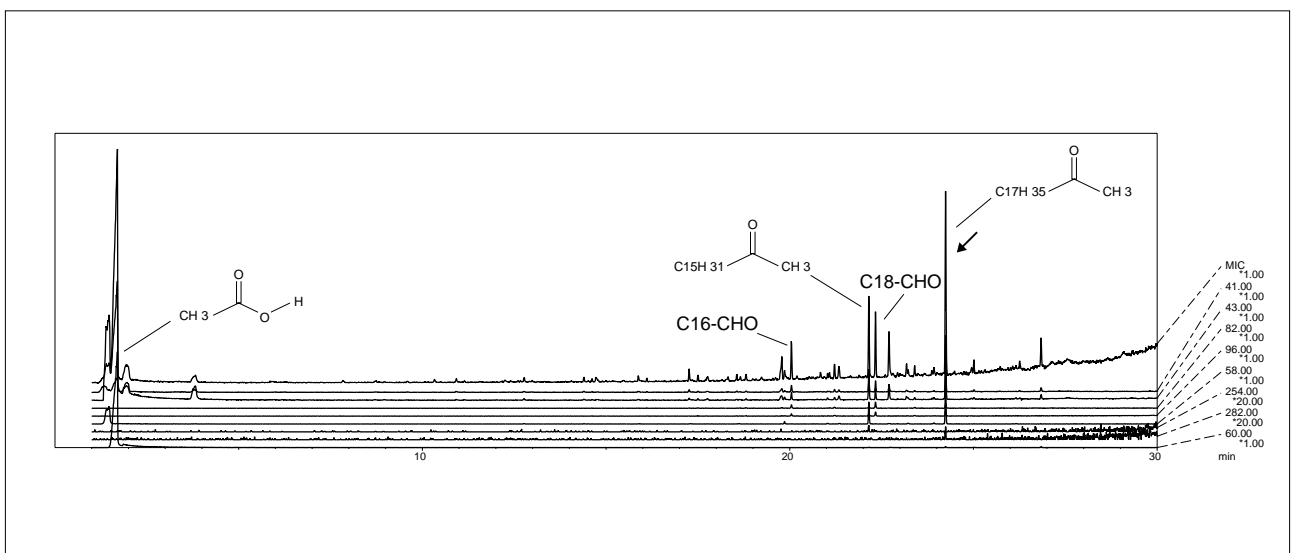


Fig. 1.6.2 Thermal decomposition chromatogram at 400 °C

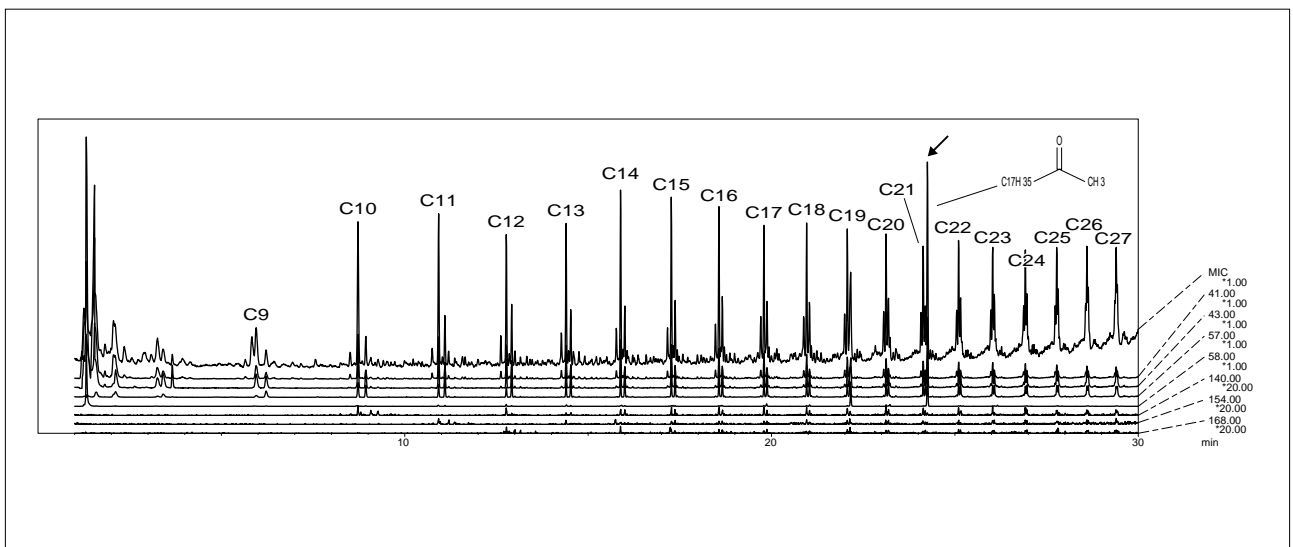
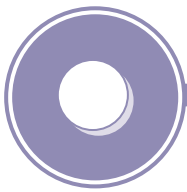


Fig. 1.6.3 Thermal decomposition chromatogram at 550 °C



1.7 Analysis of Inorganic Ions in Electrical Insulation Materials (1) - IC

■ Explanation

A number of electrical insulating materials are commonly encountered. Rubber insulation and insulating tape are examples of this. The ions contained in such materials and related materials, such as tires and pump tubing, are known to affect the quality of the material. Ion analysis provides extremely valuable information for quality control checks, such as the level of product deterioration. The following are examples of ion-chromatograph analysis of hot-water extracted samples for commonly found insulation materials.

■ Pretreatment

Fig. 1.7.1 Analysis of ions in liquid extracted from rubber tubing used on vacuum pump

Fig. 1.7.2 Analysis of ions in liquid extracted from a rubber plate

Fig. 1.7.3 Analysis of ions in liquid extracted from electrical wire insulation coating

Fig. 1.7.4 Analysis of ions in liquid extracted from insulation tape

■ Analytical Conditions

Column : Shim-pack IC-A1 (100 mm × 4.6 mm i.d.)

Mobile Phase : 2.5mM Phthalic acid
2.4mM Tris (hydroxymethyl) - aminomethane

Flow Rate : 1.5 mL/min

Temperature : 40 °C

Detection : Conductivity Detector

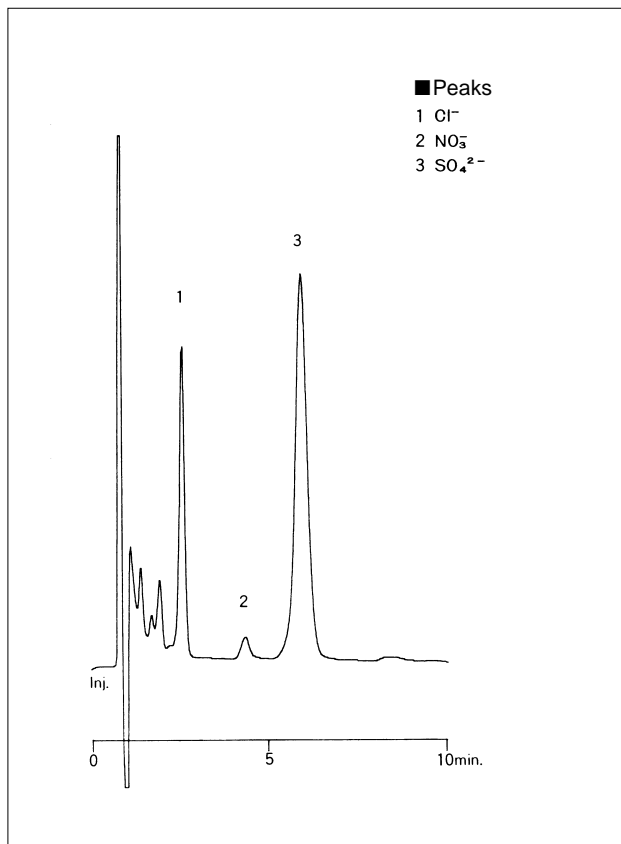


Fig. 1.7.1 Analysis of ions in liquid extracted from rubber tubing used on vacuum pump

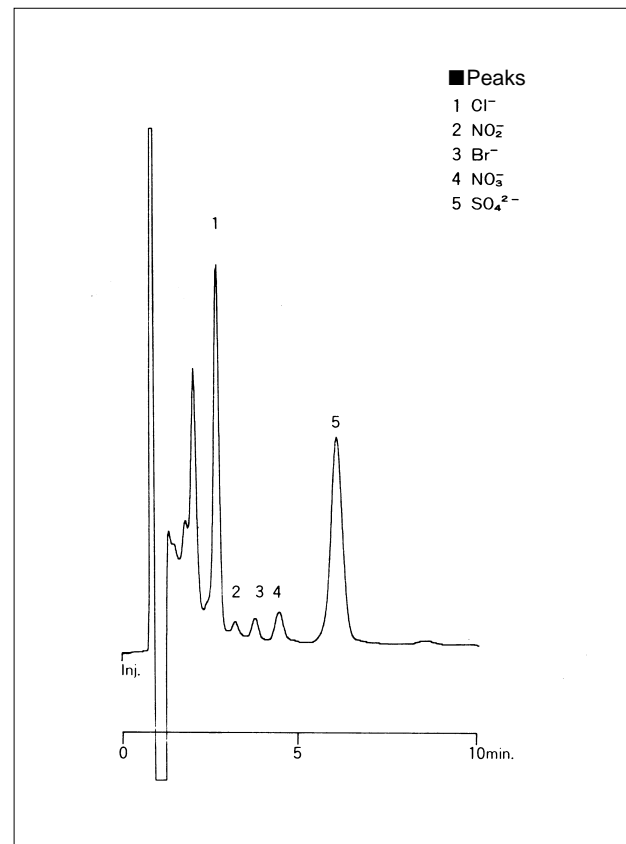


Fig. 1.7.2 Analysis of ions in liquid extracted from a rubber plate

1.7 Analysis of Inorganic Ions in Electrical Insulation Materials (2) - IC

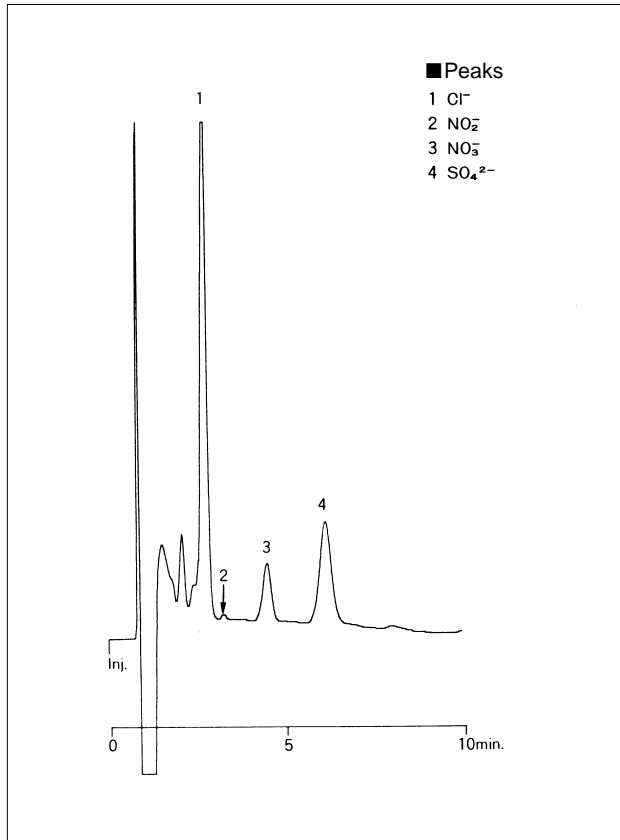


Fig. 1.7.3 Analysis of ions in liquid extracted from electrical insulation coating

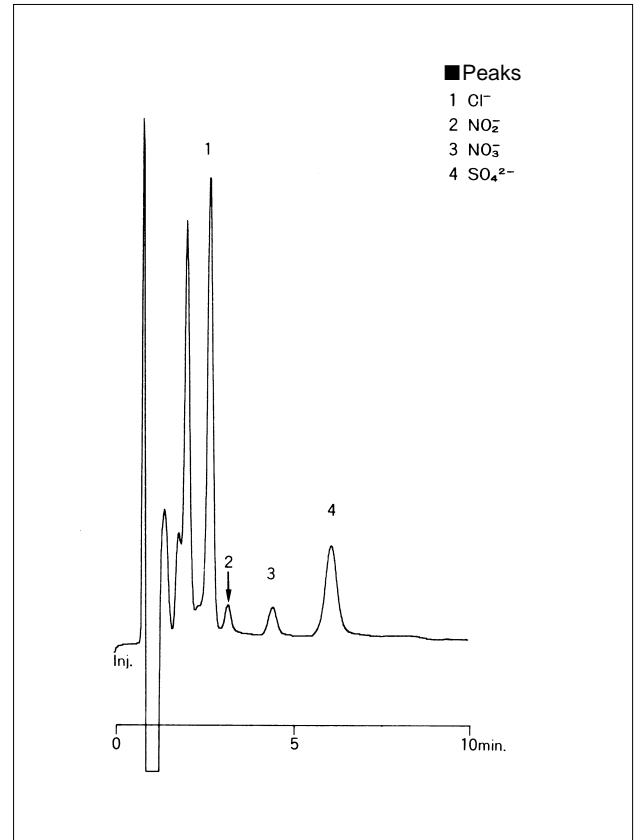
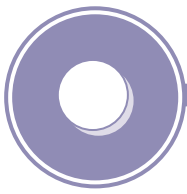


Fig. 1.7.4 Analysis of ions in liquid extracted from insulation tape



1.8 True Density Measuring of Polyethylene Pellets - PT

■Explanation

Density is one of the most fundamental characteristics of substances. Numerous measuring methods and devices for measuring density are available. Among these, the immersion method (wet process), and gas substitution method (dry process), are frequently used. The specific gravity bottle method is representative of the immersion methods and is used in several JIS standards. While, for the gas substitution method, technology advancements have raised measuring accuracy. Automation of operation and data processing have made this method to be used in fields handling powders and solids. Even so, the gas substitution method employing a dry process is rarely used in certain fields regulated to the wet process method in JIS. With this in mind, this experiment studies whether the gas substitution method could be used as a substitute for the density gradient method conventionally used in the field of plastics.

Results were identical to the density gradient method. The dry process method can be used in routine work in areas such as quality control.

■Analytical Conditions

Instrument : Micromeritics Accupyc

Measuring Temperature : 23 °C

References

Accupyc 1330 Application (S062-0711) technical material

Item	Sample A	Sample B	Sample C
Mean value \bar{X} (g/cm ³)	0.9125	0.9306	0.9330
Range R (g/cm ³)	0.0009	0.0006	0.0007
Standard deviation σ (g/cm ³)	2.41×10^{-4}	1.75×10^{-4}	2.02×10^{-4}
Measuring time	Approx. 25min	Approx. 25min	Approx. 25min

Table 1.8.1 Measuring example for polyethylene pellets using Accupyc 1330 with temperature control function

Measurement Method	Sample A	Sample B	Sample C
Accupyc 1330	0.9125	0.9306	0.9330
Density gradient method	0.9122	0.9309	0.9333

Table 1.8.2 Comparison of Accupyc 1330 with temperature control function and density gradient method Unit: g/cm³

1.9 Physical Property Evaluation of Electronic Materials Using Thermal Analysis - TA

■ Explanation

The thermal expansion coefficient is vital in components made up from the joining of metals and epoxy resin such as PCBs and ICs. For instance, breaking, cracking or warping may occur if one material only expands slightly and the other expands greatly. Ideally, both materials will expand at about the same rate. Also, the thermal expansion coefficient value for epoxy resin increases when the glass-transition temperature is reached or exceeded.

■ PCB Measuring Example

Fig. 1.9.1 shows the expansion curve when a printed circuit board is heated at 5 °C/min using a thermalmechanical analyzer (TMA). The inflection point at glass transition in the vicinity of 90 °C is visible and extreme change in the thermal expansion coefficient can be seen at about this time.

■ Diode Measuring Example

Fig. 1.9.2 shows the results of measurements taken from a diode using a simultaneous differential thermogravimetric analyzer (DTG). The figure includes a DTA curve expressing the calorific change and a TG curve expressing the weight change.

An endothermic peak appears in the DTA curve showing

meltdown of some of the components of the diode in the vicinity of 225 °C. In the vicinity of 300 °C, weight loss and calorific change show the start of decomposition.

■ Analytical Conditions

Fig. 1.9.1

Instrument	: TMA - 50
Sample Length	: 10mm
Heating Speed	: 10 °C/min
Weight	: 1g

Fig. 1.9.2

Instrument	: DTG - 60
Sample Weight	: 10.1mg
Heating Speed	: 10 °C/min
Atmosphere	: Air 100mL/min decomposition

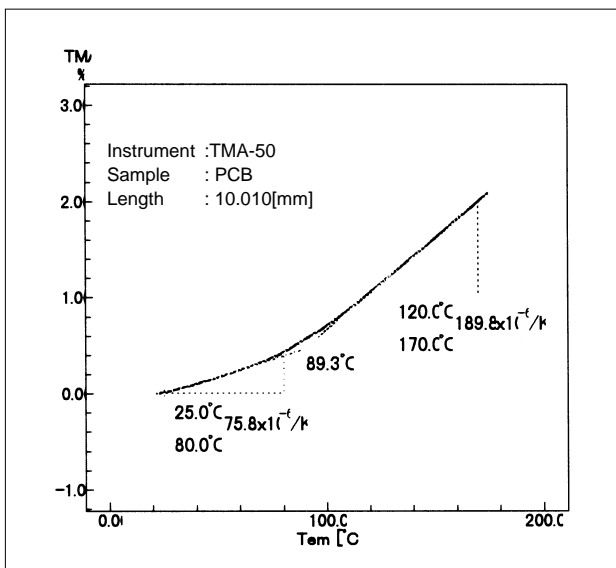


Fig. 1.9.1 Thermal expansion of PCB

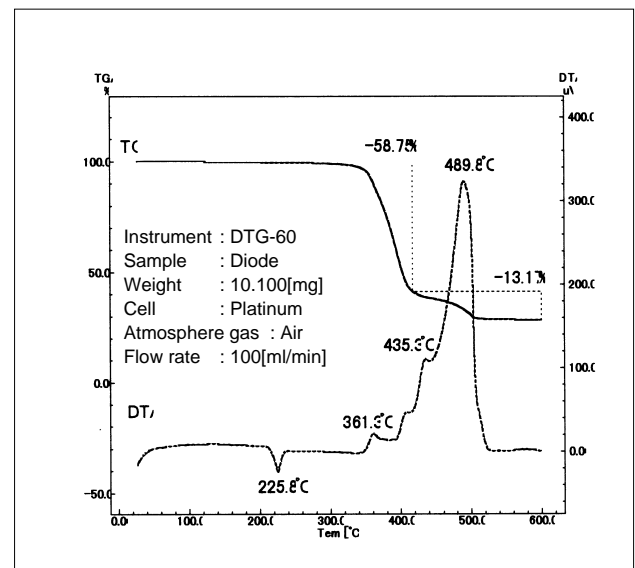


Fig. 1.9.2 Thermal characteristics of diode



1.10 Application in Thermal Analysis for Thermosetting Resins - TA

■Explanation

Thermosetting resins are widely used in molding materials, adhesives and electrical components (Printed circuit boards (PCBs), connectors, switches, etc.). These are normally combined with a reinforcing agent for hardening and forming. In other words, the hardening reaction enables solidification manufacturing. The hardening reaction's characteristics greatly vary with the variation progress of hardening due to hardening temperature and hardening time. Measurement of this progress of hardening is vital because it affects physical characteristics such as mechanical strength.

Also, thermal analysis is useful in quality control for thermosetting resins including thermal expansion coefficient and glass-transition temperature measuring and the calculation of how much reinforcing agent should be added.

Note that the thermal analyzer differs depending on the type of measurement. Generally, the following analyzers are used for the following analyses.

DSC: Glass-transition temperature, hardening

TMA: Thermal expansion coefficient

TG: Quantitation of reinforcing agent, heat resistance

■Measuring Example of Glass-transition temperature

Fig. 1.10.1 shows measurements of epoxy resin. The glass-transition temperature (Tg) was measured using DSC. Tg appears as a stepped change on baseline showing the epoxy resin to have a Tg at 114.2 °C.

■Measuring Example of Thermal Expansion Coefficient

Fig. 1.10.2 shows measurements of a Printed circuit board (PCB). The thermal expansion coefficient at operating temperature of such a board is important. The expansion coefficient increases at the Tg boundary showing great changes before and after Tg.

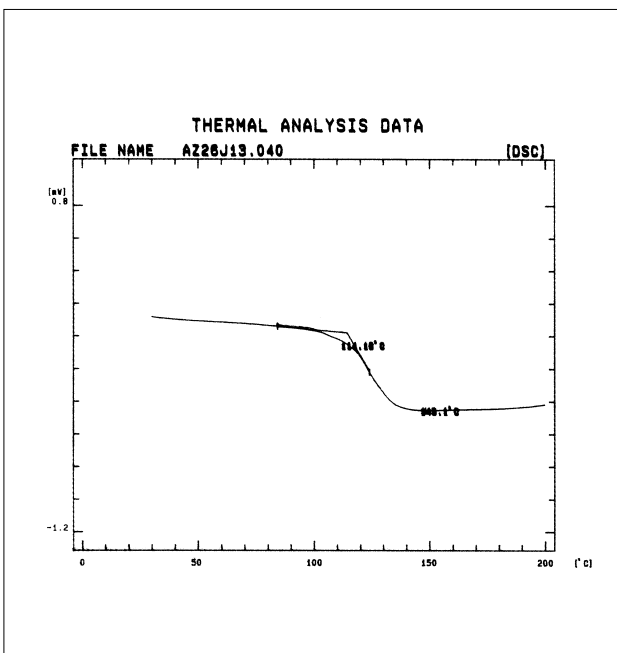


Fig. 1.10.1 Measurement of glass-transition temperature

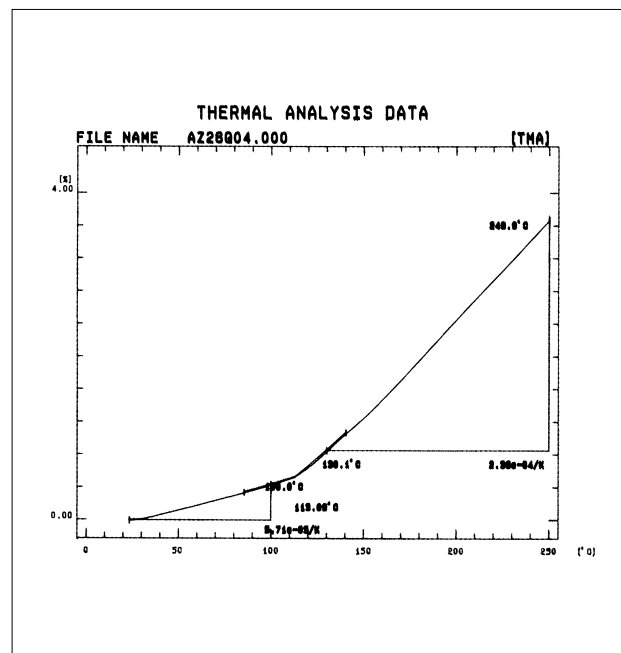


Fig. 1.10.2 Measurement of thermal expansion coefficient



2. Manufacturing Processes

2.1 FTIR Analysis of Fluorine Gases - FTIR

■ Explanation

Fluorine gases are used in the etching process of semiconductor manufacturing.

Separation using a chromatograph is not necessary because an infrared spectrum shows a pattern according to the configuration of the fluorine gas, so qualification and quantification are possible with additional components mixed in. Introduced here are quantifying tests for three freon gases.

Fig. 2.1.1 shows overlays of standard spectra for the mixed gas sample. Fig. 2.1.2 is a magnification of that low wavelength region. The CF_4 peak overlays C_4F_8 but C_4F_8 and C_2F_6 have their own particular peaks, which clearly shows that quantitative analysis is possible.

Sample: Mixed freon gas (CF_4 , C_4F_8 , C_2F_6 , CO)
(Nitrogen base in tetrapack)

Attachment: 10cm gas cell (Aperture plate: KRS-5)

■ Analytical Conditions

Resolution : 0.5cm^{-1}

Accumulation : 50

Apodization : NONE

Detector : DLATGS

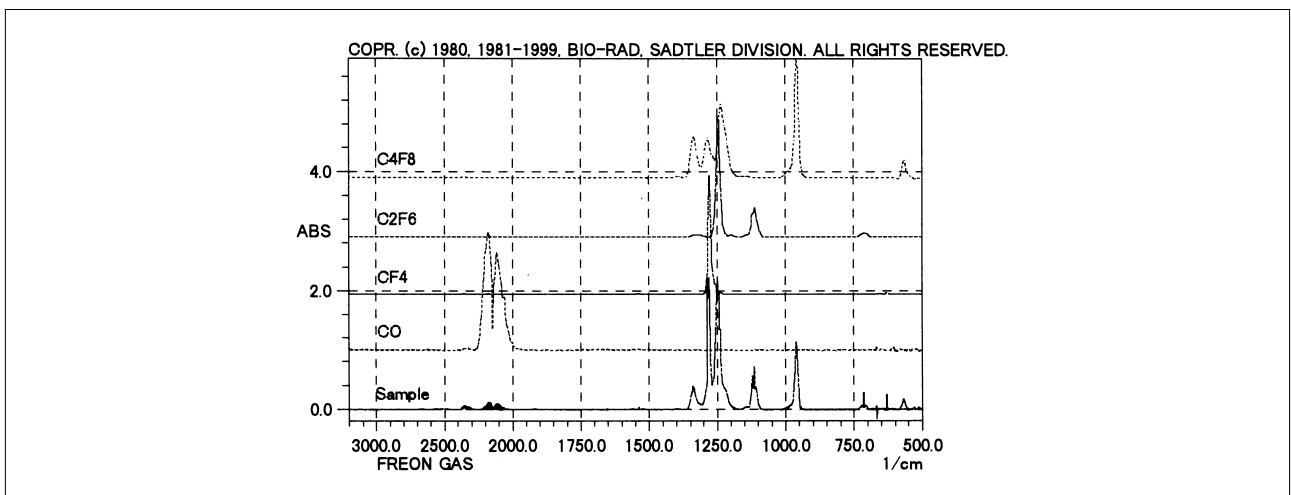


Fig. 2.1.1

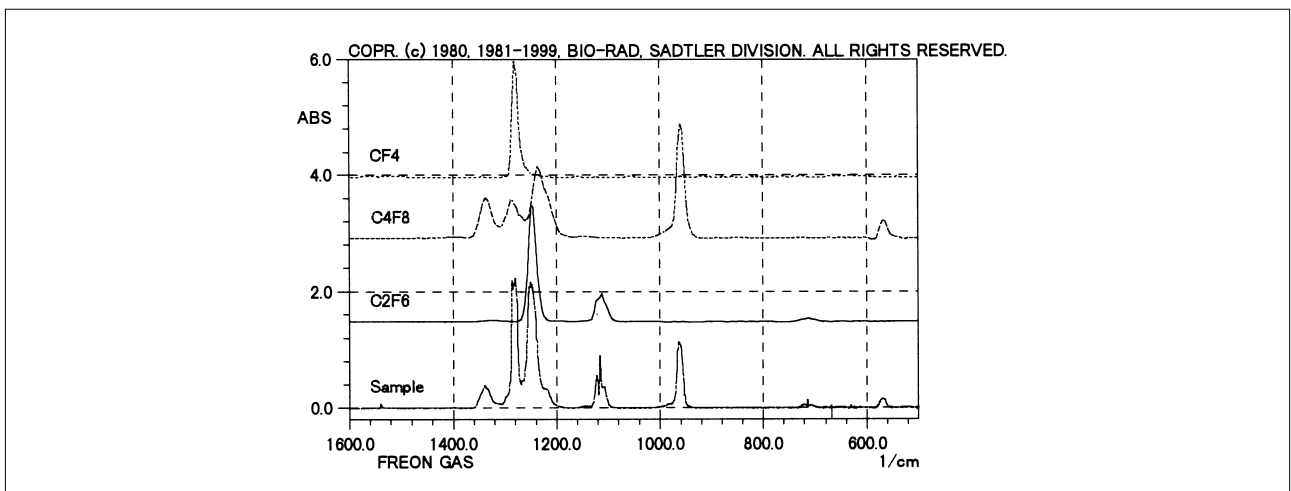


Fig. 2.1.2



2.2 FTIR Analysis of Inorganic Gases (1) - FTIR

■ Explanation

Unlike solid or liquid samples, molecules in a gaseous sample can rotate freely, which means that changes in the vibrational state will always occur together with changes in the rotational state. This means that the infrared spectrum of a gas appears as a combination of vibrational and rotational spectra. Because of this the absorption band of the infrared spectrum obtained becomes a group of spectral bands consisting of a large number of microstructures, necessitating high-resolution measurement.

For measurement of highly concentrated gas a cell length of either 10cm or 5cm is used, while for low concentration gas long optical path cell of 10 to 20m long are used. It is necessary to select the appropriate aperture plate and cell materials because some samples can be corrosive.

■ Example of SO₂ Measurement

Fig. 2.2.1 is the infrared spectra of SO₂ gas measured using a 10cm gas cell. The sample concentrations of the spectra in the diagram are, from the lowest one, 95.9ppm, 187ppm and 468ppm.

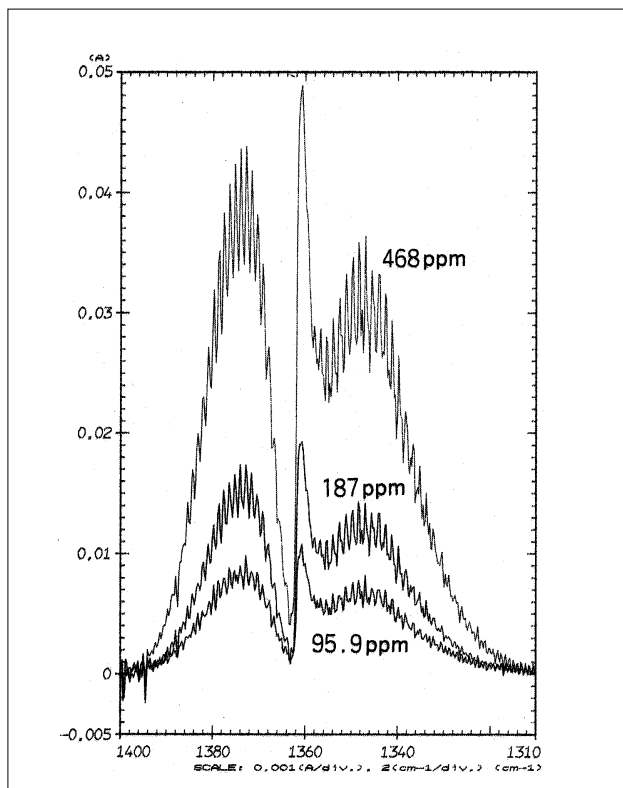


Fig. 2.2.1 Infrared spectra of SO₂ gas

187ppm and 468ppm. Fig. 2.2.2 is the calibration curve of these spectra obtained by using quantitative analysis software. A highly linear calibration curve has been obtained where the coefficient of correlation due to first order regression curve is 0.9998.

■ Example of Measurement of Other Gases

The results of measuring other gases using a 10cm gas cell are shown in Figs 2.2.3 to 2.2.6. The maximum peak region of each spectrum - NO₂, NO, N₂O and CO in order from Fig. 2.2.3-has been magnified.

■ Analytical Conditions

Resolution : 0.5cm⁻¹
 Accumulation : 100
 Apodization : Rectangular
 Detector : DLATGS

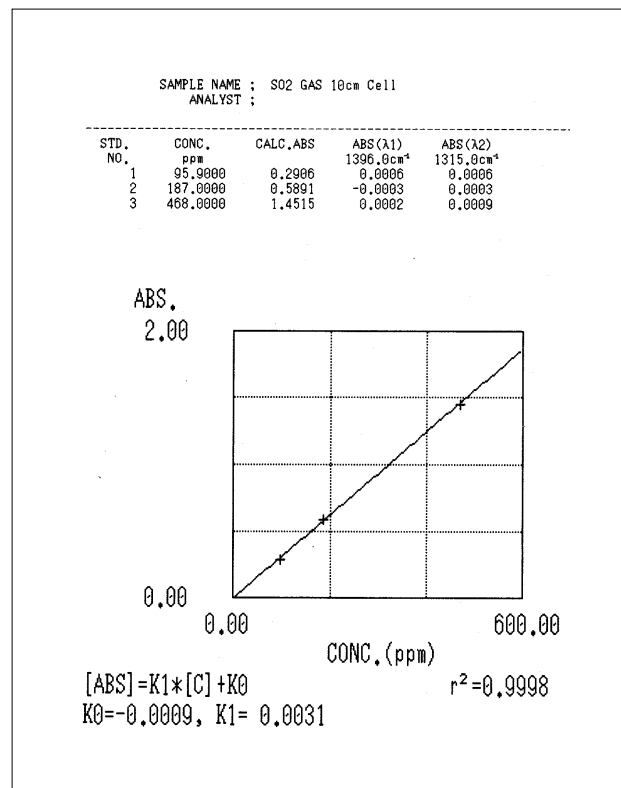


Fig. 2.2.2 Calibration curve of SO₂

2.2 FTIR Analysis of Inorganic Gases (2) - FTIR

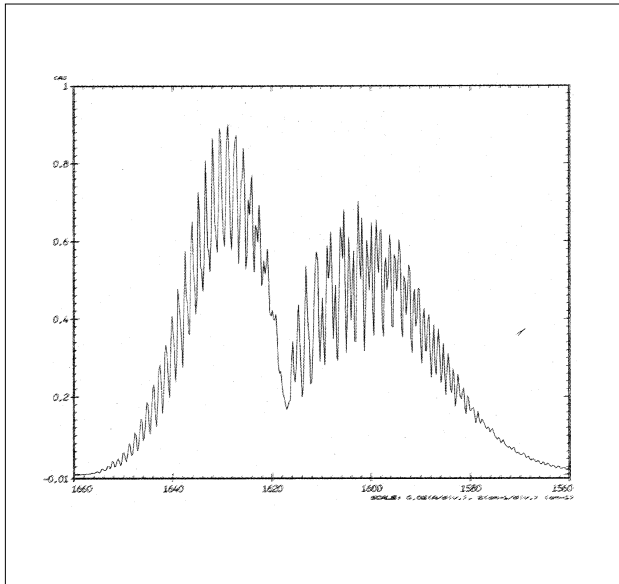


Fig. 2.2.3 Infrared spectrum of NO₂ gas

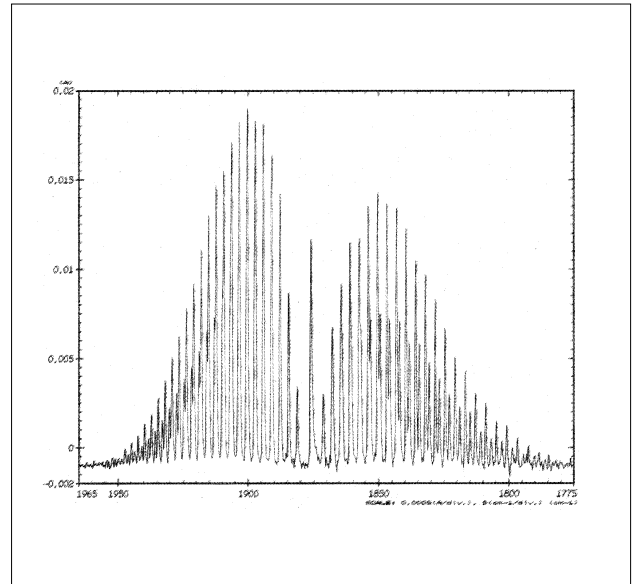


Fig. 2.2.4 Infrared spectrum of NO gas

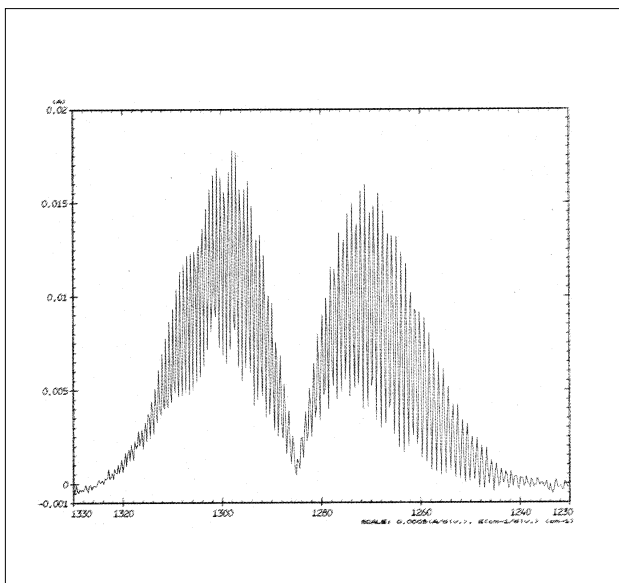


Fig. 2.2.5 Infrared spectrum of N₂O gas

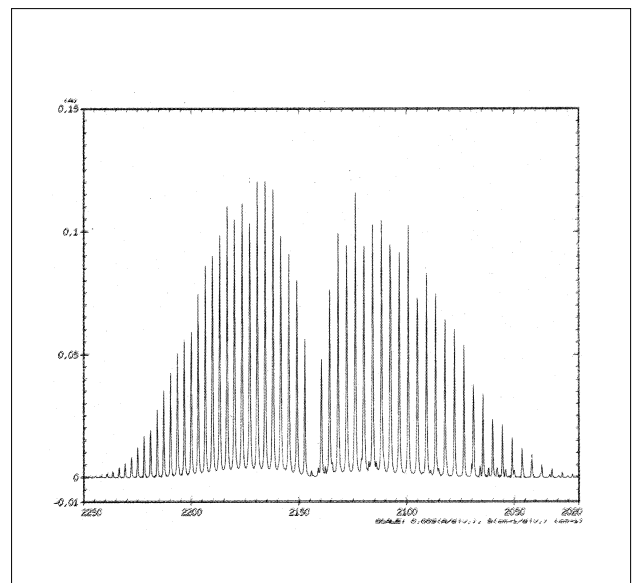


Fig. 2.2.6 Infrared spectrum of CO gas



2.3 Analysis of Freon Gas (1) - GC

■ Explanation

Introduced here as one example of analysis of freon gas using a packed column is an analysis employing the SM-6 (Chemical Industries, Ltd.)

Although the two components freon-115 and freon-12 as well as the three components freon-124, freon-22 and freon-152a cannot be separated with the normally used PorapakQ, complete separation is possible with this column.

■ Analytical Conditions

Instrument : GC-14BPT
Column : SM-6 3mm × 6m
Col.Temp. : 40 °C
Inj.Temp. : 50 °C
Det.Temp. : 50 °C (TCD)
Carrier Gas : He (20 mL/min)

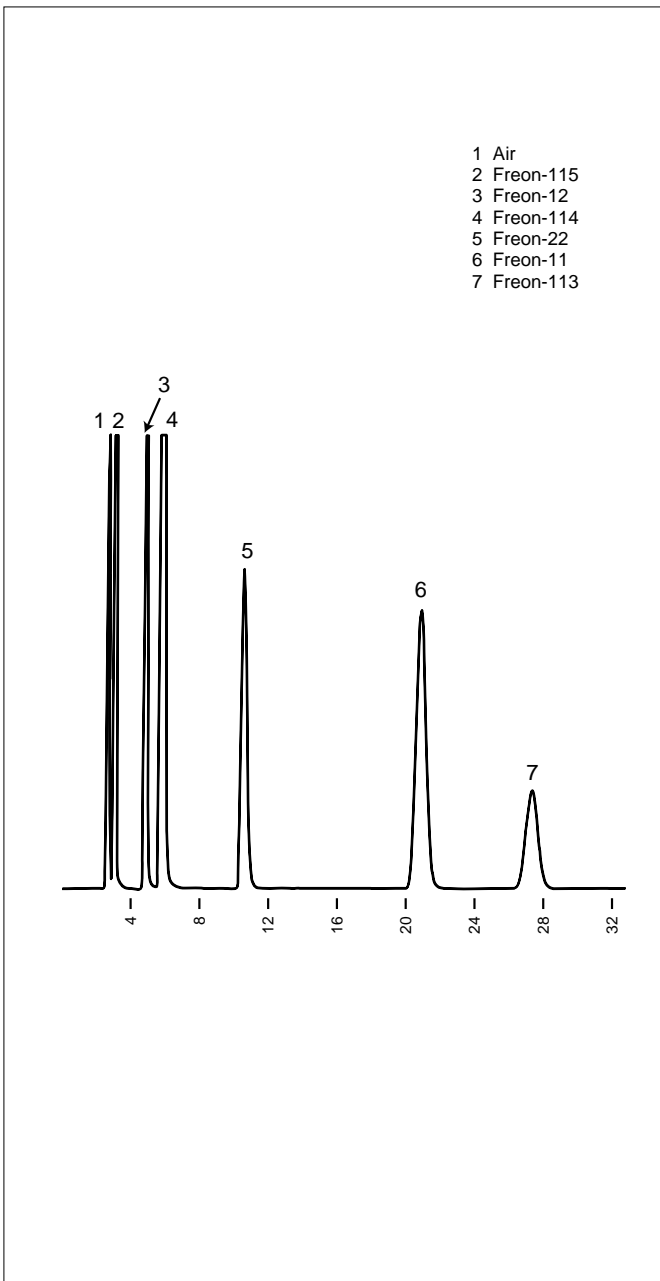


Fig. 2.3.1 Example of analysis of freon gas using a packed column

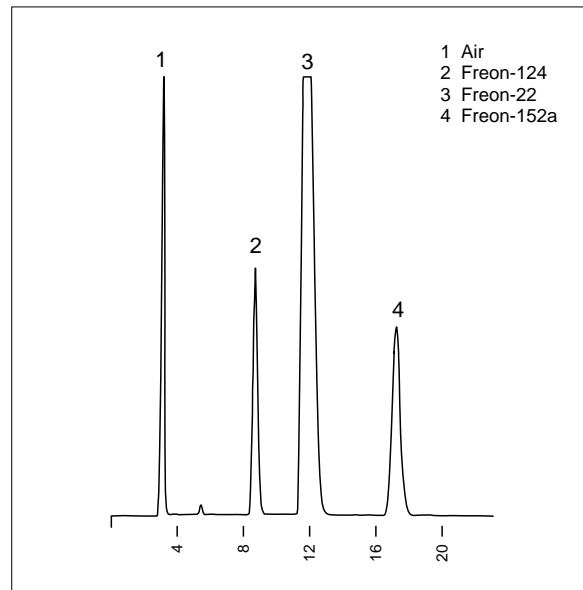


Fig. 2.3.2 Example of analysis of freon gas using a packed column

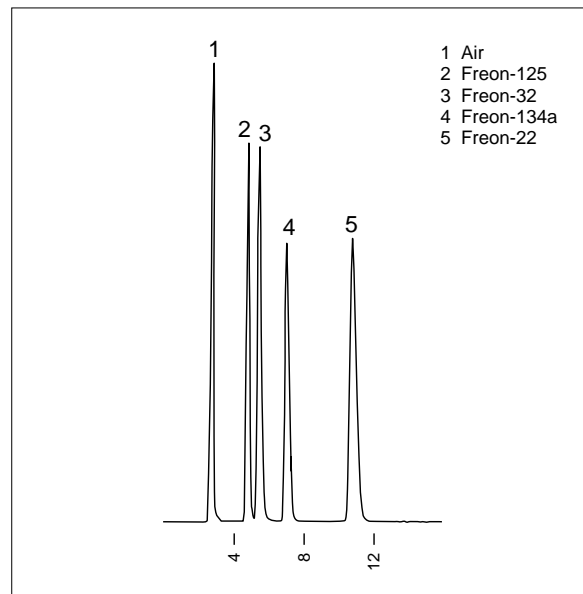


Fig. 2.3.3 Example of analysis of freon gas using a packed column

2.4 Analysis of Freon Gas (2) - GC

■ Explanation

The analysis introduced here uses the GS-ALUMINA (PLOT column) as an example of the analysis of freon gas using a capillary column.

■ Pretreatment

None.

■ Analytical Conditions

Instrument : GC-17A AFw + ECD - 17
Column : GS-ALUMINA 0.54mm × 30m
Col.Temp. : 50 °C (0min) -100 °C (5 °C/min)
 -180 °C (10 °C/min)
Inj.Temp. : 180 °C
Det.Temp. : 200 °C (ECD)
Carrier Gas : He (8.2 mL/min)
Injection : Split 1:5

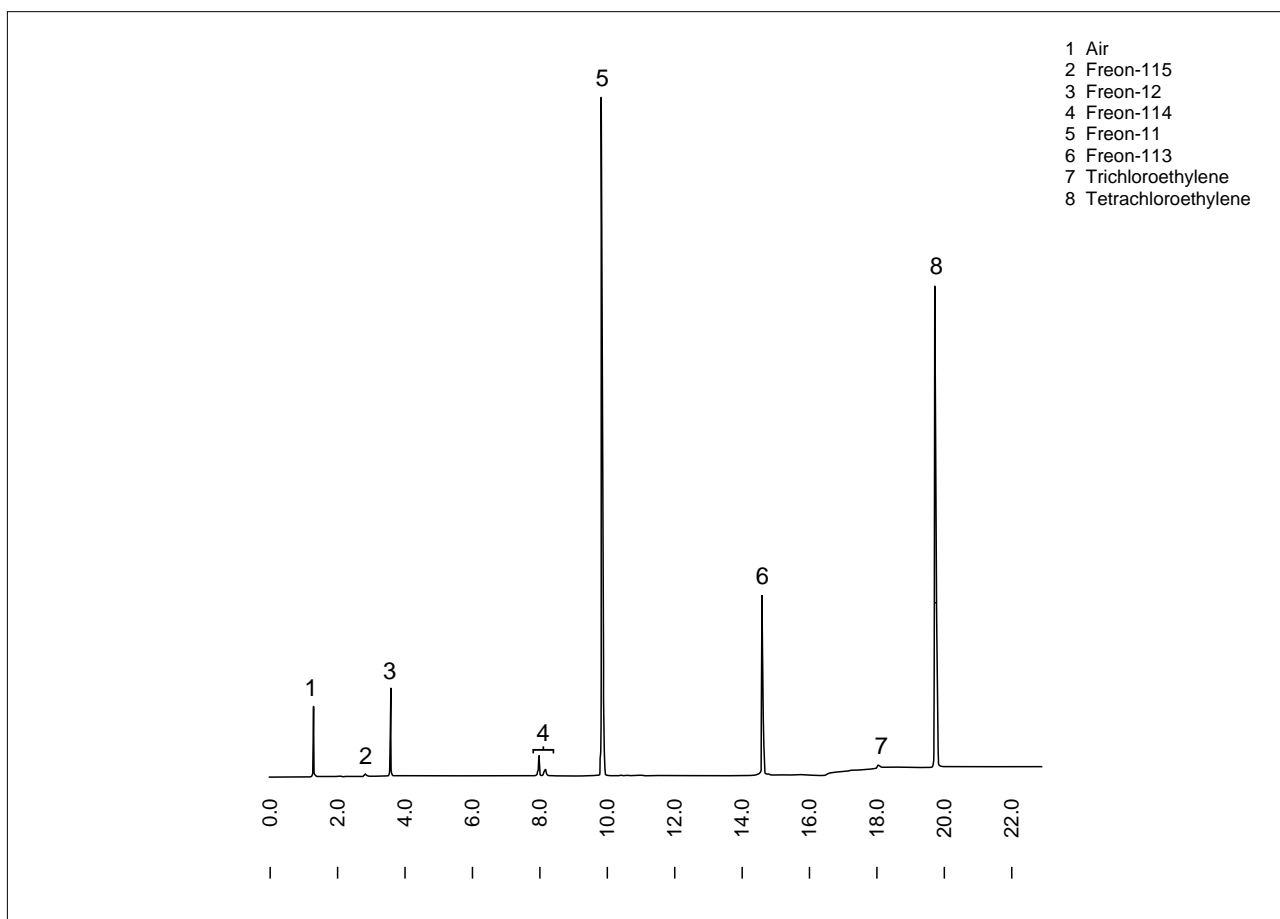


Fig. 2.4.1 Example of analysis of freon gas using capillary column



2.5 Analysis of Cyanides in Plating Solutions - LC

■Explanation

Plating solutions must be analyzed periodically at the time of spraying and during processing to ensure product stability and good productivity. A plating solution contains a base metal and various components including a complexing agent, a buffering agent and a reducing agent. These can be accurately analyzed in a short time using a HPLC. Introduced here are analysis examples for cyanides, organic acids and formaldehydes.

■Measurement Method

Cyanides contained in precious metal plating solutions such as gold or silver plating solutions are important for measurement not only for product control but also for management of plating wastewater. These cyanides can be analyzed with a cyanide analysis system, which employs a post-column derivatization method. In this method the cyanides in the sample are separated in the column and converted into cyanogen chloride by chloramine-T. It is then made to react with 4-pyridine/pyrazolone solution and the blue color obtained is measured at the absorbance of the 638nm wavelength. Shown in Figs. 2.5.1 and 2.5.2 are respectively examples of analysis of gold plating solution and silver plating solution.

(for separation)

Column : Shim-pack AMINO-Na
(100 mm × 6.0 mm i.d.)

Mobile Phase : 10mM (Sodium) Tartarate
Buffer (pH4.2)

Flow Rate : 0.6 mL/min

Temperature : 50 °C

(for detection)

<chlorination>

Reagent : 200mM (Sodium) Phosphate Buffer
Containing 2mM Chloramine T (pH6.8)

Flow Rate : 0.3 mL/min

Temperature : 100 °C

<coloring>

Reagent : A:100mM 1-Phenyl-3-methyl-5-pyrazolone
Ethanol Solution
B:20mM Pyridine-4-carboxylic Acid
Aq. Solution
A/B = 1/3 (v/v)

Flow Rate : 0.3 mL/min

Temperature : 100 °C

Detection : UV-VIS Spectrophotometric Detector
Wavelength 638nm

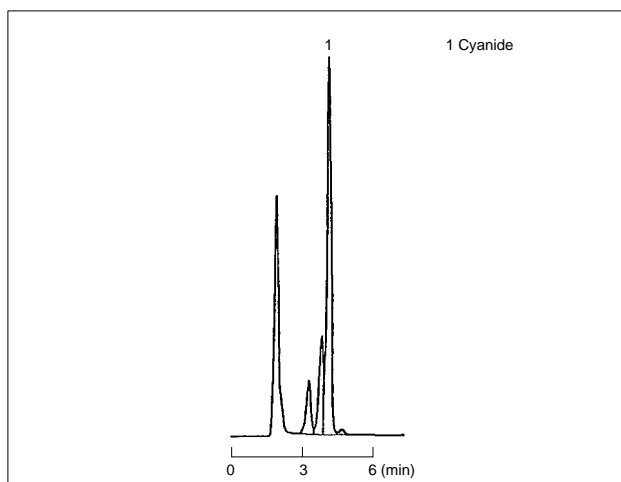


Fig. 2.5.1 Example of analysis of cyanides in gold plating solution

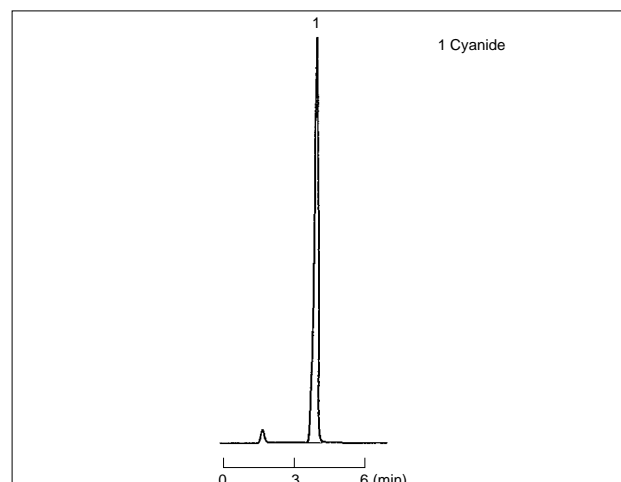


Fig. 2.5.2 Example of analysis of cyanides in silver plating solution

2.6 Analysis of Organic Acids in Plating Solutions - LC

■ Measurement Method

Organic acids are added to plating solutions as complexing agents and buffering agents. These organic acids can be selectively measured at a high sensitivity by employing an organic acid analysis system. Shown in Fig. 2.6.1 is an example of analysis of the various organic acids contained in nickel solution, while Fig. 2.6.2 shows an example of analysis of citric acids contained in gold plating solution.

■ Analytical Conditions

(for separation)

Column : Shim-pack SCR-102H
(300 mm × 8.0 mm i.d.)
× 2 (Fig. 2.6.1)
× 1 (Fig. 2.6.1)

Guard Column : Guard Column SCR-102H
(50mm × 6.0 mm i.d.)

Mobile Phase : 5mM p-Toluenesulfonic Acid

Flow Rate : 0.8 mL/min

Temperature : 40 °C

(for detection)

Reagent : 5mM p-Toluenesulfonic Acid,
20mM Bis-tris and
100 μM EDTA · 2Na

Flow Rate : 0.8 mL/min

Temperature : 43 °C

Detection : Conductivity Detector

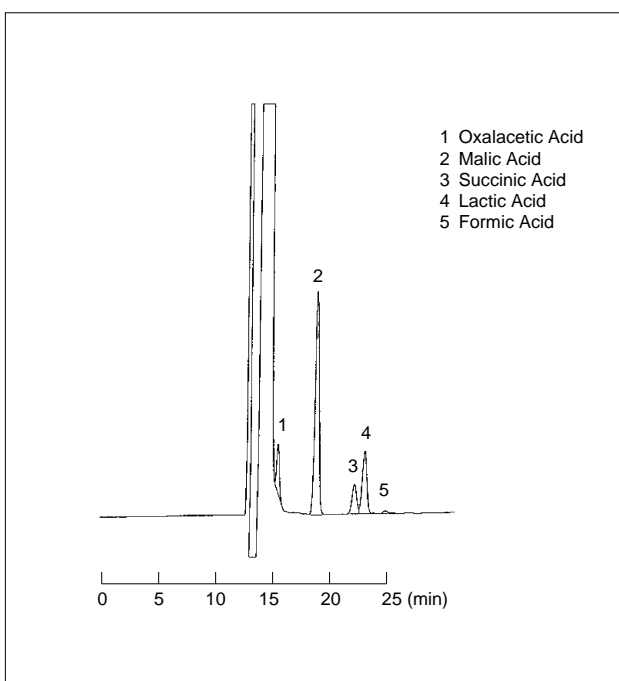


Fig. 2.6.1 Example of analysis of organic acids in nickel plating solution

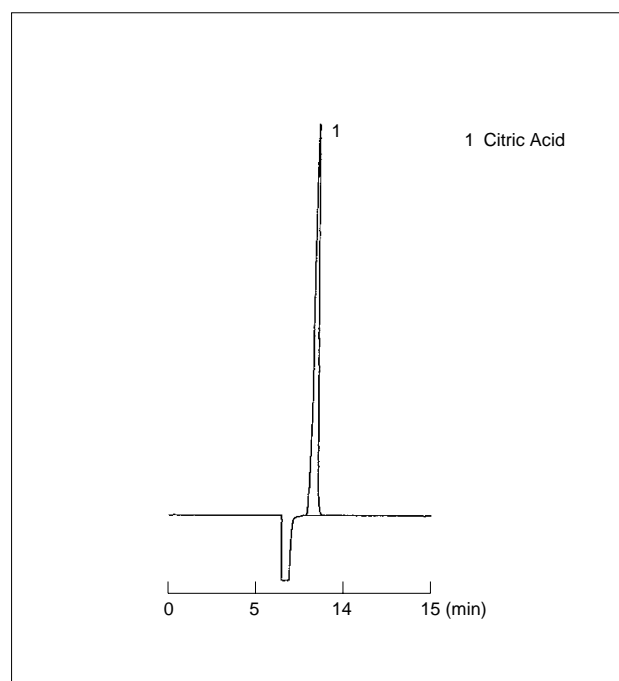


Fig. 2.6.2 Example of analysis of citric acids in gold plating solution



2.7 Analysis of Formaldehydes in Plating Solutions - LC

■ Measurement Method

An example of analysis of formaldehydes employed as reducing agents is shown in Fig. 2.7.1. 2,4-DNPH (dinitrophenylhydrazine) derivatization is performed. After column separation, the sample is measured at an absorbance of wavelength 360nm. In this example, copper pyrophosphate plating solution is used. The derivatization reaction and injection of the sample can be performed automatically with the autosampler.

■ Analytical Conditions

Column	: STR ODS-II (150 mm × 4.6 mm i.d.)
Mobile Phase	: Acetonitrile/Water = 45/55 (v/v)
Flow Rate	: 0.8 mL/min
Temperature	: 40 °C
Detection	: UV-VIS Spectrophotometric Detector Wavelength 360nm

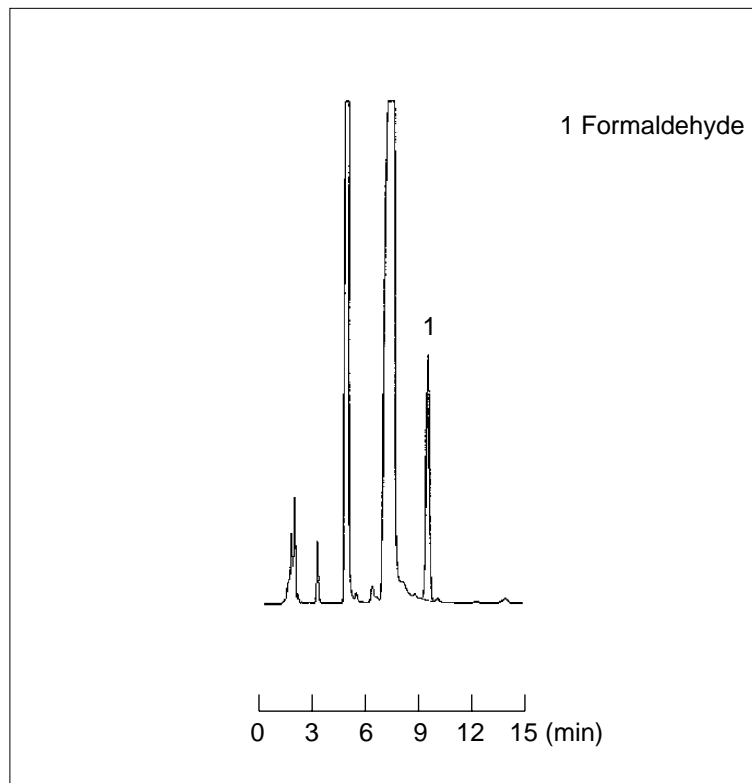


Fig. 2.7.1 Example of analysis of formaldehydes in copper pyrophosphate plating solution

2.8 Plating Solution Analysis (1) - LC

■ Explanation

Analysis of electroplating solutions, acidic etching solutions, conversion coating, rinsing solution and the waste solutions produced from all of these solutions are examples of ion chromatography employed in the electroplating industry. Notably, ion chromatography is exceptionally effective in the analysis of plating solutions, being able to quickly and accurately quantify both major and minor components.

Introduced here is an example of analysis on nickel plating solutions using a Shimadzu ion chromatograph.

Fig. 2.8.1 Plating solutions: Analysis of chloride ions and sulfate ions

■ Analytical Conditions

Column : Shim-pack IC-A1
(100 mm × 4.6 mm i.d.)

Mobile Phase : 2.5mM Phthalic acid
2.4mM Tris (hydroxymethyl)-
aminomethane
Flow Rate : 1.5 mL/min
Temperature : 40 °C
Detection : Conductivity Detector

Fig. 2.8.2 Plating solutions: Analysis of formic acid

■ Analytical Conditions

Column : Shim-pack SCR-101H
(300 mm × 7.9 mm i.d.)
Mobile Phase : 5mM Perchloric acid
Flow Rate : 0.8 mL/min
Temperature : 50 °C
Detection : UV Spectrophotometric Detector
Wavelength 210nm

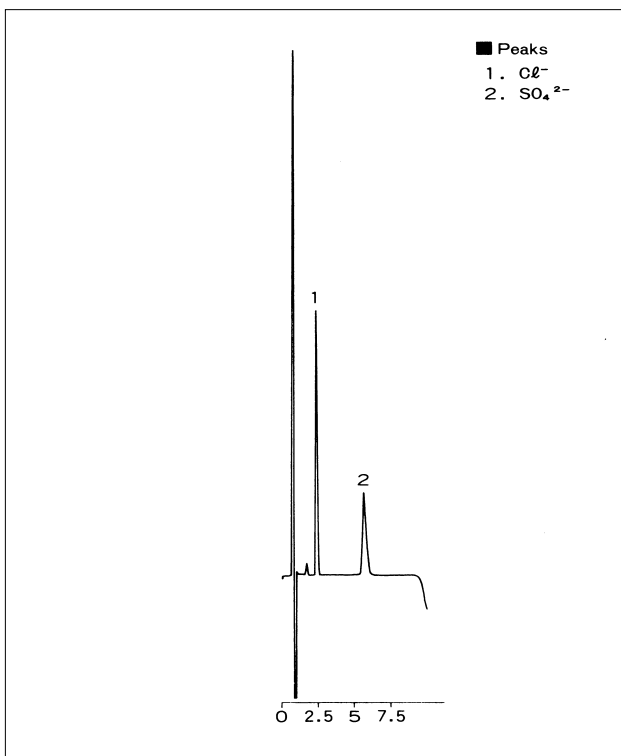


Fig. 2.8.1 Analysis of chloride ions and sulfate ions

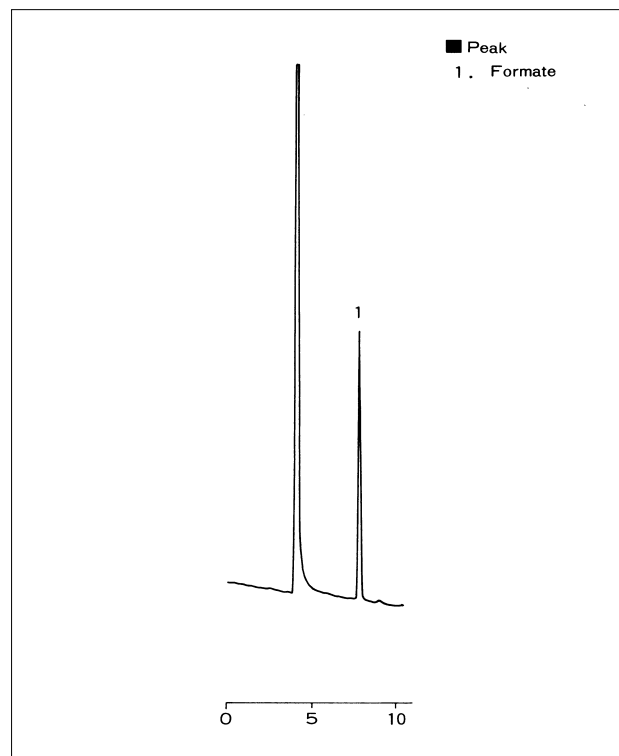


Fig. 2.8.2 Analysis of formic acid



2.8 Plating Solution Analysis (2) - LC

Fig. 2.8.3 Plating solutions: Analysis of sulfamic acid ions and inorganic anions

■ Analytical Conditions

Column : Shim-pack IC-A1
(100 mm × 4.6 mm i.d.)
Mobile Phase : 2.5mM Phthalic acid
2.4mM Tris (hydroxymethyl)-
aminomethane
Flow Rate : 1.5 mL/min
Temperature : 40 °C
Detection : Conductivity Detector

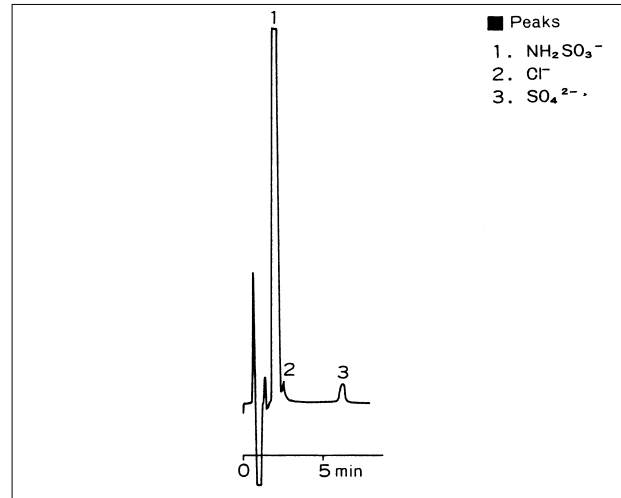


Fig. 2.8.3 Analysis of sulfamic acid ions and inorganic anions

Fig. 2.8.4 Plating solutions: Analysis of boric acid

■ Analytical Conditions

Column : Shim-pack SCR-101H
(300 mm × 7.9 mm i.d.)
Mobile Phase : 5mM Perchloric acid
Flow Rate : 0.8 mL/min
Temperature : 50 °C
Detection : Refractive Index Detector

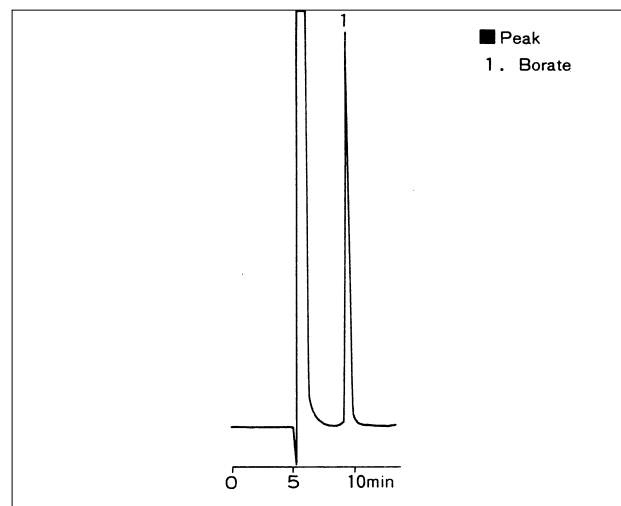


Fig. 2.8.4 Analysis of boric acid

Fig. 2.8.5 Plating solutions: Analysis of nickel ions

■ Analytical Conditions

Column : Shim-pack IC-C1
(150 mm × 5.0 mm i.d.)
Mobile Phase : 4.0mM Tartaric acid
2.0mM Ethylenediamine
Flow Rate : 1.5 mL/min
Temperature : 40 °C
Detection : Conductivity Detector

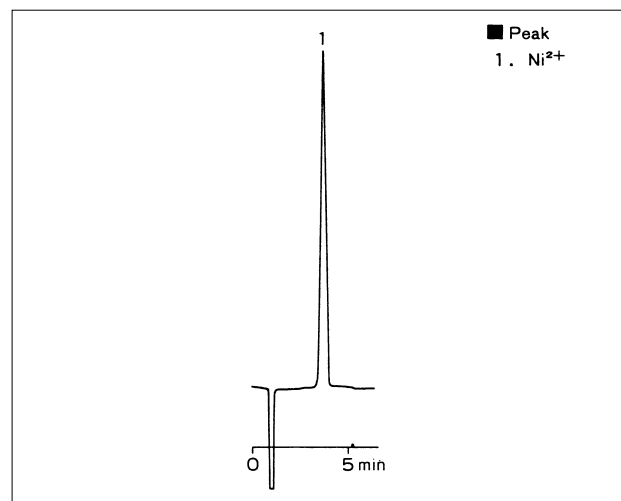


Fig. 2.8.5 Analysis of nickel ions

2.9 Analysis of Trace Inorganic Ions in Semiconductor Rinsing Solution - IC

■ Explanation

In semiconductor manufacturing an ultrapure water rinsing process is employed to remove strong acid ions that cause metal corrosion from product surfaces. Here an analysis method capable of detecting ions at several tens of parts per trillion (ppt) is required because analysis of ions in rinsing water is extremely important in the area of quality control. To meet such a need, a system equipped with a high sensitivity suppressor type ion chromatograph with solvent delivery pump and column switching valve to enable sample concentration is required.

Fig. 2.9.1 shows an example where 10mL of ultrapure water used to rinse semiconductor components is fed into the system using a solvent delivery pump, temporarily trapped in the enrichment column, fed to the separation column and then analyzed. Several parts per billion (ppb) sufficiently respond for detection. Note, also, that this chromatogram was obtained with conditions enabling

simultaneous analysis of inorganic acids such as acetic acid and formic acid.

Column : Shim-pack IC-SA1
(100 mm × 4.6 mm i.d.) × 2
Mobile Phase : 14mM Sodium hydrogen carbonate
10 μM Triethylenetetramine
Flow Rate : 1.0 mL/min
Temperature : 30 °C
Detection : Suppressed Conductivity Detector

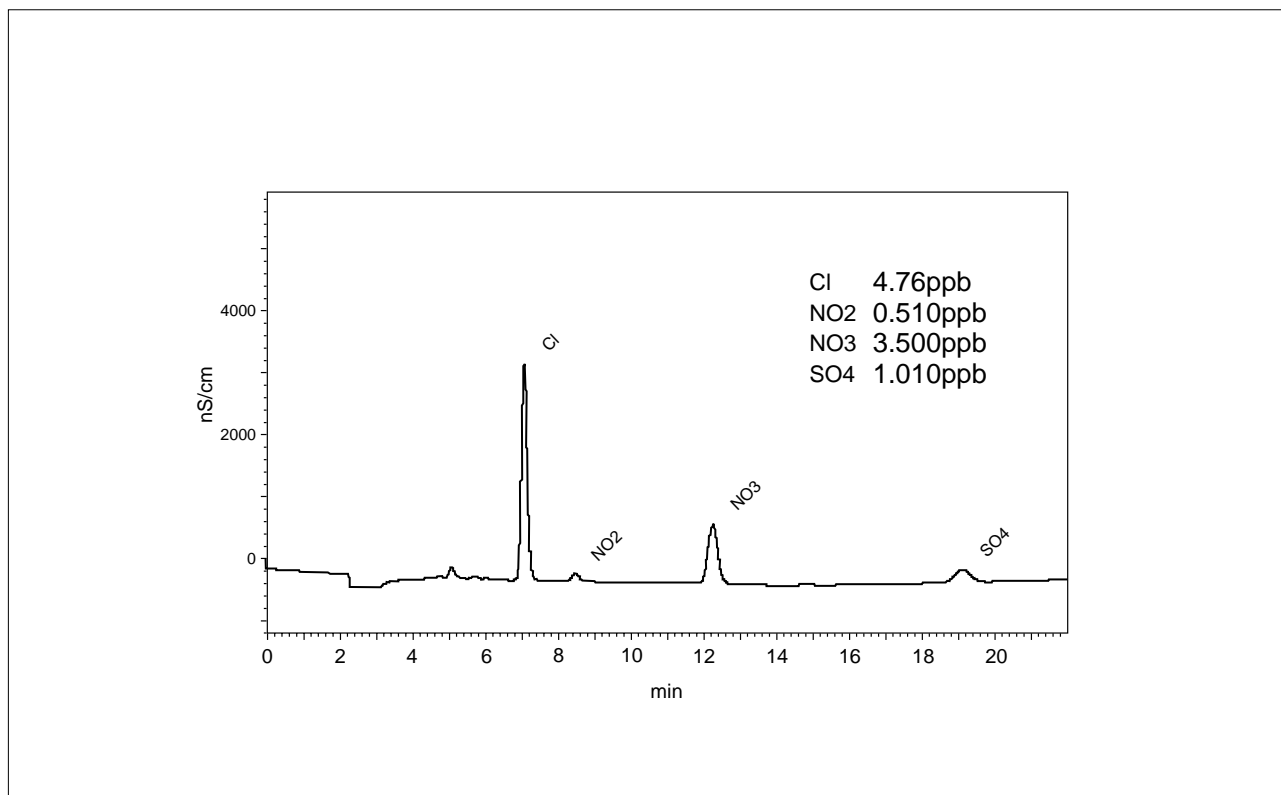


Fig. 2.9.1 Example analysis of semiconductor rinsing solution



2.10 Thermal Analysis of Lead-Free Solder - TA

■ Explanation

In recent years, research has focused on the harm caused to humans by lead; notably the problem of ground water pollution due to tin-lead solders (used in automobiles and electrical appliances) being dissolved by acid rain. Thus, a great deal of R&D work on lead-free solders is being conducted.

Knowing that the metal base of lead-free solders must be tin, and from the viewpoint of producing solders with melting points close to that of tin-lead solder (183 °C), the metals most likely to produce the best combination with tin are silver (Ag), copper (Cu), zinc (Zn), bismuth (Bi) and indium (In); however, as the combination of just two metals does not sufficiently meet requirements, the addition of a third or fourth metal is under consideration. Introduced here is a measuring example of the differing component ratios in lead-free solders.

■ Sn-Pb Solder Measuring Example

Fig. 2.10.1 shows measuring results for a conventional Sn-Pb solder with melting point at 183 °C.

■ Sn-Ag-Bi-Cu Solder Measuring Example

Figs. 2.10.2 and 2.10.3 show measuring results for a solder free of the lead component.

Instrument : DSC - 60
Sample Amount : 5 ~ 10mg
Heating Speed : 10 °C/min
Atmosphere : N₂ 50mL/min

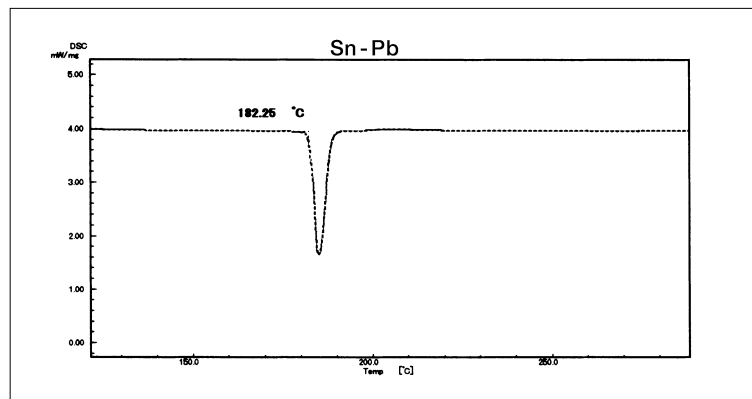


Fig. 2.10.1 Melting point of conventional Sn-Pb solder

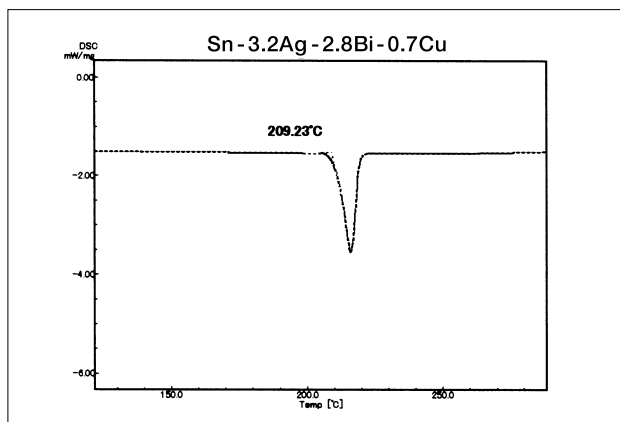


Fig. 2.10.2 Melting point of Sn-3.2Ag-2.8Bi-0.7Cu solder

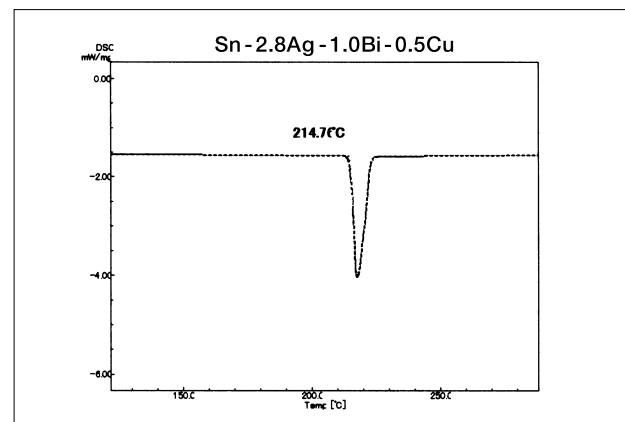


Fig. 2.10.3 Melting point of Sn-2.8Ag-1.0Bi-0.5Cu solder

2.11 Analysis of Sodium (Na) in Hydrogen Peroxide - AA

■ Explanation

It is necessary for impurities contained in chemical industrial products used for semiconductor related purposes, especially elements like Na, K, Ca and Fe, to be kept down to fairly low concentrations. As a consequence, control analysis of manufactured products requires high sensitivity measurement. Shown here is a trace analysis of Na in hydrogen peroxide using the electro-thermal atomization method.

■ Lower Limit of Quantitation

Approximately 0.1ppb

■ Measurement Method

(1) Measured by the standard addition method where hydrogen peroxide is diluted two times by the autosampler.

(2) 20 μL of hydrogen peroxide was injected, while the amount of 2ppb Na standard solution injected was varied between zero to 20 μL . The rest was prepared with purified water so that the total amount injected was always 40 μL .

■ Analytical Conditions

Wavelength : 589.0nm

Lamp Current : 12mA

Slit Width : 0.2nm

Measuring Mode : Non-BGC

Furnace Program:

(Tube type: Pyro-coated tube)

Stage	Temp (°C)	Time (sec)	Heat Mode	Ar Flow Rate (L/min)
1	150	20	RAMP	0.10
2	250	20	RAMP	0.10
3	450	10	RAMP	1.00
4	450	10	STEP	1.00
5	450	3	STEP	0.00
6	1800	3	STEP	0.00
7	2500	2	STEP	1.00

□ : Atomizing

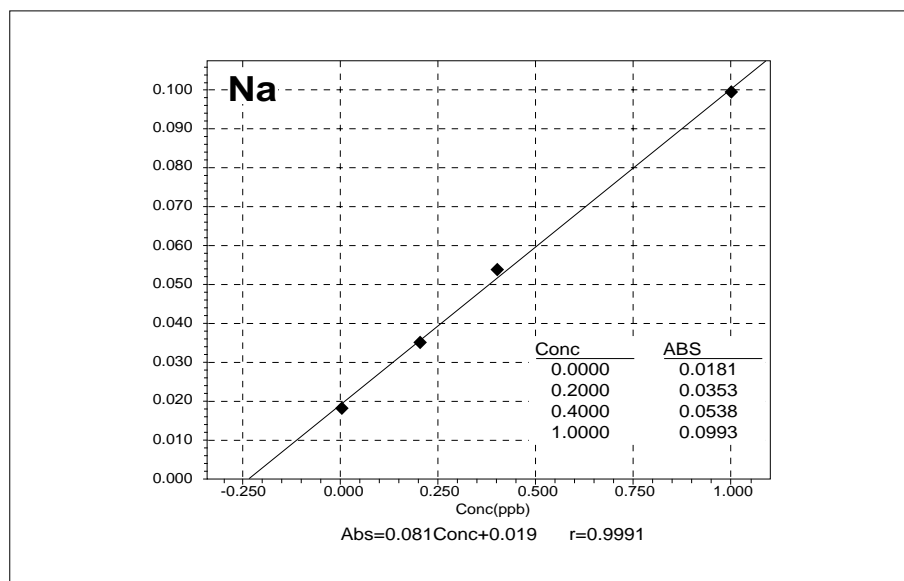
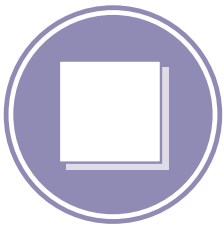


Fig. 2.11.1 Calibration curve for analysis of Na in hydrogen peroxide water by the standard addition method

Concentration within solution	Amount of sample collected	Total amount of sample injected	Concentration within stock solution
0.19 ppb	20 μL	40 μL	0.38 ppb

Table 2.11.1 Measuring results



3. Products and Evaluations

3.1 Microscopic Raman Spectroscopic Analysis of Micro Samples - Raman

■ Explanation

Raman spectroscopic analysis is used in the same way as infrared spectroscopic analysis in that it measures spectra based on molecular vibration for qualitative analysis and research related to molecule structures. In comparison to infrared spectroscopic analysis, Raman spectroscopic analysis is deficient in that it has less standard spectra, but has the advantages of requiring almost no pretreatment and being almost impervious to water.

Fig. 3.1.1 shows the configuration of the microscopic Raman system. Light emerging from the laser light source passes through a fiber and is conducted into the microscope. Now the Raman light scattered from the sample is conducted into the monochromator via the fiber again. A notched filter in the monochromator removes

Rayleigh light (scattered light with a wavelength identical to laser light) and a highly sensitive transmittance-type holographic grating forms a spectrum out of the light, which is then detected by an electronically cooled CCD camera.

■ Measurement Method

Raman spectroscopic analysis is used to evaluate the microstructure of carbon materials and is an essential form of analysis for evaluating hard carbon films.

In Fig. 3.1.2, (a) is a diamond-like film on a silicon wafer (2000 Å) and (b) is a Raman spectrum of graphite.

In the case of highly crystalline graphite, the Raman band is in the vicinity of 1582cm^{-1} , but a new Raman band appears and increases in the vicinity of 1350cm^{-1} where crystallinity drops.

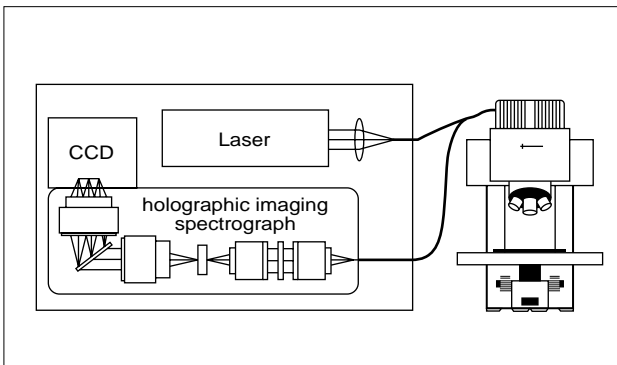


Fig. 3.1.1 Configuration diagram of microscopic Raman system

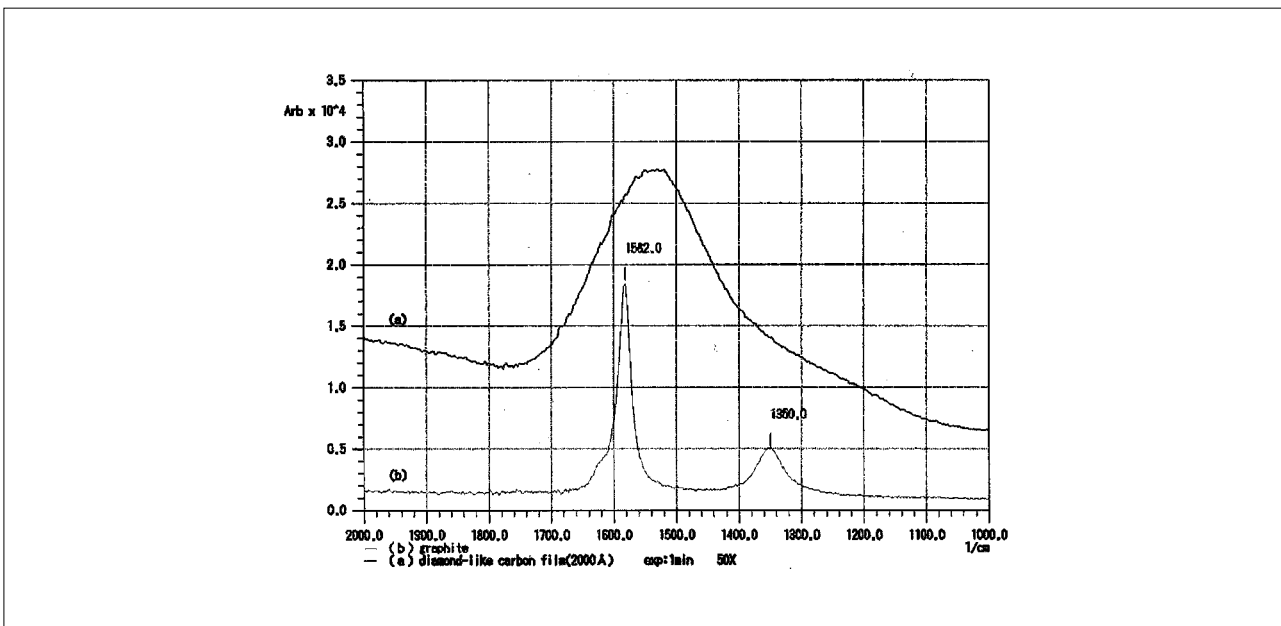


Fig. 3.1.2 Raman spectra of graphite and diamond-like film

3.2 Microscopic Infrared Mapping of Solid Surfaces - FTIR

■ Explanation

Infrared microscopes are essential for measuring microscopic areas. Measuring methods have developed from the conventional transmittance and reflection methods, to the total reflection method that measures sample surfaces using a prism.

The various modes are as follows.

● Transmittance Method

Infrared light is transmitted through a sample to obtain an absorption spectrum. To obtain a good spectrum for all regions, the sample must be just a few micrometers thick.

● Reflection Method

Infrared light is irradiated onto a sample and the reflected light detected. Pretreatment is not required, and the refractive index is obtained simultaneously, so absorption and refraction data are separated via data processing and analyzed.

● Attenuated Total Reflection Method (ATR Method)

Infrared light is irradiated via a prism (not directly) onto a sample and measured. If the prism and sample are tightly sealed together, only the thin in-contact area will be measured, which will provide a spectrum of just the surface of the sample.

■ Measurement Method

Here, ATR mapping was performed on a polynorborene resin with deteriorated surface. The normal sections were revealed with spectral analysis in the vicinity of zero to 300 μm but the deteriorated sections in the vicinity of 300 to 600 μm .

An identical location was measured using different prism materials. The upper diagram is with low-refractive-index ZnSe material and the lower diagram is with high-refractive-index Ge material. It is obvious that the deteriorated peak strength near the surface is larger when measured by the Ge prism. In this way multiple prisms can be used to map samples with varied measuring thicknesses.

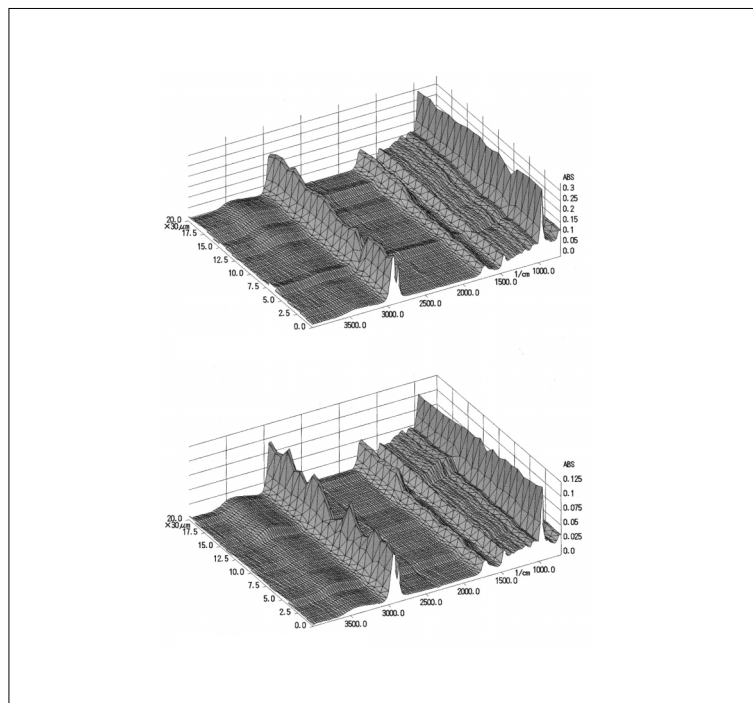
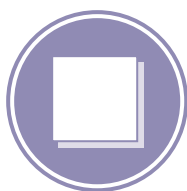


Fig. 3.2.1 ATR mapping of deteriorated resin (upper: by ZnSe prism, lower: by Ge prism)



3.3 Single-Reflection ATR Applications - FTIR

■ Explanation

The attenuated total reflection method (ATR method) requires the prism to be sealed against the sample to enable easy measurement of a sample spectrum. It is one of the most used infrared spectroscopic methods for resins and rubber.

Up to now a plate prism has been used and a multiple reflection produced to enhance sample absorption; however, thanks to the highly sensitive FTIR, the absorption of a single reflection is sufficient enough to provide a spectrum, so now even small samples can be measured. Also, warped samples such as curved plastics can be easily sealed against the prism because the required contact area is less.

The following shows the external appearance of the single-reflection ATR MIRacle.

The circular prism has a diameter of approximately 1.5mm and can be finely adjusted to press against the sample from above using the clamping screw with micrometer. The prism is fitted into the outer metal ring to form one unit, so prism swapping is easy if multiple prisms (differing materials) are to be used and optical tuning is almost unnecessary.

The following show some features of ATR prisms.

	Refractive Index	Hardness (Qty of 200g Knoop)	Hardest (cm ⁻¹)
ZnSe	2.4	250	to 550
KRS - 5	2.4	40	to 250
Diamond	2.4	Wavelength Range	to 12.5

■ Measurement Method

Resins and rubbers can be easily measured using the ATR method. For rubber measurement, prism selection is related to whether there is carbon black in the sample. The ATR method makes use of the total reflecting phenomenon so a prism with a refractive index higher than that of the sample must be used. Carbon is mixed into rubber to enhance rubber strength, but this carbon also increases the rubber's refractive index. Consequently, a Ge prism (Ge has a high refractive index of 4) must be used to measure black rubber.

Here, acrylic rubber containing carbon has been measured using Ge and ZnSe prisms. The high-refractive-index Ge prism provides a high baseline and well-defined absorption peak, but the low-refractive-index ZnSe does not fulfill the conditions for total reflection, the peaks are warped and the baseline has dropped down due to carbon absorption.

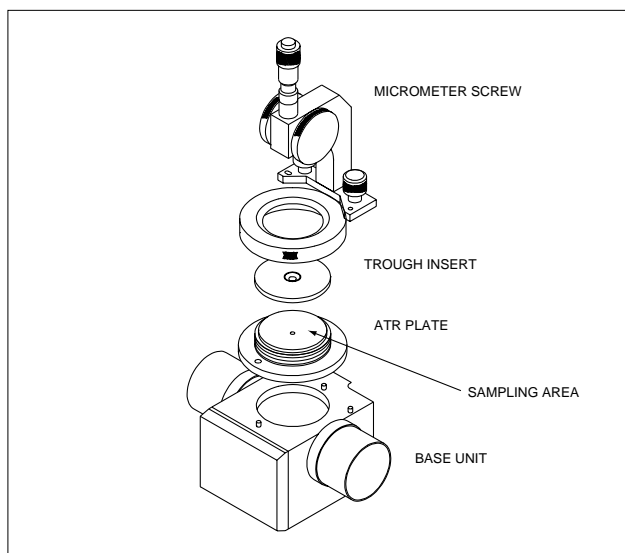


Fig. 3.3.1 External appearance of MIRacle

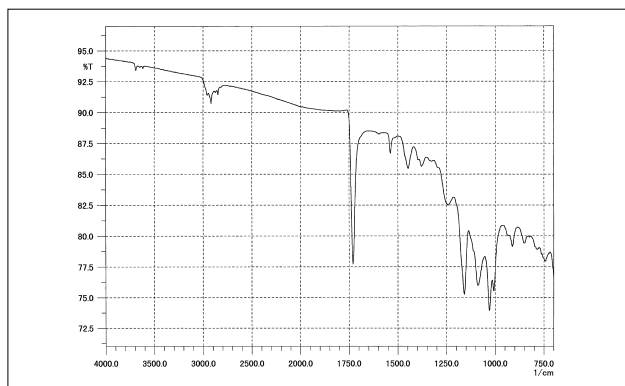


Fig. 3.3.2 Ge prism spectrum of rubber

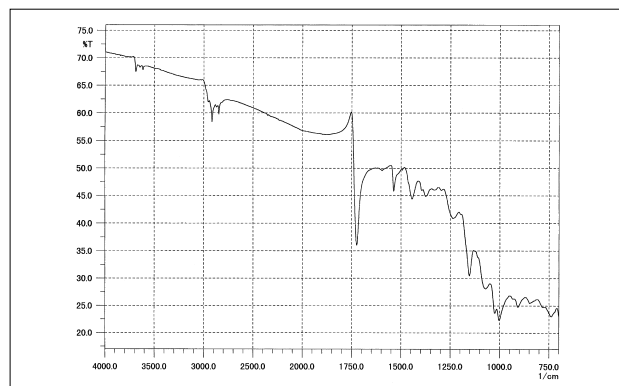


Fig. 3.3.3 ZnSe prism spectrum of rubber

3.4 Analysis of Liquid Sample Using Single Reflection ATR - FTIR

■ Explanation

The liquid membrane method and multiple reflection ATR (horizontal ATR) are often used for analysis of liquid samples. Each method has its distinct merits – absorption intensity can be changed according to film thickness with the liquid membrane method and post-measuring cleaning is easy with the horizontal ATR. However, as both methods measure without saturating peaks in the full wave number region, they must be tuned (cell thickness for the liquid membrane method and amount of sample drop down onto the prism [contact area]) for the horizontal ATR method.

Conversely, if the single reflection ATR MIRacle is used, the reflection frequency is one, which means that good spectra can be obtained without peak saturation

by just dropping the liquid sample onto the prism.

The photograph shows the external appearance of MIRacle. The device is divided into four sections (base unit, ATR prism plate, liquid sample adapter plate and clamping screw with micrometer). The liquid sample need only be dropped onto the prism for analysis. Moreover, the clamping screw with micrometer can be removed because there is no need to press the sample onto the prism.

■ Measurement Method

Additives such as antioxidants and rust-preventive agents are included in lubricating oils (that are mainly composed of mineral oil) to prolong performance. The types of additives and concentration vary with targeted use, grade and manufacturer. Introduced here is a comparison between lubricating oil for vacuum pumps and paraffin oil. The concentration of the added substance is approx. 1%, so normally those absorption peaks would be small, but peaks thought to be due to the additive can be seen in the 1300 to 750 cm^{-1} range.

Fig. 3.4.3 shows enlarged spectra of the antioxidant Tris (2,4-di-tert-butylphenyl) phosphite for comparison purposes. Results show that a phosphorous-containing substance has been added to the vacuum pump lubricating oil.



Fig. 3.4.1 Photo of MIRacle

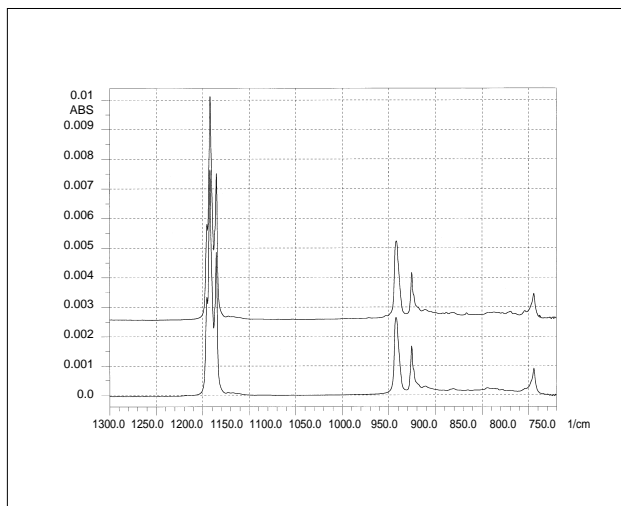


Fig. 3.4.2 Spectra of lubricating oil (upper) and paraffin oil (lower)

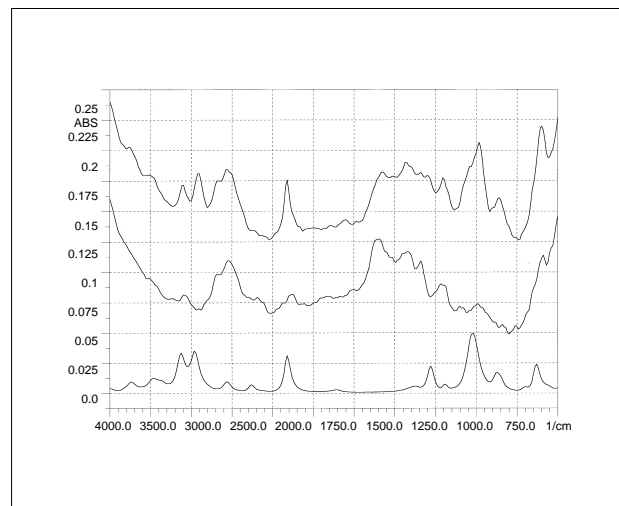
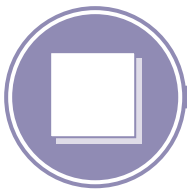


Fig. 3.4.3 Spectrum of lubricating oil (upper), paraffin oil (middle) and Tris (2,4-di-tert-butylphenyl) phosphite



3.5 Measuring the Thickness of Films - UV

■ Explanation

Various methods exist for measuring the thickness of films of substances. By using the UV-VIS spectrophotometer, measurement is simple and non-destructive. The degree to which the film thickness can be measured using a UV-VIS spectrophotometer was investigated here.

A wavy interference spectrum, which forms as a result of light reflected from the surface of the film interfering with the light reflected from the rear surface of the film is obtained in measurements using spectrophotometers. The thickness is obtained by counting the number of waves in a spectrum within a fixed range of wavelengths (note that the refractive index of the film substance is required).

The thinner the film, the lesser the number of waves in the spectrum, and the thicker the film, the greater the number of waves. Here, measurements were made to the limits of both the thinnest and thickest measurements.

It was discovered that at its thinnest, measurements can

be made down to approximately $0.5 \mu\text{m}$, as can be seen in Fig. 3.5.1, while measurements can be made to approximately $60 \mu\text{m}$ at its thickest (note: $1 \mu\text{m} = 1000\text{nm}$), as can be seen in Fig. 3.5.4. If the film is either thinner or thicker than this, a wavy interference spectrum is unobtainable and consequently the film thickness cannot be measured. For reference, Figs. 3.5.2 and 3.5.3 show measurement data for thickness in between that of those mentioned above.

■ Analytical Conditions

Mode	: Reflectance
Slit Width	: 0.5nm
Scan Speed	: Medium
Attachment	: Specular reflectance measurement attachment for 5° incident angle

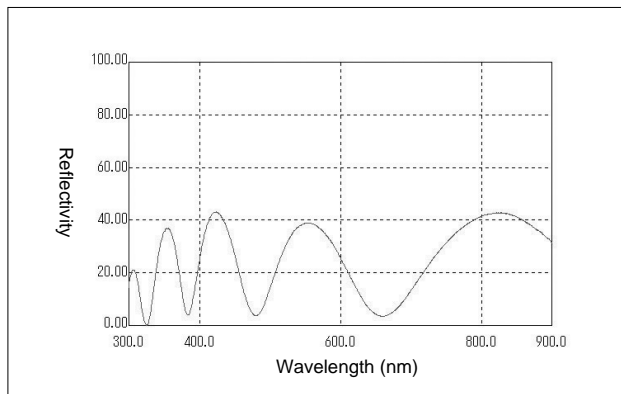


Fig. 3.5.1 $0.5 \mu\text{m}$ photoresist film (on a silicon wafer)

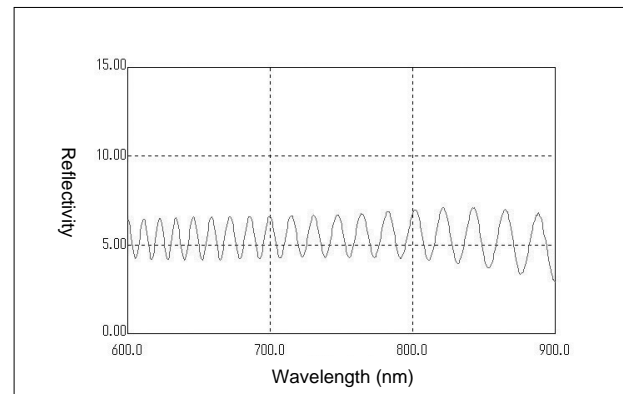


Fig. 3.5.2 $10 \mu\text{m}$ plastic wrap (polyvinylidene chloride)

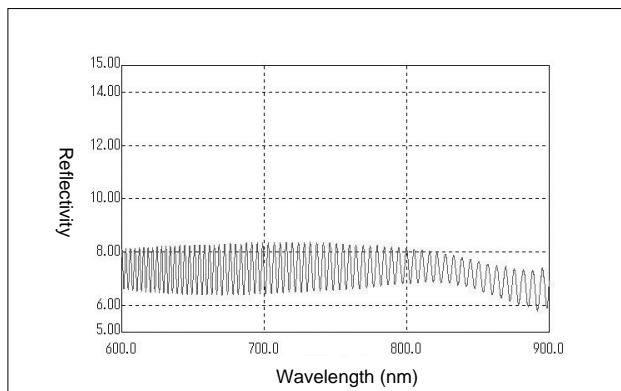


Fig. 3.5.3 $41 \mu\text{m}$ Plastic bag (polypropylene)

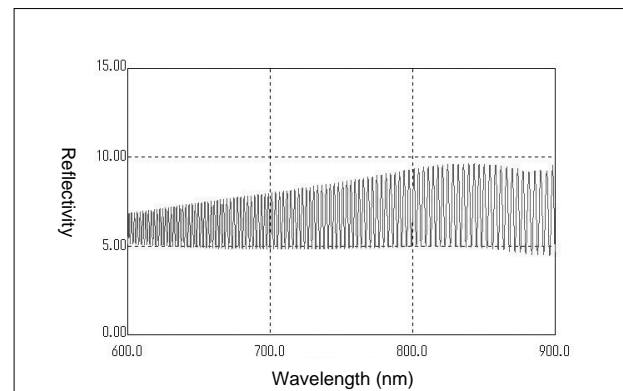


Fig. 3.5.4 $63 \mu\text{m}$ K Kuraray vinylon film (polyvinyl alcohol)

3.6 Analysis of Organic Solvents in Tape - GC

■ Explanation

Introduced here is the analysis of magnetic tape and adhesive tape using headspace GC.

■ Pretreatment

0.4mL of headspace sample was analyzed after 30cm of magnetic tape was enclosed in a vial and warmed at 120 °C for 60 minutes.

0.8mL of headspace sample was analyzed after 50cm of adhesive tape was enclosed in a vial and warmed at 100 °C for 40 minutes.

■ Analytical Conditions(magnetic tape)

Instrument : HSS-2B + GC-14BPF
Column : SP-1000 5% on Chromosorb W
60/80 3m × 3.0mm

Col.Temp. : 80 °C
Inj.Temp. : 200 °C
Det.Temp. : 200 °C (FID)
Carrier Gas : N₂ 50mL/min

■ Analytical Conditions(adhesive tape)

Instrument : HSS-2B + GC-14BPFsc
Column : CBP20-S25-050 0.33mm × 25m df 0.5 μm
Col.Temp. : 50 °C (10min)-200 °C (10 °C/min)
Inj.Temp. : 230 °C
Det.Temp. : 230 °C (FID)
Carrier Gas : He (1.6mL/min)
Injection : Split 1:33

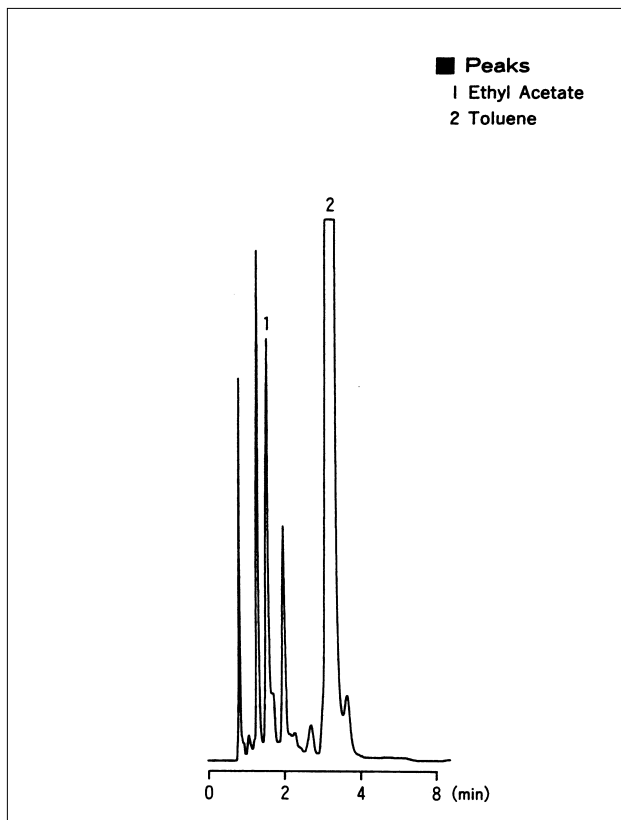


Fig. 3.6.1 Example of headspace analysis for magnetic tape

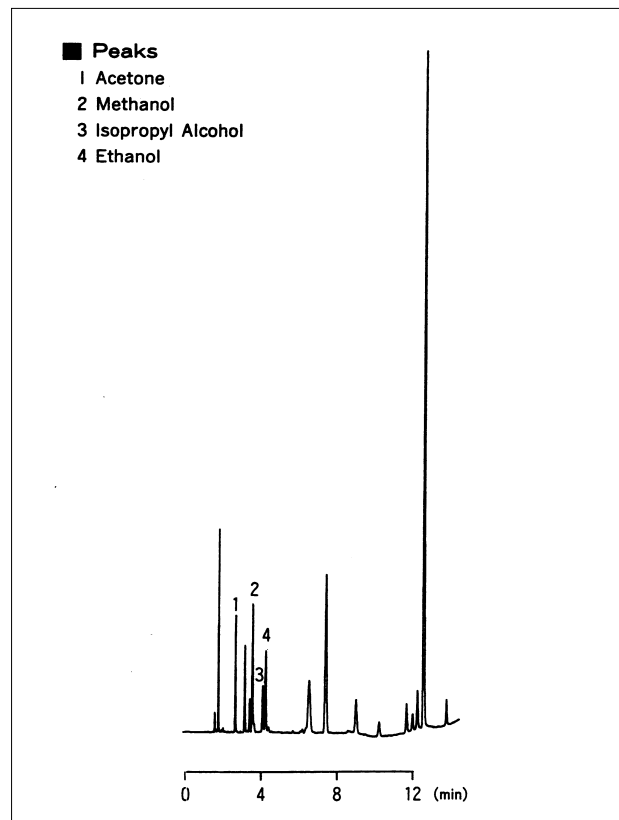
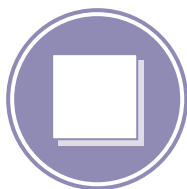


Fig. 3.6.2 Example of headspace analysis for adhesive tape



3.7 Analysis of Phenols on Electrical Wiring Surfaces - GC

■ Explanation

Phenols generated when electrical wiring (polyurethane copper wiring) was heated has been analyzed with headspace GC.

■ Pretreatment

0.8mL of headspace sample was analyzed after 8g of sample was bundled and enclosed in a vial and warmed at 150 °C for 60 minutes.

■ Analytical Conditions

Instrument	: HSS-2B + GC-14BPFsc
Column	: CBP10-S25-050 0.33mm × 25m df 0.5 μm
Col.Temp.	: 50 °C (0min)-200 °C (10 °C/min)
Inj.Temp.	: 230 °C
Det.Temp.	: 230 °C (FID)
Carrier Gas	: He (1.4mL/min)
Injection	: Split 1 : 14

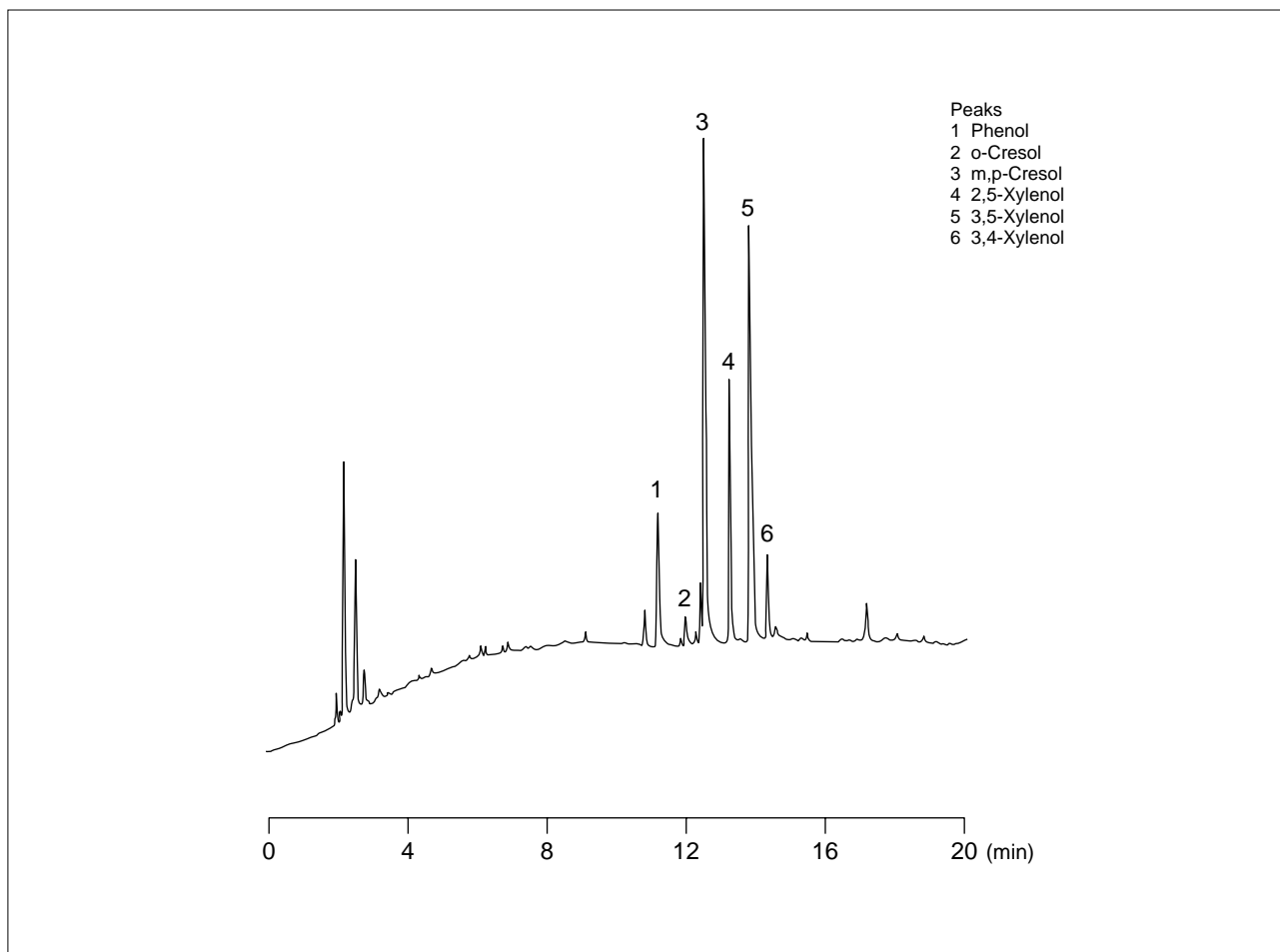


Fig. 3.7.1 Example of headspace analysis of polyurethane copper wire

3.8 Analysis of Liquid Crystals - GC

■ Explanation

Introduced here is an example of analysis on liquid crystals using a capillary column. Liquid crystals used in a toy were compared before and after use. Results show that the component ratio changes after use.

■ Pretreatment

None.

■ Analytical Conditions

Instrument : GC-17AAFw
Column : OV-17 0.25mm × 25m
Col.Temp. : 200 °C (0min)-300 °C (5 °C/min)
Inj.Temp. : 320 °C
Det.Temp. : 320 °C (FID)
Carrier Gas : He (1.2 mL/min)
Injection : Split 1 : 50

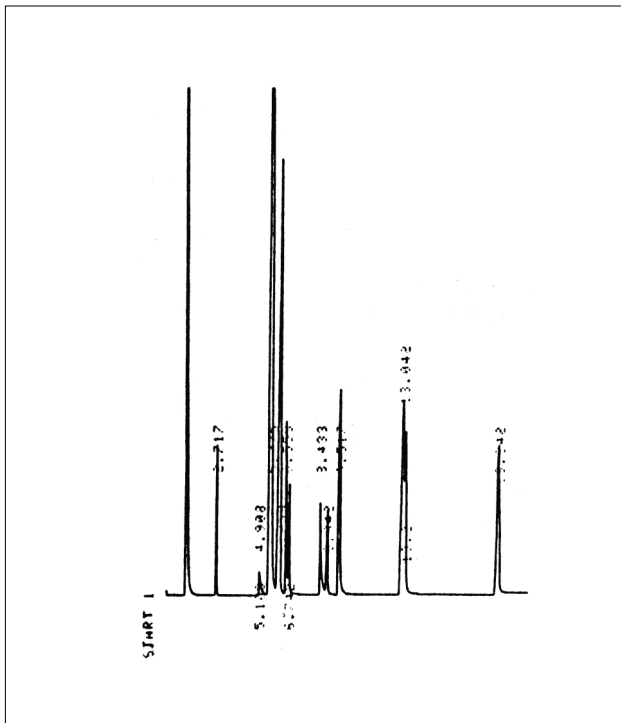


Fig. 3.8.1 Example of analysis on liquid crystals before use

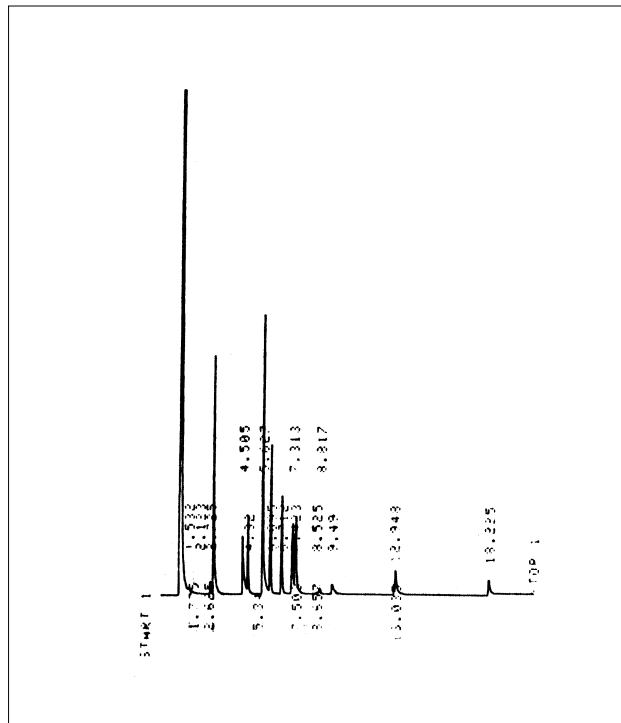
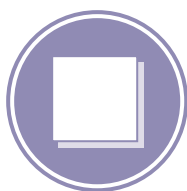


Fig. 3.8.2 Example of analysis on liquid crystals after use in a toy



3.9 Analysis of Liquid Crystals - GCMS

■ Explanation

Fig. 3.9.1 shows some structures of liquid crystals. The molecular ion peaks denoting molecular weight cannot be detected with EI for some of these compounds, which mean that the determination of molecular weight and structure are difficult. Notably, compounds with ester structures cleave at the ester section. In such cases the use of CI is essential to provide molecular weight data. Molecular structure was conjectured using the CI data together with structure data from EI.

■ Analytical Conditions

Instrument : GCMS-QP1100EX
Column : DB-101 0.24mm × 25m df 0.25 μm
Col.Temp. : 180 °C-270 °C (5 °C/min)
Inj. Temp. : 290 °C
I/F Temp. : 300 °C
Carrier Gas : 100kPa
Reagent Gas : Isobutane

References

Application News No. M72

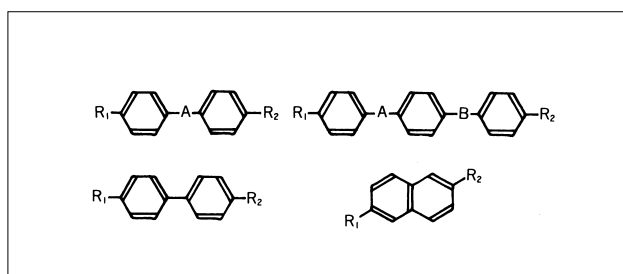


Fig. 3.9.1 Liquid crystal structure

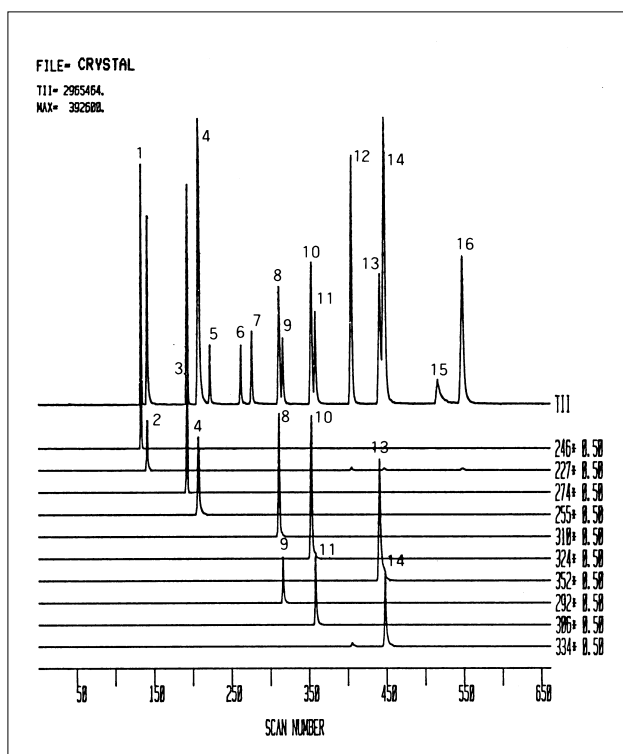


Fig. 3.9.2 MC

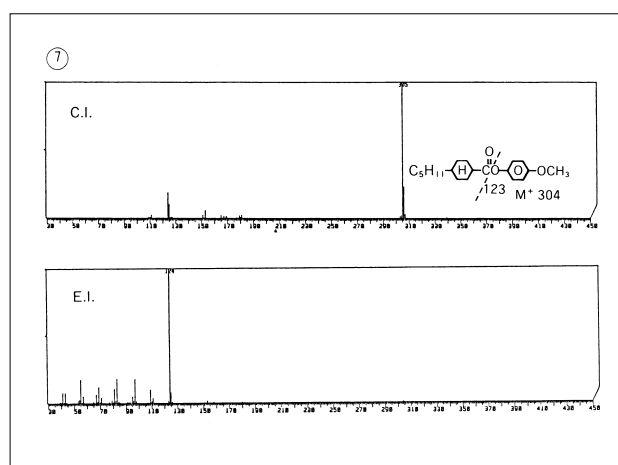


Fig. 3.9.3 Mass spectrum of peak 7

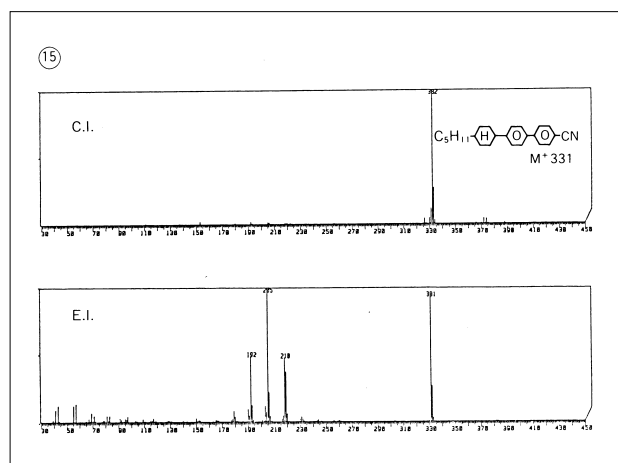


Fig. 3.9.4 Mass spectrum of peak 15

3.10 Analysis of Vinyl Acetate Adhesive - GCMS

■ Explanation

Vinyl acetate polymers and several organic solvents are contained in vinyl acetate adhesive. If an adhesive like this is thermally decomposed at high temperature, the peaks of the vinyl acetate related matter generated from heat decomposition and organic solvents will be mixed, making identification impossible. (See Fig. 3.10.3.)

To eliminate this problem, the sample is heated at 200 °C to vaporize the organic solvents without decomposing the vinyl acetate components. With the sample in this status, the organic solvents can be measured and analyzed. Next, the sample is heated to 550 °C to thermally decompose the vinyl acetate and produce a vinyl acetate pyrogram. The use of two heating stages means that the organic solvents and polymers used in the adhesive can be separately distinguished. (See Figs. 3.10.1 and 3.10.2.)

■ Analytical Conditions

Instrument : GCMS-QP5000 PYR-4A
 Column : DB-1 0.25mm × 30m df 0.25 μm
 Col.Temp. : 50 °C (1min)-300 °C (10 °C/min)
 Inj.Temp. : 300 °C
 I/F Temp. : 320 °C
 Carrier Gas : 100kPa(1min)-150kPa(2kPa/min)-
 250kPa(5kPa/min)
 Split Ratio : 1 : 10

References

Application News No. M174, M196

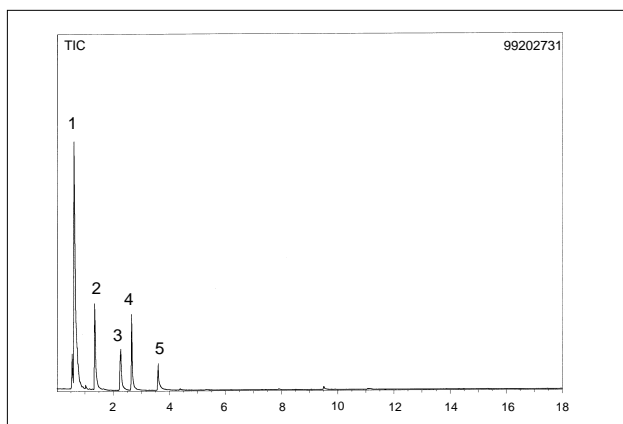


Fig. 3.10.1 Adhesive TIC (heating temperature: 200 °C)

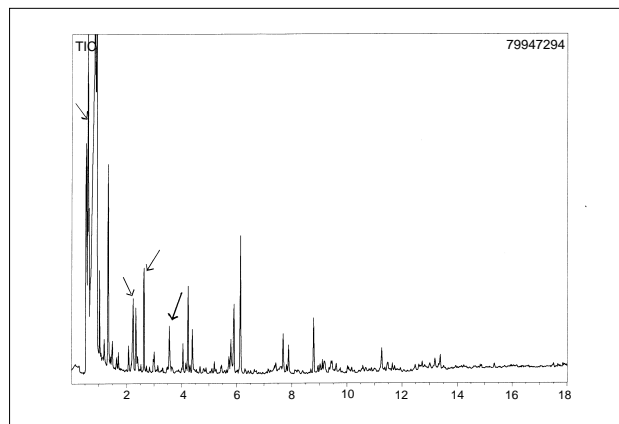


Fig. 3.10.3 Adhesive TIC (thermal decomposition temperature: room temperature to 550 °C) Arrows denote organic solvents

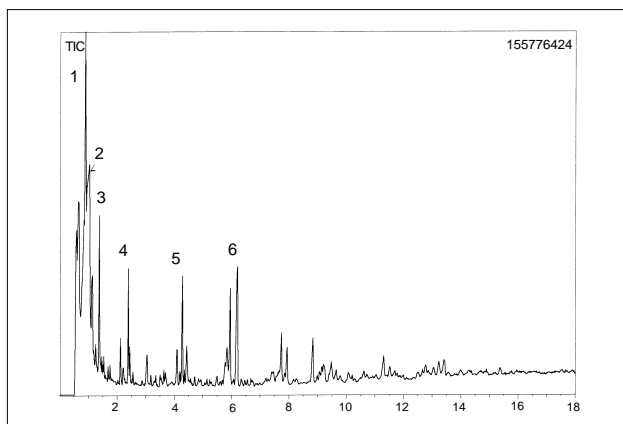


Fig. 3.10.2 Adhesive TIC (thermal decomposition temperature: 200 °C to 550 °C)

Identified Solvents (Fig. 3.10.1)

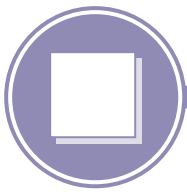
1. Methyl acetate
2. Isobutyl acetate
3. 2-Methyl-1-butyl acetate
4. n-Pentyl acetate
5. Azobis isobutyronitrile

Table 3.10.1

Identified Pyrolysis Fragments (Fig. 3.10.2)

1. Benzene
2. Acetic acid
3. Toluene
4. Styrene
5. Indene
6. Naphthalene

Table 3.10.2



3.11 Analysis of Paint Resin - GCMS

■ Explanation

Polymers and solvents coexist in the resin used in paint. Solvents remain in the paint after application. For this reason, in paint resin analysis, components generated at the thermal decomposition temperature change vastly. Introduced here are examples at thermal decomposition temperatures of 450 °C and 700 °C.

■ Analytical Conditions

Instrument : GCMS-QP1100EX PYR-4A
Column : SE30 2.6mm × 3m 10%
Col.Temp. : 60 °C-250 °C (5 °C/min)
Inj.Temp. : 300 °C
I/F Temp. : 250 °C
Carrier Gas : 30mL/min

References

Application News No. M78

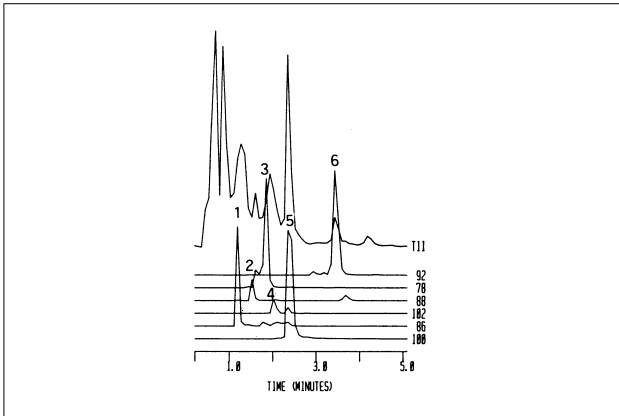


Fig. 3.11.1 Paint resin MC (450 °C)

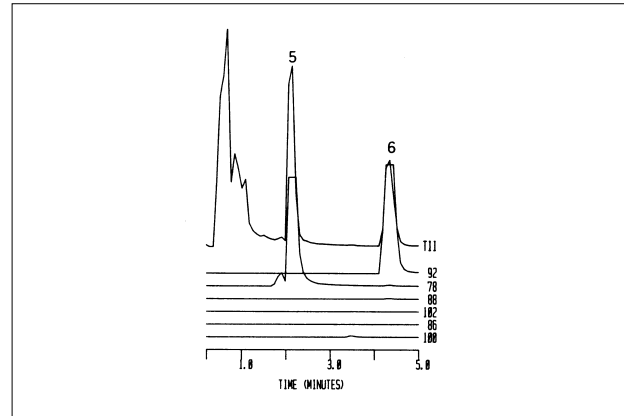


Fig. 3.11.2 Paint resin MC (700 °C)

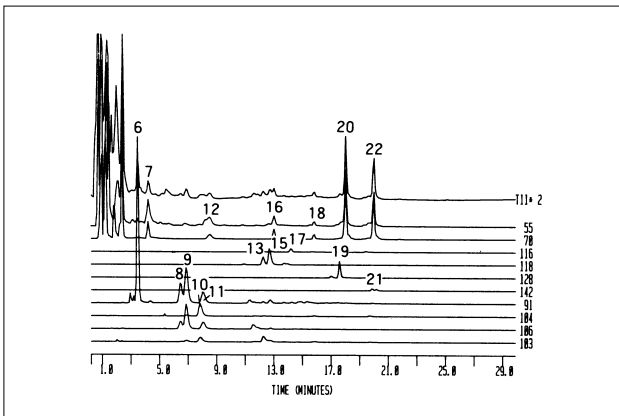


Fig. 3.11.3 Paint resin MC (450 °C)

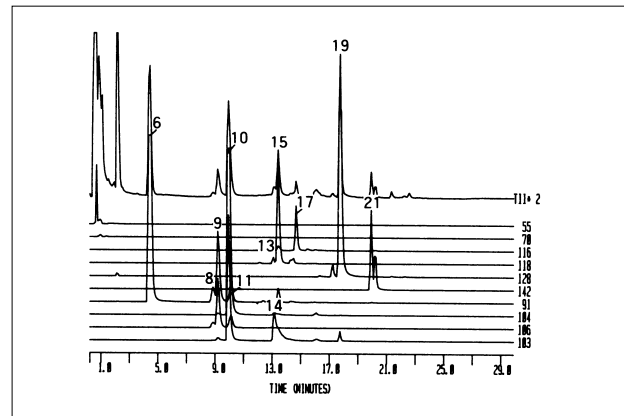


Fig. 3.11.4 Paint resin MC (700 °C)

1. Methyl acrylate
2. Methyl propanate
3. Benzene
4. Methyl isobutylate
5. Methyl meta acrylate
6. Toluene
7. 1-Octene
8. Ethyl benzene
9. m-, p-Xylene
10. Styrene
11. o-Xylene
12. 1-Nonene
13. α -Methylstyrene
14. Cyanobenzene
15. β -Methylstyrene
16. 1-Decene
17. Indene
18. 1-Undecene
19. Naphthalene
20. 1-Dodecene
21. Methyl naphthalene
22. 1-Tridecene

3.12 Analysis of Magnetic Tape - GCMS

■ Explanation

Magnetic tape contains polyethylene terephthalate (PET) for the film base and polyurethane and nitrocellulose for the binder as well as a cross linking agent.

Measurement of the magnetic tape involved thermal decomposition using a pyrolyzer and qualification of generated components.

■ Analytical Conditions

Instrument : GCMS-QP1100EX PYR-4A
 Column : PEG-20M 2.6mm × 3m 25%
 Col.Temp. : 80 °C-220 °C (4 °C/min)
 Inj.Temp. : 300 °C
 I/F Temp. : 260 °C
 Carrier Gas : 30mL/min
 Pyrolysis Temp. : 500 °C

References

Application News No. M69

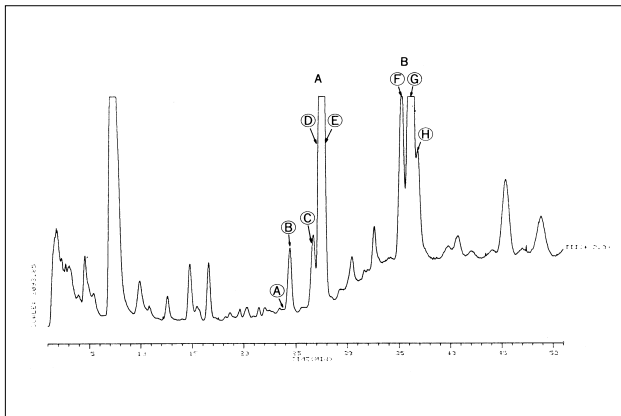


Fig. 3.12.1

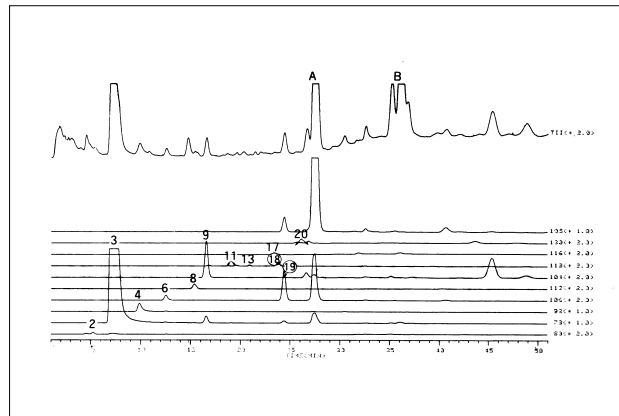


Fig. 3.12.2

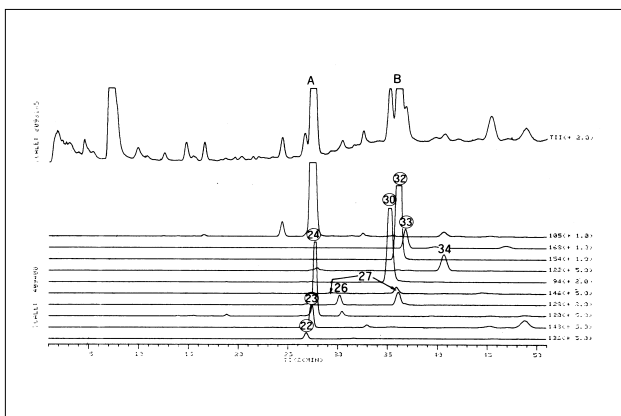


Fig. 3.12.3

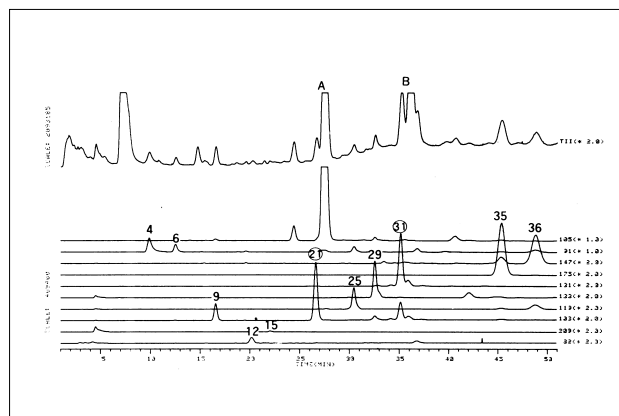
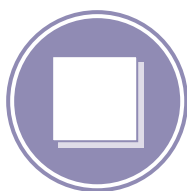


Fig. 3.12.4

Magnetic Tape TIC and MC

- A. Benzofuran B. Benzaldehyde C. Cyanobenzene D. 1,2-Propanedion-1-phenyl E. Acetophenone
 F. Phenol + ethyl cyanobenzene G. Biphenyl H. Diphenylmethane 4. Toluene 6. Ethyl benzene 9. Styrene
 21. Cyanobenzene 22. Methyl benzoic acid 23. 1,2-Propanedion-1-phenyl 24. Acetophenone 25. Phenyl isothiocyanate
 26. Naphthalene 29. Methyl phenyl isothiocyanate 30. Phenol 31. Ethyl cyanobenzene 32. Biphenyl
 33. Dipheylmethane 34. Benzoic acid



3.13 Analysis of Cellulose - GCMS

■ Explanation

Cellulose molecules are extremely large with a polymerization degree of 5000 to 6000 for the polysaccharide bonded β -1,4-glucoside. Analysis of the cellulose involved thermal decomposition using a thermal decomposer and measurement of the generated components. Also, NiCl_2 was mixed into the cellulose and the sample thermally decomposed at 500°C to generate peak 13. A molecular ion peak (providing molecular weight data) for peak 13 could not be detected with EI mass spectrum, but could be well detected with CI mass spectrum, making qualitative analysis possible.

■ Analytical Conditions

Instrument : GCMS-QP1100EX PYR-4A
Column : OV-17 2mm \times 2m 5%
Col.Temp. : 80°C - 230°C ($4^\circ\text{C}/\text{min}$)
Inj.Temp. : 300°C
I/F Temp. : 250°C
Carrier Gas : 30mL/min

References

Application News No. M62

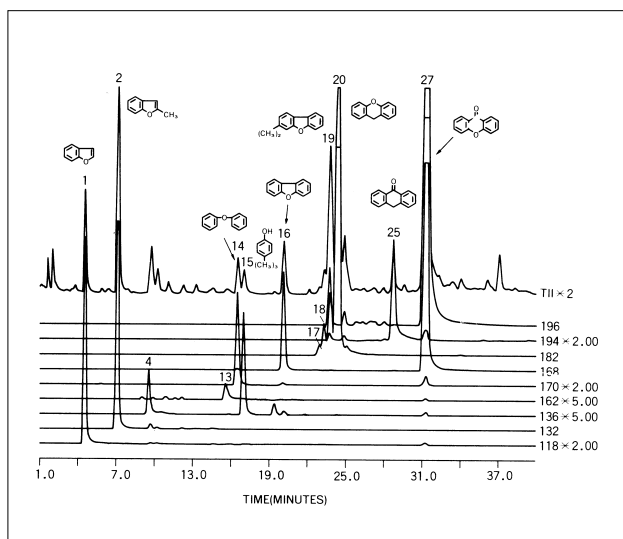


Fig. 3.13.1 Cellulose MC

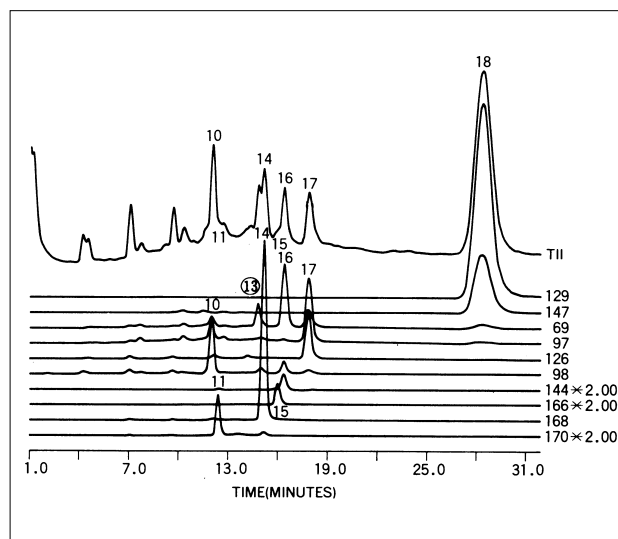


Fig. 3.13.3 Cellulose MC

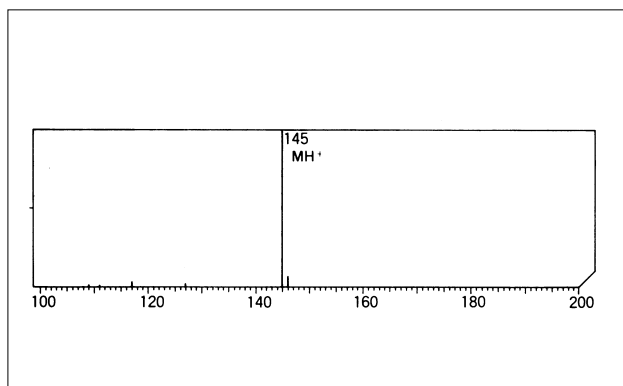


Fig. 3.13.2 EI mass spectrum of peak 13

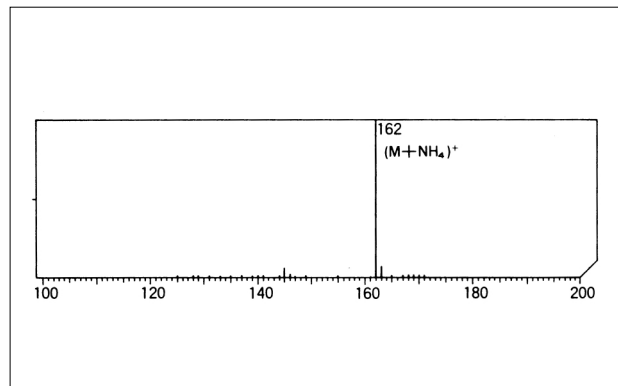


Fig. 3.14.4 CI mass spectrum of peak 13 (isobutene)

3.14 Analysis of Vulcanized Natural Rubber - GCMS

■ Explanation

Polymer samples like rubber cannot be directly injected into GC and GCMS. Normally, they are thermally decomposed using a pyrolyzer and the decomposed components qualitatively analyzed.

The product material from that decomposition is complicated and requires MC (mass chromatography) to simplify the task of qualifying the components.

Introduced here is an example of analysis targeting a sulfur compound and another example focusing on alkyl benzene and naphthalene compounds. Fig. 3.14.1 shows MC targeting the detection of the sulfur compound. Analysis shows peak A to be thiophene, peak B to be methyl thiophene, peak C to be benzothiophene and peak D to be benzothiazole. Fig. 3.14.2 shows MC with molecular weights for the targeted alkyl benzene

compound. This type of analysis enables reliable determinations of these compounds.

■ Analytical Conditions

Instrument : GCMS-QP1100 PYR-4A
Column : DB-1 0.2mm × 25m df 0.25 μm
Col.Temp. : 50 °C-250 °C (10 °C/min)
Inj.Temp. : 300 °C
I/F Temp. : 280 °C
Carrier Gas : 100kPa
Pyrolysis Temp. : 800 °C

References

Application News No. M103

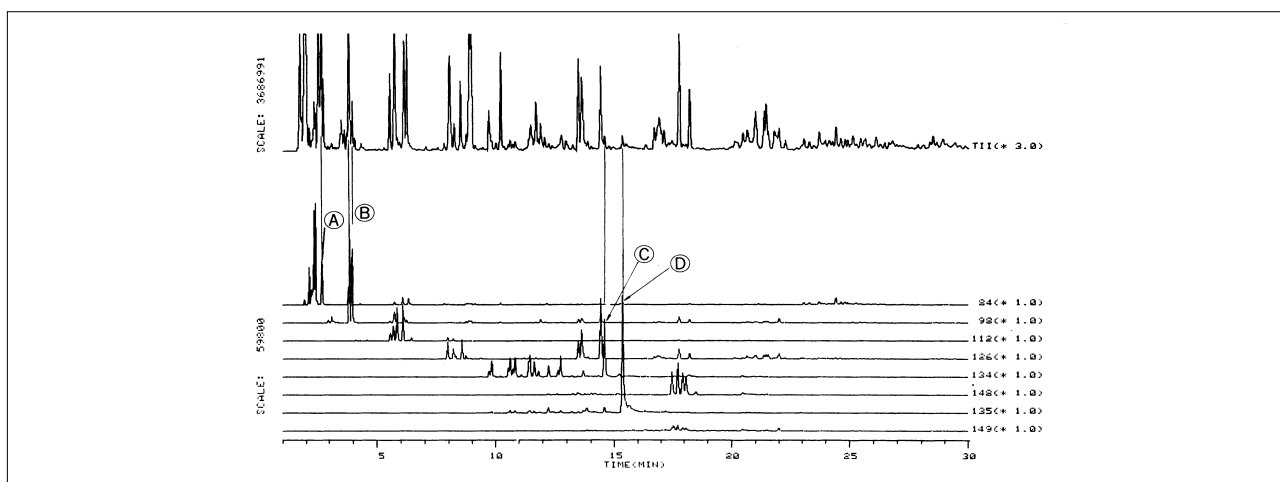


Fig. 3.14.1 Vulcanized natural rubber MC

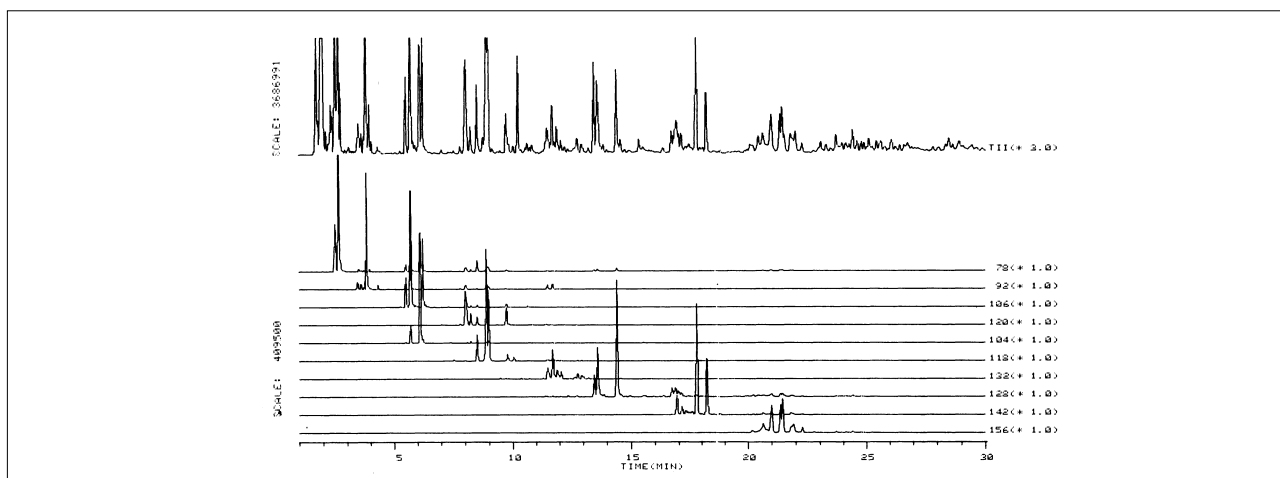
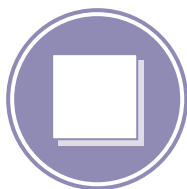


Fig. 3.14.2 Vulcanized natural rubber MC



3.15 Analysis of Tire Rubber - GCMS

■ Explanation

Large quantities of carbon black are added to the rubber components of tire rubbers. At a thermal decomposition temperature of 450 °C only the rubber components are decomposed, resulting in the detection of isoprene, its dimer and its homologue components. However, decomposition at the high temperature of 700 °C results in detection of various components. This example concentrates on sulfur constituents.

■ Analytical Conditions

Instrument : GCMS-QP1100EX
PYR-2A
Column : DB-1 0.2mm × 50m df 25 μm
Col.Temp. : 50 °C-280 °C (5 °C/min)
Inj.Temp. : 300 °C
I/F Temp. : 300 °C
Carrier Gas : 150kPa
Split Ratio : 80 : 1
Pyrolysis Temp. : 450 °C, 700 °C

References

Application News No. M104

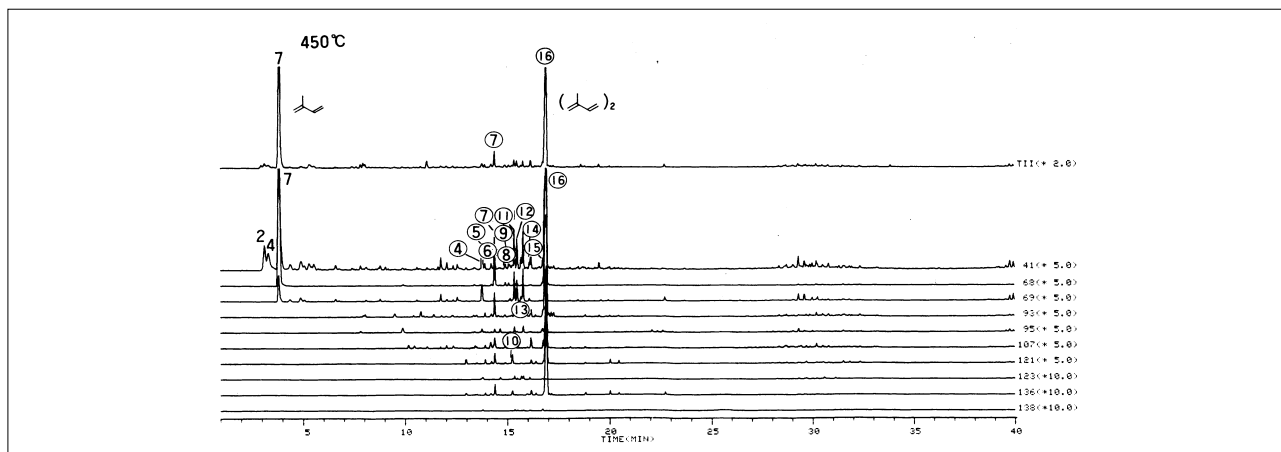


Fig. 3.15.1 MC at thermal decomposition temperature of 450 °C

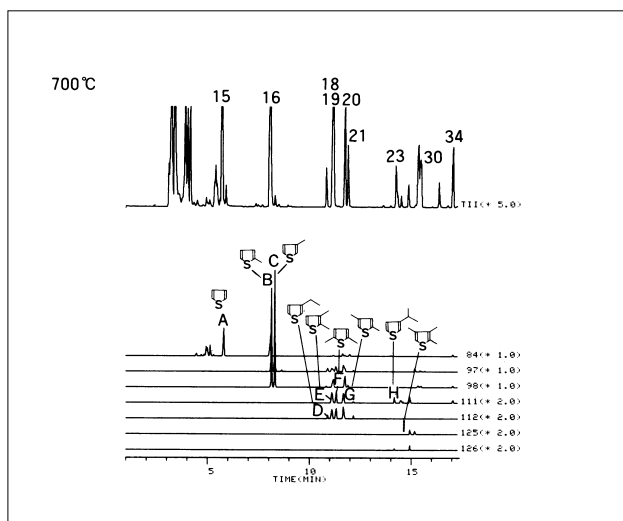


Fig. 3.15.2 1st MC at thermal decomposition temperature of 700 °C

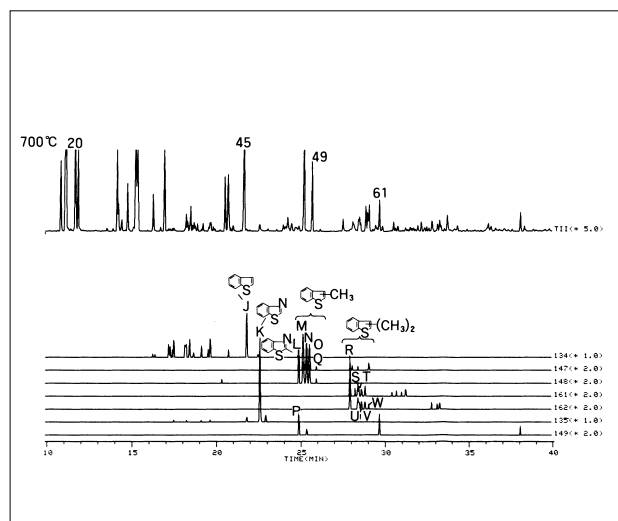


Fig. 3.15.2 2nd MC at thermal decomposition temperature of 700 °C

3.16 Analysis of Silicon Rubber - GCMS

■ Explanation

Silicon rubber is made by the hydrolysis of dimethyldichlorosilane and has excellent heat resistance properties, which is why this rubber is used in injection port septa for GC and GCMS devices. Nevertheless, the problem of bleeding from such septa is highlighted in high sensitivity analysis. Introduced here is an example of analysis using TG-MS and TG-GCMS to measure the differences in two types of septa. Fig. 3.16.1 shows the TG curve and Fig. 3.16.2 the TGMS data. Results show reduction at the low-temperature side of septum S2. Fig. 3.16.3 and Fig. 3.16.4 show the results TG-GCMS for septa S1 and S2 respectively. The detection of peak 1 (benzene) and peak 2 (methylphenylsiloxane) show the differences in the two septa. This measurement was

conducted with TGMS but could be easily measured using a double-shot pyrolyzer (PY-2020D).

■ Analytical Conditions

Instrument : GCMS-QP1100EX
Column : DB-1 0.53mm × 30m df 25 μm
Col.Temp. : 80 °C (1min)-280 °C (10 °C/min)
Inj.Temp. : 300 °C
I/F Temp. : 250 °C
Carrier Gas : 50kPa

References

Application News No. M152

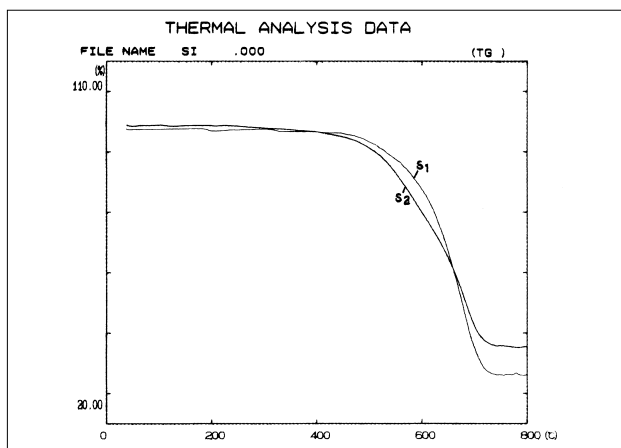


Fig. 3.16.1 TG curves of septa S1 and S2

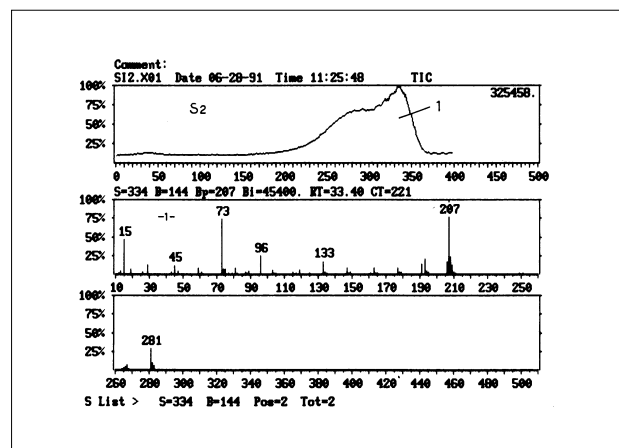


Fig. 3.16.2 TGMS of septum S2

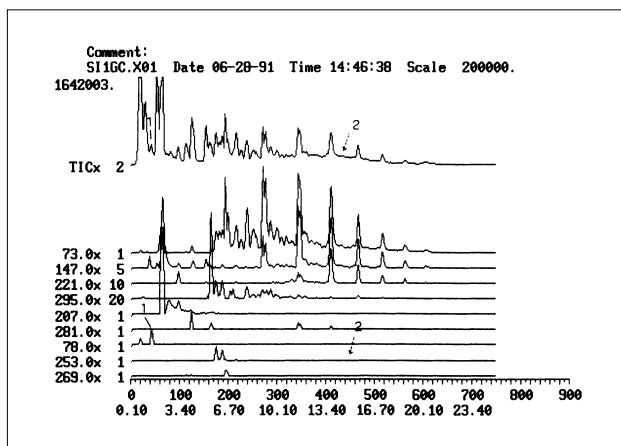


Fig. 3.16.3 TG-GCMS of septum S1

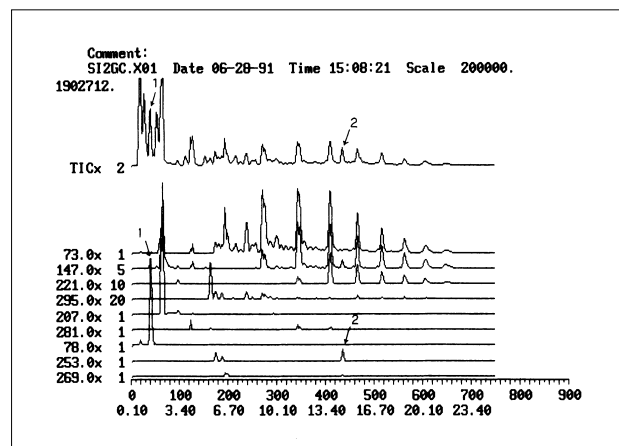
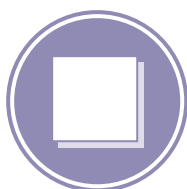


Fig. 3.16.4 TG-GCMS of septum S2



3.17 Analysis of Mending Tape - GCMS

■Explanation

Mending tape is comprised of polypropylene tape and acrylic adhesive. Analysis of samples with these two types of polymers is extremely difficult because both polymers' components are detected after thermal decomposition at 500 °C. To overcome this, and make analysis easy, thermal decomposition is performed at 350 °C where polypropylene remains intact but the acrylic adhesive decomposes and then the sample is thermally decomposed at 450 °C to produce just a thermal decomposition chromatogram of polypropylene.

■Analytical Conditions

Instrument	: GCMS-QP5000 PYR-4A
Column	: DB-1 0.25mm × 30m df 0.25 μm
Col.Temp.	: 50 °C (1min)-300 °C (10 °C/min)
Inj.Temp.	: 300 °C
I/F Temp.	: 320 °C
Carrier Gas	: 100kPa (1min)-150kPa (2kPa/min)- 250kPa (5kPa/min)
Split Ratio	: 1 : 10

References

Application News No. M174

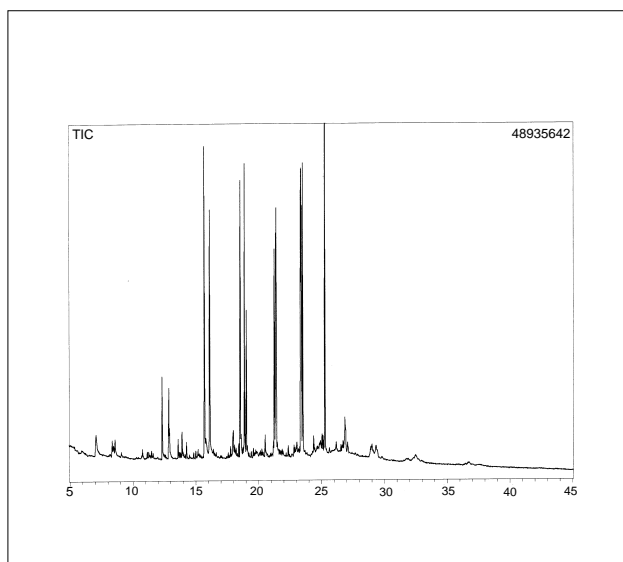


Fig. 3.17.1 Mending tape TIC (thermal decomposition temperature: 350 °C)

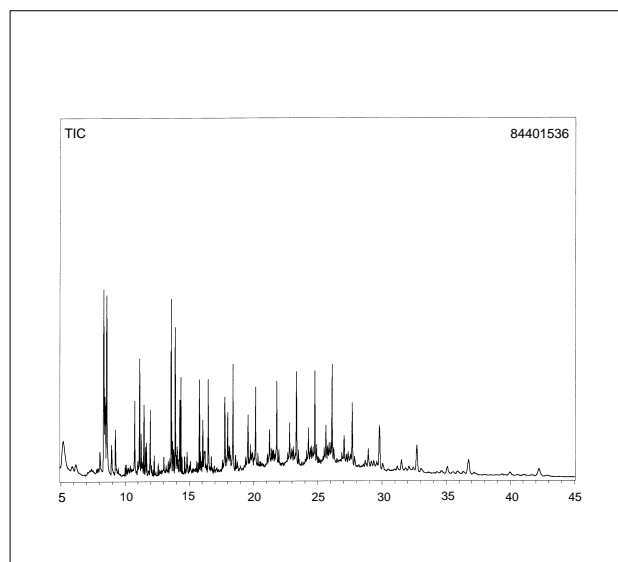


Fig. 3.17.2 Mending tape TIC (thermal decomposition temperature: 350 °C to 450 °C)



4. Environment

4.1 Water Analysis Using the Colorimetric Method - UV

■ Explanation

One of the most widely used applications of the spectrophotometer is water analysis. The UVmini-1240 is provided with a dedicated program and reagents for 55 items in water analysis. This example shows comparisons with the JIS method for water hardness and COD. Introduced here is a separation quantifying method for Fe and Al using an oxine absorptiometry as an example of

colorimetric quantification using a spectrophotometer. This method is often used because it has comparatively high sensitivity and coloration is stable. The oxine forms complexes with the Fe and Al and the discrepancies absorption spectra in both are used to enable simultaneous quantitative analysis.

		Mineral Water A			Mineral Water B		
		Total hardness	Ca hardness	Mg hardness	Total hardness	Ca hardness	Mg hardness
UV + waterpac		51.8	25.0	26.8	34.0	28.1	5.9
JIS method	AA	47.3	24.2	23.1	35.3	27.5	7.8
	Titration						

		Tap Water			Wastewater
		Total hardness	Ca hardness	Mg hardness	CODMn
UV + waterpac		41.5	30.0	11.5	7.2
JIS method	AA	38.3	28.8	9.5	
	Titration				9.2

Table 1 Water analysis results

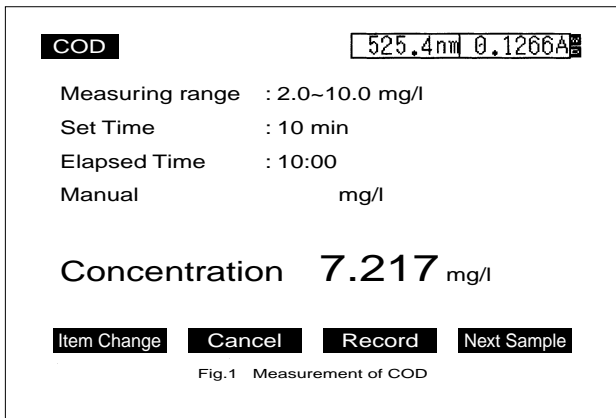


Fig. 4.1.1 Measuring results

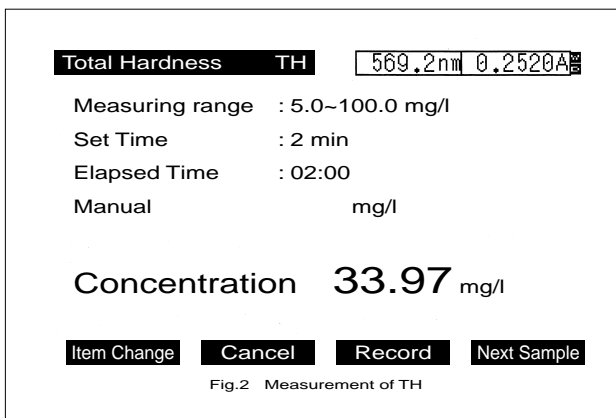


Fig. 4.1.2 Measuring results

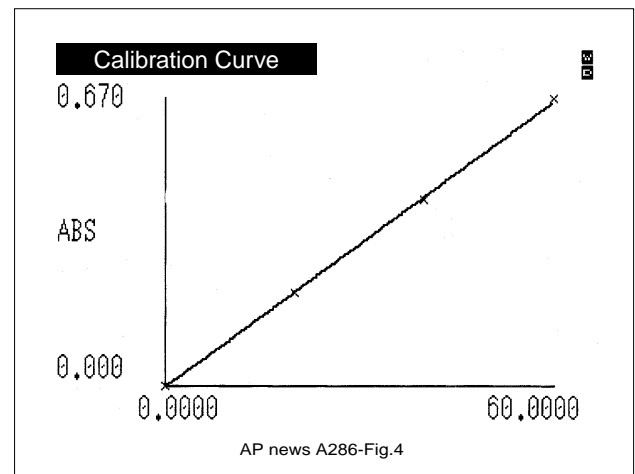


Fig. 4.1.3 Calibration curve

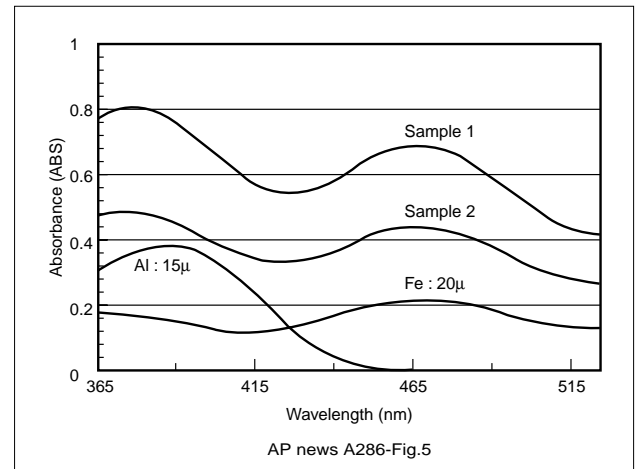


Fig. 4.1.4 Absorption spectra

	Concentration (μg)	
	Al	Fe
Sample 1	8.5	59.3
Sample 2	5.9	40.2

Table 2 Measuring results for Al and Fe



4.2 Analysis of Micro Elements in Ni-Base Solution Using Atomic Absorption Method - AA

■ Explanation

The following three officially adopted methods (JIS and USA Environment Protection Agency [EPA]) are used as background compensation methods for the atomic absorption method.

1. Deuterium lamp (D₂) method
2. Zeeman method
3. Self-reversal (SR) method

Table 4.2.1 shows the features of each method.

	D ₂ Lamp Method	SR Method	Zeeman Method
Wavelength range (nm)	190 - 430	190 - 900	190 - 900
Compensation for molecule absorption	Possible	Possible	Possible
Compensation for spectral interference	Sometimes impossible	Possible	Possible
Sensitivity	Good	Poor compared to D ₂ method	Poor compared to D ₂ method
Light loss	None	None	Some
Required instrument configuration	D ₂ Lamp	Lamp for SR light up	Polarizer, magnet
Optical axis adjustment	Necessary	Unnecessary	Unnecessary
Applicability of atomizer	Yes	Yes	Limited

Table 4.2.1 Comparison of background compensation methods

■ Measurement Method

Introduced here is an example of analysis of microelements in a solution with the main components of Ni and Fe in order to show the advantages of the SR method.

For analysis of Cd in Ni, the Cd analysis line is at 228.80nm with a background of 228.71nm existing due to Ni, so errors occur in analysis values because comprehensive compensation is not possible with the D₂ method. Likewise, for analysis of Sb in Fe, the Sb analysis line is at 217.55nm with a background of 217.58nm existing due to Ni, so errors occur in analysis values because comprehensive compensation is not possible with the D₂ method. In both of these cases, the use of the SR method enables highly accurate measuring.

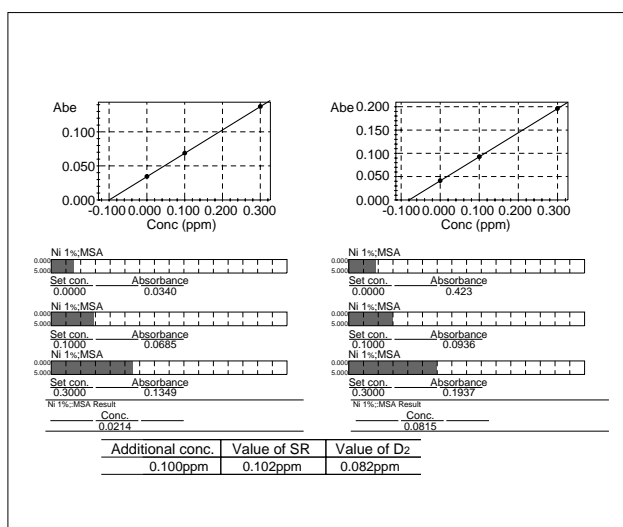


Fig. 4.2.1 Example of measuring of Cd in Ni 1% solution (left: SR method, right: D₂ method)

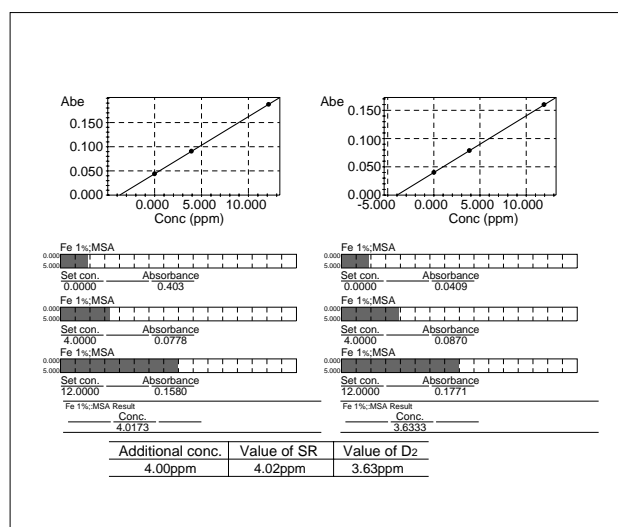


Fig. 4.2.2 Example of measuring of Sb in Fe 1% solution (left: SR method, right: D₂ method)

4.3 Measuring of As and Pb in Tap Water and River Water Using the Furnace Method - AA

■ Explanation

Liquids such as tap water and river water are not complicated and are often measured using the calibration curve method. But it is vital that advance consideration be given to interference. The possibility of interference is normally checked via an additional recovery experiment. Introduced here are As and Pb measuring examples.

■ As Heating Conditions

Furnace program:
(Tube type: Pyro-coated tube)

Stage	Temp (°C)	Time (sec)	Heat Mode	Ar Flow Rate (L/min)
1	150	20	RAMP	0.10
2	250	20	RAMP	0.10
3	900	10	RAMP	1.00
4	900	10	STEP	1.00
5	900	3	STEP	0.00
6	2000	3	STEP	0.00
7	2300	2	STEP	1.00

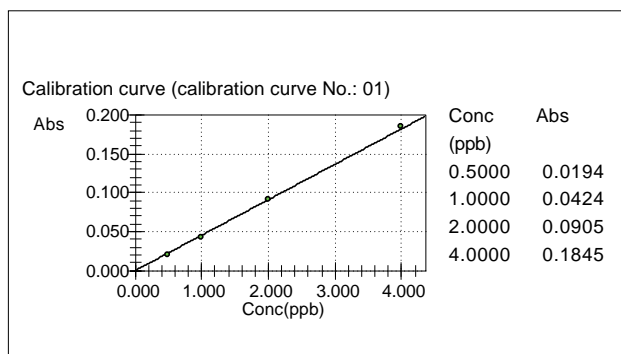


Fig. 4.3.1 As calibration curve

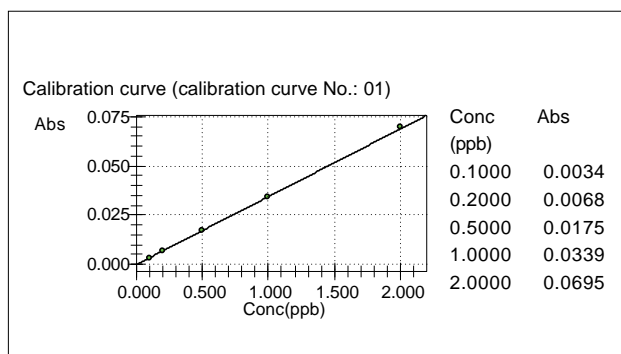


Fig. 4.3.3 Pb calibration curve

■ Pb Heating Conditions

Furnace Program:
(Tube type: Pyro-coated tube)

Stage	Temp (°C)	Time (sec)	Heat Mode	Ar Flow Rate (L/min)
1	150	20	RAMP	0.10
2	250	20	RAMP	0.10
3	800	10	RAMP	1.00
4	800	10	STEP	1.00
5	800	3	STEP	0.00
6	2000	3	STEP	0.00
7	2400	2	STEP	1.00

Pd is added as a matrix modifier in measuring for both As and Pb.

: Atomizing

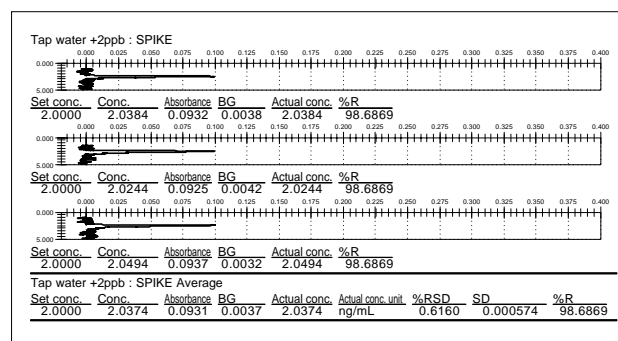


Fig. 4.3.2 Peak profile at time of As analysis

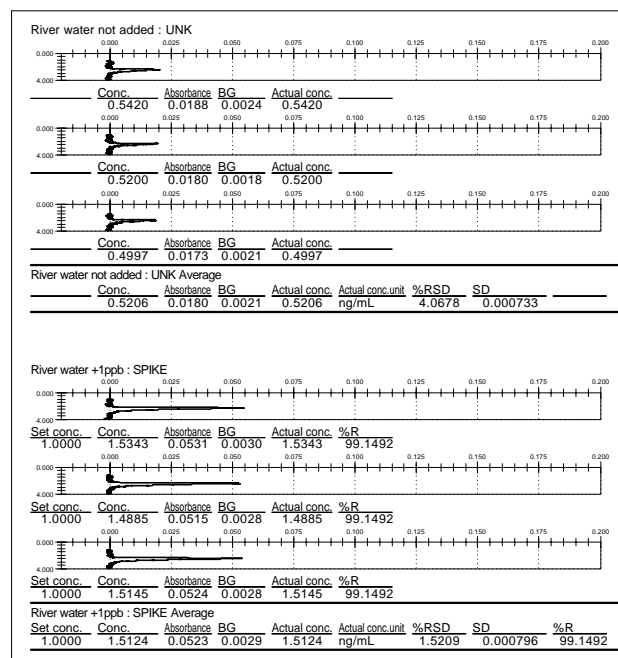


Fig. 4.3.4 Peak profile at time of Pb analysis



4.4 Measurement of As, Sb and Se Using the Hydride Vapor Generation Method - AA

■ Explanation

As, Sb and Se react with hydrogen when it is generated to form hydrides. As, Sb and Se can be measured to ppb level using an atomic absorption/flame emission spectrophotometer if a hydride generator is used. The measurement of As, Sb and Se using the hydride vapor generation method is widely adopted as the official method for testing drinking water.

■ Pretreatment

With JIS K0102:1998, a pretreatment like that shown in Table 4.4.1 is selected according to the type of element or sample concerned. Whatever method is selected, the aim is to create inorganic elements for measuring.

Normal Sample

	As	Sb	Se
Suitable amount of sample	0.1 ~ 1.0µg	0.1 ~ 0.5µg	0.05 ~ 0.3µg
Sulfuric acid (1+1)	1mL	1mL	1mL
Nitric acid	2mL	2mL	2mL
Potassium permanganate solution (3g/L)	Until solution colors	—	—
Heating method	Generate white fumes from nitric acid	White fumes begin to appear from nitric acid	Just prior to sample dry up

Samples Not Containing Organic Matter (Nitric Acid, Nitrite)

	As	Sb	Se
Suitable amount of sample	0.1 ~ 1.0µg	0.1 ~ 0.5µg	0.05 ~ 0.3µg
Hydrochloric acid	2mL (4mL for 1+1HCL)	5mL	Same amount as sample
Heating method	Several min without boiling	Several min without boiling	Approx. 10min at 90 to 100°C.

Samples Containing Large Amounts of Organic Matter

	As	Sb	Se
Suitable amount of sample	0.1 ~ 1.0µg	0.1 ~ 0.5µg	0.05 ~ 0.3µg
Sulfuric acid (1+1)	1mL	1mL	1mL
Nitric acid	2mL	2mL	2mL
Perchloric acid	3mL	3mL	3mL
Heating method	Generate white fumes	Generate white fumes	Generate white fumes

Table 4.4.1 Individual pretreatment for elements and samples

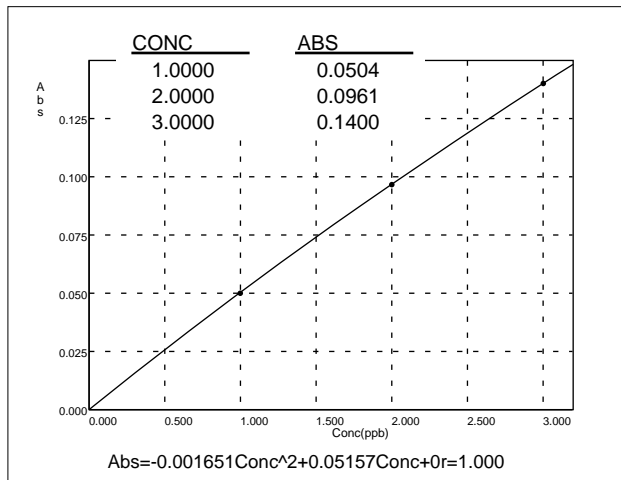


Fig. 4.4.1 Typical As calibration curve using HVG-1

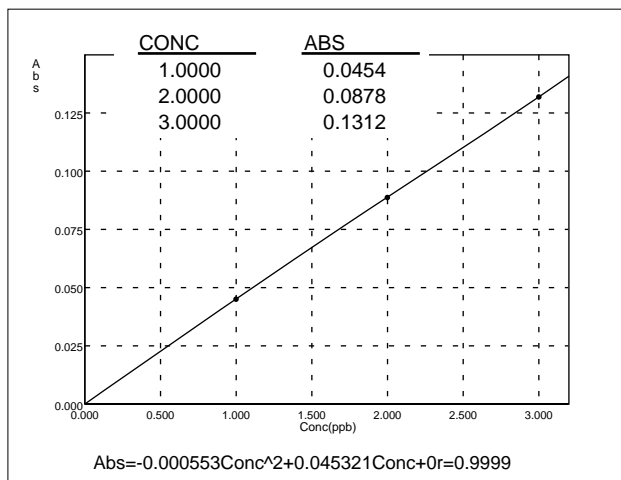


Fig. 4.4.2 Typical Sb calibration curve using HVG-1

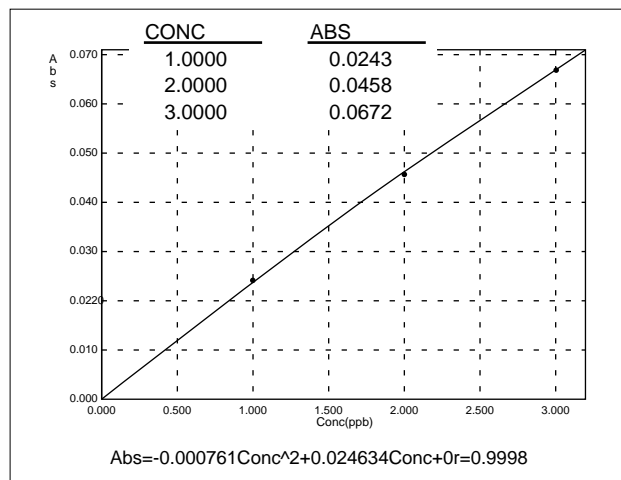


Fig. 4.4.3 Typical Se calibration curve using HVG-1

4.5 Analysis of Volatile Organic Compounds (VOCs) in Wastewater - GC

■ Explanation

GC/MS is mainly used to analyze volatile organic compounds in environment water; however, GC can be used if sample impurities are minimal. Headspace GC analysis can be used for ten items stipulated in the Japan's Waste Water regulation. Notably, GC-ECD can highly sensitively detect compounds with three or more chlorines. However, ECD cannot detect benzene, so FID must be used to analyze this. Introduced here is an example of headspace GC-ECD analysis of VOCs.

Instrument : GC-17A AFw + ECD-17
 Column : DB-VRX 0.45mm × 75m, df = 2.25 μm
 Col.Temp. : 35 °C (5min)-180 °C (5 °C/min)
 Inj.Temp. : 200 °C
 Det.Temp. : 210 °C (ECD)
 Carrier Gas : He (6 mL/min)
 Injection : Direct Injection

■ Pretreatment

10mL of wastewater and 3g of NaCl are enclosed in a headspace vial, warmed for 1hour at 50 °C and 0.2mL of headspace gas injected.

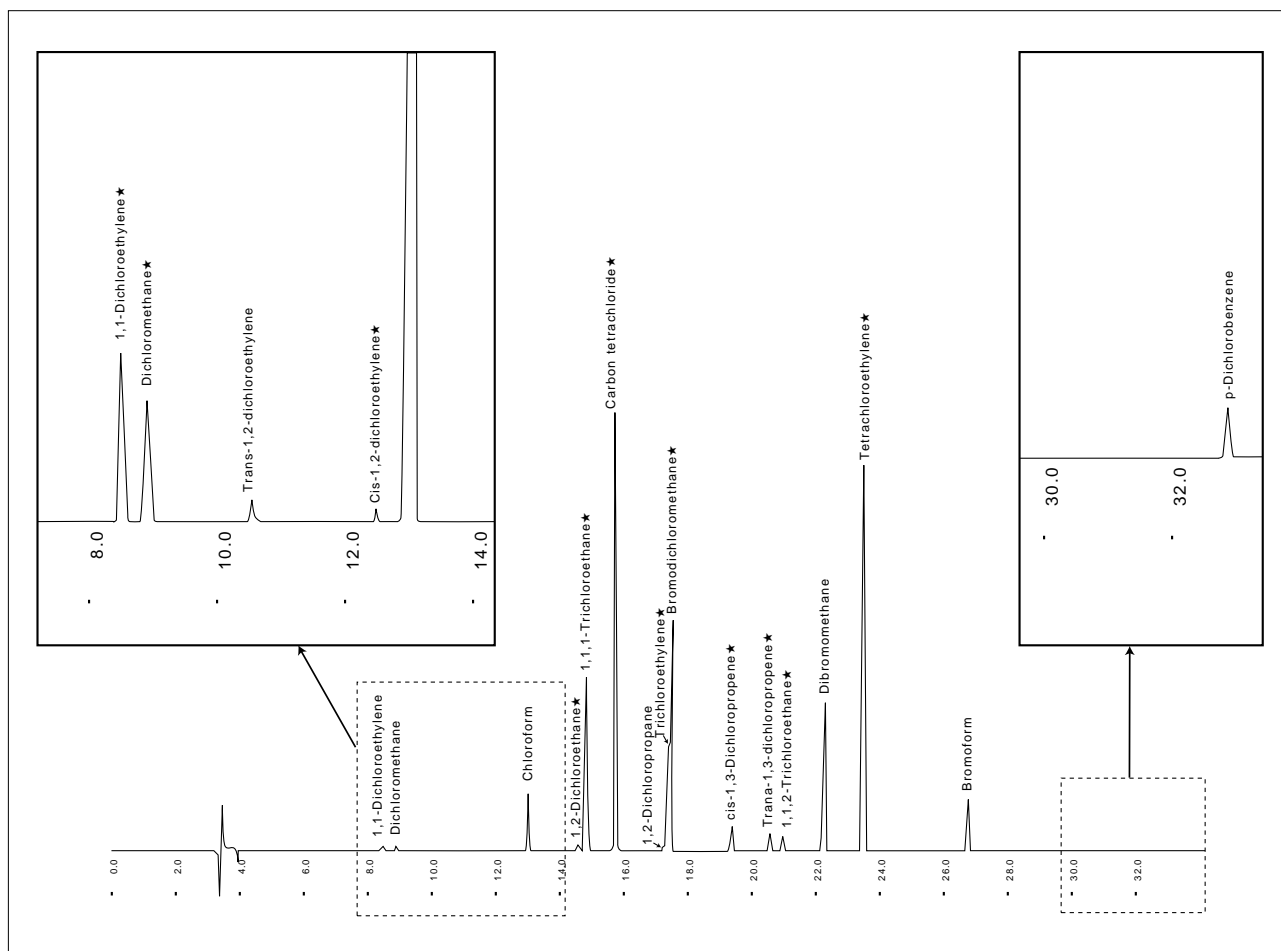


Fig. 4.5.1 Analysis example of environment water with added VOCs using headspace GC-ECD (★ denotes regulated item in Japan's Effluent Standard)



4.6 Headspace Analysis of VOCs in Wastewater - GCMS

■Explanation

The Wastewater Standard was introduced in 1994 in Japan. The standard includes 11 items for VOCs to be measured using the purge & trap method, the headspace method and the solvent extraction method.

The headspace method is particularly effective for measuring effluent VOCs because it is an easy method, with good reproducibility, minimal carryover and it is suitable for continuous measuring if an autosampler is used. Introduced here is analysis of a sample containing all 23 components regulated by the Water Works Law (all items of the Effluent Standard are included in this law).

Instrument : GCMS-QP5000 HS-40
Column : DB-624 0.32mm × 60m df 1.8 μm
Col.Temp. : 40 °C (1min)-200 °C (10 °C/min)
I/F Temp. : 230 °C
Carrier Gas : 100kPa
Sample Temp. : 60 °C
Condition Time : 30 min

References

Application News No. M170

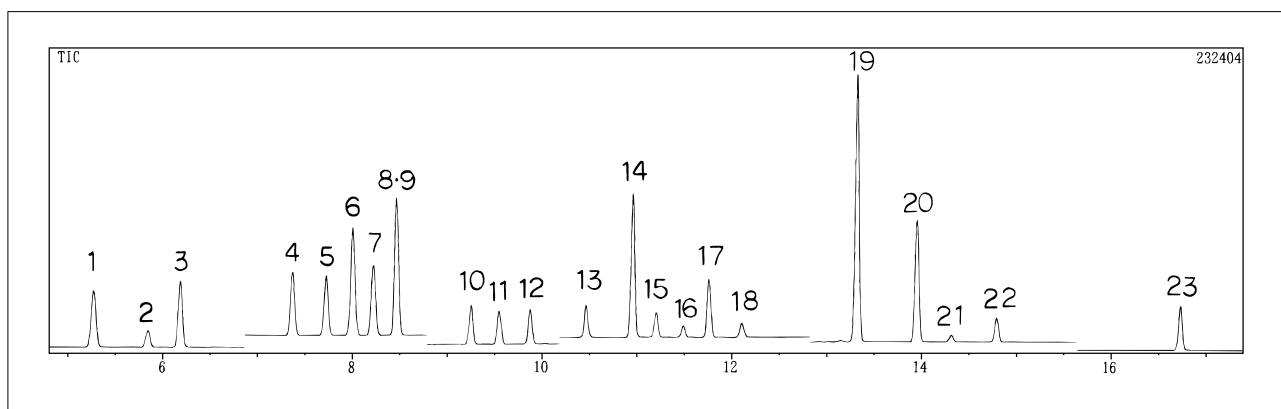


Fig. 4.6.1 TIC of 20ppb standard samples

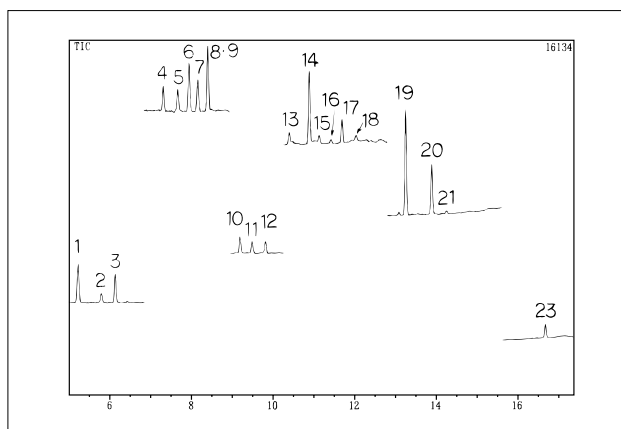


Fig. 4.6.2 SIM of 2ppb standard sample

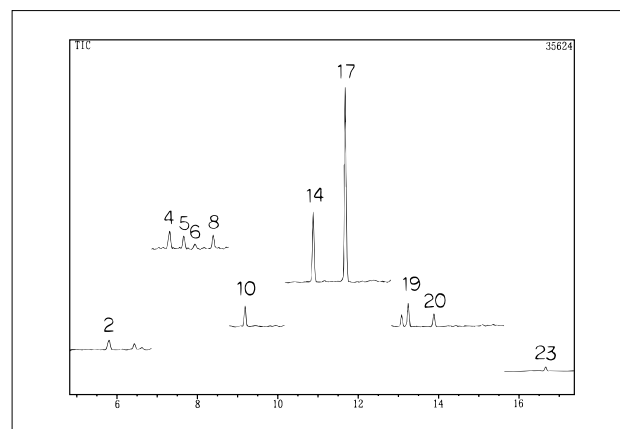


Fig. 4.6.3 Analysis example of wastewater

- 1,1-Dichloroethylene (0.2mg/L)
 - Dichloromethane (0.2mg/L)
 - Trans-1,2-dichloroethylene
 - Cis-1,2-dichloroethylene (0.4mg/L)
 - Chloroform
 - 1,1,1-Trichloroethane (0.3mg/L)
 - Carbon tetrachloride (0.02mg/L)
 - Benzene (0.1mg/L)
 - 1,2-Dichloroethane (0.04mg/L)
 10. Trichloroethylene (0.3mg/L)
 - 1,2-Dichloropropane
 12. Bromodichloromethane
 13. Cis-1,3-dichloropropane (0.02mg/L)
 14. Toluene
 15. Trans-1,3-dichloropropane
 16. 1,1,2-Trichloroethylene (0.06mg/L)
 17. Tetrachloroethylene (0.1mg/L)
 18. Dibromochloromethane
 19. m,p-Xylene
 20. o-Xylene
 21. Bromoform
 22. 1-Bromo-4-fluorobenzene (IS)
 23. 1,4-Dichlorobenzene
- Values given in parenthesis () are reference values in items of Wastewater standard.

4.7 Measurement of Inorganic Ions in Wastewater - IC

■ Measurement Method

The environmental impact of wastewater can at times be a major problem. Figs 4.7.1 and 4.7.2 show examples of analysis on inorganic anions and univalent cations in wastewater.

■ Analytical Conditions

(Inorganic anions of Fig. 4.7.1)

Column : Shim-pack IC-A1
(100 mm × 4.6 mm i.d.)
Mobile Phase : 2.5mM Phthalic acid
2.4mM Tris (hydroxymethyl)-
aminomethane
Flow Rate : 1.5 mL/min
Temperature : 40 °C
Detection : Conductivity Detector

■ Peak Components (Inorganic anions of Fig. 4.7.1)

- 1 PO_4^{3-}
- 2 Cl^-
- 3 NO_3^-
- 4 SO_4^{2-}

■ Analytical Conditions

(Univalent cations of Fig. 4.7.2)

Column : Shim-pack IC-C1
(150 mm × 5.0 mm i.d.)
Mobile Phase : 5.0mM Nitric acid
Flow Rate : 1.5 mL/min
Temperature : 40 °C
Detection : Conductivity Detector

■ Peak Components (Univalent cations of Fig. 4.7.2)

- 1 Na^+
- 2 NH_4^+
- 3 K^+

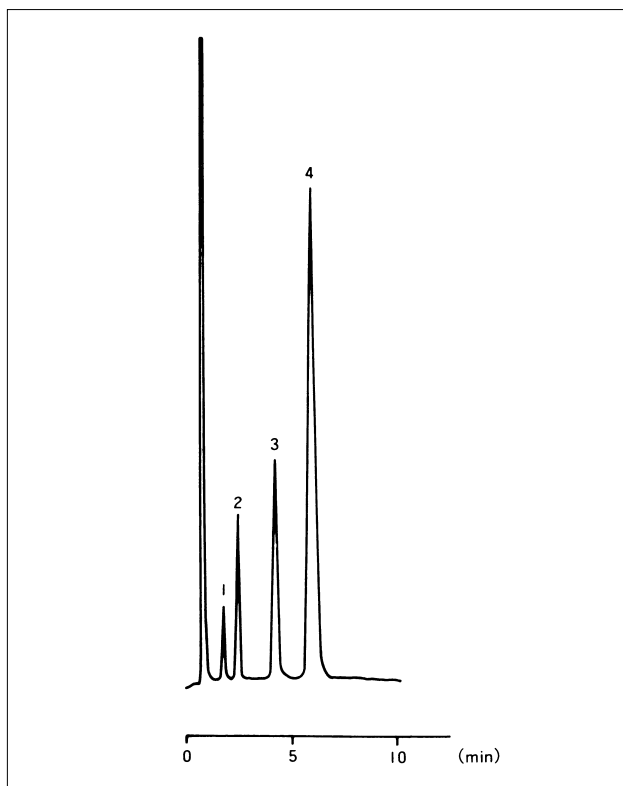


Fig. 4.7.1 (a)

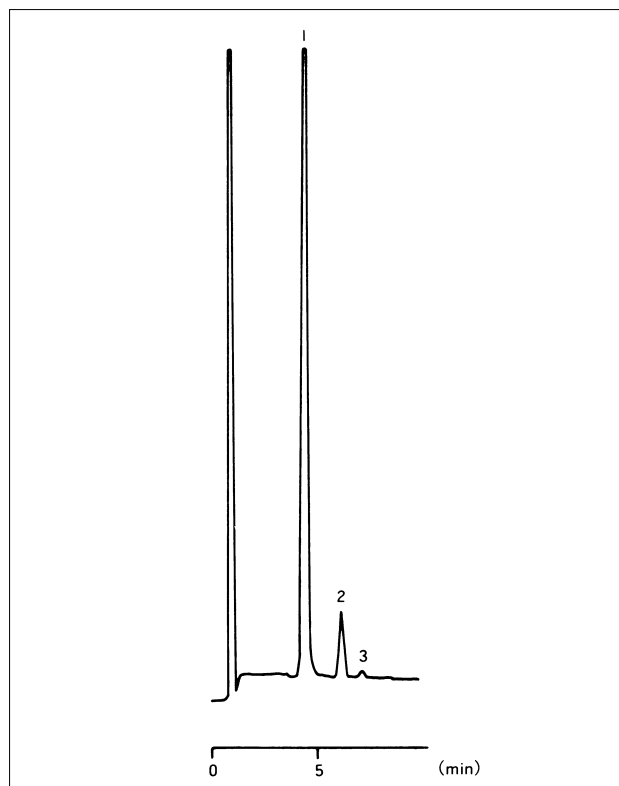


Fig. 4.7.2 (b)



4.8 Analysis of Wastewater (1) - ICP

■Explanation

Factory wastewater was analyzed using ICPS-7500. Figs 4.8.1 and 4.8.2 show spectral line profiles and semi-quantitative values occurring in qualitative analysis. Table 4.8.1 shows quantitative analysis results, Fig. 4.8.3 shows spectral line profiles occurring in quantitative analysis, and Figs. 4.8.4 and 4.8.5 show spectral line profiles and calibration curves for As and Se when a hydride vapor generator is used.

■Sample

Wastewater

■Pretreatment

Filter sample through 5C filter. Add 2mL of nitric acid to 50mL of filtrate and heat on hotplate (boil for approximately 2hrs). After cooling, dilute to 50mL with purified water and use sample.

■Analytical Conditions

- Instrument : ICPS-7500
- High-frequency Output : 1.2kW
- Cooling Gas Flow Rate : 14L/min
- Plasma Gas Flow Rate : 1.2L/min
- Carrier Gas Flow Rate : 0.7L/min
- Sample Induction : Coaxial nebulizer
Hydride Vapor Generator
HVG-1
- Sample Intake Rate : 0.6mL/min coaxial
3.5mL/min hydride
- Chamber : Cyclone chamber
- Plasma Torch : Standard torch
- Observation Method : Axial direction

Table 4.8.1 Quantitative analysis results for wastewater (unit:µg/mL)

Element	Quantifying Value
B	8.2
Cr	0.020
Mn	0.074
Fe	0.65
Ni	0.229
Cu	0.9
Zn	0.06
*As	0.0008
*Se	0.0003
Cd	0.005
Pb	0.020

* Hydride vapor generation method

4.8 Analysis of Wastewater (2) - ICP

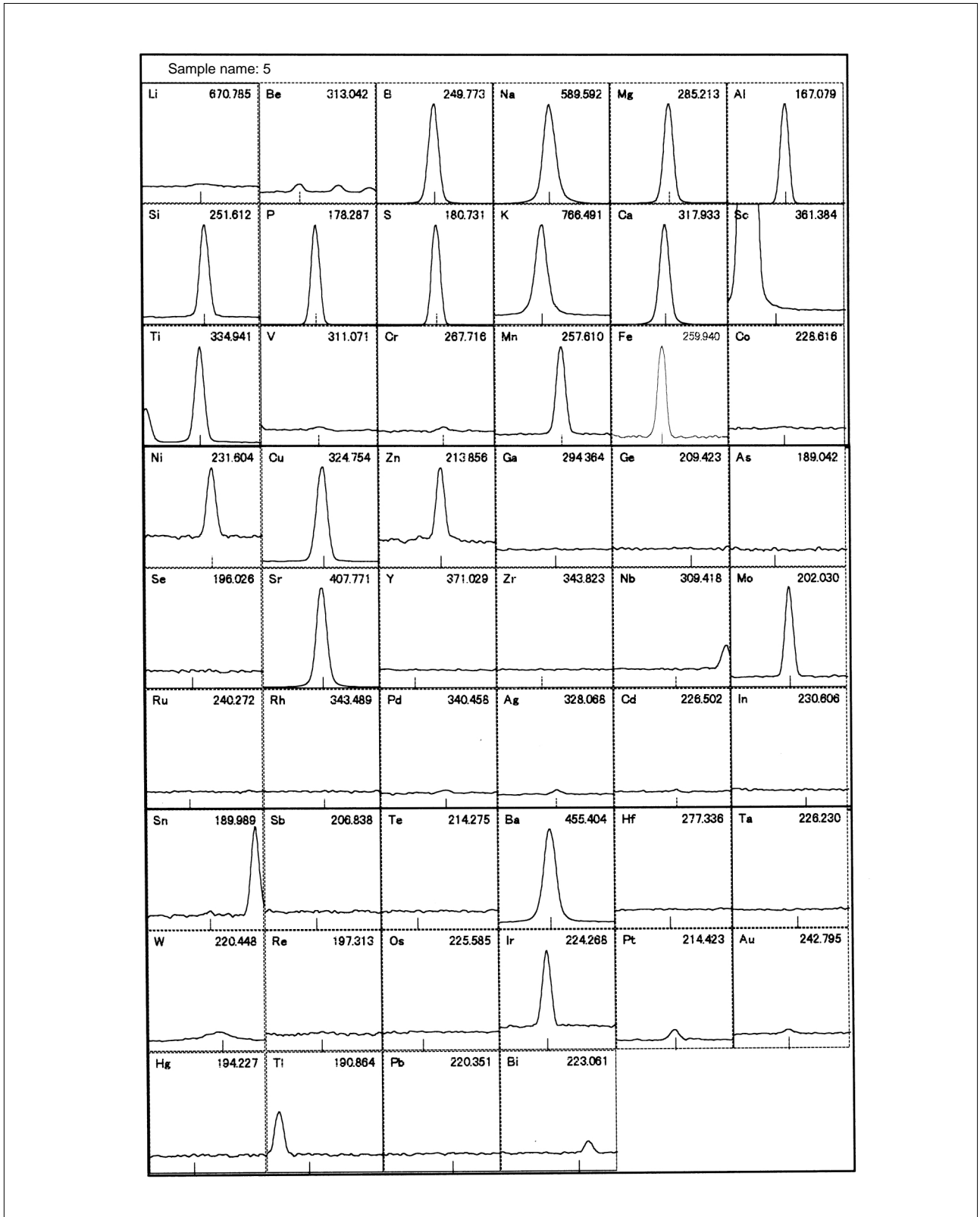


Fig. 4.8.1 Profile occurring in qualitative analysis (wastewater)



4.8 Analysis of Wastewater (3) - ICP

Sample name: Wastewater						
1000ppm or higher	Na 2700	S 2700				
10ppm or higher	B 11	Al 19	P 35	K 26	Ca 29	
1ppm or higher	Mg 4.7	Si 1.9	Cu 1.1			
0.10ppm or higher	Ti .69	Fe .58	Ni .33	Se .11	Sr .14	Mo .65
	In .11	Ba .11	W .34	Os .13	Ir .43	Pt .25
	Pb .11					
Less than 0.1ppm	Li .030	V .021	Cr .025	Mn .088	Co .010	Zn .074
	Ga .050	Ge .029	As .063	Y .0006	Ru .023	Rh .085
	Pd .084	Ag .030	Sn .092	Sb .034	Te .030	Ta .023
	Re .013	Au .042	Hg .016	Tl .044	Bi .031	
Detection not possible	Be .0023	Sc .0039	Zr .0038	Nb .0075	Cd .0078	Hf .0092

Fig. 4.8.2 Semi-quantitative value occurring in qualitative analysis of wastewater

4.8 Analysis of Wastewater (4) - ICP

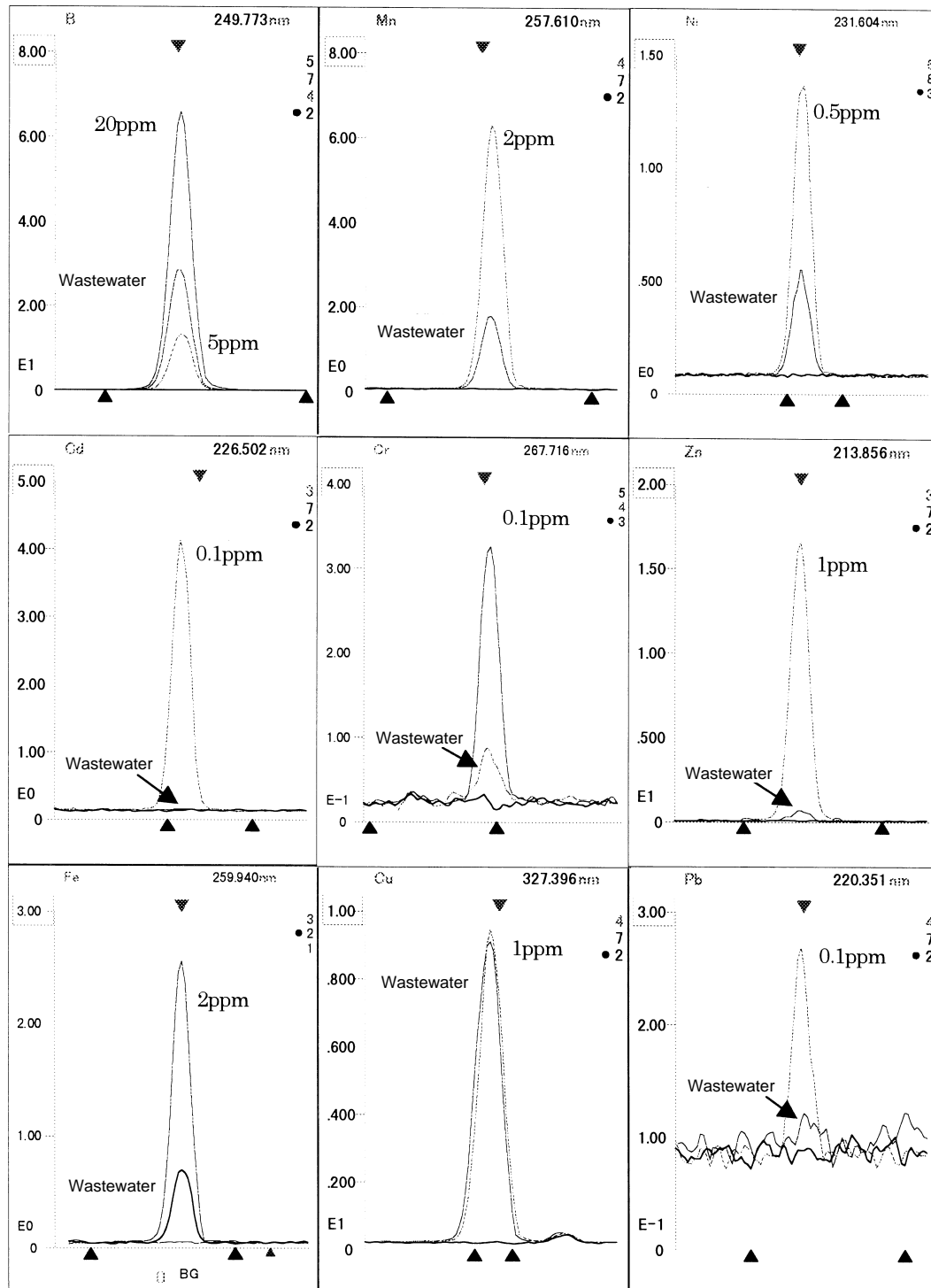


Fig. 4.8.3 Profile occurring in qualitative analysis (wastewater)



4.8 Analysis of Wastewater (5) - ICP

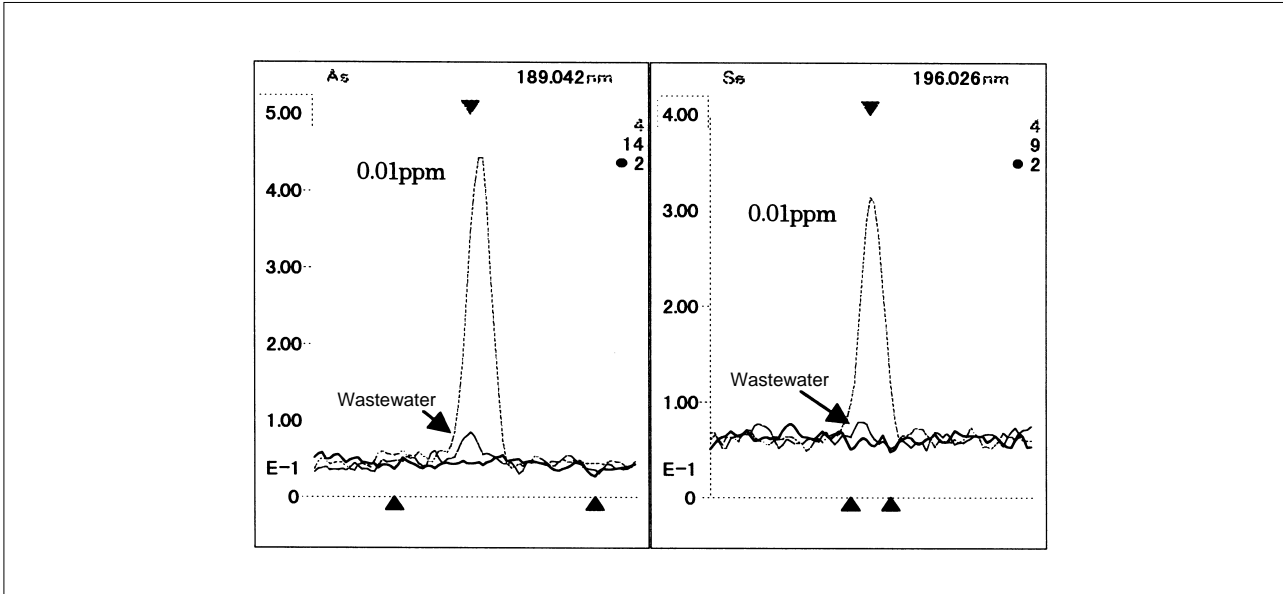


Fig. 4.8.4 As and Se profiles (hydride vapor generation method)

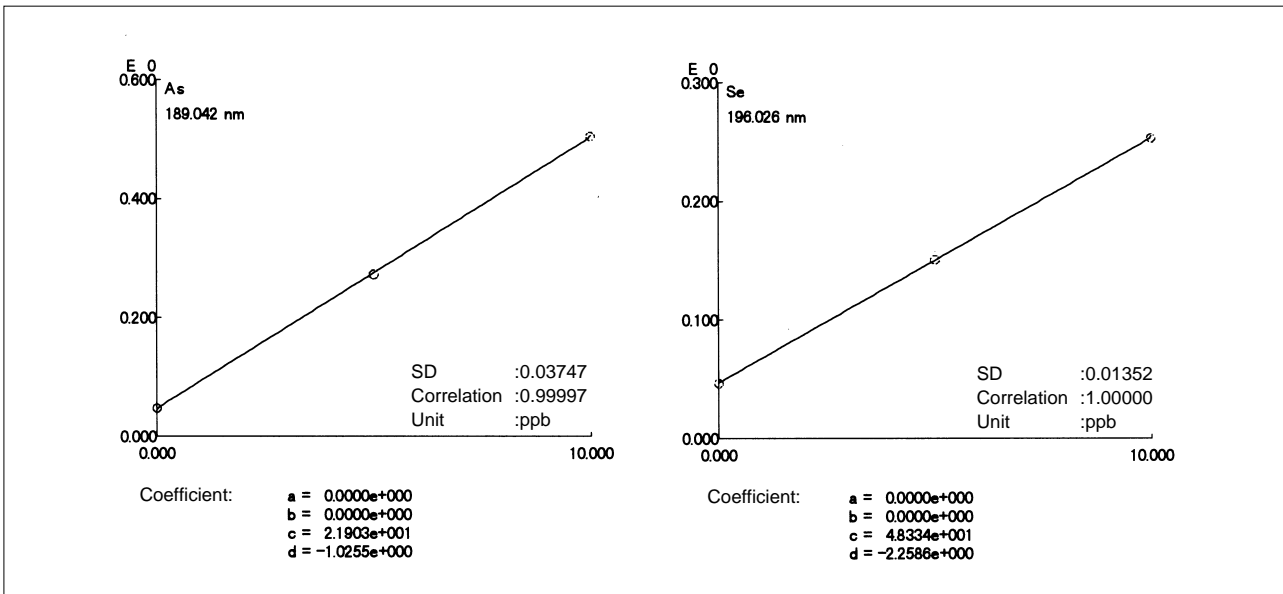


Fig. 4.8.5 As and Se calibration curve (hydride vapor generation method)

4.9 Analysis of Soil (1) - ICP-MS

Soil samples consist of extremely complicated coexisting substances that are highly concentrated, which normally makes the measurement of microelements extremely difficult. Analysis requires a highly sensitive device that is only minimally affected by coexisting substances. Introduced here is analysis of standard substances in soil using the ICPM-8500.

■ Sample

Standard soil sample (Japanese Society of Soil Science and Plant Nutrition): NDG-2 (field core soil), NDG-7,8 (paddy field soil)

■ Pretreatment: Sealed Pressure Decomposition

0.5g of standard soil sample and 5ml of highly pure nitric acid are enclosed in the pressurized decomposition container (made of Teflon) and warmed for 3hrs at 170 deg. C.. After cooling, an internal standard element is added and the sample diluted to 100ml with ultrapure water. This is filtered through a 5B filter and the filtrate diluted five times with ultrapure water to make the analysis sample.

■ Analysis Sample Provision

Analysis sample provided by the soil science research lab of Tokyo University of Agriculture

References

- Environment Agency Bulletins No. 46th (Soil Environment Standard)
- March 8, 1993 public notification of partial amendment to enforcement ordinance for Water Pollution Control Law
- JIS K0102-1998 (factory effluent testing method)
- EPA Method 200.8 Ver. 5.4

■ Calibration Curve Sample

Standard liquid (1000ppm) for atomic absorption analysis mixed into soil sample. This is then diluted appropriately using ultrapure water and 50ppb of internal standard element and 1% of nitric acid added.

■ Instrument & Conditions

Table 4.9.1 Analysis conditions

Instrument	: ICPM-8500
Plasma Unit	
High-frequency Output	: 1.2kW
Coolant Gas Flow Rate (Ar)	: 7L/min
Plasma Gas Flow Rate (Ar)	: 1.5L/min
Carrier Gas Flow Rate (Ar)	: 0.62L/min
Sample loading Unit	
Nebulizer	: Concentric nebulizer
Sample Intake Rate	: 0.4mL/min
Chamber	: Cooling-type Scott chamber
Plasma Torch	: Triple-layered tubing mini torch
Sampling Depth	: 5mm
Sampling Interface Unit	: Made of copper

■ Analysis

This involved quantitative analysis using the calibration curve method.

■ Results

Table 4.9.2 shows the quantifying results. Measuring results are multiplied by a dilution factor of 1000 and show concentrations in the solid sample. Figs. 4.9.1 to 4.9.4 show the calibration curves.



4.9 Analysis of Soil (2) - ICP-MS

Element	Sample name		NDG-2		NDG-7		NDG-8	
	M/Z	INT	Guaranteed Value	Quantifying Value	Guaranteed Value	Quantifying Value	Guaranteed Value	Quantifying Value
As	75	Rh	14.0	10.6	68.0	66.5	47.6	45.8
Se	82	Rh		1.1		0.88		0.73
Mo	98	Rh		0.099		0.54		0.26
Cd	111	Rh	0.06	0.07	2.80	2.52	1.64	1.48
Hg	202	Ho		0.023		0.38		0.38
Pb	208	Ho	28.0	26.3	72.2	72.0	59.9	59.8

Table 4.9.2 Quantifying results for decomposed soil solution (unit: µg/g)

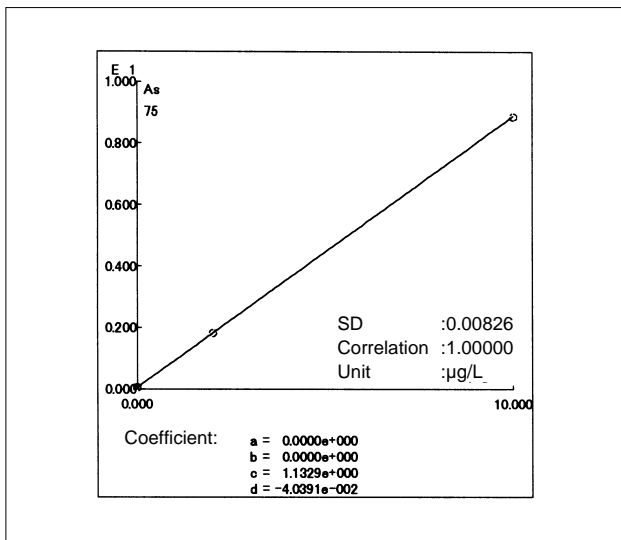


Fig. 4.9.1 As 75 calibration curve

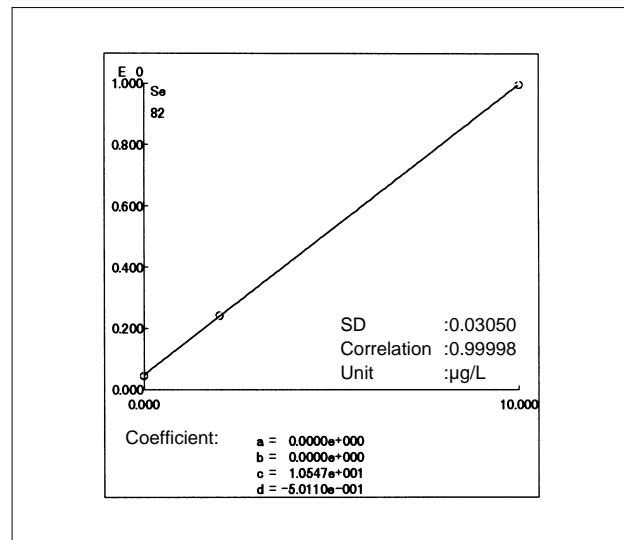


Fig. 4.9.2 Se 82 calibration curve

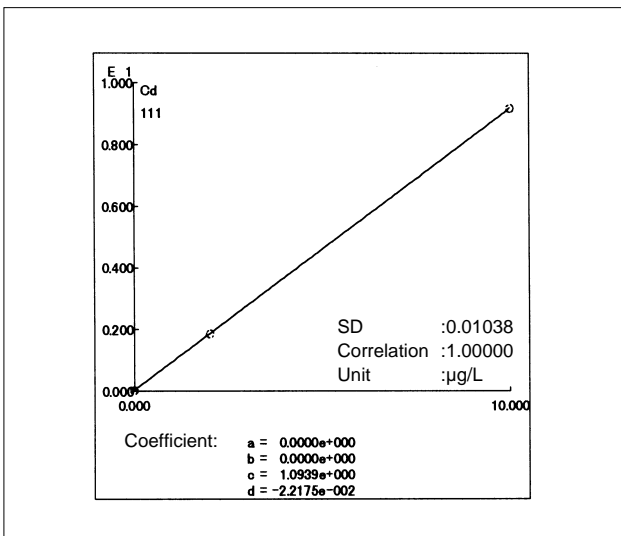


Fig. 4.9.3 Cd 111 calibration curve

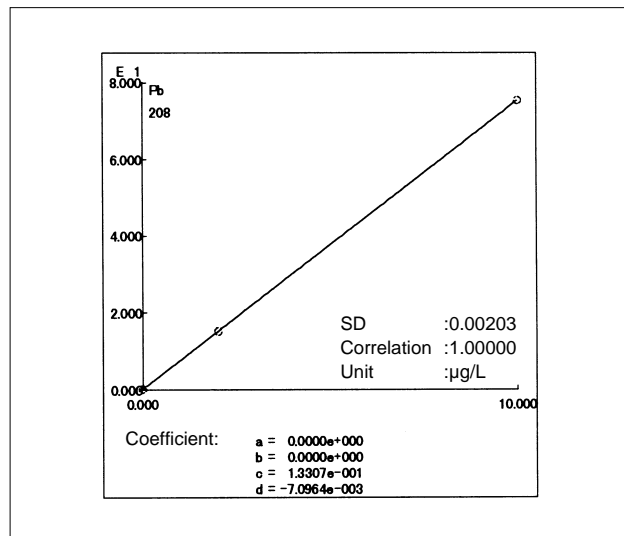


Fig. 4.9.4 Pb 208 calibration curve



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