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Analysis Guidebook

Chemical Industry Analyses

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1. Petroleum and Petroleum-based Chemicals

1.1 Analysis of all the constituents of gasoline - GC

•Explanation

With the abolition of the Japanese Provisional Measures Law on the Importation of Specific Refined Petroleum Products at the end of March 1996, the methanol, MTBE (methyl tertiary-butyl ether), benzene, and kerosene (equivalent to 14 times the volume % content of n-C13 and n-C14) present in gasoline is regulated. 4 types of GC analysis methods depending on the objective are specified in JIS K 2536-1996 (Petroleum Products - Testing Method of Constituents) for the analysis of these regulated compounds. Introduced here is the "Method for Analyzing All Constituents by GC".

An approximately 100m non-polar fused silica capillary column is used with a GC equipped with a low temperature accessory. Multistage high temperature analysis is carried out from 5°C to 200°C. The gasoline components are almost completely separated and identified. The areas of each component is multiplied by the relative sensitivity correction coefficients, and the quantities are determined by the corrected area percentage method.

References

JIS K 2536-1996 (Petroleum Products - Testing Method of Constituents)

•Pretreatment

None.

•Analytical Conditions

Model   : GC-17AAFw ver.3,CRG-17

Column   : DB-5 (2m × 0.25mm i.d. df= 1μm)
                 + GLC Petrostar (Rtx-1 PONA)
                 (100m × 0.25mm i.d. df=0.5μm)

Col.Temp.   : 5°C (10min)-5°C/min-50°C (43min)
                 -1.6°C /min-200°C (5min)

Inj.Temp.   : 250°C

Det.Temp.   : 250°C (w-FID)

Carrier Gas : He   280kPa

Injection   : Split   1 : 200

Inj.Vol.   : 0.2μL
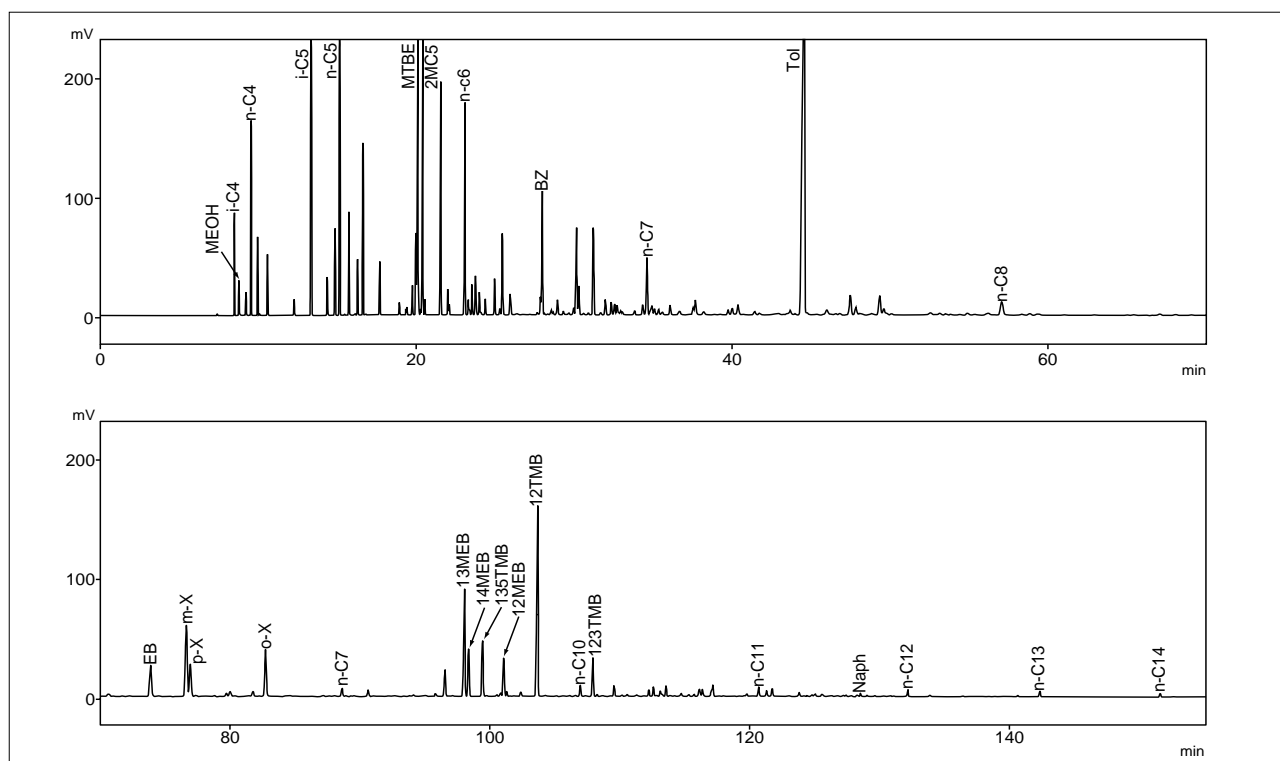
Fig.1.1.1 Gasoline with added methanol, MTBE, n-C13 and n-C14

1.2 Rapid analysis of regulated compounds in gasoline (1) - GC

•Explanation

A number of analytical methods other than the ones stipulated by the JIS are introduced here. The aforementioned "Method for Analyzing All Constituents by GC" takes approximately 150 minutes for completion of analysis. A rapid analytical method to measure chiefly the regulated components has been developed with the objective of shortening the time taken for analysis. Introduced here is the "Dual column GC analysis JPI-5S-61-99 No.2" registered as a Japan Petroleum Institute Standard in 1999.

2 different slightly polar capillary columns of 60m are connected to a split injector with a dual column adapter. The compounds of the injected sample are branched off into the 2 columns. The methanol, MTBE, and kerosene (equivalent to 14 times the volume % content of n-C13 and n-C14) are diverted into the first column, while the benzene is separated and quantified in the second column.

References

Incorporated association Japan Petroleum Institute Standard JPI-5S-61-99 No.2, Dual Column Gas Chromatograph Analysis

•Pretreatment

None.

•Analytical Conditions

Model	:	GC-17AAFwFw ver.3
		GC Gasoline Analysis System
		(Dual Column)
Column	:	No.1 60m × 0.25mm i.d. df = 1.4µm
		No.2 60m × 0.25mm i.d. df = 1.4µm
Col.Temp.	:	35°C (13min)-13°C/min-180 (14.5min)
		-15°C/min-255°C (3min)
Inj.Temp.	:	260°C
Det.Temp.	:	260°C (w-FID)
Carrier Gas	:	He 230kPa
Injection	:	Split 1 : 150
Inj.Vol.	:	0.5µL
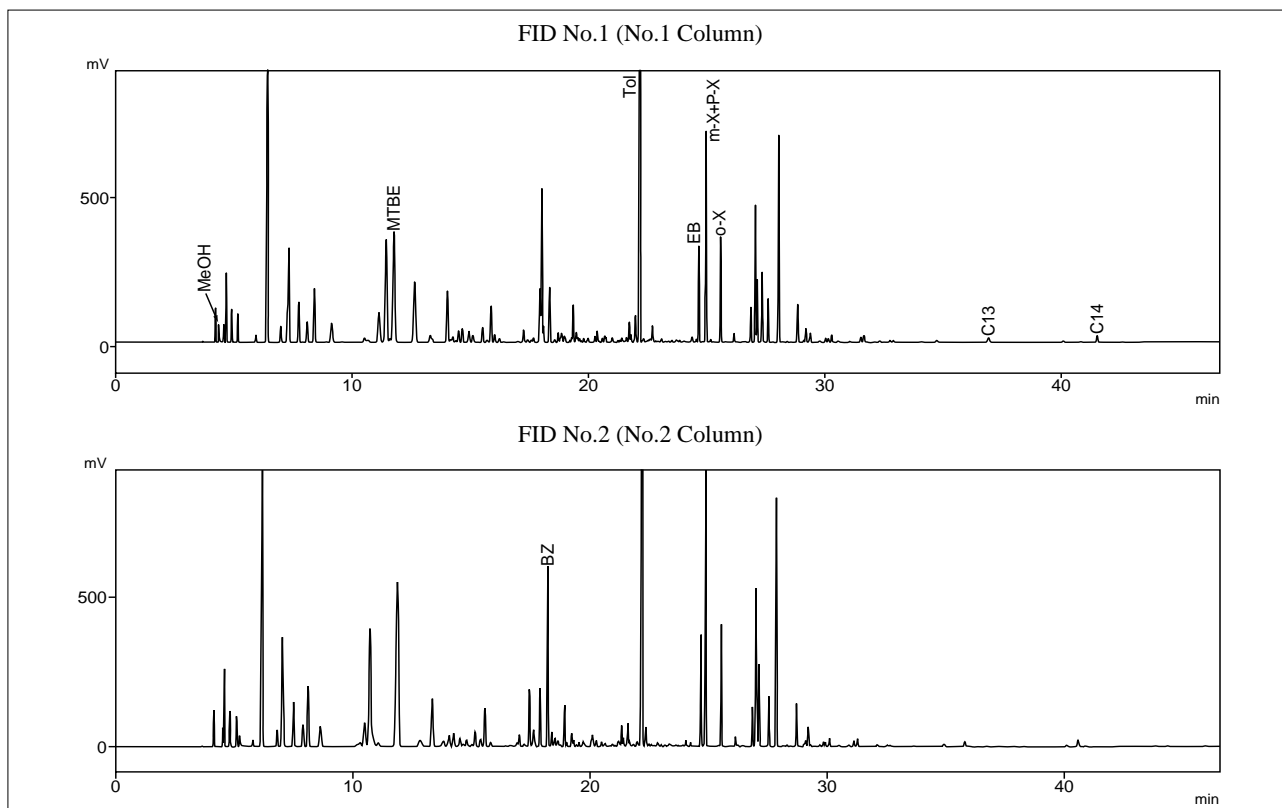
Fig.1.2.1 Gasoline with added methanol, MTBE, n-C13 and n-C14

1.2 Rapid analysis of regulated compounds in gasoline (2) - GC

•Explanation

Introduced here is a rapid analysis method to measure the regulated components of gasoline using a TCEP capillary column. This is the "Nisseki / aromatics testing method JPI-5S-61-99 No.1" registered as a Japan Petroleum Institute Standard in 1999.

The TCEP capillary column is used to elute hydrocarbons of a low molecular weight early on. The methanol, MTBE, and kerosene (equivalent to 14 times the volume % content of n-C13 and n-C14) are retained and separated. Their quantities are determined by the internal standard method.

References

Incorporated association Japan Petroleum Institute Standard JPI-5S-61-99 No.1, Nisseki / Aromatics Testing Method

•Pretreatment

"cis-decalin" is used as the substance for the internal standard.

0.4g of "cis-decalin" is weighed in a container with a hermetic seal. After 8mL of gasoline is added the substance is weighed and used as the sample.

•Analytical Conditions

Model   : GC-17AAFw ver.3
Column   : Chrompack TCEP
             (50m × 0.25mm i.d. df=0.4μm)
Col.Temp. : 35°C (6min)-2°C/min-90°C
             -5°C/min-125°C (3min)
Inj.Temp. : 250°C
Det.Temp. : 250°C (w-FID)
Carrier Gas : He   135kPa
Injection : Split   1 : 200
Inj.Vol.   : 0.3μL
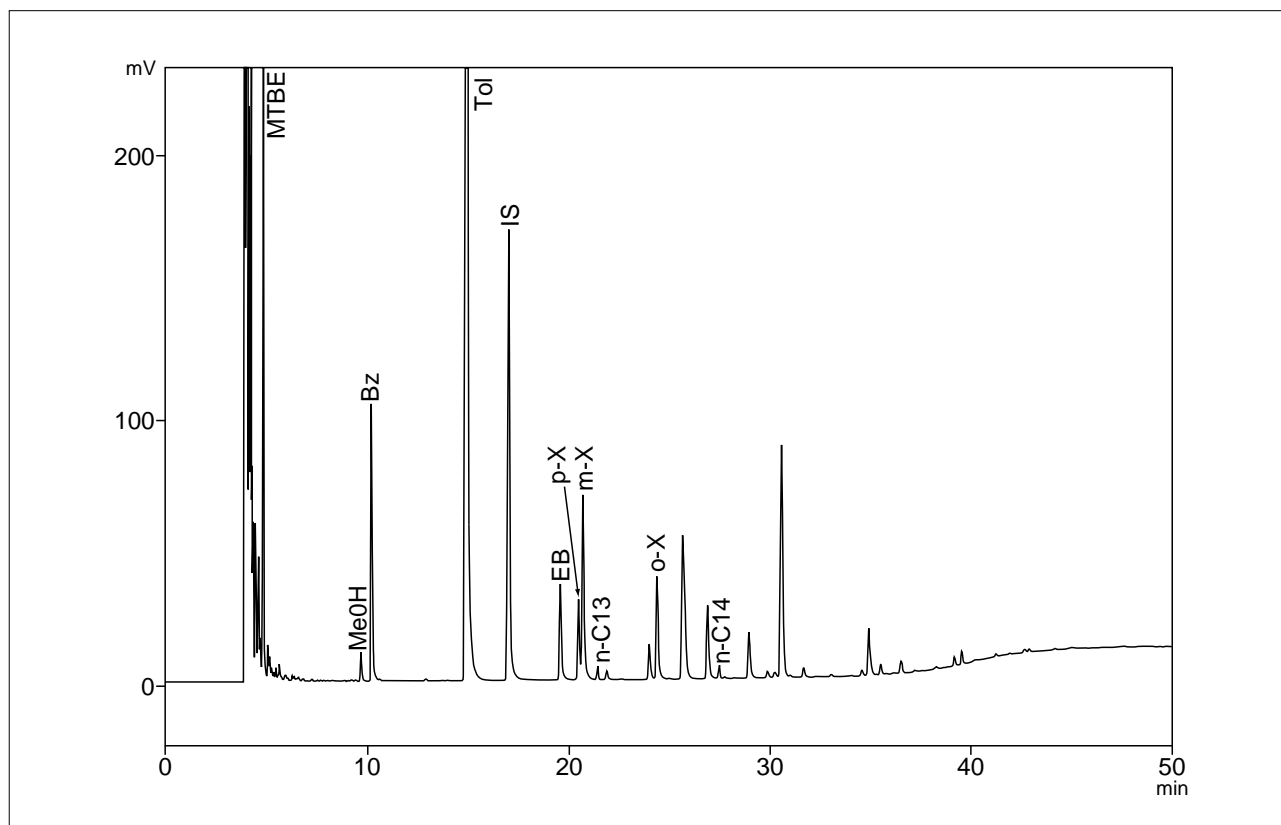
Fig. 1.2.2 Gasoline with added methanol, MTBE, n-C13 and n-C14

1.3 Analysis of kerosene and light oil - GC

•Explanation

Kerosene is a petroleum fraction with a boiling point range of approximately 180°C to 300°C. Light oil is a petroleum fraction with a boiling point range lying halfway between that of kerosene and crude oil. Like gasoline, an extremely large number of compounds are contained in both kerosene and light oil. Examples of analysis of kerosene and light oil are introduced here.
A 60m non-polar fused silica capillary column was used. Analysis was carried out by the split method.

•Pretreatment

None.

•Analytical Conditions

Model	:	GC-17AAFw ver.3
Column	:	DB-1 60m × 0.32mm i.d. df= 1.0µm
Col.Temp.	:	50°C-10°C/min-320°C (3min)
Inj.Temp.	:	300°C
Det.Temp.	:	330°C (w-FID)
Carrier Gas	:	He 30cm/sec at 50°C
Pressure Prog.	:	125kPa-2.5kPa/min-200kPa
Injection	:	Split 1 : 100
Inj.Vol.	:	0.2µL
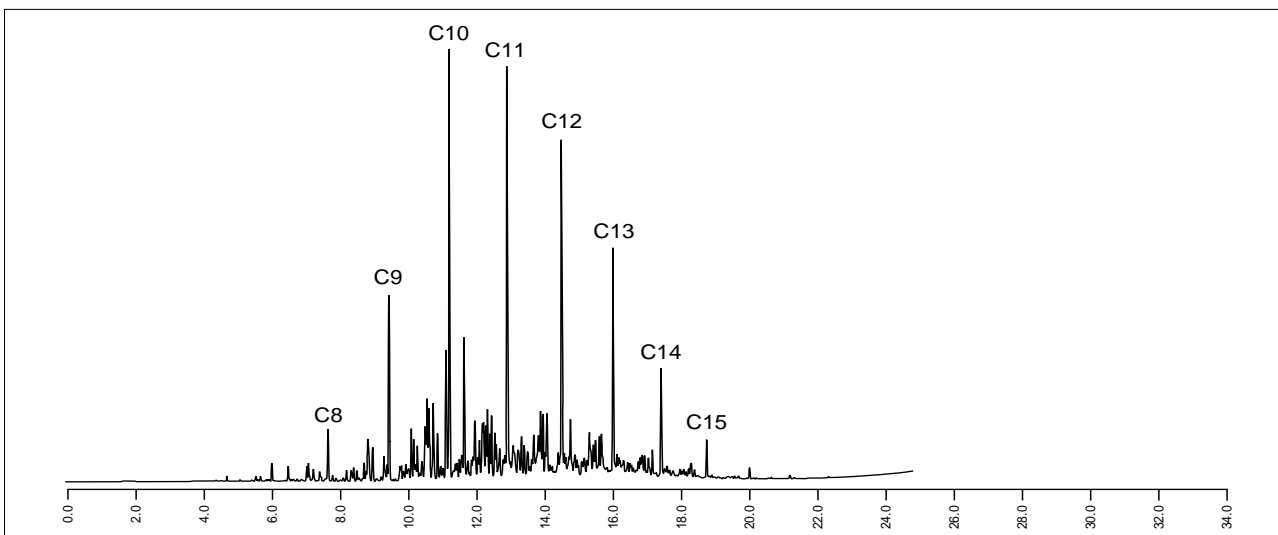
Fig. 1.3.1 Kerosene

Fig. 1.3.2 Light oil

4
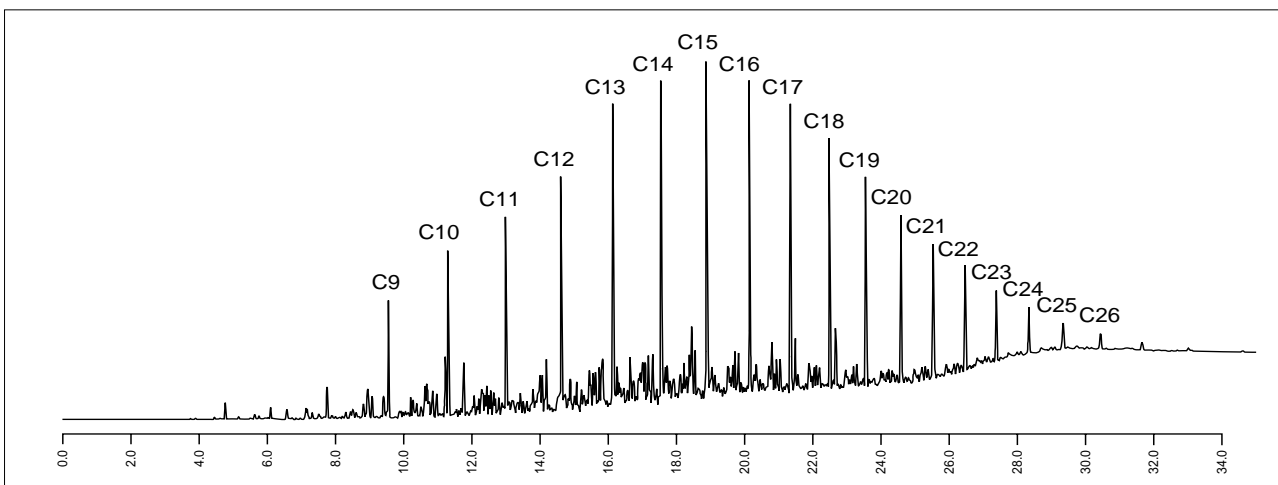
1.4 Distillation gas chromatography - GC

•Explanation

This is a technique which measures the boiling point distribution of petroleum fractions (boiling point range over approximately 55°C) etc. through gas chromatography. It is commonly called distillation gas chromatography as this is a method of testing that gives measurement results similar to the conventional distillation method.

Hydrocarbons are eluted in order of boiling points when a linear temperature analysis is carried out using a non-polar column. By analyzing a hydrocarbon mixture whose boiling point is already known, a calibration curve of the retention time and boiling point can be generated since the elution time is more or less directly proportional to the boiling point. If kerosene, light oils etc. are analyzed under the same conditions, the retention time can be converted into the boiling point.

Furthermore, the total area of the obtained chromatogram is divided into fixed time intervals, and the smaller areas within each time frame is calculated. The elution amount (%) is calculated by dividing the "sum of the smaller areas from the starting time to a particular time" by the "total area".

Introduced here is an example of analysis of kerosene by distillation gas chromatography.

•Pretreatment

None.

•Analytical Conditions

Model   : GC-17AAFw ver.3, WBI-17
Column   : CBP1 (12m × 0.53mm i.d. df= 5.0μm)
Col.Temp. : 35°C-10°C/min-215°C (2min)
Inj.Temp. : 250°C
Det.Temp. : 250°C (w-FID)
Carrier Gas : N_2 20mL/min
             40kPa-1.8kPa/min-72kPa
Injection : Direct Injection
Inj.Vol.   : 0.5μL

Conversion into the traditional method (ASTM D-86)

%OFF	°C	°F
Initial boiling point	149	300
10	167	332.5
20	177	350.9
30	185.5	366
50	203.5	398.1
70	223.5	434.4
80	235	454.7
90	247	476.9
95	256	492.5
End point	270.5	519.2

Results of quantitative calculations

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	4.012	7455615	11094			100	
		TOTAL	7455615	11094			100	

* * * Distillation properties * * *

Kerosene GC-No.3
Date   Time
Receipt No.   1   Sample No.1
CHROMATO No. 1:
DGC FILE   No. 1
Analytical parameter : Mode   @FILE1.1   3722

* *GC Data* *

%OFF	°C	°F	R t(min)
Initial boiling point	108.9	227.9	2.41
5	130	265.9	3.43
10	148.2	298.8	4.53
20	164.6	328.3	5.63
30	179	354.2	6.63
40	193.3	379.9	7.64
50	206	402.9	8.55
60	217.5	423.5	9.36
70	232.4	450.3	10.42
80	247	476.6	11.45
90	263.1	505.7	12.61
95	274.9	526.8	13.46
End point	298.5	569.2	15.17

DISTILLATION CURVE

D-86 ·······
GC-DATA ▬▬▬

Fig. 1.4.1 Distillation GC of kerosene

1.5 Analysis of impurities in DIBE - GC
(rapid analysis system by a GC equipped with a pre-cut injector)

•Explanation

With gas chromatography the duration of analysis can last a long time as it is necessary to wait for the elution of high boiling point components that may be unnecessary for identification and quantitation. In such, a GC system with a pre-column injector is used. Unnecessary high boiling point components are trapped in the pre-column and backflushed to shorten the analysis time.

Introduced here is an example of analysis of impurities in DIBE (Diisobutyl hexahydro phthalate) using a GC system with a pre-cut injector.

•Pretreatment

None.

•Analytical Conditions

Model	: GC-17AAFw ver.3 with Pre-cut GC System
Column	: DB-5 $30m \times 0.32mm$ i.d. df=$0.25\mu m$
Col.Temp.	: $60°C$ (0.2min)-$10°C$/min-$250°C$ (10min)
Inj.Temp.	: $250°C$
Det.Temp.	: $280°C$ (w-FID)
Carrier Gas	: He 30cm/sec
Injection	: Split 1 : 30
Inj.Vol.	: $1\mu L$
Precolumn	: OV-1 1.5% on Gaschrom Q 10cm
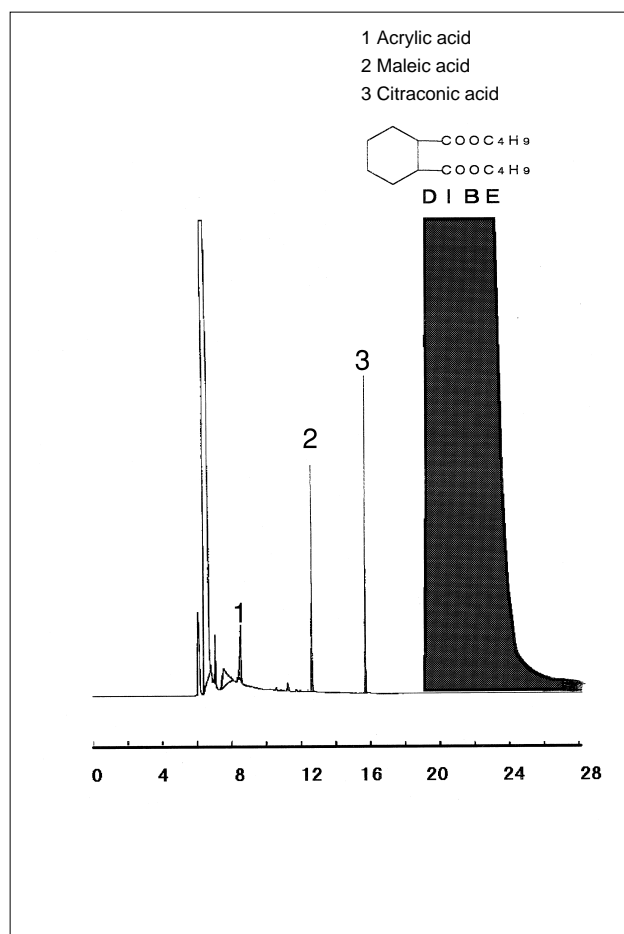
Fig. 1.5.1 Analysis of impurities within DIBE (without pre-cut)
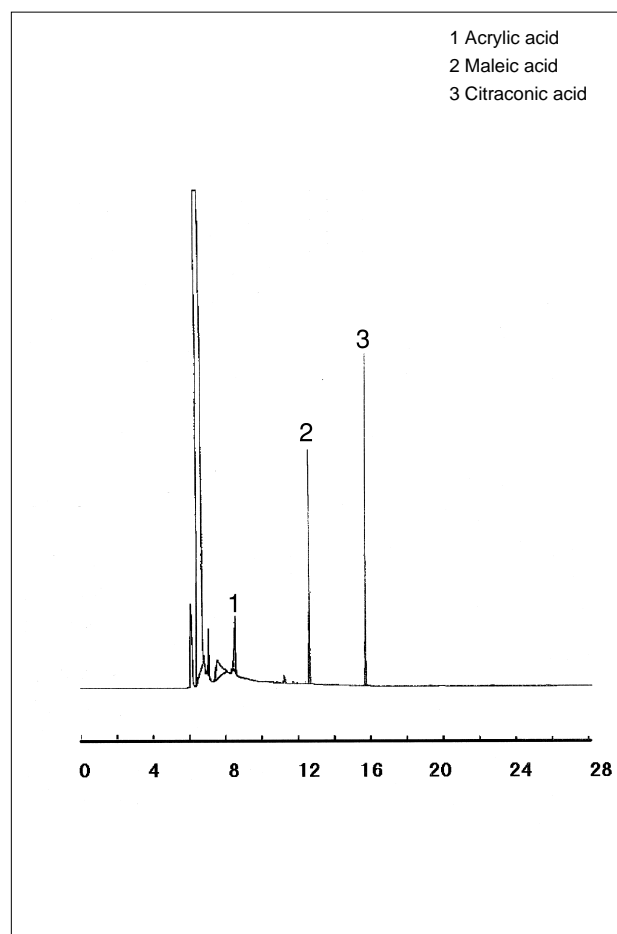
Fig. 1.5.2 Analysis of impurities within DIBE (with pre-cut)

1.6 Analysis of surfactants - LC

•Explanation

Shown in Fig. 1.6.1 is the GPC chromatogram of polyoxyethylene alkylether (POE), a surfactant. The additional mol number of the oxyethylene is 30. In addition, Fig. 1.6.2 shows polyoxyethylene phenyl ether separated by an alkyl chain by HPLC.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45μm).

•Analytical Conditions

Fig. 1.6.1

Model	: GPC
Column	: Shim-pack GPC-802 $\times$ 4
	: (Each 300mm $\times$ 8.0mm i.d.)
Mobile Phase	: Tetrahydrofuran (THF)
Flow Rate	: 1.0mL/min
Temperature	: 40°C
Detection	: Refractive Index Detector

Fig. 1.6.2

Model	: HPLC
Column	: Shim-pack CLC-ODS
	: (150mm $\times$ 6.0mm i.d.)
Mobile Phase	: Methanol/Water=4/1 (v/v)
Flow Rate	: 1.2mL/min
Temperature	: 60°C
Detection	: UV-VIS Detector 275nm

$$C_{22}H_{45}O \left[CH_2CH_2O \right]_n H$$
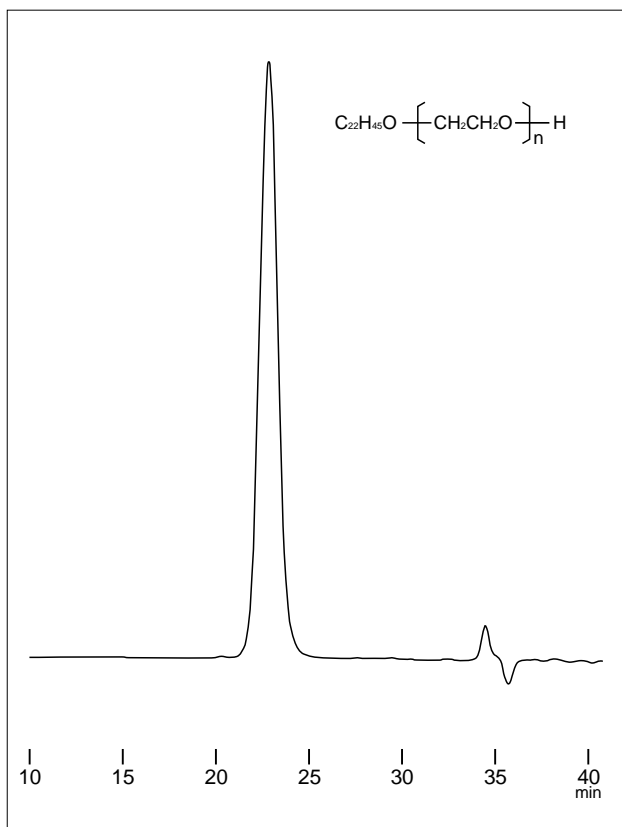
Fig. 1.6.1 Analysis of polyoxyethylene alkylether

$$R \bigcirc O \left[CH_2CH_2O \right]_n H$$
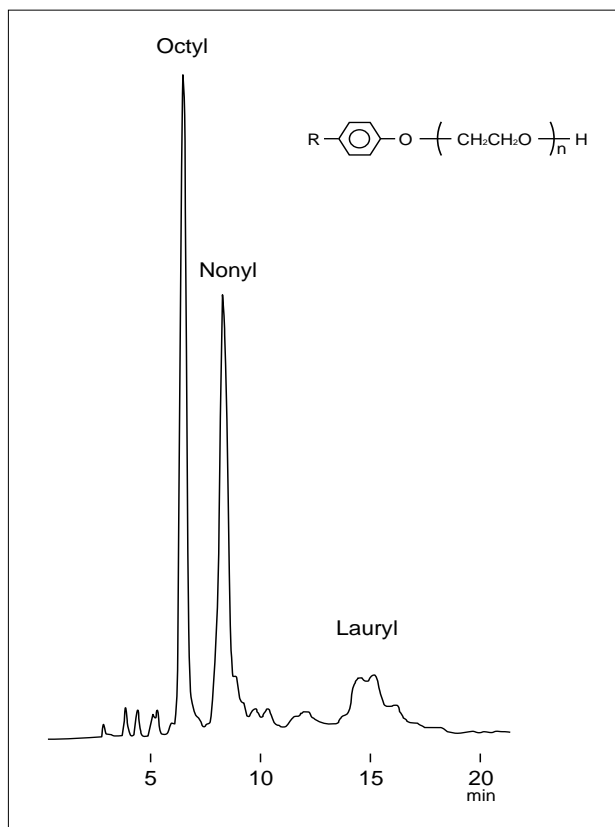
Fig. 1.6.2 Separation of polyoxyethylene phenyl ether by an alkyl chain

1.7 Analysis of gum substances in gasoline - LC
(Method to measure the gasoline oxidation product index by HPLC)

•Explanation
Among the ways of testing for existent gum in gasoline and aviation fuel, the National Petroleum Association has devised the "Measurement of Oxidation Products in Flammable Oils by the Liquid Chromatograph". Gasoline can be screened using this method. The traditional method is by the jet evaporation method stipulated in JIS K2261, but because of the hassle involved in solvent disposal, equipment, and measurement, a method utilizing a more convenient LC is accepted.

Shown in Fig. 1.7.1 is an example of measurement of the oxidation product index in gasoline, while Fig. 1.7.2 shows an analysis example of a standard item. By using the grouping processing function the oxidation product index is calculated automatically, making evaluation of the results easier.

•Pretreatment
Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions
Model   : HPLC
Column   : STR ODS- II (150mm × 4.6mm i.d.)
Mobile Phase : A ; Acetonitrile/Water=2/3 (v/v)
              : B ; Acetonitrile
Flow Rate   : 1.0mL/min
Temperature   : 40°C
Detection   : UV-VIS Detector 260nm

Gradient Program:

Time (min)	Function	Value
4.50	B.conc	0
4.51	B.conc	100
10.00	B.conc	100
18.00	B.conc	0
18.01	STOP	

•Method of calculating the oxidation product index
The oxidation product index is calculated in the following manner shown below.

Oxidation product index (%)=A/Bx100

A: The area of the chromatogram from [the retention time (minutes) of benzyl alcohol x 0.60] to the retention time (minutes) of methyl benzoate

B: The area of the chromatogram from [the retention time (minutes) of benzyl alcohol x 0.60] to [the retention time (minutes) of methyl benzoate x 3.10]
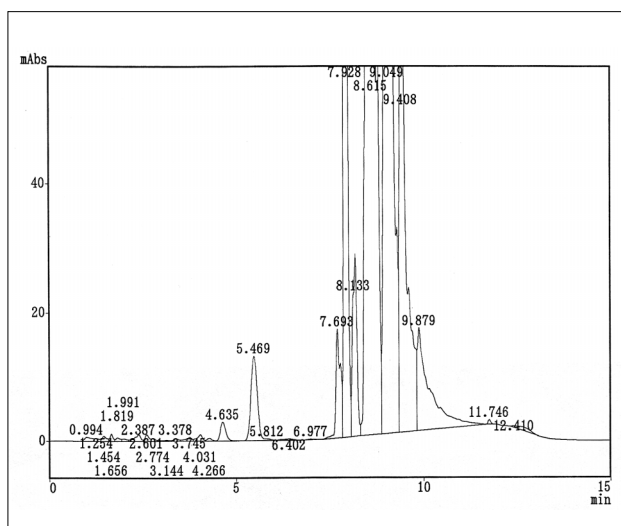
Fig. 1.7.1 Example of measurement of the oxidation product index within gasoline
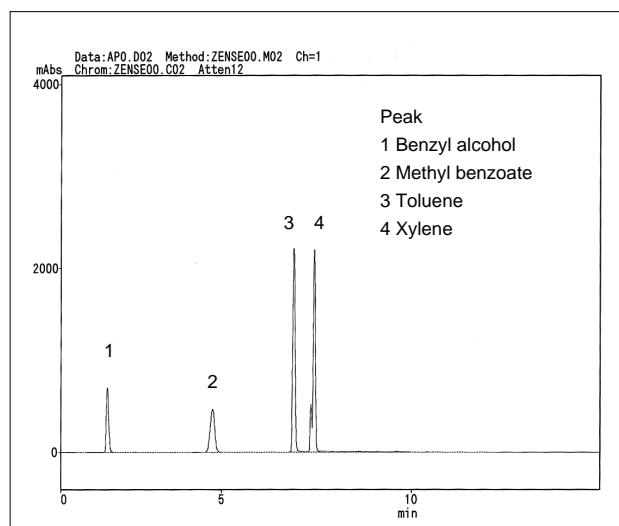
Fig. 1.7.2 Example of analysis of the standard item

1.8 Analysis of furfural in insulating oil - LC

•Explanation

The long term deterioration of oil immersed transformers is taken to be due to the weakening of the insulating paper's mechanical strength. A method to investigate this weakening involves the measurement of furfural, which is a product of the deterioration of insulating paper, to use it as an indicator for assessing the operating life of the transformer. Fig. 1.8.2 shows an example of analysis of insulating oil (new oil) to which standard furfural (1 ppm) has been added. In addition, Figs. 1.8.3 and 1.8.4 shows examples of analysis of actual transformer oil. Note that a lot of oil is still contained in the sample after pretreatment. This requires the column to be cleaned from time to time with acetonitrile, THF etc.

•Pretreatment

Refer to Fig. 1.8.1.

•Analytical Conditions

Model	: HPLC
Column	: Shim-pack CLC-ODS (M)
	(150mm × 4.6mm i.d.)
Mobile Phase	: Acetonitrile/Water=1/9 (v/v)
Flow Rate	: 0.8mL/min
Temperature	: 40°C
Detection	: UV-VIS Detector 280nm
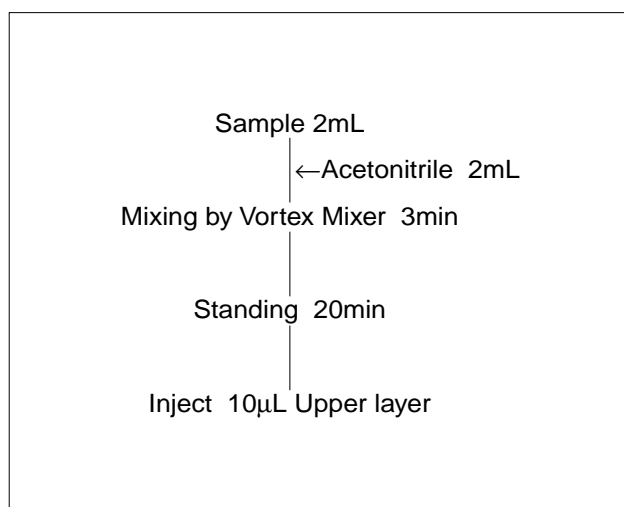
Fig. 1.8.1 Pretreatment procedure
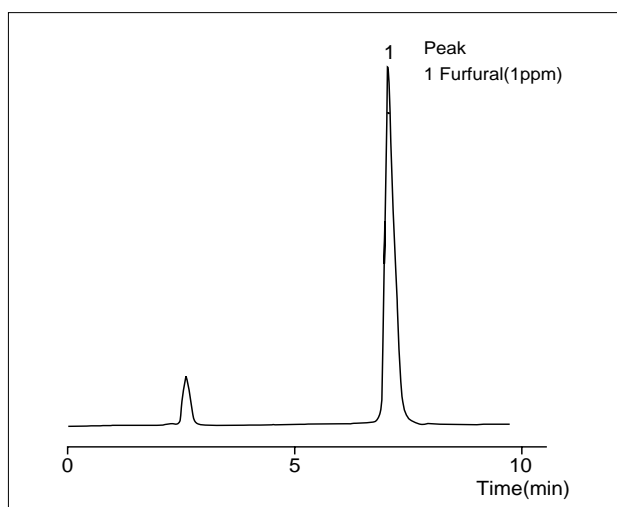
Fig. 1.8.2 Chromatogram of insulating oil with standard furfural added
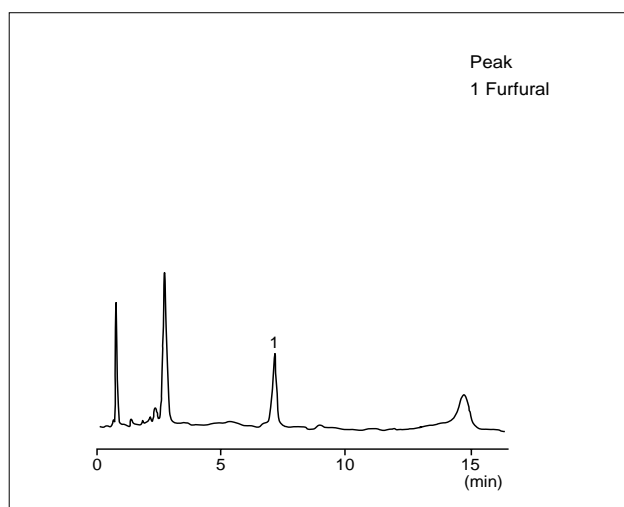
Fig. 1.8.3 Chromatogram of actual transformer oil 'A'
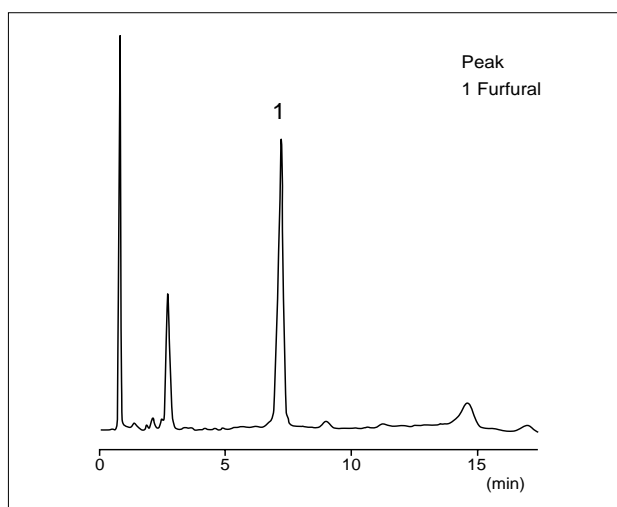
Fig. 1.8.4 Chromatogram of actual transformer oil 'B'

1.9 Analysis of kerosene (1) - GCMS

•Explanation

The primary products of petroleum - gasoline, kerosene, light oils etc – are hydrocarbon mixtures refined through distillation. A Gas Chromatography Mass Spectrometer (GCMS) is used for qualitative determination, since measurement by Gas Chromatography (GC) using a capillary column produces a large number of peaks.

Fig. 1.9.1 is the TIC of kerosene by a non-polar column (methyl silicon). Chemical compounds up to toluene can be seen because of the small amount of gasoline contained in this kerosene.

Fig. 1.9.2 is a TIC chromatogram by a polar column. This kerosene is standard and compounds up to C_8-paraffin are not contained. As shown in Fig. 1.9.3 (polar column), paraffin hydrocarbons from C_9 to C_{16} are contained, with C_{10} and C_{11} as the main components. A lot of aromatic hydrocarbons are contained as well.

•Analytical Conditions

Model   : Shimadzu GCMS-QP1000EX
Column ①   : CBJ1 0.25mm × 30m i.d. df=0.25µm
Column Temp. : 40°C (2min)-220°C (5°C/min)
Column ②   : CBP20 0.25mm × 30m i.d. df=0.25µm
Column Temp. : 80°C (2min)-5°C/min-150°C
                -15°C/min-200°C
Carrier Gas   : He 50kPa
Injector Temp. : 300°C
Interface Temp. : 200°C
Split   : 1 : 50
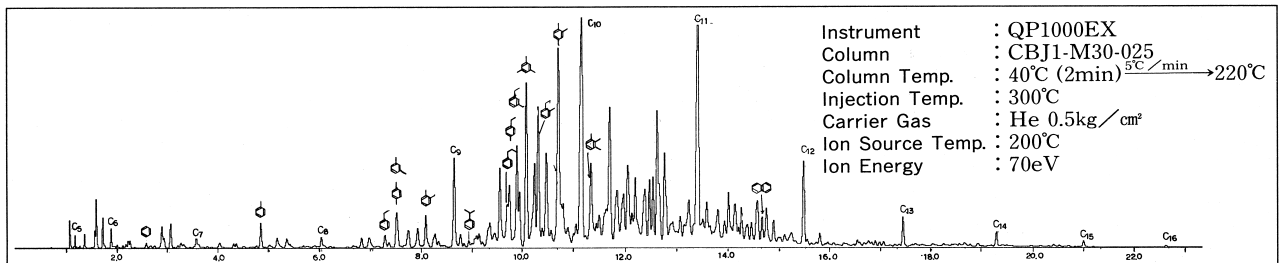
Fig. 1.9.1 TIC chromatogram by a non-polar column
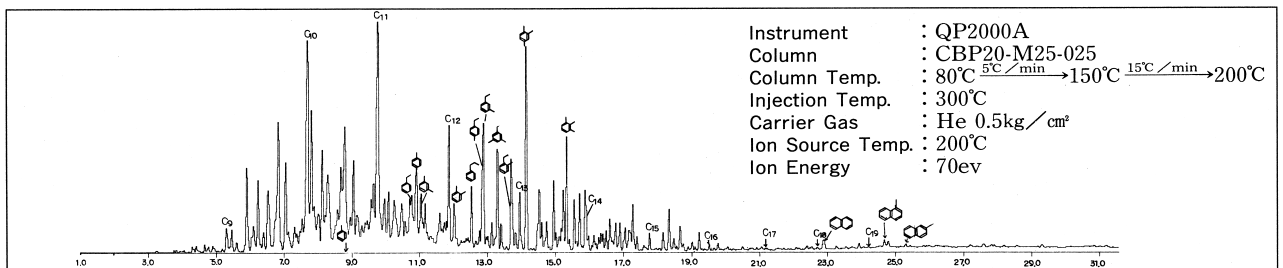
Fig. 1.9.2 TIC chromatogram by a polar column

Fig. 1.9.3 Mass chromatogram by a polar column

Petroleum and Petroleum-based Chemicals
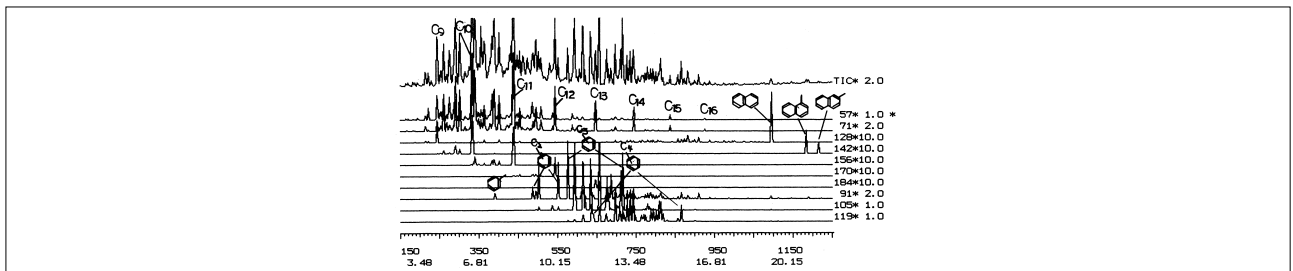
1.9 Analysis of kerosene (2) - GCMS

Fig.1.9.4 is the mass chromatogram obtained by analysis with a non-polar column. C₃-alkylbenzene is eluted from in between the main components of paraffin, n-nonane (C₉H₂₀) and n-decane (C₁₀H₂₂). Fig. 1.9.5 is the mass chromatogram obtained by a polar column (PEG). The component ratio of kerosene A and kerosene B differ somewhat, and the C₃-alkylbenzene has moved to between n-undecane (C₁₂H₂₆) and n-tetradecane (C₁₄H₃₀), and there is less interference by paraffin hydrocarbons.
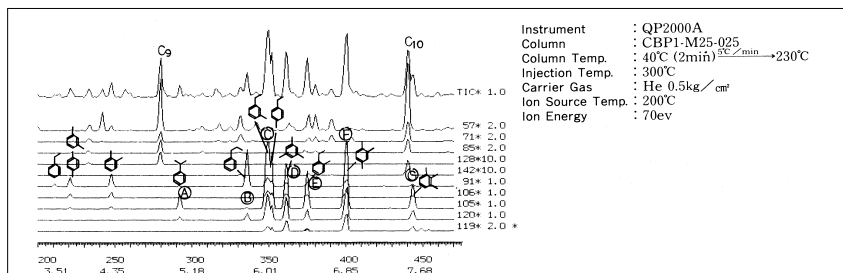
Fig. 1.9.4 Mass chromatogram by a non-polar column
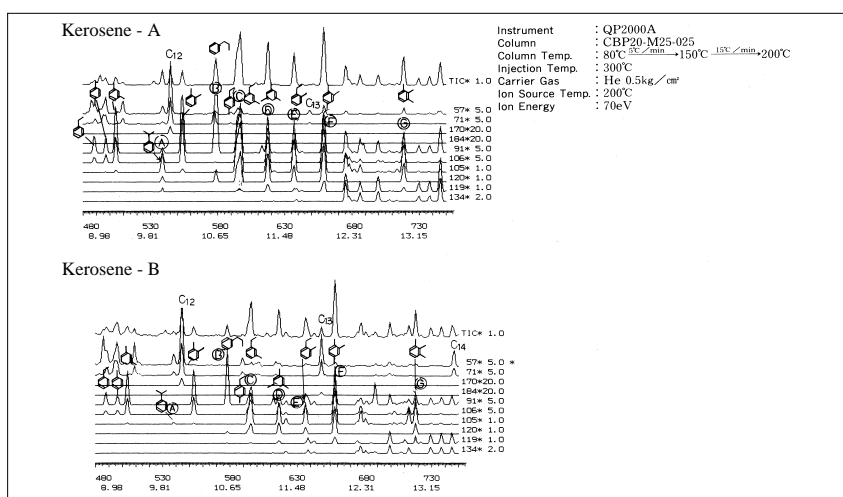
Fig. 1.9.5 Mass chromatogram by a polar column

As indicated in Fig. 1.9.6, there are 8 types of C₃-alkylbenzene isomers. Identification from the mass spectra becomes extremely difficult. In this case, if a capillary column with good separation is used, C₃-alkylbenzene can be completely separated, with the exception of m,p-ethylmethylbenzene, making identification from a mass chromatogram easy.
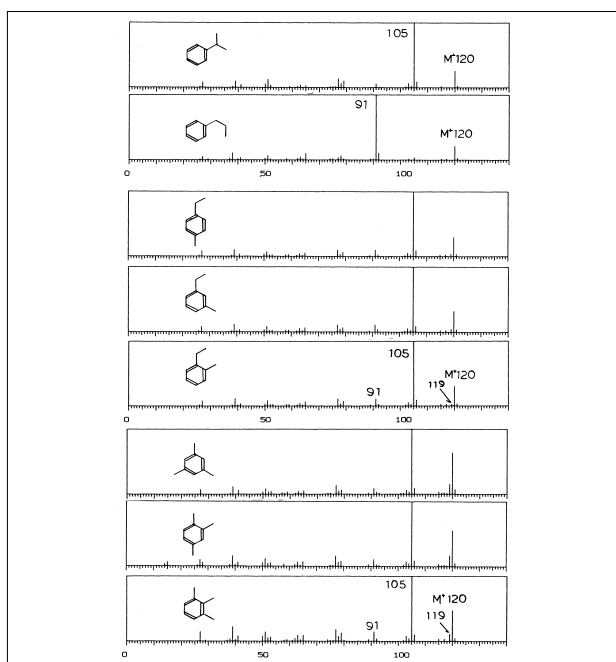
Fig. 1.9.6 Mass spectra of C₃-alkylbenzene

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1.10 Analysis of lead (Pb) in naphtha - AA

●Explanation

Shown here as an example of the measurement of heavy metals in naphtha used in the petrochemical industry is the analysis of lead (Pb) by the electro-thermal atomization method.

Lower limit of quantitation

Approximately 10ppb (depends on the dilution rate. In this case, 2 times)

●Measurement Method

(1) 4-cyclohexylbutyrate dissolved in tetrahydrofuran (THF) was used as the standard solution.

(2) The sample (naphtha) was ultimately diluted 2 times with THF, but iodine was added as an interference inhibitor to both the standard solution and sample measurement solution until the iodine level was 1000ppm. It was then measured by the calibration curve method.

●Analytical Conditions

Wavelength : 283.3 nm

Lamp Current : 10 mA

Slit Width : 0.5 nm

Lamp Mode : BGC-D$_2$

Furnace Program: (Tube type : High Density Tube)

Stage	Temp.(°C)	Time(sec)	Heat Mode	Ar Flow Rate(L/min)
1	120	15	RAMP	0.10
2	300	10	RAMP	0.10
3	600	15	RAMP	0.10
4	600	10	STEP	0.10
5	600	3	STEP	0.00
6	2200	3	STEP	0.00
7	2500	2	STEP	1.00

☐ : Atomizing Stage
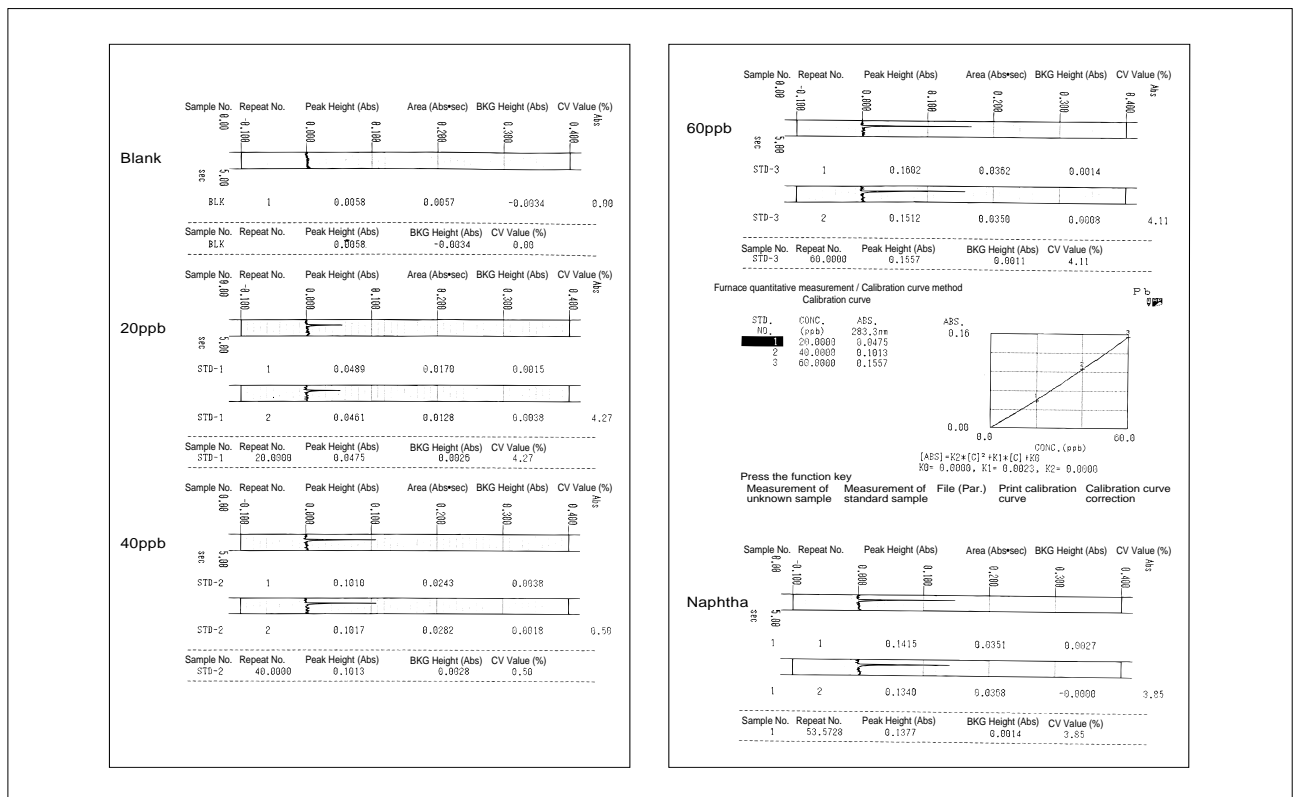
Fig.1.10.1 Example of measurement of lead in naphtha

Concentration within solution	Amount of sample collected	Amount of sample made up	Concentration within stock solution
53.6ppb	2.5mL	5.0mL	107.2ppb

Table 1.10.1 Measurement Results
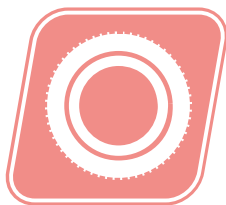
2. Plastics / Rubber

2.1 Analysis of triethylamine and tributylamine in polycarbonate resins - GC

•Explanation

Analysis of triethylamine and tributylamine by GC-FTD is one of material tests for synthetic resin utensils and packaging containers whose main component is polycarbonate. In this analysis, dichloromethane is used as the solvent in extraction and final solution.

Introduced here is an analysis of an extract from nursing bottles (liquid of 0.25ppm equivalent concentration added) as an example of analysis by a special FTD collector (parts number: 221-42512-91).

The advantages of the special FTD collector are that it recovers quickly from solvent shock even when using dichloromethane, and that it is possible to quantify triethylamine, which elutes near the solvent.

References

Details of the analytical method: Japanese Ministry of Health & Welfare Directive No. 18 (Official Bulletin No. 1329, promulgated January 31st 1994)

•Lower limit of quantitation (guide)

Approximately 0.2ppm.

•Analytical Conditions

Model   : GC-17AAFwFt
Column   : DB-1 30m × 0.32mm i.d. df=5µm
Col.Temp. : 150°C (5min)-20°C/min-250°C
Inj.Temp. : 200°C
Det.Temp. : 260°C (w-FTD)
Carrier Gas : He   80kPa, 2.3mL/min
Injection : Split 1 : 15
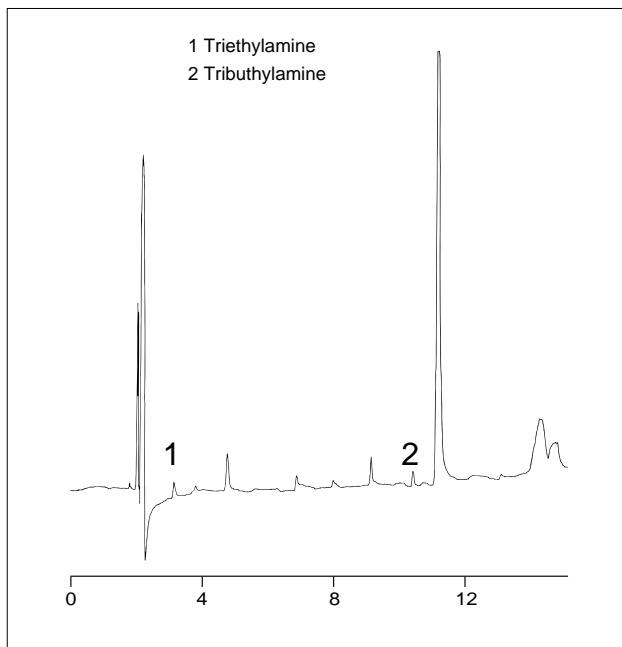
Fig. 2.1.1 Nursing bottle extract (liquid of 0.25ppm equivalent concentration added)
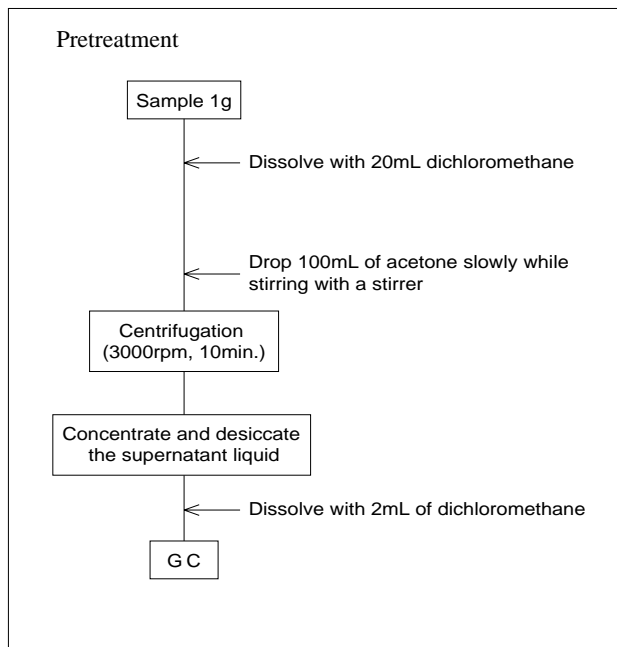
2.2 Analysis of epichlorohydrin in epoxy resin reactive diluent - GC

•Explanation

Although volatile components in a liquid sample can be analyzed by direct injection into the GC, quite a long period of time is taken for the sample to be fully eluted (in the case of this sample approximately 60 minutes) in an analysis such as epichlorohydrin where high boiling point difficult volatile compounds co-exist. In addition, compounds that are not fully eluted at end of analysis can contaminate the injector and the column. For these kinds of samples, there are instances when applying headspace GC will rapidly analyze just the low boiling point compounds. This means that there is no worry of the injector or column getting contaminated.

Comparatively accurate quantitation of liquid samples is possible with the headspace GC by using the standard addition method.

•Lower limit of quantitation (guide)

Approximately 10ppm for this particular analysis (varies greatly with the compound, sample, heating conditions).

•Pretreatment

2mL of the sample was enclosed in a 27mL vial and warmed at 100°C for 30 minutes. 0.8mL of the headspace was then injected in the GC. This being quantitation by the standard addition method, equivalent amounts of 50ppm as well as 100ppm of epichlorohydrin (ECH) were added to the analyzed sample and similarly heated and analyzed.

•Analytical Conditions

Model	: HSS-2B + GC-14BPFsc
Column	: CBP20-M25-025
	25m × 0.22mm i.d. df=0.25µm
Col.Temp.	: 50°C (5min)-10°C/min-230°C
Inj.Temp.	: 250°C
Det.Temp.	: 250°C (FID)
Carrier Gas	: He 0.85mL/min
Injection	: Split 1 : 23

With the equivalent addition of 50ppm of ECH With the equivalent addition of 100ppm of ECH
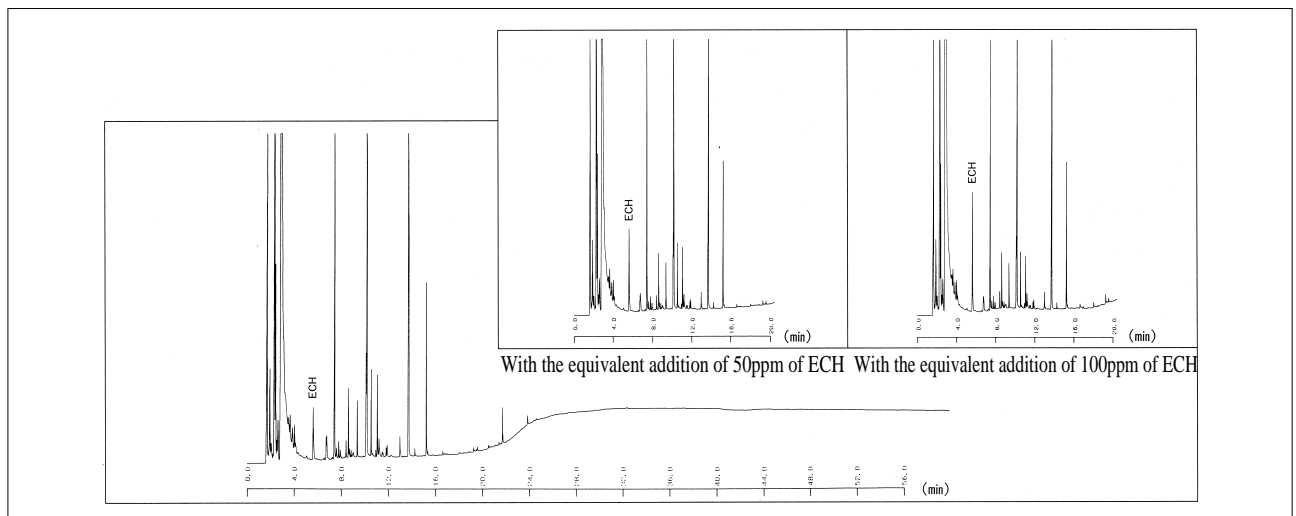
Fig.2.2.1 Headspace GC of epoxy resin reactive diluent

Standard Addition Method

The peak area is plotted on the vertical axis, and the addition volume (concentration) of ECH plotted on the horizontal axis. A straight line is drawn by the least squares method, and the absolute value of where this line intersects the horizontal axis represents the concentration of ECH in the additive free sample.

The quantity of this sample was determined to be 69ppm.

The quantity of ECH is 68.9326.
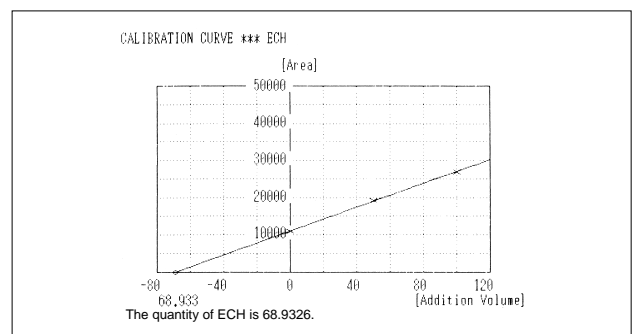
Fig. 2.2.2 Calibration curve

2.3 Analysis of acetaldehyde in PET powder - GC

•Explanation

This is the data obtained from the analysis of acetaldehydes in PET powder with headspace GC. Pretreatment is simple as analysis can be carried out by enclosing the powder directly in a vial.

However, caution is required with respect to the value being calculated as the quantitative value. In the case of dealing with solids in head space GC, the amount that is equivalent to the amount vaporized into the gas phase at that particular heating temperature is calculated as the quantitative value. Any acetaldehyde that is not vaporized and remains in the solid sample is not included in the quantitative value.

•Lower limit of quantitation (guide)

Approximately 1ppm for this particular analysis (varies greatly with the compound, sample, heating conditions etc.)

•Pretreatment

50mg or 100mg of the sample is enclosed in a 27mL vial. After it is warmed at 100°C for 30 minutes, 0.8mL of the headspace sample was injected into the GC.

•Analytical Conditions

Model   : HSS-2B + GC-14BPFsc
Column   : ULBON HR-20M
             30m × 0.53mm i.d. df=2.0μm
Col.Temp. : 40°C -10°C/min-150°C
Inj.Temp. : 165°C
Det.Temp. : 165°C (FID)
Carrier Gas : He   9.4mL/min
Injection : Direct Injection

Peak
1 Acetaldehyde(34ppm)
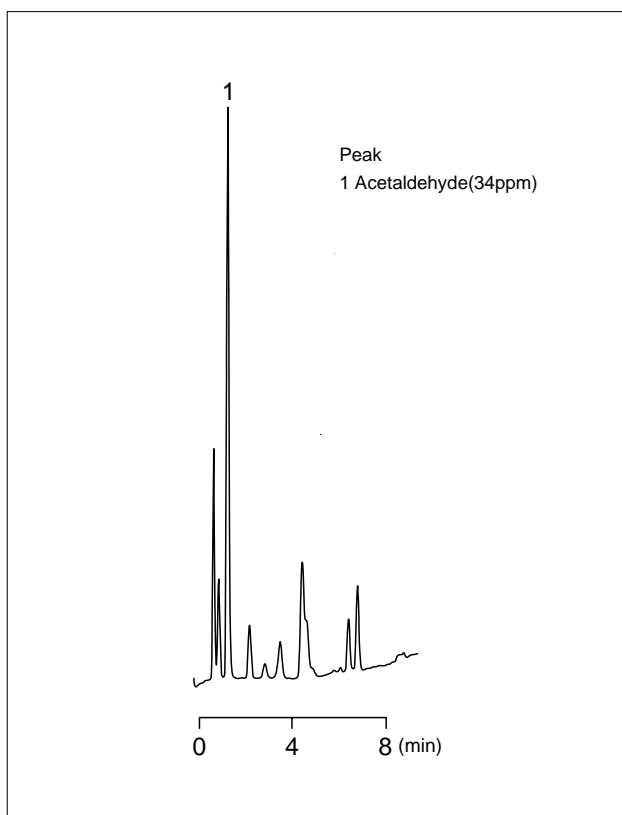
Fig. 2.3.1 PET powder 'A' (50mg contained)

Peaks
1 Acetaldehyde(0.4ppm)
2 THF(1.1ppm)
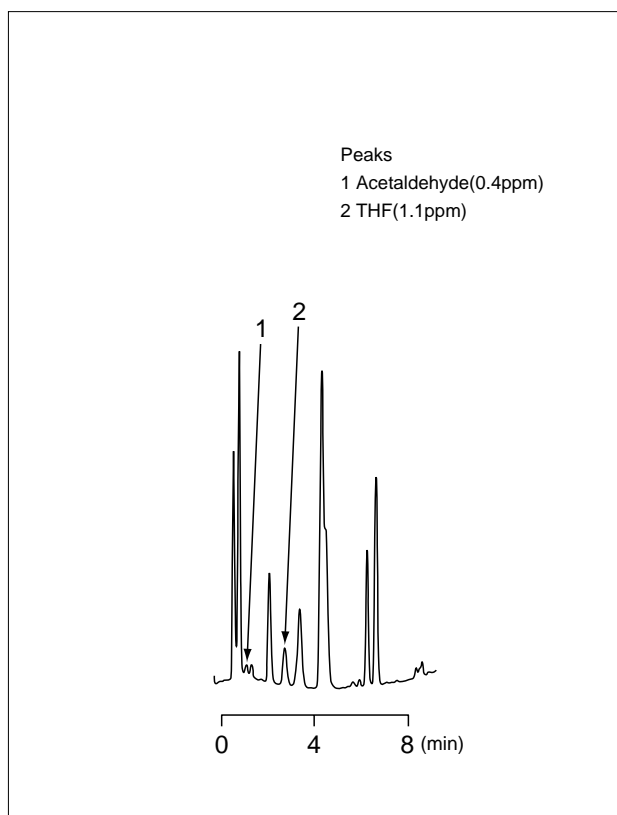
Fig. 2.3.2 PET powder 'B' (100mg contained)

2.4 Thermal decomposition gas chromatography of polymers - GC

•Explanation

The widely adopted method of using gas chromatography to analyze polymers involves thermally decomposing the polymer and analyzing the thermal decomposition products with GC.

This is used as an effective technique for characterization of polymers in polymer research and quality control.

Introduced here are pyrograms (gas chromatograms obtained by thermal decomposition GC) of polyethylene and polystyrene.

•Lower limit of quantitation (guide)

A few mg of the sample is placed in a pyrolizer set to a prescribed temperature and thermally decomposed.

•Analytical Conditions

Model   : PYR-2A + GC-14BPFsc

Column   : OV-101 25m × 0.2mm i.d.

Col.Temp.   : 70°C - 8°C/min-280°C

Inj.Temp.   : 250°C

Det.Temp.   : 330°C (FID)

Carrier Gas : He

Injection   : Split
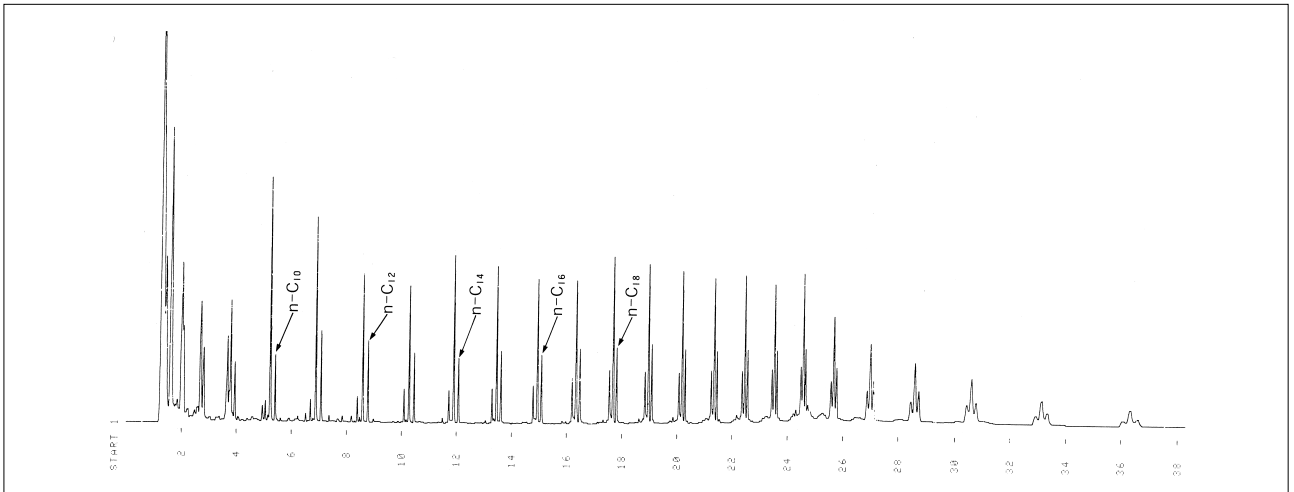
Fig. 2.4.1 Polyethylene (pyrolysis temperature: 550°C)
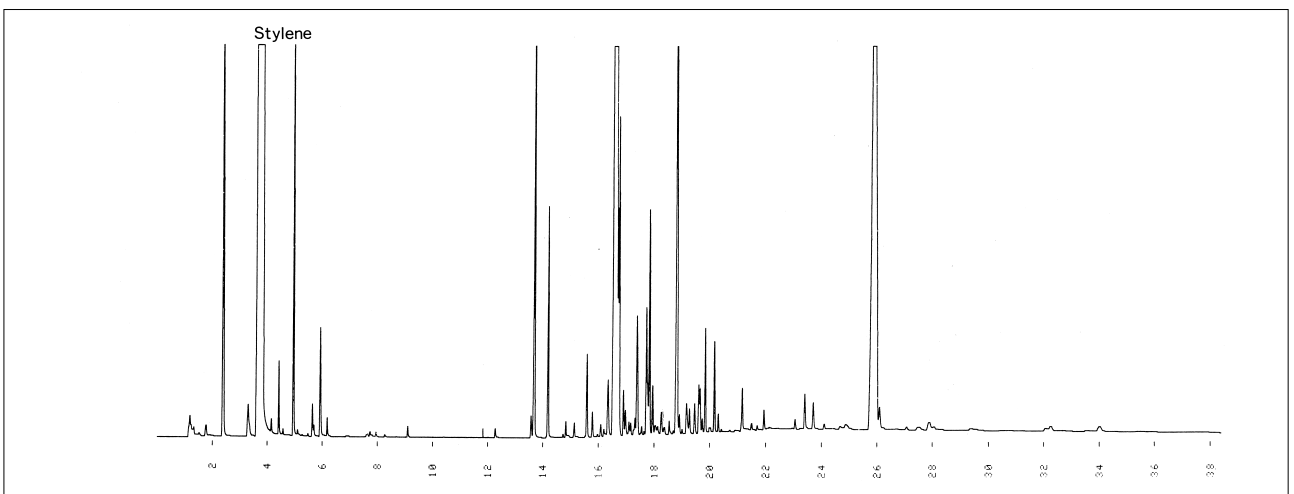
Fig. 2.4.2 Polystyrene (pyrolysis temperature: 600°C)

2.5 Thermal decomposition gas chromatography of rubber - GC

(Simultaneous FID/FTD detection)

•Explanation

It goes without saying that a column with good separation needs to be used in order to separate and identify the compounds connected to characterization from thermal decomposition products with complicated compositions. In addition, combining detectors capable of obtaining qualitative information with skill is also effective. Shown here is an example of the simultaneous FID and FTD detection of rubber thermal decomposition products by using a simultaneous detection adapter specific to the column outlet.

•Pretreatment

A few mg of the sample is placed in a thermal furnace set to a prescribed temperature and thermally decomposed.

•Analytical Conditions

Model	:	PYR-1A + GC-14BPFsc
Pyrolysis Temp.	:	600°C
Column	:	CBP1-S25-050
		25m × 0.33mm i.d. df=0.5µm
Col.Temp.	:	50°C (5min)-6°C/min-200°C
Inj.Temp.	:	250°C
Det.Temp.	:	250°C (FID)
Carrier Gas	:	He
Injection	:	Split 1 : 70
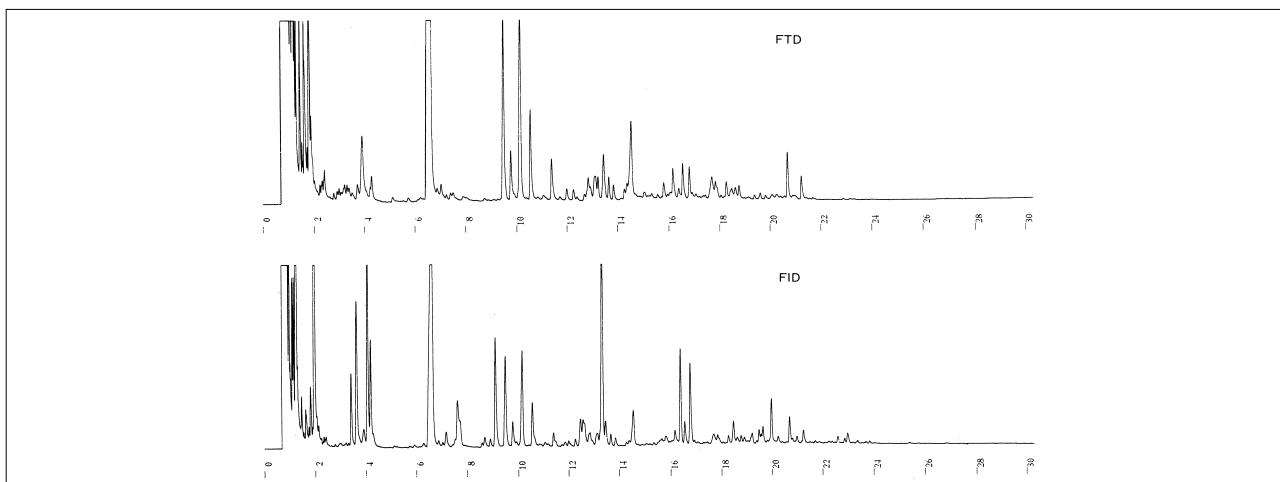
Fig. 2.5.1 NBR (acrylonitrile-butadiene rubber)
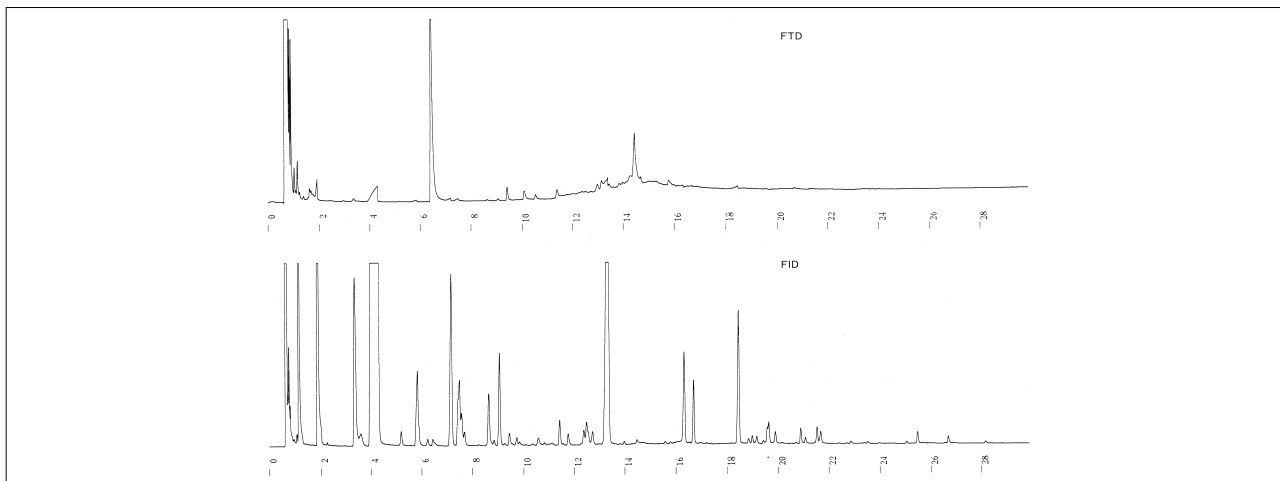
Fig. 2.5.2 styrene-acrylonitrile rubber

2.6 Simultaneous GPC-GC analysis of plasticizers and the molecular weight of polyvinyl chloride (PVC) - GPC/GC

•Explanation

The analysis of various additives that are added depending on use and the measurement of average molecular weights and molecular weight distribution is important in examining the performance and characteristics of polymeric materials and polymeric products. Of these, measuring the average molecular weight and the molecular weight distribution is relatively easy with GPC. However, complicated procedures were necessary in the measurement of additives that involved extraction with a suitable solvent, or analysis by HPLC, GC, IR etc. after separation and collection by GPC.

The GPC-GC introduced here is a system that separates the polymer and additives by GPC, after which only the additives are collected online and injected into the GC for analysis. These analyses can be done with a single injection of the sample. Introduced here is an example of analysis of polyvinyl chloride (PVC) to which 7 phthalate ester plasticizers and an internal standard substance (n-docosane) have been added.

•Pretreatment

None.

•Analytical Conditions

[GPC]

Model	:	LC-10A system
Column	:	Shim-pack GPC-80M
		30cm $\times$ 8.0mm i.d.
Mobile Phase	:	THF 1.0mL/min
Col.Temp.	:	40°C
Detector	:	RID-10A (64 $\times$ 10^{-6}RIU)

[GC]

Model	:	GC-17AAF ver.3
Column	:	DB-1 30m $\times$ 0.32mm i.d. df=1.0μm
Col.Temp.	:	55°C (5min)-12°C/min-300°C
PTV Temp.	:	64°C (1min)-30°C/min-95°C (1min)
		-250°C/min-300°C
Det.Temp.	:	320°C (w-FID)
Carrier Gas	:	He 2mL/min
Injection	:	Split 1 : 50

1 DMP : Dimethyl phthalate
2 DEP : Diethyl phthalate
3 DPP : Di-n-propyl phthalate
4 i-DBP : Di-iso-butyl phthalate
5 n-DBP : Di-n-butyl phthalate
6 IS   : n-Docosane
7 BBP : Benzyl butyl phthalate
8 DOP : Dioctyl phthalate

Results of molecular weight measurement

Number-A.M.W. MN   =66767
Weight-A.M.W. MW   =136248
Z-A.M.W. MZ   =251062
Polydispersity MW/MN =2.04066
Polydispersive MZ/MW =1.84268
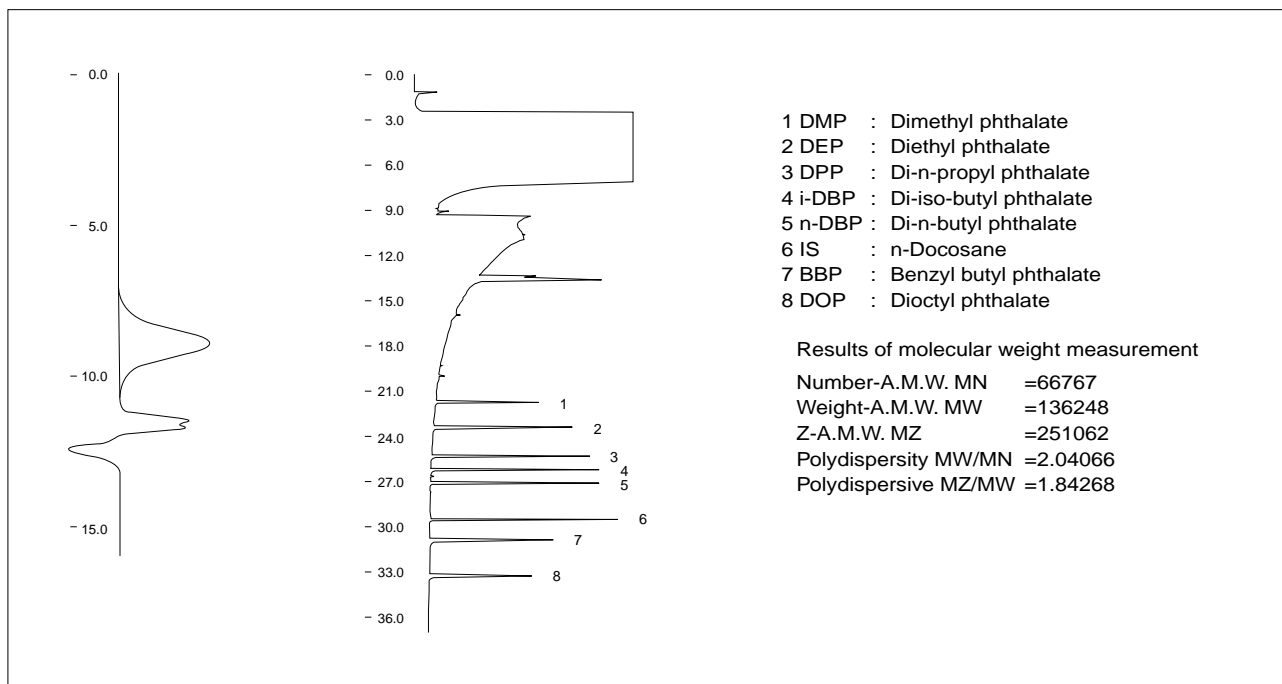
Fig. 2.6.1 GPC-GC of polyvinyl chloride (PVC)(7 phthalate ester plasticizers added)

2.7 Analysis of polyvinyl chloride resin (PVC) (1) - LC

•Explanation

PVC is used in a wide range of applications such as flexible films, sheets, leather, containers, and rigid pipes for covering electrical wiring.

Shown in Fig. 2.7.1 is the GPC chromatogram of a homopolymer. They are comparisons based on the differing degrees of polymerization (DP) of 3 types of PVCs. The differences can be clearly compared by overlaying the elution curves and the derivative and integral curves.

Fig 2.7.2 shows the results of measurement of the molecular weight distribution of PVC and the separation analysis of plasticizers contained in PVC (to which DOP 12% and DBP 5% with respect to PVC has been added) by simultaneous detection using a refractive index detector (RI) and UV-VIS absorbance detector (UV).

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).
Analytical Conditions

•Analytical Conditions

Model   : GPC
Column   : Shim-pack GPC-806,804,802
                (Each 300mm × 8.0mm i.d.)
Mobile Phase : Tetrahydrofuran (THF)
Flow Rate   : 1.0mL/min
Temperature   : 40°C
Detection   : Refractive Index Detecter
                UV-VIS Detector 254nm
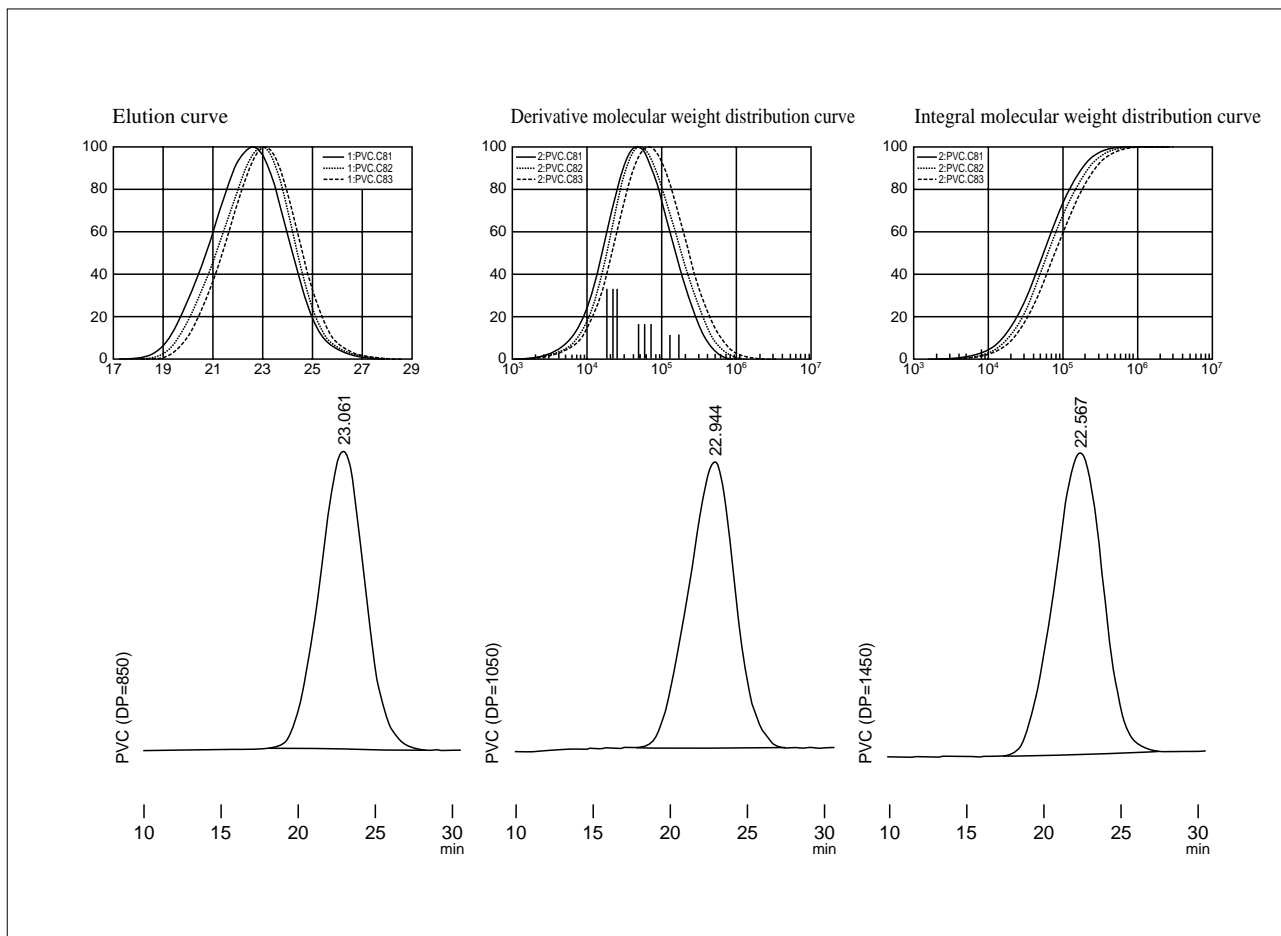
Fig. 2.7.1 Analysis of polyvinyl chloride resins with differing degrees of polymerization

2.7 Analysis of polyvinyl chloride resin (PVC) (2) *- LC*

•Analytical Conditions

Model   : GPC

Column   : Shim-pack GPC-804,802 × 2 (Each 300mm × 8.0mm i.d.)

Mobile Phase : Tetrahydrofuran (THF)

Flow Rate   : 1.0mL/min

Temperature : 40°C

Detection   : Refractive Index Detecter

                UV-VIS Detector 254nm

∗∗Results of quantitative calculations∗∗

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
2	1	25.2	13285285	544961		1	72.5095	DOP
	2	26.42	5036847	209971	V	2	27.4905	DBP
		TOTAL	18322132	754932			100	

Total data channel 1

| Time (min)	Mol. size	Height	Subtotal	%
14.87	773512	12	560031	100
15.12	501713	74	560019	99.9979
15.37	330202	1036	559945	99.9847
15.62	220541	5376	558910	99.7998
15.87	149452	13758	553533	98.8398
16.12	102732	25355	539775	96.3831
16.37	71610	37806	514420	91.8557
16.62	50602	49525	476614	85.105
16.87	36237	59078	427090	76.2618
17.12	26291	66276	368012	65.7127
17.37	19318	70210	301735	53.8783
17.62	14372	68088	231525	41.3415
17.87	10822	58431	163437	29.1836
18.12	8246	41243	105006	18.75
18.37	6355	24694	63763	11.3857
18.62	4952	13710	39069	6.9762
18.87	3901	7596	25360	4.5282
19.12	3106	4671	17763	3.1718
19.37	2497	3373	13092	2.3377
19.62	2028	2659	9719	1.7354
19.87	1663	2064	7060	1.2607
20.12	1376	1520	4996	0.8921
20.37	1149	1077	3476	0.6207
20.62	968	756	2399	0.4284
20.87	822	534	1643	0.2933
21.12	703	378	1109	0.198
21.37	606	266	731	0.1305
21.62	527	184	465	0.0831
21.87	461	122	282	0.0503
22.12	406	78	160	0.0286
22.37	360	48	82	0.0146
22.62	321	26	34	0.0061
22.87	288	8	8	0.0015

Peak information	Time (min)	Mol. size	Height
start	14.75	965384	12
peak	17.414	18440	70208
end	23	273	8

Number-A.M.W.	MN= 12642	Weight-A.	M.W. = 33802
Z-A.M.W.	MZ= 77682		
Dispersity	MW/MN= 2.67382	Dispersity	MZ/MN =6.14488

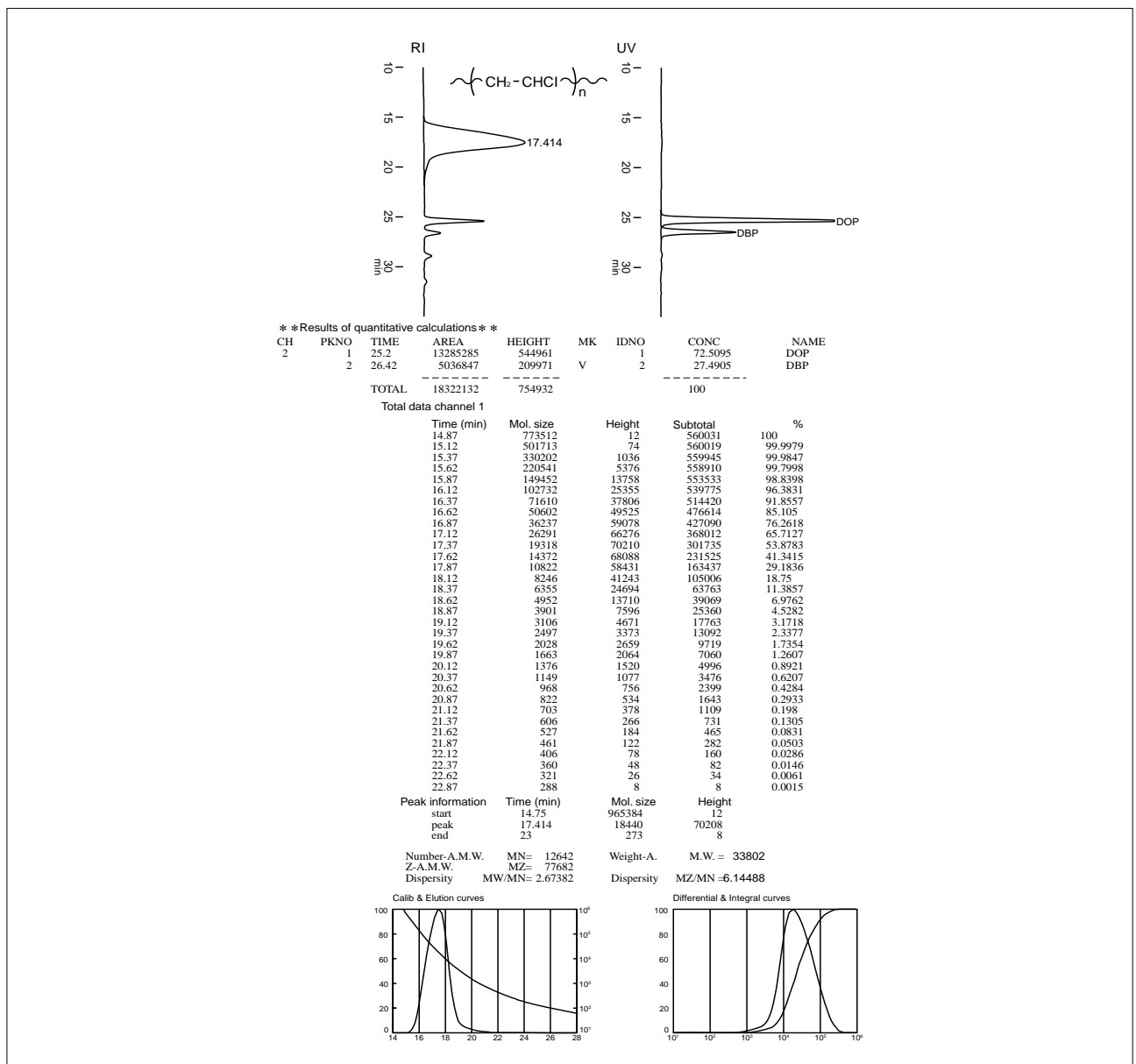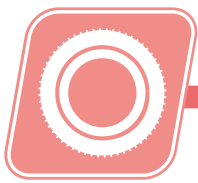Calib & Elution curves   Differential & Integral curves

Fig.2.7.2 Simultaneous analysis of plasticizers and polyvinyl chloride resin

2.8 Analysis of polystyrene resin (PS) (1) - LC

●Explanation

PS is used a lot in a variety of articles of daily use, in particular in the outer frames of products such as radios and televisions, due to the ease with which it can be molded, its transparency, and the fact that it can be painted with vivid colors.

Monodispersed polystyrene gained by anionic polymerization is widely adopted to create a calibration curve for GPC. Shown in Fig. 2.8.1 is a chromatogram measured by mixing several types of polystyrene of differing molecular weights for the purpose of generating GPC calibration curves. Shown in Fig. 2.8.2 is the chromatogram by simultaneous RI and UV detection. Additives that cannot be detected with the RI can be clearly detected with the UV.

●Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

●Analytical Conditions

Model	:	GPC
Column	:	Shim-pack GPC-806,804,802
		(Each 300mm × 8.0mm i.d.)
Mobile Phase	:	Tetrahydrofuran (THF)
Flow Rate	:	1.0mL/min
Temperature	:	40°C
Detection	:	Refractive Index Detector
		UV-VIS Detector 254nm
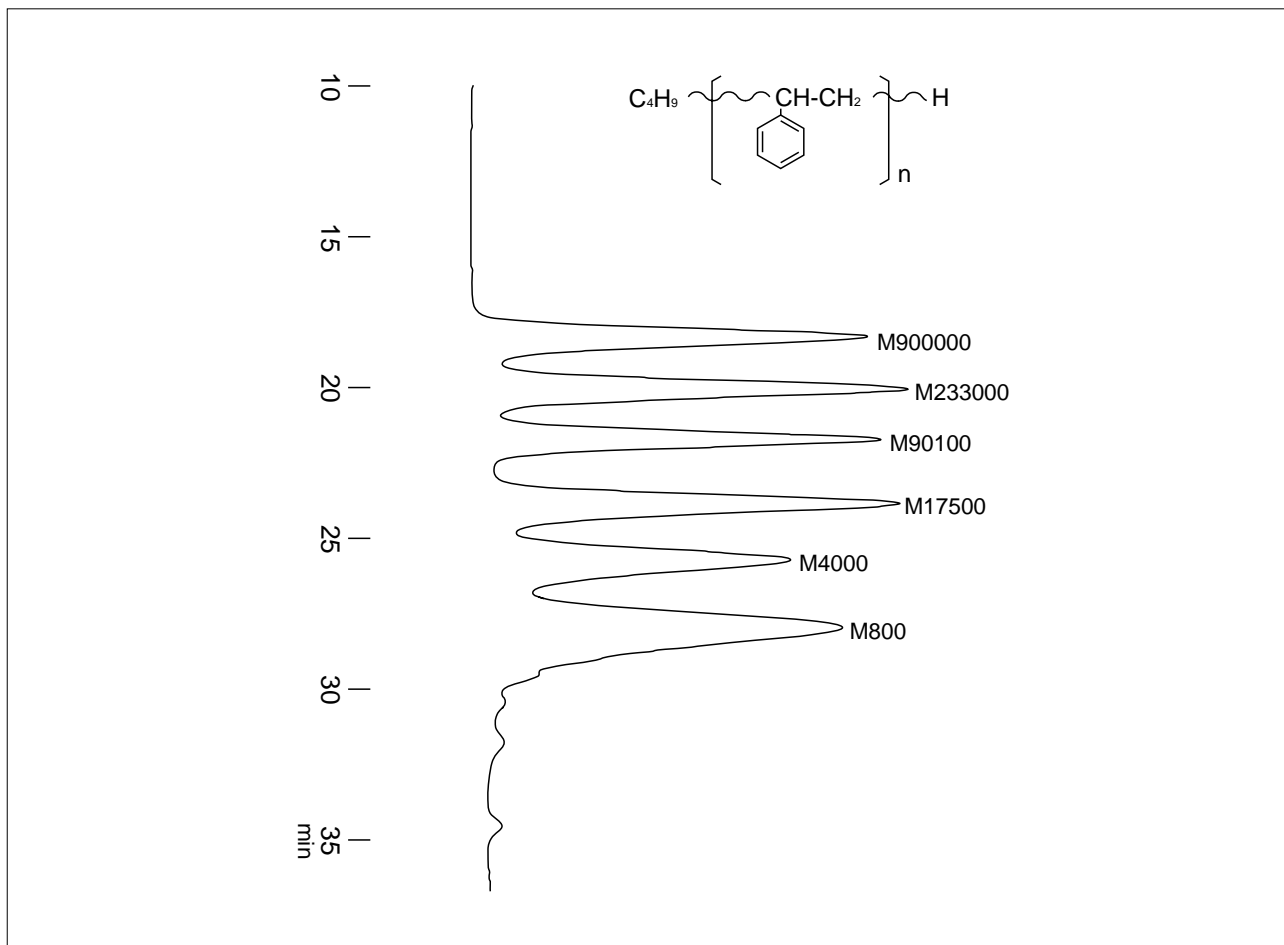
Fig. 2.8.1 Analysis of monodispersed polystyrene mixtures

2.8 Analysis of polystyrene resin (PS) (2) - LC

RI

CH-CH₂)ₙ

23.958

UV

23.811

Channel 1

Peack information	Time(min)	Mol.size	Height
start	20.333	244148	2
top	23.958	24051	82903
end	29.833	306	1

Number-A.M.W.	MN= 12612	Weight-A.M.W. MW=	26895
Z-A.M.W.	MZ= 42452		
Dispersity	MW/MN= 2.13245	Dispersity MZ/MN=	3.36592

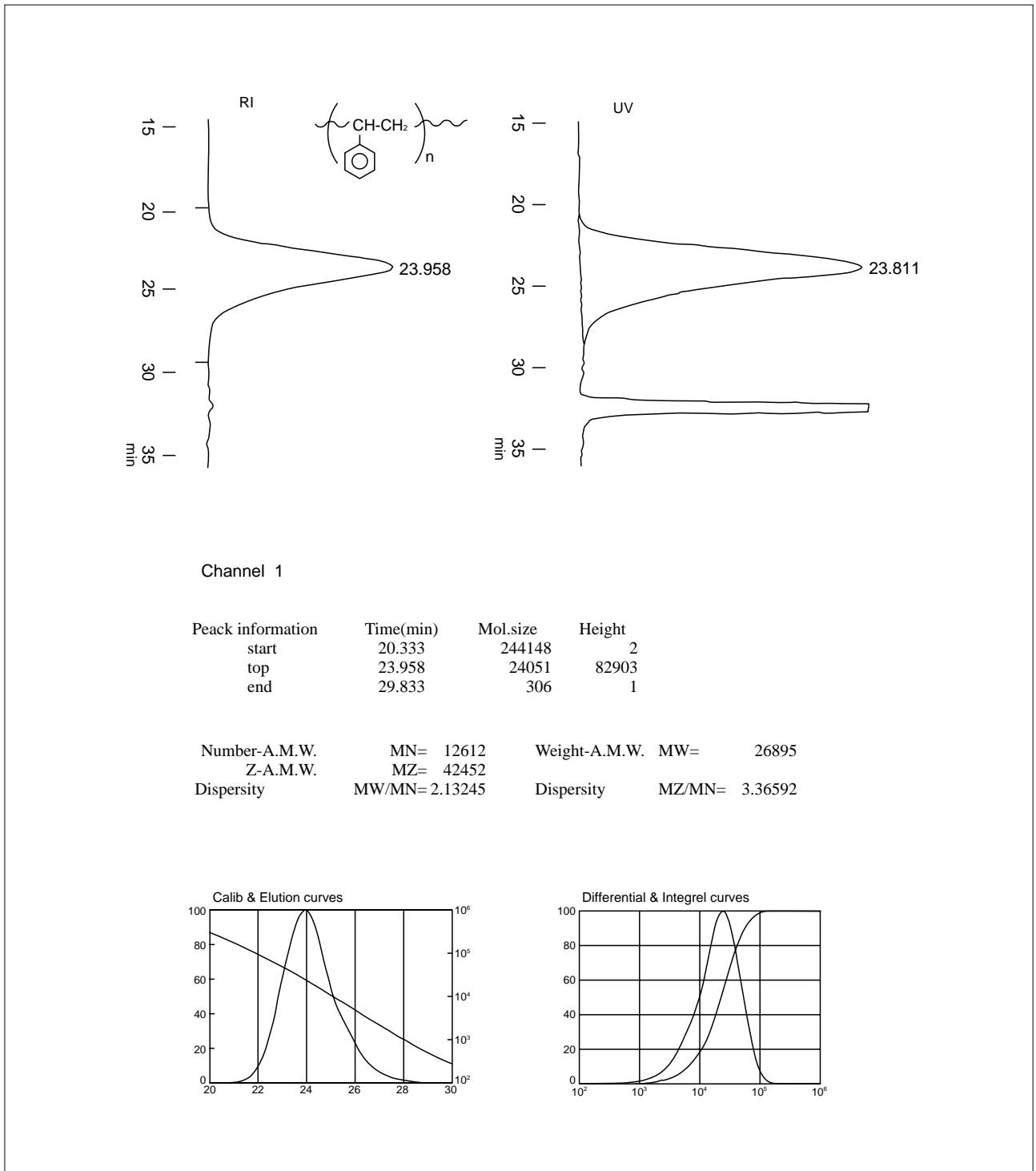Calib & Elution curves

Differential & Integrel curves

Fig. 2.8.2 Analysis of polystyrene resin

2.9 Analysis of acrylic resin (PMMA) - LC

•Explanation

PMMA is generally manufactured with methyl methacrylate, a monomer, as the main constituent. As it is the most transparent material among polymeric materials, it is used as a molded material in lighting, instrumentation, and medical purposes (such as contact lenses), as well as in adhesives, printing and paints. Shown in Fig. 2.9.1 is an example of analysis of a typical PMMA, while in Fig. 2.9.2 an example of analysis of PMMA for paints that has been dissolved 50% in xylene is shown.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

Model   : GPC
Column   : Shim-pack
                GPC-806,804,803,8025
              : (Each 300mm × 8.0mm i.d.)
Mobile Phase : Tetrahydrofuran (THF)
Flow Rate   : 1.0mL/min
Temperature   : 45°C
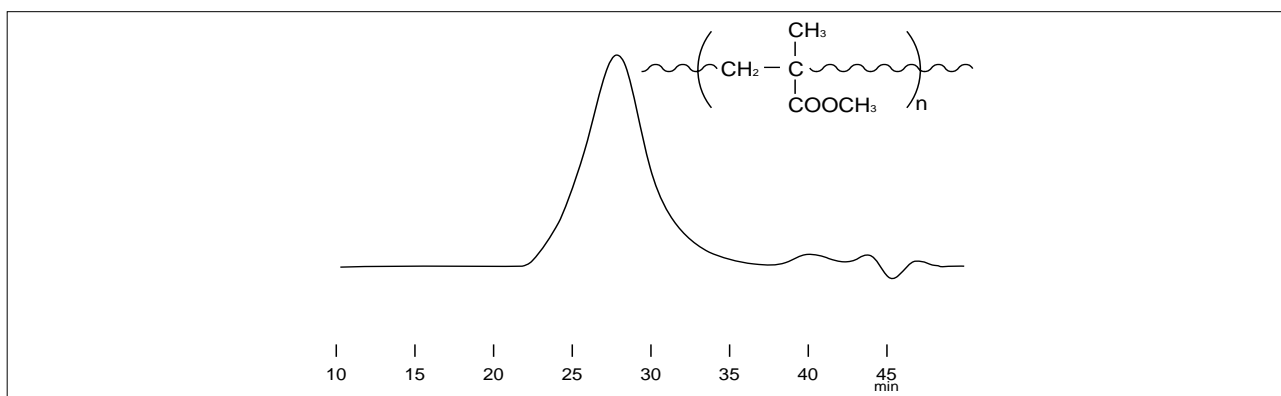Detection   : Refractive Index Detector

Fig. 2.9.1 Analysis of acrylic resin (a)
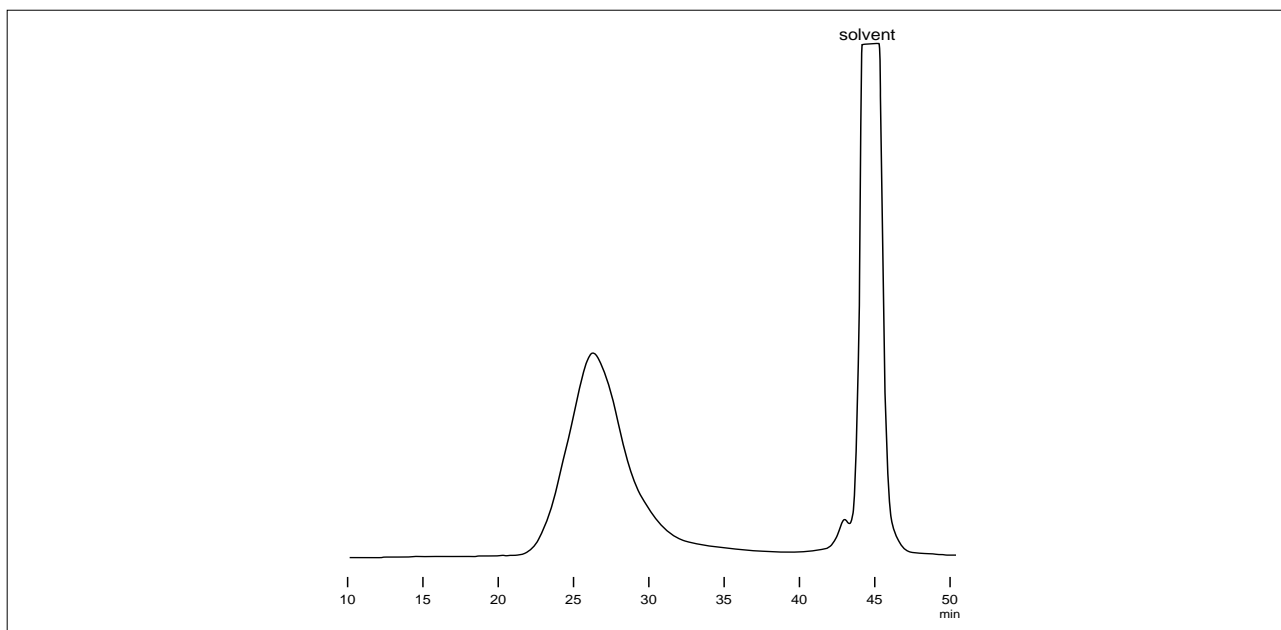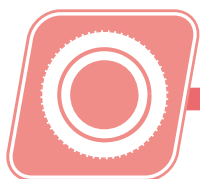

Fig. 2.9.2 Analysis of acrylic resin (b)

2.10 Analysis of polyurethane resin *- LC*

●**Explanation**

A resin with a urethane bond is produced through addition polymerization of diisocyanate (mainly toluene diisocyanate or diphenyl-methane diisocyanate) and polyol.

Polyurethane resins are mechanically strong, and in particular have excellent heat insulation properties. It is thus used in refrigerators and as a construction material in housing. It is an essential material in a wide range of fields such as energy saving and low temperature technologies. Shown in Fig. 2.10.1 is a typical chromatogram.

●**Pretreatment**

Filtered with a non-aqueous membrane filter (0.45μm).

●**Analytical Conditions**

Model	: GPC
Column	: Shim-pack GPC-806 $\times$ 2,804
	(Each 300mm $\times$ 8.0mm i.d.)
Mobile Phase	: Tetrahydrofuran (THF)
Flow Rate	: 1.0mL/min
Temperature	: 40°C
Detection	: Refractive Index Detector
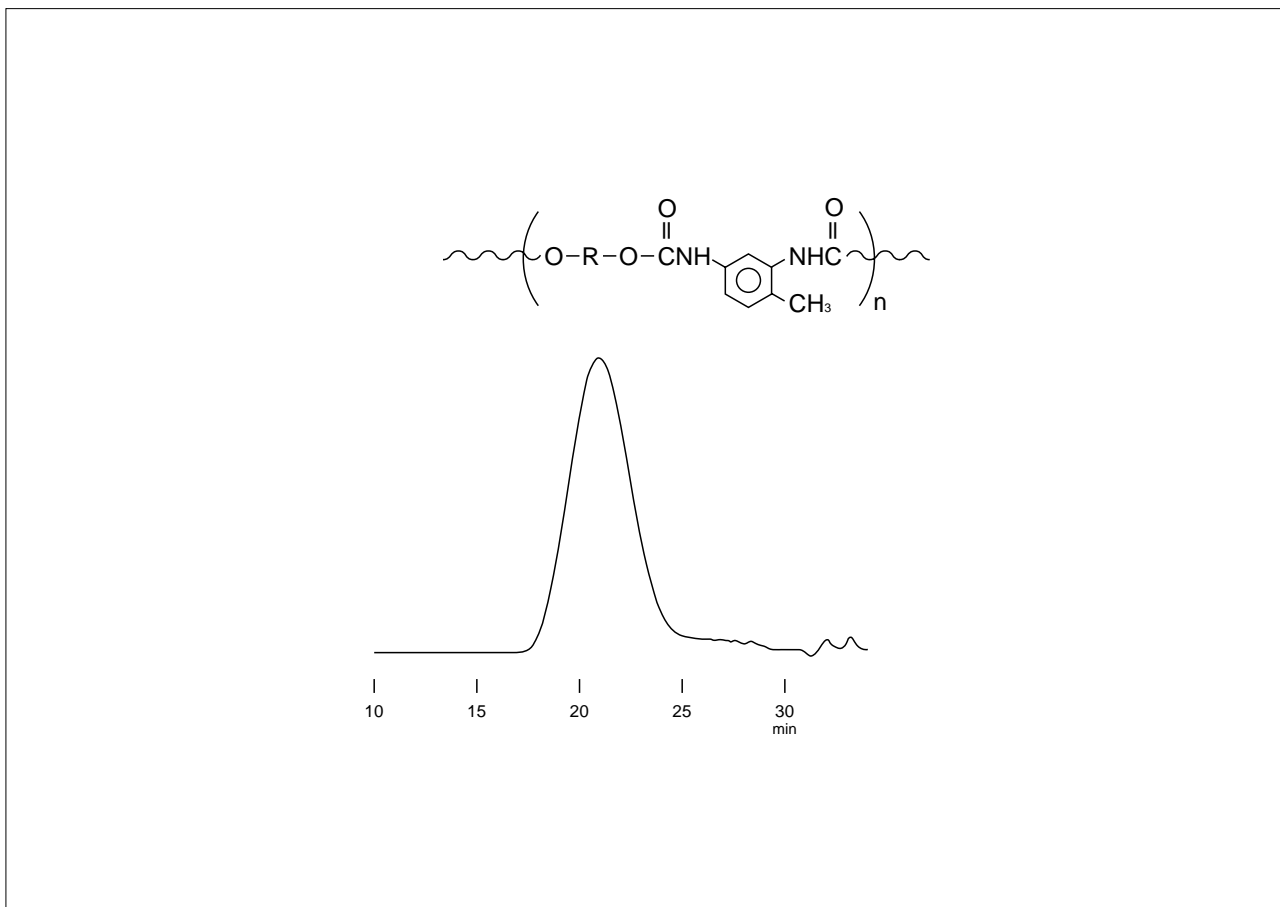
Fig. 2.10.1 Analysis of polyurethane resin

Plastics / Rubber

2.11 Analysis of plasticizers - LC

•Explanation

Plasticizers are polymer additives that either lower the elastic molulus or the glass transition point of polymers to give them an appropriate flexibility at room temperature. In addition, it also has the effect of lowering the melt viscosity to increase the workability at high temperatures. Plasticizers are added to a large number of polymeric materials, mainly to vinyl polymers. In terms of quantity, they are most used in polyvinyl chloride.

Together with anti-oxidants, they have recently been attracting attention as endocrine disrupters (environmental hormones), and there are moves to restrict their use.

Shown in Fig. 2.11.1 is an example of separation of a phthalate ester plasticizer.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

Model   : HPLC
Column   : Shim-pack CLC-ODS
               (150mm × 6.0mm i.d.)
Mobile Phase : Water/Acetonitrile=3/2(v/v)→
             : Acetonitrile 100%
             : 2%/min Linear Gradient
Flow Rate   : 1.0mL/min
Temperature : 40°C
Detection   : UV-VIS Detector 254nm

DMP (Dimethyl Phthalate)
DEP (Diethyl Phthalate)
DAP (Diallyl Phthalate)
DPP (Dipropyl Phthalate)
DBP (Dibuthyl Phthalate)
TCP (Tricresyl Phosphate)
DOP (Diocthyl Phthalate)
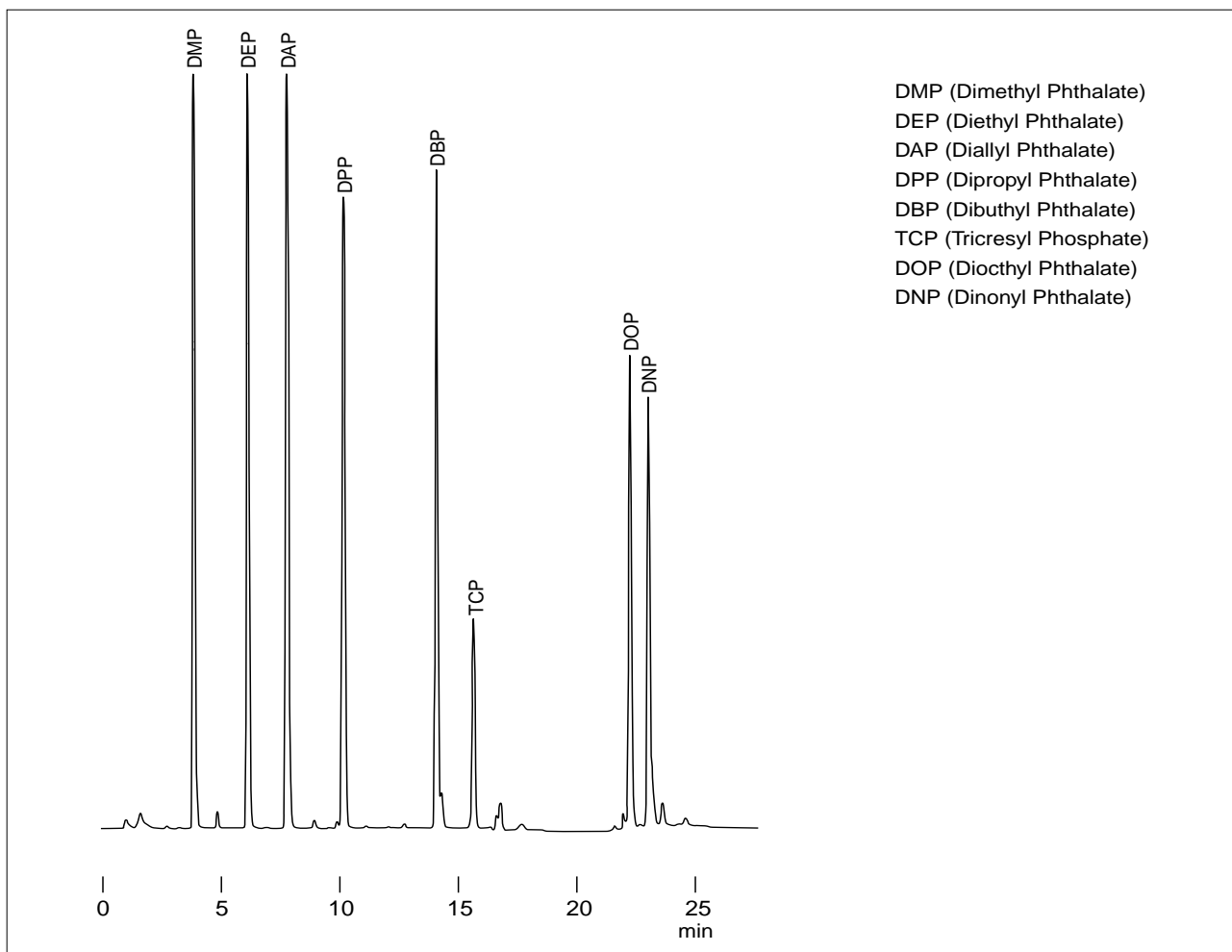DNP (Dinonyl Phthalate)

Fig. 2.11.1 Analysis of a plasticizer

2.12 Analysis of anti-oxidants (1) - LC

•Explanation

a) Radical inhibitor (hinderd phenol)

This is added to increase stability with respect to oxidation of polymeric materials. The recent trend is for those with quite a high molecular weight to be used. Anti-oxidants with a high molecular weight are better in terms of volatility, migrations, and extractability than those with a low molecular weight. Shown in Fig. 2.12.1 is an example of the separation of a typical phenol anti-oxidant.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

Model	:	HPLC
Column	:	Shim-pack CLC-ODS
	:	(150mm × 6.0mm i.d.)
Mobile Phase	:	A ; 10mM Acetic Acid
		B ; Acetonitrile/THF=1/1 (v/v)
		B,60→100%, 2%/min
		Curve#1 Gradient
Flow Rate	:	1.5mL/min
Temperature	:	50°C
Detection	:	UV-VIS Detector 270nm

1 Bisphenol A
2 BHT
3 Yoshinox BB
4 Yoshinox SR
5 Topanol CA
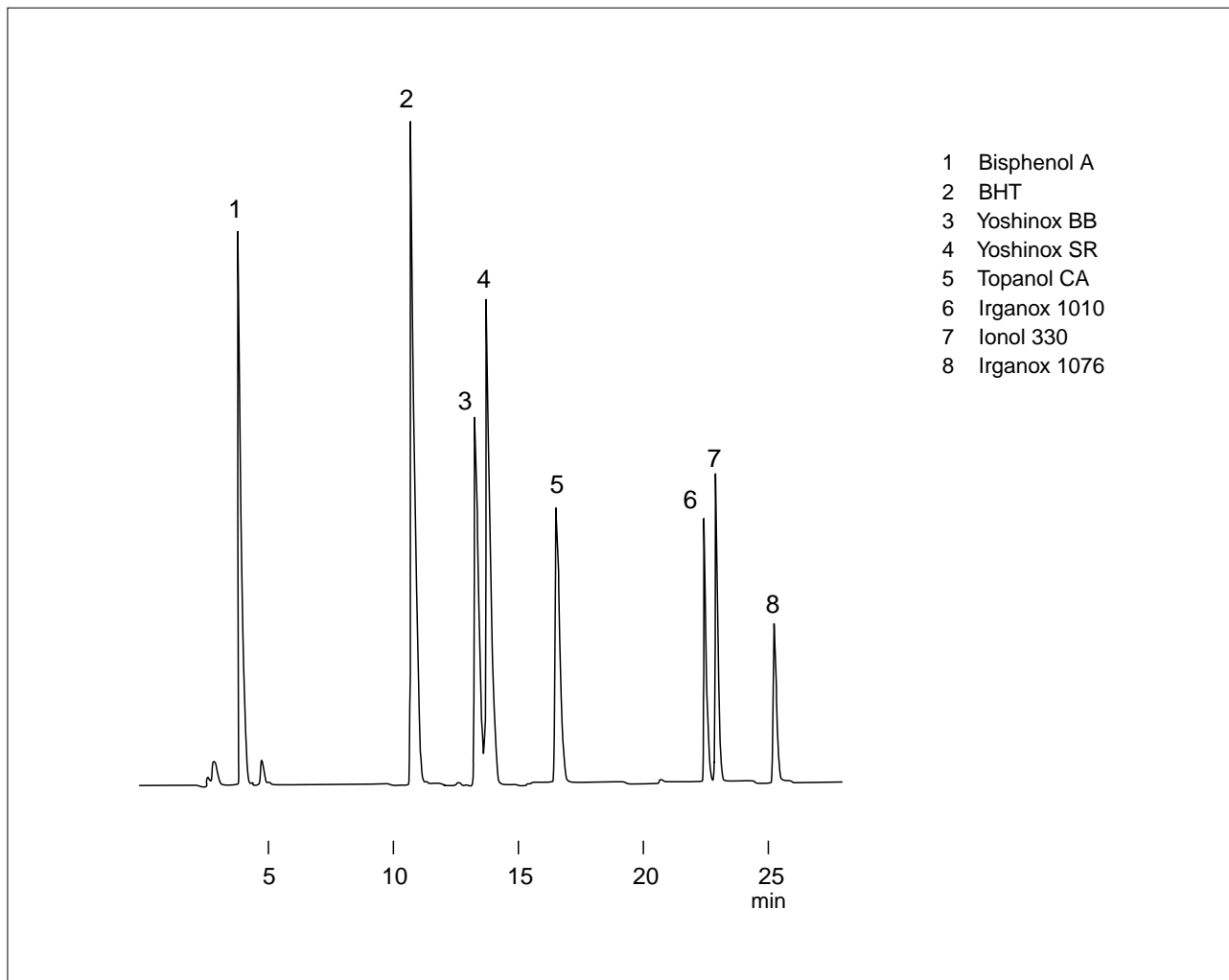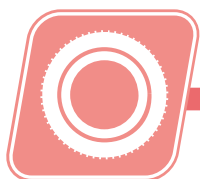6 Irganox 1010
7 Ionol 330
8 Irganox 1076

Fig. 2.12.1 Analysis of a phenol anti-oxidant

2.12 Analysis of anti-oxidants (2) *- LC*

•Explanation

b) Hydroperoxide decomposer

Shown in Fig.2.12.2 is an example of the separation of dipropionate fatty acid ester, a typical peroxide decomposer.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

Model   : HPLC

Column   : Shim-pack CLC-ODS
             (150mm × 6.0mm i.d.)

Mobile Phase : Water/Methanol/THF=2/1/1 (v/v)

Flow Rate : 1.0mL/min

Temperature : 50°C

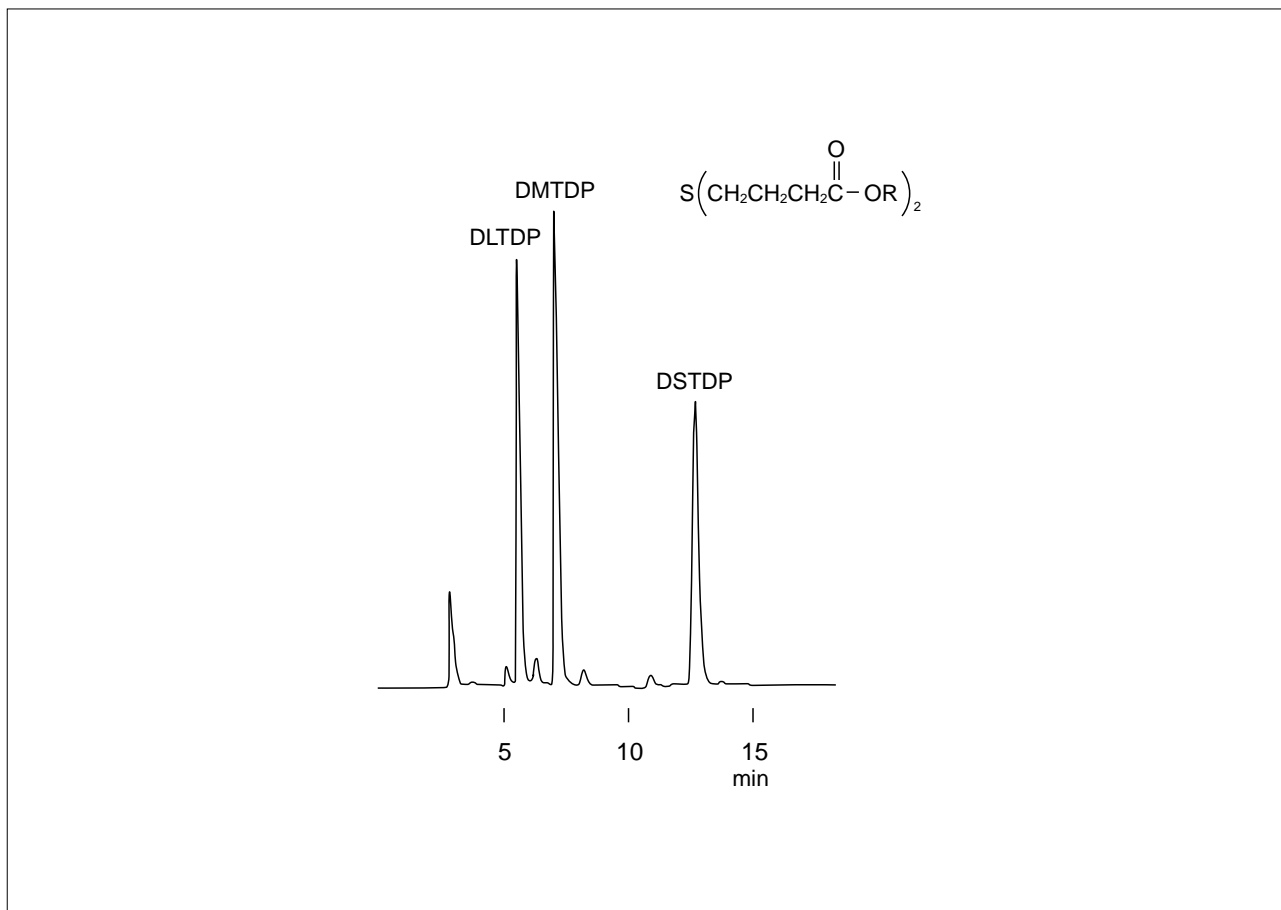Detection : UV-VIS Detector 210nm

Fig. 2.12.2 Analysis of dipropionate fatty acid ester

2.12 Analysis of anti-oxidants (3) - LC

•Explanation

c) Ultraviolet absorber

Ultraviolet absorbers fulfill the role of restricting the generation of radicals by absorbing light energy and converting it into low energy. Compounds such as salicylic acids, benzophenones and benzotriazols are used. These are generally used together with radical inhibitors and hydroperoxide decomposers. Shown in Fig. 2.12.3 is an example of the separation of an ultraviolet absorber.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

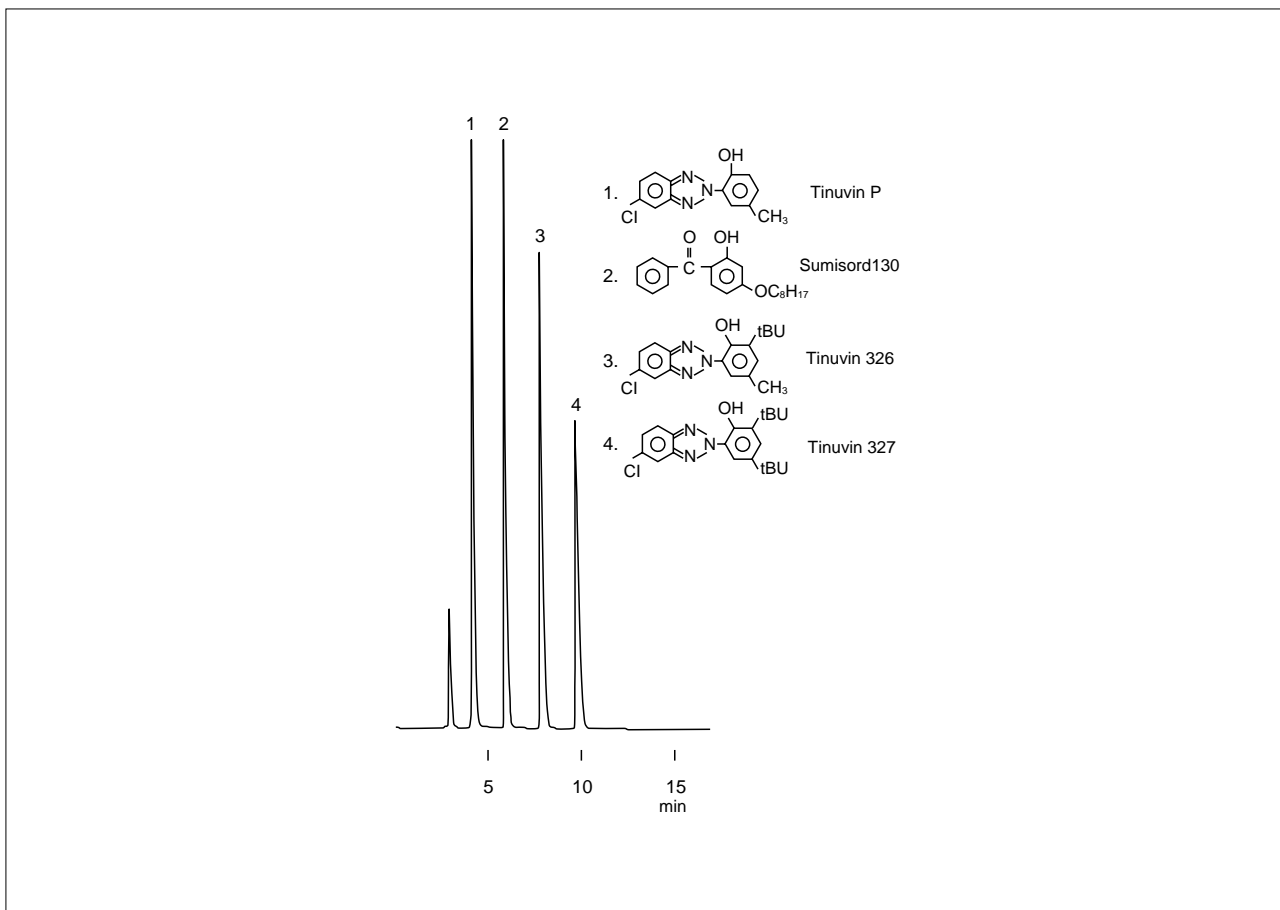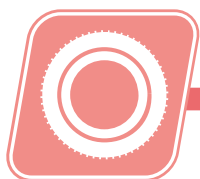|	
Model	: HPLC
Column	: Shim-pack CLC-ODS
	: (150mm × 6.0mm i.d.)
Mobile Phase	: Water/Methanol/THF=2/1/1 (v/v)
Flow Rate	: 1.0mL/min
Temperature	: 50°C
Detection	: UV-VIS Detector 210nm

Fig. 2.12.3 Analysis of an ultraviolet absorber

2.13 Analysis of lubricants - LC

•Explanation

Lubricants are important as they are additives that improve the workability of polymeric materials. Hence, by applying them effectively, the workability can be raised and productivity increased. Shown in Fig. 2.13.1 is an example of a separation of fatty acid amide, which boasts good lubricating characteristics among the numerous lubricants (internal lubricants).

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

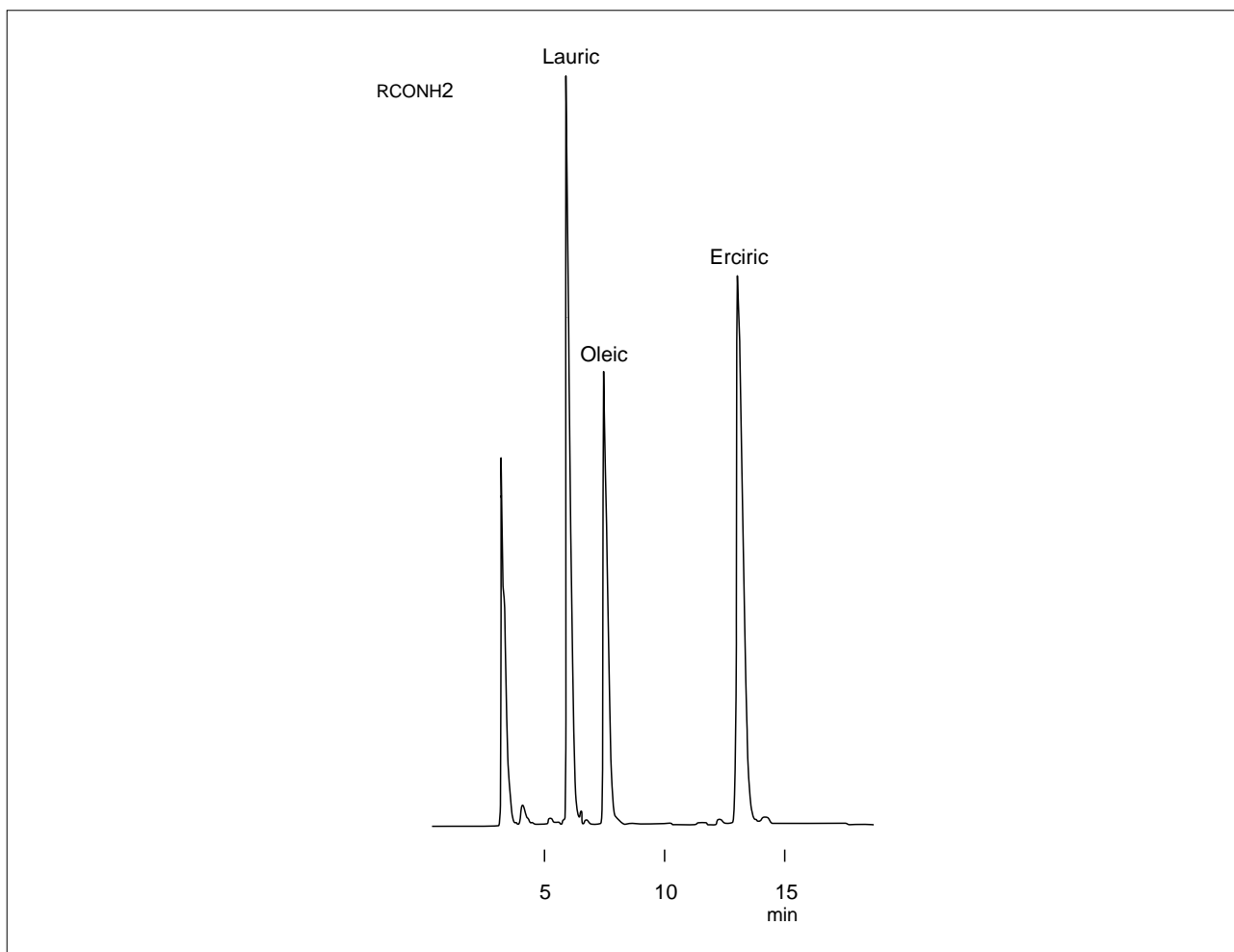|		
Model	:	HPLC
Column	:	Shim-pack CLC-ODS
	:	(150mm × 6.0mm i.d.)
Mobile Phase	:	Acetonitrile/THF=9/1 (v/v)
Flow Rate	:	1.0mL/min
Temperature	:	50°C
Detection	:	UV-VIS Detector 210nm

Fig. 2.13.1 Analysis of fatty acid amide

2.14 Analysis of polylactic acid - LC

●**Explanation**

This is an example of an analysis of polylactic acid, a material attracting attention as a biodegradable plastic (green plastics). Polylactic acid is also used in a variety of medical ingredients. Shown in Figs. 2.14.1 and 2.14.2 are the GPC chromatograms of regenerated polylactic acid.

●**Pretreatment**

Filtered with a non-aqueous membrane filter (0.45μm).

●**Analytical Conditions**

Model   : GPC
Column   : Shim-pack GPC-806,804,802
              : (Each 300mm × 8.0mm i.d.)
Mobile Phase : THF
Flow Rate   : 1.0mL/min
Temperature   : 40°C
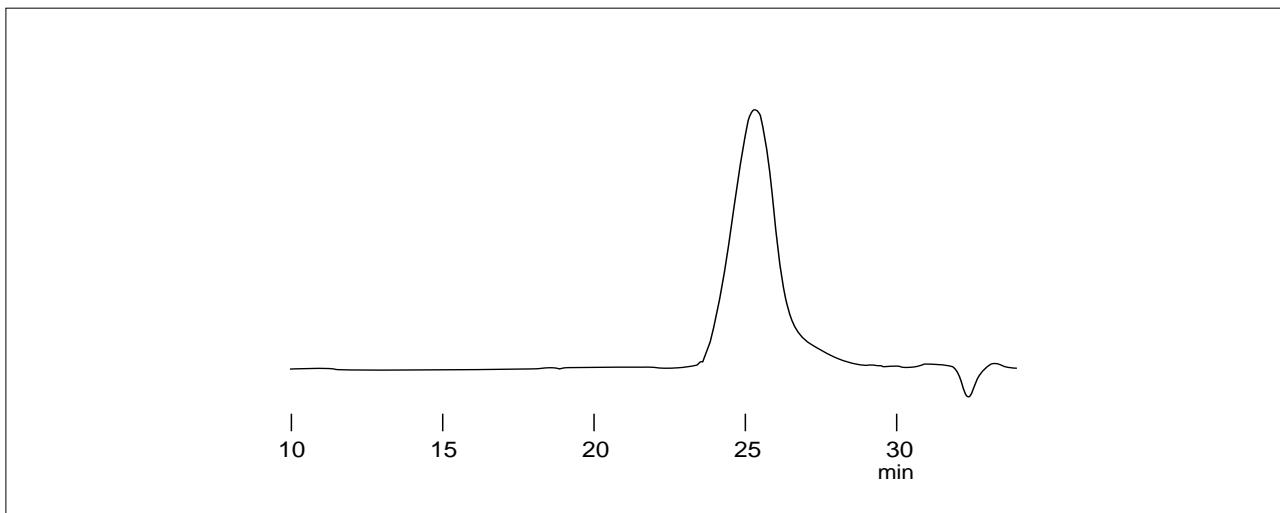Detection   : Refractive Index Detector

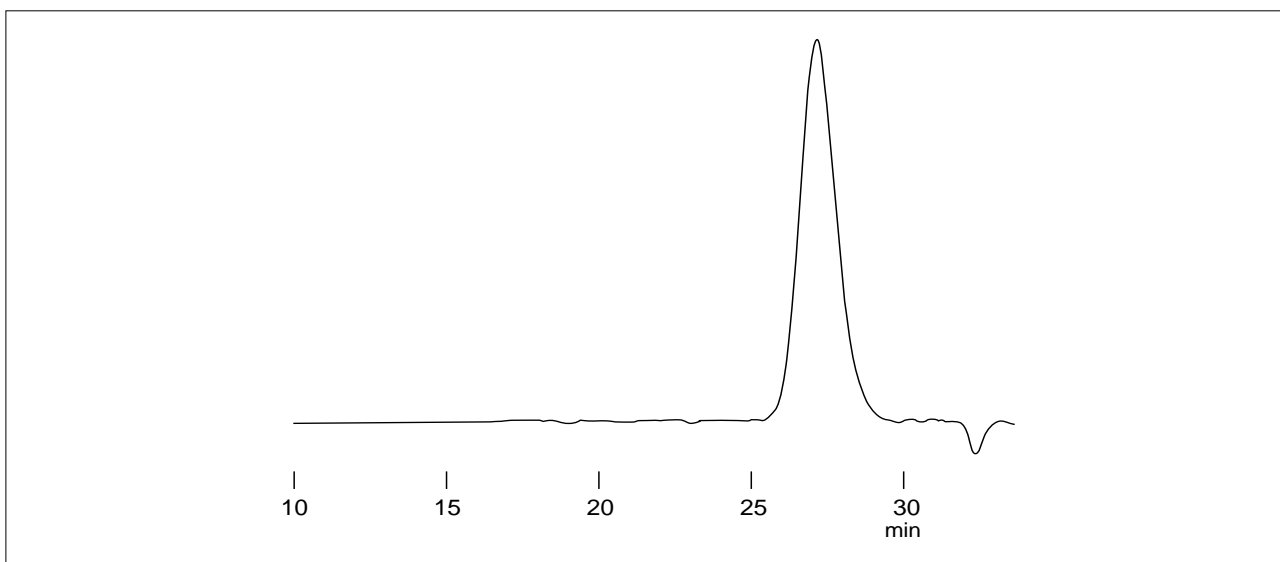Fig. 2.14.1 Analysis of regenerated polylactic acid(a)

Fig. 2.14.2 Analysis of regenerated polylactic acid(b)

2.15 Analysis of compounds dissolved in polymers (1) - GCMS

•Explanation

Some of the raw materials and additives used in the polymer manufacturing process are dissolved in the polymers. When the polymer is heated volatile components are forced out, and depending on its intended use this can be highly detrimental. In addition, solvents used in the formation of polymers and Freon gas used during foaming remain in the finished molded product as volatile components in minute quantities. The headspace gas of these volatile components are taken and measured with GC or GC/MS. Introduced here is an example of analysis of molded electrical parts.

•Analytical Conditions

Model   : Shimadzu GCMS-QP1100EX

Column   : CBP20 0.33mm × 50m i.d. df=0.5μm

Column Temp. : 50°C (1min)-10°C/min-200°C

Carrier Gas   : He 100kPa

Headspace Gas Collection

Sample Temp.   : 130°C (1hr)

Injection Volume : 0.8mL

Split Ratio   : 30 : 1

Fig. 2.15.1 is a TIC chromatogram. Peaks 1, 2 and A were examined closely.

It can be seen from the mass chromatograms (Fig. 2.15.2) of m/z41, 72, and 70 that compound A is present.

As shown in Figs. 2.15.3, 2.15.4, and 2.15.5, peak 1 (tetrahydrofuran), peak 2 (butanol), and peak A (2-methyl-propenal) could be identified from the mass spectra after a library data search.
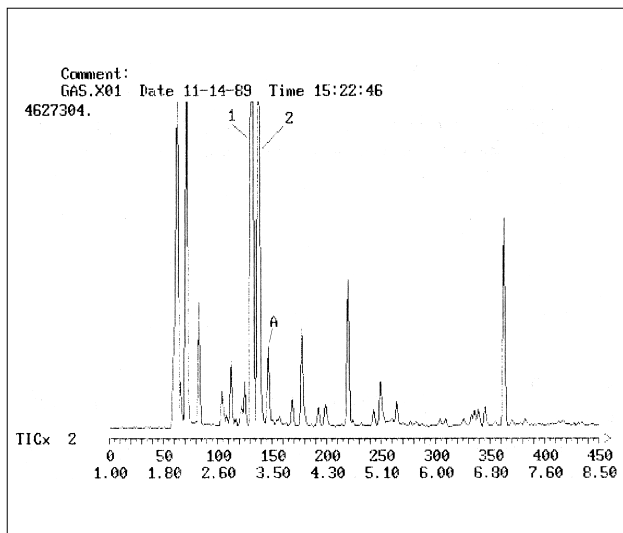

Fig. 2.15.1 TIC chromatogram of the headspace gas (130°C, 1hr) of a molded product
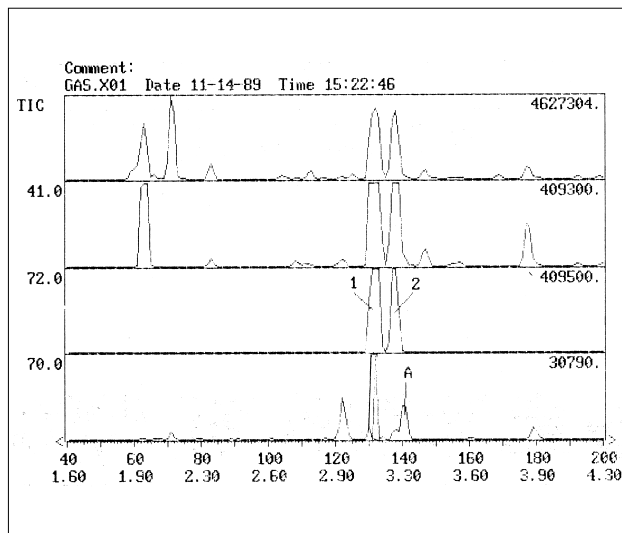

Fig. 2.15.2 Confirmation of the peaks 1, 2, and A by their mass chromatograms.

2.15 Analysis of compounds dissolved in polymers (2) - GCMS

As shown in Figs. 2.15.3, 2.15.4, and 2.15.5, peak 1 (tetrahydrofuran), peak 2 (butanol), and peak A (2-methyl-propenal) could be identified from the mass spectra after a library data search.
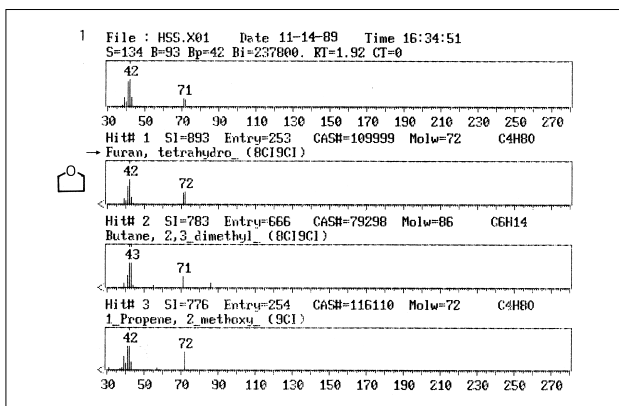

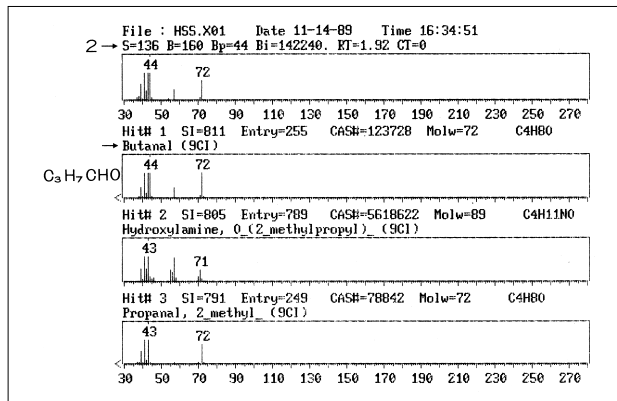Fig. 2.15.3 Data search for peak 1
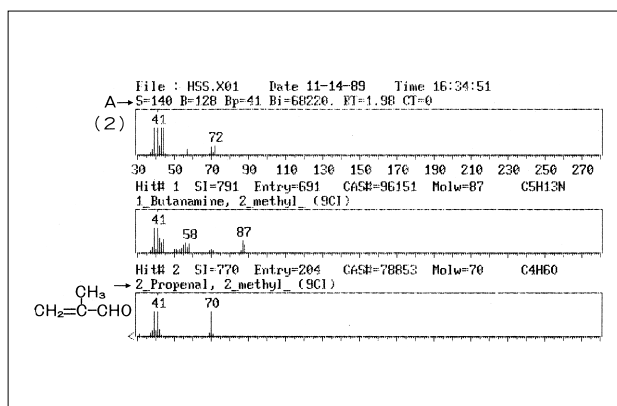

Fig. 2.15.4 Data search for peak 2

Fig. 2.15.5 Data search for peak A

Shown in Figs. 2.15.6 and 2.15.7 are the mass spectra of peaks 6 and 7. With the mass chromatograms of m/z41, 56, 91, and 106 that appears in these two mass spectra, peak 3 (toluene), peak 4 (ethyl benzene), peak 5 (p-xylene), peak 6 (butanol), peak 7 (m-xylene) and peak 8 (o-xylene) can be confirmed.
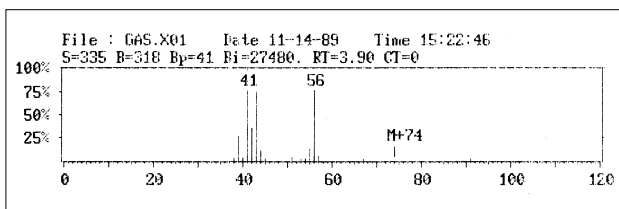

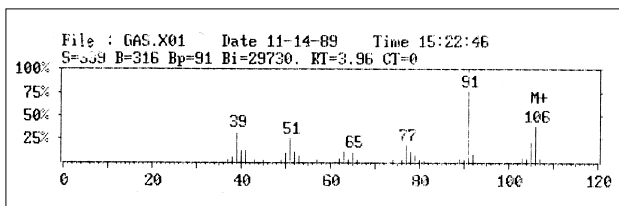Fig. 2.15.6 Mass spectrum of peak 6 (butanol)

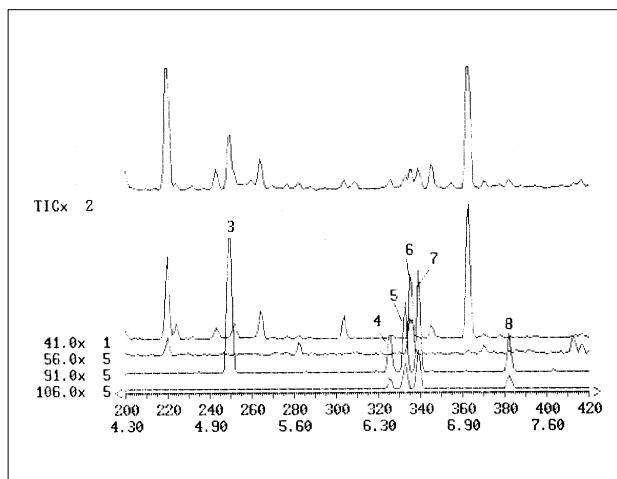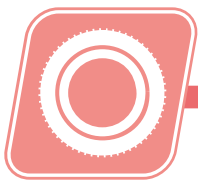Fig. 2.15.7 Mass spectrum of peak 7 (m-xylene)

Fig. 2.15.8 Confirmation of peaks 3-8 by the mass chromatogram

2.16 Analysis of tire rubber (1) - GCMS

•Explanation

Large quantities of carbon black are added to the rubber compounds of tire rubbers. As they do not dissolve in solvents, thermal decomposition gas chromatographs are use to obtain structural information. Figs. 2.16.1 and 2.16.2 are the results of analysis of gas generated at the pyrolysis temperatures of 450°C and 700°C. At 450°C only the rubber compounds are broken down, resulting in a relatively simple chromatogram. At 700°C carbon black is broken down as well, resulting in a complicated chromatogram.

•Analytical Conditions

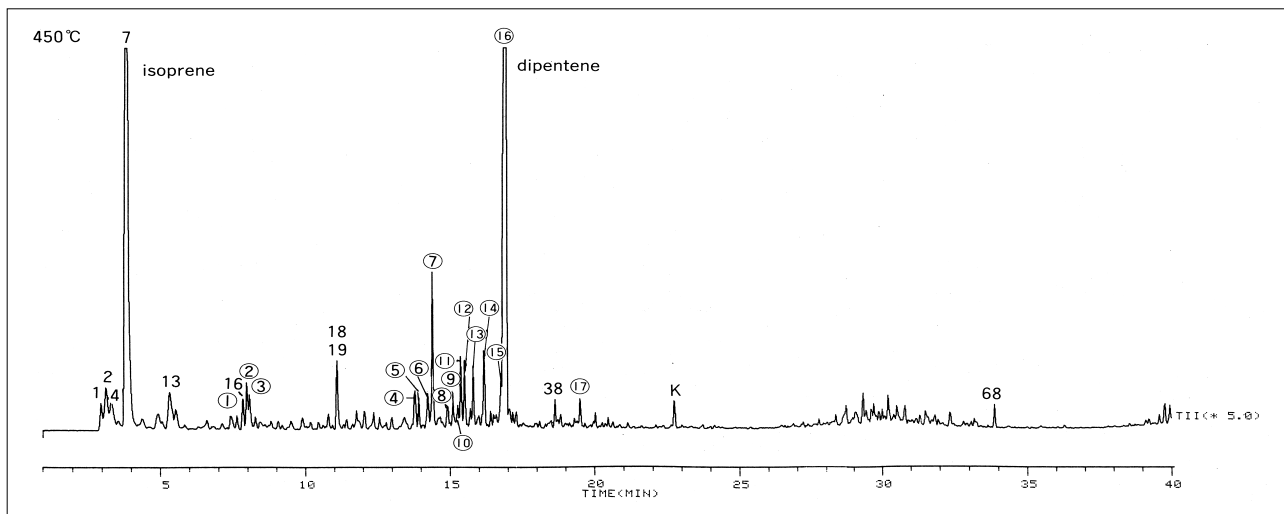|		
Model	:	Shimadzu GCMS-QP5000
Column	:	CBJ1 0.25mm × 30m i.d. df=0.25μm
Column Temp.	:	50°C (1min)-7°C/min-320°C
Carrier Gas	:	He 100kPa
PyrolysisTemp.	:	450°C,700°C
InterfaceTemp.	:	250°C
Split	:	30:1

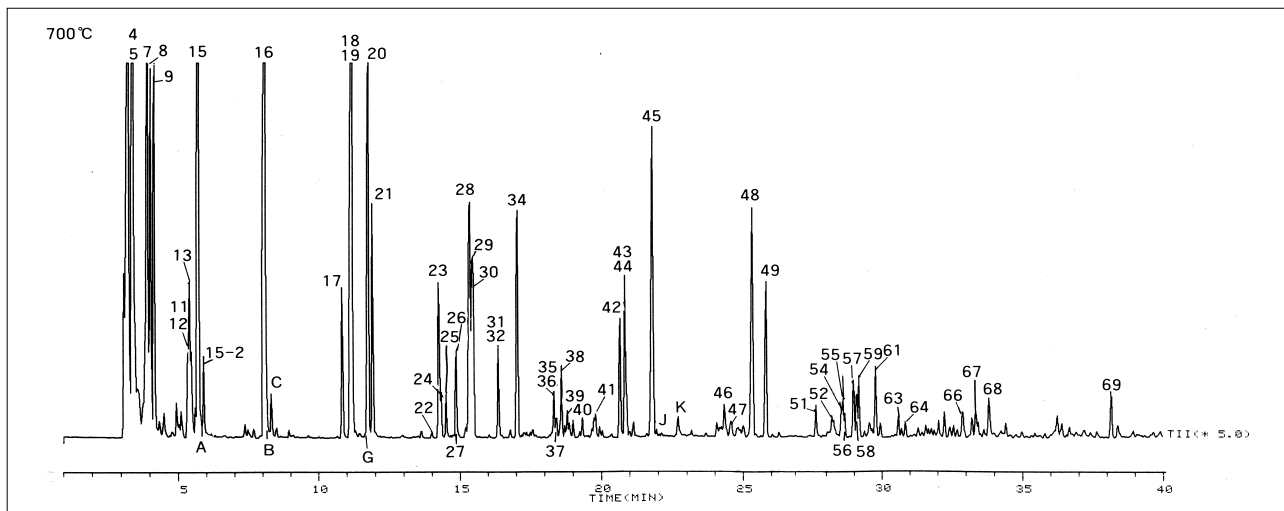Fig. 2.16.1 Total ion chromatogram of the decomposed products generated at 450°C

Fig. 2.16.2 Total ion chromatogram of the decomposed products generated at 700°C

2.16 Analysis of tire rubber (2) - GCMS

Fig. 2.16.3 is the mass chromatogram at 450°C. Isoprene (C_6H_8 peak 7) and diterpene ($C_{19}H_{16}$ peaks (5)-(16)), which are monomers of natural rubber, have been detected.
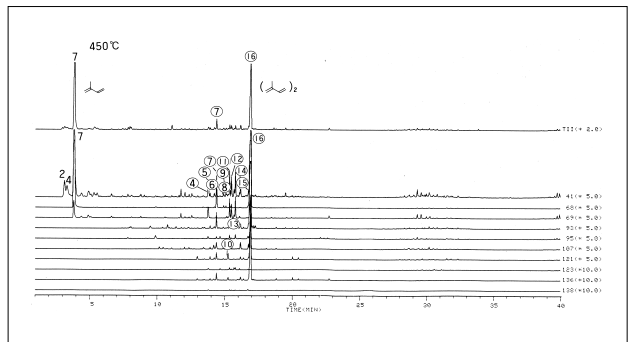
Fig. 2.16.3 Mass chromatogram at 450°C

At 700°C the decomposed products generated consist mainly of aromatic hydrocarbons, and there are less isoprene compounds. Of these many peaks, Figs. 2.16.4 and 2.16.5 examines the S-compounds.

Figs. 2.16.6 and 2.16.7 show the results of data searches on the B and J mass spectra in the chromatograms. They have been respectively identified as 2-methylthiophene and benzo thiophene.

Fig. 2.16.4 Mass chromatogram-1 examining the S-compounds

Fig. 2.16.5 Mass chromatogram-2 examining the S-compounds

Fig. 2.16.6 Results of data search on peak 'B'
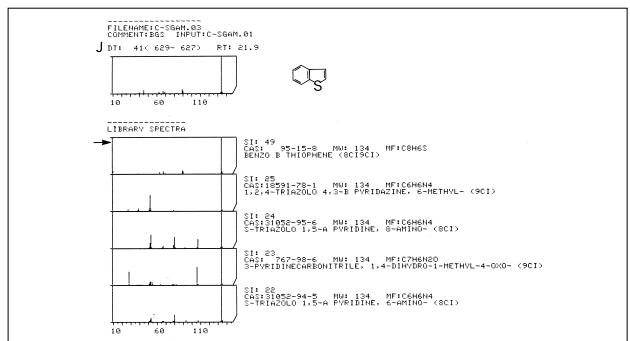
Fig. 2.16.7 Results of data search on peak 'J'

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Plastics / Rubber
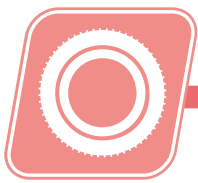
2.17 Analysis of polymers (epoxy resin) (1) - GCMS

•Explanation

Introduced here is an example of the measurement of gas generated during the hardening reaction of epoxy resin using the TG/GCMS system. This system combines 2 types of analytical instruments, the thermogravimeter device(TG) and the Gas Chromatograph Mass Spectrometer (GCMS).
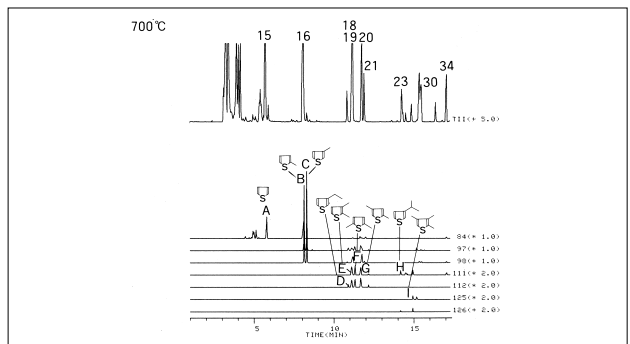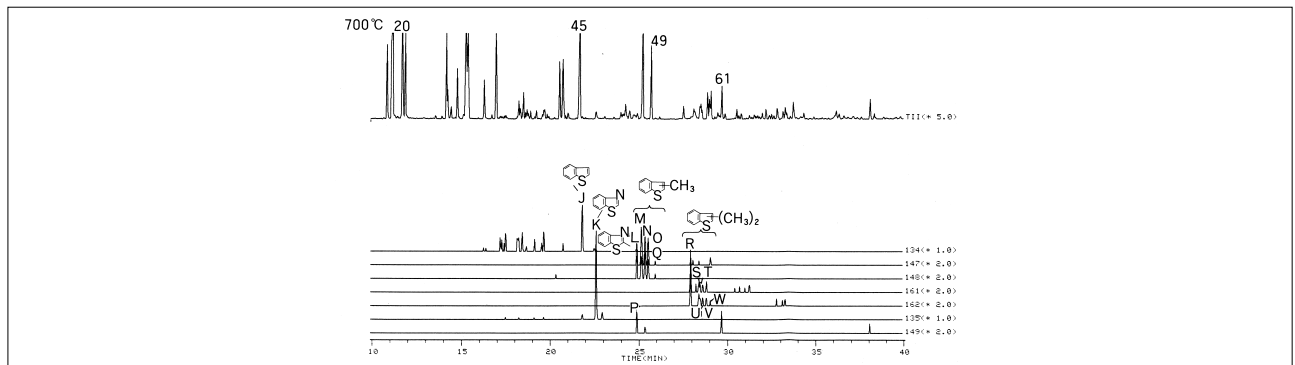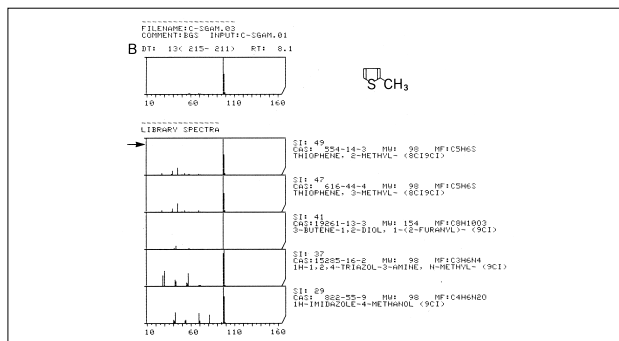
For the measurement shown in Fig. 2.17.1, Epicoat 828 from Shell was used for the epoxy resin, and heterocyclic diamine commonly available on the market (Epomate) was used as the hardener. A weight loss of approximately 1% was detected over 45°C to 240°C. In addition, the D-TG curve features a broad peak, with maximums at 125°C and 180°C. Decomposition began around 240°C after further heating.

Shown in Fig. 2.17.2 are the mass spectra of gases generated at 180°C, 300°C, 330°C and 350°C. It can be seen that H_2O (m/z18) is being generated from 180°C onwards.

•Analytical Conditions

Model   : Shimadzu GCMS-QP1000

He   : 200mL/min

Temp.   : 40°C-10°C/min-400°C

Ion Source Temp. : 250°C

TGA   : TGA-50
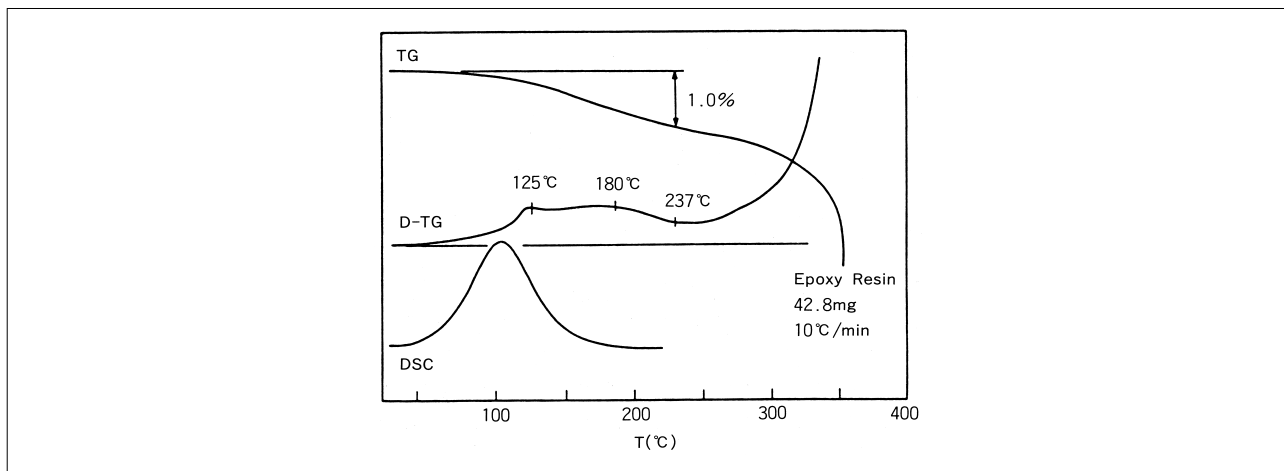
Fig. 2.17.1 DSC, TG, and D-TG curves of the epoxy resin hardening and decomposition reactions
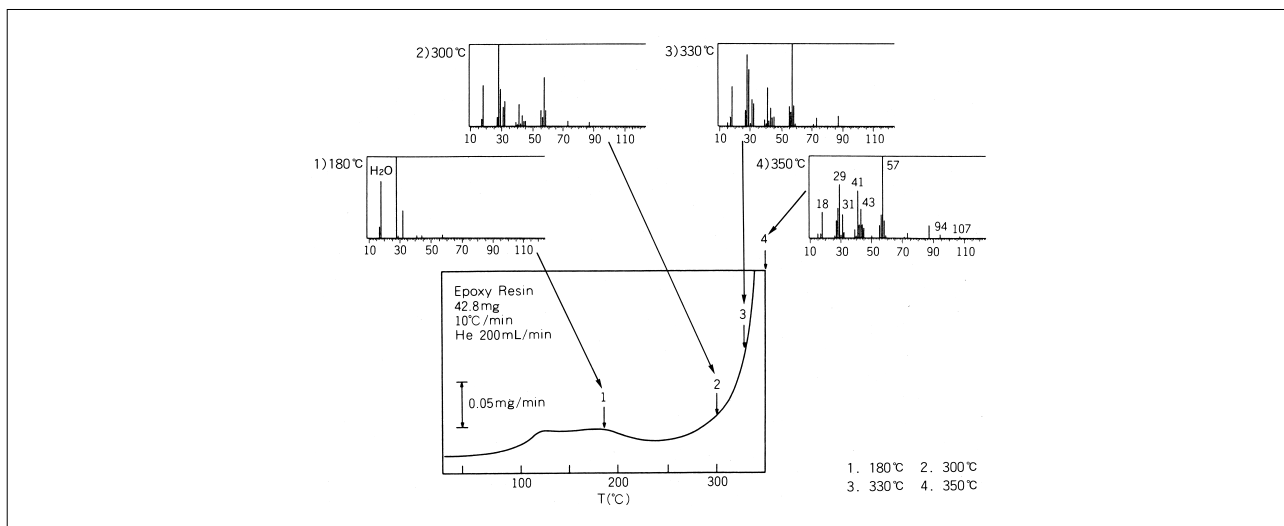
Fig. 2.17.2 D-TG curve of epoxy resin

2.17 Analysis of polymers (epoxy resin)(2) - GCMS

Shown in Fig. 2.17.3 is the mass chromatogram of the ions (m/z) seen in the mass spectra that was measured. The mass chromatogram of m/z18 (H_2O) matches the D-TG curve in Fig. 2.17.1 with the broad peak and the two maximums.
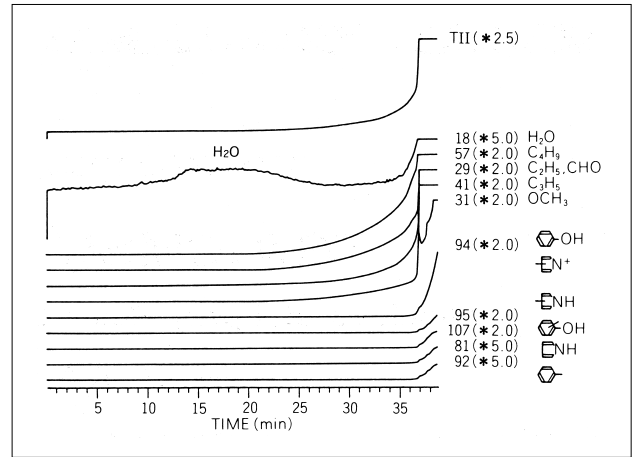
Fig. 2.17.3 Mass chromatogram of gas generated from epoxy resin

For Fig. 2.17.4, all the gas compounds generated have been measured by gas chromatography employing the GCMS. Fig. 2.17.5 estimates the components which correspond to epoxy resin out of the compounds detected.
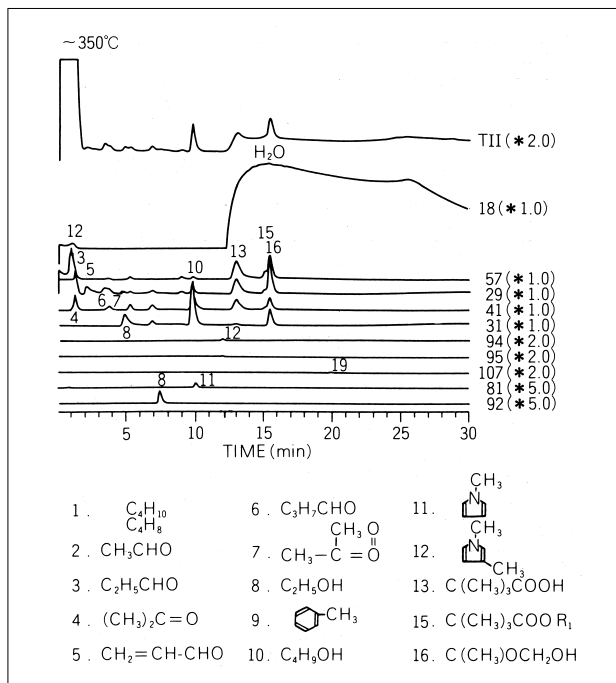
Fig. 2.17.4 GCMS chromatogram by the thermal decomposition GC of epoxy resin

Column   : 25% PEG -1000
Column Temp. : 80°C
Carrier Gas   : He 40mL/min
Interface Temp. : 250°C
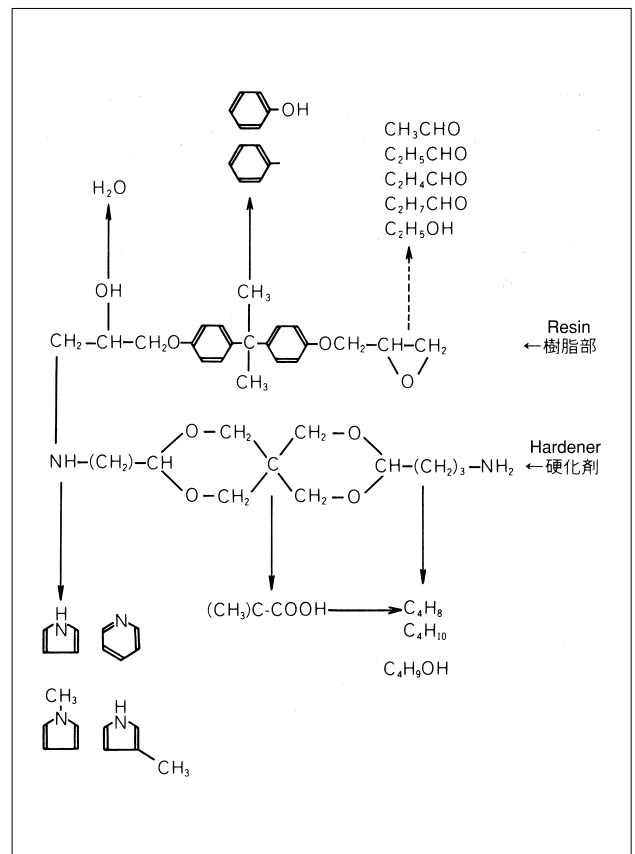
Fig. 2.17.5 Structural formula of epoxy resin

2.18 Analysis of polymers (polystyrene) - GCMS

•Explanation

Various analytical methods are used in the analysis of polymeric materials. When using gas chromatography (GC) or a gas chromatography mass spectrometer (GCMS), the polymer is broken down by heating and the gas generated is analyzed. Introduced here is an example of analysis of polystyrene using a pyrolyzer (PYR-4A).

Shown in Fig. 2.18.1 are the mass chromatograms (MC) of the molecular ions of each component. In table 2.18.1 the results of qualitative determination are shown.

•Analytical Conditions

Model	:Shimadzu GCMS-QP5000
Column	:CBJ1 0.25mm $\times$ 30m df=0.25
Column Temp.	:50°C (1min)-7°C/min-280°C
Carrier Gas	:He 100kPa
PyrolysisTemp.	:500°C
Interface Temp.	:250°C
Split	:50:1

1 CO₂

2 C — ⬡ Toluene

3 C=C — ⬡ Styrene

4 C=C(C) — ⬡ α-Styrene

5 C—C=C — ⬡ Propynyl Benzene

6 C—⬡—C—⬡,⬡—C—C—⬡

7 C—C—⬡—C—⬡

8 C=C—⬡—C—C—⬡ Dimer

9 C=C—⬡—C=C—C—C—⬡

10 C=C—⬡—C—C—⬡—C—C—⬡ Trimer

Table 2.18.1 Results of qualitative determination
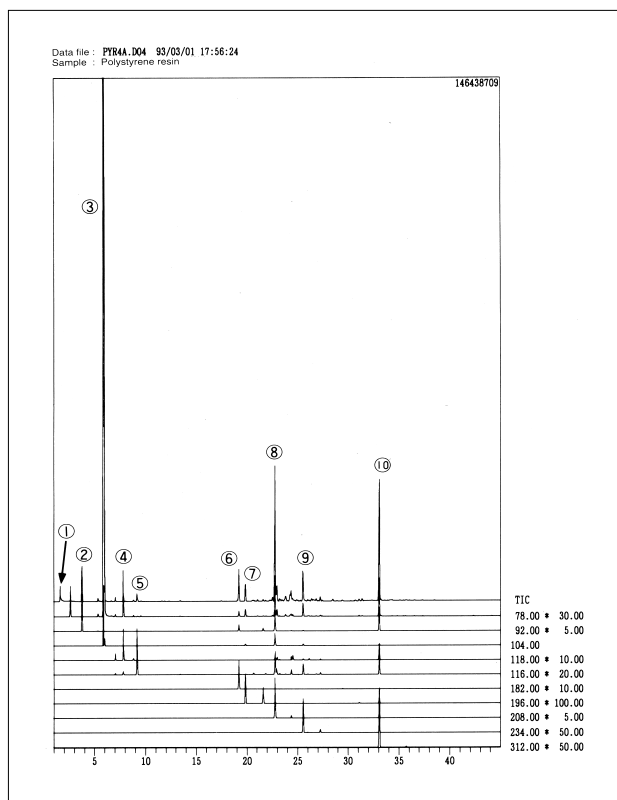
Fig. 2.18.1 Mass chromatogram of polystyrene (MC)

2.19 Analysis of polyethylene using the SiC sampler - FTIR

•Explanation

The amount of time and work involved in the pretreatment of samples has become significantly reduced due to developments in measurement methods utilizing the FTIR and its accessories.

For example, for large molded goods or plastic pellets etc., methods of measurement include thinly slicing and removing a part of the sample, or crushing the sample into powder form and measuring it with the KBr pellet method. With the SiC sampler a sample can be scraped with the SiC (silicon carbide) sandpaper stuck onto the holder and the sampling carried out directly on the sandpaper. The spectrum can be measured by mounting the holder onto the diffuse reflection accessory.

•Results

In Fig. 2.19.1 the SiC sampler was employed to scrape the surface of the polyethylene tank before and after use. The spectra were measured by the diffuse reflection method.

When the 2 results are compared, the spectrum of the polyethylene tank after use features a >C=O group peak due to peroxides, ester, and ketone around the $1700cm^{-1}$ region, and a peak of the hydroxyl group in the $3400cm^{-1}$ region. This is due to ultraviolet radiation.

In addition, for Fig. 2.19.2 the surface of 3 types of polyethylene plates were scraped employing the SiC sampler and their spectra measured using the diffuse reflection method. The 3 polyethylene plates differ in the temperatures at which they were formed.

The difference in the degree of oxidation due to the heating appears in the $1700cm^{-1}$ and $3400cm^{-1}$ regions.

•Analytical Conditions

Accessories   : DRS-8000, SiC Sampler

Resolution   : $4cm^{-1}$

Accumulation   : 200 (Fig. 2.19.1)

                           400 (Fig. 2.19.2)
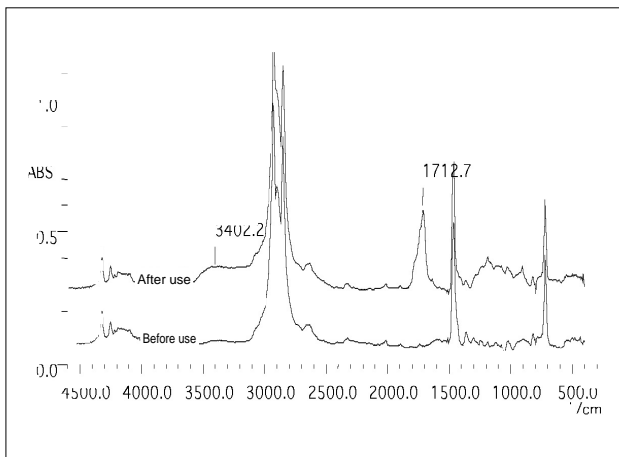
Apodization   : Happ-Genzel

Detector   : DLATGS

Fig. 2.19.1 Spectra of the polyethylene tank before and after use
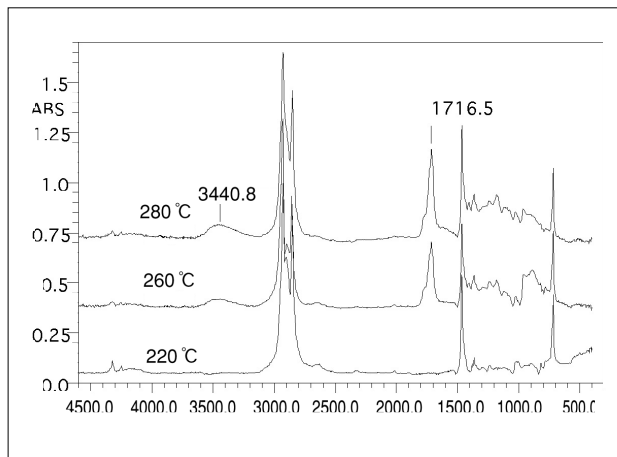
Fig. 2.19.2 Polyethylene plates of different heating temperatures
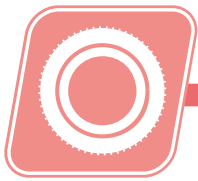
2.20 Analysis of the state of polyethylene deterioration - FTIR

•Explanation

Polymeric materials such as plastics and rubber deteriorate when exposed to light or heat. Oxygen plays a major role in the deterioration (oxidation) of polymers, and this bonding with oxygen appears in the infrared region. When polymers are oxidized, the state of oxidation on the surface differs greatly from that of the insides of the polymer. An effective method of investigating the state of oxidation from the surface to the interior is to use an infrared microscope.

Polyethylene was thermally oxidized for 10 minutes at 200°C and then cut to a thickness of approximately 80µm using a microtome. It was then measured by the transmission method using a microscope.

•Results

Fig. 2.20.1 is a spectrum of the surface layer. Due to thermal oxidation, absorption appears in the 3,422 cm^{-1} region due to the -OH group, the 1,780 cm^{-1} region due to the peroxide >C=O group, the shoulder peak in the 1,740 cm^{-1} region due to the ester >C=O group, the ketone >C=O group in the 1,717 cm^{-1} region, and the -C-O-C- group in the 1,173 cm^{-1} region. The spectra for every 100µm of the sample to a depth of 1000µm from the surface is overlaid in Fig. 2.20.2. It can be seen that the diffusibility of oxygen due to thermal oxidation decreases with depth.

•Analytical Conditions

Resolution   :4cm^{-1}
Accumulation :100
Apodization   :Happ-Genzel
Detector   :MCT
Aperture   :20 × 100µm
Step   :100µm
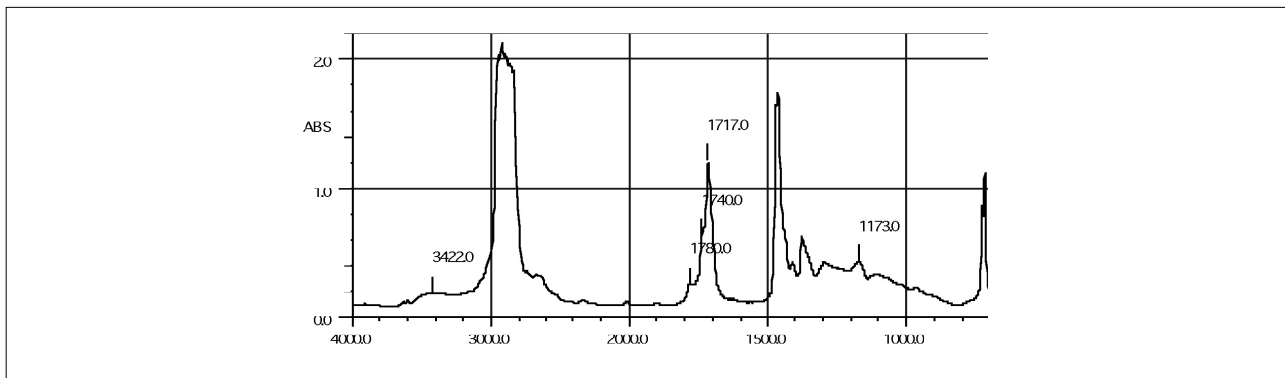
Fig. 2.20.1 Spectrum of the surface layer of polyethylene thermal oxides
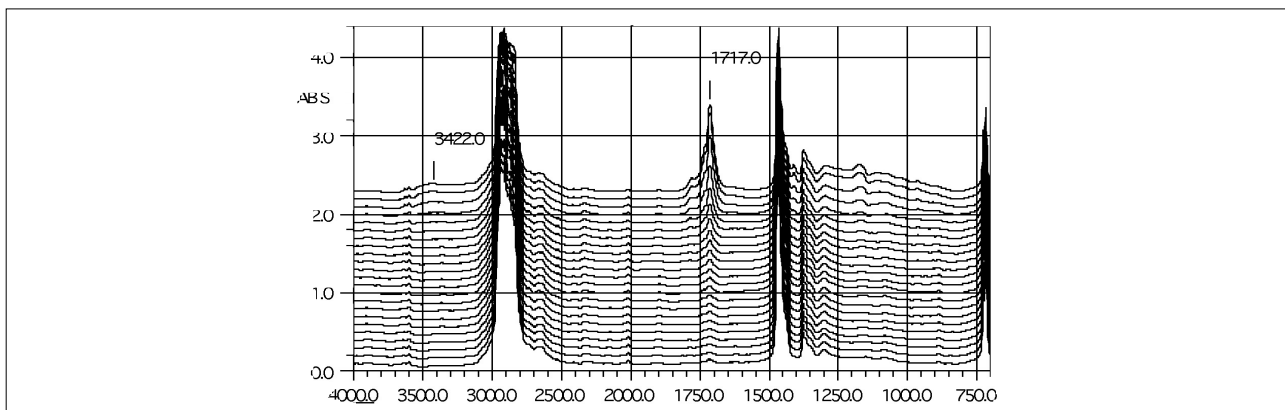
Fig. 2.20.2 Spectra of each layer of polyethylene thermal oxides

2.21 Analysis of multi-layer films using an infrared microscope - FTIR

•Explanation

Multi-layer films are often used in the packaging of food products and medical supplies. The most common method used to identify the components in each layer of multi-layer films involves slicing a section of the film and measuring the sample fragment gained by the transmission method using an infrared microscope. With this method, the spectrum of a layer can be measured if the film thickness is more than approximately 10µm.

•Pretreatment / Results

A section of the film was sliced using a microtome set to a thickness of 10µm. The fragment gained is placed on top of the diamond cell and crushed. The resultant substance is measured using an infrared microscope. Fig. 2.21.1 is a magnified image of the sample fragment before crushing, and Fig. 2.21.2 is the magnified image after crushing.

The spectra of each layer 1 to 7 indicated in Fig. 2.21.2 are shown in Fig. 2.21.3. The spectra of each layer shows absorption thought to be due to polyethylene terephthalate for the 1st layer, polyethylene for layers 2, 6, & 7, nylon for the 3rd layer, and ethylene vinyl acetate for the 4th and 5th layers.

•Analytical Conditions

Resolution : $8 cm^{-1}$

Accumulation : 100

Apodization : Happ-Genzel

Detector : MCT
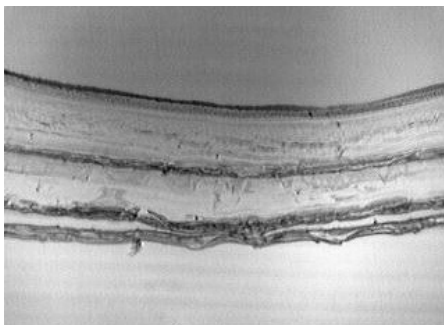
Fig. 2.21.1 Magnified image of the sample fragment
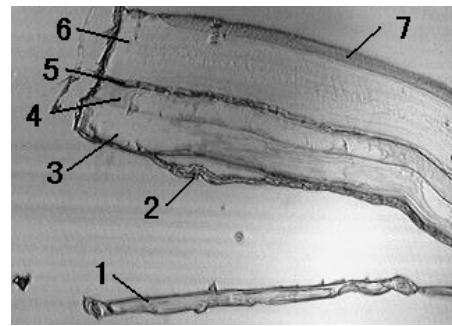
Fig. 2.21.2 Magnified image of the sample fragment after compression
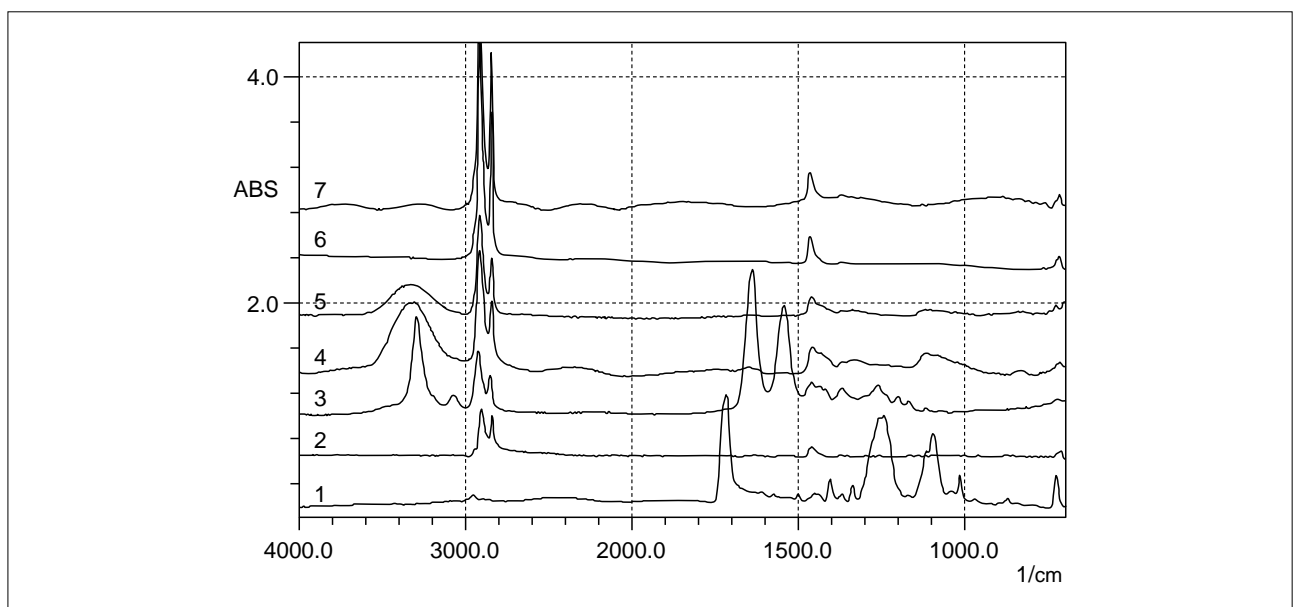
Fig. 2.21.3 Infrared spectra of each layer

2.22 Analysis of the hardening process of epoxy adhesive (1) - FTIR

•Explanation

Among polymeric materials there are those whose molecular structure changes over time as they are heated, exposed to light, or mixed. FTIR is an effective method of measurement for tracking these changes. It's advantage is that it can track multiple absorption peaks at the same time. As an example of such a measurement, the measurement of the hardening process of epoxy adhesive is introduced here.

Epoxy adhesive hardens upon mixing of the main ingredient and a hardener, following the process shown in Fig. 2.22.1. This process was measured over a fixed time interval, and the nature of the changes in the functional groups investigated.

•Pretreatment

2 liquid mixture type epoxy adhesive was mixed and then smeared on the KBr aperture plate of a high temperature heating cell. Measurement was carried out at 5 minute intervals over 60 minutes at 80°C.

•Results

From the spectrum in Fig. 2.22.2 it can be seen that there are hardly any changes in the absorption peculiar to the alkyl groups, carbonyl groups, and benzene rings. On the other hand it can be seen that the peaks of the epoxy, amino and hydroxyl groups are gradually changing. In Figs. 2.22.3 and 2.22.4 the peak regions of the epoxy and hydroxyl groups are magnified. Shown in Fig. 2.22.5 are the time course curves of the surface integrals of 3,650 to 3,140cm^{-1} (hydroxyl group) and 925 to 899cm^{-1} (epoxy group). In addition, shown in Fig. 2.22.6 are the time course curves of the epoxy group measured at the cell temperatures of 60°C, 80°C, and 100°C.

•Analytical Conditions

Accessory   : High temperature cell

Resolution   : 8cm^{-1}

Accumulation : 1min

Apodization   : Rectangular

Detector   : DLATGS
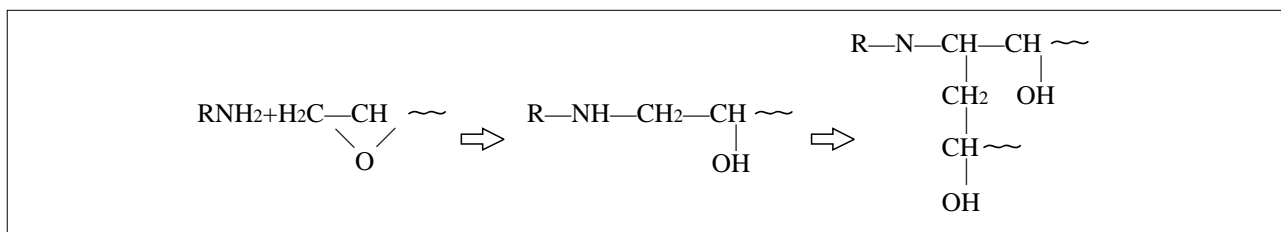
Fig. 2.22.1 Hardening process of epoxy adhesive
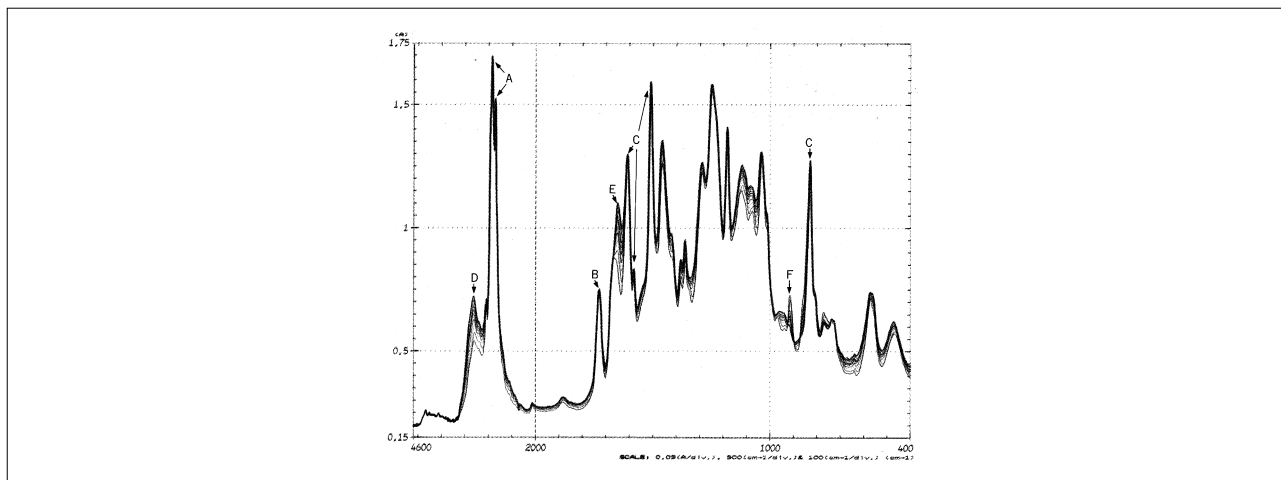
Fig. 2.22.2 Infrared spectrum of epoxy adhesive
(A: alkyl group B: carbonyl group C: benzene ring D: hydroxyl group E: amino group F: epoxy group)

2.22 Analysis of the hardening process of epoxy adhesive (2) - FTIR
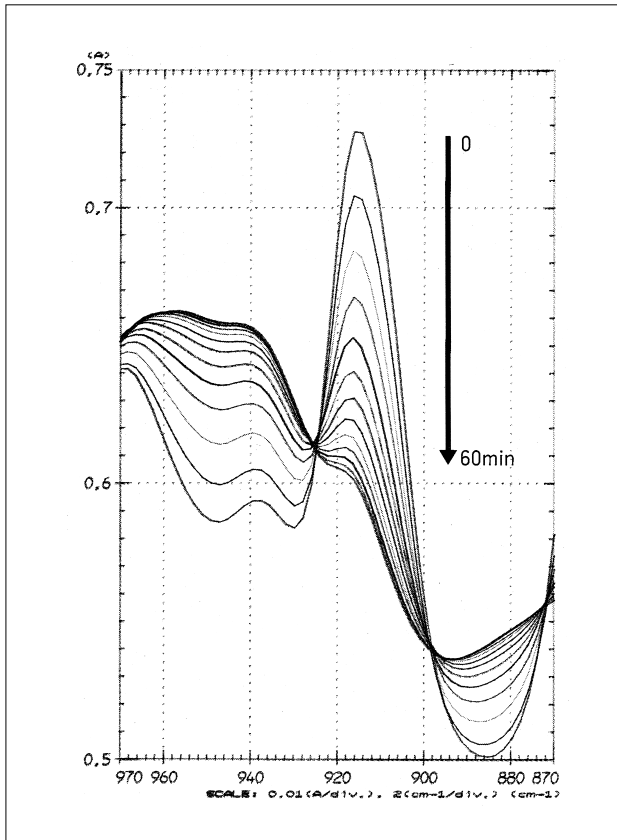
Fig. 2.22.3 Infrared spectra of the epoxy group
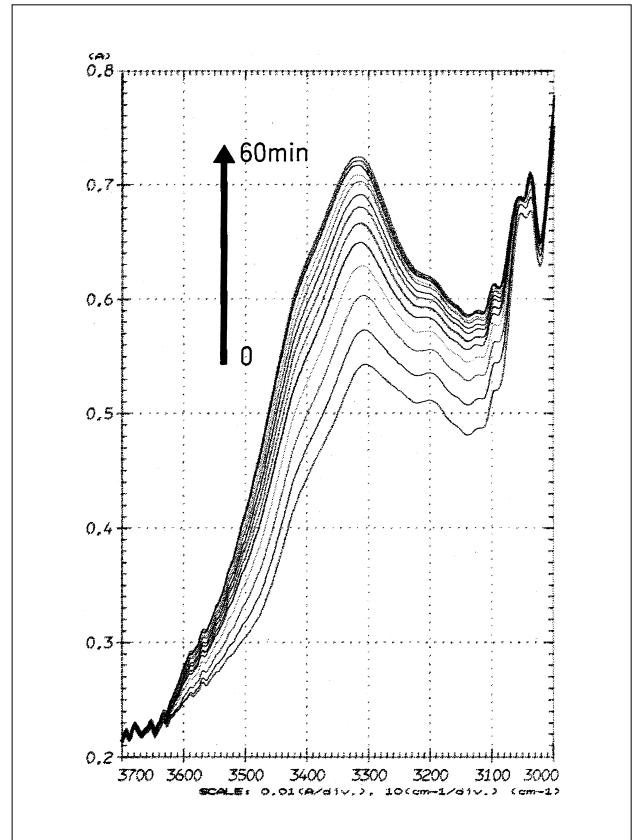
Fig. 2.22.4 Infrared spectra of the hydroxyl group
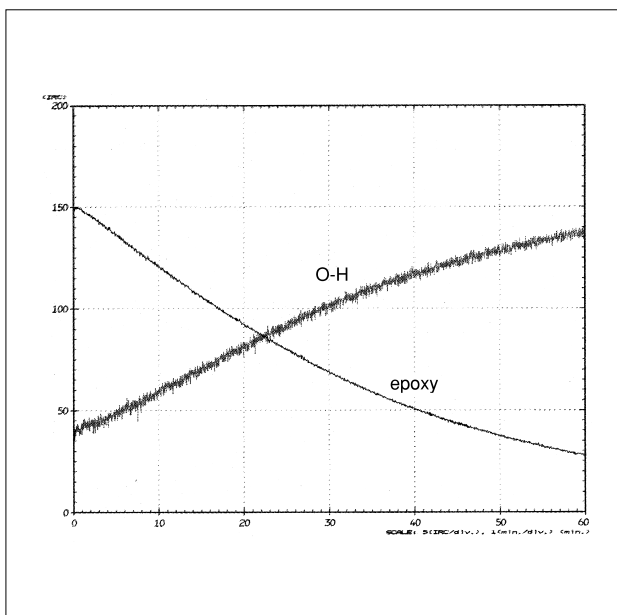
Fig. 2.22.5 Time course curves of the hydroxyl and epoxy group
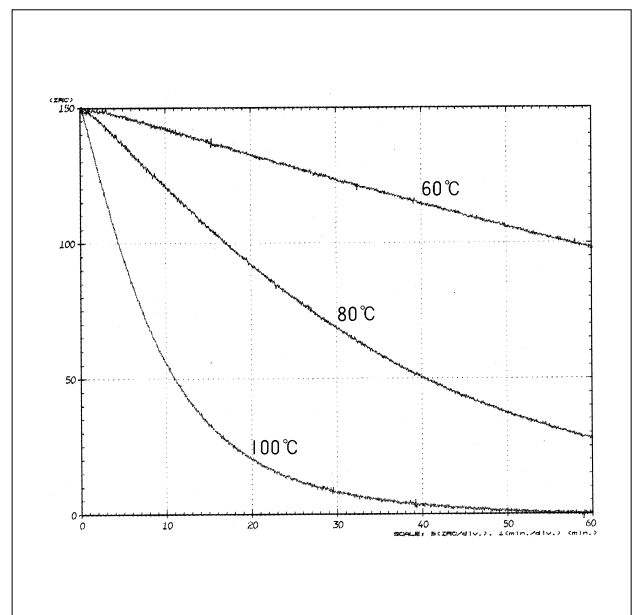
Fig. 2.22.6 Time course curves of the epoxy group at each temperature

2.23 Analysis of black rubber using the ATR method - FTIR

•Explanation

The infrared spectrum of rubber is commonly measured by either measuring the liquid components obtained by dry distillation using a liquid cell, or by direct measurement using the ATR method (Attenuated Total Reflection method). The ATR method has the advantage of requiring no pretreatment, making measurement simple. However, when measuring black rubber, which contains a lot of carbon, the KRS-5 or ZnSe prisms that are normally used do not work very well, and in such cases a Ge prism with a higher refractive index needs to be used.

When a Ge prism is used to measure black rubber, the peak intensity is weakened and the baseline of the absorbance spectrum tends to rise on the right when compared to other prisms. In addition, a characteristic of the peak intensities in the ATR method are that, the lower the wavenumber, the greater the peak intensity. Therefore, the intensity should be corrected (ATR correction) after measurement with the reciprocal of the wavelength to bring it closer to the transmittance spectrum, so that there is a greater hit rate when running a library search.

•Results

Fig. 2.23.1(a) shows the ATR spectrum of black rubber, (b) shows the ATR corrected spectrum, while (c) shows the spectrum after further correction to the baseline. The results of searching the library database for this spectrum is shown in Fig. 2.23.2. The lower spectrum in Fig. 2.23.2 is the unknown spectrum, while the upper spectrum is a spectrum from the library that resembles the unknown spectrum. From this, it is expected that the unknown spectrum is that of an acrylonitrile-butadiene compound.

•Analytical Conditions

Accessory   : ATR-8000(IRE : Ge)

              (IRE : Internal Reflection Element)

Resolution   : 4cm^{-1}

Accumulation : 100

Apodization   : Happ-Genzel

Detector   : DLATGS
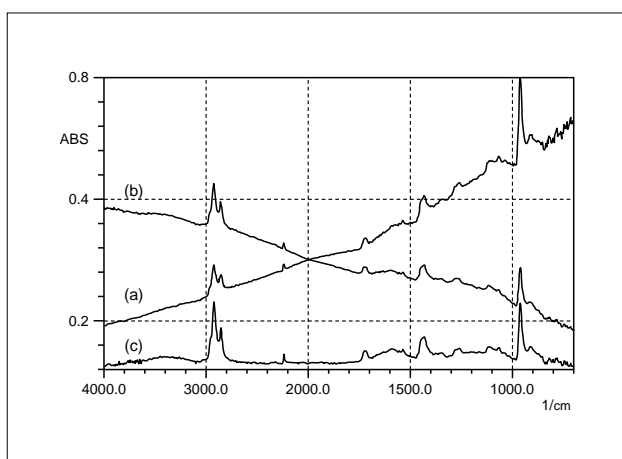
Fig. 2.23.1 ATR spectrum of black rubber
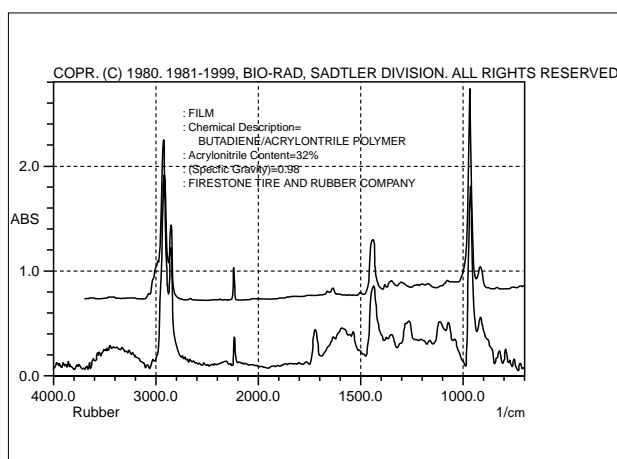
Fig. 2.23.2 Search results

2.24 Quantitation of vinyl acetate in EVA - FTIR

•Explanation

Ethylene/vinyl acetate Copolymer (EVA) has a good degree of transparency and is used in a variety of applications such as fertilizer bags, wrapping film, bottles, and tubes. The elasticity and thermoplasticity of EVA increases with the amount of vinyl acetate contained. There are a number of ways of quantifying the vinyl acetate content in EVA, and the method introduced here is the comparatively simple ATR method using the FTIR.

References

Polymer Analysis Handbook, Japan Society for Analytical Chemistry, Polymer Analysis Research Group Issue, Asakura Publishing (Japanese)

•Results

Shown in Fig. 2.24.1 are the results of the measurement of samples with vinyl acetate contents of 0, 5, and 7% using a horizontal ATR system. It can be seen that the greater the content of vinyl acetate, the greater the intensity of the C=O peak in the $1,740cm^{-1}$ region. Fig. 2.24.2 is a calibration curve generated by taking the peak ratio to the C-H peak of the $1,460cm^{-1}$ region. Fig. 2.24.3 shows the result of measuring the unknown sample using this calibration curve.

•Analytical Conditions

Accessory	: Horizontal ATR(IRE : ZnSe)
Resolution	: $4cm^{-1}$
Accumulation	: 40
Apodization	: Happ-Genzel
Detector	: DLATGS
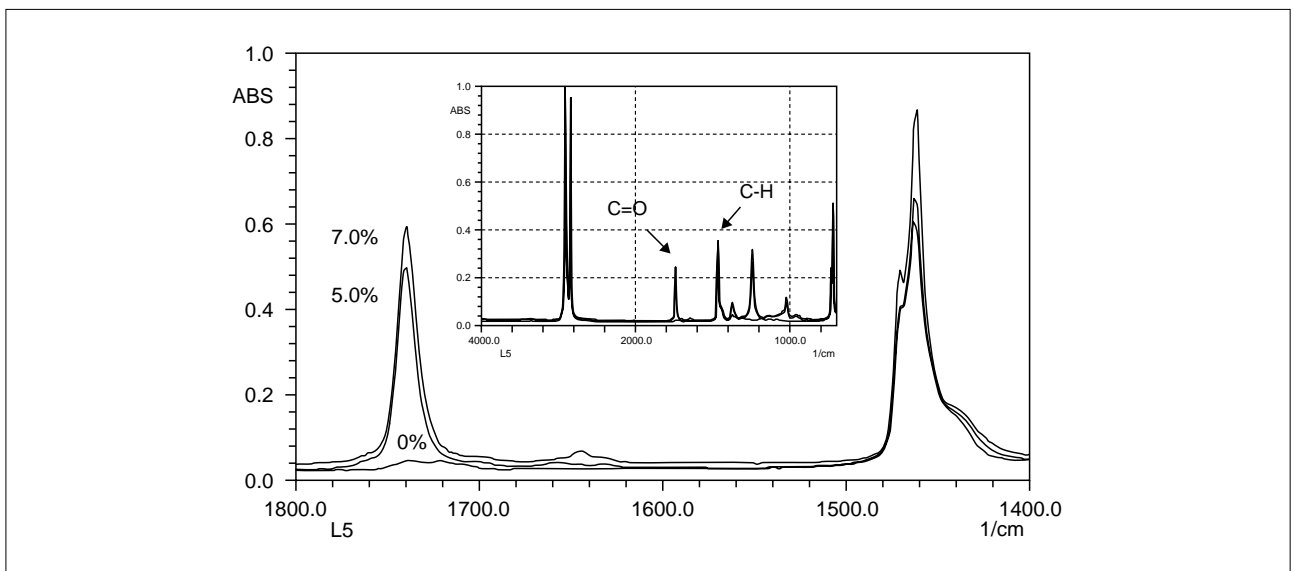
Fig. 2.24.1 ATR spectra of EVA
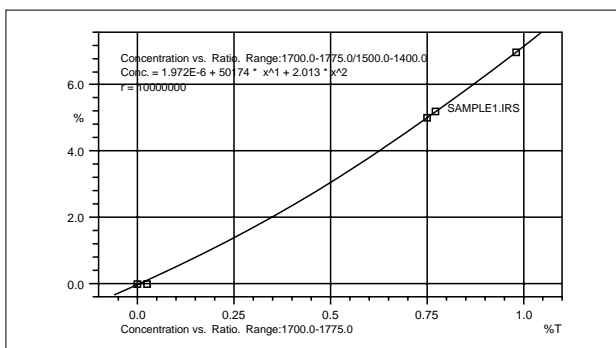
Fig. 2.24.2 Calibration curve of vinyl acetate

Text   : sample①
Cal. file : C:¥peak2.CAL
Time   : Sun Oct 17 12:48:49 1999

Range		Ratio	Conc. [%]
1700.0	1775.0	0.771	**5.184**
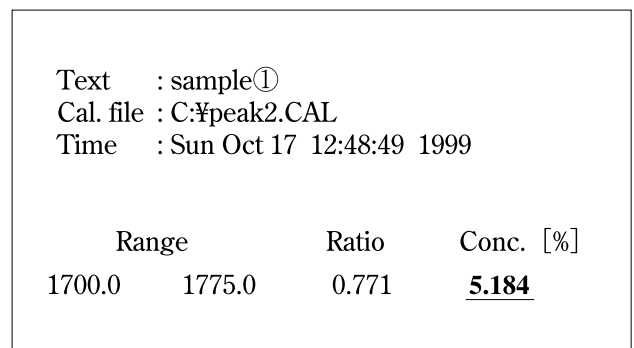
Fig. 2.24.3 Result of quantitation
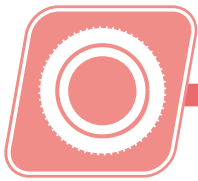
2.25 Measuring the thickness of films - UV

•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 an 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 0.5µm, as can be seen in Fig. 2.25.1, while measurements can be made to approximately 60µm at its thickest (note: 1µm =1000nm). 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. 2.25.2 and 2.25.3 show measurement data for thickness in between that of those mentioned above.

•Analytical Conditions

Measuring Mode : Reflectance
Slit Width   : 0.5nm
Scan Speed   : Medium
Attachment   : Specular reflectance attachment
                  for 5°incident angle
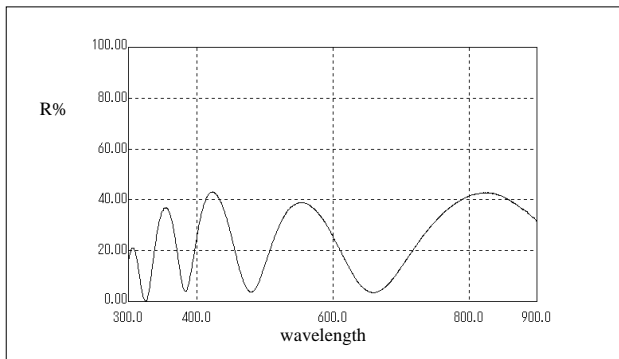
Fig. 2.25.1 0.5µm photoresist film (on a silicon wafer)
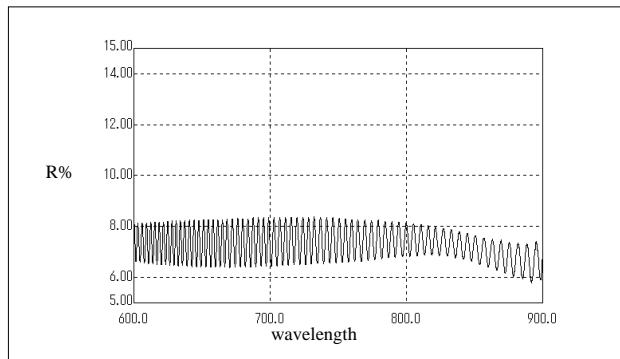
Fig. 2.25.3 4↓µm alphand Pu (polypropylene)
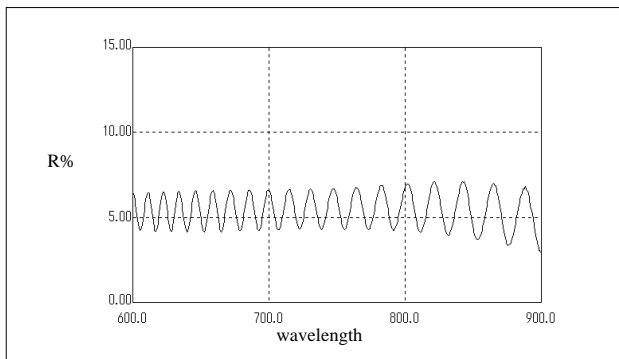
Fig. 2.25.2 10µm Sran Wrap (polyvinylidene chloride)
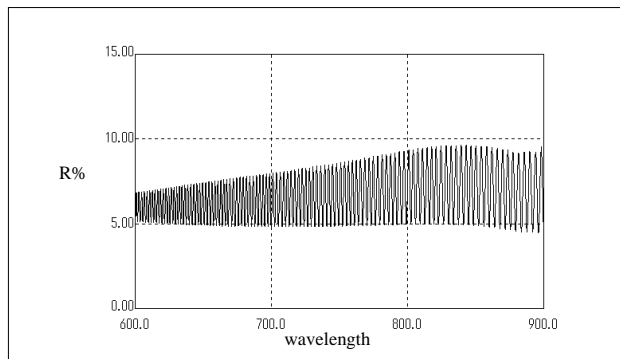
Fig. 2.25.4 63µm K Kuraray vinylon film (polyvinyl alcohol)

2.26 Analysis of copper (Cu) in polymers - AA

•Explanation

Sometimes metallic components are contained in polymer additives, and it is important that these are measured. Introduced here is an example of analysis of copper (Cu) by the electro-thermal atomization method.

Lower limit of quantitation (guide)

Approximately 2ppb (depends on the throughput. In this instance, 2g/50mL).

•Pretreatment

(1) 2g of the sample is collected in a platinum crucible and incinerated in an electric furnace.
(2) It was then extracted with nitric acid, diluted with purified water, and made up to 50mL for use as the sample stock solution.

•Analytical Conditions

Wavelength : 324.8 nm

Lamp Current : 6 mA

Slit Width : 1.0 nm

Lamp Mode : BGC-D$_2$

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

Stage	Temp.(°C)	Time(sec)	Heat Mode	Ar Flow Rate(L/min)
1	120	20	RAMP	0.10
2	250	10	RAMP	0.10
3	800	15	RAMP	0.10
4	800	10	STEP	0.10
5	800	3	STEP	0.00
6	2200	3	STEP	0.00
7	2500	2	STEP	1.00

☐ :Atomizing Stage

Abs=-0.00129Conc^2+0.0833Conc+-0.0005   r=0.9999

CONC	ABS
0.0000	0.0026
2.0000	0.1552
6.0000	0.4568
10.0000	0.7024
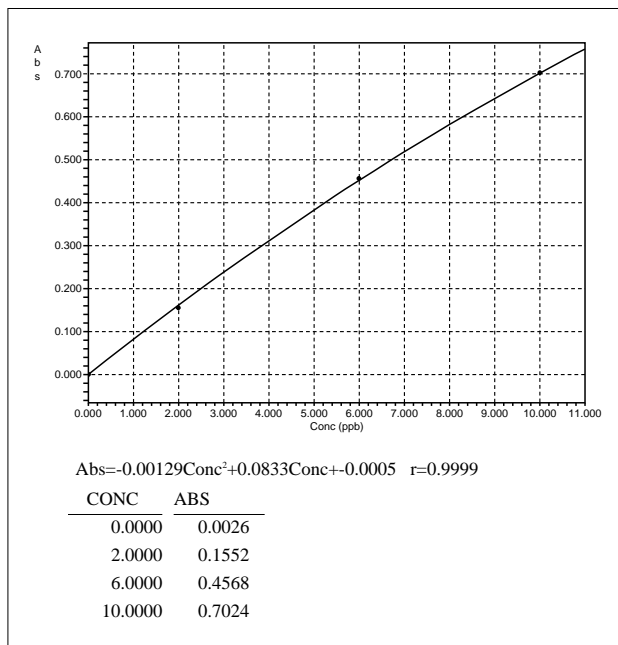
Fig. 2.26.1 Calibration curve
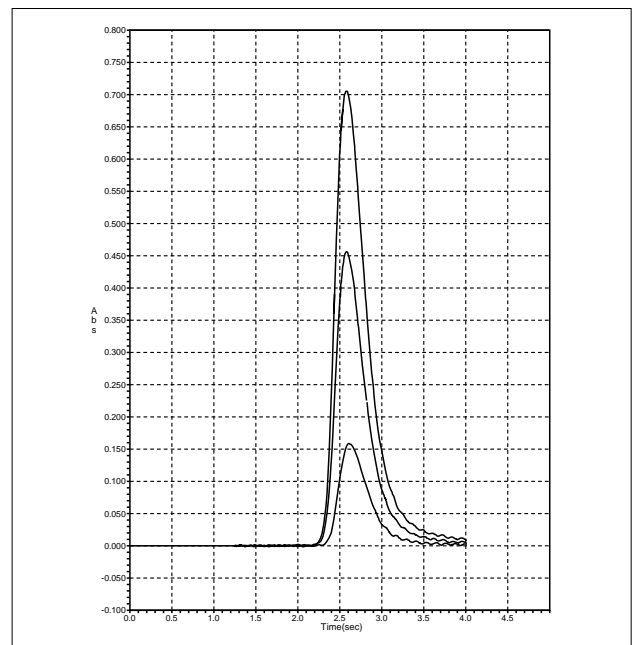
Fig. 2.26.2 Peak profile

Sample	Concentration within solution	Amount of sample collected	Amount of sample made up	Concentration within stock solution
Polypropylene	6.8 ppb	2.0g	50mL	170ppb

Table 2.26.1 Measurement Results
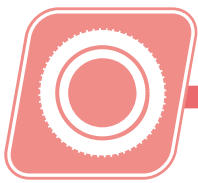
2.27 Analysis of calcium (Ca) in electronic industrial materials - AA

•Explanation

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

Lower limit of quantitation (guide)

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
Lamp Mode   : BGC-D$_2$

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

HIHot Injection

☐ :Atomizing Stage

Abs=-0.001Conc²+0.1267Conc+0.0009   r=0.9997

CONC	ABS
0.0000	0.0024
1.0000	0.1222
2.0000	0.2548
3.0000	0.3706
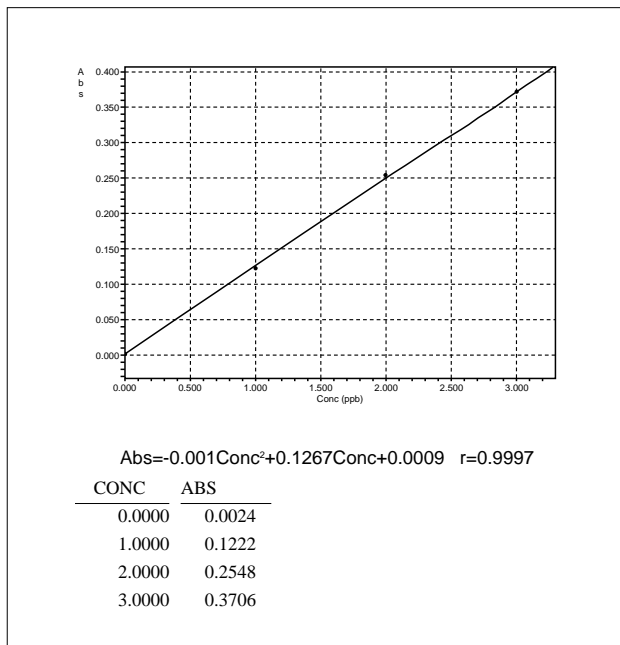
Fig. 2.27.1 Calibration curve
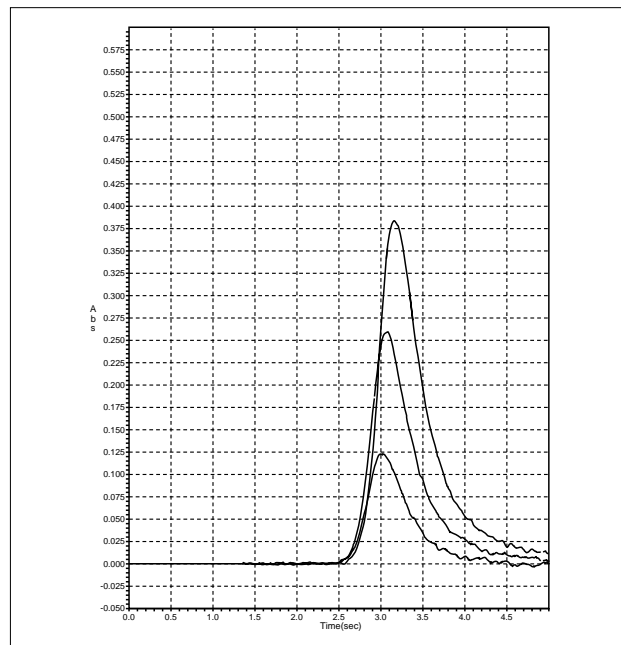
Fig. 2.27.2 Peak profile

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

Table 2.27.1 Measurement Results

3.1 Separation of organic solvents using 3 types of capillary columns of different polarity (1) - GC

•Explanation

Although it is possible to analyze a large number of organic solvents at once using a capillary column, the separation varies with the polarity of the liquid phase. Shown here is the analysis of 85 types of organic solvents using 3 different capillary columns under the same conditions.

•Pretreatment

Samples were mixed into virtually equal amounts. Approximately 0.1μL was injected for analysis.

•Analytical Conditions

Model : GC-17AAFw ver.3

Col.Temp. : 40°C -4°C/min-250°C

Inj.Temp. : 230°C

Det.Temp. : 250°C(w-FID)

Carrier Gas : He 30cm/sec

Injection : Split

The organic solvents analyzed and their abbreviations

This is a list of the 85 organic solvent compounds. Abbreviations were used in the data (Figs. 3.1.1, 3.1.2, 3.1.3).

Solvent	Abbreviation	Solvent	Abbreviation
Acetaldehyde	AA	Acetonitrile	AcNt
		Acrylonitrile	AcryNt
Methanol	MeOH		
Ethanol	EtOH	Ethyl Acrylate	EtAcry
Isopropanol	IPA	Methyl Methacrylate	MMAcry
n-Propanol	nPrOH	Butyl Acrylate	BuAcry
2-Butanol	2BuOH	2-Ethylhexyl Acrylate	2EHAcry
Isobutanol	iBuOH		
n-Butanol	nBuOH	Dichloromethane	DCM
Isoamyl Alcohol	iAmOH	trans-1,2-Dichloroethylene	tr12DCE
n-Amyl Alcohol	nAmOH	cis-1,2-Dichloroethylene	cis12DCE
Cyclohexanol	cycHeOH	Chloroform	CRF
Methylcyclohexanol	MecycHeOH	1,1,1-Trichloroethane	111TCEa
Isooctanol	iOctOH	Tetraachloromethane	CCl4
Benzyl Alcohol	BzOH	1,2-Dichloroethane	12DCEa
o-Cresol	o-Crsl	Epichlorohydrin	ECH
p-Cresol	p-Crsl	Trichloroethylene	TCEy
m-Cresol	m-Crsl	Tetrachloroethylene	4CEy
		Chlorobenzene	ClBz
Ethyl Ether	EE	1,1,2,2-Tetrachloroethane	1122TCEa
Methyl tert.-Butyl Ether	MTBE	o-Dichlorobenzene	o-DCBz
Isopropyl Ether	IPE		
		n-Hexane	C6
Tetrahydrofuran	THF	Benzene	Bz
1,4-Dioxane	14D	Cyclohexane	cycC6
		Toluene	Tol
Acetone	Actn	Ethylbenzene	EB
Methyl Ethyl Ketone	MEK	m-Xylene	m-X
Methyl Isobutyl Ketone	MiBK	p-Xylene	p-X
Methyl Butyl Ketone	MBK	o-Xylene	o-X
Cyclohexanone	chxon	Styrene	Sty
2-Methylcyclohexanone	2Mechxon		
3-Methylcyclohexanone	3Mechxon	Methyl Cellosolve	Mecel
4-Methylcyclohexanone	4Mechxon	Ethyl Cellosolve	Etcel
Isophorone	Isphon	Ispropyl Cellosolve	iPrcel
Methyl Ethyl Ketoxime	MEKoxm	Butyl Cellosolve	Bucel
		Hexyl Cellosolve	C6cel
Methyl Acetate	MeAc	2-Ethylhexyl Cellosolve	2EHcel
Ethyl Acetate	EtAc	Cellosolve Acetate	CelAc
Isopropyl Acetate	iPrAc		
n-Propyl Acetate	nPrAc	Ethyl Carbitol	Etcabi
Isobutyl Acetate	iBuAc	Ethyl Carbitol Acetate	EtcabiAc
m-Butyl Acetate	nBuAc	Butyl Carbitol	Bucabi
Isoamyl Acetate	iAmAc	Butyl Carbitol Acetate	BucabiAc
m-Amyl Acetate	nAmAc		
		N,N-Dimethylfolmamide	DMF
n-Paraffine	Cn		

Table 3.1.1

3.1 Separation of organic solvents using 3 types of capillary columns of different polarity (2) - GC

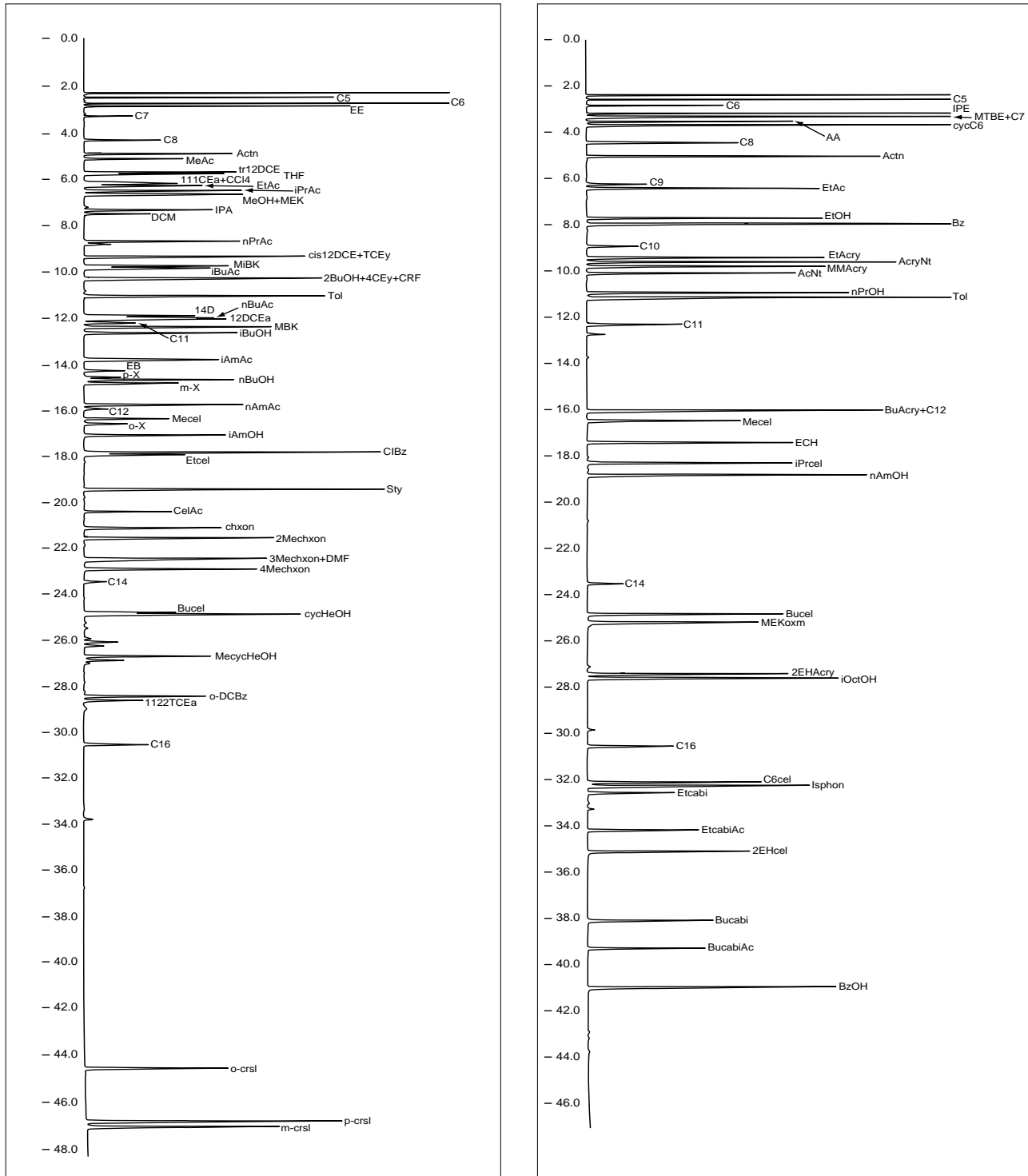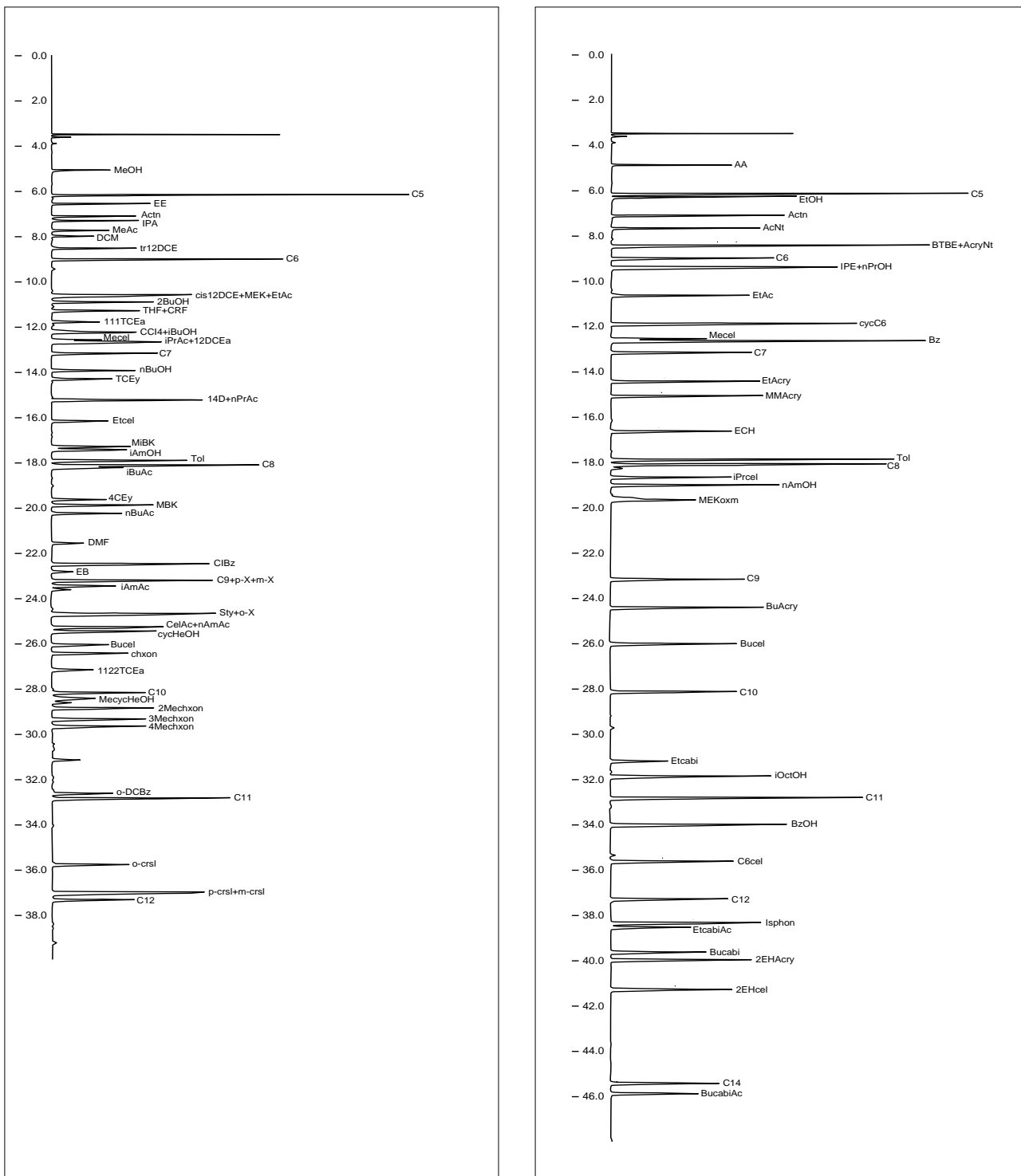Fig. 3.1.1 DB-WAX (50m × 0.32mm i.d. df=1.0µm)

Fig. 3.1.2 DB-624 (60m × 0.32mm i.d. df=1.8μm)

3.1 Separation of organic solvents using 3 types of capillary columns of different polarity (4) - *GC*
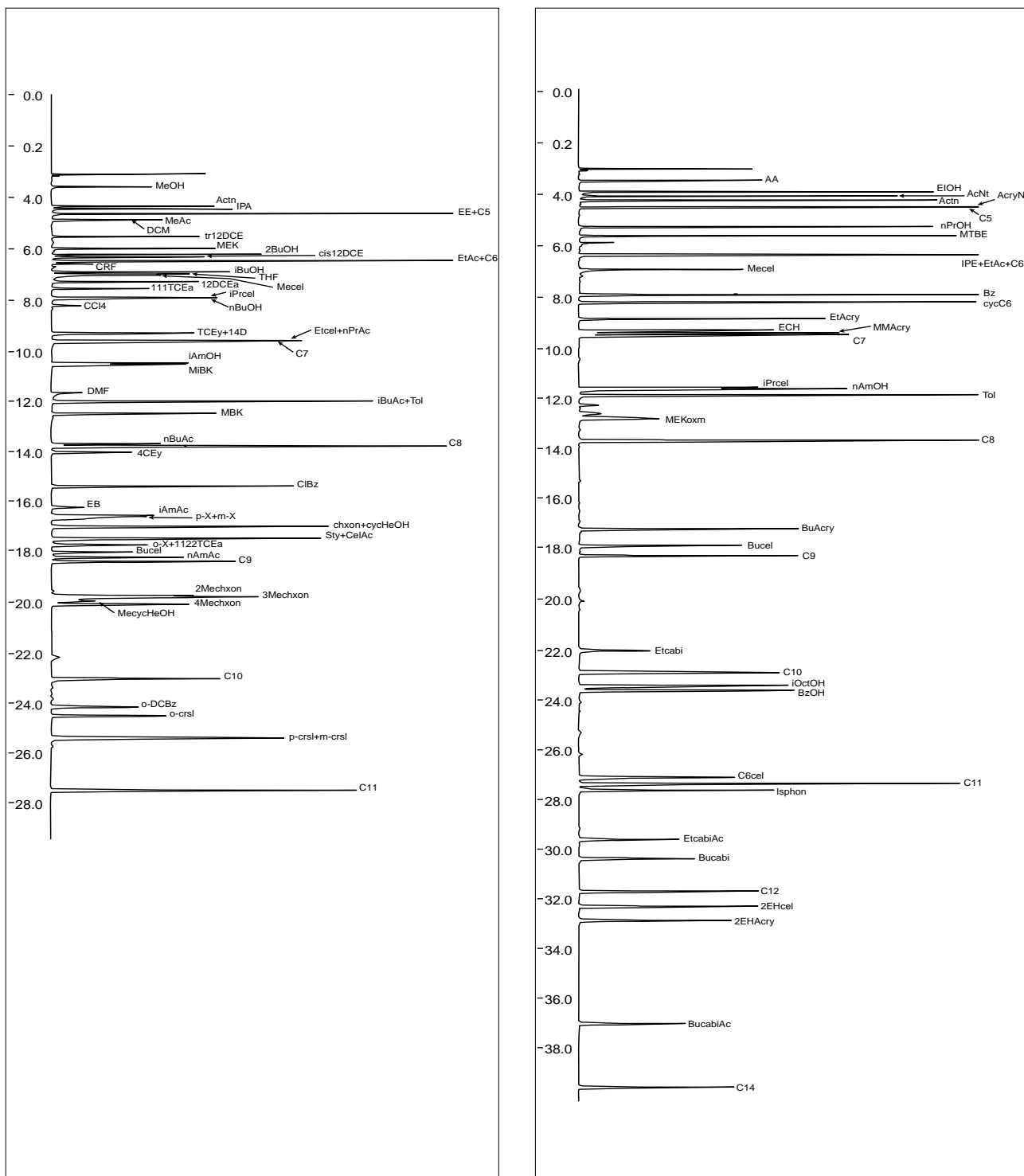

Fig. 3.1.3 DB-1 (60m × 0.32mm i.d. df=1.0μm)

3.2 Analysis of trace impurities in organic solvents - *GC*

•Explanation

When analyzing organic compounds using a normal FID, the sensitivity range is switched depending on the concentration. It is switched to high sensitivity for low concentration components, and to low sensitivity for high concentration components. In other words, it may be necessary to switch the sensitivity range to suit the target component even when analyzing a single sample.

To counter this, the wide range FID has a broad dynamic range of over 10^7 which makes switching ranges unnecessary and thus allows analysis of low to high concentration components at once.

Here, a wide range FID was used to analyze a sample consisting of n-hexane analytical grade reagent to which 5ppm (0.0005%) of n-octane and n-decane has been added.

The values shown for n-octane and n-decane (0.0004, 0.0005) in the CONC column of the quantitative calculation results are virtually correct, and it can also be seen that the purity of n-hexane is about 96.6%.

Note: Relative sensitivity correction using a standard sample is required to obtain an accurate determination of the quantity.

•Lower limit of quantitation (guide)

Approximately 0.5ppm.

•Pretreatment

None.

•Analytical Conditions

Model   : GC-17AAFw + WBI-17

Column   : CBP1-W25-500 25m × 0.53mm i.d.
             df=5.0µm

Col.Temp. : 40°C -5°C/min-120°C

Inj.Temp. : 200°C

Det.Temp. : 200°C(w-FID)

Carrier Gas : He   9 mL/min

Injection : Direct Injection

＊＊Results of quantitative calculations＊＊

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	0.619	481	258			0.0001	
	10	1.409	21794	8026			0.0037	
	13	2.023	442	80			0.0001	
	14	2.463	3053629	513011			0.5177	
	15	2.698	4032460	588307	V		0.6836	
	16	3.103	570088064	65743532	V		96.6442	←n-C6
	17	3.525	7593108	1298551	SV		1.2872	
	18	3.958	18152	4052	T		0.0031	
	19	4.226	4853044	710481	SV		0.8227	
	20	4.553	40351	7415	T		0.0068	
	21	4.793	68255	5443	T		0.0116	
	22	5.169	106897	18511	T		0.0181	
	23	5.785	1469	202			0.0002	
	35	8.113	2603	389			0.0004	←n-C8
	54	14.704	2908	390	SV		0.0005	←n-C10
		TOTAL	589883392	68898608			100	

Fig. 3.2.1 n-hexane (5ppm each of n-octane and n-decane added)

3.3 Analysis of organic solvents in film *- GC*

•Explanation

This is an example of analysis of organic solvents on the surface of photographic film. The data is obtained by analysis with headspace GC.

•Pretreatment

0.8mL of the headspace sample was analyzed after 9cm of the film was enclosed in a vial and warmed at 90°C for 30 minutes.

•Analytical Conditions

Model   : HSS-2B + GC-14BPFsc
Column   : ULBON HR-20M 50m × 0.22mm i.d.
             df=0.25µm
Col.Temp. : 80°C
Inj.Temp. : 250°C
Det.Temp. : 250°C (FID)
Carrier Gas : He   1.1mL/min
Injection   : Split   1 : 20
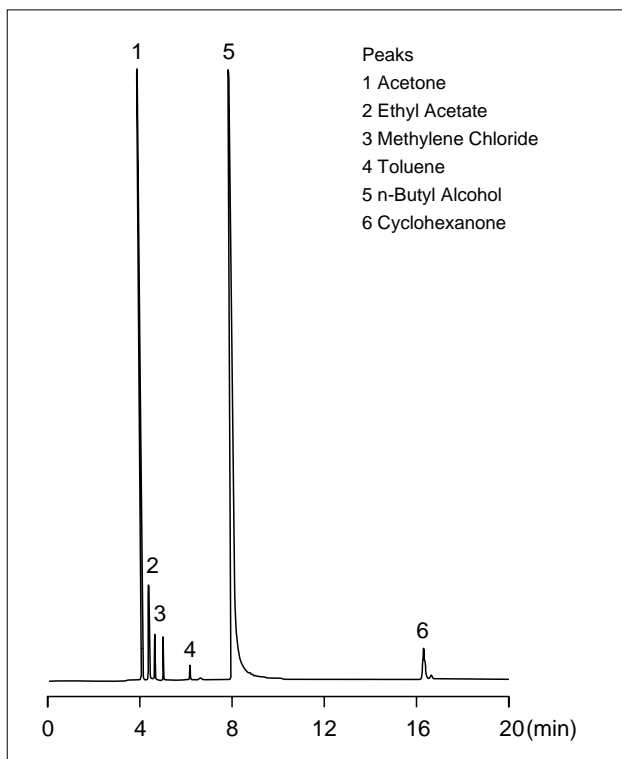
Fig. 3.3.1 Color film
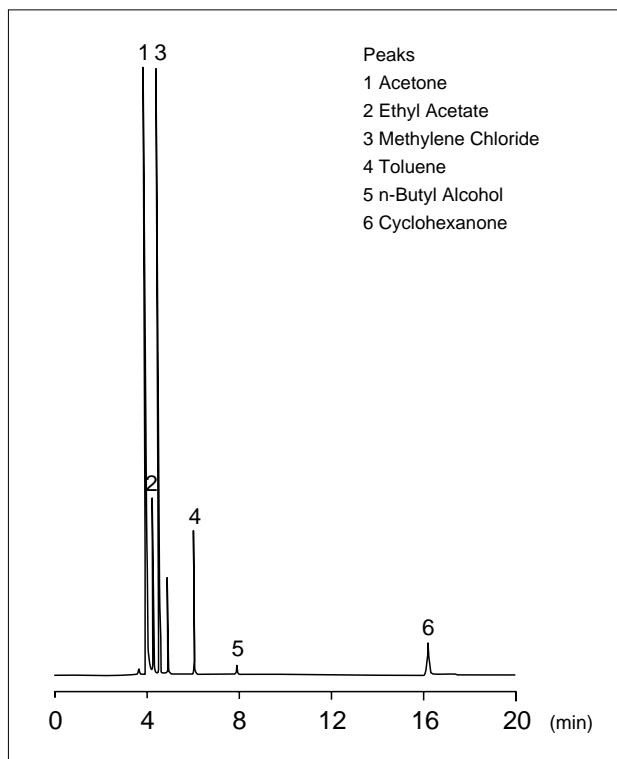
Fig. 3.3.2 Black and white film

3.4 Analysis of organic solvents of paint scrapings - GC

•Explanation

Directly injecting paint sample into a GC can contaminate the GC injector and the column because of the non-volatile pigments in paint. Organic solvents contained in samples such as paints, pigments, and coatings can be analyzed relatively easily using headspace GC. In general, samples with a very high content concentration are common, so amounts are kept as small as possible (few mg to a few tens of mg) when enclosed for analysis.

•Pretreatment

0.8mL of the headspace sample was analyzed after 50mg of the sample was enclosed in a vial and warmed at 80°C for 30 minutes.

•Analytical Conditions

Model   : HSS-2B + GC-14BPFsc
Column   : CBP20-S25-050   25m × 0.33mm i.d.
             df=0.5µm
Col.Temp. : 50°C (5min)-10°C/min-200°C
Inj.Temp. : 230°C
Det.Temp. : 230°C (FID)
Carrier Gas : He   1.4mL/min
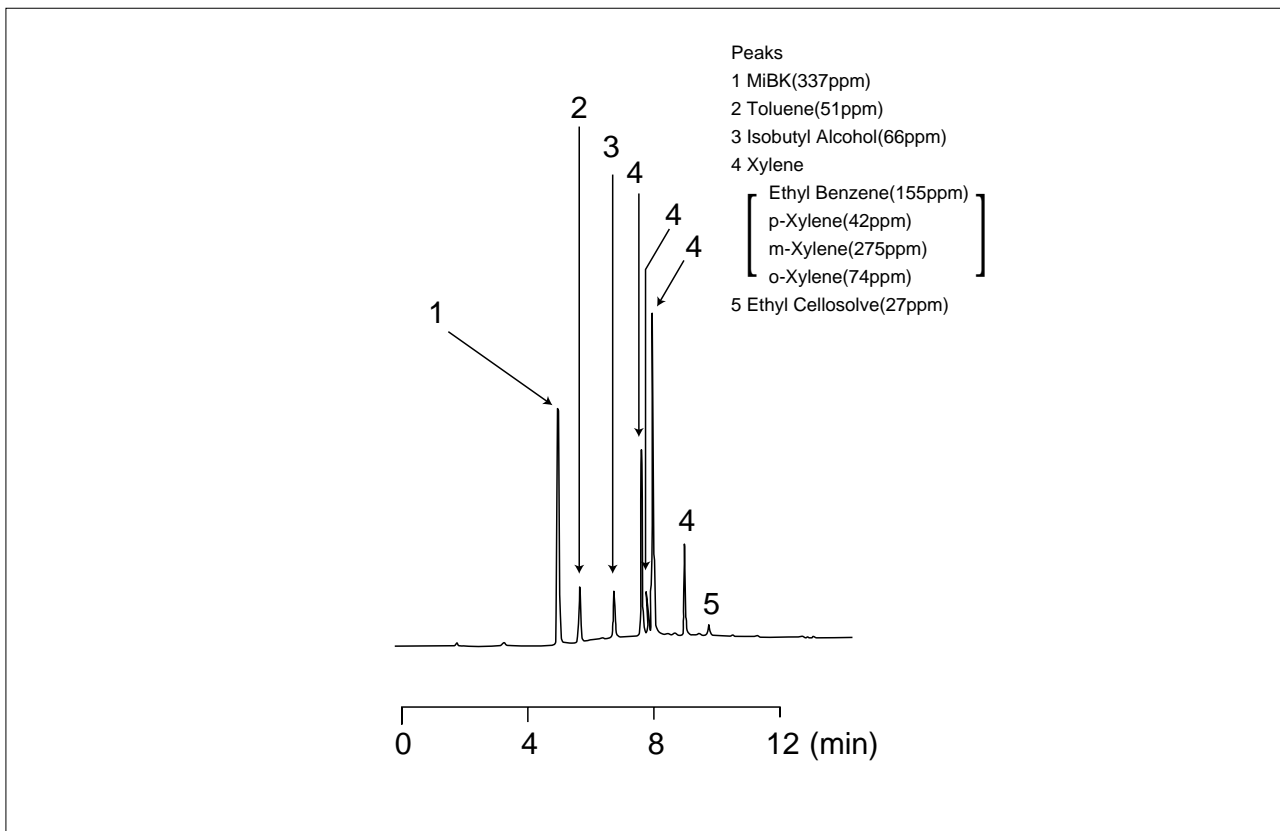Injection : Split   1 : 17

Peaks
1 MiBK(337ppm)
2 Toluene(51ppm)
3 Isobutyl Alcohol(66ppm)
4 Xylene
    Ethyl Benzene(155ppm)
    p-Xylene(42ppm)
    m-Xylene(275ppm)
    o-Xylene(74ppm)
5 Ethyl Cellosolve(27ppm)

Fig. 3.4.1 Analysis of paint scrapings

3.5 Analysis of automobile coatings using an infrared microscope - FTIR

•Explanation

The measurement of automobile coating fragments in criminal investigations by the police are carried out by scraping a part of the coating fragment and employing the transmission method. In actuality, because automobile coatings feature a 3 layer structure consisting of an undercoat, intermediate coat and a final coat, measurements are carried out by sampling each layer. This sampling operation requires skill, and depending on the way it is carried out the quality of the spectrum may vary.

If the size of the sample is over a few mm the edge of the coating can be scraped off with sandpaper, allowing the use of the microscopic ATR method. Troublesome sampling can thus be omitted.

•Pretreatment / Results

Fig. 3.5.1 is a schematic diagram of the automobile coating scraped off with sandpaper. An ATR objective prism (made of Ge) was pressed onto each layer and measured. The spectra for the final coat, intermediate coat, and the undercoat are shown in Figs. 3.5.2, 3.5.3, and 3.5.4 respectively. For reference, the undercoat was measured with the transmission method, and overlaid in Fig. 3.5.5 with the result of the ATR correction of Fig. 3.5.4.

From this it can be seen that a spectrum similar to the transmission method can be obtained with the microscopic ATR method.

•Analytical Conditions

Accessory   : ATR Objective(IRE : Ge)

Resolution   : 8cm^{-1}

Accumulation : 40

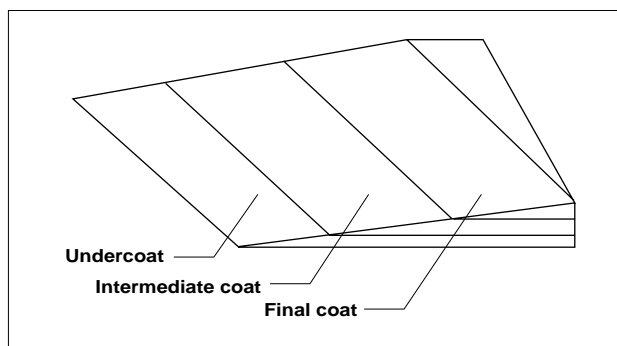Apodization   : Happ-Genzel

Detector   : MCT

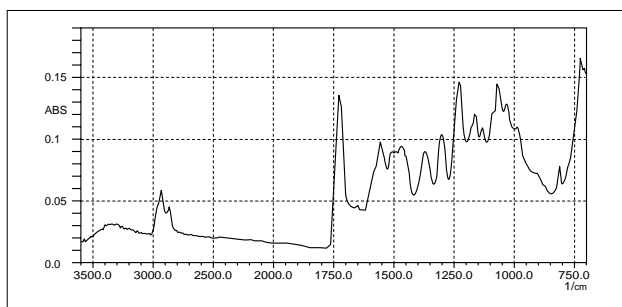Fig. 3.5.1 Magnified image of the paint fragment

Fig. 3.5.2 ATR spectrum of the final coat
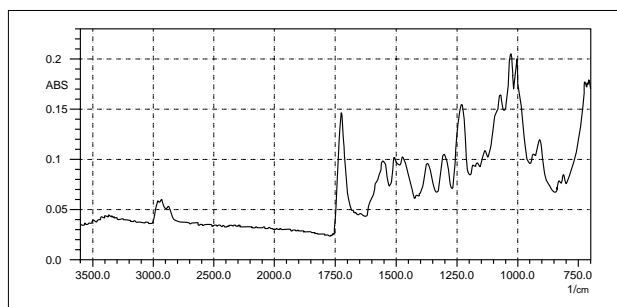

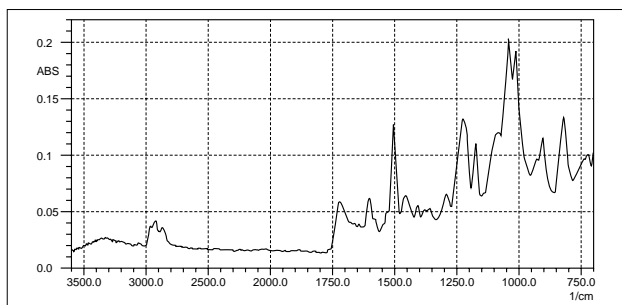Fig. 3.5.3 ATR spectrum of the intermediate coat

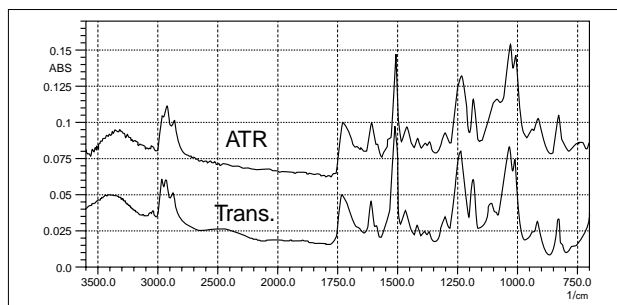Fig. 3.5.4 ATR spectrum of the undercoat

Fig. 3.5.5 Transmittance spectrum and ATR spectrum of the undercoat

3.6 Analysis of paint scrapings using an infrared microscope - FTIR

•Explanation

There are a number of ways of analyzing paint scrapings employing the FTIR. Measurement can be carried out by crushing the collected paint scrapings and employing the KBr pellet method or diffuse reflection method; or by measuring the surface of a coating with the ATR method; or by measuring the minute sample with an infrared microscope.

Introduced here is an example of measurement of paint scrapings from a timber surface.

•Pretreatment / Results

Measurement was carried out by the transmission method using an infrared microscope after a part of the paint on a chip of wood was scraped off with a needle and crushed using a diamond cell. Fig. 3.6.1 is a magnified image of the paint scraping after being crushed. It's size is about 70x40μm.

When measuring the paint scraping shown in Fig. 3.6.1, measurement was carried out with a 30x10μm aperture size, altering the location a few times. The spectra consequently obtained varied slightly with the location (Fig. 3.6.2). Out of these, a difference spectrum was obtained by subtracting spectrum (3) from spectrum (2).

This is shown in Fig. 3.6.3 (bottom). By searching the paint database a spectrum (on the top in Fig. 3.6.3) that matched well with the difference spectrum was found. From this it can be inferred that a pigment thought to be TOLUIDINE RED L (an azo compound) is contained in this paint scraping.

•Analytical Conditions

Resolution : $8cm^{-1}$

Accumulation : 100
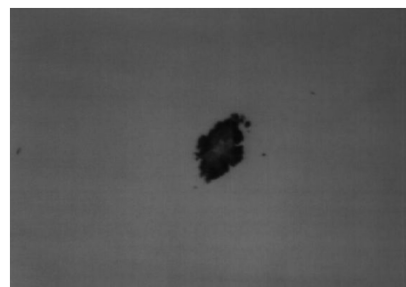
Apodization : Happ-Genzel

Detector : MCT

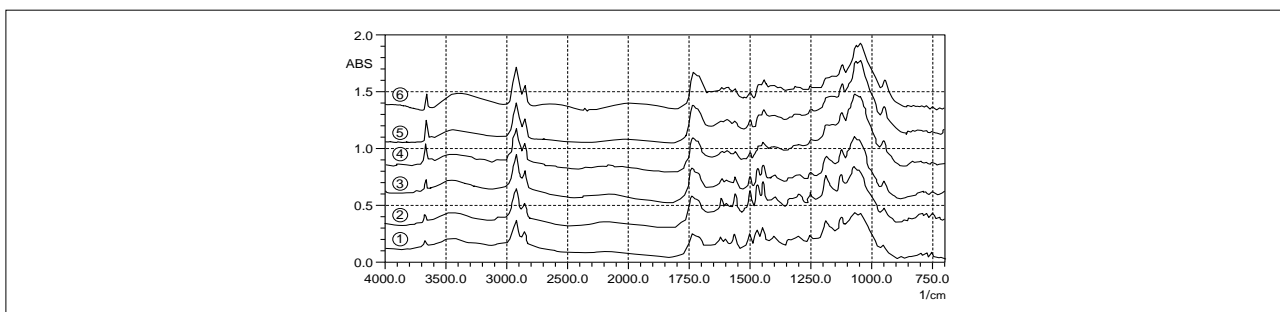Fig. 3.6.1 Magnified image of the paint scraping
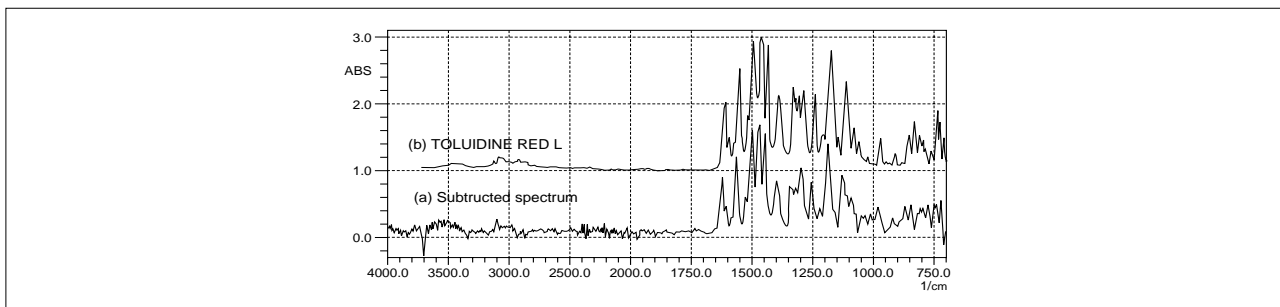

Fig. 3.6.2 Infrared spectra of the paint scraping

Fig. 3.6.3 Difference spectrum and the spectrum of TOLUIDINE RED L

3.7 Analysis of lead (Pb) in paint - AA

•Explanation

Lead is contained in some paints, and since they affect the environment it is necessary to measure the concentration of the lead content. Shown here is an example of analysis of SRM 2528, a standard substance for measurement of Pb in powder paint supplied by the NIST (National Institute of Standard and Technology).

Lower limit of quantitation (guide)

Approximately 50mg/kg (depends on the throughput. In this instance, 1g/50mL).

•Pretreatment

(1) Approximately 1g of the sample that has been dried for 2 hours at 105°C is placed in a beaker and weighed precisely.
(2) 5mL of nitric acid (65%) is added, and then heated over a sand bath.

(3) A further 5mL of nitric acid (65%) is added. 2mL of perchloric acid is then added. Heating is then continued over a sand bath until white smoke is generated and it has virtually evaporated to dryness.
(4) After cooling the residue was filtered and transferred to a 50mL measuring flask. It was then made up with purified water and used as the measurement sample.

•Analytical Conditions

Wavelength   : 283.3 nm
Lamp Current : 10 mA
Slit Width   : 0.5 nm
Lamp Mode   : BGC-D_2

Flame   : Air-C_2H_2
C_2H_2 Flow Rate : 2.0 L/min

Measure Calibration Curve

Abs.=0.0211 Conc+0.000
Cor. Coef. (r)=0.99982

Concn.(ppm)	Abs
2	0.0443
4	0.0845
6	0.1265
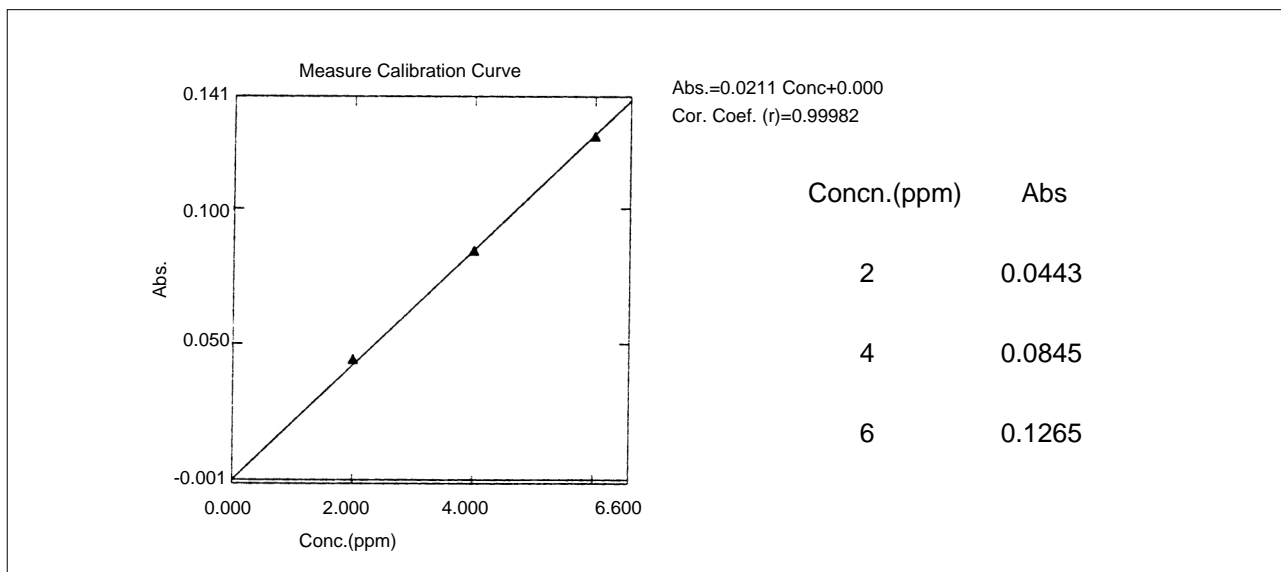
Fig. 3.7.1 Calibration curve used in the measurement of Pb in paint

Concentration within solution	Amount of sample collected	Amount of sample made up	Concentration within solid	Certified value
4.12 μg/mL	0.988g	50mL	208.4mg/kg	208.2±4.9mg/kg

Table 3.7.1 Measurement Results

3.8 Measurement of ink for color printers (1) - UV

•Explanation

Calibration curves were generated by the multilinear regression quantitation mode based on the inks used in color printers (yellow, magenta, cyan). Using this calibration curve 2 samples with different composition ratios were measured, and a classified quantitation of the 3 components was attempted. The absorption spectra of the 3 components which formed the basis is shown in Fig. 3.8.1. In Fig. 3.8.2 the absorption spectra and results of quantitation of the 2 samples measured are shown. Good results have been obtained since 0.3, 0.2, and 0.5 are the correct values for sample 1, while 1, 1, and 1 are the correct values for sample 2.

•Analytical Conditions

Measuring Apparatus : MLS-1500

Cell : Standard quartz cell

Scan Range : 190nm-780nm

Sampling Interval : 1.0nm

Accumulations : 1
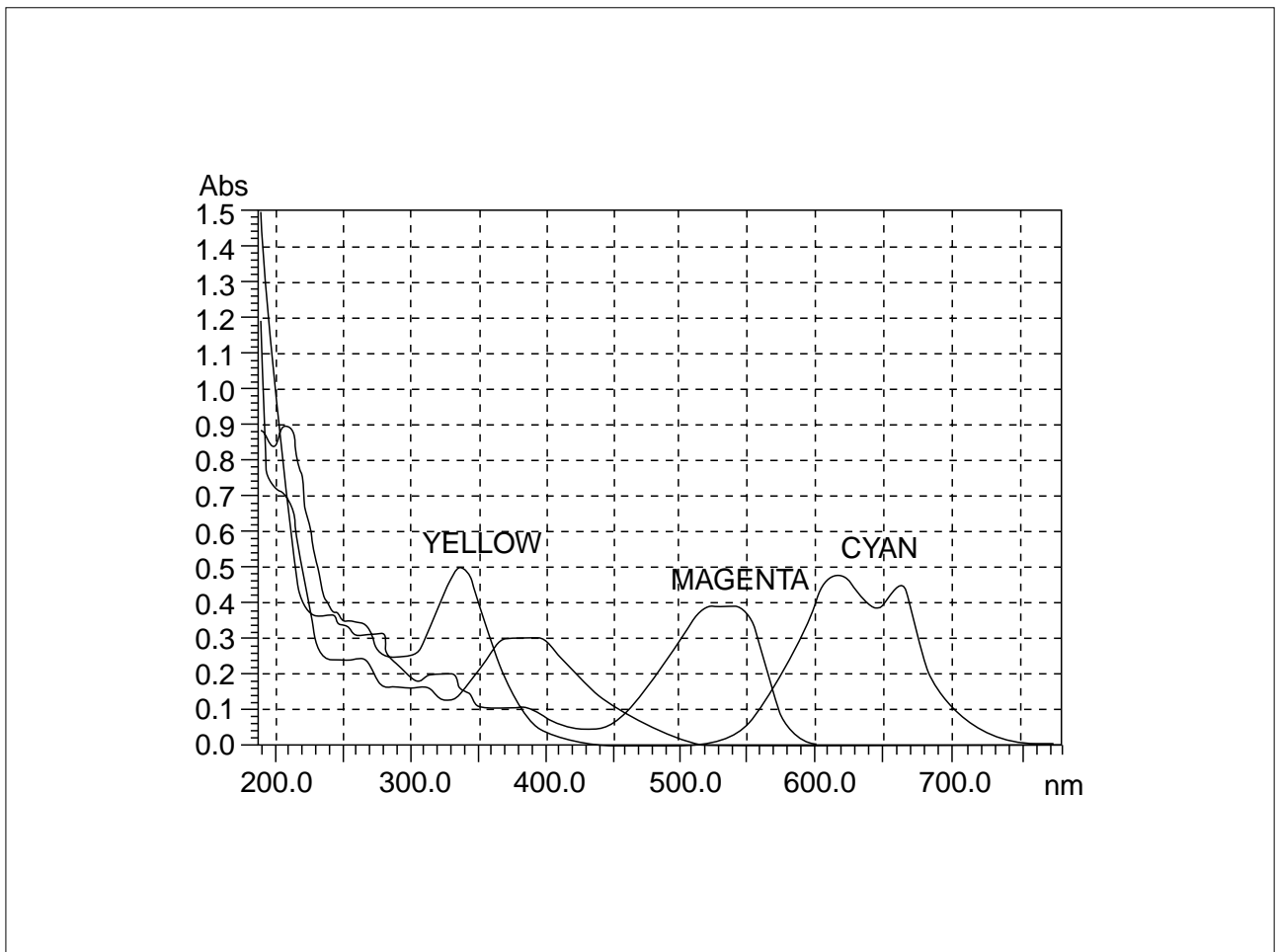
Fig. 3.8.1 Absorption spectra for color printer ink (Yellow, Magenta, Cyan)

3.8 Measurement of ink for color printers (2) - UV

●**Measurement Results**

Fesult of NLR analysis

Operator   : Shimadzu Customer
Origin   : Laboratory
Date   : 97/10/15 17:09:25
Time   : Mon Oct 15 17:09:25 1997
Calibration file : C:¥an¥nulti1‾1¥914150‾1¥dye¥dye1.nlr
Description   : dye
Dataset   : C:¥AN¥NILTI1‾1¥944150‾1¥DYE¥N2YSC5.DVD
Textinfo   : Source:A:¥N2YSC5.SPC
Evaluation   : K-Matrix
Rangeset   : UV-VIS. RNG
Range 1   : 190.00-780.00nm

Compound 1	Concetration [ ]
yellow	0.3113
magenta	0.1964
cyan	0.5000

Compound 2	Concentration [ ]
yellow	1.0675
magenta	1.0185
cyan	1.00

Fig. 3.8.2 Absorption spectra and the quantitation results

4. Gas

4.1 Analysis of inorganic gases (1) - GC

•**Explanation**

As column packing material, molecular sieves, activated carbon, silica gels, activated alumina, and porous polymer beads are use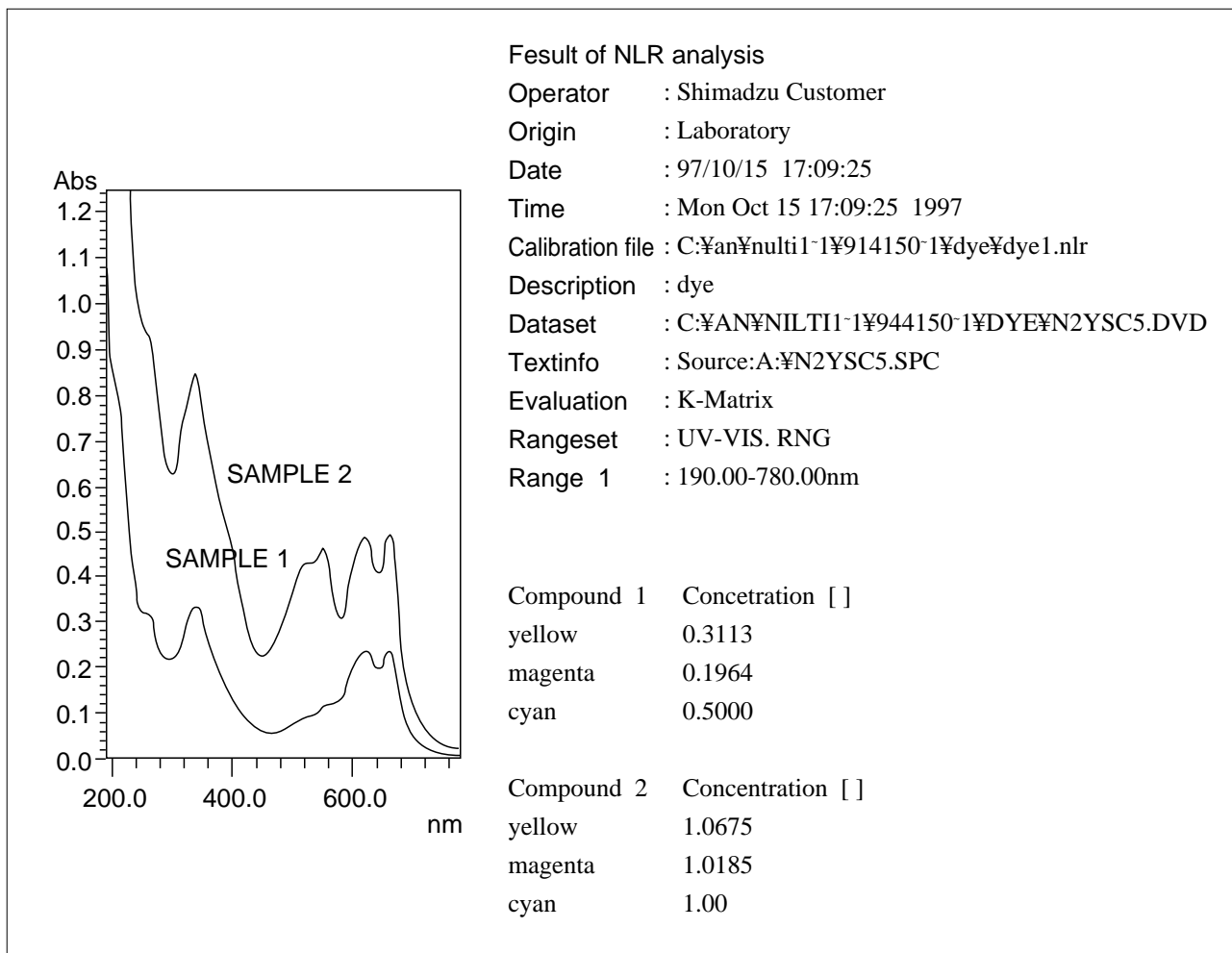d in the analysis of inorganic gases. Of these, molecular sieve 5A is the most widely used as it can separate O_2 and N_2, although CO_2 will not be eluted as it is adsorbed.

Introduced here is an example of analysis using SHINCARBON T (Shinwa Chemical). A single column can analyze O_2, N_2, CO, CH_4, CO_2, N_2O, C_2H_4, and C_2H_6 at the same time.

•**Pretreatment**

None.

•**Analytical Conditions**

Model   : GC-14BPT

Column   : SHINCARBON T 60/80 mesh
             6m × 2mm i.d.

Col.Temp. : 50°C (8min)-10°C/min-260°C

Inj.Temp. : 200°C
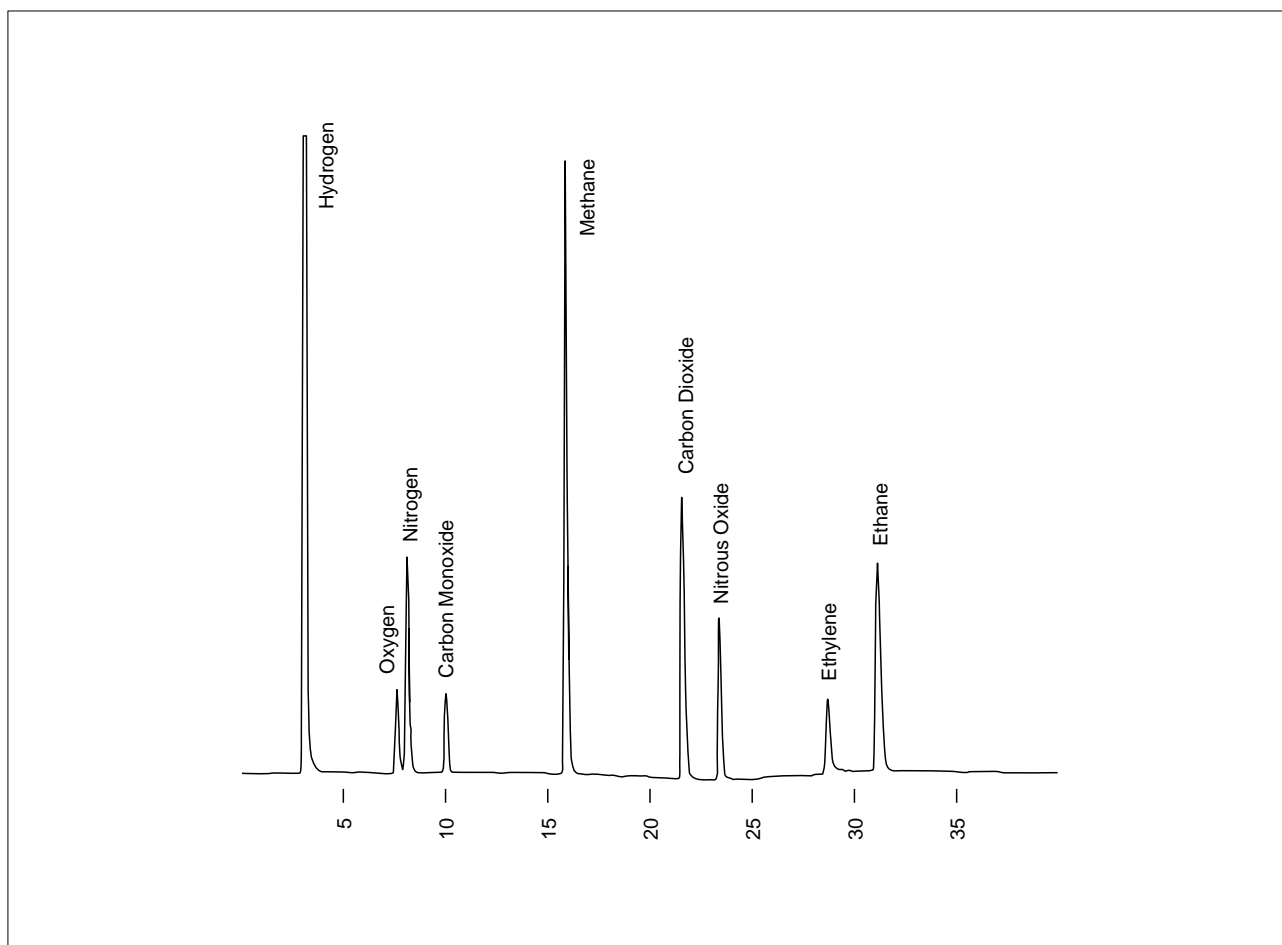
Det.Temp. : 200°C (TCD)

Carrier Gas : Ar 20mL/min

Fig. 4.1.1 Example of analysis of inorganic gas and low grade hydrocarbons with a packed column

Gas

4.1 Analysis of inorganic gases (2) - GC

•Explanation

Until about a awhile ago, the great foundation of "gas analysis" was the "packed column". This was because with a capillary column coated with a normal liquid phase, there was not much retention of compounds gaseous at room temperature. This made separation difficult.

However, gaseous components can be separated and analyzed using a capillary column where the adsorbent is chemically bonded to the inner surface (this is called the Porous Layer Open Tubular column: PLOT). Introduced here are examples of analyses of air, CO, and methane employing a MS-5A (molecular sieve 5A) PLOT column. The detector used was the μ-TCD (a TCD for capillary columns, it has a small cell volume).

•Pretreatment

None.

•Analytical Conditions

Model : GC-17AAT ver.3
Column : MS-5A   25m × 0.32mm i.d.
Col.Temp. : 130°C
Inj.Temp. : 200°C
Det.Temp. : 200°C(μ-TCD)
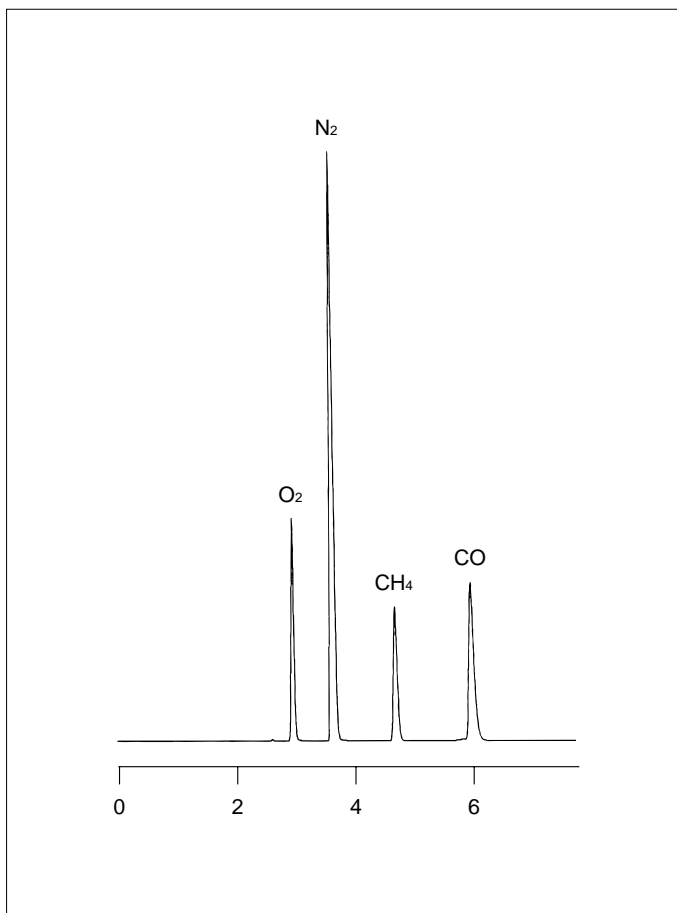Carrier Gas : He   1.5mL/min
Injection : Split   1 : 15

Fig. 4.1.2 Example of analysis of an inorganic gas using a capillary column

4.2 Analysis of organic gases (1) - GC

•Explanation

Adsorbents such as activated alumina and porous polymer beads are used to separate C_1 to C_2 in the analysis of organic gases.

For the separation of gases beyond C_2, high concentration distributors are utilized. Introduced here is an example of analysis of C_2 to C_4 hydrocarbons using a sebaconitrile column.

•Pretreatment

None.

•Analytical Conditions

Model   : GC-14BPF

Column   : Sebaconitrile 25%
             on Shimalite 60/80 mesh
             $11m \times 3mm$ i.d.

Col.Temp. : 43°C

Inj.Temp. : 40°C

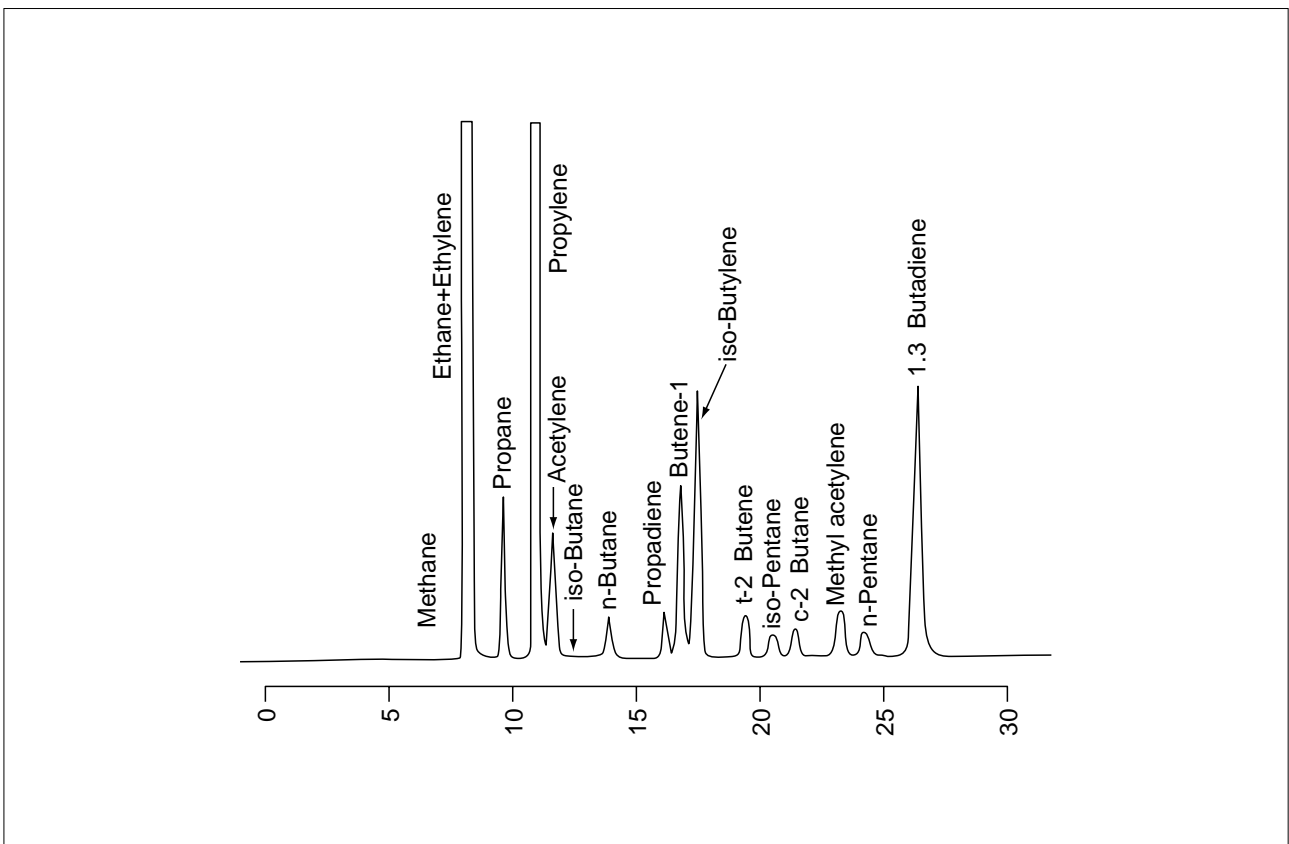Det.Temp. : 100°C (FID)

Carrier Gas : N_2 (45 mL/min)

Fig. 4.2.1 Example of analysis of C_2 to C_4 hydrocarbons with a packed column

4.2 Analysis of organic gases (2) - *GC*

•Explanation

Introduced here is an example of analysis of C_2 to C_4 hydrocarbons using GS-ALUMINA, which is an activated alumina PLOT column.

•Pretreatment

None.

•Analytical Conditions

Model   : GC-17AAT ver.3
Column   : GS-ALUMINA 30m × 0.53mm i.d.
Col.Temp. : 45°C (3min)-15°C/min-180°C
Inj.Temp. : 200°C
Det.Temp. : 200°C (μ-TCD)
Carrier Gas : He   5 mL/min
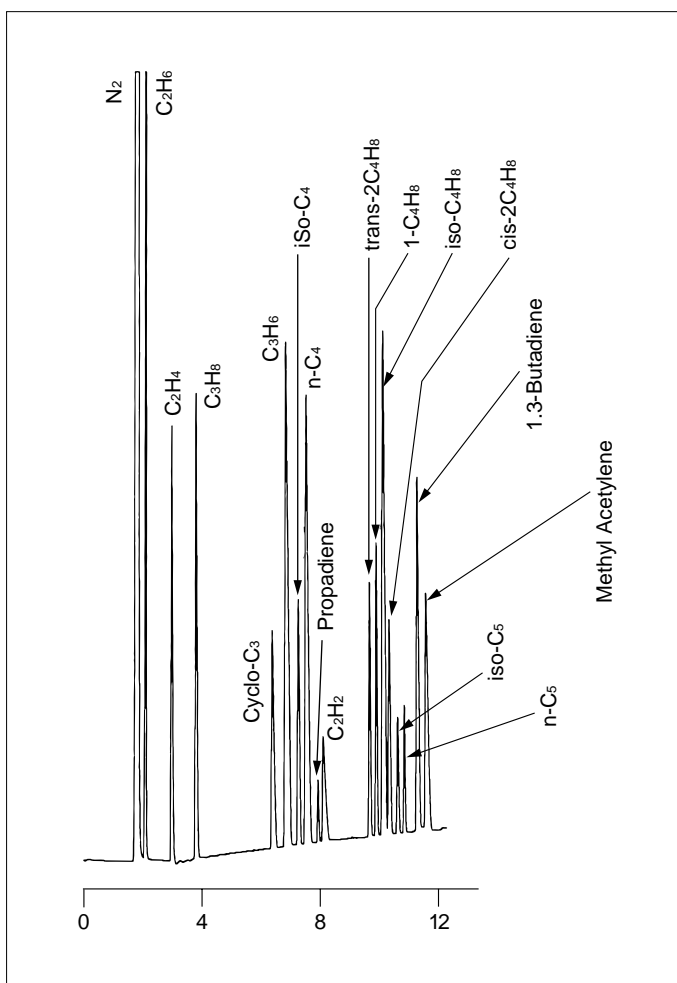Injection : Split 1 : 1

Fig. 4.2.2 Example of analysis of C_2 to C_4 hydrocarbons using a capillary column

4.3 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 (Shinwa Chemical).

Although the 2 components Freon-115 and Freon-12, as well as the 3 components Freon-124, Freon-22 and Freon-152a cannot be separated with the normally used PorapakQ, with this column complete separation is possible.

●**Pretreatment**

None.

●**Analytical Conditions**

Model   : GC-14BPT

Column   : SM-6   6m × 3mm i.d.

Col.Temp.   : 40°C

Inj.Temp.   : 50°C

Det.Temp.   : 50°C (TCD)

Carrier Gas : He   20mL/min

1 Air
2 Freon-115
3 Freon-12
4 Freon-114
5 Freon-22
6 Freon-11
7 Freon-113

1 Air
2 Freon-124
3 Freon-22
4 Freon-152a

1 Air
2 Freon-125
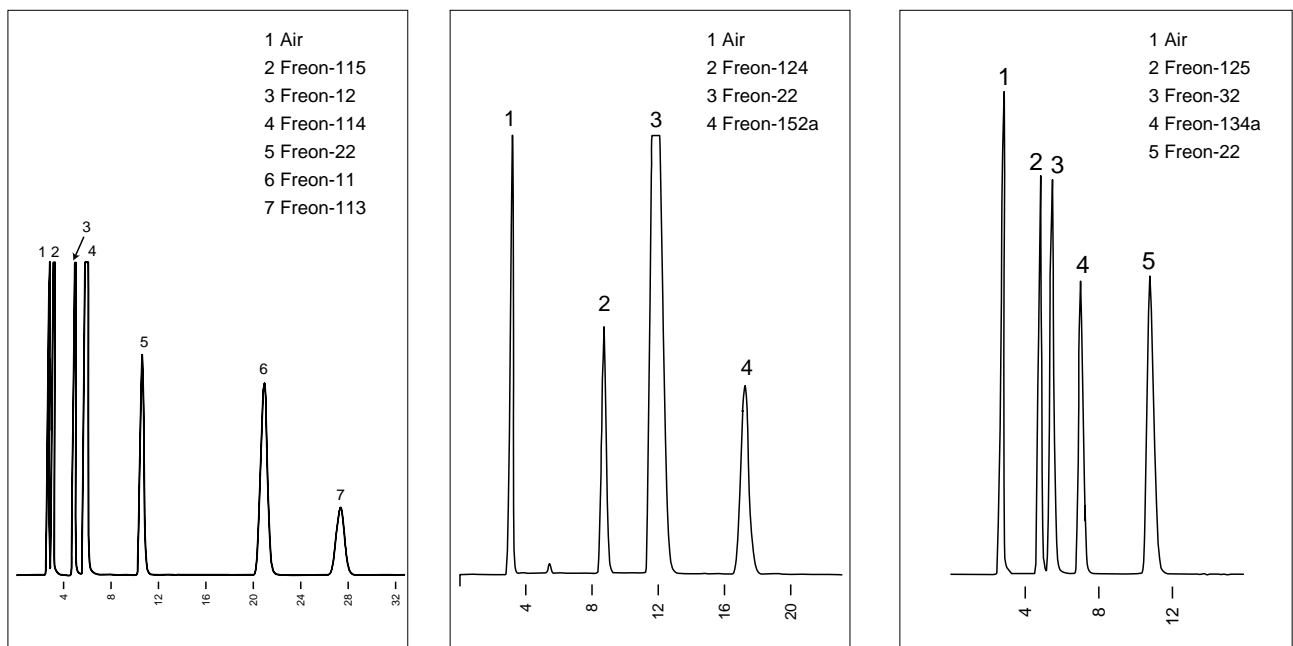3 Freon-32
4 Freon-134a
5 Freon-22

Fig. 4.3.1 Example of analysis of Freon gas using a packed column

4.3 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

Model : GC-17AAFw + ECD-17

Column : GS-ALUMINA 30m × 0.54mm i.d.

Col.Temp. : 50°C (0min)-5°C/min-100°C
10°C/min-180°C

Inj.Temp. : 180°C

Det.Temp. : 200°C (ECD)

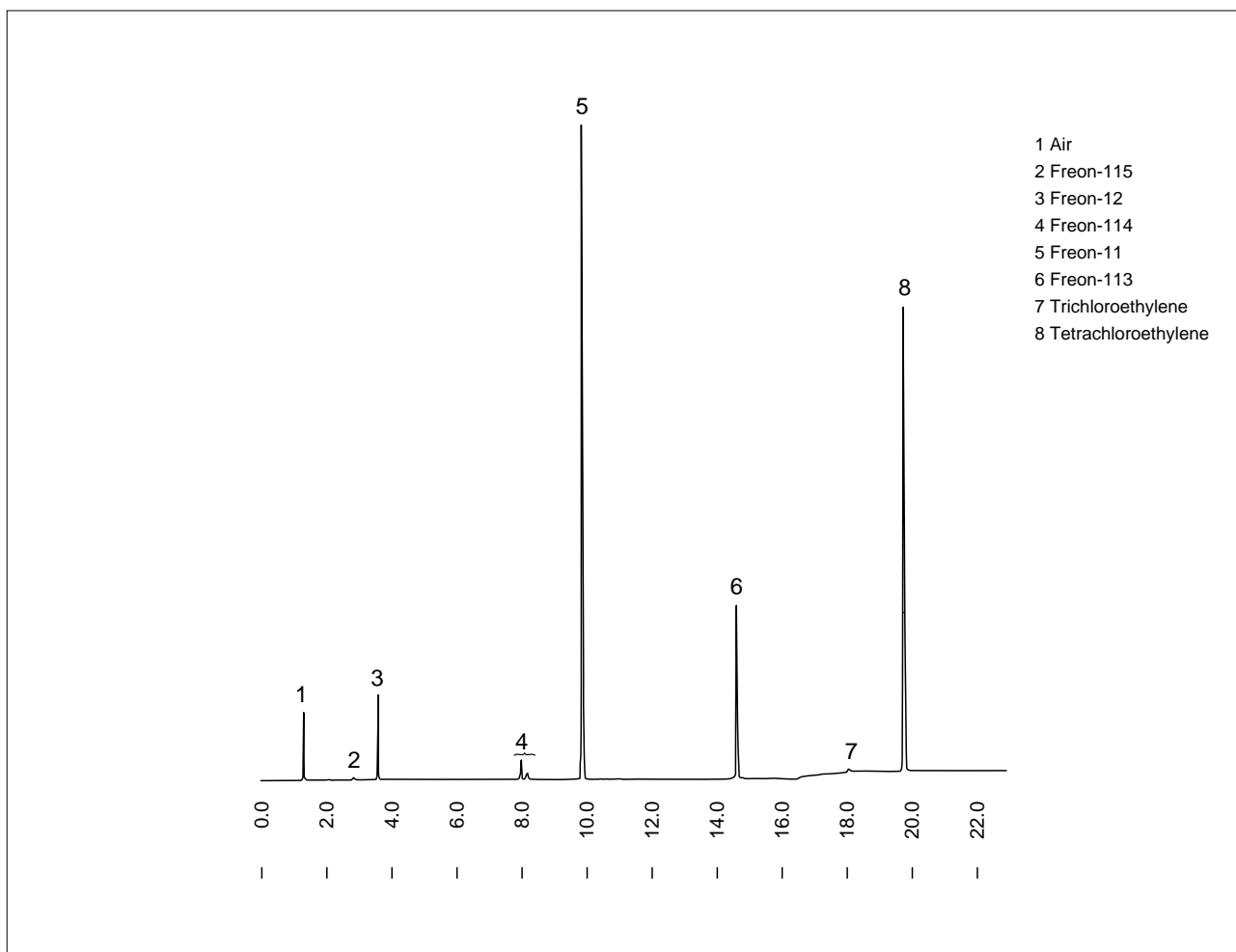Carrier Gas : He 8.2 mL/min

Injection : Split 1 : 5

1 Air
2 Freon-115
3 Freon-12
4 Freon-114
5 Freon-11
6 Freon-113
7 Trichloroethylene
8 Tetrachloroethylene

Fig. 4.3.2 Example of analysis of Freon gas using a capillary column

4.4 Analysis of inorganic gases using FTIR *(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 gas appears as a combination of the 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 gases long optical path cells that are 10, 20mLong are used. It is necessary to select the appropriate window plate and cell materials because some samples can be corrosive.

•Example of SO_2 Measurement

Fig. 4.4.1 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. 4.4.2 is the calibration curve of these spectra obtained by using quantitation 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. 4.4.3 to 4.4.6. The maximum peak region of each spectrum - NO_2, NO, N_2O, CO in order from Fig. 4.4.3 - has been magnified.

•Analytical Conditions

Accessory   : 10cm Gas cell

Resolution   : $0.5cm^{-1}$

Accumulation : 100

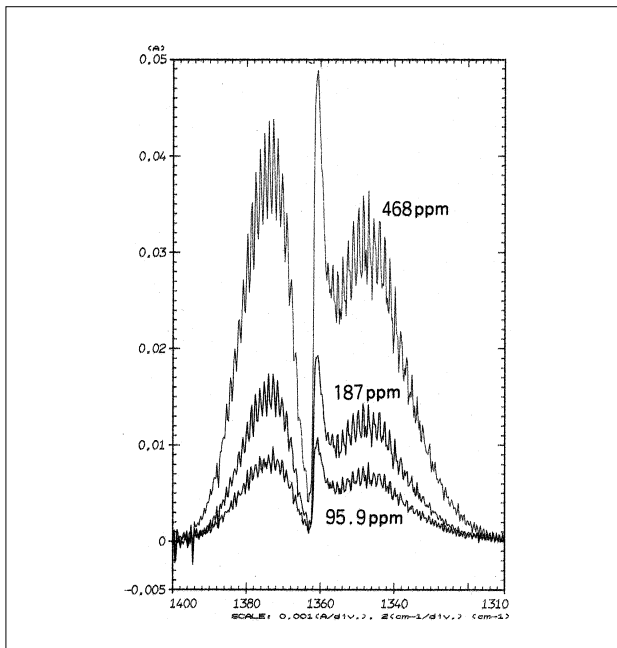Apodization   : Rectangular

Detector   : DLATGS
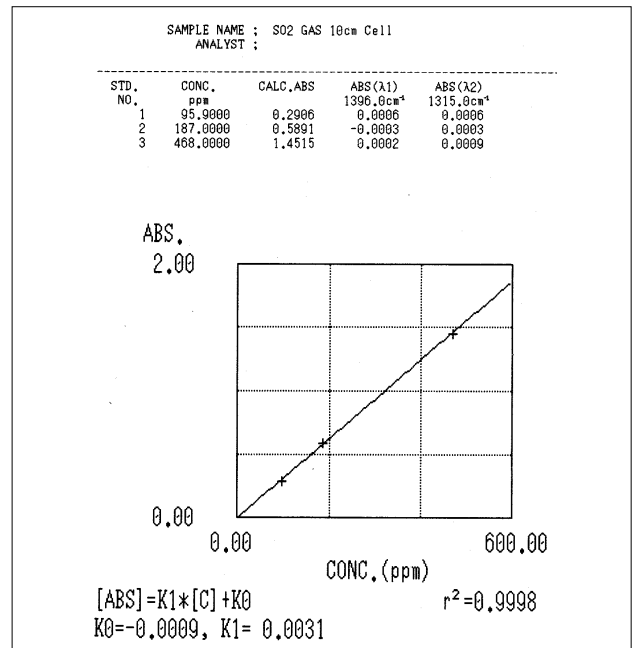

Fig. 4.4.1 Infrared spectra of SO_2 gas

Fig. 4.4.2 Calibration curve of SO_2

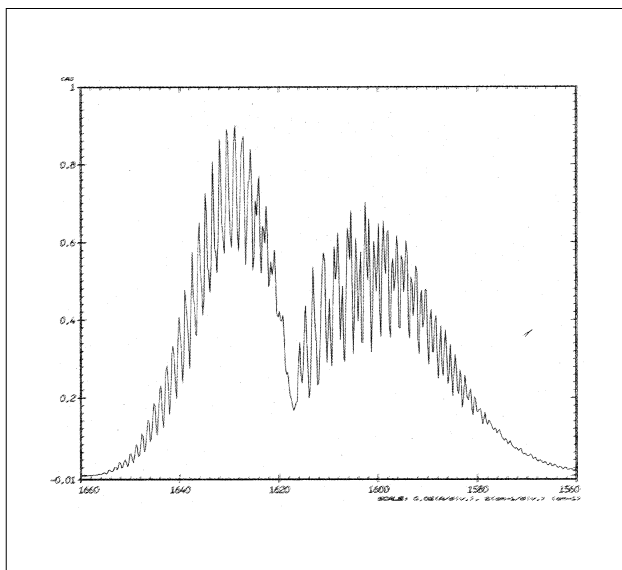# 4.4 Analysis of inorganic gases using FTIR (2) - FTIR

Fig. 4.4.3 Infrared spectrum of NO_2 gas of the $1,600cm^{-1}$ region
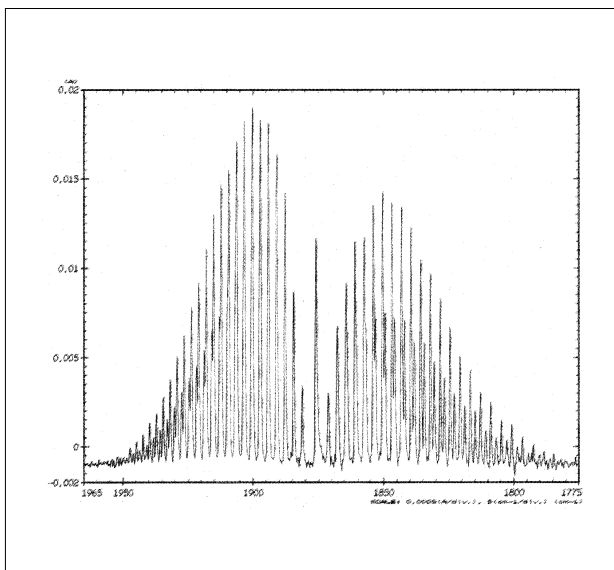

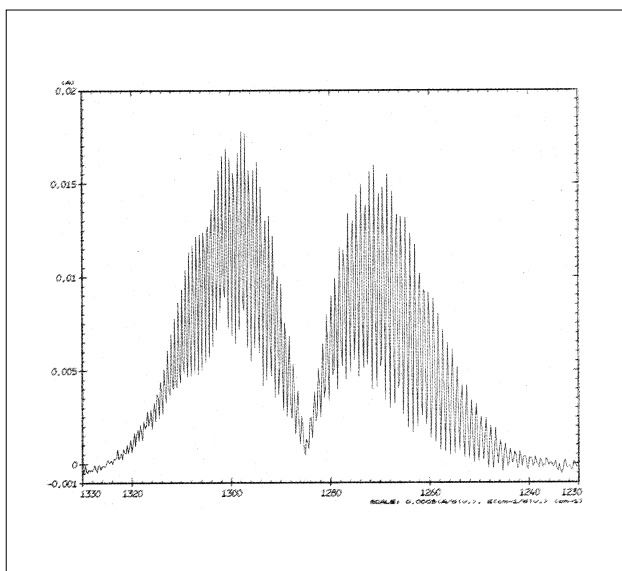
Fig. 4.4.4 Infrared spectrum of NO gas

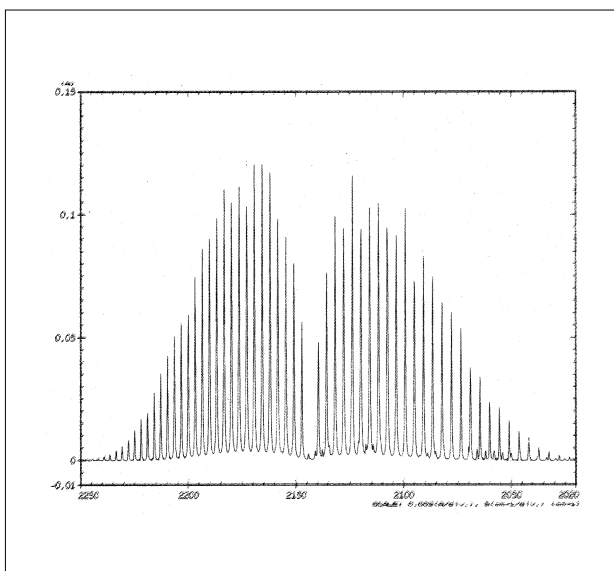Fig. 4.4.5 Infrared spectrum of N_2O gas

Fig. 4.4.6 Infrared spectrum of CO gas

5. Metals

5.1 Analysis of phenols on electrical wiring surfaces - GC

•Explanation
Phenols generated when electrical wiring (polyurethane copper wiring) is heated were analyzed with headspace GC.

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

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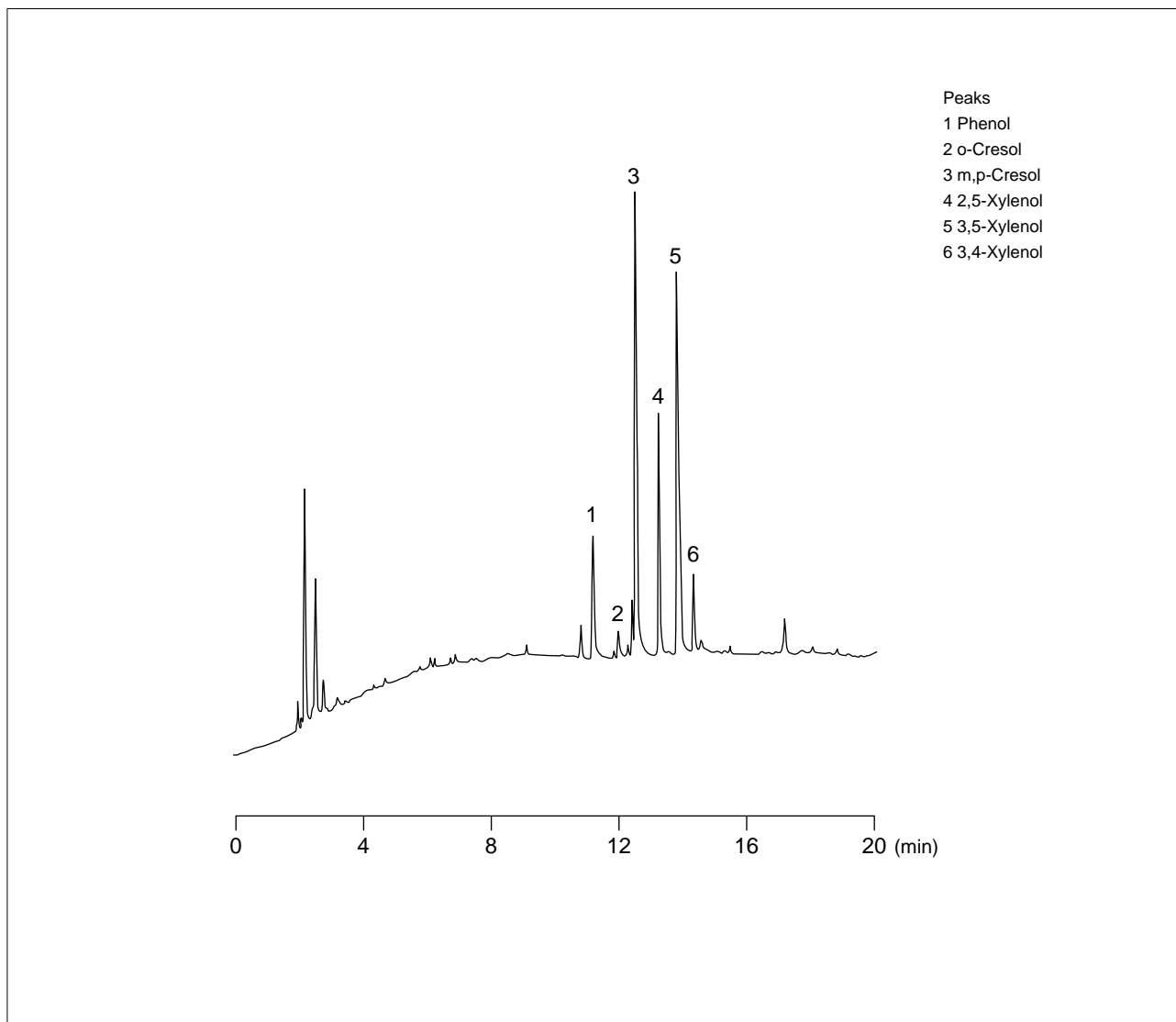Carrier Gas : He   1.4mL/min
Injection   : Split 1 : 14

Peaks
1 Phenol
2 o-Cresol
3 m,p-Cresol
4 2,5-Xylenol
5 3,5-Xylenol
6 3,4-Xylenol

Fig. 5.1.1 Headspace GC of polyurethane copper wire

5.2 Analysis of cyanogens in plating solutions - LC

•Explanation

Cyanides contained in precious metal plating solutions such as gold or silver plating solutions are important objects for measurement not only for product control but also for management of plating waste water. These cyanides can be analyzed with the cyanogen analysis system which employs the 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 reacted with 4-pyridine / pyrazolone solution and the blue color obtained is measured at the absorbance of the 638nm wavelength. Shown in Figs. 5.2.1 and 5.2.2 are respectively examples of analysis of gold plating solution and silver plating solution.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

Model   : HPLC

for separation

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

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

  Flow Rate   : 0.6mL/min

  Temperature   : 50°C

Detective Condition (Post Column)

[chlorination]

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

  Flow Rate   : 0.3mL/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   : 0.3mL/min
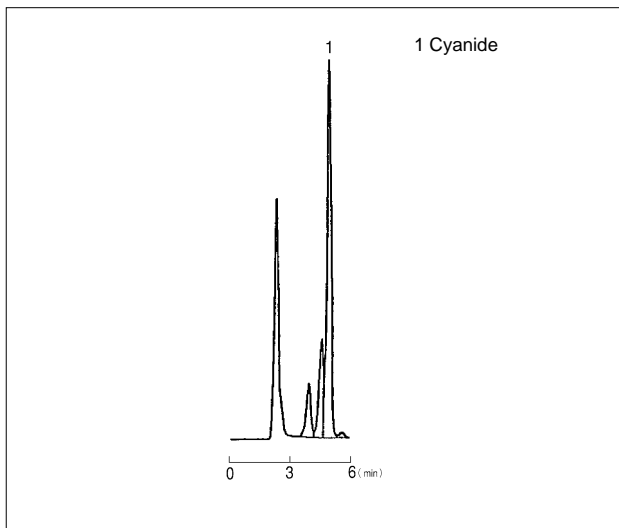
  Temperature   : 100°C

  Detector   : UV-VIS Detector 638nm

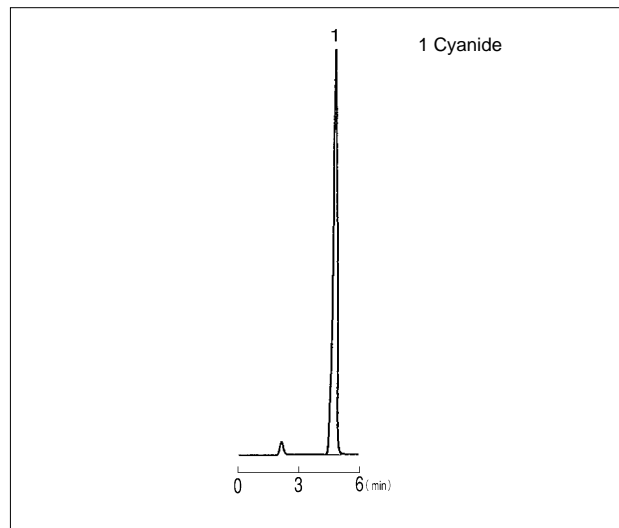Fig. 5.2.1 Example of analysis of cyanides in gold plating solution

Fig. 5.2.2 Example of analysis of cyanides in silver plating solution

5.3 Analysis of organic acids in plating solutions - LC

•Explanation

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. 5.3.1 is an example of analysis of the various organic acids contained in nickel plating solution, while Fig. 5.3.2 shows an example of analysis of citric acids contained in gold plating solution.

•Pretreatment

Filtered with a non-aqueous membrane filter (0.45µm).

•Analytical Conditions

Model   : HPLC

for separation

  Column   : Shim-pack SCR-102H

            (300mm × 8mm i.d.) × 2(Fig. 5.3.1)

                           × 1(Fig. 5.3.2)

Guard Column : Guard Column SCR-102H

                     (50mm × 6.0mm i.d.)

Mobile Phase : 5mM p-Toluenesulfonic Acid

Flow Rate   : 0.8mL/min

Temperature : 40°C

for detection

  Reagent   : 5mM p-Toluenesulfonic Acid

               20mM Bis-Tris

               100µM EDTA-2Na

  Flow Rate   : 0.8mL/min

  Detector   : Conductivity Detector

1 Oxalacetic Acid
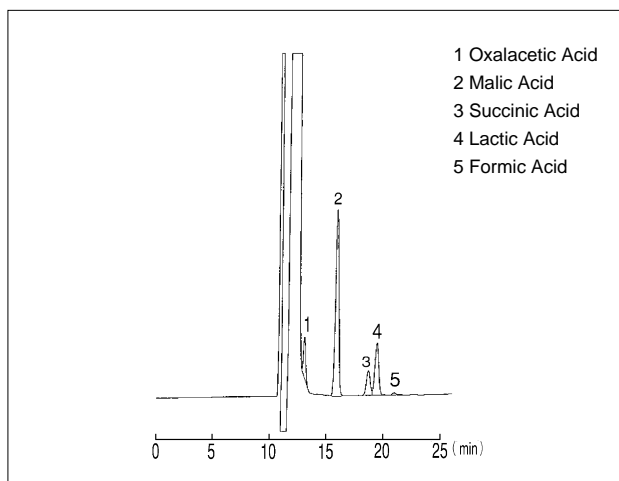2 Malic Acid
3 Succinic Acid
4 Lactic Acid
5 Formic Acid

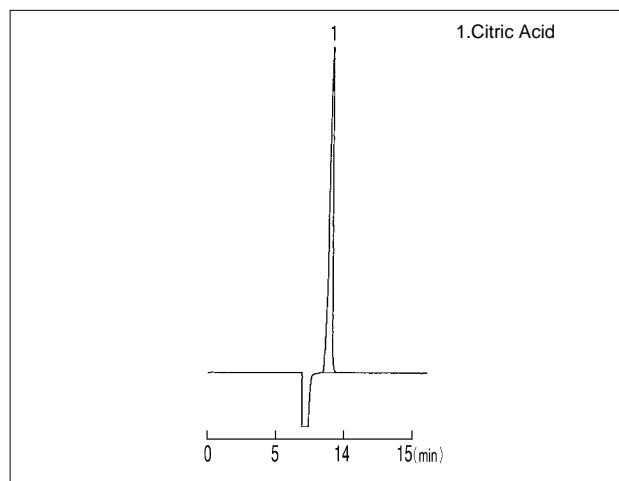Fig. 5.3.1 Example of analysis of organic acids in nickel plating solution

1.Citric Acid

Fig. 5.3.2 Example of analysis of citric acids in gold plating solution

5.4 Analysis of formaldehydes in plating solutions - LC

•Explanation

An example of analysis of formaldehydes employed as reducing agents is shown in Fig. 5.4.1. 2,4-DNPH (dinitrophenylhydrazine) derivatization is carried out. After it is separated in the column, measurement is carried out at an absorbance of wavelength 360nm. Using copper pyrophosphate plating solution in this case, the derivatization reaction and injection of the sample can be done automatically with the auto-injector.

•Pretreatment

2,4-DNPH (dinitrophenylhydrazine) derivatization (refer to chart 5.4.1 for details).

•Analytical Conditions

Model   : HPLC

Column   : STR ODS-Ⅱ

              (150mm × 4.6mm i.d.)

Mobile Phase : Acetonitrile/Water=45/55(v/v)

Flow Rate   : 0.8mL/min

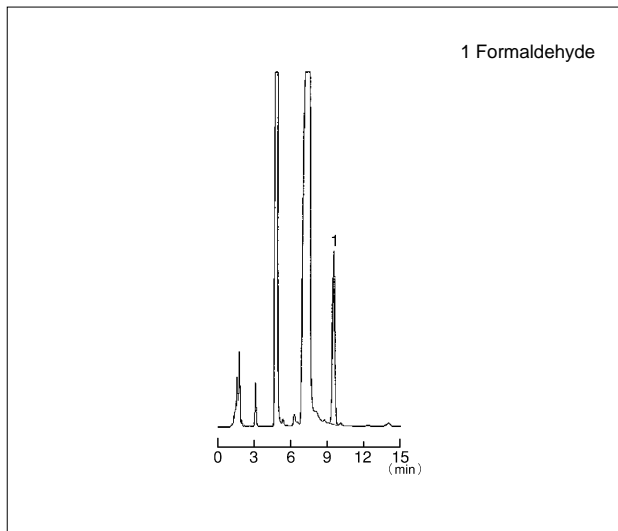Temperature   : 40°C

Detection   : UV-VIS Detector 360nm

Fig. 5.4.1 Example of analysis of formaldehydes in copper pyrophosphate plating solution
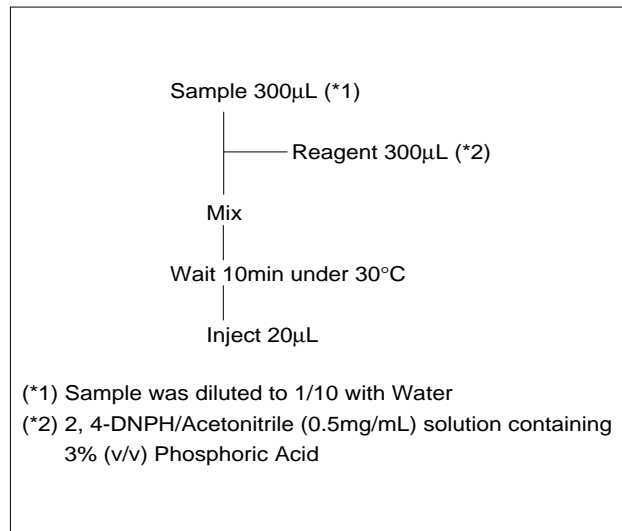

Chart 5.4.1 Conditions for automatic derivatization

5.5 Analysis of magnesium (Mg) in aluminum alloys - AA

•Explanation

Atomic absorption analysis is an effective method of identifying compounds within alloys. Shown here is an example of analysis of magnesium in aluminum alloy by the flame atomization method.

Lower limit of quantitation (guide)

Approximately 0.004% (varies with throughput. In this instance, 0.5g/100mL diluted 10 times).

•Pretreatment

(1) 0.5g of the sample is placed and weighed in a beaker.
(2) 30mL of hydrochloric acid (1+1) is added and thermally decomposed over a sand bath.
(3) 1mL of hydrogen peroxide water (30%) is added. It is heated some more to sufficiently decompose the sample, so that the hydrogen peroxide is expelled.
(4) After cooling the sample is made up to 100mL with purified water and used as the sample stock solution.
(5) In the case of Mg measurement the sample stock solution was diluted a further 10 times. For the

standard solution Al and strontium were added to 500ppm and 1,000ppm respectively, while strontium was added to 1,000ppm to the sample solution used in measurement. Measurement was carried out with the calibration curve method. In the actual measurement the burner angle was set to approximately 30 degrees, and the sensitivity adjusted.

•Analytical Conditions

Wavelength   : 285.2 nm

Lamp Current   : 8 mA

Slit Width   : .5 nm

Lamp Mode   : BGC-D$_2$

Flame   : Air-C$_2$H$_2$

C$_2$H$_2$ Flow Rate : 1.8 L/min

Burner Angle   : 30 degree

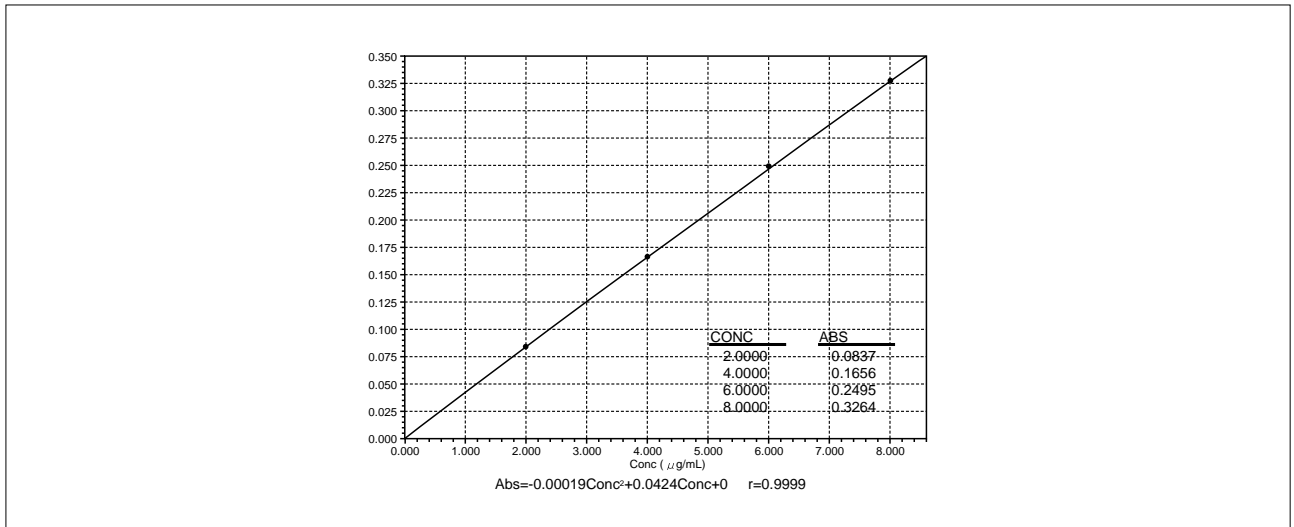| CONC	ABS
2.0000	0.0837
4.0000	0.1656
6.0000	0.2495
8.0000	0.3264

Abs=-0.00019Conc^2+0.0424Conc+0   r=0.9999

Fig. 5.5.1 Calibration curve

Sample	Concentration within solution	Amount of sample collected	Amount of sample made up	Dilution rate	Concentration within solid
001	0.397 ppm	0.5 g	100mL	10	0.079 %
002	0.888 ppm	0.5 g	100mL	10	0.177 %

Table 5.5.1 Measurement Results

5.6 Analysis of manganese (Mn) in steel - AA

•Explanation

Atomic absorption analysis is an effective method of identifying components within steel. Shown here is an example of analysis by the flame atomization method of magnesium within an aluminum alloy in steel.

Lower limit of quantitation (guide)

Approximately 0.01% (varies with throughput. In this instance, 1.0g/100mL diluted 100 times).

•Pretreatment

(1) 1.0g of the sample is placed and measured in a beaker.
(2) 20mL of hydrochloric acid (1+1) is added to the sample and thermally decomposed gently over a sand bath.
(3) 5mL of hydrogen peroxide water (30%) is then carefully added, little by little. The sample is heated so that as the sample is sufficiently decomposed the hydrogen peroxide is expelled.
(4) The sample is filtered with filter paper (5 type A), and the solids on the filter paper washed using warm hydrochloric acid (2+100). The sample is washed a further 3, 4 times with warm purified water. The filtrate and the washings are collected in a 100mL measuring flask.
(5) After cooling the sample is made up to 100mL with purified water and used as the sample stock solution.
(6) In the case of Mn measurement the sample stock solution is diluted a further 100 times, and Fe is added to 100ppm to the standard solution. It is then measured by the calibration curve method.

•Analytical Conditions

Wavelength   : 279.5 nm
Lamp Current : 6 mA
Slit Width   : 0.2 nm
Lamp Mode   : BGC-D_2

Flame   : Air-C_2H_2
C_2H_2 Flow Rate : 2.0 L/min

CONC	ABS
0.5000	0.0495
1.0000	0.1064
1.5000	0.1538
2.0000	0.2087

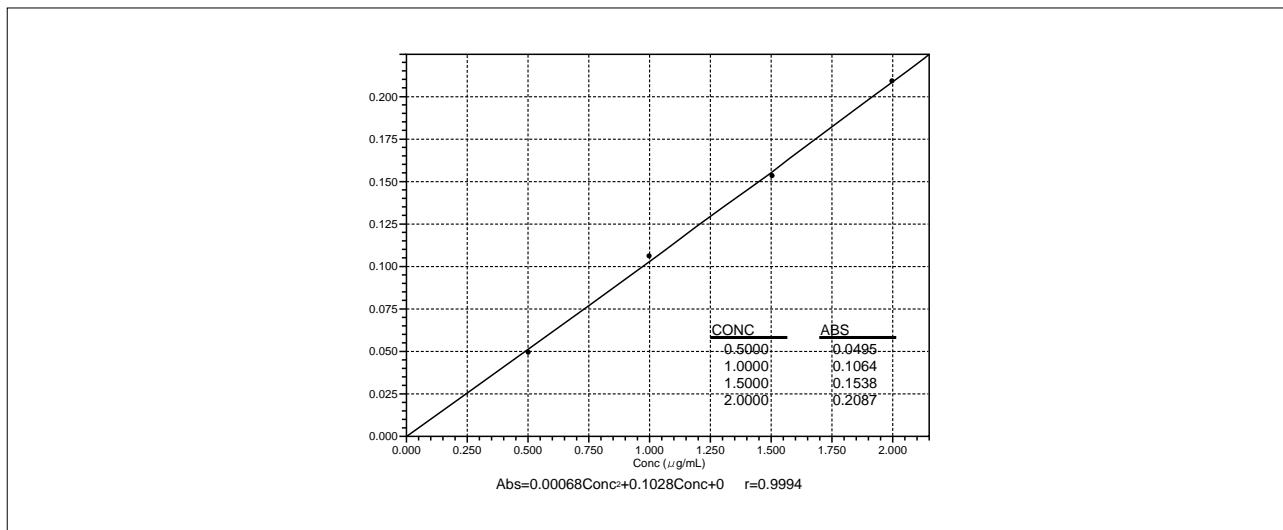$Abs = 0.00068 Conc^2 + 0.1028 Conc + 0$ $r = 0.9994$

Fig. 5.6.1 Calibration curve

Sample	Concentration within solution	Amount of sample collected	Amount of sample made up	Dilution rate	Concentration within solid
001	0.885 ppm	1.00 g	100mL	100	0.88 %
002	1.836 ppm	1.00 g	100mL	100	1.84 %

Table 5.6.1 Measurement Results

6. Glass / Ceramic Products

6.1 Analysis of iron (Fe) in clay minerals - AA

•Explanation

Montmorillonite, a type of clay mineral, is used in applications like adsorbents, catalysts, and binding agents in casting. A characteristic of montmorillonite is that its thermal properties changes with the Fe and Mg content. Shown here is an example of analysis of iron (Fe) by the flame atomization method.

Lower limit of quantitation (guide)

Approximately 0.2% (varies with throughput. In this instance, 0.2g/50mL diluted 50 times).

•Pretreatment

(1) 0.2g of the sample is placed and weighed in a platinum crucible.
(2) 10mL of hydrofluoric acid and 5mL of perchloric acid is added. The sample is thermally decomposed over a sand bath until the white smoke of the perchloric acid is generated.

(3) After cooling, 10mL of hydrochloric acid (1+1) is added, and then boiled.
(4) After cooling the sample was made up to 50mL with purified water, and this was used as the sample stock solution.
(5) In the case of Fe measurement the sample stock solution was diluted a further 50 times, and measured by the calibration curve method.

•Analytical Conditions

Wavelength	: 248.3 nm
Lamp Current	: 12 mA
Slit Width	: 0.2 nm
Lamp Mode	: BGC-D$_2$

Flame	: Air-C$_2$H$_2$
C$_2$H$_2$ Flow Rate	: 2.0 L/min

CONC	ABS
0.8000	0.0570
1.6000	0.1060
2.4000	0.1602
3.2000	0.2160

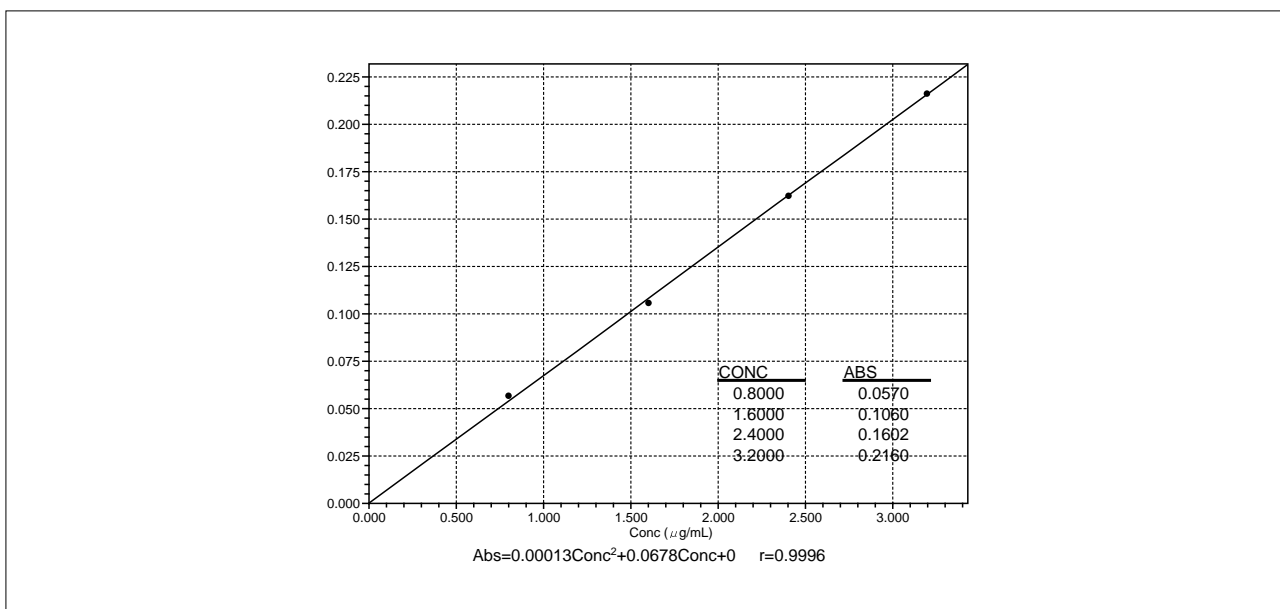$$Abs = 0.00013 Conc^2 + 0.0678 Conc + 0 \quad r = 0.9996$$

Fig. 6.1.1 Calibration curve

Sample	Concentration within solution	Amount of sample collected	Amount of sample made up	Dilution rate	Concentration within solid
001	1.51 ppm	0.2 g	50mL	50	1.89 %
002	2.30 ppm	0.2 g	50mL	50	2.88 %

Table 6.1.1 Measurement Results

6.2 Analysis of chrome (Cr) in fine ceramics - AA

•Explanation

In order to make high quality fine ceramics, technology and quality control is necessary at every step of the manufacturing process. As a part of this, the analysis of trace elements contained within fine ceramics becomes important. Shown here is an example of analysis of chrome (Cr) by the electro-thermal atomization method.

Lower limit of quantitation (guide)

Approximately 1ppm (varies with throughput and dilution rate. In this instance 0.2g/25mL, diluted 10 times).

•Measurement

(1) 0.2g of the sample was thermally decomposed using hydrofluoric acid.
(2) After cooling, the total amount was made to 25mL with purified water, and used as the sample stock solution.
(3) In the case of measurement of chrome, the sample stock solution was diluted 5 times. It was measured by the calibration curve method as the influence of the matrix was not accepted.

•Analytical Conditions

Wavelength   : 357.9 nm

Lamp Current : 10 mA

Slit Width   : 0.5 nm

Lamp Mode   : BGC-D_2

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

Stage	Temp.(°C)	Time(sec)	Heat Mode	Ar Flow Rate(L/min)
1	120	15	RAMP	0.10
2	300	10	RAMP	0.10
3	700	15	RAMP	0.10
4	700	10	STEP	0.10
5	700	3	STEP	0.00
6	2600	3	STEP	0.00
7	2700	2	STEP	1.00

☐ :Atomizing Stage

CONC.   ABS.
0.0000   0.0027
1.0000   0.0805
3.0000   0.2397
5.0000   0.3941
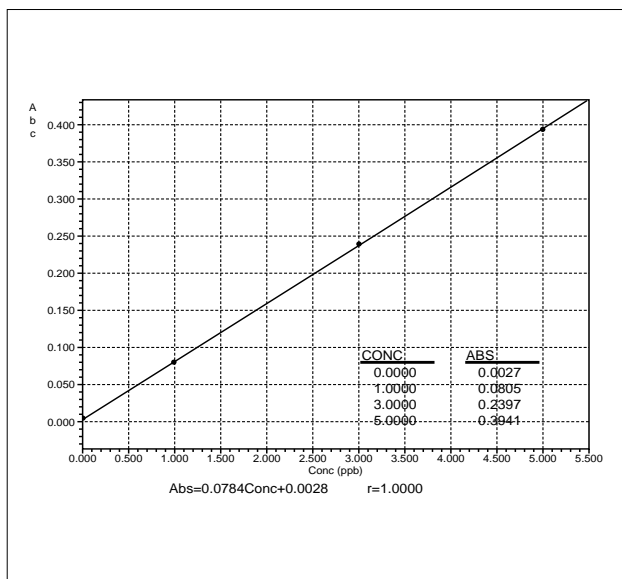
Abs=0.0784Conc+0.0028   r=1.0000
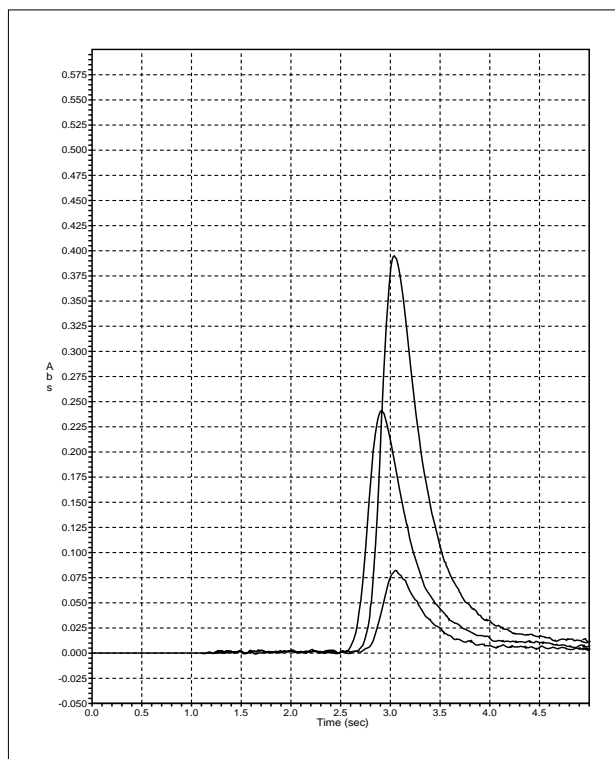
Fig. 6.2.1 Calibration curve

Fig. 6.2.2 Peak profile

Concentration within solution	Amount of sample collected	Amount of sample made up	Dilution rate	Concentration during weight loss
2.83ppb	0.2g	25.0mL	10	35.4ppm

Table 6.2.1 Measurement Results

6.3 Measurement of the solar transmittance (reflectance) of flat glass - UV

•Explanation

Glass is a familiar material which, owing to its characteristics (transparency, corrosion resistant, easiness of manufacture), has always been a part of our lives. Glass in windows is a typical example of application. A lot of high performance flat glass is being produced which, in addition to its classical properties of keeping out the wind and rain while letting in sunlight, also features characteristics such as allowing visible light through but not heat waves (infrared and near infrared). Introduced here is a method of testing the properties of such high performance flat glass (JIS-R3106), and an example of measurement employing a system that conforms to this standard.

Testing method on transmittance, reflectance of flat glass, and evaluation of solar heat gain coefficient of flat glass

This standard (JIS-R3105) standardizes the test for the whole range of energy saving glass, including double glazing and heat wave absorption flat glass, with respect to their daylight, solar radiation, and heat reflection capabilities. With respect to the radiant flux of sunlight incident on window glass, the solar transmittance (reflectance) is defined as the ratio of transmission radiant flux (reflection radiant flux) to the incident radiant flux. Its equation is stipulated as follows.

References

JIS-R3105

$\tau e = \Sigma^{1800}_{340} E\lambda \cdot \Delta\lambda \cdot \tau(\lambda)$ (Solar reflectance)

$\rho e = \Sigma^{1800}_{340} E\lambda \cdot \Delta\lambda \cdot \rho(\lambda)$ (Solar transmittance)

$\alpha e = 1 - \tau e - \rho e$ (Solar absorption rate)

Here $E\lambda \cdot \Delta\lambda$ is the load coefficient,

$\tau(\lambda)$ is the spectral reflectance,

$\rho(\lambda)$ is the spectral transmittance.

Measurement was carried out on the following 3 items:

1. Float glass
2. High performance heat reflection glass
3. High insulation double glazing

•Analytical Conditions

Measuring Apparatus : UV-3100

Attachment : MPC-3100
                          Special Color Measurement
                          Software

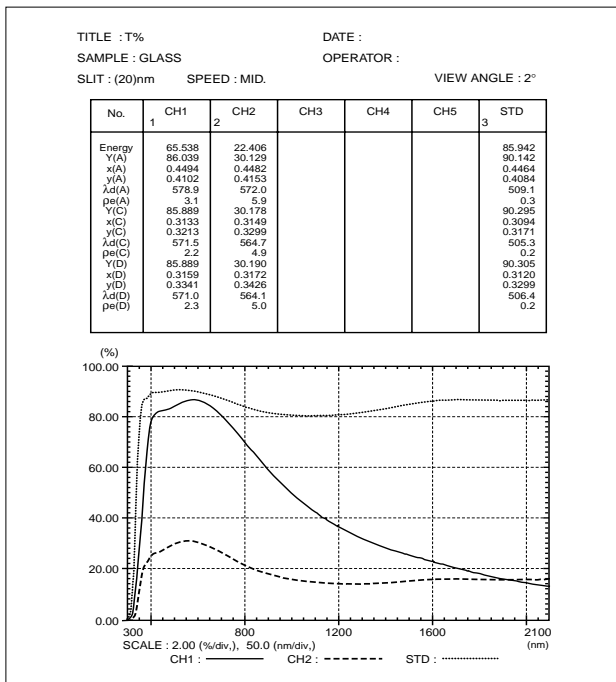Scan Range : 300nm-2,100nm

Sampling Interval : 2.0nm

Slit Width : 20nm

Fig. 6.3.1 Measurement data of the solar transmittance of flat glass
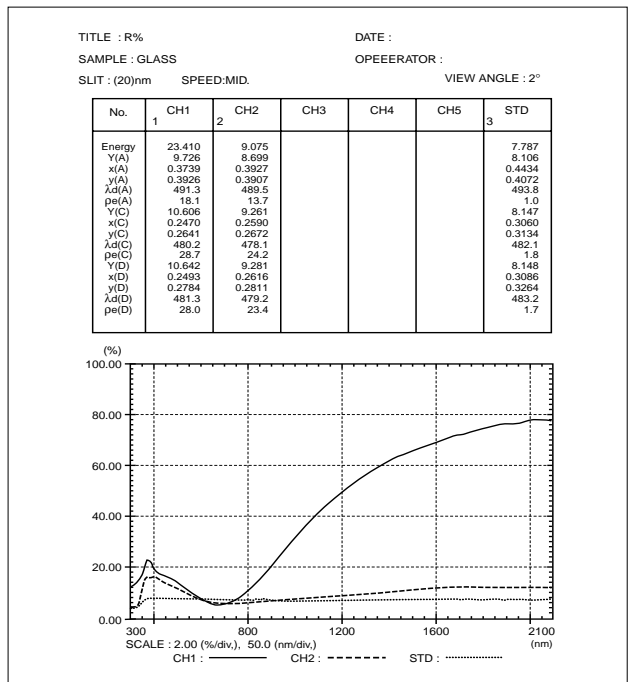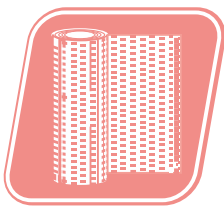

Fig. 6.3.2 Measurement data of the solar reflectance of flat glass

7.1 Headspace gas analysis of indoor construction materials - *GC*

•Explanation

As a basic means of assessing indoor pollution, it is extremely useful to know how much of what compounds are being generated from construction materials and interior materials. Introduced here is an example of analysis by headspace GC of gas generated by plasterboards used as wallpaper backing for interior materials / indoor construction materials.

The amount detected varies greatly depending on whether it is warmed at 50°C or at 100°C. It can be surmised that when it is warmed at a lower temperature the compounds on the surface of the construction material are vaporized, whereas at the higher temperature the compounds enclosed within the material are expelled into the gaseous phase as well.

•Pretreatment

2 pieces of the sample 1cm x 4cm were enclosed in a vial, and their headspace sample analyzed after being warmed at 50°C and 100°C for 60 minutes.

•Analytical Conditions

Model   : HS-40XL + GC-17AAFw ver.3
Column   : DB-1   30m × 0.32mm i.d. df=5μm
Col.Temp. : 40°C (5min)-10°C/min-200°C
Inj.Temp. : 250°C
Det.Temp. : 250°C (w-FID)
Carrier Gas : He   3mL/min
Injection : Direct Injection

Peaks
1 Methanol + Acetaldehyde
2 Ethanol
3 Acetone
4 Vinyl acetate
5 Ethyl acetate
6 n-Butanol
7 1-Metoxy-2-propanol
8 Toluene
9 Hexanal
10 m.p-Xylene
11 Cyclohexanon
12 2-Ethylhexanol

Thermostatting Temp. 50 °C

Thermostatting Temp. 100 °C
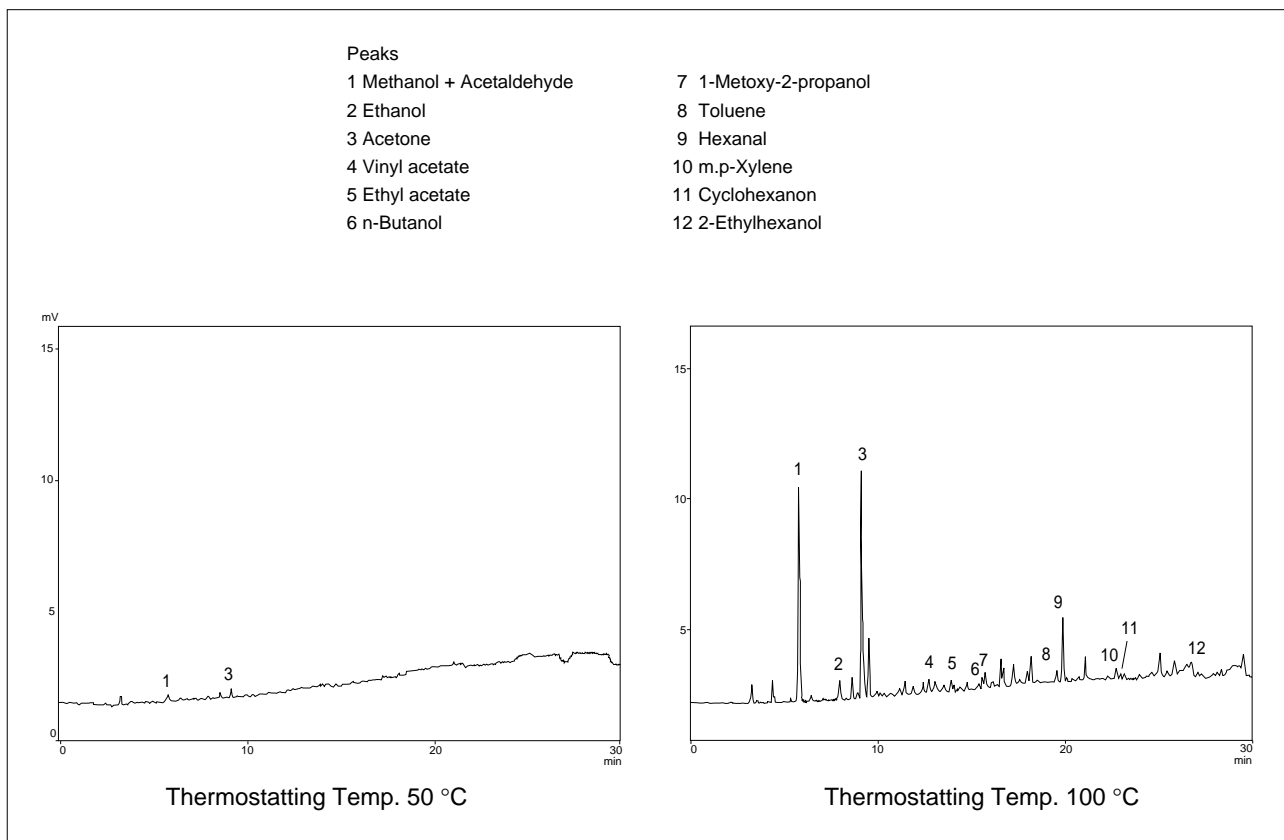
Fig. 7.1.1 Headspace GC of plasterboard for wallpaper backing

7.2 Analysis of sodium (Na) in hydrogen peroxide - AA

•Explanation

It is necessary for impurities contained in chemical industrial goods 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 goods requires high sensitivity measurement. Shown here is a trace analysis of Na in hydrogen peroxide by the electro-thermal atomization method.

Lower limit of quantitation (guide)

Approximately 0.1ppb.

•Measurement

(1) Measured with the standard addition method when the hydrogen peroxide is diluted 2 times by the auto-sampler.
(2) 20µL of hydrogen peroxide was injected, while the amount of 2ppb Na standard solution injected was varied between 0 to 20µL. The rest was made up with purified water so that the total amount injected was always 40µL.

•Analytical Conditions

Wavelength   : 589.0 nm

Lamp Current : 12 mA

Slit Width   : 0.2 nm

Lamp 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 Stage

Conc	ABS
0.0000	0.0181
0.2000	0.0353
0.4000	0.0538
1.0000	0.0993

Abs=0.081Conc+0.019   r=0.9991
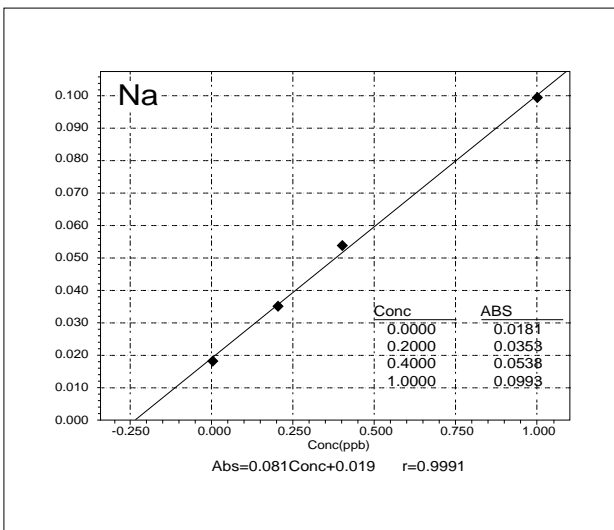
Fig. 7.2.1 Analysis of Na in hydrogen peroxide water by the standard addition method
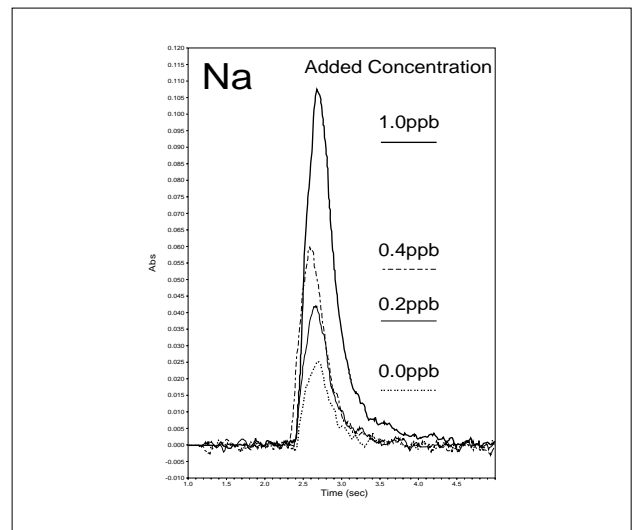
Fig. 7.2.2 Overlay of the peak profiles of Na in hydrogen peroxide water

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

Table 7.2.1 Measurement Results
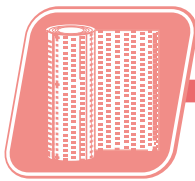
7.3 Analysis of formaldehydes remaining on underwear (1) *- UV*

•Explanation

Formalin (formaldehyde) is used during the manufacture of clothing to prevent loss of shape and color. However, formaldehyde left on clothing is a cause of skin complaints such as itchiness / rashes, and hence manufacturers need to ensure that residual amounts are below regulated values. Amongst clothing, underwear and infant clothing are especially regulated by the standards established in "JIS-L1041(1983)", with testing methods standardized in the "Ministry of Health and Welfare 1974 Ordinance No. 34".

A number of analytical methods are presented in the JIS, and of these the "acetylacetone method" is often used for its convenience.

•Lower limit of quantitation (guide)

Approximately 0.01ppm (varies with the sample).

•Pretreatment

An example of the measurement of formaldehydes in underwear and baby underwear is shown on the next page. The sample is cut finely, and a fixed quantity of the sample is immersed in a fixed quantity of water. This is warmed at 40 degrees for 30 minutes. After it is left to cool, the action of acetylacetone in excess ammonium acetate produces the yellow 3,5-diacetyl-1, 4-dihydrolutidine which has its absorption maximum in the 415nm region. Using this absorption, the formaldehyde liquid diluted with water is made the standard solution and measurement carried out by the calibration curve method.

•Analytical Conditions

Measuring Apparatus :UV-1600
Cell   :Standard Quartz Cell
Scan Range   :412.0nm
Slit Width   :2.0nm

The calibration curve and absorption spectra of the standard sample (1 to 4μg/mL) by the acetylacetone method
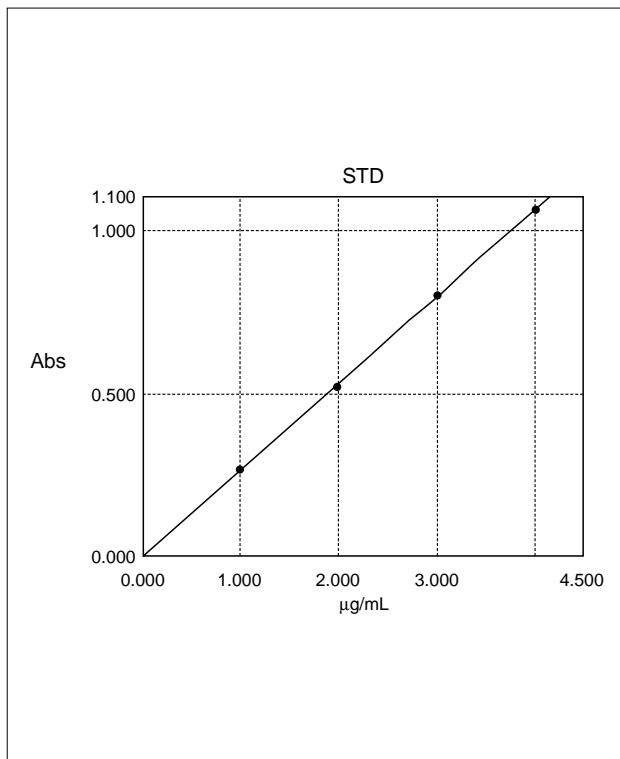
Fig. 7.3.1 Calibration curve
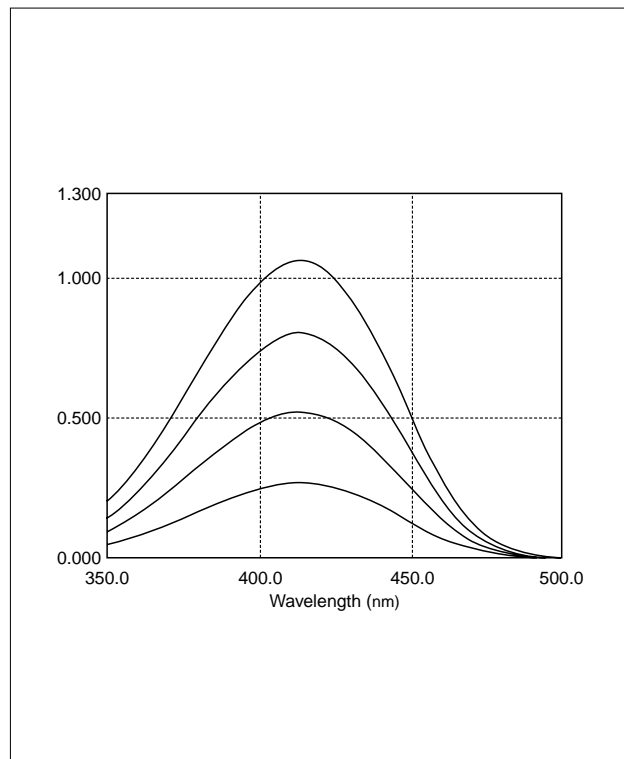
Fig. 7.3.2 Absorption spectra
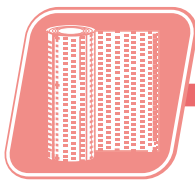
7.3 Analysis of formaldehydes remaining on underwear (2) - UV

[Reference 1] Measurement Results

ID	Concentration (µg/mL)	Absorbance	
1	0.03336	0.010	
1	0.03411	0.010	
Average :	0.03373	0.010	←Result of underwear measurement
Standard deviation : 0.000			
2	0.01475	0.005	
2	0.01437	0.005	
Average :	0.01456	0.005	←Result of baby underwear measurement
Standard deviation :		0.0001	

[Reference 2] Measurement Principle (Chemical Equation)

$2CH_3COCH_2COCH_3 \ + \ CH_3COONH_4 \ + \ HCHO \ \rightarrow$

(Acetylacetone)   (Ammonium Acetate)

$+3H_2O+CH_3COOH$
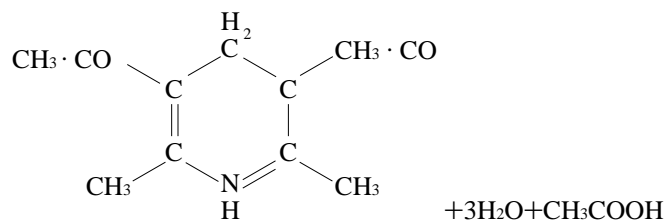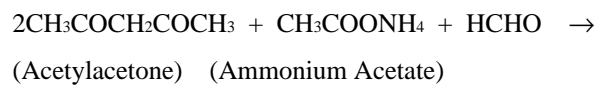
7.4 Measuring the transmission and reflection spectra of optical materials - UV

•Explanation

By combining the Shimadzu recording spectrophotometer UV-3100 and the multi-purpose large sample compartment MPC-3100 with built-in integrating sphere, the transmittance and reflection spectrum can be measured with a high degree of precision over a wide range of wavelengths from the near infrared to the ultraviolet. Large samples can be measured without having to break them down. 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 : 20 nm
Attachment : Multi purpose compartment
                       MPC-3100
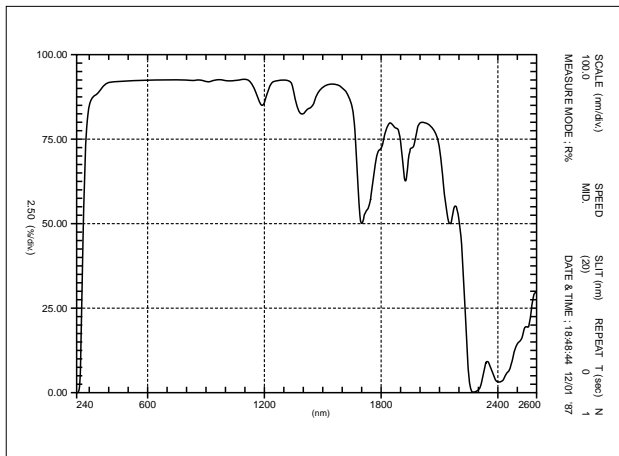
Fig. 7.4.1 Transmittance spectrum of a CD substrate
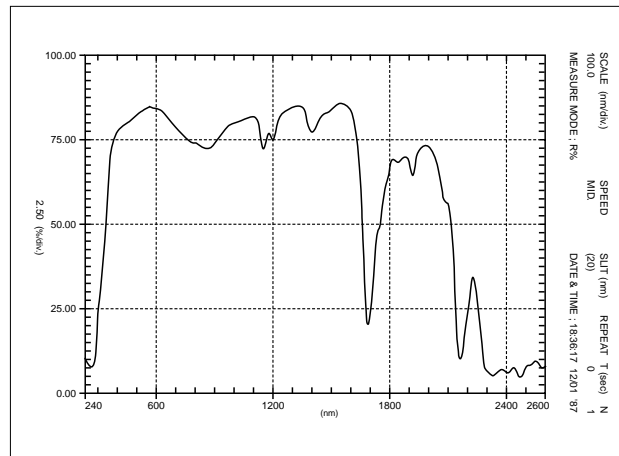
Fig. 7.4.3 Reflection spectrum of a silicon wafer
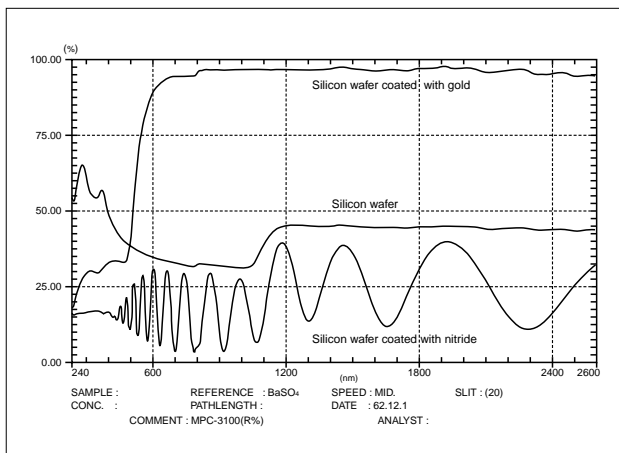
Fig. 7.4.2 Reflection spectrum of a CD
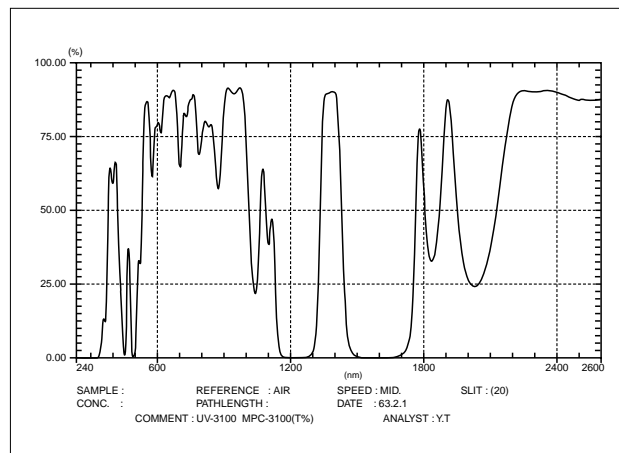
Fig. 7.4.4 Transmittance spectrum of a bandpass filter

7.5 Analysis of paper using the horizontal ATR method (1) - FTIR

•Explanation

Cellulose separated from timber is the raw material of paper. A binder is added to the cellulose and pressed, and a sizing agent to preserve its strength and prevent ink bleed is applied together with pigments and clay etc. In addition, the paper can be coated with a range of substances for special applications. Paper containers for food products, adhesive tape, release paper and coated paper are examples of these. Measurement by the ATR method using the FTIR is the optimal way of analyzing these paper surfaces with ease.

The ATR method of measurement involves contacting the sample to the surface of a plate prism made of a material with a high refractive index. Although the roughness of the paper surface varies with the type of paper, the surface spectrum of most kinds of paper can be measured by applying a greater force when pushing the paper down onto the prism to ensure a greater degree of contact.

•Pretreatment

Although there are cases when the size of the sample is adjusted to fit the size of the prism, pretreatment will not normally be particularly required if a sample 1cm wide and a few cmLong is secured. However, a characteristic of the ATR method is that, the lower the wavenumber, the greater the peak intensities. Therefore there are instances when, upon completion of measurement, the spectrum data is processed to correct the data with the reciprocal of the wavenumber (ATR correction) in order to bring it closer to the transmittance spectrum.

•Analytical Conditions

Accessory : Horizontal ATR(IRE : ZnSe)

Resolution : 4cm^{-1}

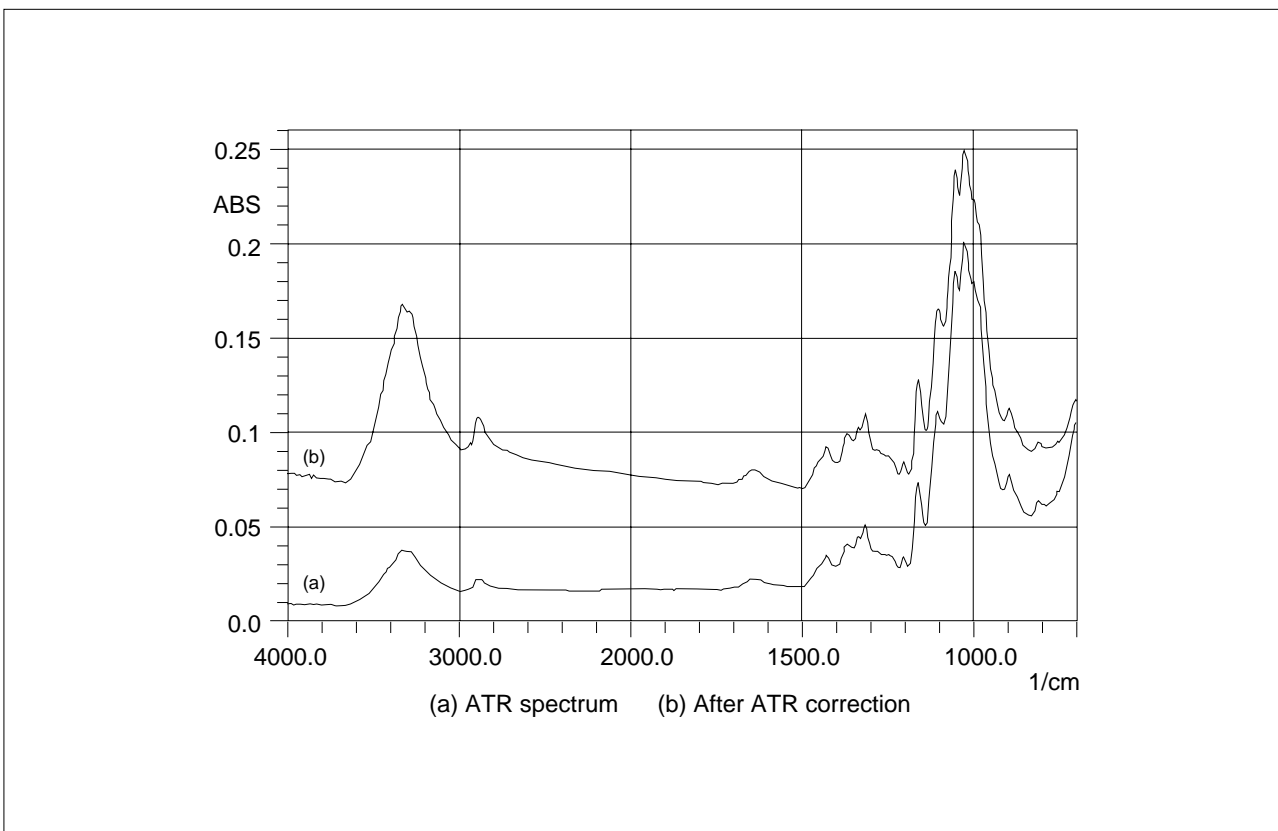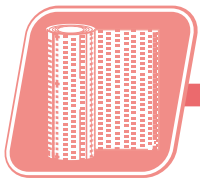Accumulation : 100

Apodization : Happ-Genzel

Detector : DLATGS

(a) ATR spectrum   (b) After ATR correction

Fig. 7.5.1 ATR spectra of facial tissue

7.5 Analysis of paper using the horizontal ATR method (2) - FTIR

●**Measurement Example**

Shown in Figs. 7.5.2 to 7.5.5 are the results of measuring 4 types of paper: cardboard, coated paper, milk carton, and release paper. The spectra for the face and back of each paper are shown overlaid on each other. Peaks that closely resemble those of kaolin and SiO2 can be identified in the spectra for the face of the cardboard and coated paper. In addition, absorption that resembles polyethylene and poly (dimethylsiloxane) can be identified in the carton of milk and release paper.
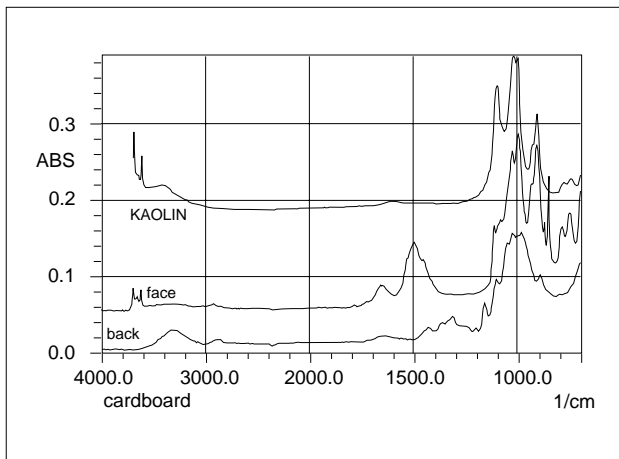
Fig. 7.5.2 ATR spectrum of cardboard
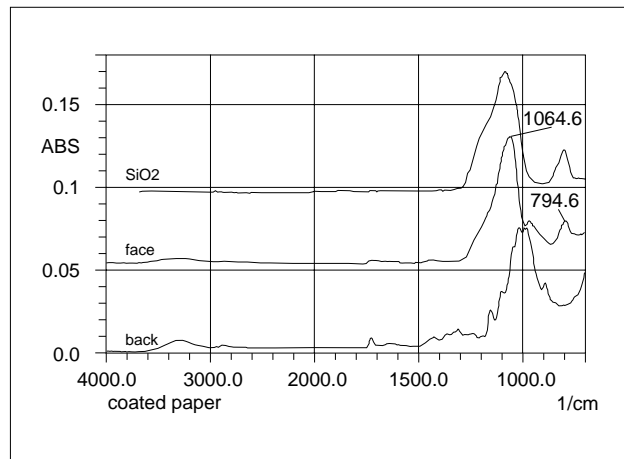
Fig. 7.5.3 ATR spectrum of coated paper
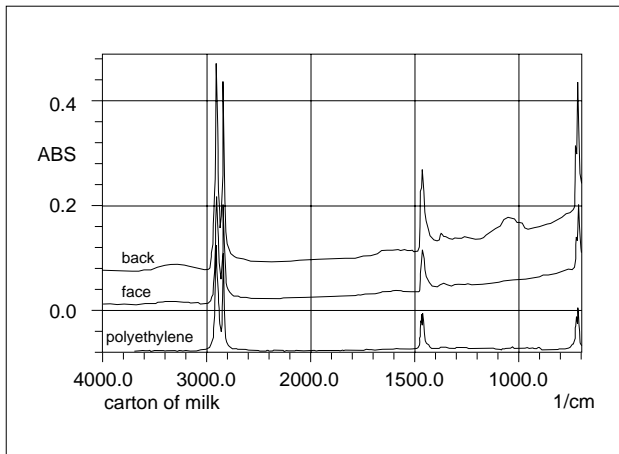
Fig. 7.5.4 ATR spectrum of a carton of milk
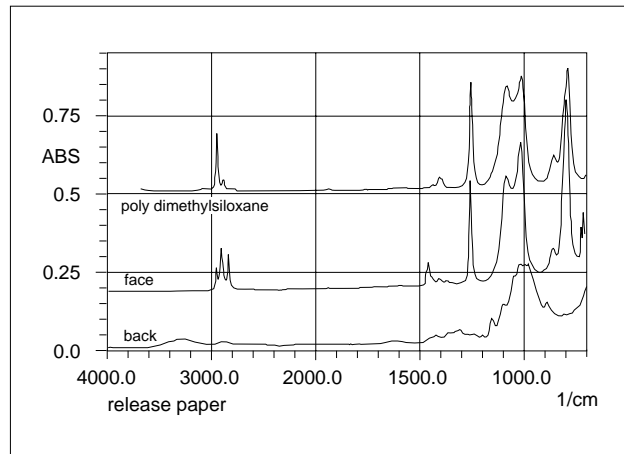
Fig. 7.5.5 ATR spectrum of release paper

7.6 Analysis of contaminants on paper - FTIR

•Explanation

Analysis of minute contaminants is important in quality control. The infrared microscope is capable of measuring minute contaminants quickly and easily, hence lending it to use in a wide variety of fields. Among these the microscopic ATR method does not require any pretreatment such as scraping the sample or adjusting its thickness. It is also not influenced by the interference fringe often seen in transmission measurement, nor is it influenced by the roughness of the surface of the contaminant or the reflection and absorption etc. due to the base seen in reflection measurement. It is thus highly effective in the analysis of deposits and surface contaminants.

Measurement with the microscopic ATR method involves contacting the contaminant with the prism. A relatively hard base will allow the sample to make good contact with the prism. If the base is soft, the contaminant will be buried in the base resulting in the inclusion of the absorption by the base as well. Thus, when measuring contaminants etc. on paper, the spectrum of the paper, which in this instance is the base, needs to be measured so that any influence by the base on the results of the measurement of the contaminant can be identified.

•Results

Shown in Fig. 7.6.1 is a microscopic photograph of the contaminant, and shown in Fig. 7.6.2 are the spectra of the contaminant and the base (paper). In this measurement the contaminant was sufficiently big to allow it to attain good contact with the prism. As a result a good spectrum showing hardly any influence from the paper was obtained.

This spectrum shows absorption by 2nd grade amides, suggesting the contaminant to be a piece of skin.

•Analytical Conditions

Accessory   : ATR Objective(IRE : Ge)

Resolution   : 8cm^{-1}

Accumulation   : 60

Apodization   : Happ-Genzel

Detector   : MCT

Fig. 7.6.1 Magnified photograph of the
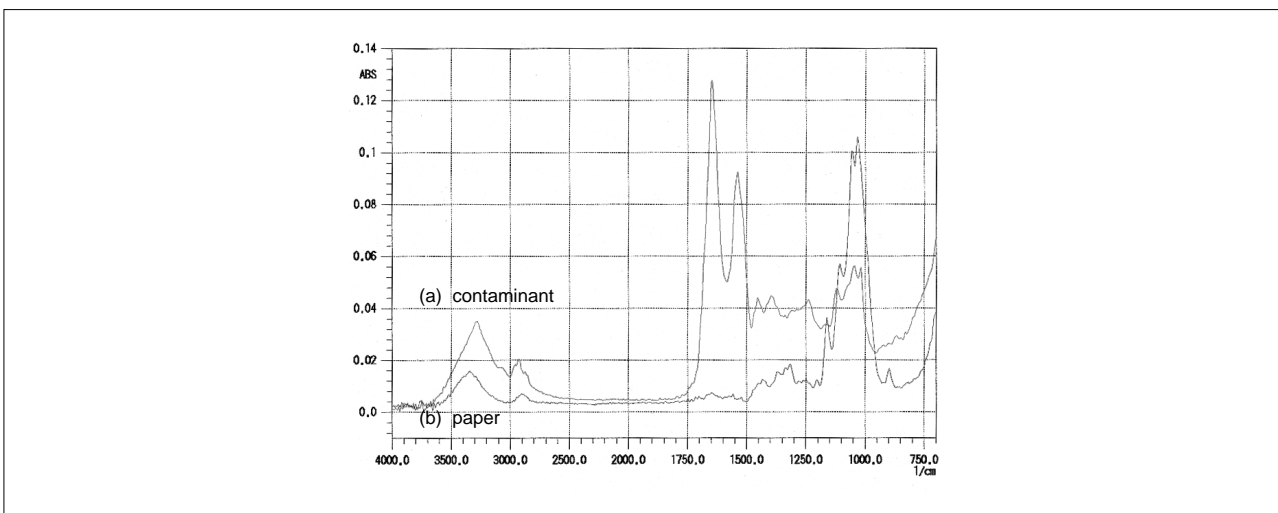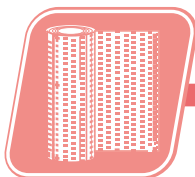contaminant deposited on the paper

Fig. 7.6.2 ATR spectrum of contaminant (a) and paper (b)

7.7 Analysis of contaminants on filters - FTIR

•Explanation

With the microscopic ATR method, measurement is carried out by contacting the contaminant with the prism. It is known that if the surface of the sample is flat, approximately 20 to 30µmø of the sample is in contact with the prism. This means that if a sample smaller than this is measured, it is likely that absorption by a substance other than the target substance will be measured. However, if the sample protrudes above the base, the measurement will not be influenced by the base.

Introduced this time is an example of measurement of a fiber (breadth approximately 10µm) deposited on a nitrocellulose filter.

•Results

The microscopic photograph of the contaminant is shown in Fig. 7.7.1. The measurement results in the form of the spectra of the fiber and the nitrocellulose that is the base are shown in Fig. 7.7.2 . The spectrum of this fiber is not affected by the base, and moreover shows absorption of polyethylene terephthalate.

•Analytical Conditions

Accessory	: ATR Objective (IRE : Ge)
Resolution	: 8cm^{-1}
Accumulation	: 60
Apodization	: Happ-Genzel
Detector	: MCT

Fig. 7.7.1 Magnified image of the fiber deposited on the filter
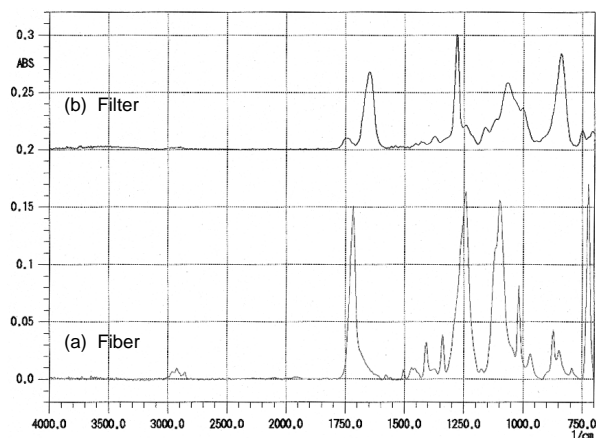
Fig. 7.7.2 ATR spectrum of fiber (a) and filter (b)

SHIMADZU