Solutions for Innovation

Polymeric Materials Analysis by JEOL Mass Spectrometers

- A Guidebook -

Overview of various analytical methods and instruments

Introduction

■ GC-MS

■ Various ionization methods
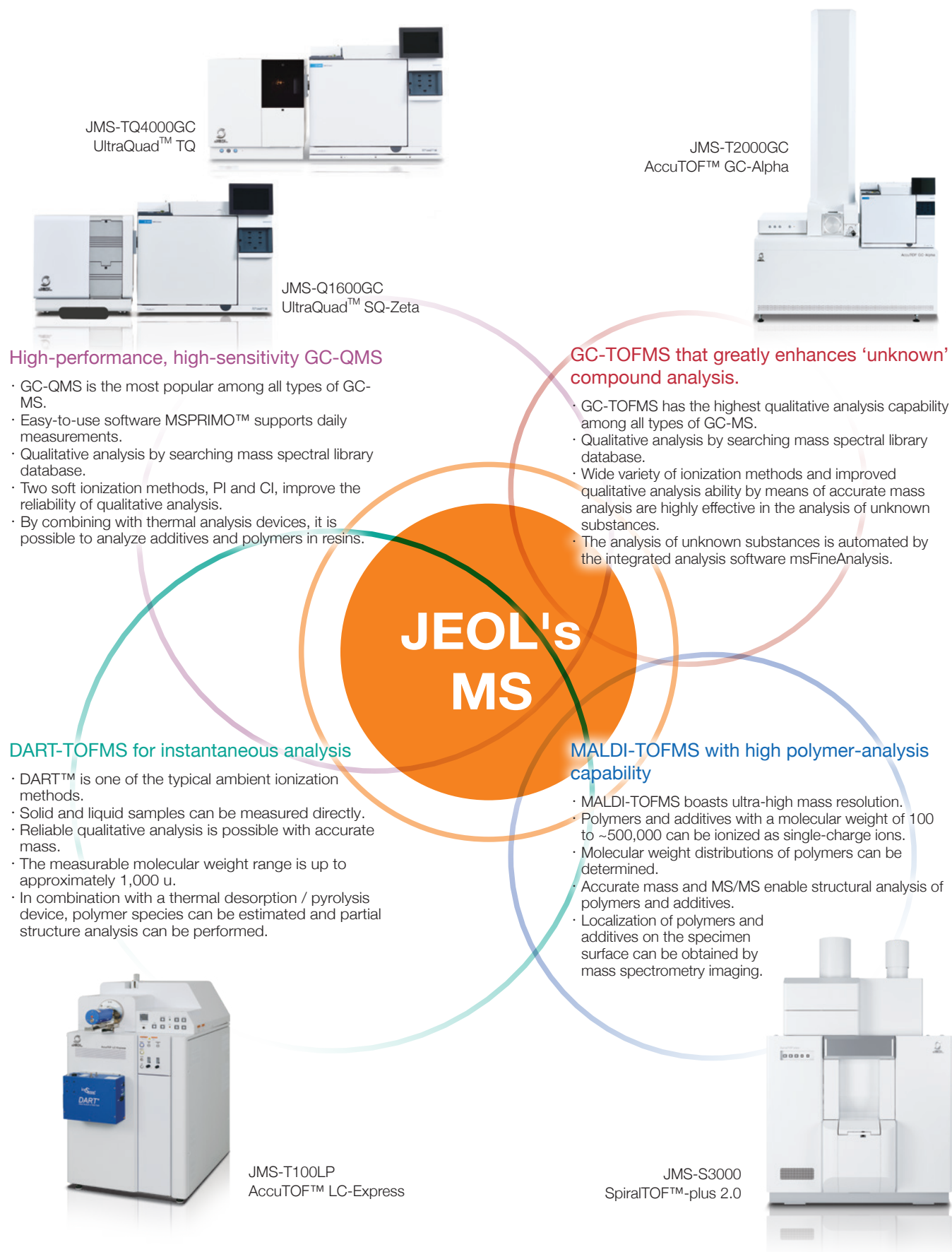   GC-MS (EI, PI, FI, CI)
   MALDI
   DART™

Applications

■ JMS-TQ4000GC UltraQuad™ TQ
   JMS-Q1600GC UltraQuad™ SQ-Zeta

■ JMS-T2000GC AccuTOF™ GC-Alpha

■ JMS-S3000 SpiralTOF™-plus 2.0

■ JMS-T100LP AccuTOF™ LC-Express + DART™

JEOL Ltd.

Mass spectrometry (MS) is a method that can perform qualitative and quantitative analyses of polymers and additives contained in polymeric materials by ionizing them and analyzing their molecular masses.
There are multiple ionization methods, mass spectrometer types, and data analysis technologies, and it is possible to obtain more comprehensive information by combining them.

In this guidebook, we will introduce polymeric material analysis solutions that make full use of JEOL's high-performance mass spectrometers.

JMS-TQ4000GC
UltraQuad™ TQ

JMS-T2000GC
AccuTOF™ GC-Alpha

JMS-Q1600GC
UltraQuad™ SQ-Zeta

High-performance, high-sensitivity GC-QMS

· GC-QMS is the most popular among all types of GC-MS.
· Easy-to-use software MSPRIMO™ supports daily measurements.
· Qualitative analysis by searching mass spectral library database.
· Two soft ionization methods, PI and CI, improve the reliability of qualitative analysis.
· By combining with thermal analysis devices, it is possible to analyze additives and polymers in resins.

GC-TOFMS that greatly enhances 'unknown' compound analysis.

· GC-TOFMS has the highest qualitative analysis capability among all types of GC-MS.
· Qualitative analysis by searching mass spectral library database.
· Wide variety of ionization methods and improved qualitative analysis ability by means of accurate mass analysis are highly effective in the analysis of unknown substances.
· The analysis of unknown substances is automated by the integrated analysis software msFineAnalysis.

JEOL's MS

DART-TOFMS for instantaneous analysis

· DART™ is one of the typical ambient ionization methods.
· Solid and liquid samples can be measured directly.
· Reliable qualitative analysis is possible with accurate mass.
· The measurable molecular weight range is up to approximately 1,000 u.
· In combination with a thermal desorption / pyrolysis device, polymer species can be estimated and partial structure analysis can be performed.

MALDI-TOFMS with high polymer-analysis capability

· MALDI-TOFMS boasts ultra-high mass resolution.
· Polymers and additives with a molecular weight of 100 to ~500,000 can be ionized as single-charge ions.
· Molecular weight distributions of polymers can be determined.
· Accurate mass and MS/MS enable structural analysis of polymers and additives.
· Localization of polymers and additives on the specimen surface can be obtained by mass spectrometry imaging.

JMS-T100LP
AccuTOF™ LC-Express

JMS-S3000
SpiralTOF™-plus 2.0

Overview of various analytical methods and instruments

	JMS-Q1600GC & JMS-TQ4000GC GC-QMS	JMS-T2000GC GC-TOFMS	JMS-S3000 MALDI-TOFMS	JMS-T100LP DART-MS
	P.7-9	P.10-12	P.13-18	P.19-21
Pyrolysis analysis of polymer	✓✓ · Elucidation of polymer class · Differential analysis	✓✓✓ · Elucidation of polymer class based on measured accurate masses · Differential analysis		✓ · Elucidation of polymer class by using a thermal desorption / pyrolysis device
Confirmation of molecular weight distribution of soluble polymer		✓✓ · ≤ 6,000 Da · Confirmation of monomer unit · Confirmation of end groups based on measured accurate masses	✓✓✓ · ≤ 500,000 Da · Confirmation of monomer unit · Confirmation of end groups based on measured accurate masses and MS/MS	✓ · ≤ 2,000 Da · Confirmation of monomer unit
Identification of additives	✓✓ · Mass spectral library database search · Differential analysis	✓✓✓ · Mass spectral library database search · Unknown compound analysis by accurate mass · Differential analysis	✓ · Analysis of high molecular weight additives · Molecular formula list search	✓✓ · Instantaneous analysis · Molecular formula list search
Regulation compliance analysis	✓✓✓ · RoHS · TSCA			
Surface analysis			✓✓✓ · Analysis of adhered foreign matter · Degradation analysis	✓✓ · Analysis of adhered foreign matter
Thermal characterization / TG-MS	✓✓✓ · Evolved gas analysis (including hydrogen)	✓✓✓ · Evolved gas analysis · High mass-resolution measurement		

Gas Chromatography / Mass Spectrometry (GC/MS)

Comprehensive analysis of a mixture is possible by separating volatile components with GC and then mass-separating each component with MS for detection.
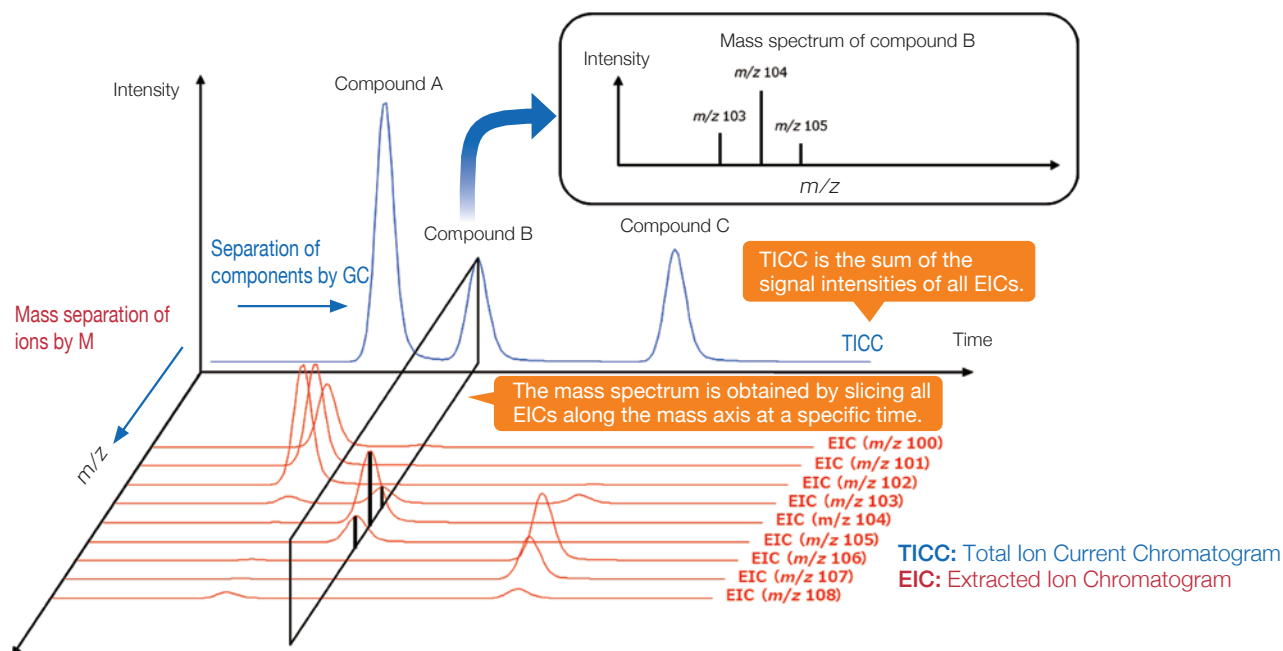

Flow of polymeric material analysis using gas chromatograph - mass spectrometer (GC-MS)

To analyze polymers using GC-MS, there are three different methods depending on the purpose. Polymers cannot be analyzed directly, as they cannot pass through a GC column. Therefore, we pyrolyze polymer samples and analyze low molecular weight pyrolysis products (pyrolyzate). Since the pyrolysis products reflect the structure of the original polymer, it is possible to identify the polymer and analyze its degradation.

① Evolved Gas Analysis (EGA)

The evolved gas from a heated sample is analyzed in real time. A blank tube is installed in the GC, because component separation is not performed in the GC. By monitoring the change in the amount of evolved gas versus temperature, it is possible to determine the appropriate temperature for thermal desorption of additives or thermal decomposition of polymers.

① EGA：40 → 10 °C/min → 600 °C
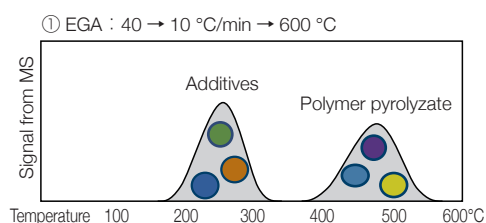
② Thermal desorption (TD) / GC / MS analysis

A separation column is installed in the GC. The components are separated and detected, and qualitative analysis is performed. In thermal desorption, components (additives, etc.) evolved at relatively low temperatures are detected with as little thermal pyrolysis as possible.

② Thermal desorption：40 °C → 10 °C/min → 300 °C

The same sample can be analyzed with 'double shot'.
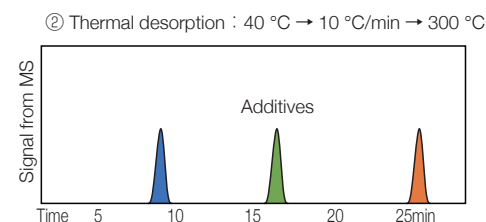
③ Pyrolysis (Py) / GC / MS analysis

Similar to thermal desorption, this analysis involves GC separation, but thermal pyrolysis products generated by instantaneous heating are detected.

Additives and polymer pyrolyzates are detected at the same time in measurements that involve only pyrolysis (single shot). By sequentially performing thermal desorption and pyrolysis on the same sample (double shot), it is possible to extract the information of polymer pyrolyzates only.

③ Pyrolysis：600 °C（constant）
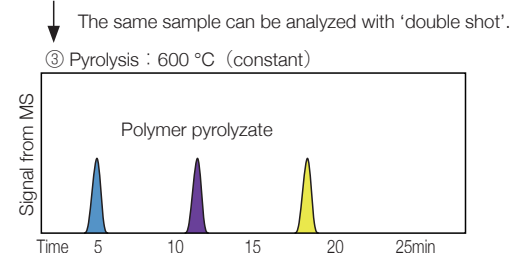
Sample preparation devices for GC-MS

For analyzing a solid sample, a GC sample preparation device is used to generate the sample gas by heating.

Multi-shot pyrolyzer

Maximum heating temperature: 1,050 °C
Maximum sample amount: several tens of milligrams
For EGA and TD or Py / GC / MS analysis

Thermogravimetry (TG)

Maximum heating temperature: 1,600 °C*
Maximum sample amount: approximately 1 g
Simultaneous measurement of EGA and thermogravimetry

*Note: The maximum heating temperature varies depending on the model.

Direct sample introduction

Liquid or solid samples can be introduced directly into the mass spectrometer using direct probes.

Although component separation of a sample mixture is not possible, it is possible to analyze high boiling point / high-mass components that cannot pass through a GC column. Since the analysis time is as short as 1 to 2 minutes, it can also be used for screening. For QMS, direct insertion probe (DIP) and direct exposure probe (DEP) are available. For TOFMS, field desorption probe (FDP) is available in addition to DIP and DEP.

■ DEP (Direct Exposure **Probe)**

Platinum filament

▶ Sample dissolved or dispersed in solvent is applied to the filament at the tip
▶ Suitable for high boiling point and/or thermally labile compounds
▶ Compatible with EI and CI

■ DIP (Direct Insertion Probe)

Glass sample tub

▶ Solid sample can be introduced in the glass sample tube
▶ Suitable for high boiling point and/or insoluble compounds
▶ Compatible with EI and CI

■ FDP (Field Desorption Probe)
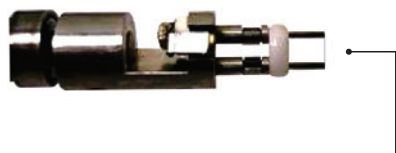
▶ Sample dissolved or dispersed in solvent is applied to the carbon emitter at the tip
▶ Suitable for high boiling point, high molecular weight, and/or thermally labile compounds
▶ Suitable for low- to mid-polar metal complexes
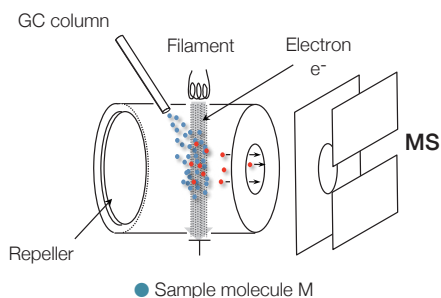▶ Used for field desorption (FD) and field ionization (FI) (see below)

Schematics of FD

Carbon Emitter

Anode (Emitter)

Current

Condensed phase molecules (neutral)

M$^{+\cdot}$, [M+H]$^+$, etc.

Cathode

MS

10kV

Schematics of FI

Carbon Emitter

Anode (Emitter)

GC column

Gas phase molecules (neutral)

M$^{+\cdot}$, [M+H]$^+$, etc.

Cathode

e$^-$

MS

10kV
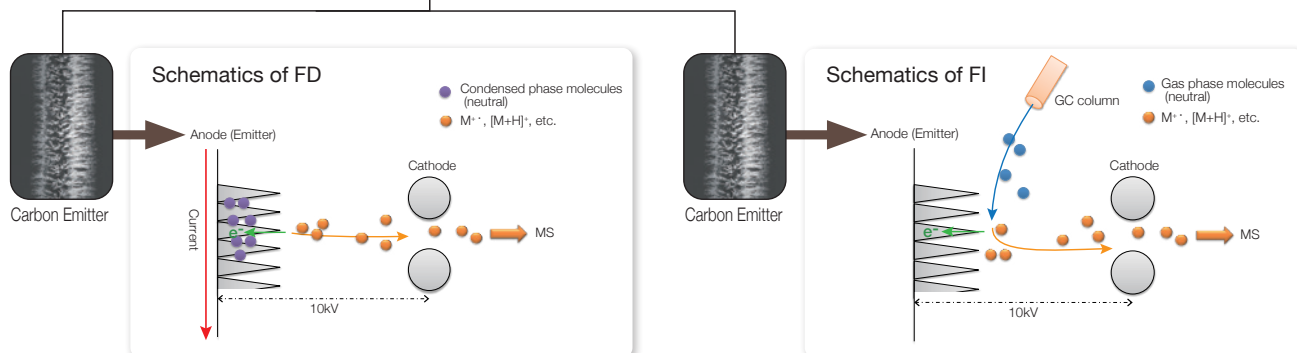
In FI and FD, ionization occurs by the removal of electrons from neutrals via the action of a high electric field.
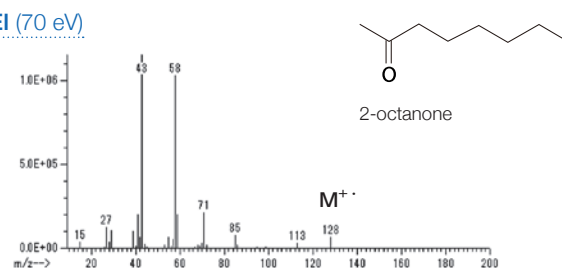
Proper choice of various ionization methods for GC-MS

The basis of qualitative analysis is electron ionization (EI), which has rich library databases. On the other hand, soft ionization methods, such as field ionization (FI), photoionization (PI), and chemical ionization (CI), can selectively detect molecular ions, so the molecular weight and formula can be determined. It is effective for qualitative analysis of unknown compounds not registered in the library databases.
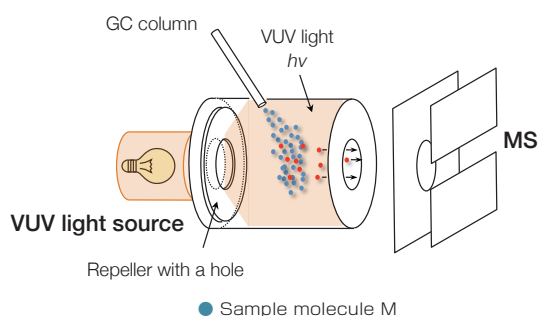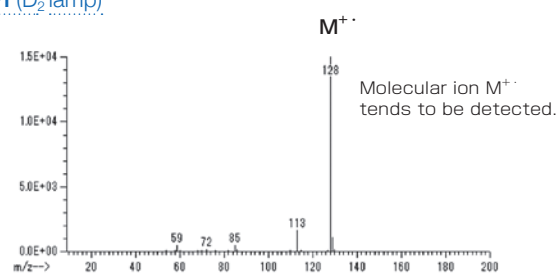
Schematics of EI

EI (70 eV)

2-octanone

$M^{+ \cdot}$

Schematics of PI

PI (D$_2$ lamp)

$M^{+ \cdot}$

Molecular ion M$^{+ \cdot}$ tends to be detected.

Schematics of FI

FI (-10kV)

$M^{+ \cdot}$

Molecular ion M$^{+ \cdot}$ tends to be detected.
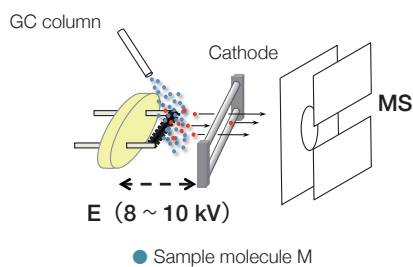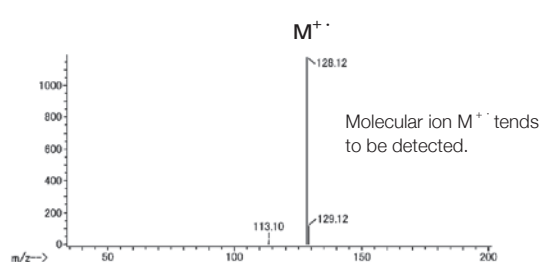
Schematics of CI
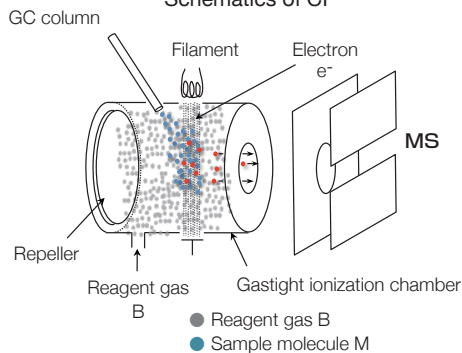
CI (Reagent gas: isobutane)

$[M+H]^+$

Protonated molecule [M+H]$^+$ tends to be detected.
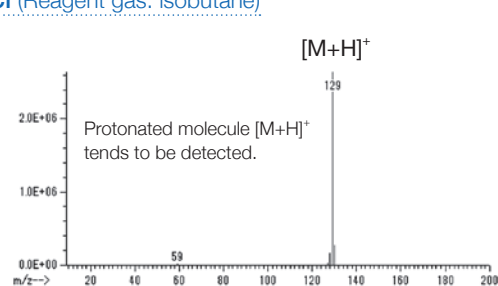
Matrix-Assisted Laser Desorption/Ionization (MALDI)

In the MALDI method, a solution of matrix compound, which assists ionization, and a sample solution are mixed and deposited on a stainless steel target plate. When the mixture dries, a co-crystal of sample and matrix will form. The sample molecules are desorbed and ionized by irradiating the co-crystal with an ultraviolet laser. By selecting an appropriate matrix compound according to the sample, it is possible to ionize macromolecules with molecular weights of hundreds to hundreds of thousands. Since single-charge ions are mainly generated, the horizontal axis of the mass spectrum is equivalent to the mass of the ions, making the mass spectrum easier to interpret. JEOL's MALDI-TOFMS has three measurement modes (Linear mode, Spiral mode, and TOF-TOF mode), and it is possible to analyze samples in a wide molecular weight range.

1. UV laser irradiation

3. Sample and matrix are desorbed and ionized.

2. Laser is absorbed by matrix.

● ··· Matrix
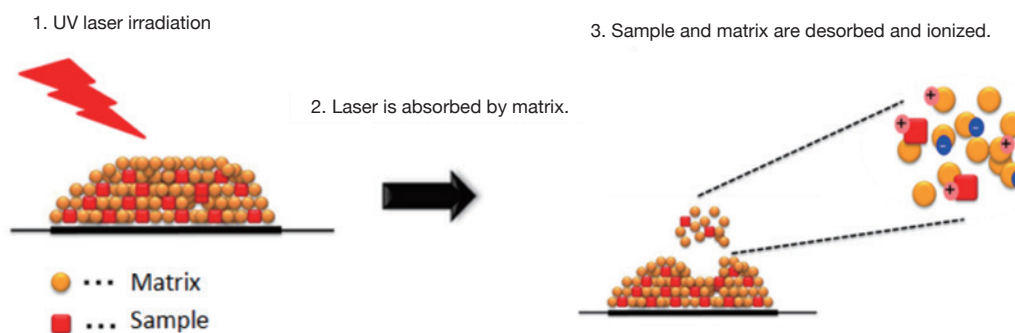
■ ··· Sample

DART™ (Direct Analysis in Real Time)

DART™ is one of the typical ambient ionization methods. Ionization in DART™ is based on the interaction of excited atoms or molecules with atmospheric gases and samples. Plasma is generated by the discharge at the needle electrode in the helium gas stream introduced into DART™. The plasma contains ions, electrons, excited state (metastable) atoms and molecules, but most of the charged particles in the plasma are removed by the grounded electrode, and only the excited state neutrals are released tothe atmosphere. By heating the DART™ gas with the heater as needed, it promotes the vaporization and thermal desorption of analytes from the substrate surface. Excited helium atoms efficiently ionize water molecules in the atmosphere, and protonated water clusters produced as a result of the ion molecule reaction donate protons to the sample molecules to generate the protonated molecule of the sample. The protonated molecules of the sample are analyzed with high mass accuracy by TOFMS. By combining with a thermal desorption / pyrolysis device, it is possible to handle various resin samples. Compared to Pyrolysis(Py)-GC-MS, oligomers with a molecular weight of up to 1,000 Da can be ionized, and partial structure information of polymeric materials can be obtained.

Schematics of DART™ ion source

Needle electrode

Grid electrode

Mass spectrometer inlet (Orifice 1)

Gas (He)

glow discharge

+ e⁻ −

metastables

sample gap

Grounded electrode

Gas heater
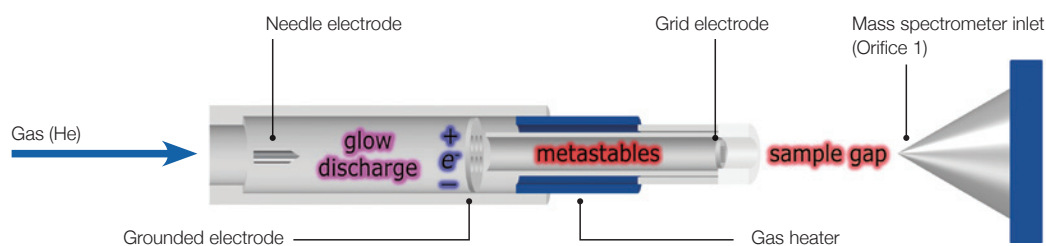
EGA and pyrolysis analysis of PET resin using a pyrolyzer

In EGA, a peak of the evolved gas, which is presumed to be the pyrolysis product of PET, was observed around 400 to 500 °C. In the pyrolysis analysis, many peaks resulting from the decomposition of the ester groups and the decarboxylation reaction were confirmed.
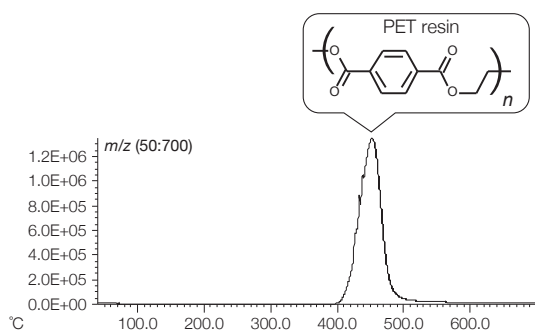
PET resin analysis results by Direct-EGA (TIC chromatogram)
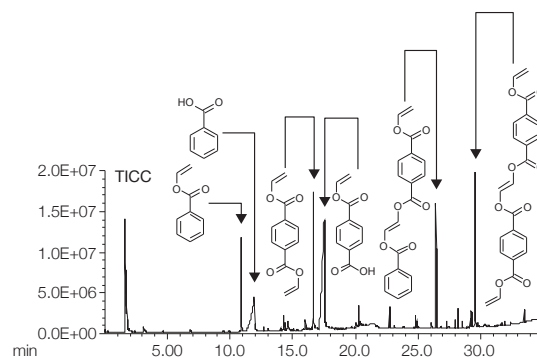
PET resin analysis results by Py/GC/MS (TIC chromatogram)

Thermal desorption analysis of additives in PVC resin using a pyrolyzer

In thermal desorption analysis, heating is terminated before the pyrolysis of the main component (PVC), so it is possible to selectively detect only additives. In addition, quantification is possible by creating a calibration curve using standard samples.
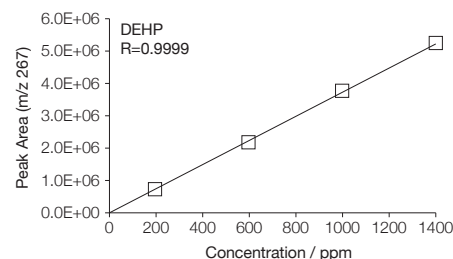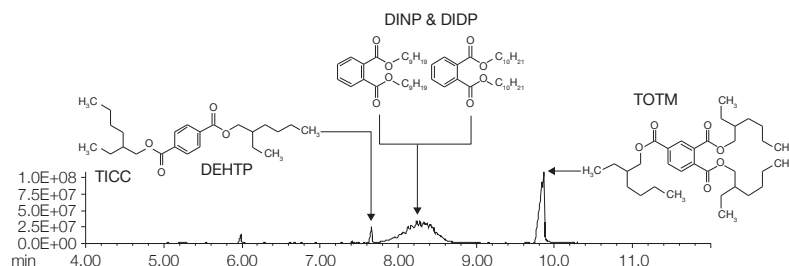
Absolute calibration curve for DEHP

Rapid analysis of an antioxidant (Irganox MD 1024) using direct sample introduction (DEP) (MSTips No. 278)

Irganox MD 1024 (BASF) is a compound with a boiling point of 652.6 °C, but by using DEP, it was possible to measure within 1 minute. The structure was assigned by NIST library search of the obtained EI mass spectrum.

**Irganox MD 1024 measurement results using DEP**

TICC

EI mass spectrum
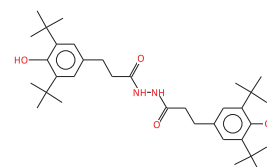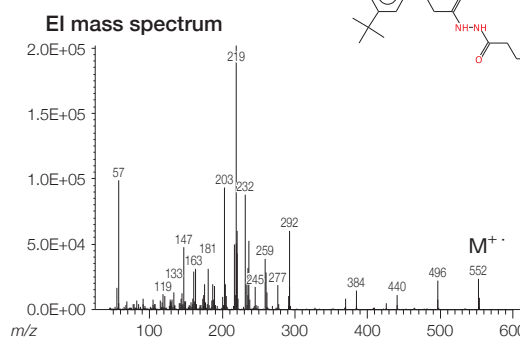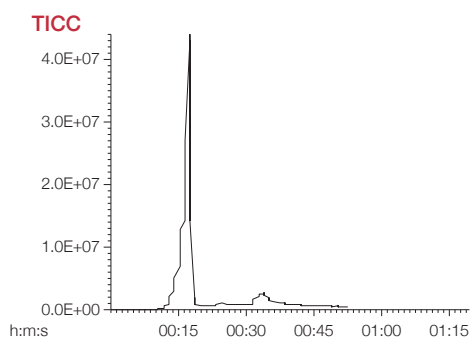
Irganox MD 1024
Formula: $C_{34}H_{52}N_2O_4$
Molecular weight: 552
Melting point: 224-229 °C
Boiling point: 652.6 °C

Ultraviolet (UV) degradation analysis of styrene foam using a pyrolizer (MSTips No. 257)

Using differential analysis of samples before and after UV irradiation, it was possible to extract the degradation products 1-propenylbenzene (A) and Acetophenone (B).

Differencial analysis of styrene foam before and after UV irradiation
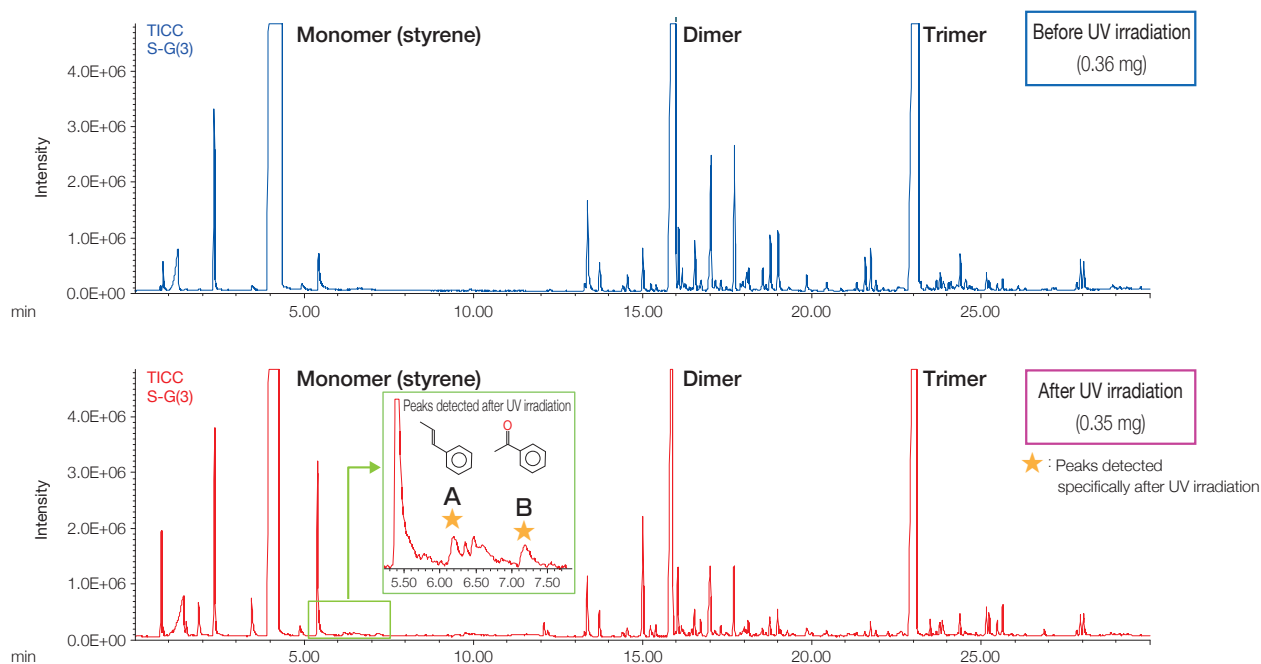
EGA of polystyrene under oxidative atmosphere with TG (MSTips No. 320)

Standard electron ionization (EI) filaments can break easily due to oxidation in an oxidizing atmosphere, and as such, cannot be used for long periods of time. A low-vacuum filament with oxidation resistant coating enables stable measurement for a long time. As the oxygen concentration increased, styrene decreased as benzaldehyde increased.

EGA of polystyrene under different oxygen concentrations
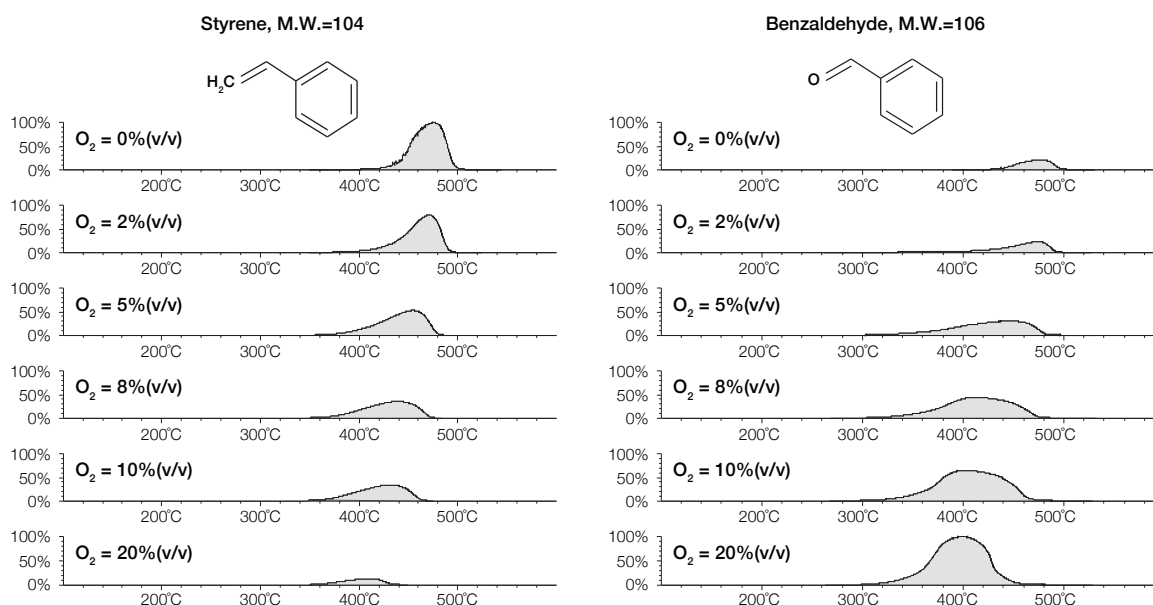
Integrated analysis of acrylic resin using a pyrolyzer (MSTips No. 300)
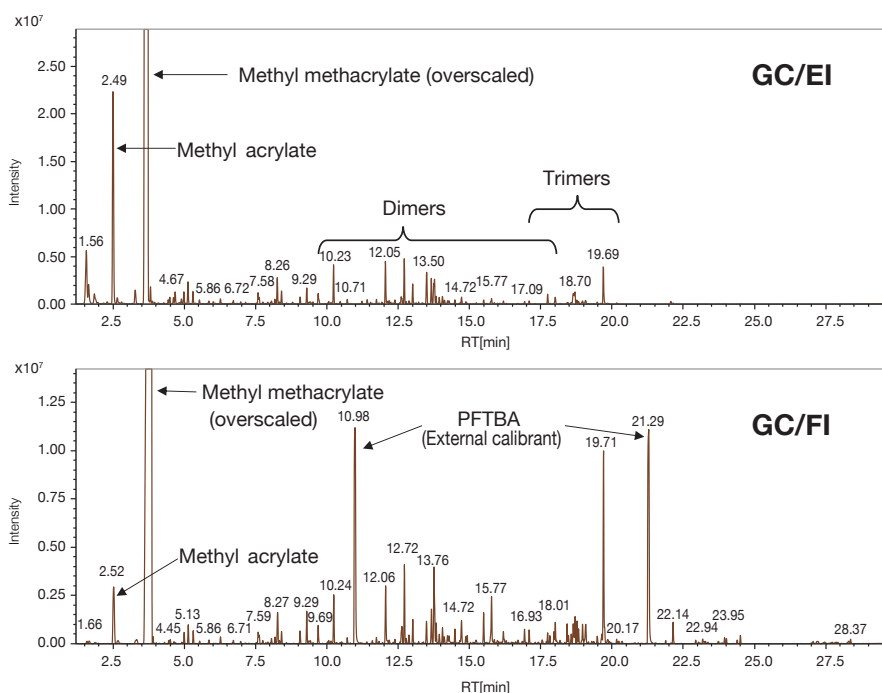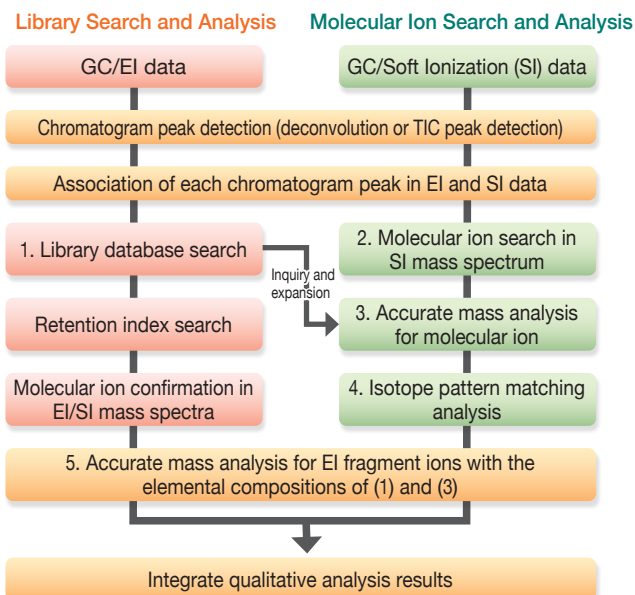
Many of the components detected by Py/GC/MS analysis of polymeric materials, such as acrylic resin, have not been registered in the library database, and QMS cannot provide sufficient qualitative information.

In such unknown compound analysis, anyone can easily and quickly obtain qualitative information on pyrolysis products by using TOFMS, which can be equipped with various ionization methods, and msFineAnalysis, an integrated qualitative analysis software.

To carry out the integrated analysis, one measurement is performed by EI, and the other by a soft ionization method (FI, PI, CI, etc.) Afterward, msFineAnalysis automatically performs the integrated analysis of the data obtained by EI and by the soft ionization method.
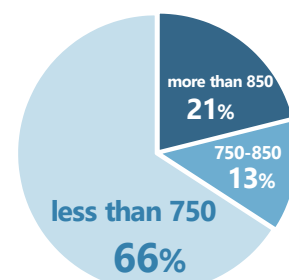
For 151 components detected in the analysis of acrylic resin, only 21% of the components had an Match Factor score of 850 or higher, which ensures sufficient reliability in the library database search. In the integrated analysis by msFineAnalysis, unique molecular formula candidates have been identified for 96% of the components.
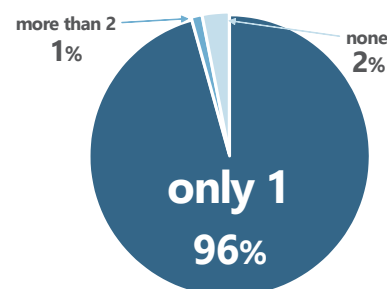
Integrated Analysis Workflow

Library Search and Analysis | Molecular Ion Search and Analysis

GC/EI data | GC/Soft Ionization (SI) data

Chromatogram peak detection (deconvolution or TIC peak detection)

Association of each chromatogram peak in EI and SI data

1. Library database search → 2. Molecular ion search in SI mass spectrum

Inquiry and expansion

Retention index search → 3. Accurate mass analysis for molecular ion

Molecular ion confirmation in EI/SI mass spectra | 4. Isotope pattern matching analysis

5. Accurate mass analysis for EI fragment ions with the elemental compositions of (1) and (3)

Integrate qualitative analysis results

■ Identified ■ Maybe? ■ Not identified

more than 850 **21%**

750-850 **13%**

less than 750 **66%**

Qualitative Analysis by Library DB Search Only

more than 2 **1%**

none **2%**

only 1 **96%**

Integrated Analysis by msFineAnalysis

Pyrolysis(Py)/GC/MS analysis results of acrylic resin (top: EI, bottom: FI)

GC/EI — Methyl methacrylate (overscaled), Methyl acrylate, Dimers, Trimers

GC/FI — Methyl methacrylate (overscaled), Methyl acrylate, PFTBA (External calibrant)

Foreign substance analysis in PP/PE copolymer using a pyrolyzer (MSTips No. 330)

The differential analysis function of msFineAnalysis is effective for identifying foreign substances in polymeric materials.

Chromatogram deconvolution and statistical analysis (with measurements of n = 3 or 5) provide reliable differential analysis results, even for trace components. An overview of the statistical analysis results can be visually confirmed using a volcano plot. (In case of n = 1 measurement, statistical analysis is not performed and simple comparison is performed.)

The following are the components detected only in defective products by the differential analysis function of msFineAnalysis. The detection of acrylonitrile, styrene, and presumed hybrid trimers of these components suggests that the foreign substance mixed in may be an acrylonitrile/styrene (AS) copolymer.

Differential analysis workflow of msFineAnalysis

Library Search and Analysis	Molecular Ion Search and Analysis
A : GC/EI data (n=1, 3, 5) B : GC/EI data (n=1, 3, 5)	A : GC/SI data (n=1) B : GC/SI data (n=1)

Chromatogram peak detection (deconvolution)

Data alignment

Differential analysis

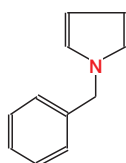Association of each chromatogram peak in EI and SI data

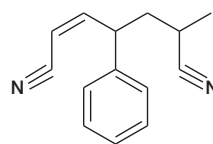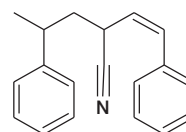Subsequent workflow is the same as the integrated analysis
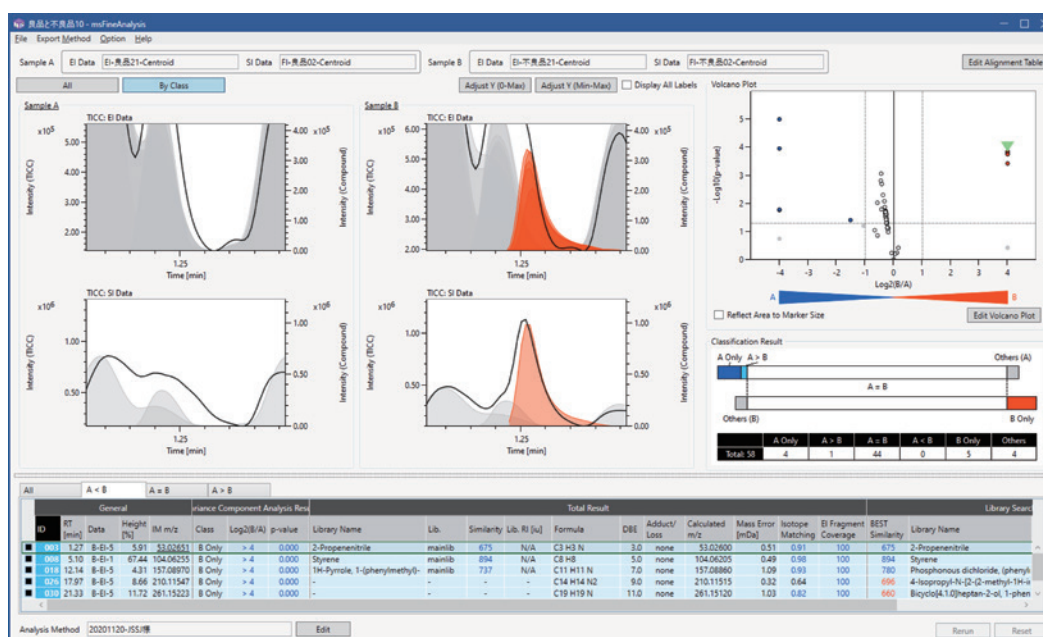

ID003
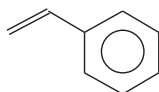
ID008

ID018

Inferred structure of ID 026 (Not in library DB)

Inferred structure of ID 030 (Not in library DB)

Thermal analysis of fluorocarbon polymer using TG-MS (MSTips No. 249)

From approximately 500 °C, weight loss and evolved gas due to pyrolysis of the fluorocarbon polymer were observed. Ions up to *m/z* 2,500 were confirmed from the mass spectrum around 550 °C. It was shown that the mass range that can be measured by TG-TOFMS is wider than that of TG-QMS, and that it is effective for measuring synthetic polymers in the oligomer region.
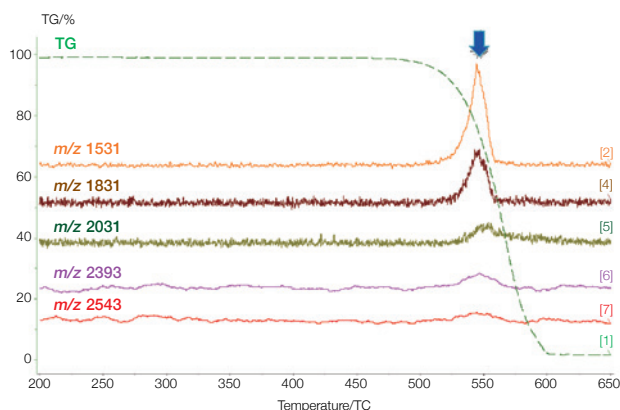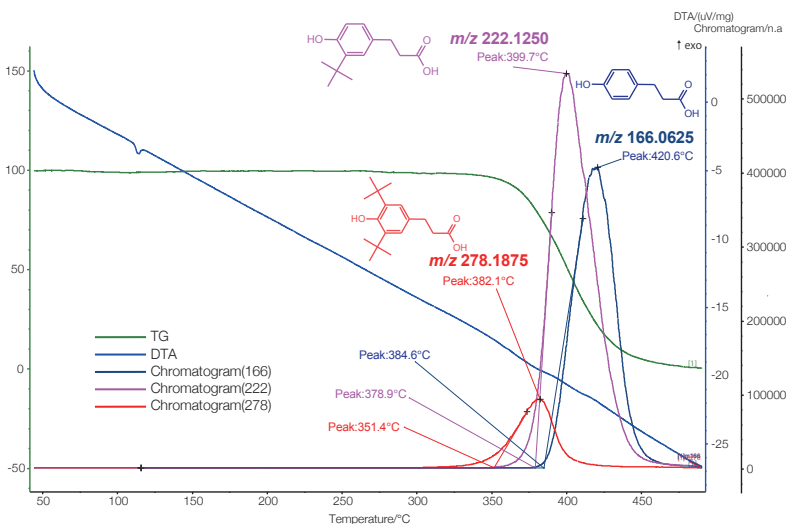

TG curve and EGA data (EICs)
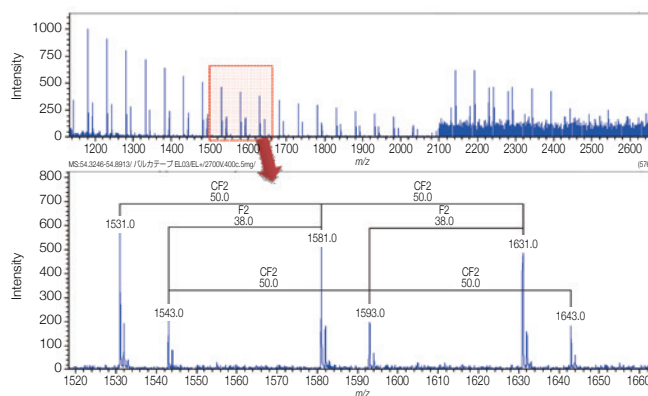
EI mass spectrum at the EGA peak (approx. 550°C)

Thermal pyrolysis analysis of antioxidant additive by TG-MS. (MSTips No. 250)

Fragment ions detected by the EI method are often common to multiple components, and are not suitable as qualifier ions for confirming thermal behavior. Conversely, molecular ions detected by the PI method are component-specific, so they are ideal for checking the thermal behavior of each component. Even in TG-MS without chromatogram separation, it is possible to efficiently perform thermal analysis of polymer materials and additives by utilizing soft ionization.


TG curve and EGA data
(EICs from PI)
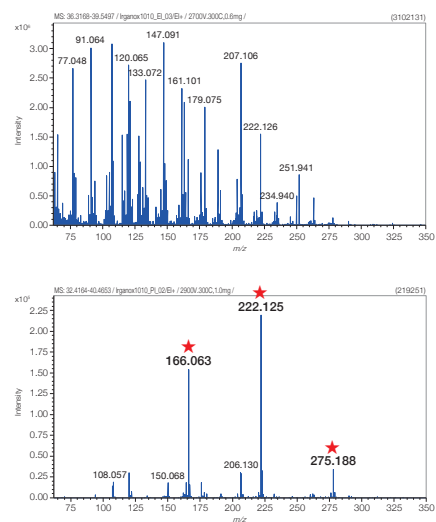
Mass spectra of evolved gas
(Top: EI, bottom: PI)

Polymer Analysis by FD and Kendrick Mass Defect (KMD) Analysis

Field desorption (FD) is an ionization method in which the analyte molecules applied to the emitter are desorbed and ionized by a high electric field. The electric current running through the emitter is gradually increased during the measurement to heat the analyte to assist desorption/ionization. Since the optimal emitter current for ionization depends on the analyte, components can desorb at different times. Separation of components in a mixture is possible, and mass spectra for a specific class of compounds can be extracted.
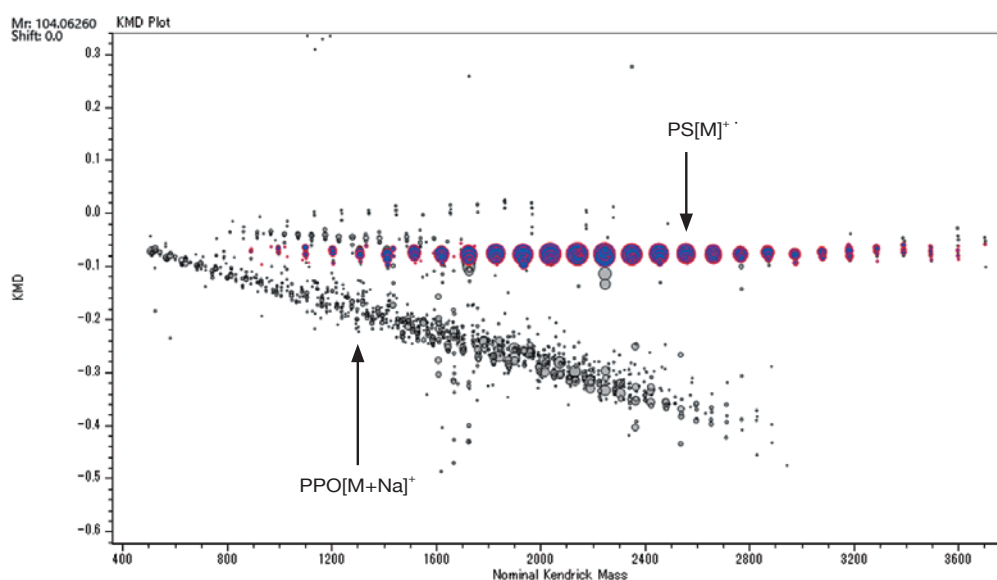
Furthermore, even when compounds are not separated in time during desorption/ionization, target components can still be clearly separated by creating KMD plots.
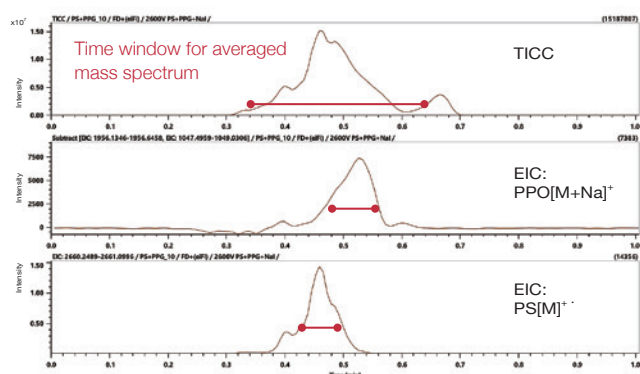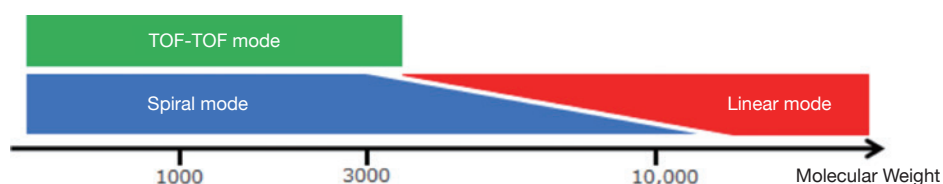

FD Measurement Data
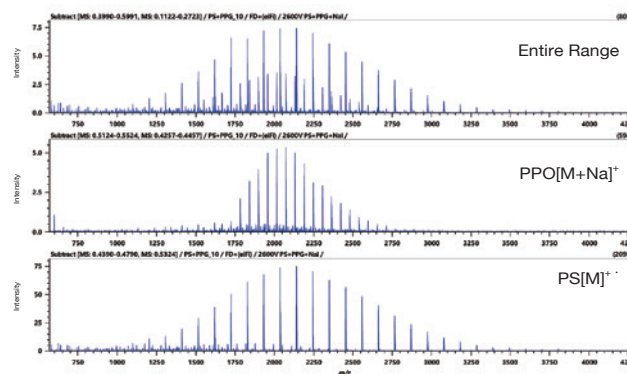
FD Mass Spectra

KMD plot for the entire range mass spectrum (base unit: C_8H_8)

MALDI-TOFMS can analyze synthetic polymer materials effectively by using its three available measurement modes.

Confirmation of molecular weight distribution of high-molecular-weight polymers

Using linear mode, you can check the molecular weight distribution of polymers with molecular weights of ~500 to ~500,000. If the molecular weight distribution is wide, it is possible to confirm a molecular weight distribution with better reliability by fractionating the sample with a technique such as size exclusion chromatography.

Molecular weight distributions of high molecular weight polymers

PMMA 48 kDa

PS 100 kDa
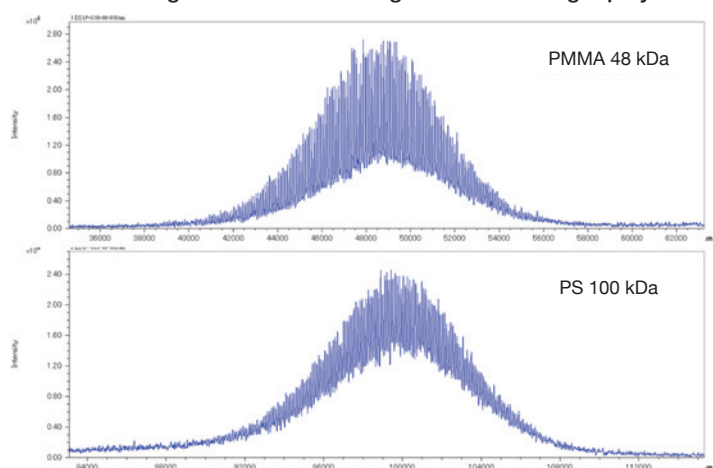
High resolution analysis of polymers over wide mass range

The Spiral mode enables high resolution measurements of polymers with molecular weights up to 10,000. Structural analysis of homopolymers and copolymers is possible from the peak intervals in the mass spectrum. If there is an putated sub-structure, the existence of the corresponding series can be confirmed from the accurate masses of ions.
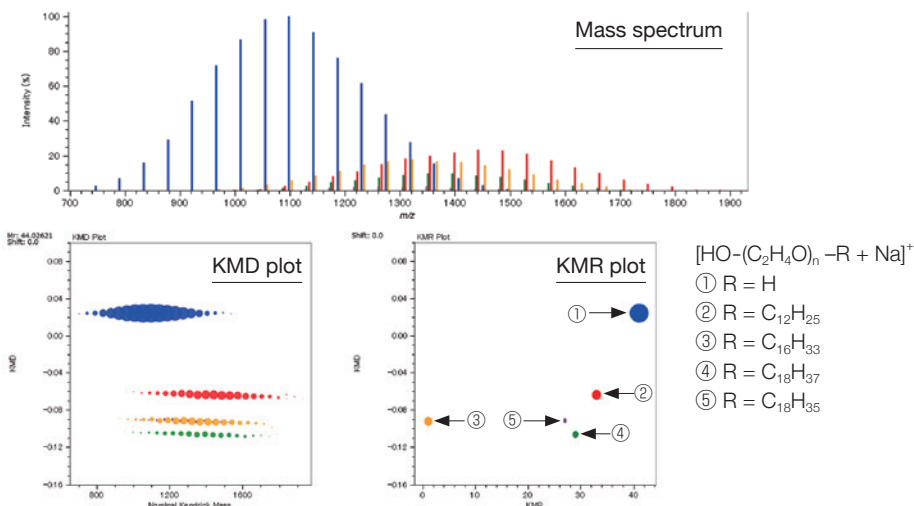
Mass spectrum of PMMA (*m/z* 1000 -10000)

R ~ 27000 (*m/z* 2027)

R ~ 77000 (*m/z* 5030)

R ~ 67000 (*m/z* 8033)
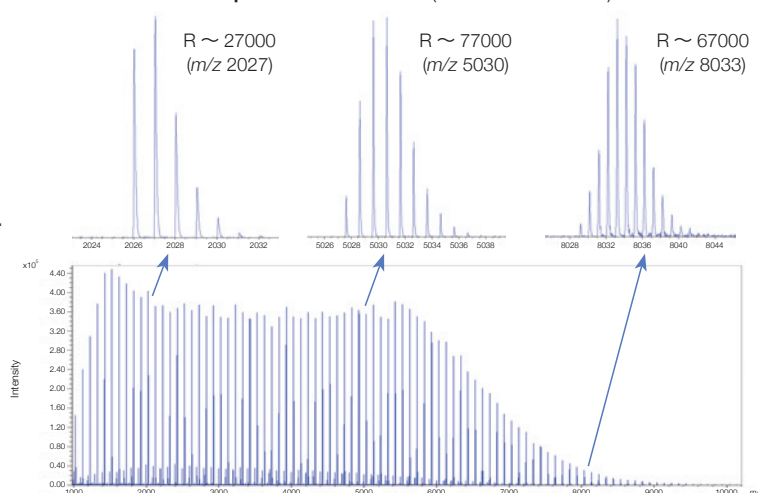
End group analysis of polymers

By using JEOL's polymer analysis software msRepeatFinder, mixtures of homopolymers with different end groups can be separated and grouped. For each group, it is possible to calculate the index values of molecular weight distribution (number average molecular weight, weight average molecular weight, and polydispersity). It is also possible to elucidate the elemental compositions of polymer end groups from the accurate masses. However, it is not possible to determine the degree of polymerization (or the mass of an end group) or adduct ion information of a polymer species from the accurate mass alone. By utilizing the functions of the TOF-TOF option, it is possible to determine such information.

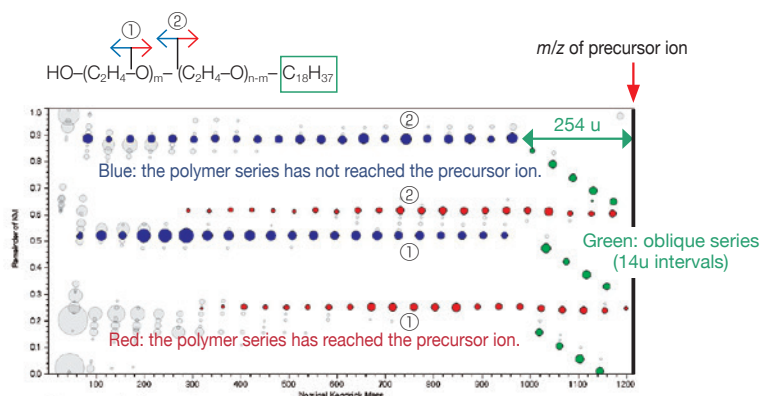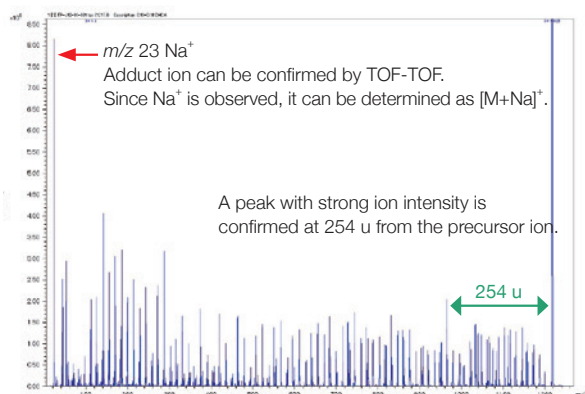**Mass spectrum of a polyethylene oxide mixture with different end groups**

Mass spectrum

KMD plot

KMR plot

$[HO-(C_2H_4O)_n -R + Na]^+$
① R = H
② R = $C_{12}H_{25}$
③ R = $C_{16}H_{33}$
④ R = $C_{18}H_{37}$
⑤ R = $C_{18}H_{35}$

	Total ion intensity	Weighted-average of KMD	Weighted-average of NKM	Number average molecular weight (Mn)	Weight average molecular weight (Mw)	Polydispersity
①	826378	0.0245	1092.1	1092.8	1109.3	1.015
②	239802	-0.0635	1433.7	1434.5	1453.0	1.013
③	175311	-0.0920	1347.5	1348.3	1366.1	1.013
④	90119	-0.1060	1371.1	1371.9	1387.5	1.011
⑤	17689	-0.0912	1279.8	1280.5	1291.2	1.008

The elemental composition elucidation result of the end group for group ④ is shown. The 4 candidates have the same elemental composition, but different degree of polymerization. The information obtained from TOF-TOF measurement was used to narrow down the candidates. Since a *m/z* 23 peak was observed in the product-ion mass spectrum, it is known to be an Na adduct ion. The characteristic neutral loss indicates that the size of one end group is about 254 u and the other is relatively small. As a result, we could estimate that it was polyethylene oxide, which has an end group of $C_{18}H_{37}$ /OH.

No.	End group composition formula	Monomer	n	Adduct ion	Mass	DBE	Mass Error (modulus; mDa)	Mass error (mDa)	Mass Error (modulus; ppm)	Mass Error (ppm)
①	$C_{16}H_{34}$	C_2H_4O	22	Na	1217.83200	-0.5	2.2767	-2.2767	1.8695	-1.8695
②	$C_{18}H_{38}O$	C_2H_4O	23	Na	1217.83200	-0.5	2.2767	-2.2767	1.8695	-1.8695
③	$C_{20}H_{42}O_2$	C_2H_4O	20	Na	1217.83200	-0.5	2.2767	-2.2767	1.8695	-1.8695
④	$C_{22}H_{46}O_3$	C_2H_4O	19	Na	1217.83200	-0.5	2.2767	-2.2767	1.8695	-1.8695

Product-ion mass spectrum and RKM plot of group ④

m/z 23 Na⁺
Adduct ion can be confirmed by TOF-TOF. Since Na⁺ is observed, it can be determined as [M+Na]⁺.

A peak with strong ion intensity is confirmed at 254 u from the precursor ion.

254 u

m/z of precursor ion

$HO-(C_2H_4-O)_m-(C_2H_4-O)_{n-m}-C_{18}H_{37}$

254 u

Blue: the polymer series has not reached the precursor ion.

Green: oblique series (14u intervals)

Red: the polymer series has reached the precursor ion.

Analysis of an anionic surfactant (MSTips No. 333)

It is sometimes highly effective to analyze an anionic surfactant, which has a sulfate group or phosphate group as an end group, in negative-ion mode. Below are the analysis examples of detergent samples containing alkyl ether sulfate ester (AES) and polyoxyethylene alky ether (POEAE). While POEAE was mainly observed in positive-ion, only AES was observed in negative-ion mode. By obtaining a product-ion mass spectrum in the negative-ion mode with the TOF-TOF option, it can be estimated that the end groups are an alkyl chain($C_{14}H_{29}$) and a sulfate group, respectively.

Mass spectrum in negative-ion, Spiral mode

KMD plot in negative-ion, Spiral mode

$C_{14}H_{29}O(C_2H_4O)_nSO_3^-$

$C_{12}H_{25}O(C_2H_4O)_nSO_3^-$

Product-ion mass spectrum in negative-ion, TOF-TOF mode.

$C_{14}H_{29}O(C_2H_4O)_{11}SO_3^-$

SO_3^- SO_4H^-

198.2

$-C_{14}H_{30}$

Gel permeation chromatography (GPC) combined with MALDI-TOFMS (MSTips No. 269)

A combination of GPC fractionation and MALDI-TOFMS is effective for the analysis of polymers with high polydispersity. The compositional distribution can be visualized by simultaneously displaying the mass spectrum of each fraction on the Remainder of Kendrick Mass (RKM) plot.

Mass spectra of the five GPC fractions of high polydispersity polycaprolactone

Overlaid RKM plots of the mass spectra of all fractions

* The data was acquired in collaboration with the National Institute of Advanced Industrial Science and Technology.

Analysis of copolymers

It is important to use high mass resolution to analyze copolymers, which consist of two or more species of monomer. An ultra-high mass resolution TOFMS can separate many isobaric ion peaks (which have the same nominal mass but different accurate mass) on a mass spectrum. Due to the complexity of copolymer mass spectra, it is not practical to assign peaks one by one. The KMD analysis using msRepeatFinder makes it possible to visualize the distribution of polymer species. Below is an example of EO-PO block copolymer. The enlarged mass spectrum shows that peaks that are less than 0.03 u apart are still clearly separated due to high mass resolution. By visualizing the mass spectrum using KMD plot (base unit: PO), a lattice is seen reflecting the PO distribution on horizontal axis and the EO distribution in a diagonal direction.

Mass spectrum and KMD plot of EO-PO block copolymer
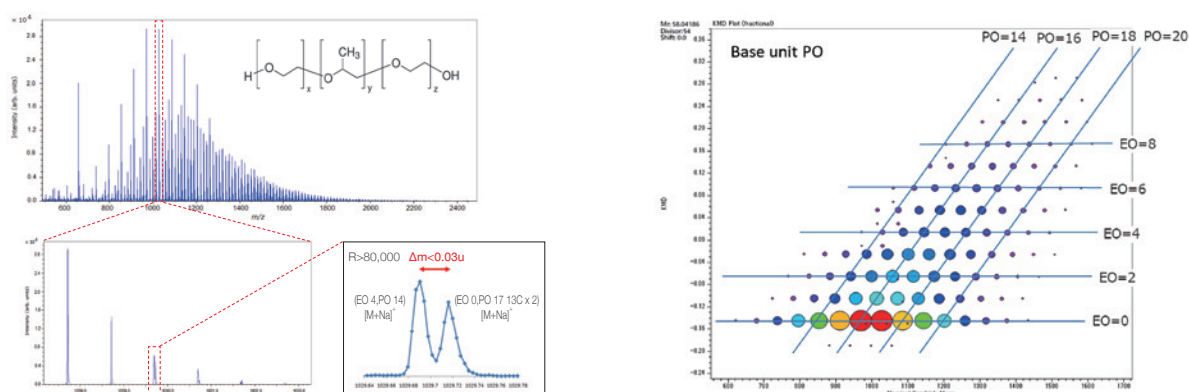
Differential analysis of 2 polymer samples

The differential analysis of the end groups and molecular weight distributions of polymer samples are very important for checking the degradation of a sample, differences between production lots, and differences in synthesis processes. msRepeatFinder can perform the differential analysis of two samples. On the right is an example application for the degradation analysis of polyethylene terephthalate. The top shows the mass spectra before and after the degradation. The major components observed before degradation were cyclic oligomers, whereas those after degradation were linear oligomers having COOH/COOH end groups. For performing differential analysis, each sample was measured three times. The bottom left is the result of the differential analysis shown in KMD plots. The red shows the stronger peaks before the degradation, while the green shows the stronger peaks after the degradation. In addition, a volcano plot can be created to confirm the components that differ with statistical significance between 2 samples.
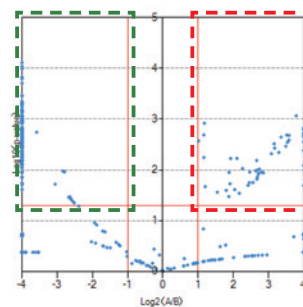
Mass spectra of PET samples before and after degradation
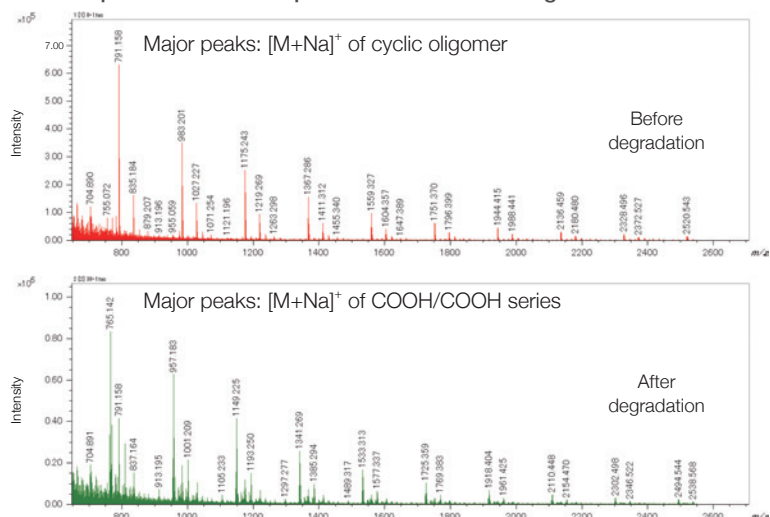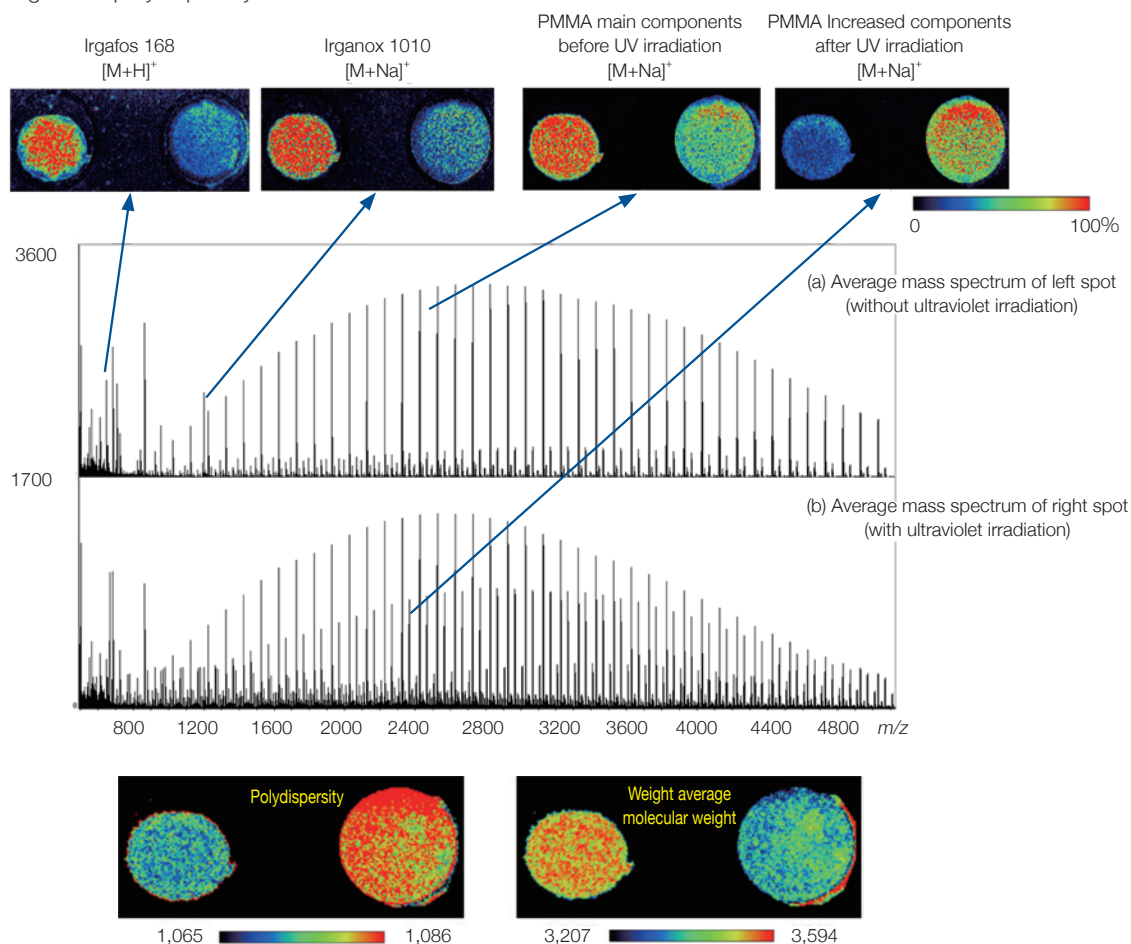

KMD plot of differential analysis result
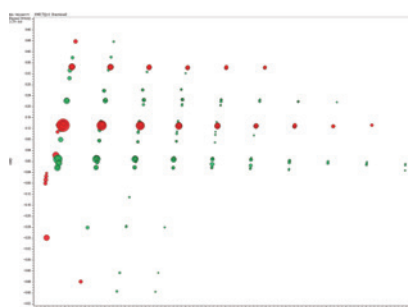
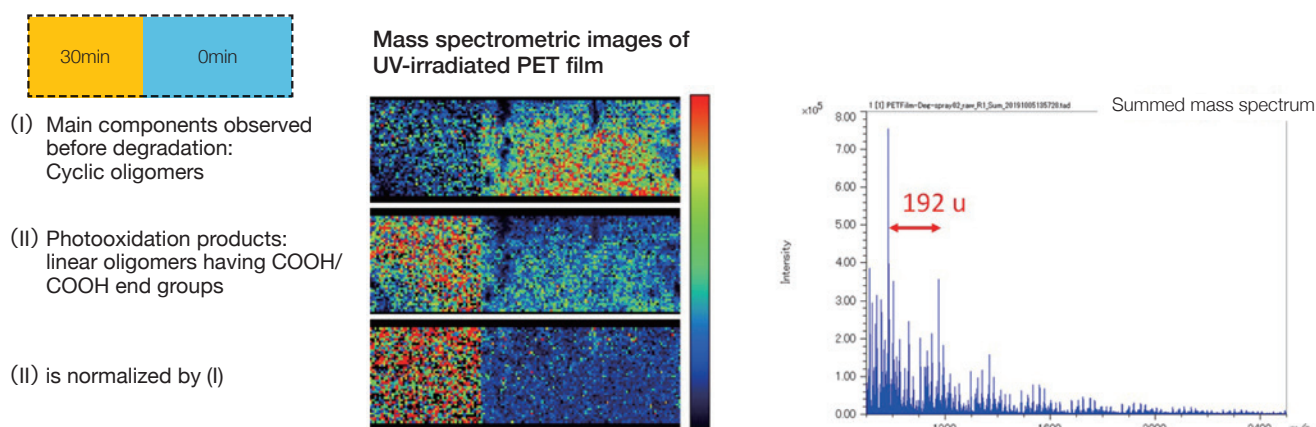**Volcano plot of differential analysis result**

Mass spectrometry imaging of polymeric materials

Mass spectrometry imaging can be applied to polymeric materials. Two spots are prepared by adding two antioxidants - Irgafos 168 (BASF) and Irganox 1010 (BASF) - to polymethylmethacrylate (PMMA). Ultraviolet irradiation was performed to the right spot only and its degradation was visualized by using mass spectrometry imaging. For polymers, it is possible to visualize the quantitative change in both polymers and additives. It is also possible to capture the changes in the average molecular weight and polydispersity.

Irgafos 168
[M+H]$^+$

Irganox 1010
[M+Na]$^+$

PMMA main components
before UV irradiation
[M+Na]$^+$

PMMA Increased components
after UV irradiation
[M+Na]$^+$

0   100%

(a) Average mass spectrum of left spot
(without ultraviolet irradiation)

(b) Average mass spectrum of right spot
(with ultraviolet irradiation)

800 1200 1600 2000 2400 2800 3200 3600 4000 4400 4800 *m/z*

Polydispersity

Weight average
molecular weight

1,065   1,086

3,207   3,594

Degradation analysis of polymer surface (Applications Note HS05)

Mass spectrometry imaging can also be used to analyze the sample surface. The figure below visualizes the changes in oligomers on the surface of polyethylene terephthalate film due to oxidative photodegradation caused by UV irradiation.

30min   0min

(I) Main components observed
before degradation:
Cyclic oligomers

(II) Photooxidation products:
linear oligomers having COOH/
COOH end groups

(II) is normalized by (I)

**Mass spectrometric images of
UV-irradiated PET film**

Summed mass spectrum

×10^5 1 [1] PETFilm-Deg-spray02.raw_R1_Sum_20191005195720.tad

8.00

7.00

6.00

5.00

4.00

3.00

2.00

1.00

0.00

Intensity

192 u

1200   1600   2000   2400   *m/z*

Analysis of a mixture of additives

MALDI-TOFMS is also applicable to the analysis of additives. The results of the mixture of five additives are shown below. There are many structural isomers in additives, but they cannot be distinguished by their accurate masses. MS/MS is an effective method for identifying isomers. The product-ion mass spectra of the structural isomers, diethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DNOP), are shown below. They can be distinguished from the pattern of product-ion spectra.

DEHP
$C_{24}H_{38}O_4$

DNOP
$C_{24}H_{38}O_4$

Irganox1010
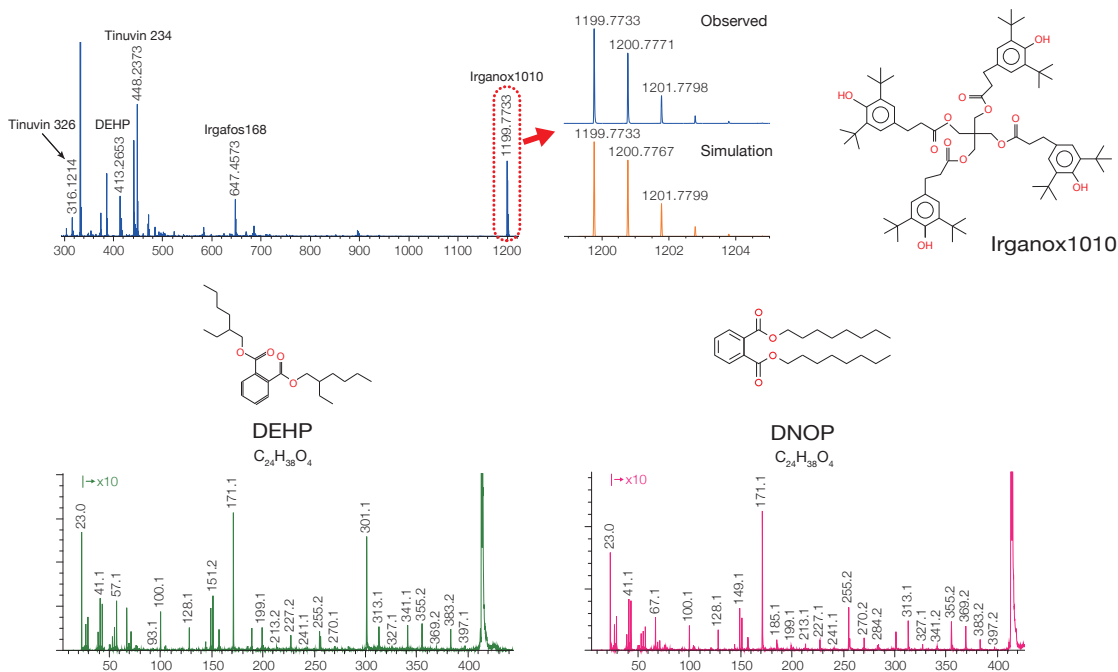
Analysis of high molecular weight hindered amine light stabilizers

MALDI-TOFMS can also analyze a high molecular weight hindered amine light stabilizer (HALS), ADK STAB LA-68 (ADEKA). It is also possible to confirm the molecular weight distribution in Linear mode and to elucidate the structure by accurate mass measurement in Spiral mode.

Linear mode: *m/z* 200-8000
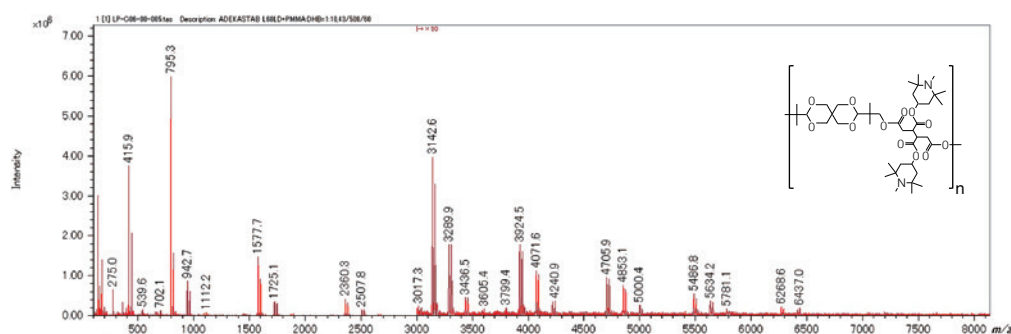
Spiral mode: *m/z* 750-2700
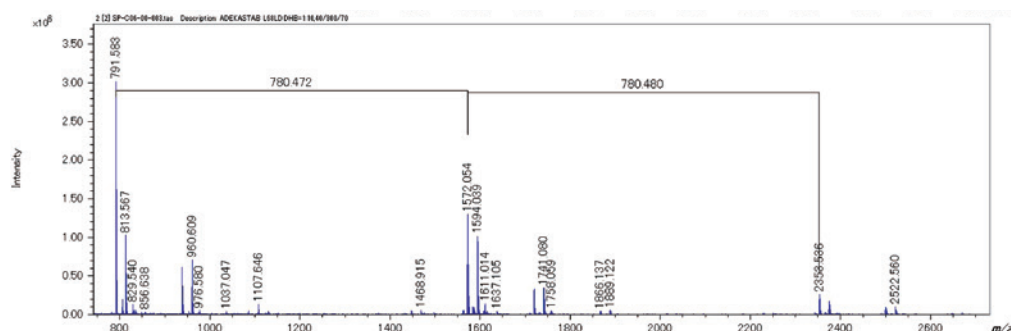
Sample introduction method

There are two sample introduction methods. One is to measure the liquid, gas, and solid state samples directly without pretreatment. The other is to use a thermal desorption/pyrolysis device. The thermal desorption/pyrolysis device allows heating of the sample with an independent furnace.

Direct analysis of a mixture sample of additives

The additive mixture sample was adhered to a glass rod and measured directly. All additives in the mixture were detected and mass measurement errors after drift correction were less than 1 mDa.
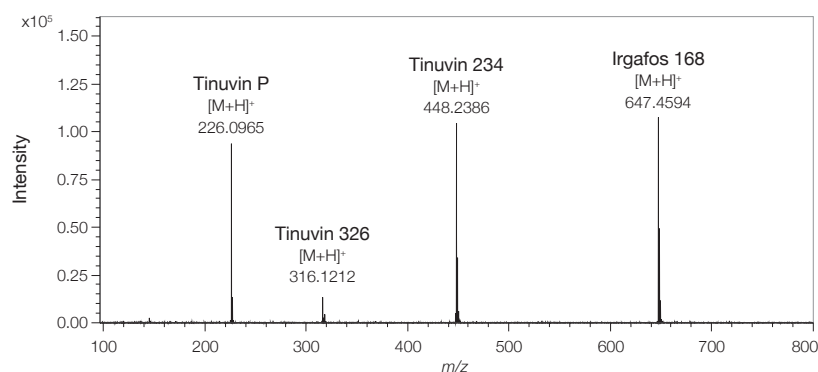
Compound	Observed m/z	Calculated m/z [M+H]$^+$	Error mDa
Tinuvin P	226.0965	226.0975	1.0
Tinuvin 326	316.1212	316.1211	0.1
Tinuvin 234	448.2386	448.2383	0.3
Irgafos 168	647.4594	647.4588	0.6

Direct analysis of phthalates in polyvinyl chloride (PVC) resin

A PVC resin was directly analyzed and the contained phthalates were detected. It is not so easy to find phthalates from a complex mass spectrum. However, by using the analysis software Mass Mountaineer, automatic analysis using a list of elemental compositions can be performed. As a result, seven types of phthalates were detected.
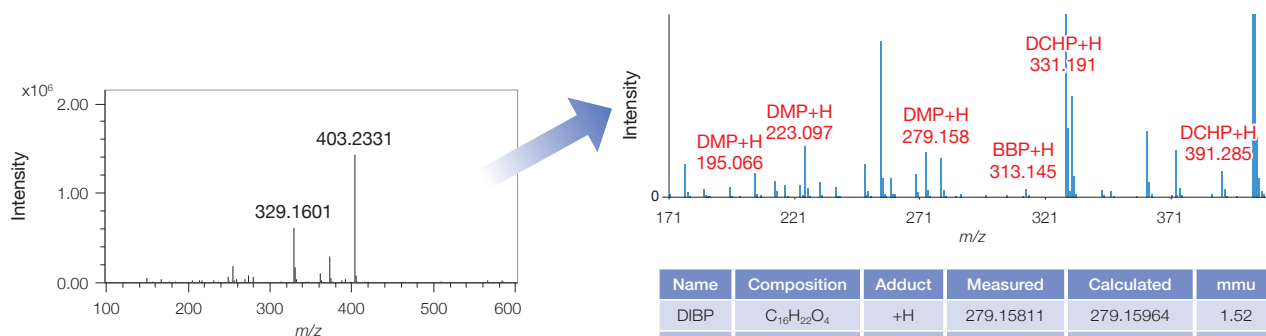
Name	Composition	Adduct	Measured	Calculated	mmu
DIBP	$C_{16}H_{22}O_4$	+H	279.15811	279.15964	1.52
DBP	$C_{16}H_{22}O_4$	+H	279.15811	279.15964	1.52
DEHP	$C_{24}H_{38}O_4$	+H	391.28525	391.28484	-0.41
DEP	$C_{12}H_{14}O_4$	+H	223.097	223.09704	0.03
DMP	$C_{10}H_{10}O_4$	+H	195.06567	195.06574	0.06
BBP	$C_{19}H_{20}O_4$	+H	313.14462	313.14399	-0.64
DCHP	$C_{20}H_{26}O_4$	+H	331.1907	331.19094	0.23

Direct analysis of brominated flame retardants added to high impact polystyrene (MSTips No. 287)

Decabromodiphenyl ether, tris(tribromophenoxy)triazine, tetrabromobisphenol A, and hexabromocyclododecane added to high impact polystyrene were detected. Even with brominated flame retardants, which are easily decomposed, molecular ions and related signals were quickly detected.
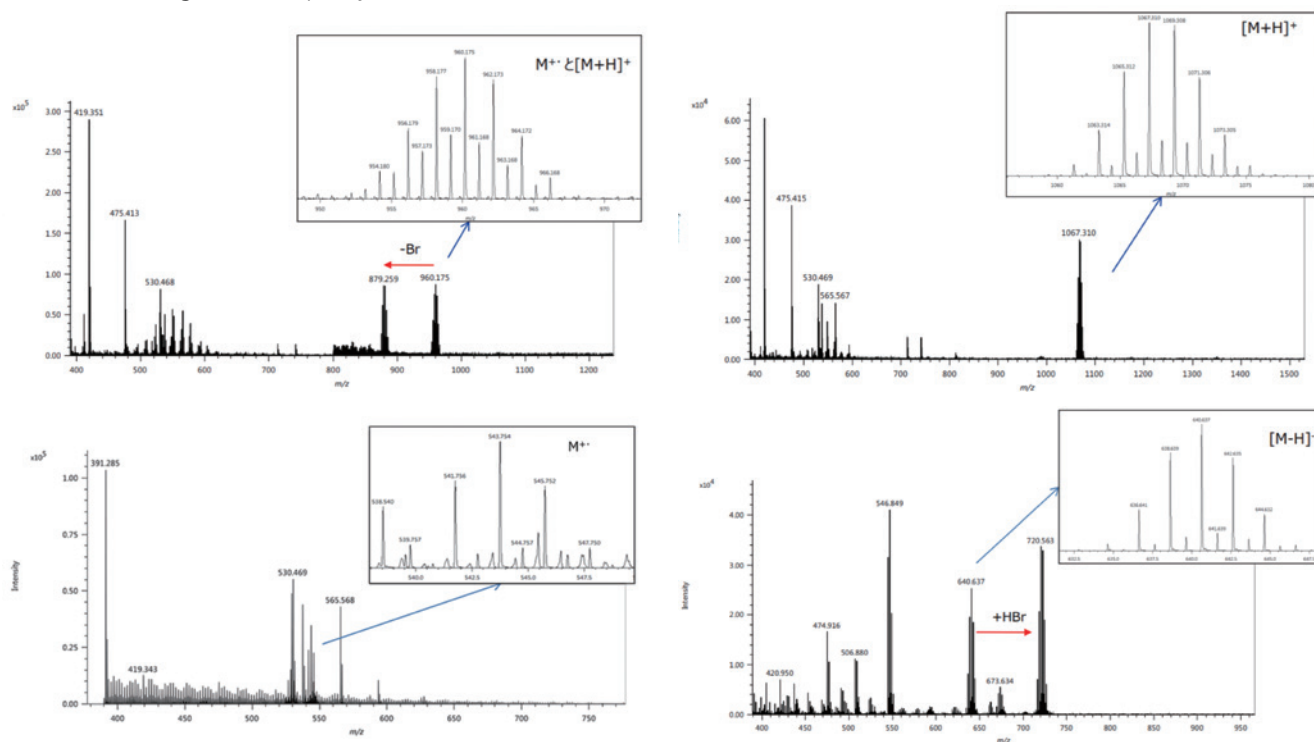
Direct analysis of oligomers

Surfactants and lubricants with relatively small molecular weight can be analyzed directly with DART™. The structure of the oligomers can be elucidated from the accurate masses. Below are the measurement results of PEG600. Signals were observed at intervals of 44 u, which is a repeating unit of PEG. Based on the accurate masses, they are mostly [M+H]$^+$ and [M+NH$_4$]$^+$. In addition, msRepeatFinder can be used to visualize the mass spectrum of PEG and to calculate important indicators for polymer analysis such as number average molecular weight.

Number average molecular weight	Weight average molecular weight	Polydispersity
476.76	499.03	1.05
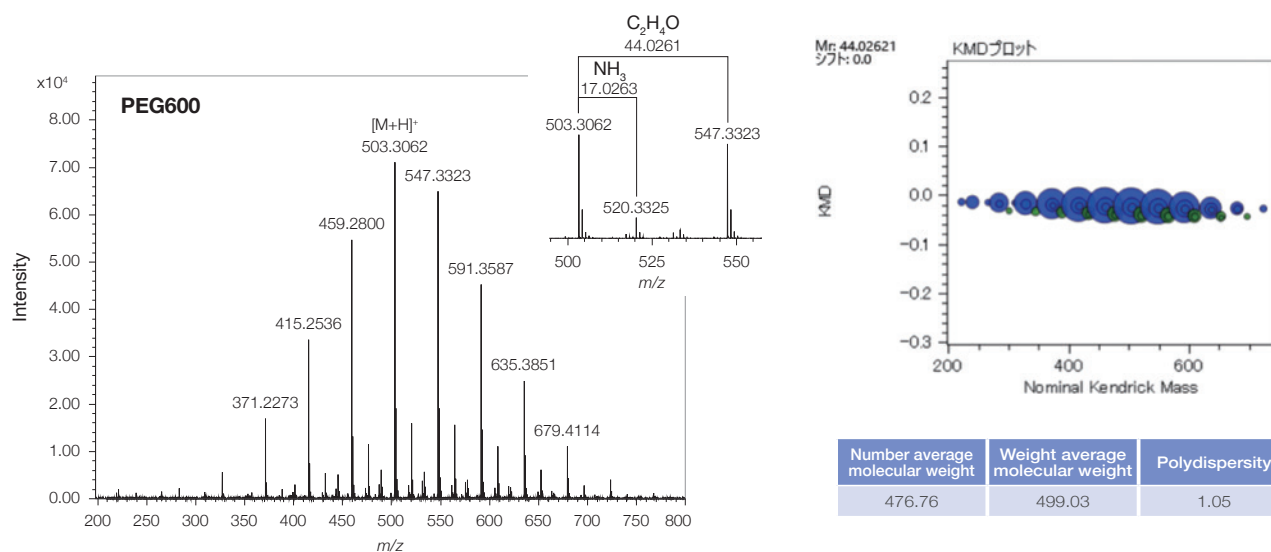
End group analysis of high-molecular-weight, insoluble polymer by combining DART™ and thermal desorption/pyrolysis device

Using a thermal desorption/pyrolysis device, the sample was heated from 100 °C to 600 °C, and the oligomer components generated by thermal desorption and pyrolysis were ionized with DART™ to elucidate the end groups. Polyphenylene sulfide (PPS) was used as the sample. End group analysis is very important because there are multiple synthetic methods for PPS, and the difference is reflected in the structure of the end groups. As a result, multiple signals were observed at 108 u intervals, which is the repeating unit of PPS, and the end groups were inferred from the accurate masses and isotope peak patterns. Since the end group contains chlorine, it is presumed that this sample was synthesized by the Phillips method.

PPS

C_6H_4S
108.003

* The data courtesy of the Research Institute of Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST)
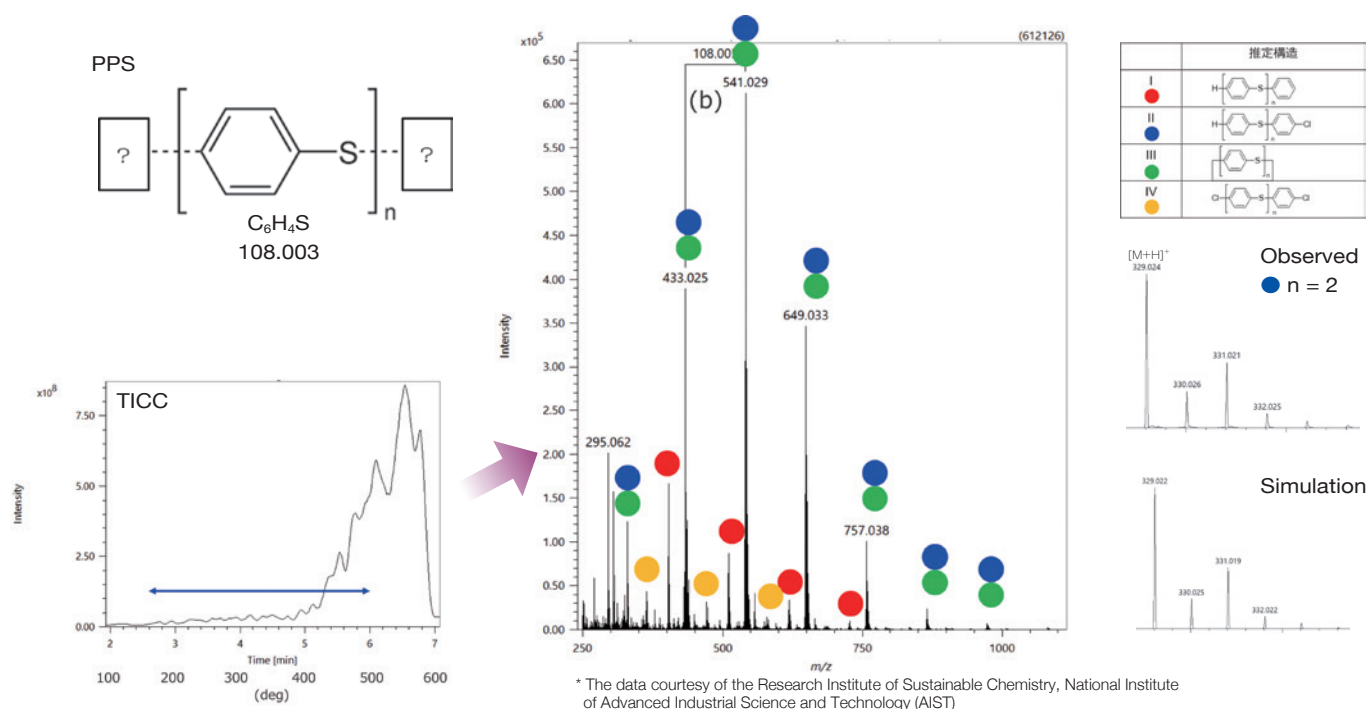
Analysis of Organic Contaminant on Metal Surface (MSTips No. D030)

Organic contamination on a metal surface was wiped off with a ceramic fiber sheet and measured. At the same time, greases and other organic substances used for metal parts were also measured and compared. As a result, it was found that the contaminant was a silicone vacuum grease.
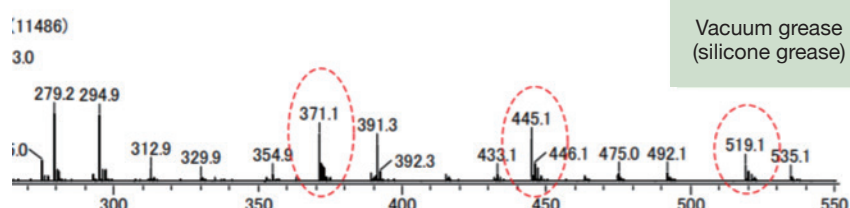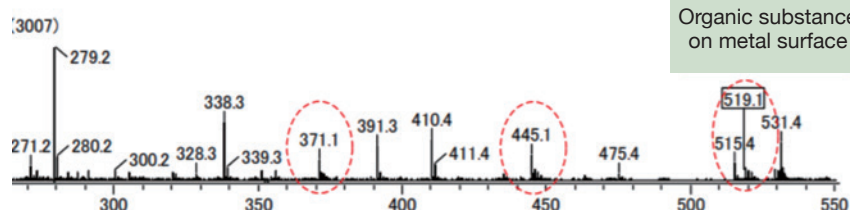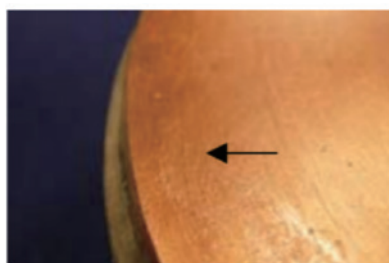
JEOL Mass Spectrometry Guidebooks
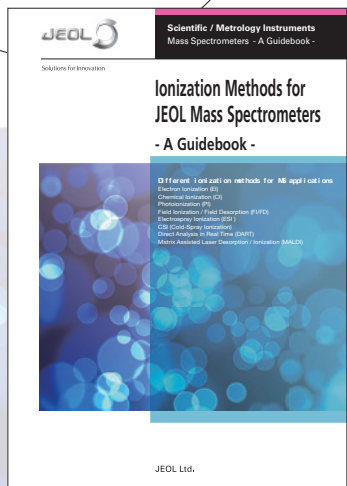
Ionization Methods for JEOL Mass Spectrometers
-A Guidebook-

JEOL mass spectrometers support a variety of ionization methods, including ionization combined with chromatography, ionization using direct sample loading, hard ionization, soft ionization, etc. This guidebook will describe the principles and characteristics of these methods and introduce their applications.

JEOL GC-MS Primer
- A Guidebook -

Gas Chromatograph - Mass Spectrometer (GC-MS) consists of a gas chromatograph that separates a mixture, and a mass spectrometer that detects the separated components, which makes it an excellent instrument for analyzing volatile compounds.

JEOL offers various types of GC-MS systems, such as a gas chromatograph - quadrupole mass spectrometer (GC-QMS), a gas chromatograph - triple quadrupole mass spectrometer (GC-TQMS), and a gas chromatograph - time-of-flight mass spectrometer (GC-TOFMS), depending on the application. This guidebook explains the basics of GC-MS and the features and applications of each type GC-MS in an easy-to-understand manner.
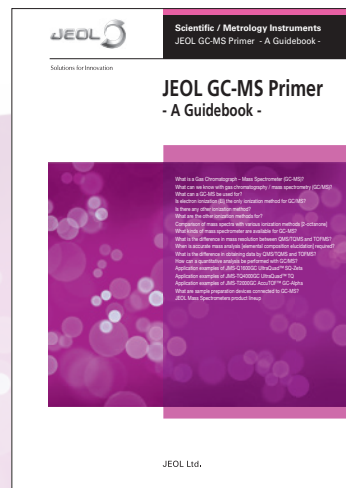
JEOL Ltd.

3-1-2 Musashino Akishima Tokyo 196-8558 Japan   Sales Division Tel. +81-3-6262-3560   Fax. +81-3-6262-3577
www.jeol.com   ISO 9001 • ISO 14001 Certified

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