

# AccuTOF™ GC series

## Materials and Chemistry Applications Notebook

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# MultiAnalyzer – Unknown Compounds Analysis System

## New Gas Chromatograph Time-of-Flight Mass Spectrometer

### JMS-T2000GC “AccuTOF™ GC-Alpha”

Masaaki Ubukata MS Business Unit, JEOL Ltd.

The JMS-T2000GC AccuTOF™ GC-Alpha is the 6th generation JEOL GC-TOFMS and has an improved ion optics system to achieve ultra-high resolution. The AccuTOF™ GC-Alpha is an orthogonal-acceleration time-of-flight mass spectrometer (oaTOFMS) with dual stage reflectron. It employs an ideal ion optical system realizing both high ion transmission (=sensitivity) and ultra-high resolution. The dedicated qualitative software msFineAnalysis makes full use of the high-quality data obtained by the JMS-T2000GC AccuTOF™ GC-Alpha, thus providing a new approach to qualitative analysis for identification of unknown compounds. JEOL can offer real unknown compounds analysis solution with the powerful combination with JMS-T2000GC AccuTOF™ GC-Alpha and msFineAnalysis.

## Introduction

Modern mass spectrometers (MS) are used for a variety of applications and scientific fields. Among these MS systems, the gas chromatograph-mass spectrometer (GC-MS) is suitable for both qualitative and quantitative analyses of volatile compounds and plays a crucial role in the analysis of materials, forensics, foods, environmental contaminants, etc. For qualitative analysis, GC-MS analysis typically involves collecting electron ionization (EI) mass spectra and then using these spectra for library database searches to identify each analyte. While this technique is effective for compounds found within these libraries, there are still many compounds that are not registered in the databases. As a result, additional tools are necessary to perform non-targeted analysis of unregistered components that can often appear during the analysis of materials and environmental samples. To address this situation, JEOL has continuously enhanced and improved upon our GC-MS products to include a variety of advanced capabilities, as shown in **Fig. 1**. The features improved upon include:

- 1) A Time-of-Flight Mass Spectrometer (TOFMS) that can acquire mass spectra with high resolution (HR) and high mass accuracy
- 2) Soft ionization techniques that are essential for determining the molecular weight and molecular formula of unknown substances
- 3) User-friendly software that automatically performs accurate mass analysis for the measured data

Our 6<sup>th</sup> generation GC-TOFMS, the JMS-T2000GC “AccuTOF™ GC-Alpha,” was introduced into the market this year with significantly enhanced capabilities for higher mass resolution and higher mass accuracy. In this report,

we will provide an overview of the AccuTOF™ GC-Alpha instrumentation as well as its basic performance capabilities.

## Overview of the Instrument

The new AccuTOF™ GC-Alpha system is shown in **Fig. 2** and represents a significant design change from the previous models shown in **Fig. 1**. Specifically, the orthogonal acceleration (oa)-TOFMS ion trajectory was changed from the conventional “V”-like trajectory to a new “A”-like trajectory in order to extend the ion flight distance from 2 m to 4 m as shown in **Fig. 3**. Additionally, the oa-TOFMS was equipped with an improved ion acceleration system that spatially focuses the ion beam and an improved reflectron system that temporally focuses the ion beam. Because the system is a HRTOF-MS, the instrument is always operating in high resolution mode. Furthermore, by optimizing these components (along with the longer flight path), the AccuTOF™ GC-Alpha represents a significant improvement in both mass resolving power and mass accuracy. The AccuTOF™ GC-Alpha provides 6 times higher resolution than our 1<sup>st</sup> generation “AccuTOF™ GC”.

## Basic High-Performance System for Non-Targeted Analysis

The basic performance of the AccuTOF™ GC-Alpha are as follows:

- Sensitivity: OFN 1 pg, S/N > 300
- Mass Resolving Power: > 30,000 (FWHM,  $m/z$  614)
- Mass Accuracy: < 1 ppm (RMS, EI standard ion source)
- Mass Range:  $m/z$  4 – 6,000
- Spectrum Recording Speed: Up to 50 spectra/sec
- Ionization Methods: EI, CI, PI, FI, DEI, DCI, and FD

**Fig. 1 History of JEOL GC-HR-TOFMS**



**Fig. 2 JMS-T2000GC "AccuTOF™ GC-Alpha"**



**Fig. 3 Schematics of ion optical system**



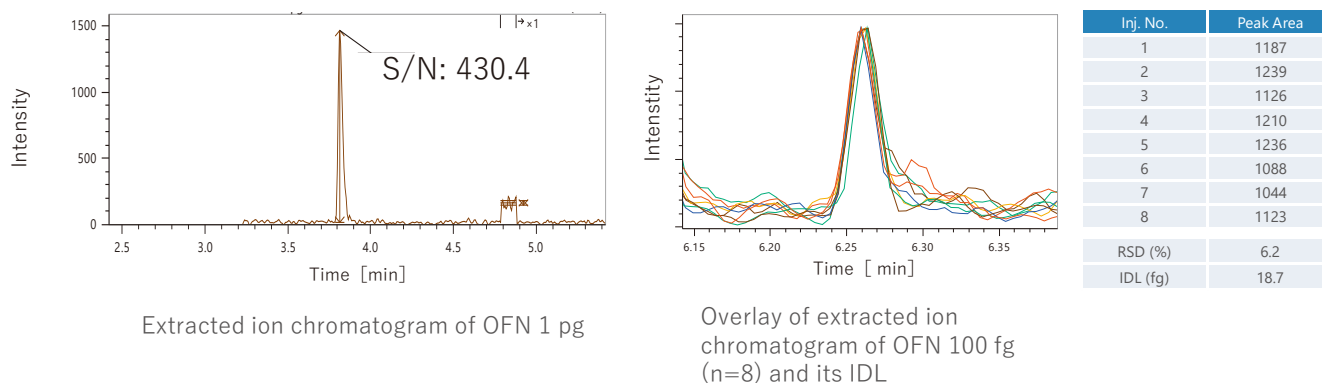
### High Sensitivity

The new AccuTOF™ GC-Alpha has maintained the same sensitivity specifications as the previous generation system, despite the longer flight path and completely redesigned hardware. **Fig. 4a** shows the  $m/z$  271.9867 extracted ion chromatogram (EIC) for 1 pg of octafluoronaphtalene (OFN) in which the GC-Alpha was able to easily achieve a  $S/N > 300$ . **Fig. 4b** shows the OFN EICs for the instrument detection limit (IDL) measurements in which 100 fg of OFN was injected 8-times. Additionally, **Fig. 4b** includes a table of peak areas, the calculated relative standard deviation (RSD) for these peak areas of 6.2%, and the calculated IDL of 18.7 fg. These results clearly demonstrate that the AccuTOF™ GC-Alpha provides both high sensitivity and high stability even for trace components analysis.

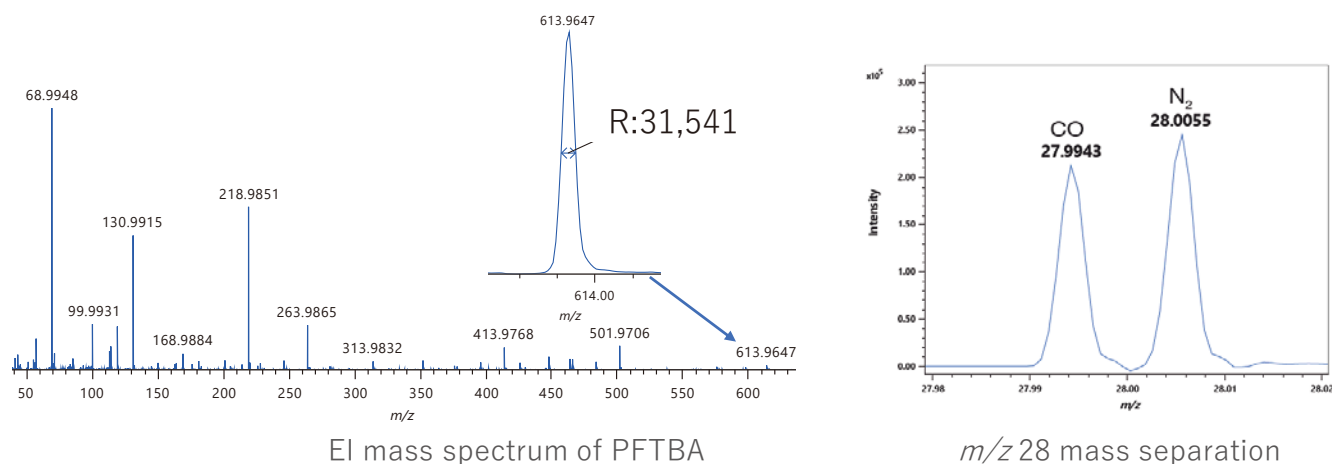
### High Mass-Resolving Power

The AccuTOF™ GC-Alpha has a much higher mass-resolving power than the previous generations of the instrument. To demonstrate this new resolution capability, **Fig. 5a** shows the EI mass spectrum for PFTBA in which the  $m/z$  614 peak was enlarged to clearly display the FWHM resolution of  $>30,000$ , which is the new resolution specification. To further highlight how this improved resolving power can enhance sample analysis, **Fig. 5b** shows the baseline separation of  $\text{CO}^+$  ( $m/z$  27.9949) and  $\text{N}_2^+$  ( $m/z$  28.0061) which was not possible with the previous generation instruments. These results clearly demonstrate that the high mass-resolution of the AccuTOF™ GC-Alpha can easily separate closely related ions (same nominal mass) and thus can be a powerful tool for a wide range of analyses and applications involving analytes with the same nominal mass but different elemental compositions.

**Fig. 4 OFN 1 pg sensitivity and IDL for OFN 100 fg measurement**



**Fig. 5 EI mass spectrum of PFTBA and  $m/z$  28 mass separation**



## High Mass-Accuracy

Along with higher mass resolving power, the AccuTOF™ GC-Alpha also has higher mass accuracy with a new specification of less than 1 ppm. An EI mass spectrum of methyl stearate along with the accurate mass analysis results for all observed ions are shown in **Fig. 6**. These results demonstrate that high mass accuracy is maintained over the entire mass range (from  $m/z$  43 corresponding to the lowest mass fragment ion up to  $m/z$  298 corresponding to the molecular ion), thus simplifying the determination of each compositional formula. Furthermore, the average mass error for these 10 ions was only 0.05 mDa / 0.45 ppm.

Also, worth noting here, the AccuTOF™ GC-Alpha produces high mass-accuracy mass spectra independent of the ionization method used for the measurements. This is important because the new system also offers all of the same ionization options that were available with the previous models - electron ionization (EI), chemical ionization (CI), photo ionization (PI), field ionization (FI) for GC-MS and desorption electron ionization (DEI), desorption chemical ionization (DCI), and field desorption (FD) methods for direct probe sample introduction. Therefore, the high mass accuracy of the AccuTOF™ GC-Alpha can be used with hard ionization (EI) for library searches / fragment ion formula determination and with soft ionization (CI, PI, FI) for molecular formula determination for the observed molecular ion / molecular ion adduct. This combination of mass accuracy and hard / soft ionization is a powerful tool for qualitative analysis of unknown compounds.

## Powerful Capabilities for GC-MS Qualitative Analysis

- The AccuTOF™ GC-Alpha simultaneously achieves high sensitivity, high mass resolution and high mass accuracy.
- The AccuTOF™ GC-Alpha is suitable for not only target analysis but also non-targeted analysis of samples, even at trace levels.

## Wide Mass Range

The AccuTOF™ GC-Alpha maintains the wide mass range ( $m/z$  4-6000) of the previous generation systems. While GC-

MS analysis is typically limited to analytes under  $m/z$  1000, this increased mass range unlocks the analyst's ability to directly analyze samples like polymers and organometallics by using direct probe MS in which the sample is directly introduced into the ion source (not through the GC). The AccuTOF™ GC-Alpha accommodates two direct sample introduction probes (Direct Exposure Probe and Direct Insertion Probe) for direct EI measurement and direct CI measurement. Additionally, the optional FD probe allows the analyst to use a soft ionization direct probe method that is easy to use for the analysis of materials like polymers and higher molecular weight petrochemicals. Most commercial GC-MS instruments are dedicated only to GC-MS measurement, but the AccuTOF™ GC-Alpha can also be used as a direct MS instrument.

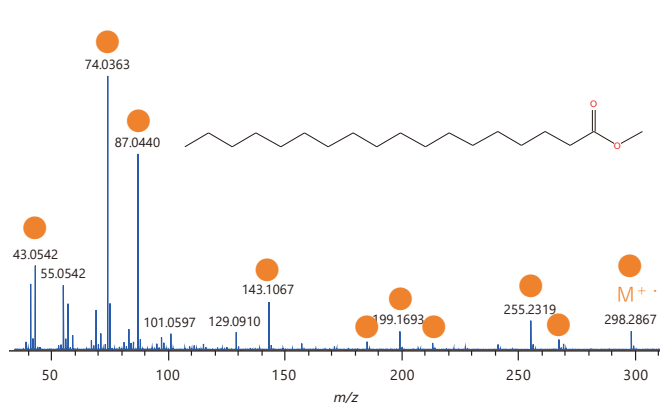
## High-Speed Data Acquisition

The AccuTOF™ GC-Alpha maintains the high-speed data acquisition rate (up to 50 spectra/sec) of the previous generation systems as well. This capability is critical for doing Fast GC and GCxGC measurements which both require fast spectrum recording intervals. In particular, the AccuTOF™ GC-Alpha allows the user to bring together GCxGC separation, high resolution MS, high mass accuracy, EI, and soft ionization (CI, PI, FI) to analyze samples that are typically too complex for standard GC-MS separations.

## Combined EI Method and Soft Ionization Methods – two combination ion sources –

As mentioned previously, library database searches are typically used for GC-MS qualitative analysis. However, for unknown compounds that are not registered in the MS databases, it can be difficult to identify these unknowns by using EI data alone. EI is a hard ionization method that typically produces many fragment ions as well as molecular ions. With that said, it is not uncommon for EI to produce minimal or no molecular ion signal in the mass spectrum. Consequently, the analyst can have difficulty deciding if

**Fig. 6 EI mass spectrum of methyl stearate and the mass accuracy**



EI mass spectrum of methyl stearate

Obs. $m/z$	Formula	Calc. $m/z$	Error	
			[mDa]	[ppm]
43.0542	C3 H7	43.0542	-0.06	-1.42
74.0363	C3 H6 O2	74.0362	0.10	1.40
87.0440	C4 H7 O2	87.0441	-0.01	-0.16
143.1067	C8 H15 O2	143.1067	0.03	0.22
185.1537	C11 H21 O2	185.1536	0.05	0.26
199.1693	C12 H23 O2	199.1693	0.04	0.19
213.1850	C13 H25 O2	213.1849	0.08	0.39
255.2319	C16 H31 O2	255.2319	0.03	0.11
267.2683	C18 H35 O	267.2682	0.05	0.18
298.2867	C19 H38 O2	298.2866	0.06	0.20
Averaged mass error (Abs.)			0.05	0.45

there is a molecular ion present in the EI spectrum, thus complicating the data analysis. To overcome this problem, it can be very effective to use soft ionization methods to confirm the molecular ion / molecular adduct ion. The AccuTOF™ GC-Alpha has two optionally available combination ion sources that can be used to switch between EI and a soft ionization method (**Fig. 7**).

The EI/FI/FD combination ion source offers the combination of EI (hard ionization) and FI (soft ionization) for GC-MS measurements and FD (soft ionization) for direct probe MS measurements of heavier materials that do not go through the GC. Basically, this combination ion source allows the analyst to do GC/EI, GC/FI and FD measurements without breaking vacuum. All that is required to switch between ionization modes is the exchanging of the EI repeller probe with the FI/FD probe through a vacuum interlock that goes directly into the ion source. FI is the softest ionization method available (\*Note) and will even produce molecular ions for saturated hydrocarbons.

The EI/PI combination ion source allows the AccuTOF™ GC-Alpha to be switched from GC/EI (hard ionization) to GC/PI (soft ionization) measurements without breaking vacuum. In this case, the ion source only requires switching between ON/OFF for the EI filament and ON/OFF for the PI ultraviolet-light lamp when switching between each ionization method. PI is particularly effective and sensitive for producing molecular ions for substances that can absorb ultraviolet light (e. g. aromatic compounds).

These unique combination ion sources are options only available with the AccuTOF™ GC-Alpha (see Fig. 1). They are extraordinarily powerful in that these sources allow the user to switch between GC/EI and GC/soft ionization without breaking vacuum while also capitalizing on the high mass resolution and high mass accuracy provided by the TOFMS. Thus, the AccuTOF™ GC-Alpha used with these combination ion sources simplifies the process of doing non-targeted,

qualitative analysis of unknown compounds.

\*Note: This case is applicable for ionization methods available with the AccuTOF™ GC-Alpha.

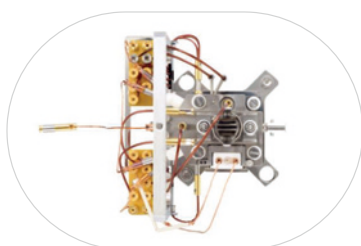
## Automatic Qualitative Analysis Software “msFineAnalysis”

Originally released in 2018 as an option for the previous generation JMS-T200GC Series, the latest version of the “msFineAnalysis” software is now included with the basic AccuTOF™ GC-Alpha system. This software was designed to automatically identify compounds in a sample measured by GC-MS. More specifically, msFineAnalysis uses a new workflow that integrates GC/EI (hard ionization) high resolution data with GC/soft ionization (FI, PI, CI) high resolution data to automatically generate a color-coded qualitative analysis report for a measured sample. **Fig. 8** shows the integrated workflow used by the software in which five different analysis steps are automatically combined to produce fast, high-accuracy qualitative analysis results. The msFineAnalysis software is already widely acknowledged as a powerful tool for non-targeted analysis.

The latest version of msFineAnalysis (Version 3) streamlines the software operation and adds a new function in which two similar samples can be directly compared in order to identify sample differences. This feature can be particularly useful for comparing complex materials that have subtle differences. Identifying these differences can be critically important for addressing changes in material synthesis or manufacturing processes in which product quality is critically important.

As a starting point, the difference analysis function uses multiple GC/EI data to determine the components observed within the two samples (here referred to as A and B). Then, a t-test statistical analysis is done to extract the components that are different. Afterwards, a full integrated analysis (Fig. 8) is performed using the GC/EI data and GC/SI data. If a characteristic component in A or B is not registered in the library database, the

**Fig. 7 Two combination ion sources**



### EI/FI/FD combination ion source

- EI and FI are switchable **without breaking a vacuum**.
- Replacement of the EI repeller probe and the FI emitter probe is needed.
- **FD (direct MS) measurement** is also possible.



### EI/PI combination ion source

- EI and PI are switchable **without breaking a vacuum**.
- Replacement of the hardware is not required.
- PI ionization energy is about 10.3 eV.



integrated analysis will still determine an elemental composition for the unknown component. **Fig. 9** shows the difference analysis window which includes a volcano plot, classification section (A only, B only, A>B, A<B and A=B), intensity ratio ( $\text{Log}_2(\text{B/A})$ ), p value, etc. For each class, the components and analysis results are color coded to distinguish them from each other in order to enable a quick visual understanding of the different components.

As an example of difference analysis using msFineAnalysis Version 3, the evolved gas analysis results of two epoxy types of adhesives are shown in **Fig. 10**. A headspace GC-MS method was used for this analysis. The difference analysis parameters were as follows: Acquisition numbers were 5 for each GC/EI measurements, the significance level was 5%, and the threshold for intensity difference was set to 2. The upper section of Fig. 10 shows the TIC chromatograms (solid lines) as well as the detected peaks from chromatographic deconvolution. Each peak is color coded with blue indicating a characteristic component for adhesive A, red indicating a characteristic component for adhesive B, and yellow indicating a component that is observed in both A and B (no difference). The blue and red color scheme is also applied to the integrated analysis report in the lower section of the window, but white is used in this case to identify the components observed in both A and B (no difference). The difference analysis results for this example showed:

- Toluene was observed in both adhesives.
- Adhesive A had a high intensity peak for butanol that was not observed from adhesive B.

- Adhesive B had several aromatic compounds such as ethylbenzene and xylene.
- Adhesive B had cyclic siloxanes.

For conventional GC-MS difference analysis, if the extracted characteristic component is not registered in the library database, then it can be difficult to identify this unknown component. However, using msFineAnalysis Version 3 makes it possible to automatically identify these components using the integrated analysis workflow that is subsequently performed after the difference analysis. This innovative 2-sample comparison solutions can be broadly applied to not only the materials field but also to a variety of other research and application fields.

## Conclusions

The new JMS-T2000GC “AccuTOF™ GC-Alpha” is a new high-resolution GC-TOFMS that represents a significant improvement over the previous generation instruments. The hardware was completely redesigned for improved resolving power, mass accuracy, sensitivity and stability. Along with the improved hardware of the AccuTOF™ GC-Alpha, the automatic qualitative analysis software “msFineAnalysis” was also upgraded to incorporate difference analysis between two-samples while also continuing to capitalize on the integrated analysis workflow that this software is known for. The combination of AccuTOF™ GC-Alpha and msFineAnalysis is a truly powerful solution for GC-MS qualitative analysis.

**Fig. 8 msFineAnalysis: Integrated analysis workflow**

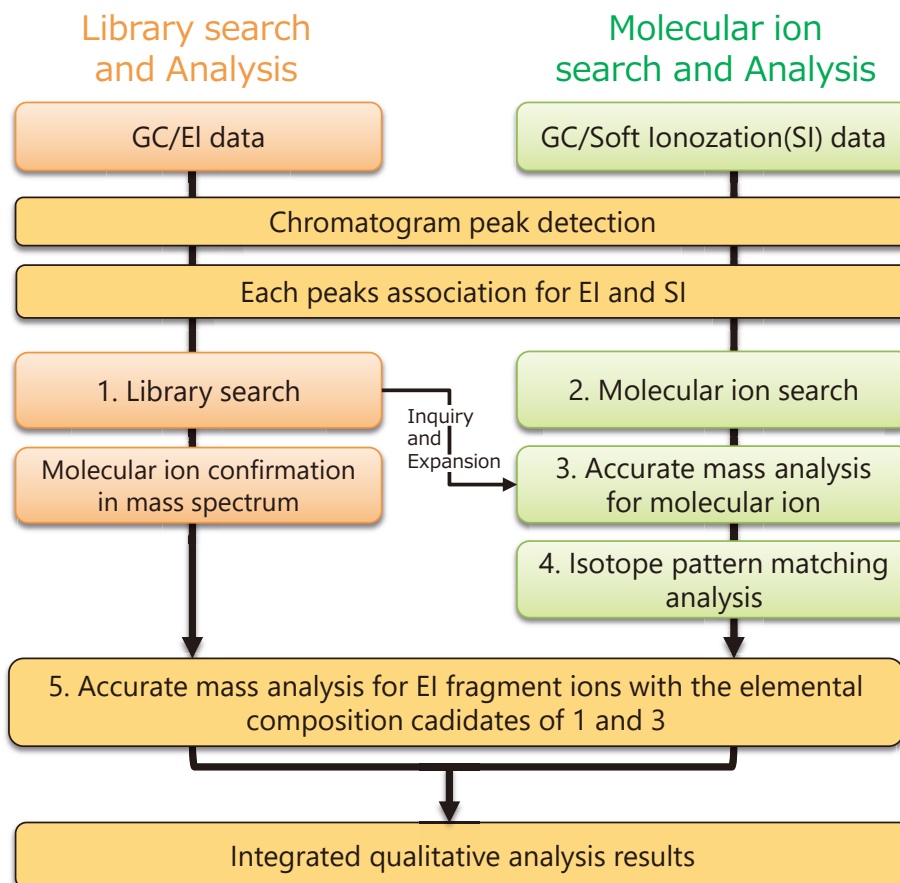




Fig. 9 msFineAnalysis Ver.3: 2-samples comparison GUI

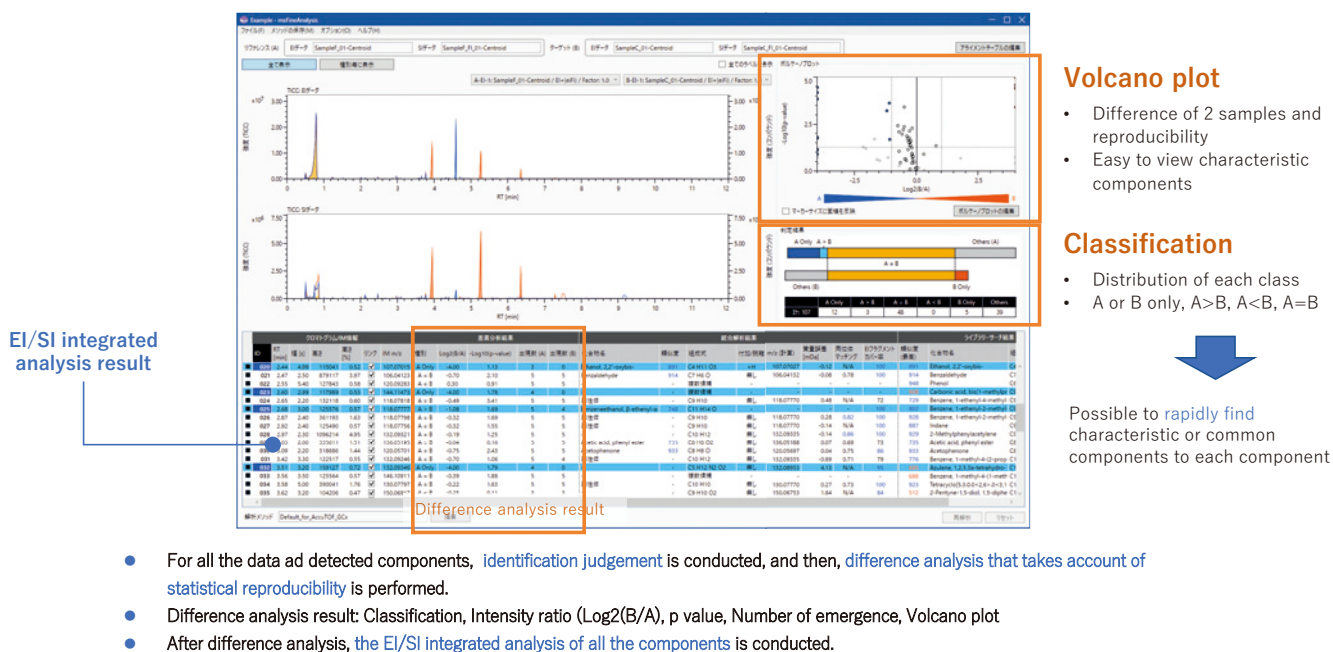
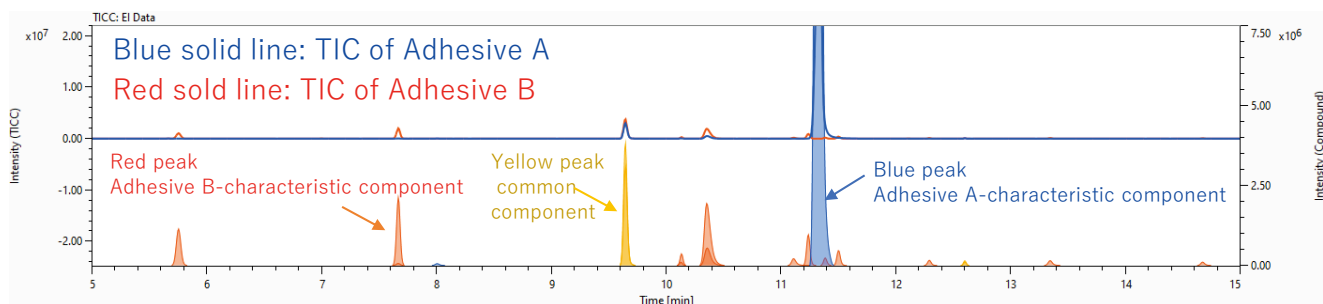


Fig. 10 Evolved-gas difference analysis of material components using HS-GC-TOFMS



Difference analysis + Integrated analysis result

クロマトグラム/IM情報						差異分析結果						統合解析結果							
ID	RT [min]	幅 [s]	高さ	高さ [%]	リンク	IM m/z	種別	Log2(B/A)	-Log10(p-value)	出現数 (A)	出現数 (B)	化合物名	類似度	組成式	付加/脱離	m/z (計算)	質量誤差 [mDa]	同位体 マッチング	EIフラグメント カバー率
001	5.75	8.00	1139828	2.54	✓	222.05689	B Only	4.00	4.68	0	5	Cyclotrisiloxane, hexamethyl-	957	C6 H18 O3 Si3	無し	222.05583	1.06	N/A	100
002	7.66	6.00	2120025	4.73	✓	281.05042	A < B	4.00	4.42	5	5	Cyclotetrasiloxane, octamethyl-	902	C7 H21 O4 Si4	-CH3	281.05114	-0.72	0.89	100
003	8.00	6.80	597118	0.13	✓	130.13524	A Only	-4.00	5.00	5	0	n-Butyl ether	867	C8 H18 O	無し	130.13522	0.03	N/A	100
004	9.64	7.60	3812139	8.50	✓	92.06221	A = B	0.12	1.28	5	5	Toluene	960	C7 H8	無し	92.06205	0.15	0.97	100
005	10.12	4.80	361148	0.81	✓	355.06898	A < B	1.76	5.00	5	5	Cyclopentasiloxane, decamethyl-	933	C9 H27 O5 Si5	-CH3	355.06993	-0.95	0.66	100
006	10.36	12.80	1936628	4.32	✓	74.07312	A < B	1.70	4.83	5	5	1-Propanol, 2-methyl-	819	C4 H10 O	無し	74.07262	0.51	0.69	100
007	11.11	11.60	208814	0.47	✓	90.06757	B Only	4.00	5.00	0	5	2-Propanol, 1-methoxy-	824	C4 H10 O2	無し	90.06753	0.03	0.39	100
008	11.24	6.80	960683	2.14	✓	106.07748	B Only	4.00	5.00	0	5	Ethylbenzene	963	C8 H10	無し	106.07770	-0.22	0.79	100
009	11.33	12.40	44842834	100.00	✓	74.07291	A Only	-4.00	5.00	5	0	1-Butanol	803	C4 H10 O	無し	74.07262	0.29	N/A	100
010	11.38	5.60	233859	0.52	✓	106.07764	B Only	4.00	5.00	0	5	p-Xylene	952	C8 H10	無し	106.07770	-0.07	N/A	100
011	11.50	6.80	461857	1.03	✓	106.07784	B Only	4.00	5.00	0	5	Benzene, 1,3-dimethyl-	967	C8 H10	無し	106.07770	0.13	0.95	100
012	12.29	6.80	159354	0.36	✓	106.07822	B Only	4.00	5.00	0	5	p-Xylene	954	C8 H10	無し	106.07770	0.51	0.93	100
013	12.60	4.80	153832	0.34	✓	429.08815	A = B	0.34	3.19	5	5	Cyclohexasiloxane, dodecamethyl-	932	C11 H33 O6 Si6	-CH3	429.08872	-0.57	0.65	100
014	13.34	8.40	148724	0.33	✓	119.10627	B Only	4.00	5.00	0	5	Ethanol, 2-(1,1-dimethylethoxy)-	872	C6 H15 O2	+H	119.10666	-0.39	N/A	100
015	14.67	7.20	103236	0.23	✓	73.05243	B Only	4.00	5.00	0	5	Formamide, N,N-dimethyl-	863	C3 H7 N O	無し	73.05222	0.21	0.69	100

Blue line: Adhesive A-characteristic component

Red line: Adhesive B-characteristic component

White line: Common component



## Introduction of AI Structure Analysis Function in Automatic Structure Analysis Software msFineAnalysis AI

Product used : Mass Spectrometer (MS)

### Introduction

Electron ionization (EI) is one of the most popular ionization methods used in gas chromatography-mass spectrometry (GC-MS). Consequently, compounds are typically identified by a mass spectral database search using EI mass spectra. Because molecular ions are often weak or absent in 70 eV EI mass spectra, identification of unknowns can be difficult by EI alone. In these cases, soft ionization (SI) can be very helpful for producing and identifying molecular ions. Recently, JEOL began developing an integrated qualitative analysis workflow that automatically combines and interprets the information from EI and SI data. And then in 2018, we introduced our integrated qualitative analysis software "msFineAnalysis" which uses both EI and SI data to improve compound identification for GC-MS applications.

Despite the fact that msFineAnalysis was automatically able to determine the molecular formula and partial structure information from EI fragment ion formulas, the actual structural formulas still required manual analysis using chemical compositions. To address this, we then developed an automated structure analysis software package entitled "msFineAnalysis AI" which uses artificial intelligence (AI) to predict EI mass spectra from chemical structures. We have used our newly-developed AI model to create a database of predicted EI mass spectra for around 100 million compounds. In this work, we introduce AI structure analysis function in automatic structure analysis software msFineAnalysis AI.

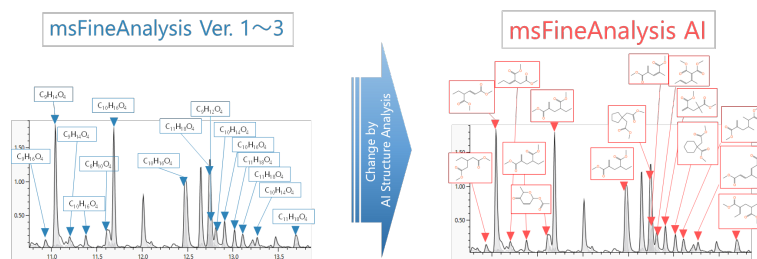


Figure 1 Image of analysis result in msFineAnalysis AI

### About AI Structure Analysis Function

AI structure analysis function performs automatic structure the analysis for unknown compounds using two AIs (main AI, support AI) that complementarily combine machine learning and deep learning.

Figure 2 shows the workflow of AI structural analysis by the main AI. In the main AI, a model for EI mass spectra prediction from structural formulas was constructed using deep learning, and predicted EI mass spectra of 100 million compounds were included in the software as an "AI library" database. The database search function using the "AI library" is implemented similarly to traditional library searches using the commercially available EI mass spectra database. Structural formula candidates are narrowed down by molecular formulas uniquely determined by integrated qualitative analysis, so more correct structural formulas can be obtained quickly. The predicted EI mass spectra were compared with measured EI mass spectra, then the scores were calculated from the spectral patterns, and candidate structural formulas were arranged in order of highest score. Finally, the correct structural formula is selected by combining the obtained structural formula candidates with the sample information and the knowledge and know-how obtained from the previous analysis.

Figure 3 shows the workflow of partial structure prediction by the support AI. The support AI assists interpreting analysis results by predicting the partial structure from the measured EI mass spectrum. It is possible to analyze the composition formula of fragment ions and neutral losses obtained from accurate mass analysis and assist in the interpretation of structural information proposed by the main AI.

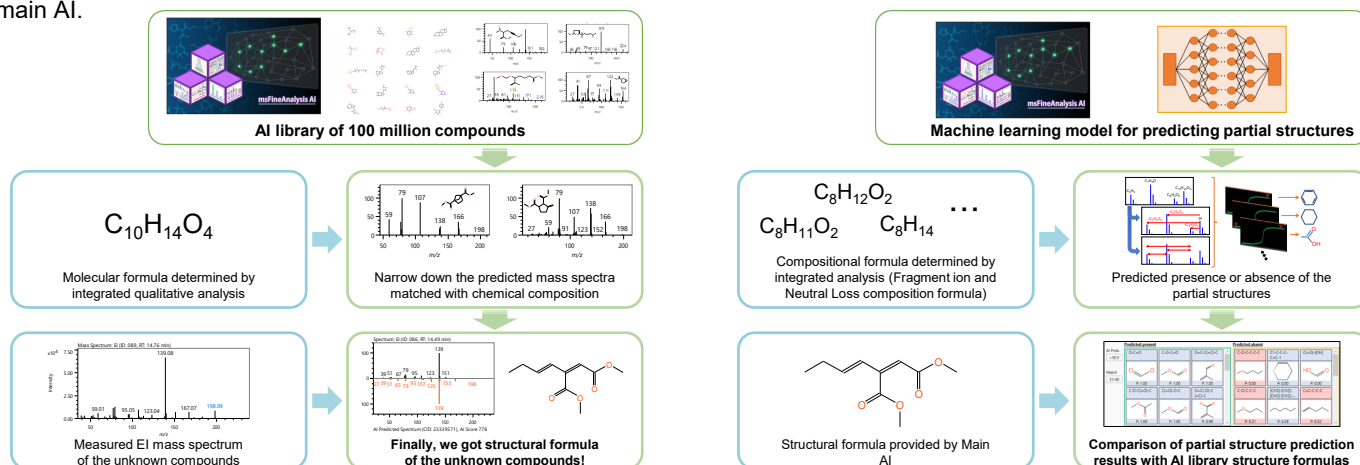


Figure 2 Main AI workflow

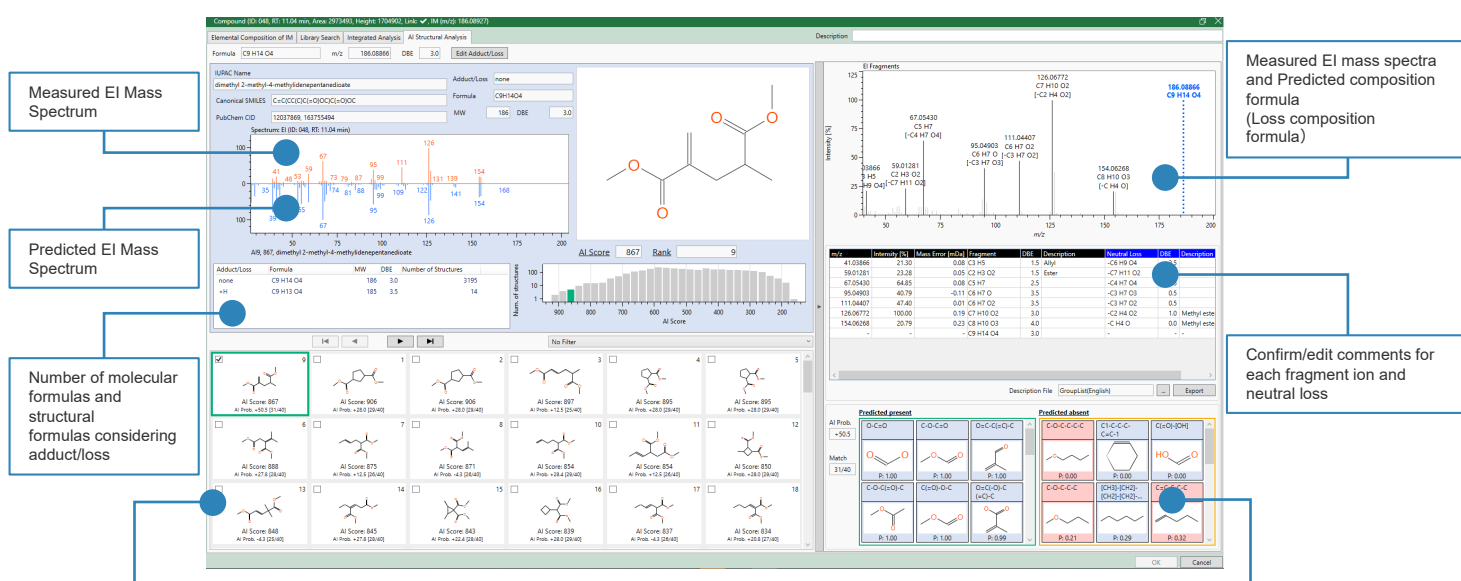
Figure 3 Support AI workflow

## GUI of AI Structure Analysis Result

Figure 4 shows the AI structure analysis result of Acrylic Resin Oligomers by msFineAnalysis AI. The target of analysis is a dimer component that is not registered in the NIST library database. The left side of the analysis result screen shows the structure candidates by the main AI, and the right side shows the analysis results by the support AI. Detailed structural information can be obtained even for unknown compounds that have not been registered in the database.

On the main AI analysis result screen, a list of predicted structural formulas is shown at the bottom of the screen, and it is possible to check the AI structural analysis results all at once. The AI score indicates the similarity between the AI library and the measured mass spectrum, and it is shown at the bottom of each structural formula. Furthermore, information on the selected structural formula is posted at the top of the screen. We can see where the selected structural formula is in the histogram. It also includes a filtering function by partial structure and monomer, which enables structural analysis results to reflect the presence or absence of substructures predicted by the support AI is described below.

On the support AI analysis result screen, predicted partial structure information is shown at the bottom of the screen. On the list, the left side is the partial structure predicted to be present, and the right side is the partial structure predicted not to be present. The partial structure with blue background matches the structural formula selected in the main AI, while the partial structure with red background does not match. Measured mass spectrum and the predicted composition formula of each fragment ion/neutral loss is posted at the top of the screen. It is also possible to confirm and edit comments for each estimated composition formula.



### Structural Formula Prediction by Main AI

- Displays ranked structural formulas in list.
- Selecting a structural formula updates the information that is displayed.
- Below each structural formula is an AI score that indicates the match percentage between structural formula and mass spectrum.

### Partial Structure Prediction by Support AI

- Displays the predicted partial structure information
- Partial structure predicted and present are on the left, predicted and absent are on the right.
- Those with a blue background are the partial structures that match the selected structural formulas. Those with a red background are those that do not match.

Figure 4 GUI of msFineAnalysis AI

## Conclusion

In this MSTips, we introduced our newly-developed software msFineAnalysis AI, which contains AI structural analysis functionality to enhance qualitative analysis workflow. This software performs automatic structure analysis for unknown compounds using two AIs (main AI, support AI) that complementarily combine machine learning and deep learning. No knowledge of mass spectrometry and AI are required as the software automatically interprets complex mass spectra.

Qualitative analysis of GC-MS data can be greatly assisted by using EI and SI data together with msFineAnalysis AI, especially when trying to identify unknown compounds in complex samples.

## JMS-T2000GC AccuTOF™ GC-Alpha

### Sensitivity in nitrogen carrier gas ① - EI / PI ion source

Related products: Mass spectrometer (MS)

#### Introduction

Due to the global shortage of helium gas supply, the demand for alternative gas for GC-MS carrier gas is increasing. Nitrogen gas is the most suitable gas due to its availability and high safety, but it is known that the influence of nitrogen ions generated by the MS ion source causes a decrease in sensitivity. So we have checked the influences of nitrogen carrier gas on JMS-T2000 GC AccuTOF™ GC-Alpha, and report on MS Tips No. 374-376. This report shows the results of the EI (Electron Ionization) / PI (Photo Ionization) combination ion source, which is one of the characteristic multi-ionization ion sources of JMS-T2000 GC AccuTOF™ GC-Alpha.

#### Measurement

Table 1 shows the details of the measurement conditions in this experiment. In the EI method, 1 µL of OFN (octafluoronaphthalene) 100 pg / µL was injected. In the PI method, 1 µL of benzophenone 10 ng / µL was injected. Helium and nitrogen were used as carrier gases, and the S/N sensitivity, the similarity to the library spectrum (M.F.), and the mass accuracy (error) of molecular ions were compared. The carrier gas flow rate was set to 1.0 mL / min in helium and 0.55 mL / min in nitrogen based on the optimum linear velocity of each carrier gas. The ionization energy in the EI method was measured at 70eV and 20 eV, which is expected to suppress the ionization of nitrogen.

**Table 1. Measurement conditions**

GC : 8890GC (Agilent Technologies, Inc.)		TOFMS : JMS-T2000GC AccuTOF™ GC-Alpha	
Injection volume	1 µL	Ion source	EI/PI combination ion source
Mode	Splitless	Ionization	①EI, ②PI
Column	DB-5MS UI (Agilent Technologies, Inc.) 30m x 0.25mm, 0.25µm	EI Ionization energy (filament current)	70eV (300µA), 20eV (200µA)
Oven temperature	40°C(1min)-30°C/min -250°C(2min)	Mass Range	<i>m/z</i> 35-600
Carrier flow	He : 1.0 mL/min N <sub>2</sub> : 0.55 mL/min	Detector voltage	①2600V, ②2800V

## Results ① EI method

Figure 1 shows the extracted ion chromatograms ( $m/z$  272.98  $\pm$  0.10) of the OFN measurement results in the EI method. The sensitivity was greatly decreased to about 1/30 in nitrogen (70 eV). In the nitrogen (20 eV), the sensitivity was slightly decreased to about 1/3. It was confirmed that the decrease in sensitivity was suppressed by changing the ionization energy.

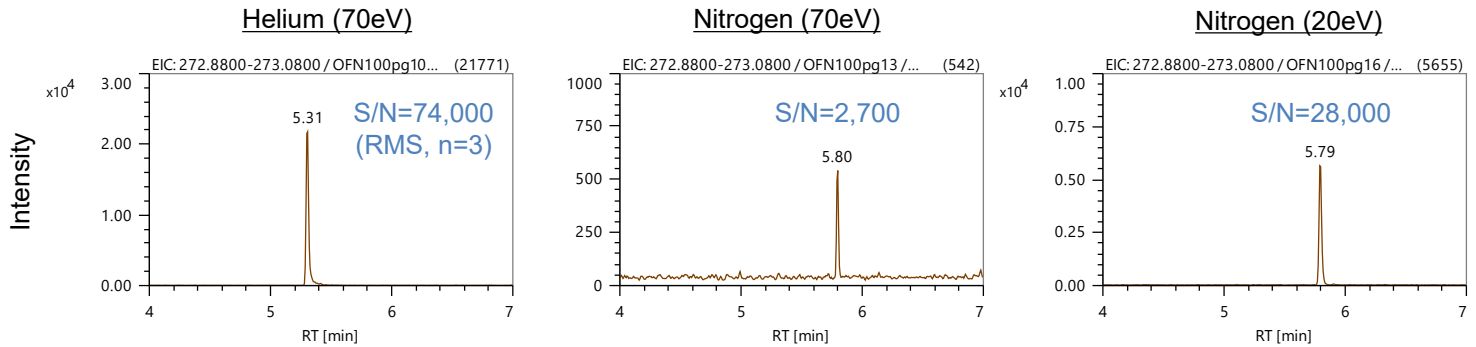


Figure 1. EICs of OFN (EI method)

Figure 2 shows the mass spectra of the OFN measurement results in the EI method. The similarities to the library spectra (M.F.) were good at 800 or more in helium (70eV) and nitrogen (70eV). It was slightly decreased to about 760 in nitrogen (20eV), since the low energy ionization suppressed the fragments and changed the spectrum. The mass errors of the molecular ions  $M^{+}$  ( $m/z$  271.9867) were as good as 1 mDa or less in all results.

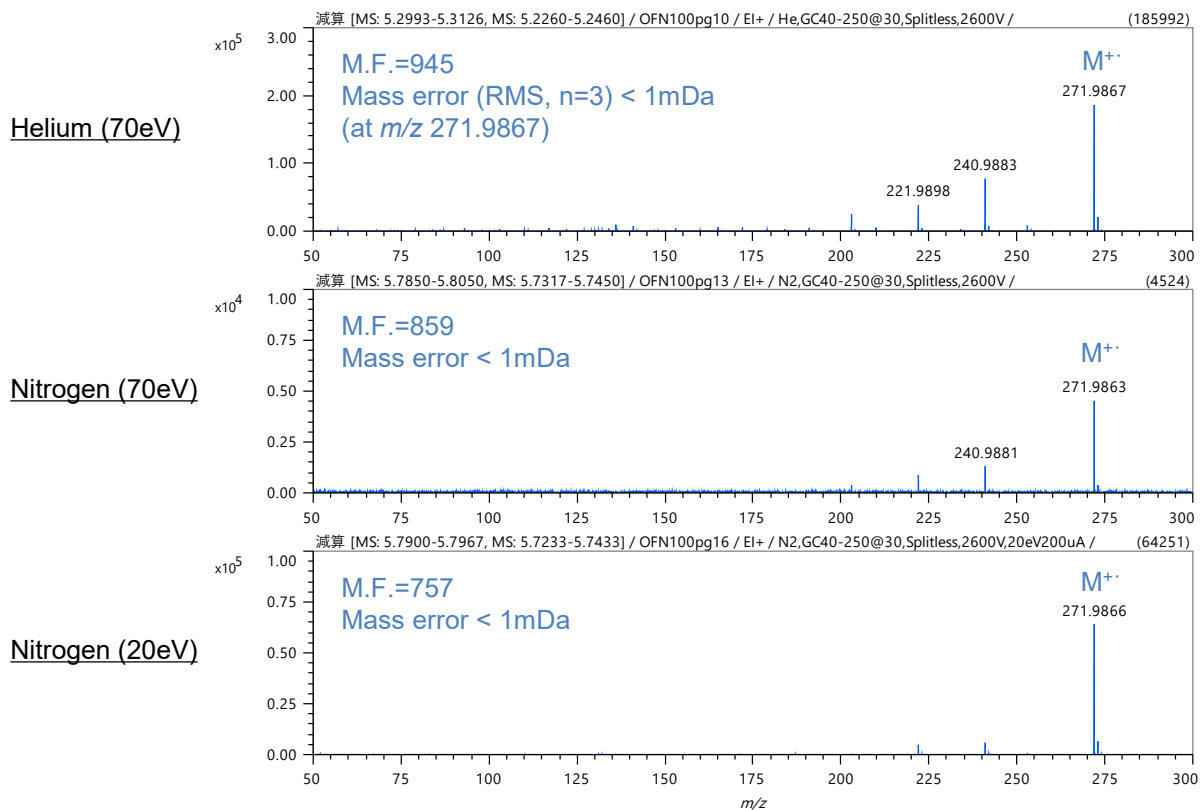
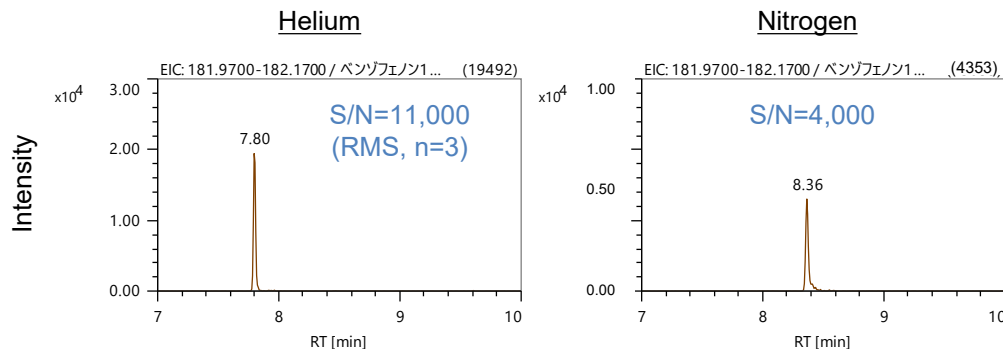


Figure 2. Mass spectra of OFN (EI method)

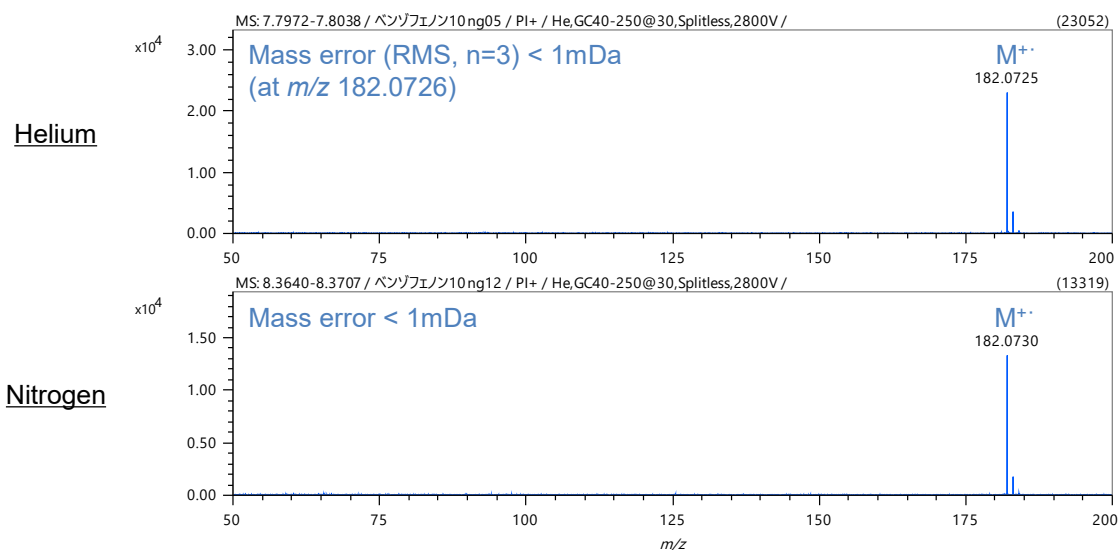
## Results ② PI method

Figure 3 shows the extracted ion chromatograms ( $m/z$  182.07  $\pm$  0.10) of the benzophenone in the PI method. The sensitivity was slightly decreased to about 1/3. In the PI method, which is soft ionization, nitrogen is hardly ionized, but the sensitivity is slightly reduced due to the influence of a large amount of nitrogen molecules.



**Figure 3. EICs of benzophenone (PI method)**

Figure 4 shows the mass spectra of the benzophenone in the PI method. The mass errors of the molecular ions  $M^{+}$  ( $m/z$  182.0726) were as good as 1 mDa or less in both results.



**Figure 4. Mass spectra of benzophenone (PI method)**

## Conclusion

The influences of nitrogen carrier on the EI / PI combination ion source of JMS-T2000GC AccuTOF™ GC-Alpha were checked. In the EI method, the sensitivity was greatly decreased to about 1/30, but it could be suppressed by changing the ionization energy. In the PI method, the sensitivity was slightly decreased to about 1/3. The mass errors of the molecular ions were as good as 1 mDa or less in both EI method and PI method.







## JMS-T2000GC AccuTOF™ GC-Alpha

### Sensitivity in nitrogen carrier gas ② - EI / FI ion source

Related products: Mass spectrometer (MS)

#### Introduction

Due to the global shortage of helium gas supply, the demand for alternative gas for GC-MS carrier gas is increasing. Nitrogen gas is the most suitable gas due to its availability and high safety, but it is known that the influence of nitrogen ions generated by the MS ion source causes a decrease in sensitivity. So we have checked the influences of nitrogen carrier gas on JMS-T2000 GC AccuTOF™ GC-Alpha, and report on MS Tips No. 374-376. This report shows the results of the EI (Electron Ionization) / FI (Field Ionization) combination ion source, which is one of the characteristic multi-ionization ion sources of JMS-T2000 GC AccuTOF™ GC-Alpha.

#### Measurement

Table 1 shows the details of the measurement conditions in this experiment. In the EI method, 1 µL of OFN (octafluoronaphthalene) 100 pg / µL was injected. In the FI method, 1 µL of hexadecane 10 ng / µL was injected. Helium and nitrogen were used as carrier gases, and the S/N sensitivity, similarity to the library spectrum (M.F.), and mass accuracy (error) of molecular ions were compared. The carrier gas flow rate was set to 1.0 mL / min in helium and 0.55 mL / min in nitrogen based on the optimum linear velocity of each carrier gas. The ionization energy in the EI method was measured at 20 eV, which is expected to suppress the ionization of nitrogen, in addition to the general 70 eV.

**Table 1. Measurement conditions**

GC : 8890GC (Agilent Technologies, Inc.)		TOFMS : JMS-T2000GC AccuTOF™ GC-Alpha	
Injection volume	1 µL	Ion source	EI/FI combination ion source
Mode	Splitless	Ionization	①EI, ②FI
Column	DB-5MS UI (Agilent Technologies, Inc.) 30m x 0.25mm, 0.25µm	EI Ionization energy (filament current)	70eV (300µA), 20eV (200µA)
Oven temperature	40°C(1min)-30°C/min -250°C(2min)	Mass Range	<i>m/z</i> 35-600
Carrier flow	He : 1.0 mL/min N <sub>2</sub> : 0.55 mL/min	Detector voltage	2600V

## Results ① EI method

Figure 1 shows the extracted ion chromatograms ( $m/z$  272.98  $\pm$  0.10) of the OFN measurement results in the EI method. The sensitivity was decreased about 1/3 in nitrogen (70 eV). Since the EI / FI shared ion source has an open structure without a chamber, nitrogen retention in the ion source is small. Therefore, it is considered that the influence of nitrogen ions was small and the sensitivity decrease was suppressed. In nitrogen (20eV), which was expected to suppress the sensitivity decrease, the sensitivity was further decreased. It was confirmed that it is not necessary to change the ionization energy in the EI / FI ion source.

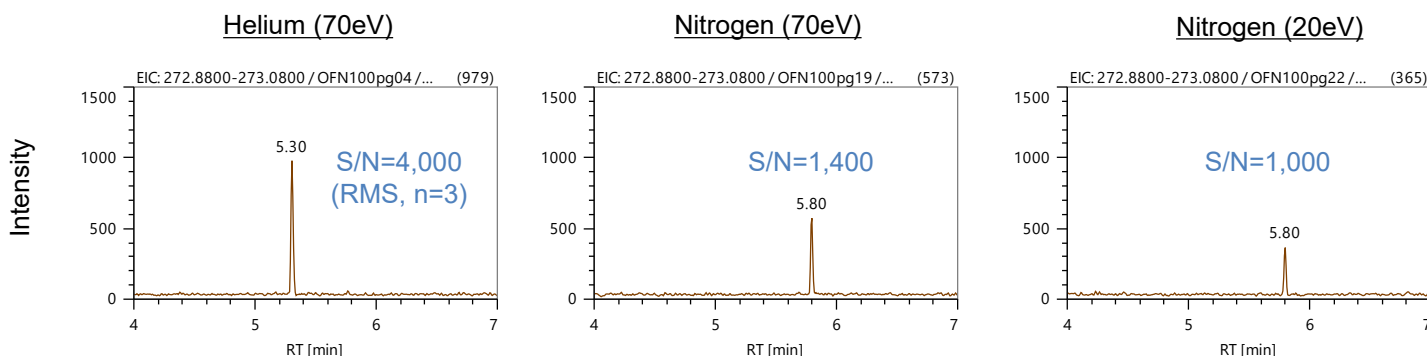


Figure 1. EICs of OFN (EI method)

Figure 2 shows the mass spectra of the OFN measurement results in the EI method. The similarities to the library spectra (M.F.) were good at 800 or more in helium (70eV) and nitrogen (70eV). It was decreased to about 590 in nitrogen (20eV), since the low energy ionization suppressed the fragments and changed the spectrum. The mass error of the molecular ion  $M^{+}$  ( $m/z$  271.9867) was 1 mDa or less in helium (70 eV). They were decreased to 2 mDa or less in nitrogen (70 eV) and nitrogen (20 eV).

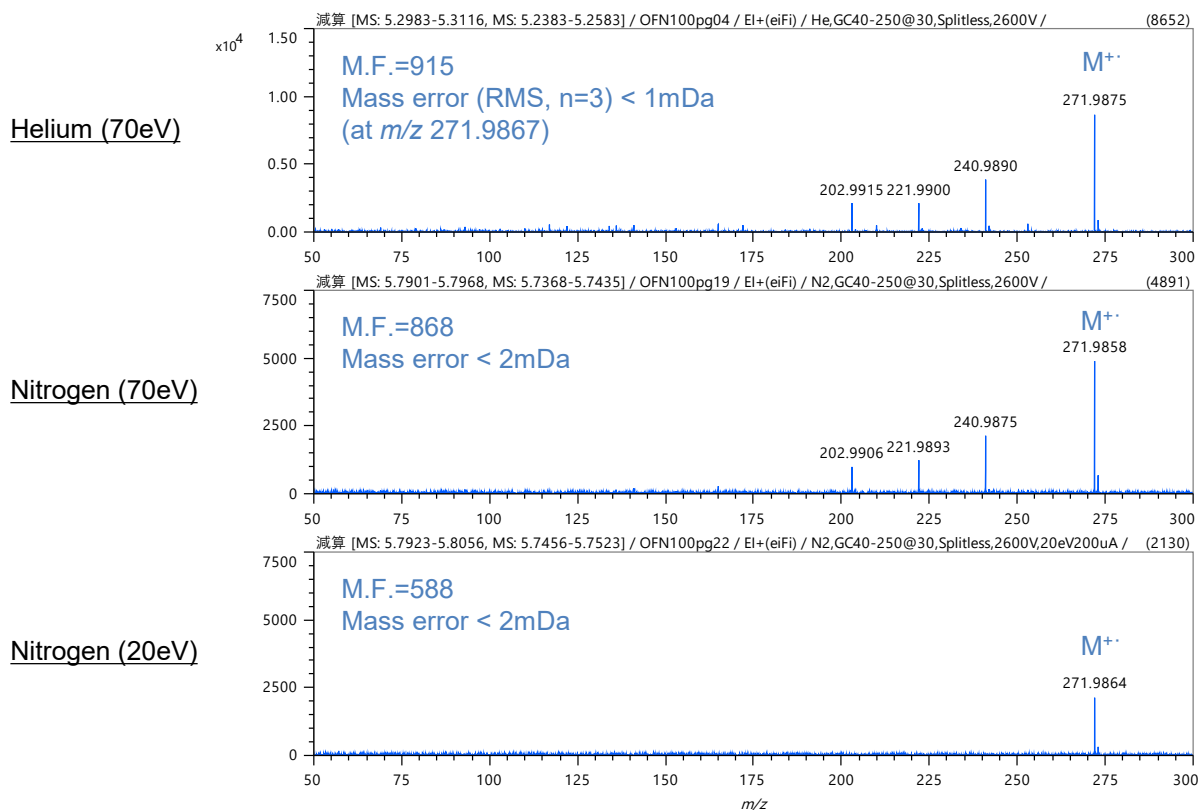


Figure 2. Mass spectra of OFN (EI method)

## Results ② FI method

Figure 3 shows the extracted ion chromatograms ( $m/z$  226.26  $\pm$  0.10) of the hexadecane measurement result in the FI method. The sensitivity was almost the same in helium and nitrogen. Since nitrogen is hardly ionized in the FI method, which is soft ionization, the decrease in sensitivity was suppressed.

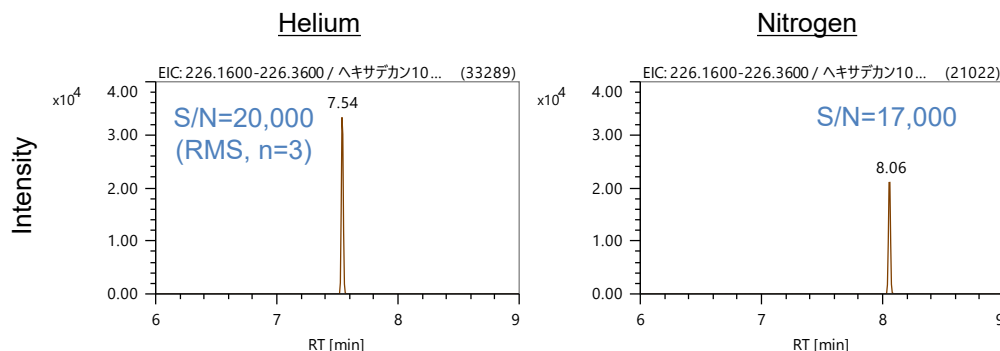


Figure 3. EICs of hexadecane (FI method)

Figure 4 shows the mass spectra of the hexadecane measurement results in the FI method. The mass error of the molecular ions  $M^{+•}$  ( $m/z$  226.2655) were 2 mDa or less in both results.

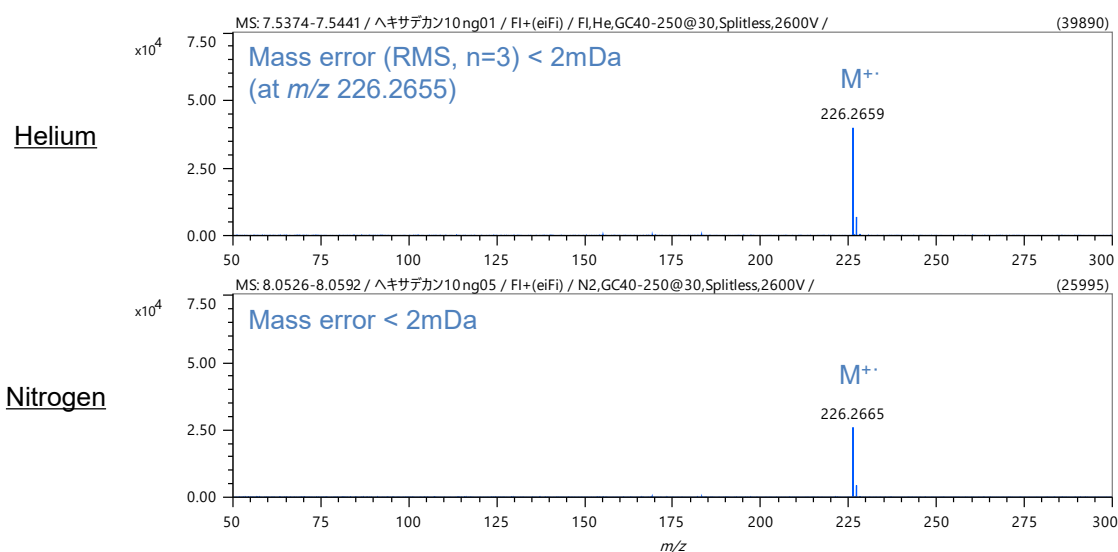


Figure 4. Mass spectra of hexadecane (FI method)

## Conclusion

The influences of nitrogen carriers on the EI / FI combination ion source of JMS-T2000GC AccuTOF™ GC-Alpha were checked. In the EI method, the sensitivity was decreased to about 1/3. In the FI method, the sensitivity was not decreased. The mass errors of the molecular ions were as good as 2 mDa or less in both EI method and FI method.



## JMS-T2000GC AccuTOF™ GC-Alpha

### Sensitivity in nitrogen carrier gas ③ - CI ion source

Related products: Mass spectrometer (MS)

#### Introduction

Due to the global shortage of helium gas supply, the demand for alternative gas for GC-MS carrier gas is increasing. Nitrogen gas is the most suitable gas due to its availability and high safety, but it is known that the influence of nitrogen ions generated by the MS ion source causes a decrease in sensitivity. So we have checked the influences of nitrogen carrier gas on JMS-T2000 GC AccuTOF™ GC-Alpha, and report on MS Tips No. 374-376. This report shows the results of the CI (Chemical Ionization) ion source.

#### Measurement

Table 1 shows the details of the measurement conditions in this experiment. In the positive ion CI (CI+) method, 1 µL of benzophenone 100 pg / µL was injected. In the negative CI (CI-) method, 1 µL of OFN (octafluoronaphthalene) 10 pg / µL were injected. Helium and nitrogen were used as carrier gases, and the S/N sensitivity and mass accuracy (error) of molecular ions were compared. The carrier gas flow rate was set to 1.0 mL / min in helium and 0.6 mL / min in nitrogen based on the optimum linear velocity of each carrier gas.

**Table 1. Measurement conditions**

GC : 8890GC (Agilent Technologies, Inc.)		TOFMS : JMS-T2000GC AccuTOF™ GC-Alpha	
Injection volume	1 µL	Ion source	CI ion source
Mode	Splitless	Ionization	①CI+, ②CI-
Column	DB-5MS UI (Agilent Technologies, Inc.) 30m x 0.25mm, 0.25µm	CI reaction gas	Methane
Oven temperature	50°C(1min)-40°C/min -250°C(2min)	Ionization energy (filament current)	200eV (300µA)
Carrier flow	He : 1.0 mL/min N <sub>2</sub> : 0.6 mL/min	Mass Range	m/z 100-500
		Detector voltage	2500V

## Results ① CI+ method

Figure 1 shows the extracted ion chromatograms ( $m/z$  183.08  $\pm$  0.02) of the measurement result of benzophenone in the CI+ method. The sensitivity was decreased to about 1/2 in nitrogen. Since nitrogen is difficult to ionize in the CI method, which is soft ionization, the decrease in sensitivity was suppressed.

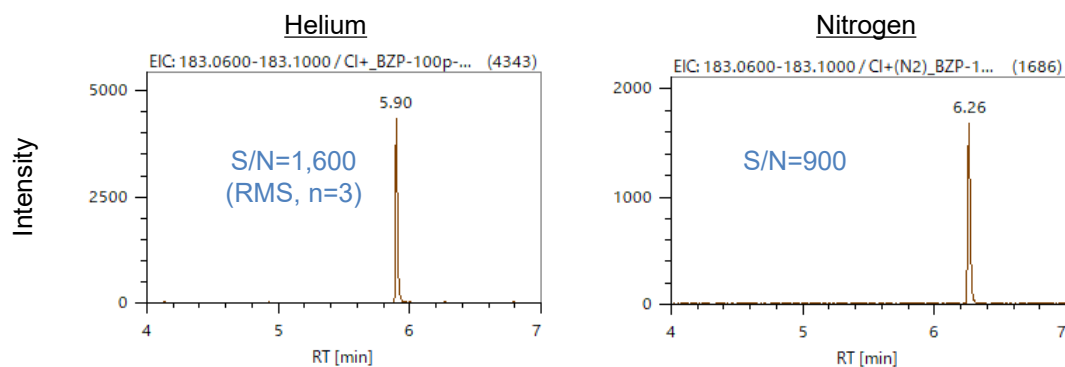


Figure 1. EICs of benzophenone (CI+ method)

Figure 2 shows the mass spectra of the benzophenone measurement result in the CI+ method. Protonated ions  $[M+H]^+$  ( $m/z$  183.0804) were strongly observed, and their mass errors were as good as 1 mDa or less in both results.

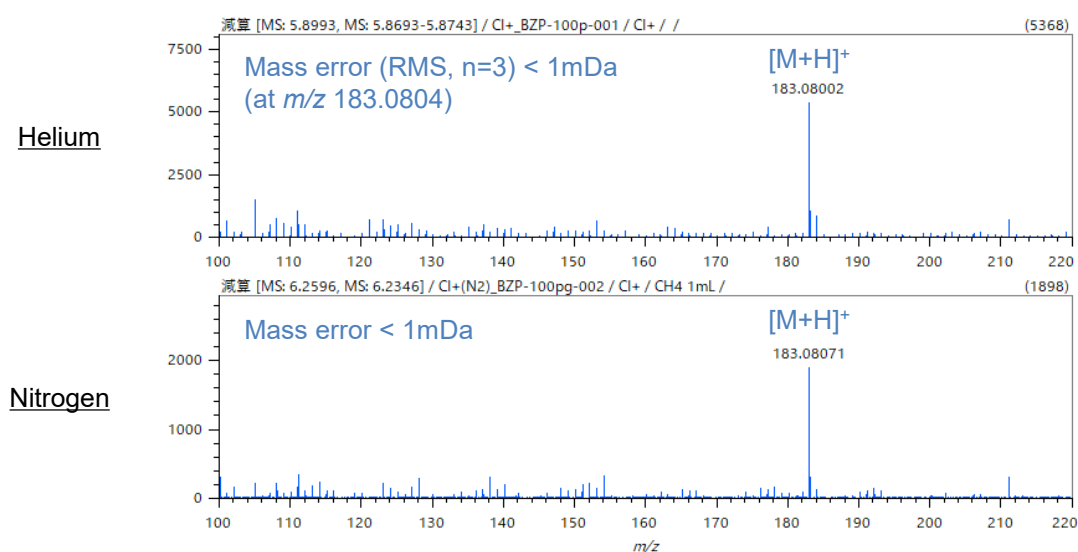


Figure 2. Mass spectra of benzophenone (CI+ method)

## Results ②CI- method

Figure 3 shows the extracted ion chromatograms ( $m/z$  271.99  $\pm$  0.02) of the OFN measurement result in the CI- method. The sensitivity was improved about twice in nitrogen. Since it was difficult to ionize reaction gas impurity in addition to nitrogen in CI- method, which is soft ionization, it is considered that the sensitivity was improved.

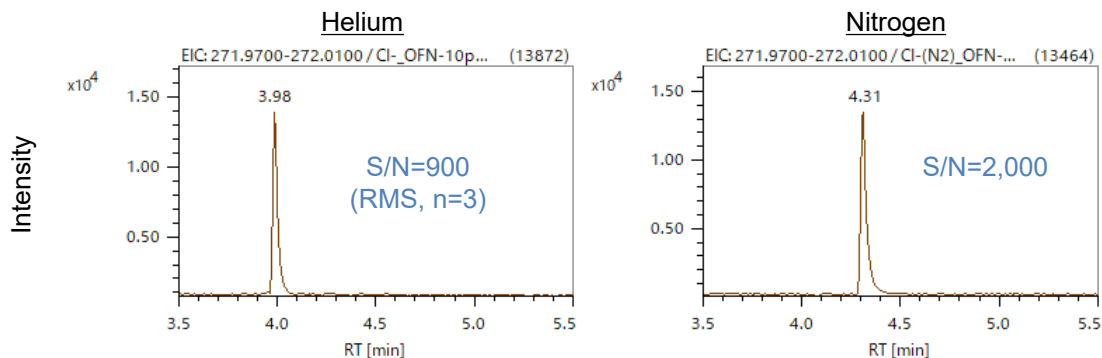


Figure 3. EICs of OFN (CI- method)

Figure 4 shows the mass spectra of the OFN measurement result in the CI- method. The mass errors of the molecular ions  $M^+$  ( $m/z$  271.9878) were as good as 1 mDa or less in both results.

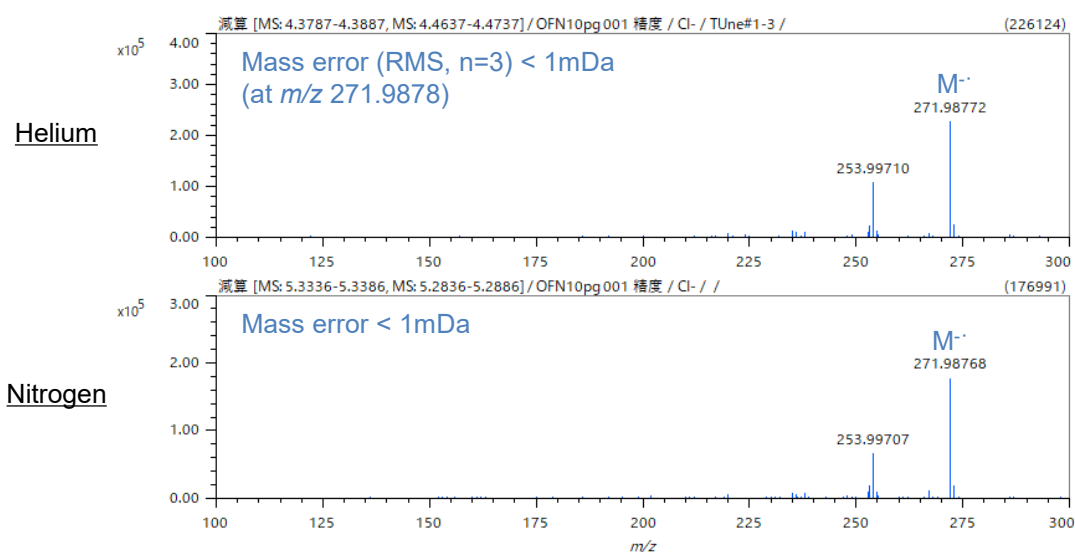


Figure 4. Mass spectra of OFN (CI- method)

## Conclusion

The influences of nitrogen carriers on the CI ion source of JMS-T2000GC AccuTOF™ GC-Alpha were checked. In the CI+ method, the sensitivity was decreased to about 1/2. In the CI- method, the sensitivity was not decreased. The mass errors of the molecular ions were as good as 1 mDa or less in both CI+ method and CI- method.





## Effect of JMS-T2000GC high mass resolution on the analysis result —KMD Plot comparison using msRepeatFinder—

Related Product: Mass Spectrometer(MS)

### Introduction

Recently, JEOL announced the release of the JMS-T2000GC “AccuTOF™ GC-Alpha”, which is the 6th generation GC-HRTOFMS in the JEOL “AccuTOF™ GC” series (Fig. 1). The GC-Alpha achieves three times higher mass resolving power (10,000→30,000 @  $m/z$  614) and three times higher mass accuracy (3ppm→1ppm, EI standard ion source) than the previous model. In this work, we used direct probe field desorption (FD) of crude oil (a very complex mixture) to monitor the effects of improved resolution. Additionally, the JEOL msRepeatFinder software was used to examine the crude oil data by using Kendrick mass defect (KMD) plots in order to more clearly visualize the effects of improved mass resolution on the analysis results.



Fig. 1 JEOL GC-HRTOFMS systems: JMS-T2000GC

### Experimental

Crude oil from the Gulf of Mexico (SRM2779, NIST) was used as the sample. The previous generation JMS-T200GC and new generation JMS-T2000GC equipped with EI/FI/FD combination ion sources were used for the sample analysis. Table 1 shows the measurement conditions for these systems. The data from each system was then analyzed by using msRepeatFinder to confirm the effect of improved mass-resolving power on the analysis results.

Table 1. Measurement and analysis conditions

MS conditions	
Spectrometer	JMS-T2000GC (JEOL Ltd.) JMS-T200GC (JEOL Ltd.) (Previous model)
Ion Source	EI/FI/FD combination ion source
Ionization	FD+: -10kV, 0→51.2mA/min→50mA
Mass Range	$m/z$ 35-1,600
Data processing condition	
Software	msRepeatFinder (JEOL Ltd.)

## Result

Fig. 2 shows the FD mass spectrum obtained by both instruments. Although the overall spectrum patterns were very similar, a closer inspection of the peaks showed that the peak separation differed significantly for each instrument. The JMS-T2000GC (Fig. 2(a)) showed a clear mass separation of each hydrocarbon component, even in the high mass range above  $m/z$  600, that is the result of the new system having a higher mass resolving power. In contrast, the mass separation for the previous model was insufficient, particularly in the high mass range, to adequately resolve the mass peaks from each other.

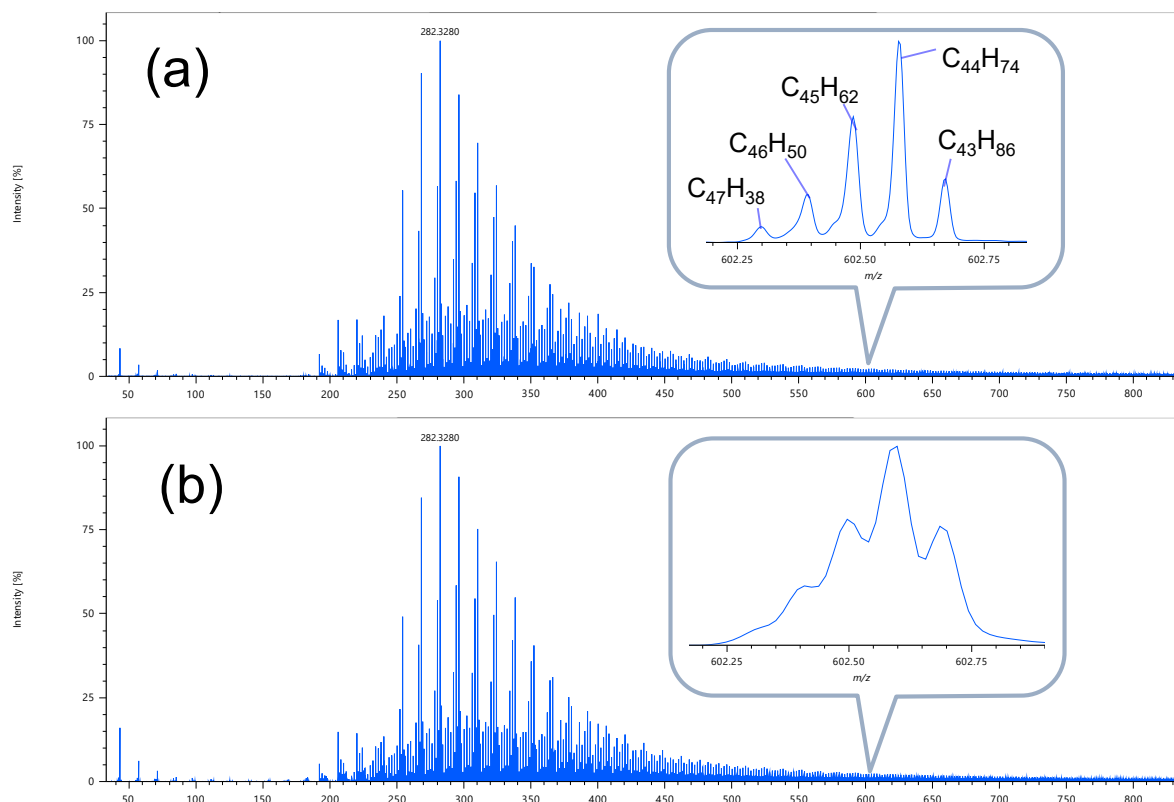


Fig. 2 FD mass spectra for crude oil: (a) JMS-T2000GC data, (b) Previous model data

Next, msRepeatFinder was used to visualize each FD mass spectrum with KMD plots (Fig. 3). The JMS-T2000GC KMD plot (Fig. 3(a)) clearly showed the family of components over the full mass range (including the components above  $m/z$  600). This outcome is a direct result of the improved peak separation, as shown in Fig. 2. On the other hand, the KMD plot for the previous model showed very poor results for the peaks above  $m/z$  600, with many components disappearing because of insufficient mass separation. Basically, the unresolved peaks are being treated as single components despite the fact that there are multiple components, thus resulting in the loss of KMD Plot information in the high mass range.

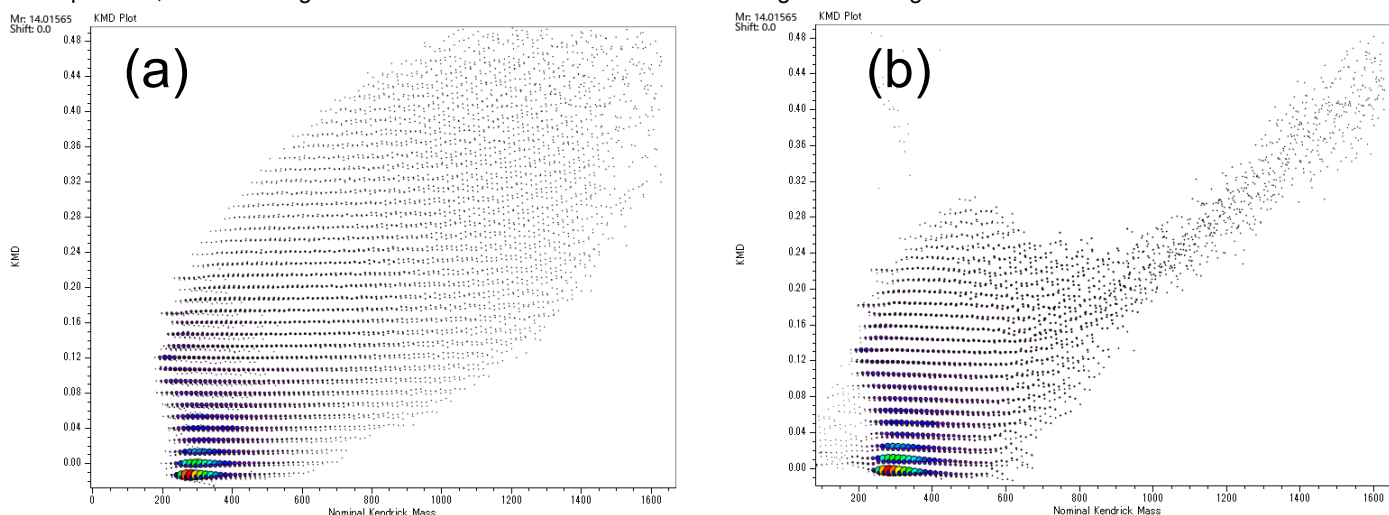


Fig. 3 KMD Plots of FD mass spectrum: (a) JMS-T2000GC data, (b) Previous model data

## Conclusions

The above results confirmed that the high resolving power achieved by the JMS-T2000GC was particularly effective for direct mass measurements (FD probe) of complex materials like crude oil. Additionally, the KMD plots clearly showed that the T2000GC high mass-resolution dramatically increased the number of detected components as a result of the improved mass separation.

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## Effect of high mass accuracy on the analysis result by JMS-T2000GC—Effect to narrow down the result of msFineAnalysis integrated analysis—

Related Product: Mass Spectrometer(MS)

### Introduction

JEOL Ltd. recently announced the JMS-T2000GC “AccuTOF™ GC-Alpha” which is the 6<sup>th</sup> generation GC high resolution time-of-flight MS (GC-HRTOFMS) in the “AccuTOF™ GC” series that was first released in 2004. The GC-Alpha (Fig. 1) represents a significant improvement in capabilities over the previous model with three times higher mass resolving power (10,000→30,000 @  $m/z$  614) and three times higher mass accuracy (3ppm→1ppm, EI standard ion source). In this work, we used the thermal decomposition of an acrylic resin to evaluate how improved mass accuracy can affect the analysis results for a complex sample. Additionally, the msFineAnalysis Version 3 software included with the JMS-T2000GC was used to quickly determine the impact of improved mass accuracy on the qualitative analysis results.

### Experimental

Table 1 shows the measurement conditions for the pyrolysis GC-MS measurements. A JMS-T2000GC equipped with a Frontier Lab pyrolyzer and the JEOL EI/FI combination ion source was used for the measurements, and a commercially available acrylic resin was used as the sample -- 0.2mg for EI method and 1.0mg for FI method, respectively. The resulting data was then analyzed by using the msFineAnalysis integrated workflow (next section, Fig. 2) to examine the effects of high mass accuracy on the analysis results.

**Table 1. Measurement and analysis conditions**

Pyrolysis conditions		MS conditions	
Pyrolyzer	EGA/PY-3030D(Frontier Lab)	Spectrometer	JMS-T2000GC (JEOL Ltd.)
Pyrolysis Temperature	600°C	Ion Source	EI/FI combination ion source
GC conditions		Ionization	EI+:70eV, 300μA FI+: -10kV, 40mA/30msec
Gas Chromatograph	8890A GC (Agilent Technologies)	Mass Range	$m/z$ 35-800
Column	ZB-5MSi (Phenomenex) 30m x 0.25mm, 0.25μm	Data processing condition	
Oven Temperature	40°C(2min)-10°C/min -320°C(15min)	Software	msFineAnalysis (JEOL Ltd.)
Injection Mode	Split mode (100:1)	Library database	NIST17
Carrier flow	He:1.0mL/min	Tolerance	±5mDa, ±2mDa



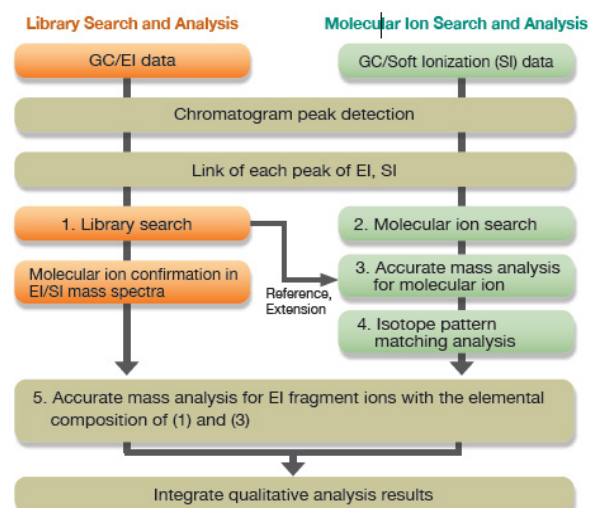
**Fig. 1 JEOL GC/HR-TOFMS systems: JMS-T2000GC**

### msFineAnalysis Software

Fig. 2 shows the msFineAnalysis workflow in which GC/EI data and GC/soft ionization (SI) data are analyzed together to automatically produce an integrated qualitative analysis report. The 5 qualitative analysis steps that are automatically executed are:

1. Library database search using EI mass spectrum
2. Automatic search of molecular ion in the SI mass spectrum
3. Accurate mass analysis for the molecular ion
4. Isotope pattern matching analysis to narrow down the candidate molecular formulas
5. Accurate mass analysis of EI fragment ion and narrowing down molecular formula candidates by using the composition condition of molecular formula candidate obtained in 1 and 4.

By combining the accurate mass analysis of the EI and SI mass spectra, msFineAnalysis cannot only identify components registered in the library but can also determine the elemental composition for unregistered components.

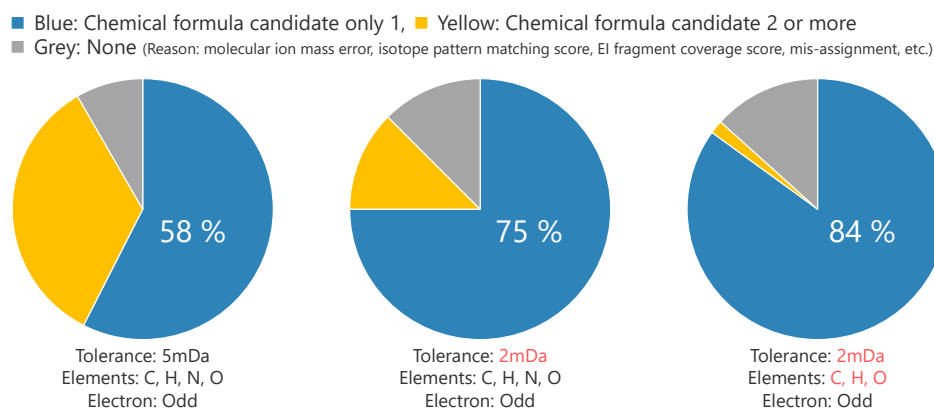


**Fig. 2 msFineAnalysis workflow**

## Result

For accurate mass analysis, an error tolerance is specified based on the mass accuracy capabilities of the instrument. The previous generation models (i.e. JMS-T2000GC) required an error tolerance of  $\pm 5$  mDa for the elemental compositions. However, with the higher mass accuracy of the JMS-T2000GC, it is possible to narrow this error tolerance, which in turn lowers the number of possible elemental compositions calculated for each analyte. The goal of these experiments was to examine the effect of error tolerance for the 120 components (Intensity  $\geq 0.05\%$ ) that were observed during thermal decomposition of the acrylic resin.

Fig. 3 shows the results for the automatic analysis for the pyrolysis of acrylic resin using msFineAnalysis. The blue color shows the percentage of components that resulted in one molecular formula candidate, the yellow shows the percentage that had two or more molecular formula candidates, and the gray shows the percentage with no clear molecular formula candidate. The left pie chart shows the analysis results when using an error tolerance of  $\pm 5$  mDa. Because of this wider tolerance, there were many analytes with more than one candidate molecular formula (yellow). Consequently, only 58% of the 120 components were narrowed down to a single molecular formula candidate. Next, the error tolerance was lowered to  $\pm 2$  mDa, and the results are shown in the Fig.2 central pie chart. The narrower tolerance eliminated many false positive candidates and increased the number of components with only one molecular formula candidate to 75%. Next, the elements used for the elemental composition calculations were narrowed to include only C/H/O because the acrylic resin substructure only includes these elements. The pie chart on the right shows the results of removing nitrogen from the search while continuing to use the narrower tolerance of  $\pm 2$  mDa. As a result, the number of components identified with one molecular formula increased to 84% (101 components).

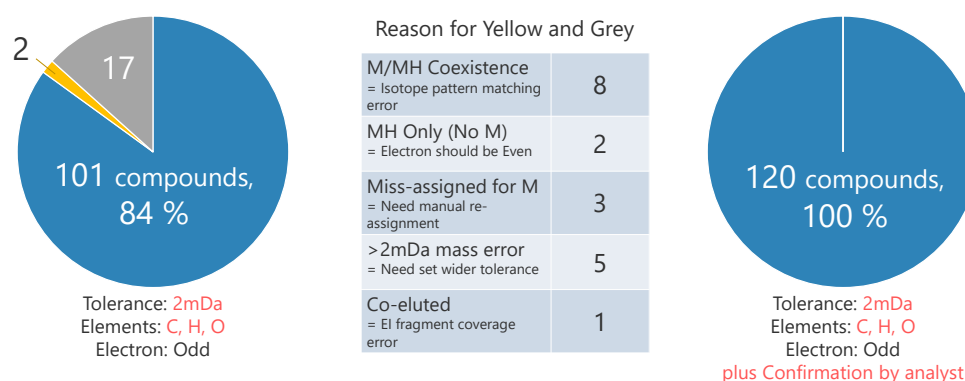


**Fig. 3 Comparison of automatic analysis results for 120 components**

The remaining 19 components were not automatically narrowed down to a single candidate composition for the following reasons:

- $[M]^+$  and  $[M+H]^+$  were present together so the isotope pattern did not match.
- Only  $[M+H]^+$  were observed (since the number of electrons in the proton-added molecule is even, the Odd electron search constraint did not give the correct result).
- The relative intensity of the molecular ion was lower than the default threshold of 10% for ion peak detection and was not correctly assigned.
- The absolute intensity of the molecular ion was low and the peak shape was poor, resulting in a mass error of more than 2mDa.
- It was considered to be a fully co-eluting component, and the EI fragment ion coverage was low.

By manually verifying the measurement data and analysis results for these final 19 components, we were able to narrow down the list to one candidate molecular formula (Fig. 4), thus identifying a single elemental composition for all 120 components that resulted from the pyrolysis of acrylic resin.



**Fig. 4 Confirmation by analyst for 19 components**

## Conclusions

The high mass accuracy of the new JMS-T2000GC allows the analyst to use narrower mass error tolerances within msFineAnalysis. As a result, the software was able to automatically narrow down the number of molecular formula candidates to a single possibility for the majority of the observed components. For components that had more than one candidate formula (yellow) or did not have a formula candidate (gray), the analyst was able to quickly focus on these components and manually verify the mass spectrum and analysis results. The combination of the JMS-T2000GC with the automatic analysis capabilities of the msFineAnalysis software provides a powerful solution that simplifies the qualitative analysis of complex samples.

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# Development of an Integrated Analysis Method for the JMS-T200GC High Mass-Resolution GC-TOFMS by Electron Ionization and Soft Ionization Methods

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We have developed a new software package with a new workflow for identifying unknown compounds from GC-high resolution MS (GC-HRMS) data. In this newly designed workflow, unknown compounds are determined by correlating the data results obtained by using a hard ionization method such as Electron Ionization (EI) and a soft ionization method such as Field Ionization (FI) with high-resolution mass spectrometry.

The new data reduction software 'msFineAnalysis' was used to identify unknown compounds in the data from pyrolysis/GC-HRMS analysis of vinyl acetate resin. The new workflow implemented in this software improved the accuracy of identification and eliminated misidentification of unknown compounds.

## Introduction

When a sample composed of unknown compounds is analyzed by using GC-MS (gas chromatograph mass spectrometer), the compound peaks separated by the GC are identified by using their corresponding mass spectra. Electron Ionization (EI) is widely used for GC-MS [1] because of the availability of mass spectral databases that contain hundreds of thousands of spectra for compounds that are frequently analyzed by GC-MS. EI mass spectra are typically acquired using the standard ionizing electron energy of 70 eV which produces fragmentation patterns that are directly related to the compound's structure. Additionally, the relative intensity ratios for the fragment peaks are always constant if the ionizing electron energy is kept constant. Consequently, the mass spectrum of the same compound acquired with the same ionization energy, exhibits a reproducible spectral pattern. Mass spectral database searches (commonly called "library searches") utilize this feature of EI for compound identification [2].

While mass spectral library searches are very simple to implement for identifying compounds acquired by GC-MS, this method has the following disadvantages. 1) For compounds having similar structures (in particular for compounds whose elemental compositions of substituents are slightly different from each other), the mass spectra acquired by using EI can be very similar, and therefore, the chemical compounds may not be identified from the library search result. 2) For compounds which are not included in the library search databases (i.e. pyrolyzed products detected by pyrolysis analysis), it is impossible to identify them with a library search. In case 1),

if the molecular ion peaks are found in the mass spectra, it can be possible to determine the elemental composition of the target compound. However, because EI is a high-energy ionization method, the chemical structure of a given compound can fragment extensively, making it difficult, if not impossible, to observe the molecular ions. If a low-resolution mass spectrometer is used for the measurement, even if molecular ions are observed, their mass-to-charge ratios are only reported as integer values. An integer value for the molecular ion  $m/z$  is not sufficient for determining the elemental composition because there are many combinations of elemental masses that can have a specific integer mass. A high-resolution mass spectrometer (HRMS) can provide accurate mass measurements with a precision in the 3<sup>rd</sup> or 4<sup>th</sup> decimal place which in turn allows for more accurate elemental composition assignments. For case 2), identification of chemical compounds that are not present in the databases cannot be obtained by library searches alone so using the HRMS accurate mass information for molecular ions (as well as fragment ions) can help narrow down the possibilities.

In this work, we used the JMS-T200GC AccuTOF™ GCx-plus GC-high resolution time-of-flight MS (GC-HRTOFMS) equipped with both EI and Soft Ionization (SI) to generate molecular ions. We then used the newly developed software application 'msFineAnalysis' to combine the information obtained from the EI library searches with the SI molecular ion accurate mass and isotope analysis to identify the sample components [3, 4]. The details of the msFineAnalysis qualitative analysis work flow will be introduced along with the application of this software to the thermal analysis of resin products.



## Analysis Flow

**Figure 1** shows the qualitative analysis work flow using only library search by the conventional EI method (left) and using the new integrated analysis work flow utilized in the msFineAnalysis software (right). The procedures for the new analysis work flow are as follows:

1. For the data acquired by the EI and SI methods, the peaks in the total ion chromatogram (TIC) are detected to create mass spectra.
2. For the mass spectra acquired by each ionization method, each spectrum is associated with a corresponding chromatographic peak retention time, and then, the mass spectra with the same retention times are assigned as the same component.
3. The EI mass spectra are library searched for matches. ①
4. The SI mass spectra are used to determine the molecular ions for each analyte. ②
5. An accurate mass analysis is done for each of the detected molecular ions. This analysis involves directly comparing the possible elemental composition formulas to the statistically-significant EI library search results from Step 3 in order to narrow down the most likely elemental composition candidates for a given analyte. ③
6. An isotope pattern analysis is conducted to further refine the molecular ion elemental composition candidates. ④
7. Using these possible molecular ion composition formulas as the search constraints, an accurate mass analysis is performed for the fragment ions in the EI mass spectra. If a given molecular ion formula is not correct, then the EI fragment ions will not show good matches and will result in a low EI fragment ion interpretation ratio.
8. The interpretation ratio is used to further refine the molecular-ion formula candidates. ⑤
9. Finally, all of these analysis results are integrated together into a qualitative analysis report for the peaks detected in the sample. ⑥

## Analysis Examples: Pyrolysis data analysis of vinyl acetate resin

### (1) Analytical Condition

A JMS-T200GC equipped with a pyrolyzer was used to measure a commercially-available vinyl acetate resin. A combination EI and Field Ionization (FI) source was used with the system to measure the samples. The measurement conditions for the GC-HRTOFMS and pyrolyzer are listed in **Table 1**. Since an EI/FI combination ion source was used for this work, it was not necessary to exchange sources when switching between the EI and FI methods.

The EI and FI sample measurements were subjected to the new msFineAnalysis work flow. Afterwards, these analysis results were compared to an analysis with only EI library search results to confirm the improved capabilities of this new, innovative analysis work flow.

### (2) Analysis Results

The EI and SI total ion current chromatograms (TICCs) for the resin sample were automatically analyzed by msFineAnalysis using the analysis work flow shown in Fig. 1. In total, 33 components were detected during the sample measurement (**Fig. 2**). Each component was categorized according to the reliability of its identification results. The three classification types are shown as different colors in the report (**Fig. 3**).

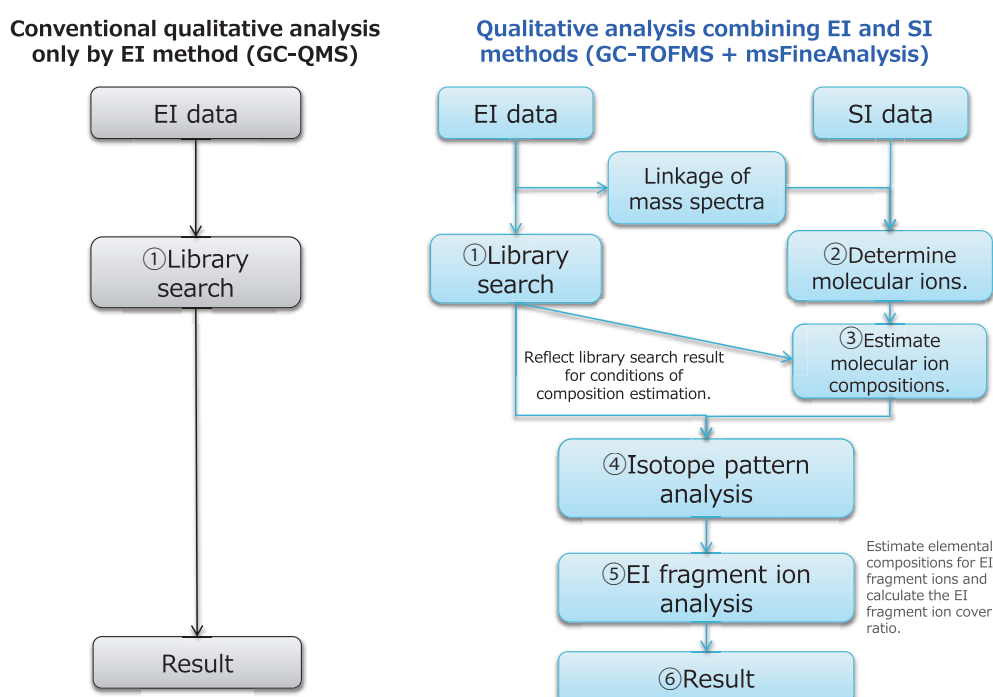
Green: EI search result had high similarity score and matched the identified SI molecular ion. High probability that the analyte has been identified correctly.

Orange: Multiple candidates with significant molecular elemental composition formulas were obtained.

White: No significant molecular composition formula was obtained.

A comparison between the integrated analysis results acquired by msFineAnalysis and the conventional GC/EI analysis

**Fig. 1 Analysis flow comparison with conventional GC-MS qualitative analysis**



results are shown in **Fig. 4**. Conventional EI data analysis only resulted in the high-confidence identification of one-fourth of the components. However, the new msFineAnalysis work flow, which also included molecular ion formula estimation and isotopic analysis, enabled the determination of more than 90% of the components. Furthermore, the new software used the EI fragment ion formulas to obtain additional structural information for the analytes. For the library-registered components (similarity: high), the new analysis method showed highly reliable qualitative analysis results that involved combining the library search results and the molecular composition formulas. Even for unknown components that do not show a good library match (similarity: low) and are thus difficult to identify by using the conventional GC/EI method (left in Fig. 1), msFineAnalysis also estimated the molecular composition formulas obtained with soft ionization. Consequently, the new analysis method, irrespective of high or low similarity, uses the accurate mass

molecular ion information to estimate elemental compositions that can further refine the candidate identification. Furthermore, these results showed that msFineAnalysis provides a very effective work flow for the qualitative analysis of GC-MS data.

To demonstrate the details of the new analysis method, we will present two kinds of identification examples that are typical for qualitative analysis.

### (3) Example 1: Peaks detected at a retention time around 2.49 min

Mass spectra acquired by EI and FI are shown in **Fig. 5**. A library search of the EI mass spectra resulted in several matches. However, all of the matching spectra had similarity scores of less than 700, indicating that there is a low probability that the related peaks correspond to these compounds. On the other hand, the SI mass spectra showed clear peaks at  $m/z$  106.06 and  $m/z$  128.12. The  $m/z$  128.12 (larger  $m/z$ ) was selected as the

**Table 1 Measurement Condition**

[Pyrolysis condition] Pyrolysis Temperature	600 °C
[GC Condition] Column Oven Temperature Injection Mode	DB-5msUI, 15 m × 0.25 mm, 0.25 μm 50 °C (1 min) - 30 °C /min - 330 °C (1.7 min) Split mode (100:1)
[MS condition] Spectrometer Ion Source Ionization	JMS-T200GC (JEOL Ltd.) EI/FI combination ion source EI+ : 70 eV, 300 μA FI+ : -10 kV, 6 mA/10 msec, Carbotec emitter

**Fig. 2 Total Ion current chromatograms for Py-GC/TOFMS analysis of vinyl acetate sample**

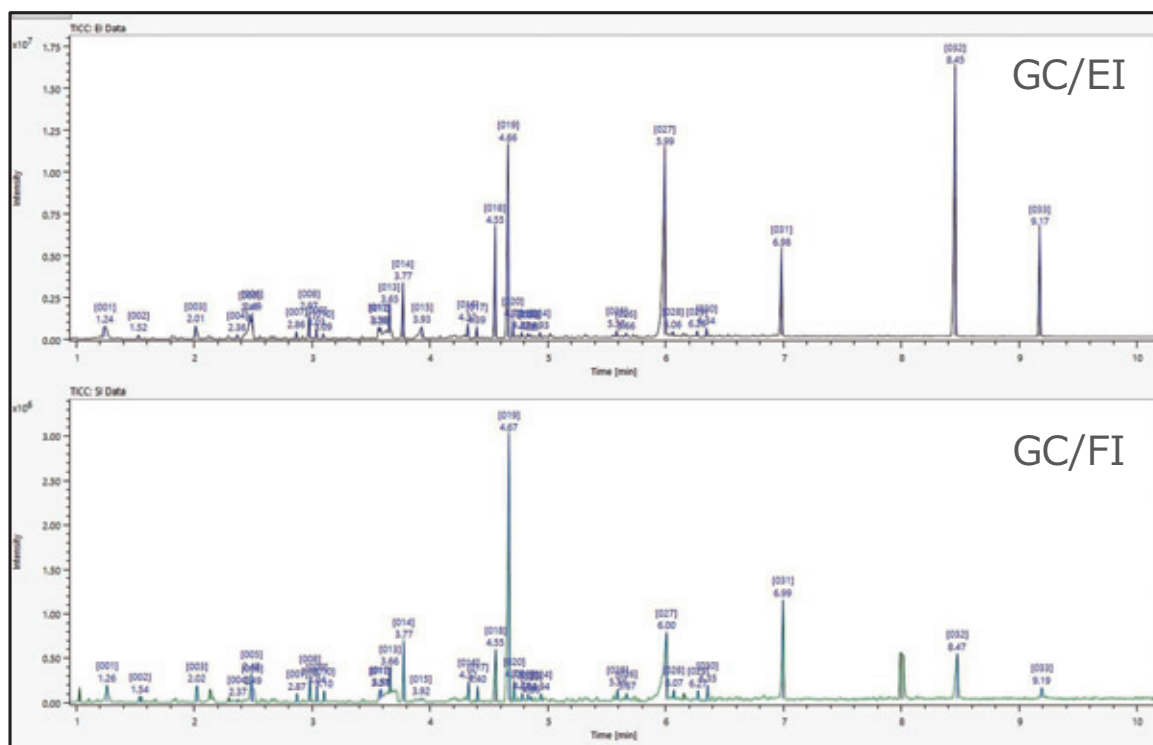


Fig. 3 Data analysis results of vinyl acetate sample by msFineAnalysis software

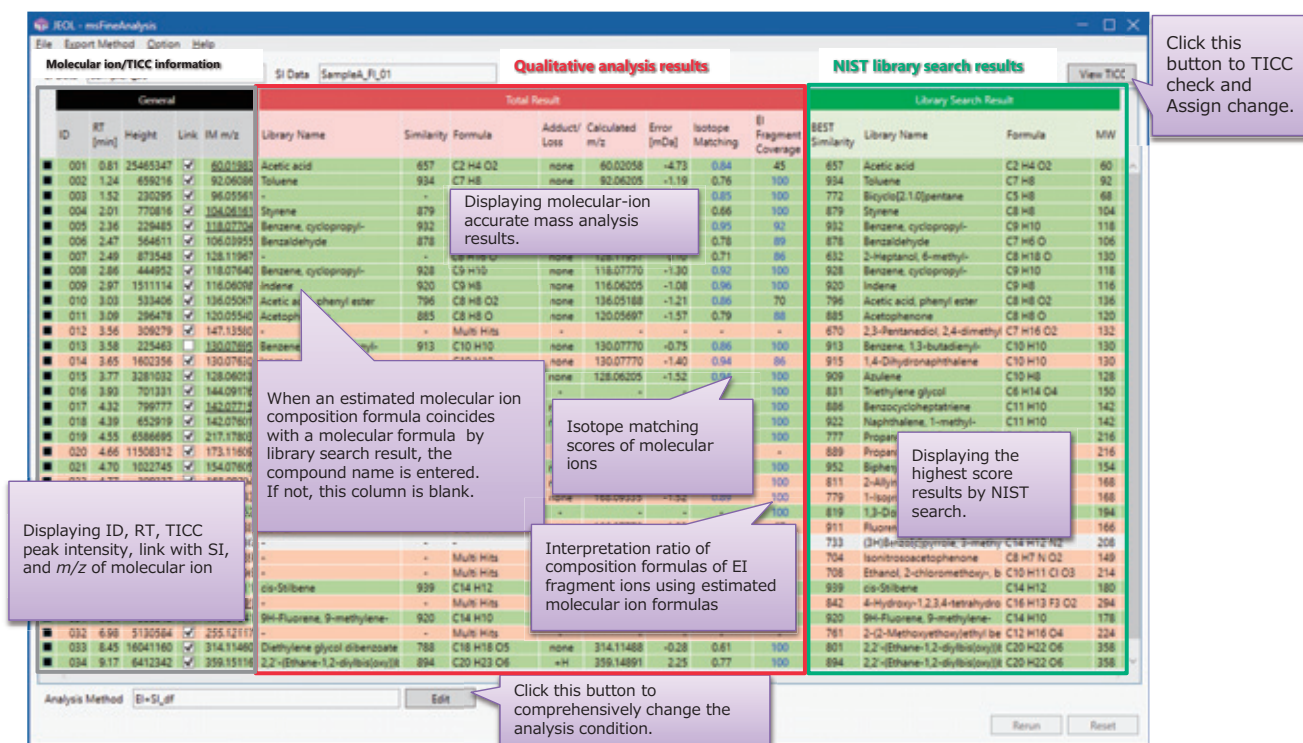
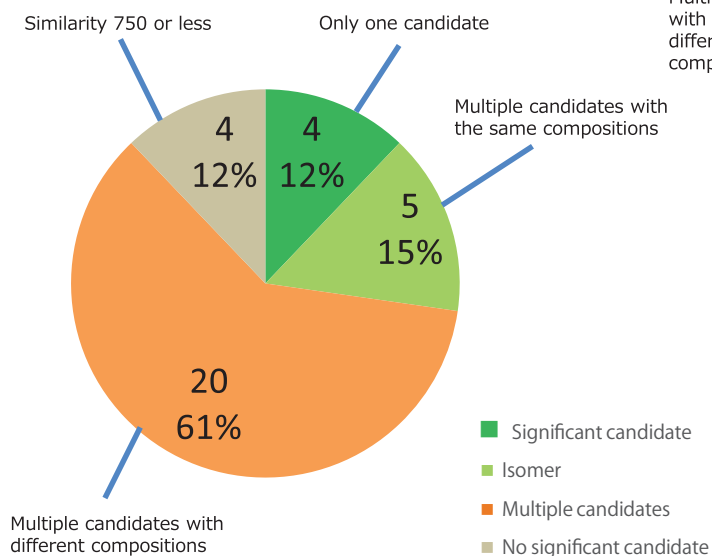
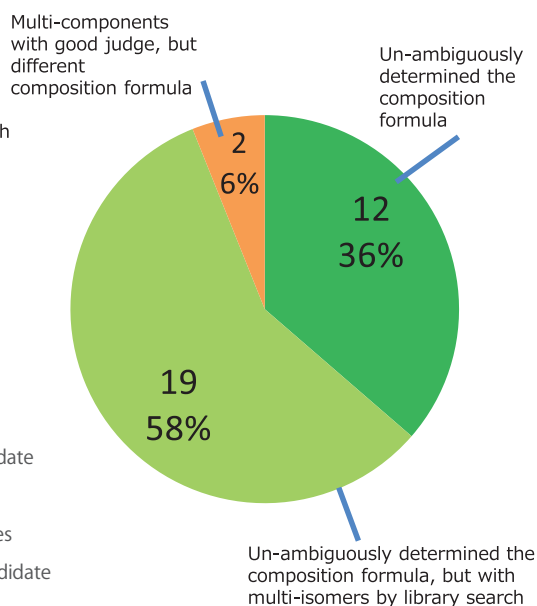


Fig. 4 Comparison of number of peaks that were identified between conventional data analysis flow and new work flow with msFineAnalysis software

**Conventional GC-MS qualitative analysis**  
(by NIST library search, similarity threshold : 750)



**Integrated analysis of EI and SI methods**  
(by msFineAnalysis, able/disable to determine composition)





molecular ion peak, and its accurate mass was used to estimate an elemental composition of  $C_8H_{15}O$  (error 0.1 mDa). Next, this composition " $C_8H_{15}O$ " was used as the element limits to estimate the fragment ion formulas in the EI mass spectrum. The results showed that 6 out of the 7 higher intensity peaks were likely a product of the " $C_8H_{16}O$ " elemental composition. These results also suggested that 1 of the 7 peaks may not be a peak derived from  $C_8H_{16}O$ . To explore this possibility, extracted ion current chromatograms (EICC) for both peak types ( $C_8H_{16}O$ :  $m/z$  55.05, 97.10 and non- $C_8H_{16}O$ :  $m/z$  75.04) were created, and the results showed that there was a clear difference in the chromatographic peak shapes/times in each chromatogram (Fig. 6). These results suggested that ion peaks produced by different chemical species were co-eluting at a retention time of ~2.49 min. To test this hypothesis, a library search was conducted using only a mass spectrum produced from the latter part of the peak at 2.49 min, so as to exclude as much as possible the contribution from the co-eluted components. The search came up with "3-Penten-1-ol, 2,2,4-trimethyl- :  $C_8H_{16}O$ " with a similarity of over 800. Furthermore, the composition for this compound exactly matched the initially-estimated elemental composition of  $C_8H_{16}O$ .

The peak at 2.49 min analyzed by using the conventional GC/EI method (only library search of the EI mass spectra) did not provide enough information to narrow down the candidate compounds. However, the msFineAnalysis work flow using the combined EI and FI mass spectral information resulted in a single, strongly supported candidate "3-Penten-1-ol, 2,2,4-trimethyl-".

#### (4) Example 2: Peaks detected at a retention time around 8.15 min

Mass spectra acquired by EI and FI are shown in Fig. 7. A library search of the EI mass spectrum revealed one compound with a similarity of 801 (2,2'-(Ethane-1,2-diylbis(oxy)) bis(ethane-2,1-diyl) dibenzoate) along with 7 other compounds

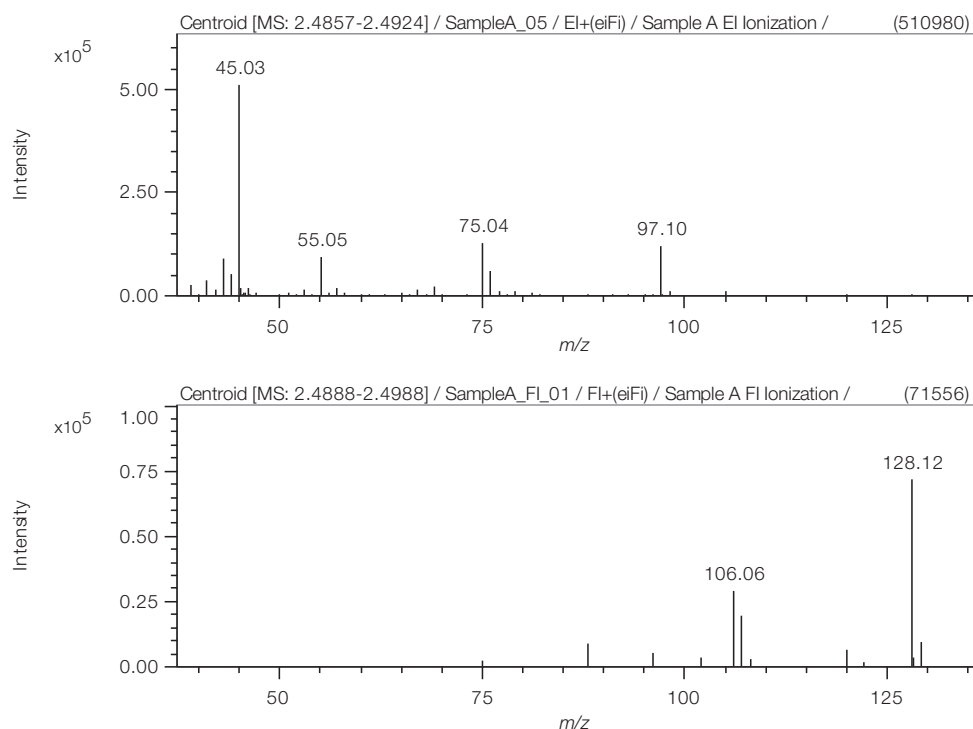
with similarities of more than 750 (shown on Table 2). Consequently, it was difficult to make an unambiguous identification using only the library search results. The SI mass spectra showed a clear peak appearing at  $m/z$  315.12, suggesting that this peak is likely to be the molecular ion. Table 3 shows the possible elemental composition formulas calculated using the accurate mass of this peak. All four compositions had calculated values that were within 3 mDa of the measured value. Next, a comparison of Table 2 and Table 3 showed that "Diethylene glycol dibenzoate" (similarity of 788) had an elemental composition that matched  $C_{18}H_{18}O_5$ . Next, this composition " $C_{18}H_{18}O_5$ " was used as the element limits to estimate the fragment ion formulas for 5 high intensity peaks in the EI mass spectrum. All of the peaks produced elemental compositions (errors less than 3 mDa) consistent this compound (Table 4). These results all strongly support "Diethylene glycol dibenzoate" as the peak detected at retention time ~8.45 min.

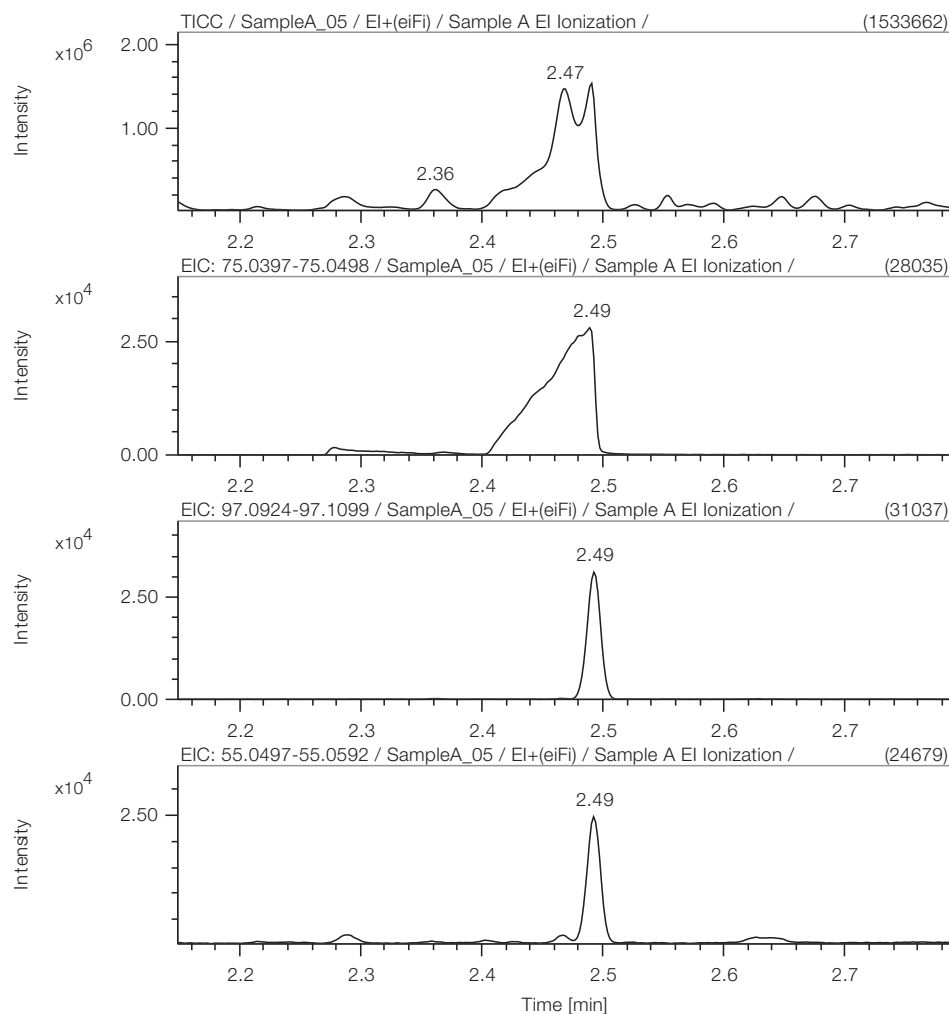
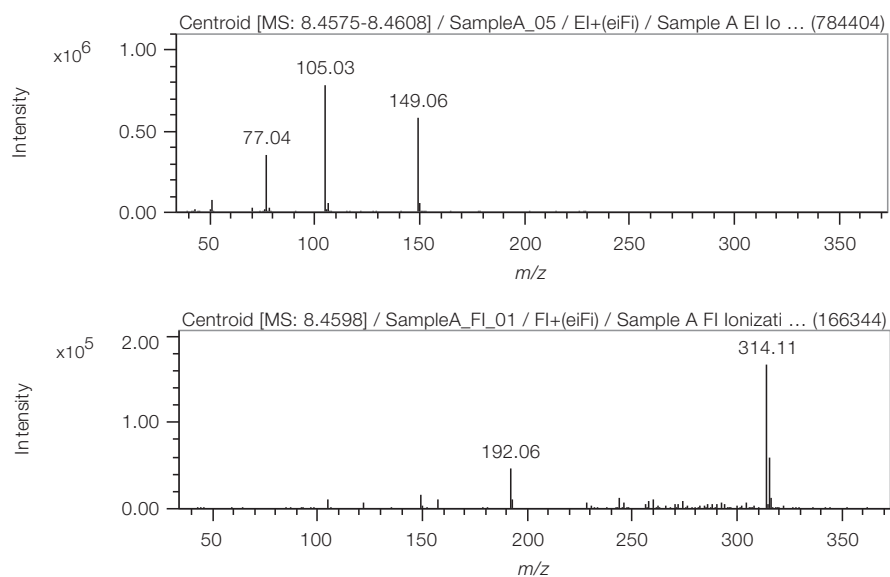
As described above, the peak detected at a retention time around 8.45 min was difficult to identify through an EI library search result alone, as there were a number of possible candidates with close similarity matches. However, the msFineAnalysis software, with its ability to combine EI and SI data analysis, resulted in a single, strongly supported candidate "Diethylene glycol dibenzoate".

### Summary

For the analysis of unknown compounds using GC-TOFMS with high-mass resolution, a new analytical work flow was devised that combined conventional EI library search, molecular ion elemental compositions acquired using a SI method (FI for this work), and the EI fragment ion accurate mass information to identify the targeted chemical species. This innovative analysis work flow led to the development of the new GC-HRMS analysis software msFineAnalysis.

**Fig. 5 Mass spectra at around retention time 2.49 min measured by EI and FI**



**Fig. 6 TICC and EICC at around retention time 2.49 min****Fig. 7 Mass spectra at around retention time 8.45 min measured by EI and FI**

**Table 2 Results of library search for the mass spectrum of peak at 8.45 min retention time**

No	Compound Name	Similarity	Formula
1	2, 2'-(Ethane-1, 2-diylbis(oxy))bis(ethane-2, 1-diyl) dibenzoate	801	C <sub>20</sub> H <sub>22</sub> O <sub>6</sub>
2	Diethylene glycol dibenzoate	788	C <sub>18</sub> H <sub>18</sub> O <sub>5</sub>
3	1, 3-Dioxolane, 2-(methoxymethyl)-2-phenyl-	787	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>
4	Benzoic acid, 2-(3-nitrophenyl)ethyl ester	778	C <sub>15</sub> H <sub>13</sub> NO <sub>4</sub>
5	Benzoic acid, 2-(4-nitrophenoxy)ethyl ester	776	C <sub>16</sub> H <sub>13</sub> NO <sub>5</sub>
6	3, 6, 9, 12-Tetraoxatetradecane-1, 14-diyl dibenzoate	764	C <sub>24</sub> H <sub>30</sub> O <sub>8</sub>
7	Ethanol, 2-(4-phenoxyphenoxy)-, benzoate	752	C <sub>21</sub> H <sub>18</sub> O <sub>4</sub>
8	1, 3-Dioxolane, 2-phenyl-2-(phenylmethyl)-	750	C <sub>16</sub> H <sub>16</sub> O <sub>2</sub>
9	Benzoic acid, 2-(2-chlorophenoxy)ethyl ester	730	C <sub>15</sub> H <sub>13</sub> ClO <sub>3</sub>
10	3, 4-Pyridinedicarboxylic anhydride	703	C <sub>7</sub> H <sub>3</sub> NO <sub>3</sub>

**Table 3 Results of estimation of elemental composition for the MS peak of 314.11462**

Formula	Calculated <i>m/z</i>	Error/mDa
C <sub>18</sub> H <sub>18</sub> O <sub>5</sub>	314.11488	-0.26
C <sub>16</sub> H <sub>16</sub> N <sub>3</sub> O <sub>4</sub>	314.11353	1.09
C <sub>19</sub> H <sub>14</sub> N <sub>4</sub> O	314.11621	-1.59
C <sub>21</sub> H <sub>16</sub> NO <sub>2</sub>	314.11756	-2.94
C <sub>13</sub> H <sub>18</sub> N <sub>2</sub> O <sub>7</sub>	314.11085	3.77

**Table 4 The results of estimation of elemental compositions for the peaks in mass spectrum at 8.45 min peak**

<i>m/z</i> of peak	Formula	Error/mDa
51.02244	C <sub>4</sub> H <sub>3</sub>	-0.48
77.03809	C <sub>6</sub> H <sub>5</sub>	-0.49
105.03439	H <sub>7</sub> H <sub>5</sub> O	0.9
105.08898	C <sub>5</sub> H <sub>13</sub> O <sub>2</sub>	-2.02
149.05995	C <sub>9</sub> H <sub>9</sub> O <sub>2</sub>	0.25

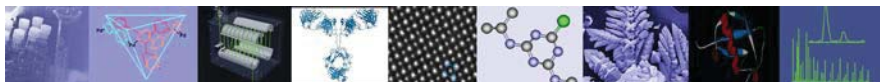
Using this software for library-registered compounds (similarity: high), it is possible to provide highly reliable qualitative analysis results that combine the EI library search results with the SI molecular ion elemental composition results. Furthermore, the msFineAnalysis software made it possible to estimate the molecular ion elemental composition as well as the fragment ion elemental compositions for unknown compounds that do not show a good library match (similarity: low). These results provided a stronger foundation for identifying unknowns than using the conventional EI with library search method alone.

Irrespective of high or low similarity, the new analysis method enables the estimation of molecular composition formulas and to refine candidates for identification. Thus, msFineAnalysis is very effective for qualitative analysis of GC-HRMS (JMS-T200GC) data.

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# AccuTOF-GCx Series

## Comparison of performance between PI and FI by using GC-HRTOFMS

### Introduction

Electron ionization (EI) is a common ionization technique for gas chromatography/mass spectrometry (GC/MS). However, EI often does not produce strong molecular ions ( $M^{+}$ ) because the excess energy generates fragment ions during the ionization process.

The detection of the molecular ion is very important for confirming the molecular weight of the target compounds. Therefore, a soft ionization technique is often necessary to determine the molecular weight information.

Field ionization (FI) is well known as one of the softest ionization techniques commercially available. Similarly, photoionization (PI) can produce molecular ions. In this application note, the characteristics of PI and FI were investigated by using various compounds. Furthermore, the performance between EI, FI and PI for these compounds in diesel fuel were investigated.

### Experiment

All samples were analyzed by using JMS-T100GCV (JEOL Ltd.) with the optionally available EI/FI combination ion source and PI ion source. EI data was acquired by using the standard 70eV ionization energy with the EI/FI combination source. FI data was acquired by using a 5 $\mu$ m carbon emitter (Carbotec Analytik) with the combination EI/FI source. A deuterium lamp with a magnesium fluoride window (Hamamatsu Photonics K.K.) was used as the PI source. This lamp has an irradiation wavelength range from 115 to 400 nm (equivalent to the energy range from 3.1 to 10.7 eV) in which the maximum radiation intensity is at 160 nm (7.7 eV). And finally, the EI, FI and PI measurements were done with the same detector voltage so that the peak intensities could be directly compared for each ionization method.

Table 1. Measurement Conditions

Instrument	JMS-T100GCV "AccuTOF GCv 4G" (JEOL Ltd.)
Inlet temp.	280°C
Injection mode	Standard reagents : Split 30:1 Diesel fuel : Split 100:1
Column	ZB-5MSi, 30 m x 0.25 mm, film thickness 0.25 $\mu$ m
Oven temp. program	50°C (1 min) => 10°C /min => 320°C (10min)
Carrier gas	He (Constant flow : 1.0 mL/min)
Sample volume	Standard reagents : 1 $\mu$ L Diesel fuel : 0.1 $\mu$ L
Ionization mode	EI(+) : 70 eV, 300 $\mu$ A PI(+) : D <sub>2</sub> lamp (Hamamatsu Photonics K.K.) FI(+) : -10 kV, 0 mA ; Baked at 8 mA (20 msec) after recording interval
Transfer line temp.	270°C
Chamber temp.	EI : 300°C, FI and PI : 100°C
m/z range	35-800
Data acquisition interval	0.5 sec

## Results

- All compounds produced molecular ions by FI.
- Several compounds produced very low intensity molecular ions by PI.
- Aromatic compounds such as 2,6- dimethyl phenol produced high intensity molecular ions by PI.
- *n*-Octanol produced fragment ions by both PI and FI. These fragment ions were different from the EI fragment ions.
- EI did not show a molecular ion for *n*-octanol.

Various *n*-alkanes and aromatic compounds were detected in the diesel fuel (Fig.2 and Fig.3). The TICC in Figure 2 for EI, FI and PI show the *n*-alkanes as the highest intensity peaks (blue circles) observed in the diesel fuel. Additionally, the average FI mass spectrum in Figure 3 shows high intensity molecular ions for the *n*-alkanes.

However, the average PI mass spectrum showed higher relative intensity molecular ions for the aromatic compounds than for the *n*-alkanes. Even so, more fragmentation was observed in the average PI mass spectrum relative to the average FI mass spectrum. The average EI mass spectrum for the diesel fuel was dominated by hydrocarbon fragments in the low mass region.

## Conclusion

FI showed strong molecular ions for all compounds measured in this application. PI also showed molecular ions but also produced more fragment ions relative to FI. Also, PI is sensitive for the measurement of aromatic compounds, making it particularly useful for looking at polycyclic aromatics. This application note confirms that PI and FI are soft ionization techniques that can be used to complement the EI results.

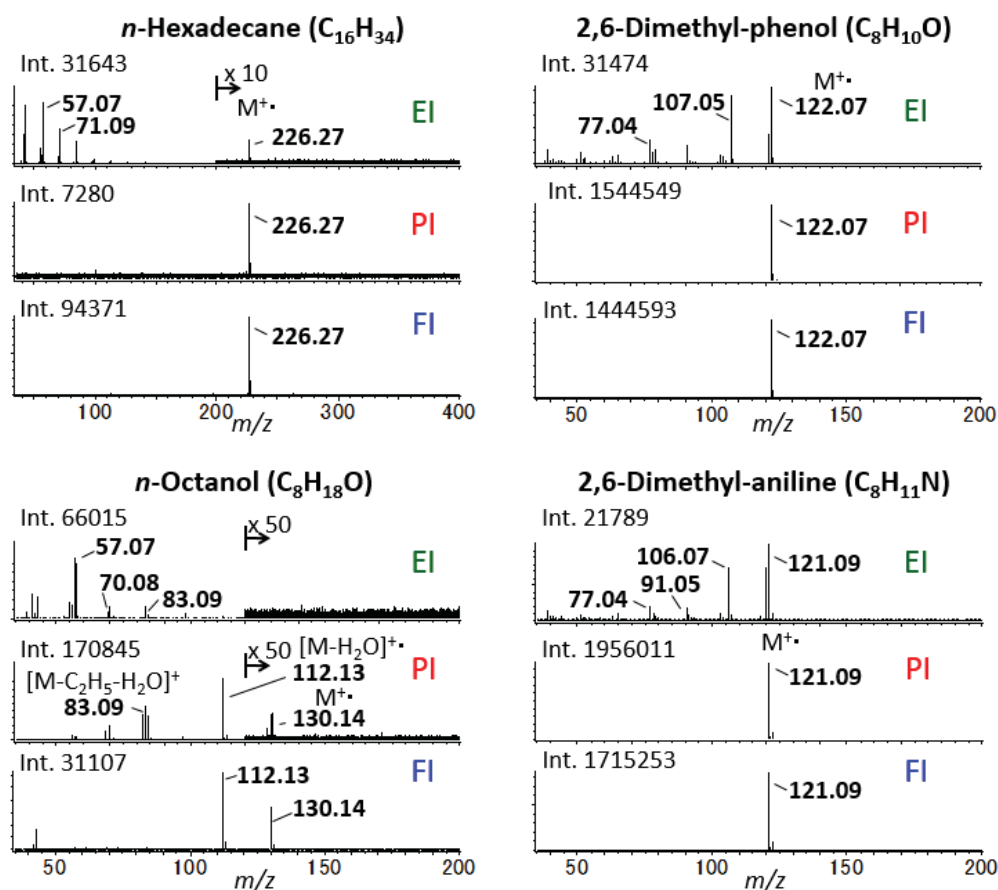


Fig. 1. Compared mass spectra by EI (top), PI (middle) and FI (bottom)

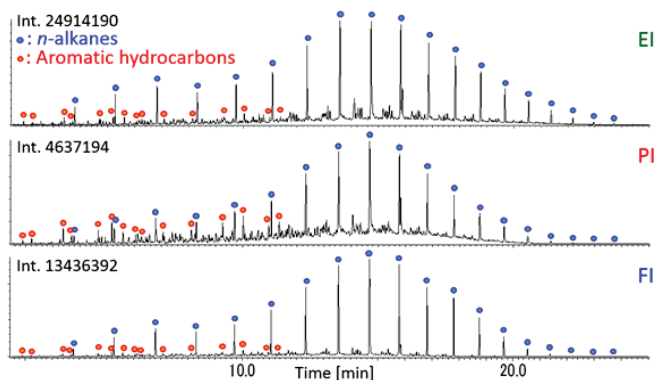
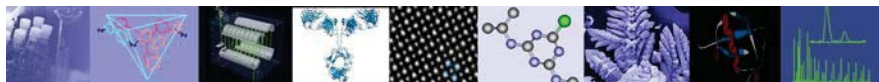


Table 2. Comparison of the molecular-ion detection by FI and PI

F.I. : Fragment ion

Compounds name	FI		SPI	
	Sensitivity	F.I.	Sensitivity	F.I.
<i>n</i> -Hexadecane	++	+	+	+
Naphthalene	+	+	++	+
<i>n</i> -Octanol	++	-	+	--
2,6-Dimethyl phenol	+	+	++	+
2-Octanone	++	-	+	-
Benzophenone	++	+	+	+
2,6-Dimethyl aniline	+	+	++	+
Methyl stearate	++	+	+	+

Fig.2. TICC chromatograms of diesel fuel

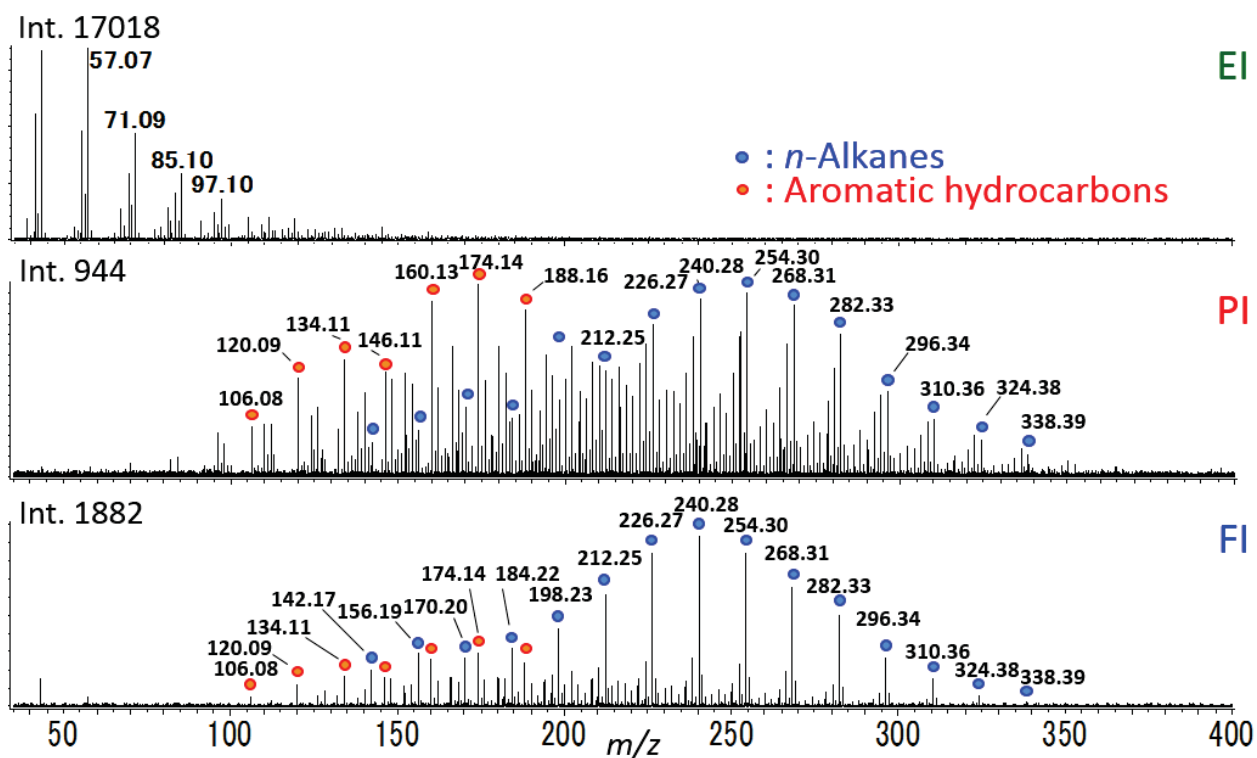
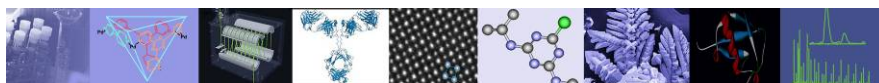


Fig.3. Average mass spectra of diesel fuel







# AccuTOF-GCv Series

## High-speed 50 Hz Data Acquisition Capability for Comprehensive 2-dimensional GC Measurements

### Introduction

The comprehensive 2-dimensional GC (GC x GC) technique provides higher-separation capabilities for complex mixtures than the typical 1-dimensional GC measurements. However, the GC x GC technique requires high speed data acquisition, e. g. > 20 Hz, for the GC detectors due to the shorter 2<sup>nd</sup> GC column which elutes samples within just a few seconds (comparable to those used for the ultra-fast GC measurements).

Recently, JEOL has developed a new generation GC-HRTOFMS system called the “AccuTOF GCv 4G”. The AccuTOF GCv 4G has high sensitivity, high resolution, high mass accuracy and high speed data acquisition, all simultaneously. In fact, this instrument can measure data using up to a 50 Hz data acquisition speed which is more than sufficient to do not only fast GC measurements but also GC x GC measurements.

In this work, we measured diesel fuel and crude oil using the GC x GC technique with the 50 Hz data acquisition speed available on the AccuTOF GCv 4G.

### Experimental

Sample information and measurement condition are shown in Table 1.

### Results

To start, the sensitivity for the GCxGC/HR-TOFMS system was tested by measuring 1pg of octafluoronaphthalene (OFN). The signal to noise ratio (S/N) for this sample was checked with both the modulator OFF and then ON. These results confirmed that the GCxGC column condition and modulator were working well. The OFN mass chromatograms for each scenario are shown in Figure 1.

The S/N values for the 1pg OFN sample were over 100 for both modulator statuses. These results clearly showed high sensitivity even when the high speed 50 Hz acquisition capability is used. Additionally, 2-dimensional and 3-dimensional mass chromatograms were constructed for the OFN sample, and then the data was analyzed by using both a NIST library search and the accurate mass measurements for the sample (Figure 2).

Condition	System check	Oil application
Sample	OFN	Diesel Fuel, Crude Oil
Concentration	1 pg/uL (Hexane)	1/100 (Hexane)
GCxGC system	ZX2 thermal modulator (ZOEX)	
1st column	Rxi-5SiMS, 30 m x 0.25 mm, 0.25 um	
2nd column	Rxi-17SiMS, 2 m x 0.15 mm, 0.15 um	
Modulator	Deactivated fused silica, 1.5 m x 0.15 mm	
Modulator period	6 sec	8 sec
Modulator duration	400 msec	
Hot jet temp.	270 C	
Hot jet gas pressure	40 psi	
Cold jet flow	18 L/min	
Inlet pressure	200 kPa (Out flow: 2mL/min)	
Inlet mode	Splitless	Split 10:1
Oven temp.	50 C(1min) -> 3 C/min -> 300 C(6min)	
GC-HRTOFMS system	AccuTOF GCv 4G (JEOL)	
Ion source	EI standard (High sensitivity)	EI/FI/FD combination
Ionization mode	EI+ (70 eV, 300 uA)	
m/z range	m/z 35-500	
Acquisition speed	50 Hz	

Table 1. Measurement Condition.

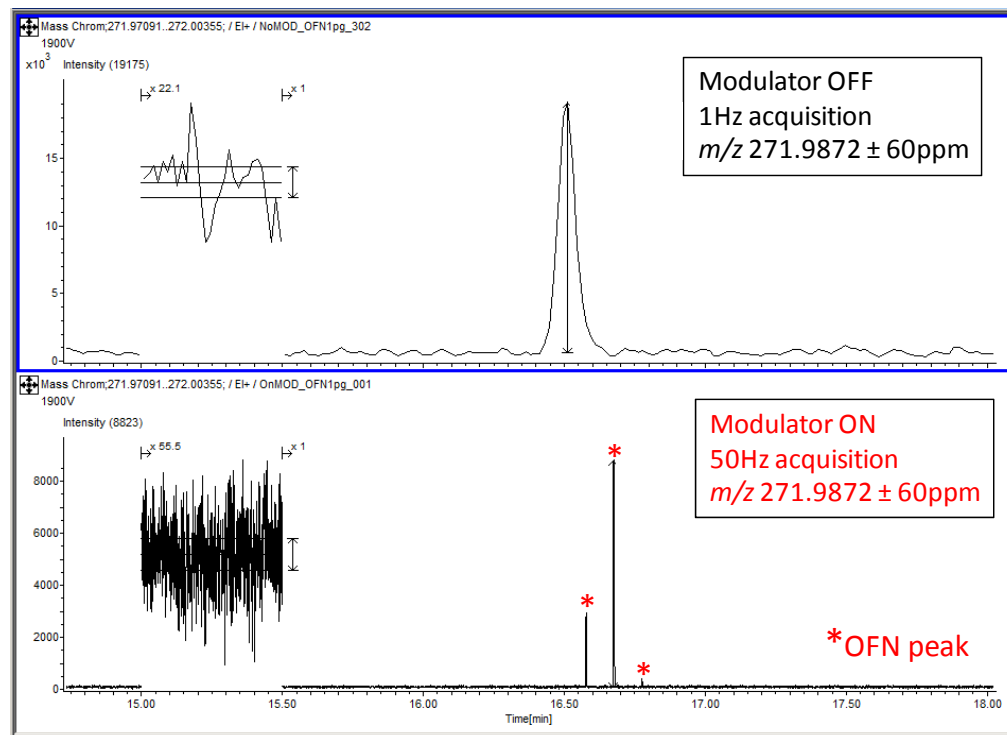


Figure 1. Mass chromatograms of OFN 1pg, Raw data, Mass windows:  $m/z$  271.9872 ± 60ppm  
Upper: modulator OFF, 1 Hz acquisition,  
Lower: modulator ON, 50 Hz acquisition

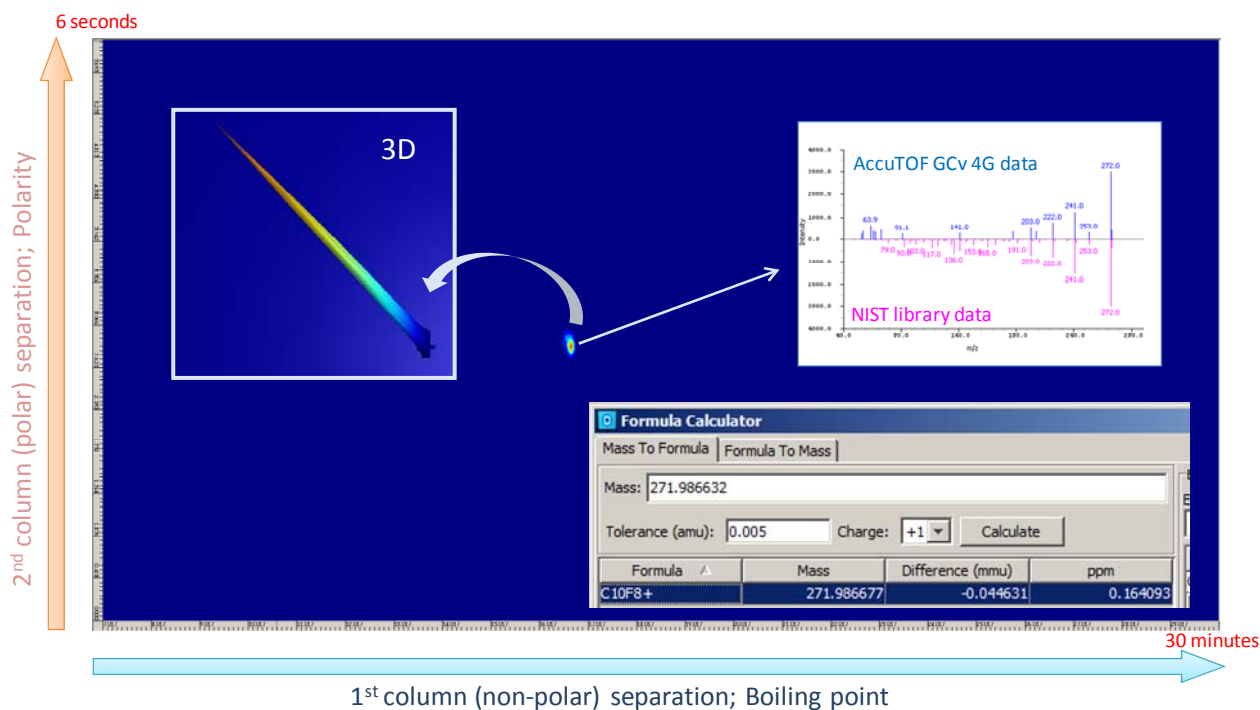


Figure 2. 2-dimensional and 3-dimensional mass chromatograms, library search result and accurate mass measurement results using the OFN 1pg data.

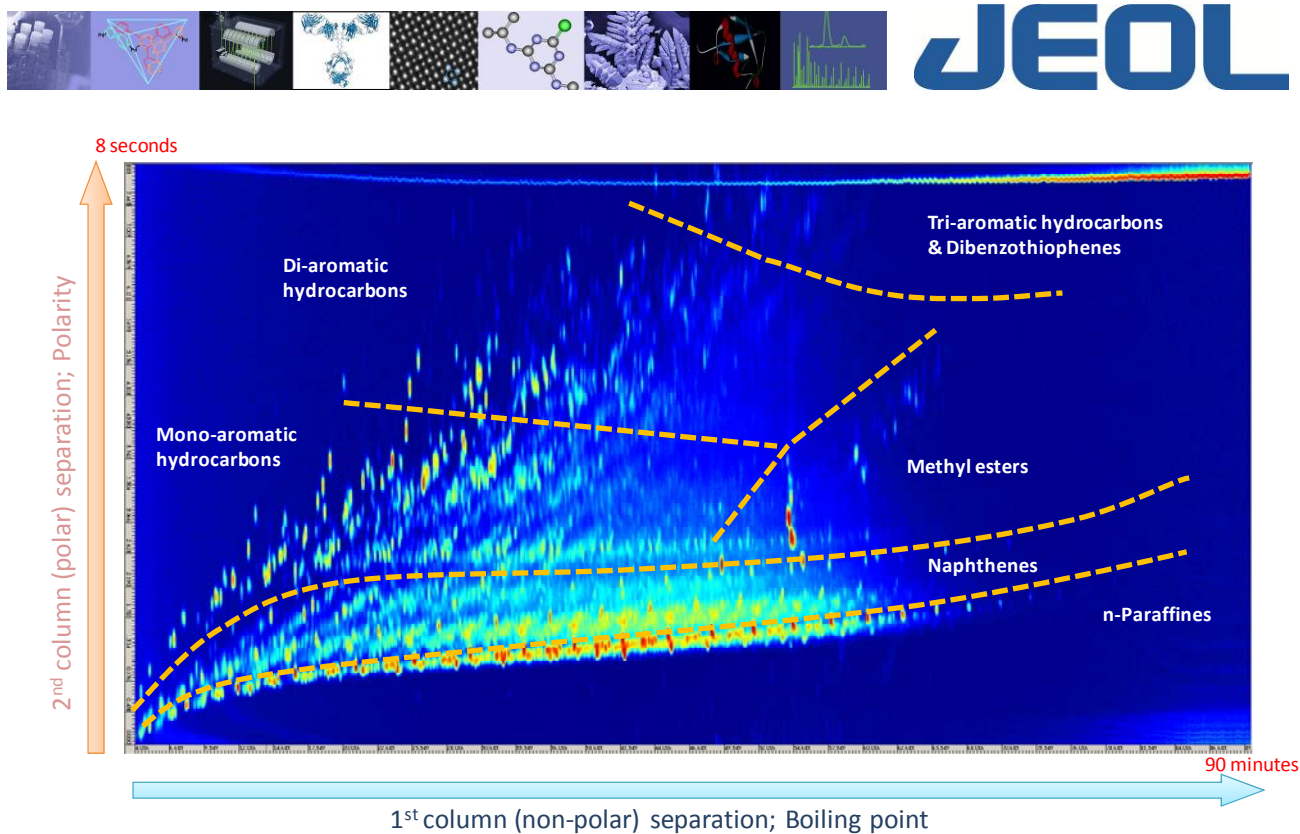


Figure 3. 2-dimensional TIC chromatogram for diesel fuel (50 Hz data acquisition).

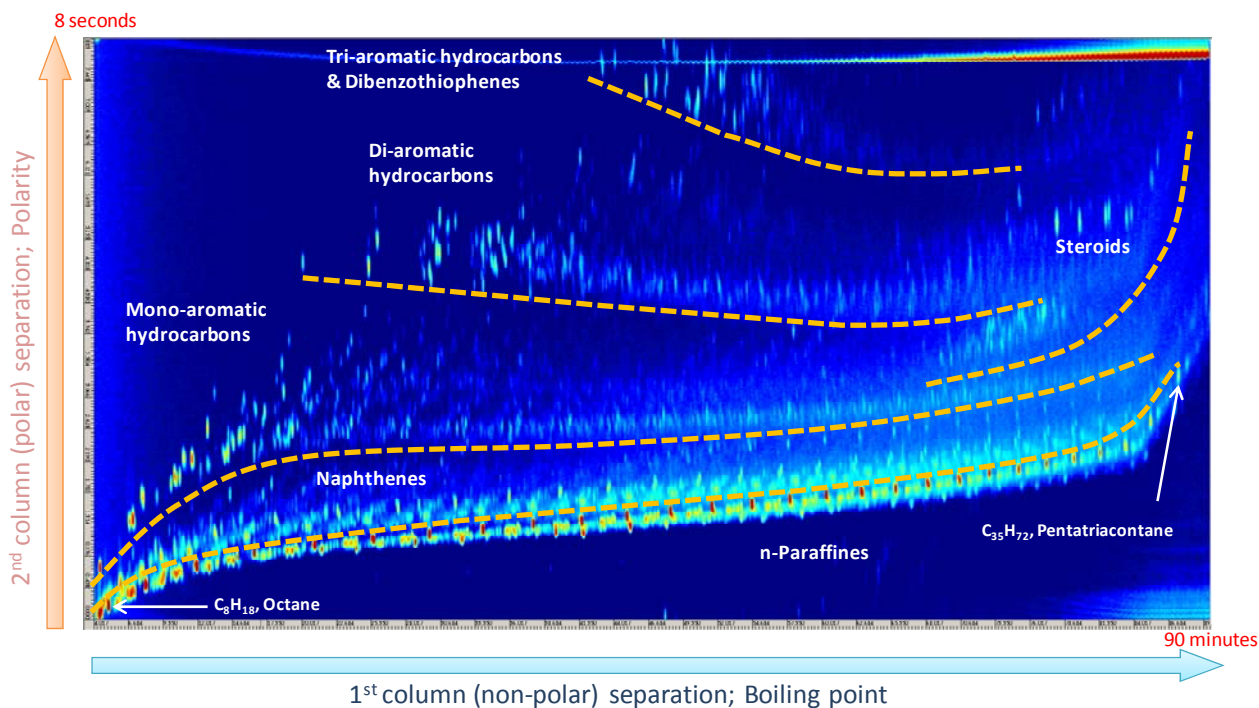


Figure 4. 2-dimensional TIC chromatogram for crude oil (50 Hz data acquisition).

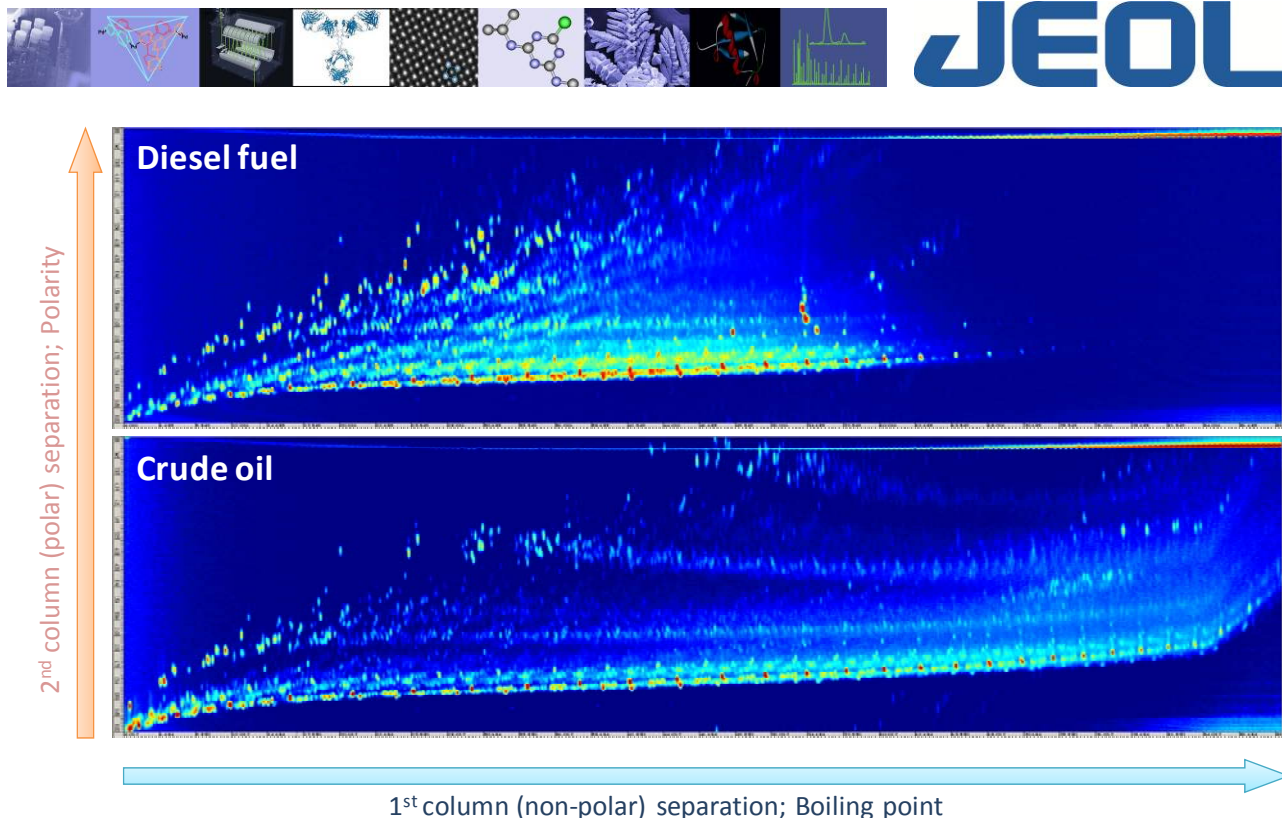


Figure 5. Comparing the 2-dimensional TIC chromatograms for diesel fuel and crude oil.

The data showed good spectral matching to the NIST data for OFN (also shown in Figure 2). Additionally, the mass accuracy obtained for the measurement was less than 1 mDa for the molecular ion ( $C_{10}F_8^+$ ,  $m/z$  271.9872) using an external one-point calibration for a GC column background ion ( $m/z$  207.0329). These results clearly show that the AccuTOF GCv 4G is a powerful tool for the qualitative analyses of samples using the NIST library search and the accurate mass measurements for GC x GC data.

Next, the diesel fuel and crude oil samples were analyzed using similar GC x GC conditions (See Table 1). The GC x GC results showed a large number of chromatographic peaks present in the TICs for both samples (Figure 3 and 4). Each analysis showed good peak shapes and good peak separations as a result of the 50 Hz acquisition capability of the AccuTOF-GCv 4G. Further inspection of the mass spectral data

allowed us to denote where the major hydrocarbon compound groups are located in the 2D plots, as labeled in Figures 3 and 4. Figure 5 shows a comparison between the GC x GC chromatograms, which visually highlights the qualitative differences between each sample.

### Conclusion

In this work, we showed the 50 Hz acquisition capability of the AccuTOF-GCv 4G for GC x GC measurements. This system can provide high sensitivity, high resolution, high mass accuracy and high speed data acquisition measurements, all simultaneously. Additionally, the GC x GC/EI measurements showed very good sensitivity that was on the order of a few picograms. Furthermore, these results showed that the AccuTOF GCv 4G is a powerful tool for the qualitative analyses of samples using the NIST library search and the accurate mass measurements, even when using an external one-point calibration, for GC x GC data.




**JEOL**

## AccuTOF-GCv Series

### The Qualitative Analysis of an Antioxidant Additive Using the Full Capabilities of the EI/FI/FD Combination Ion Source

#### Introduction

JEOL has developed a unique EI/FI/FD combination ion source for the “AccuTOF GCv 4G”, a high-resolution GC-time-of-flight (TOF) MS system. This unique ion source provides the capabilities of GC/EI, GC/FI and FD measurements without having to break vacuum in order to switch between each ionization mode. Additionally, this combination is particularly powerful in that it provides library searchable fragmentation information by using EI and high mass accuracy molecular ion information by using FI and FD. In this work, we measured an antioxidant additive by using each ionization mode available on the AccuTOF GCv 4G combination ion source (EI/FI/FD).

#### Experimental

Sample information and measurement condition are shown in Table 1.

#### Results

The GC/EI and GC/FI total ion chromatograms (TICs) for the antioxidant sample are shown in Figure 1. Both chromatograms showed the presence of 8 components in the sample. The corresponding EI and FI mass spectra for each component are shown in Figure 2 and Figure 3.

The FI mass spectra for each of the 8 components showed very simple mass spectra that were dominated by their molecular ions. Additionally, the exact masses measured for these compounds showed that there were several isomers present in the antioxidant additive—(A) one at  $m/z$  225, (B) three at  $m/z$  281, (C) two at  $m/z$  337, and (D) two at 393. The accurate mass and calculated elemental composition results are shown in Table 2. The ions generally showed good mass accuracy with less than 1 mDa for both EI and FI mode.

Condition	Measurement		
	GC/EI	GC/FI	FD
Sample	Antioxidant additive		
Concentration	100 ng/uL		10 ug/uL
GC-TOFMS system	AccuTOF GCv 4G (JEOL)		
Ion source	EI/FI/FD combination ion source		
Ionization mode	EI+	FI+	FD+
Ionization condition	70 eV, 300 uA	-10 kV, 45 mA (30 msec refresh between every stored spectrum)	-10 kV, 0 mA → 51.2 mA/min → 45mA
$m/z$ range	$m/z$ 35–800		$m/z$ 35–1600
GC column	DB-5ms, 30 m x 0.25 mm, 1.0 um		
Inlet mode	Splitless		
Oven temp.	35 C(2min) → 10 C/min → 300 C(22 min)		

Table 1. Measurement condition.

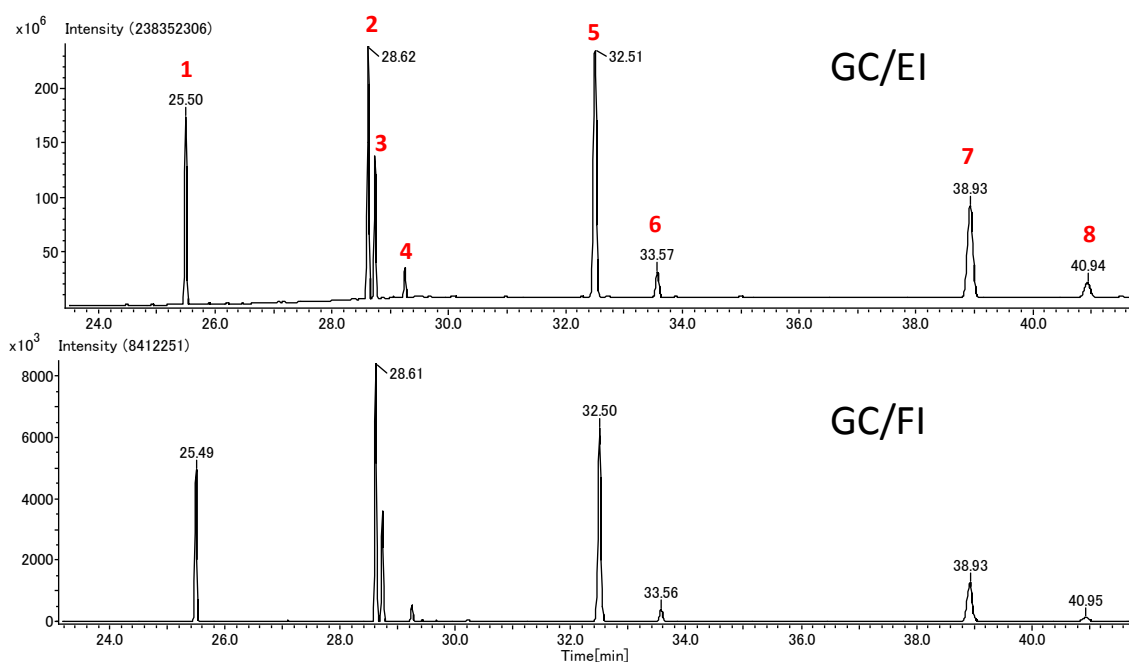
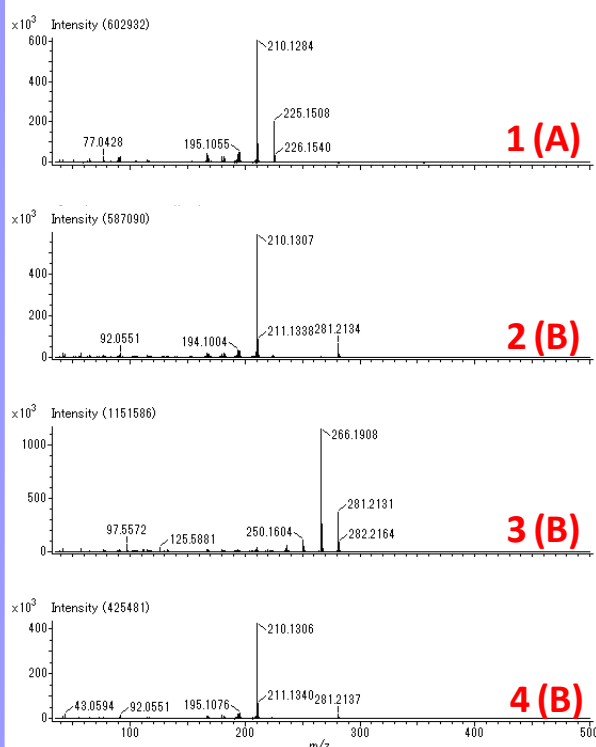


Figure 1. The TICs for GC/EI and GC/FI

## EI mass spectra



## FI mass spectra

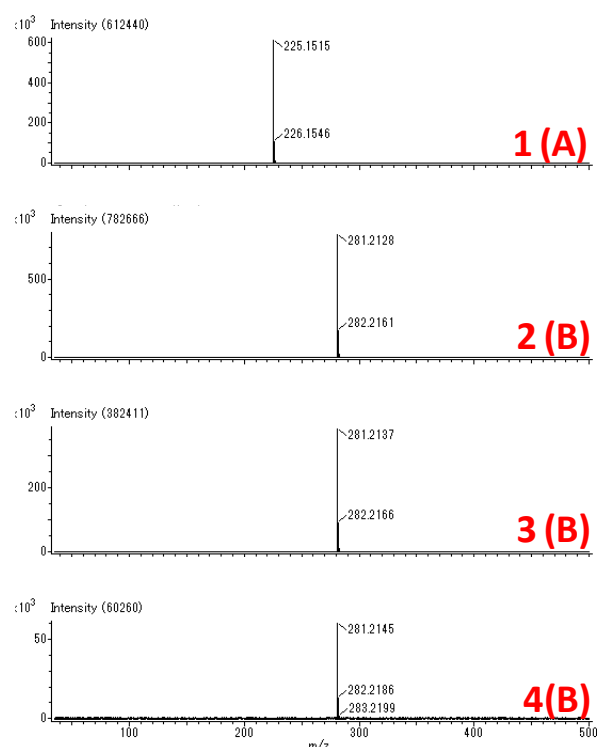


Figure 2. Mass spectra of component1-4, left: EI mass spectra, right: FI mass spectra (A,B: Isomer group)

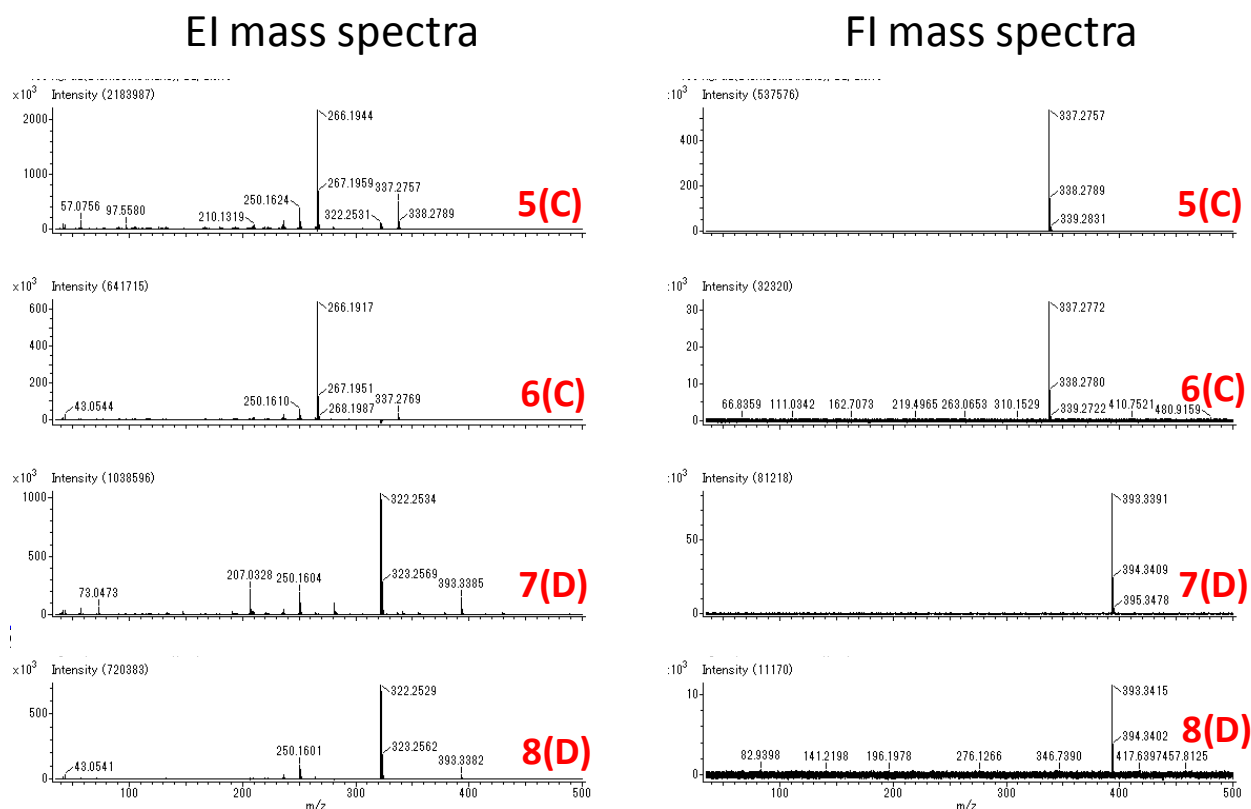


Figure 3. Mass spectra of component 5-8, left: EI mass spectra, right: FI mass spectra (C,D: Isomer group)

Component (Isomer group)	Ionization mode	Obs. $m/z$	Theo. $m/z$	Error (mDa)	Formula
1(A)	EI	210.1284	210.1283	0.1	$C_{15}H_{16}N$
		225.1508	225.1518	-1.0	$C_{16}H_{19}N$
	FI	225.1515	225.1518	-0.3	$C_{16}H_{19}N$
2(B)	EI	266.1908	266.1909	-0.1	$C_{19}H_{24}N$
		281.2131	281.2144	-1.3	$C_{20}H_{27}N$
	FI	281.2137	281.2144	-0.6	$C_{20}H_{27}N$
5(C)	EI	266.1917	266.1909	0.8	$C_{19}H_{24}N$
		337.2769	337.2770	-0.1	$C_{24}H_{35}N$
	FI	337.2772	337.2770	0.3	$C_{24}H_{35}N$
7(D)	EI	322.2534	322.2535	-0.1	$C_{23}H_{32}N$
		393.3385	393.3396	-1.1	$C_{28}H_{43}N$
	FI	393.3396	393.3396	-0.4	$C_{28}H_{43}N$

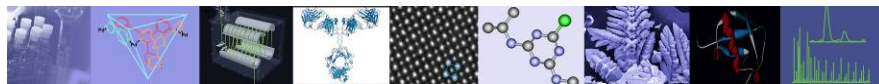
Table 2. Accurate mass measurement results

## MS061813



Figure 5. FD measurement result





As an example of how the EI data is library searchable, the EI spectrum for component 5 was exported to the NIST database which in turn showed that the top candidate for this EI fragmentation pattern is butyl-octyl-diphenylamine (Figure 4). To further support this match, the elemental composition of this compound ( $C_{24}H_{35}N$ ) exactly matches the composition identified through the EI and FI accurate mass measurements. Moreover, butyl-octyl-diphenylamine is an antioxidant which further supports this identification for component 5.

Next, the same antioxidant additive mixture was measured using FD mode, in which the sample is loaded directly onto the emitter probe. Figure 5 shows both the TIC and mass spectrum for this analysis. The measurement was completed within 1 minute and confirmed that the same four compositions were observed in this experiment ( $m/z$  225.2, 281.2, 337.3

and 393.3) as were observed in the GC/EI and GC/FI analyses. Additionally, the dimers for several of these ions were also observed in the mass spectrum. While FD is not able to determine the presence of multiple isomers (like the chromatography techniques), the analysis speed (less than 1min) is very useful for quickly evaluating the types of constituents that are present in a given sample.

### Conclusion

In this work, we showed a brief study for an antioxidant additive using each ionization mode available on the AccuTOF GCv 4G EI/FI/FD combination ion source. Furthermore, each technique was accessed without changing out the ion source or breaking vacuum. The EI/FI/FD combination ion source used in conjunction with the high resolution capabilities of the AccuTOF GCv 4G is a powerful tool for doing chemical qualitative analysis.



## Structural Analysis of Polyethylene Terephthalate Film by using a Py-GC-HRTOFMS and msFineAnalysis AI

Product used : Mass Spectrometer (MS)

### Introduction

Electron ionization (EI) is one of the most popular ionization methods used in gas chromatography-mass spectrometry (GC-MS). Consequently, compounds are typically identified by mass a spectral database search using EI mass spectra. Because molecular ions are often weak or absent in 70 eV EI mass spectra, identification of unknowns can be difficult by EI alone. In these cases, soft ionization (SI) can be very helpful for producing and identifying molecular ions. Recently, JEOL began developing an integrated qualitative analysis workflow that automatically combines and interprets the information from EI and SI data. And then in 2018, we introduced our integrated qualitative analysis software “msFineAnalysis” which uses both EI and SI data to improve compound identification for GC-MS applications.

Despite the fact that msFineAnalysis was automatically able to determine the molecular formula and partial structure information from EI fragment ion formulas, the actual structural formulas still required manual analysis using chemical compositions. To address this, we then developed an automated structure analysis software package entitled “msFineAnalysis AI” which uses artificial intelligence (AI) to predict EI mass spectra from chemical structures. We have used our newly-developed AI model to create a database of predicted EI mass spectra for around 100 million compounds. In this work, we introduce a polymer materials application that uses msFineAnalysis AI for structural analysis.

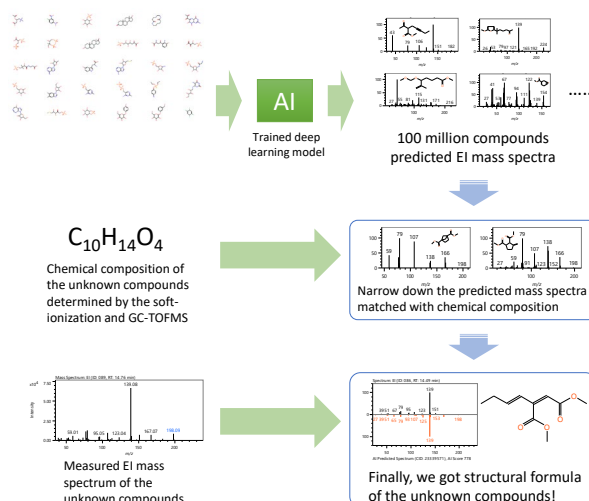
### AI Structural Analysis

The AI structural analysis workflow is shown in Figure 1. In this method, we used deep learning to construct an AI model that can predict the EI mass spectrum from a structural formula. We then submitted approximately 100 million compound structure formulas to our AI model in order to generate predicted EI mass spectra. The structural formula and the predicted EI mass spectra associated with each compound are included with the software as an “AI library” database that also includes database search function based on the mass spectral pattern. Additionally, msFineAnalysis AI uses the molecular formulas uniquely determined during automatic integrated qualitative analysis in order to narrow down the possible candidate structural formulas.

The predicted EI mass spectrum narrowed down by molecular formula and the actual EI mass spectrum are used to then calculate a score from the similarity of their spectral pattern, and the candidate structural formulas are then listed in order of high similarity to low similarity.

### Experimental

A commercially-available polyethylene terephthalate film was used as a test sample in this study. We performed Py-GC-HRTOFMS measurements using both EI and field ionization (FI) modes with a combination EI/FI ion source. The qualitative data processing was performed with msFineAnalysis AI (JEOL). Measurement conditions are shown in Table 1.



**Figure 1: Workflow for structural analysis of unknowns using msFineAnalysis**

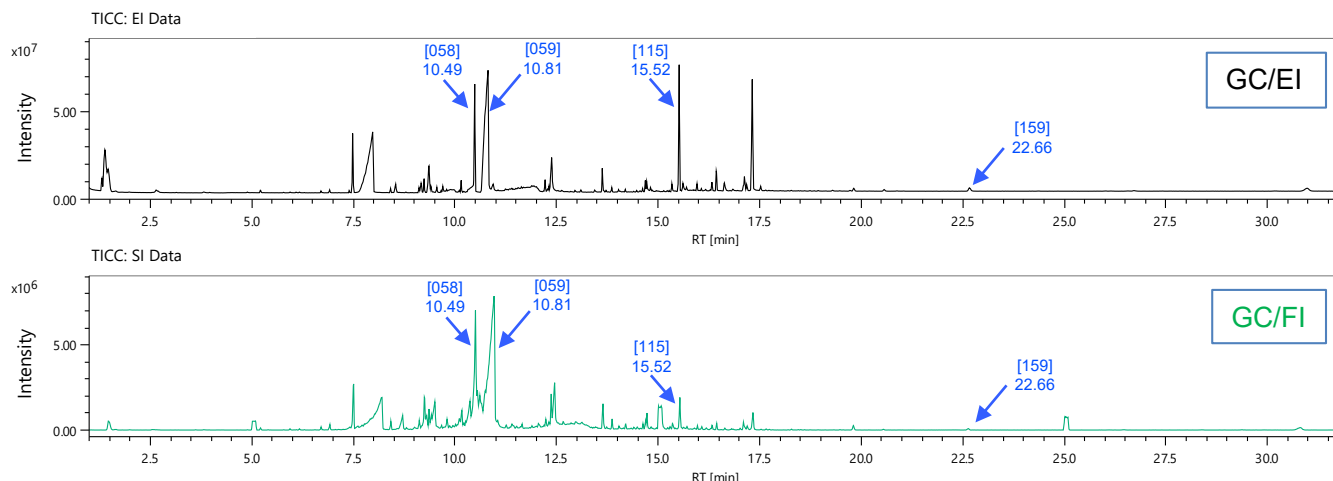
**Table 1: Measurement and analysis conditions**

Pyrolysis conditions		MS conditions	
Pyrolyzer	EGA/PY-2020D(Frontier Lab)	Spectrometer	JMS-T200GC (JEOL Ltd.)
Pyrolysis Temperature	600°C	Ion Source	EI/FI combination ion source
GC conditions		Ionization	EI+:70 eV, 300 µA FI+: -10 kV
Gas Chromatograph	7890 GC (Agilent Technologies)	Mass Range	<i>m/z</i> 29 - 600
Column	ZB-5MSi (Phenomenex) 30 m x 0.25 mm, 0.25 µm	Data processing condition	
Oven Temperature	40°C (2 min) - 20°C/min -320°C (30 min)	Software	msFineAnalysis AI (JEOL Ltd.)
Injection Mode	Split mode (100:1)	Library database	NIST20, AI Library (JEOL Ltd.)
Carrier flow	He:1.0 mL/min		

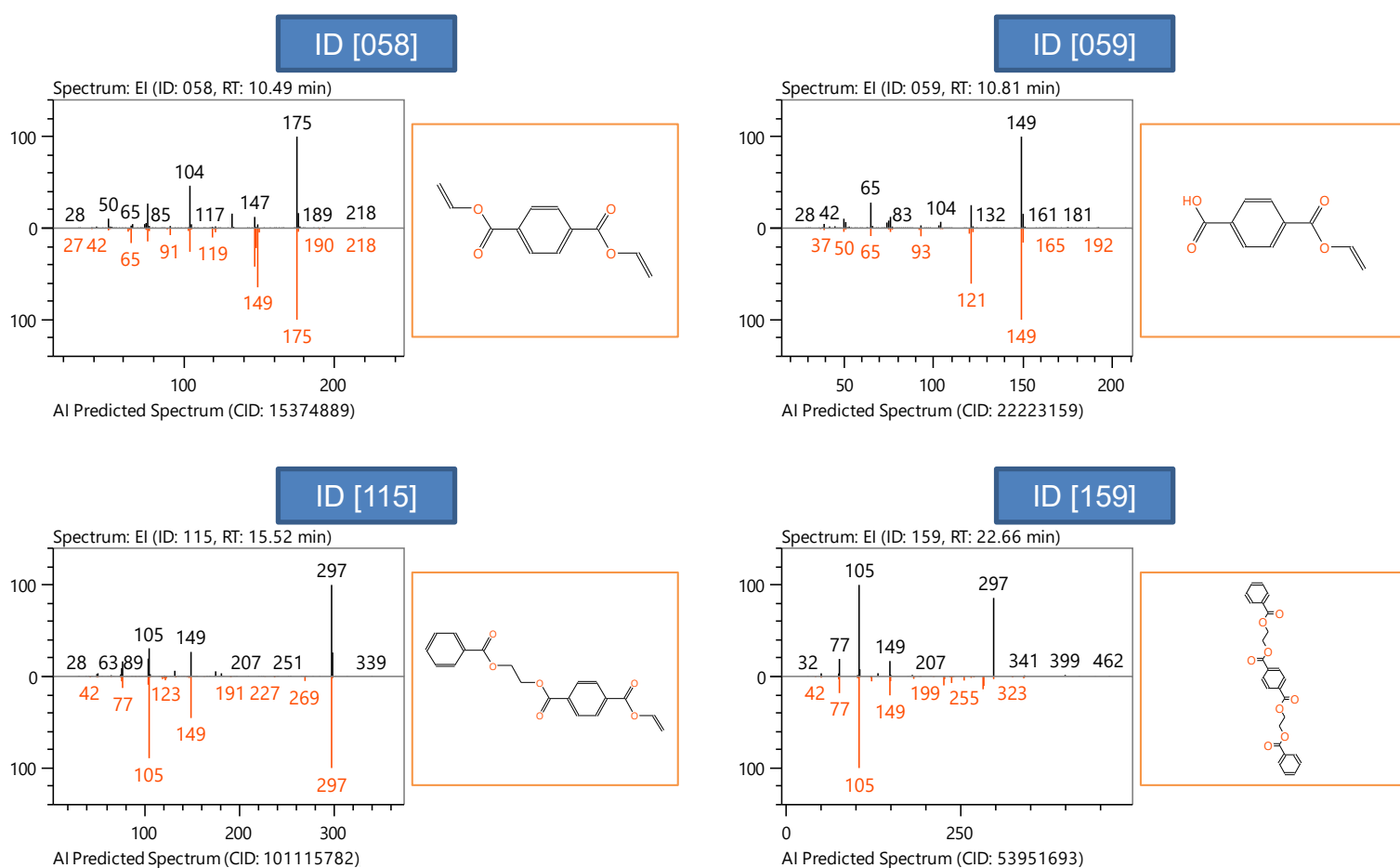
## Results and Discussion

### Comparison of AI structural analysis results and references

Among the observed polyethylene terephthalate (PET) pyrolysis products, AI structural analysis was performed for four components not registered in the NIST library database and for which structural formulas were proposed in reference [1]. Figure 2 shows the TIC chromatograms obtained from the Py-GC-EI and FI measurements. The peaks with IDs [058], [059], [115], and [159] in Figure 2 are the four components analyzed in this study. Figure 3 shows the measured EI mass spectra for these four components (upper, black), the structural formula proposed in the reference literature (right side of the spectrum), and its predicted EI mass spectrum (lower, red).



**Figure 2: Py-GC-EI and FI TIC chromatograms for Poly(ethylene terephthalate)**



**Figure 3: Measured EI mass spectra and predicted EI mass spectra of the proposed structural formula in reference [1]  
for ID[058], [059], [115], [159] in Figure 2**

AI structural analysis results are shown in Table 2. In the table, the "AI Score" is a score (up to 999) calculated by msFineAnalysis AI that represents the cosine similarity between the measured and predicted EI mass spectra. "Rank" indicates the score rank of the structural formulas listed in Figure 3, and "Total" indicates the number of candidate structural formulas. Three of the four components analyzed in this study (ID [058], [059], [115]) obtained over 800 score which means a high degree of similarity, and the fragment ions observed in the measured mass spectra and the predicted mass spectra were in good agreement. The number of candidate structural formulas were about 970-1400, and the structural formulas proposed in the reference were obtained as within the top two.

For ID [159], the AI Score was calculated at 510 score, and although this score was lower than the other components, the structural formula proposed in the reference literature was obtained at #3 rank in 311 candidates.

As a result, it was found that the structural formulas proposed in the reference literature were obtained in the top three positions for all the components evaluated in this study.

**Table 2: AI structural analysis result**

Reference [1] data		msFineAnalysis AI result						
Notation	Assignment of Main Peaks	ID	RT(min)	IUPAC name	PubChem CID	AI Score	Rank	Total
C	CH2=CHOCOC6H4COOCH=CH2	058	10.49	bis(ethenyl) benzene-1,4-dicarboxylate	15374889	820	2	1471
D	CH2=CHOCOC6H4COOH	059	10.81	4-ethenoxycarbonylbenzoic acid	22223159	914	2	1013
F	C6H5COOCH2CH2OCOC6H4COOCH=CH2	115	15.52	1-O-(2-benzoyloxyethyl) 4-O-ethenyl benzene-1,4-	101115782	877	1	975
H	C6H5COOCH2CH2OCOC6H4COOCH2CH2OCOC6H5	159	22.66	bis(2-benzoyloxyethyl) benzene-1,4-dicarboxylate	53951693	510	3	311

## Conclusion

In this MSTips, we introduced our newly-developed software msFineAnalysis AI, which contains AI structural analysis functionality to enhance qualitative analysis workflow. Additionally, a polymer application using msFineAnalysis AI to identify components of a pyrolyzed PET film was also presented.

Structural analysis using AI was performed on four components not registered in the NIST library database, and results were compared with structural formulae proposed in the reference literature.

In spectral pattern comparisons, Three of the four components analyzed in this study (ID [058], [059], [115]) cosine similarity scores were over 800, indicating that AI-predicted mass spectra showed a high degree of similarity to measured mass spectra. The number of candidate structural formulas were about 970-1400, and the structural formulas proposed in the reference were obtained as within the top two. For ID [159], the AI Score was calculated at 510 score, and although this score was lower than the other components, the structural formula proposed in the reference literature was obtained at #3 rank in 311 candidates. The prediction by AI showed high accuracy, indicating that the method is effective for structural analysis of pyrolysis products.

Qualitative analysis of GC-MS data can be greatly assisted by using EI and SI data together with msFineAnalysis AI, especially when trying to identify unknown compounds in complex samples.

## Reference

[1]Shin Tsuge, Hajime Ohtani, Chuichi Watanabe (2011), Pyrolysis - GC/MS Data Book of Synthetic Polymers, Elsevier





## Structural Analysis of Additives and Related Compounds in Vinyl Acetate by using a Py-GC-HRTOFMS and msFineAnalysis AI

Product used : Mass Spectrometer (MS)

### Introduction

Electron ionization (EI) is one of the most popular ionization methods used in gas chromatography-mass spectrometry (GC-MS). Consequently, compounds are typically identified by a mass spectral database search using EI mass spectra. Because molecular ions are often weak or absent in 70 eV EI mass spectra, identification of unknowns can be difficult by EI alone. In these cases, soft ionization (SI) can be very helpful for producing and identifying molecular ions. Recently, JEOL began developing an integrated qualitative analysis workflow that automatically combines and interprets the information from EI and SI data. And then in 2018, we introduced our integrated qualitative analysis software “msFineAnalysis” which uses both EI and SI data to improve compound identification for GC-MS applications.

Despite the fact that msFineAnalysis was automatically able to determine the molecular formula and partial structure information from EI fragment ion formulas, the actual structural formulas still required manual analysis using chemical compositions. To address this, we then developed an automated structure analysis software package entitled “msFineAnalysis AI” which uses artificial intelligence (AI) to predict EI mass spectra from chemical structures. We have used our newly-developed AI model to create a database of predicted EI mass spectra for around 100 million compounds. In this work, we introduce a polymer materials application that uses msFineAnalysis AI for structural analysis.

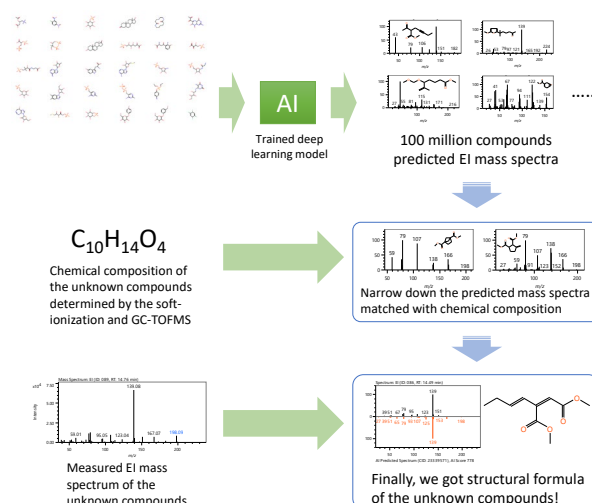
### AI Structural Analysis

The AI structural analysis workflow is shown in Figure 1. In this method, we used deep learning to construct an AI model that can predict the EI mass spectrum from a structural formula. We then submitted approximately 100 million compound structure formulas to our AI model in order to generate predicted EI mass spectra. The structural formula and the predicted EI mass spectra associated with each compound are included with the software as an “AI library” database that also includes database search function based on the mass spectral pattern. Additionally, msFineAnalysis AI uses the molecular formulas uniquely determined during automatic integrated qualitative analysis in order to narrow down the possible candidate structural formulas.

The predicted EI mass spectrum narrowed down by molecular formula and the actual EI mass spectrum are used to then calculate a score from the similarity of their spectral pattern, and the candidate structural formulas are then listed in order of high similarity to low similarity.

### Experimental

A commercially-available vinyl acetate resin was used as a test sample in this study. We performed Py-GC-HRTOFMS measurements using both EI and field ionization (FI) modes with a combination EI/FI ion source. The qualitative data processing was performed with msFineAnalysis AI (JEOL). Measurement conditions are shown in Table 1.



**Figure 1: Workflow for structural analysis of unknowns using msFineAnalysis**

**Table 1: Measurement and analysis conditions**

Pyrolysis conditions		MS conditions	
Pyrolyzer	EGA/PY-2020D(Frontier Lab)	Spectrometer	JMS-T200GC (JEOL Ltd.)
Pyrolysis Temperature	600°C	Ion Source	EI/FI combination ion source
GC conditions		Ionization	EI+:70eV, 300μA FI+:~10kV, 6mA/10msec (Carbotec)
Gas Chromatograph	7890 GC (Agilent Technologies)	Mass Range	<i>m/z</i> 35-800
Column	DB-5msUI (Agilent) 15m x 0.25mm, 0.25μm	Data processing condition	
Oven Temperature	50°C(1min)-30°C/min -330°C(1.7min)	Software	msFineAnalysis AI (JEOL Ltd.)
Injection Mode	Split mode (100:1)	Library database	NIST20, AI Library (JEOL Ltd.)
Carrier flow	He:1.5mL/min		



## Results and Discussion

Figure 2 shows the TIC chromatograms obtained from the Py-GC-EI and FI measurements. Diethylene Glycol Dibenzoate used as a plasticizer was detected at RT 8.45 min (ID [134]). In addition, compounds presumed to be pyrolysis products of Diethylene Glycol Dibenzoate were detected in the RT 5.02 min (ID [085]), RT 5.98 min (ID [108]) and RT 6.98 min (ID [127]). All of these compounds were not registered in the NIST library database. Therefore, we performed AI structural analysis on these three components and compared them with the structural formulas of pyrolysis products expected to be generated from Diethylene Glycol Dibenzoate.

The measured EI mass spectra of these three components (top, black) and the predicted structural formula (right side of the spectrum) and its predicted EI mass spectrum (bottom, red) are shown in Figure 3. Regarding Diethylene Glycol Dibenzoate, the EI mass spectrum registered in the NIST library database is displayed in blue at the bottom, not the predicted EI mass spectrum.

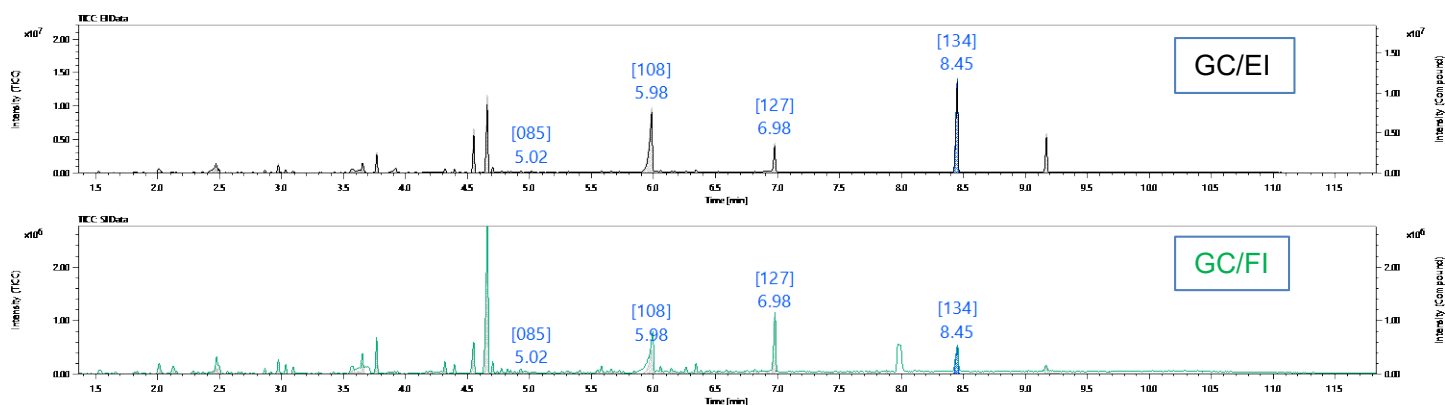
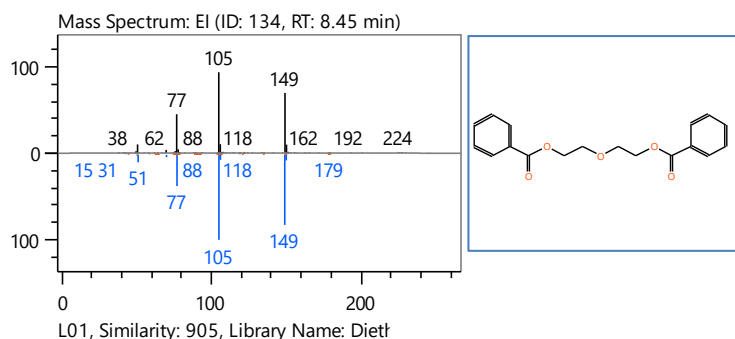
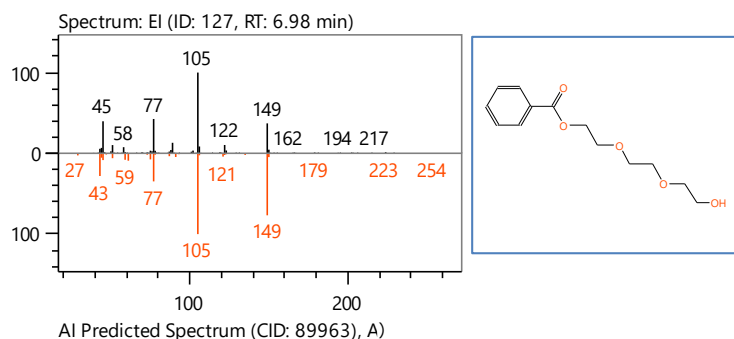


Figure 2: Py-GC-EI and FI TIC chromatograms for Poly(vinyl acetate)

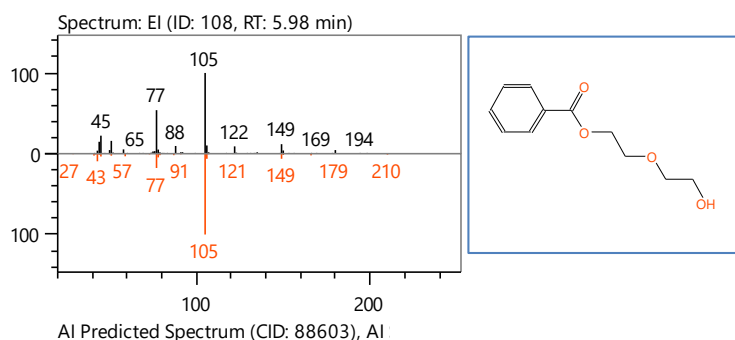
### [134] Diethylene Glycol Dibenzoate



### [127]



### [108]



### [085]

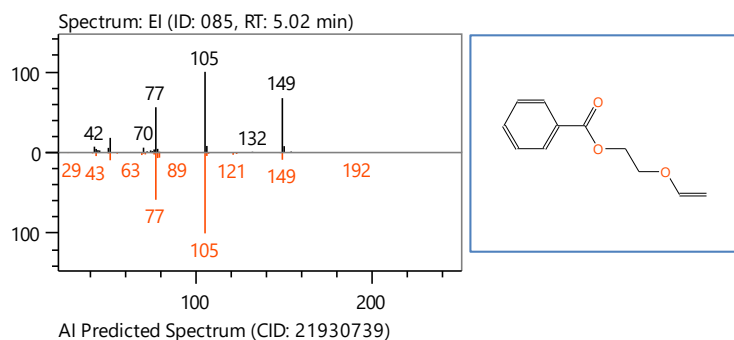


Figure 3: Measured EI mass spectra and predicted EI mass spectra of the proposed structural formula for ID[085], [108], [127], [134] in Figure 2

AI structural analysis results are shown in Table 2. In the table, the "AI Score" is a score (up to 999) calculated by msFineAnalysis AI that represents the cosine similarity between the measured and predicted EI mass spectra. "Rank" indicates the score rank of the structural formulas listed in Figure 3, and "Total" indicates the number of candidate structural formulas. All three of the components analyzed in this study obtained a score of 850 or higher, indicating a high degree of similarity, and the fragment ions observed in the measured mass spectra and the predicted mass spectra were in good agreement. The number of candidate structural formula all exceeded 2,000 for each of the components, the presumed structural formula was obtained as the first or second candidate for all three components.

**Table 2: AI structural analysis result**

msFineAnalysis AI result						
ID	RT(min)	IUPAC name	PubChem CID	AI Score	Rank	Total
085	5.02	2-Ethenoxyethyl benzoate	21930739	858	1	4600
108	5.98	2-(2-Hydroxyethoxy)ethyl benzoate	88603	857	2	4544
127	6.98	2-[2-(2-Hydroxyethoxy)ethoxy]ethyl benzoate	89963	872	1	2433

## Conclusion

In this MSTips, we introduced our newly-developed software msFineAnalysis AI, which contains AI structural analysis functionality to enhance qualitative analysis workflow. Additionally, the structural analysis application of additives and related compounds in vinyl acetate using msFineAnalysis AI was also presented.

Structural analysis using AI was performed on three components not registered in the NIST library database, and results were compared with the structures of pyrolysis products expected from Diethylene Glycol Dibenzoate. In spectral pattern comparisons, all cosine similarity scores were over 850, indicating that AI-predicted mass spectra showed a high degree of similarity to measured mass spectra. Even though the number of candidate structural formula exceeded 2,000 for each of the components, the presumed structural formula was obtained as the first or second candidate for all three components. The prediction by AI showed high accuracy, indicating that the method is effective for structural analysis of pyrolysis products and additives.

Qualitative analysis of GC-MS data can be greatly assisted by using EI and SI data together with msFineAnalysis AI, especially when trying to identify unknown compounds in complex samples.

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## Structural Analysis of Acrylic Resin Oligomers by using a Py-GC-HRTOFMS and msFineAnalysis AI

Product used : Mass Spectrometer (MS)

### Introduction

Electron ionization (EI) is one of the most popular ionization methods used in gas chromatography-mass spectrometry (GC-MS). Consequently, compounds are typically identified by a mass spectral database search using EI mass spectra. Because molecular ions are often weak or absent in 70 eV EI mass spectra, identification of unknowns can be difficult by EI alone. In these cases, soft ionization (SI) can be very helpful for producing and identifying molecular ions. Recently, JEOL began developing an integrated qualitative analysis workflow that automatically combines and interprets the information from EI and SI data. And then in 2018, we introduced our integrated qualitative analysis software “msFineAnalysis” which uses both EI and SI data to improve compound identification for GC-MS applications.

Despite the fact that msFineAnalysis was automatically able to determine the molecular formula and partial structure information from EI fragment ion formulas, the actual structural formulas still required manual analysis using chemical compositions. To address this, we then developed an automated structure analysis software package entitled “msFineAnalysis AI” which uses artificial intelligence (AI) to predict EI mass spectra from chemical structures. We have used our newly-developed AI model to create a database of predicted EI mass spectra for around 100 million compounds. In this work, we introduce a polymer materials application that uses msFineAnalysis AI for structural analysis.

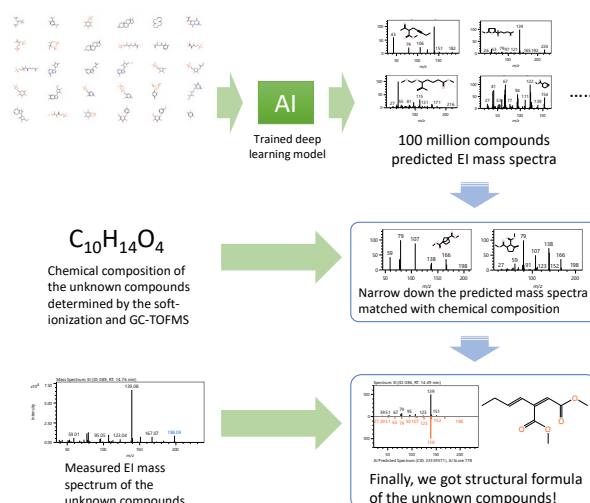
### AI Structural Analysis

The AI structural analysis workflow is shown in Figure 1. In this method, we used deep learning to construct an AI model that can predict the EI mass spectrum from a structural formula. We then submitted approximately 100 million compound structure formulas to our AI model in order to generate predicted EI mass spectra. The structural formula and the predicted EI mass spectra associated with each compound are included with the software as an “AI library” database that also includes database search function based on the mass spectral pattern. Additionally, msFineAnalysis AI uses the molecular formulas uniquely determined during automatic integrated qualitative analysis in order to narrow down the possible candidate structural formulas.

The predicted EI mass spectrum narrowed down by molecular formula and the actual EI mass spectrum are used to then calculate a score from the similarity of their spectral pattern, and the candidate structural formulas are then listed in order of high similarity to low similarity.

### Experimental

A commercially-available acrylic resin was used as a test sample in this study. We performed Py-GC-HRTOFMS measurements using both EI and field ionization (FI) modes with a combination EI/FI ion source. The qualitative data processing was performed with msFineAnalysis AI (JEOL). Measurement conditions are shown in Table 1.



**Figure 1: Workflow for structural analysis of unknowns using msFineAnalysis**

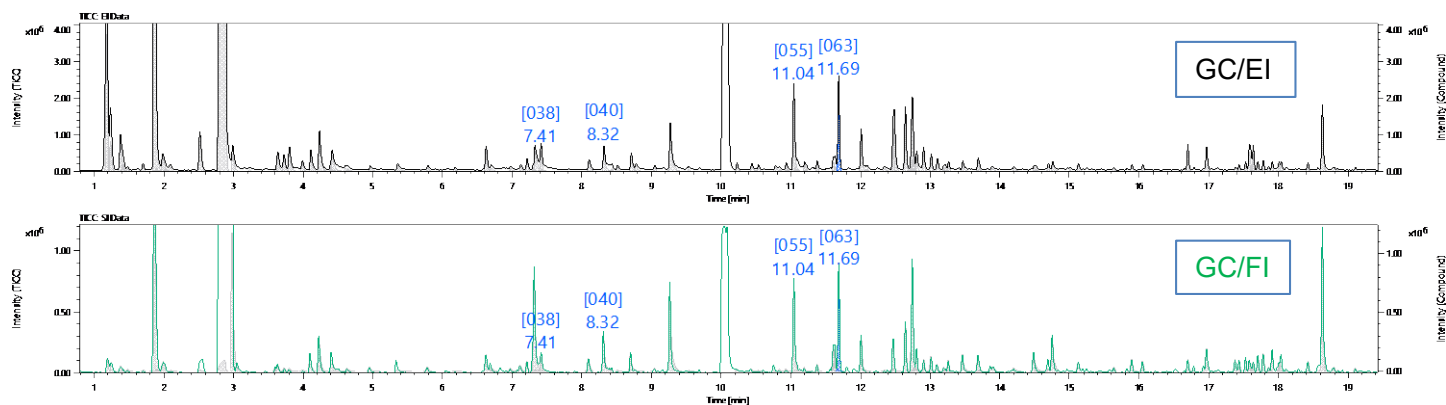
**Table 1: Measurement and analysis conditions**

Pyrolysis Conditions		MS Conditions	
Pyrolyzer	EGA/PY-3030D(Frontier Lab)	Spectrometer	JMS-T2000GC (JEOL Ltd.)
Pyrolysis Temperature	600°C	Ion Source	EI/FI combination ion source
GC Conditions		Ionization	EI+:70eV, 300μA FI+: -10kV, 40mA/30msec
Gas Chromatograph	8890 GC (Agilent Technologies)	Mass Range	<i>m/z</i> 35-800
Column	ZB-5MSi (Phenomenex) 30m x 0.25mm, 0.25μm	Data Processing Conditions	
Oven Temperature	40°C(2min)-10°C/min -320°C(15min)	Software	msFineAnalysis AI (JEOL Ltd.)
Injection Mode	Split mode (100:1)	Library database	NIST20, AI Library (JEOL Ltd.)
Carrier flow	He:1.0mL/min		

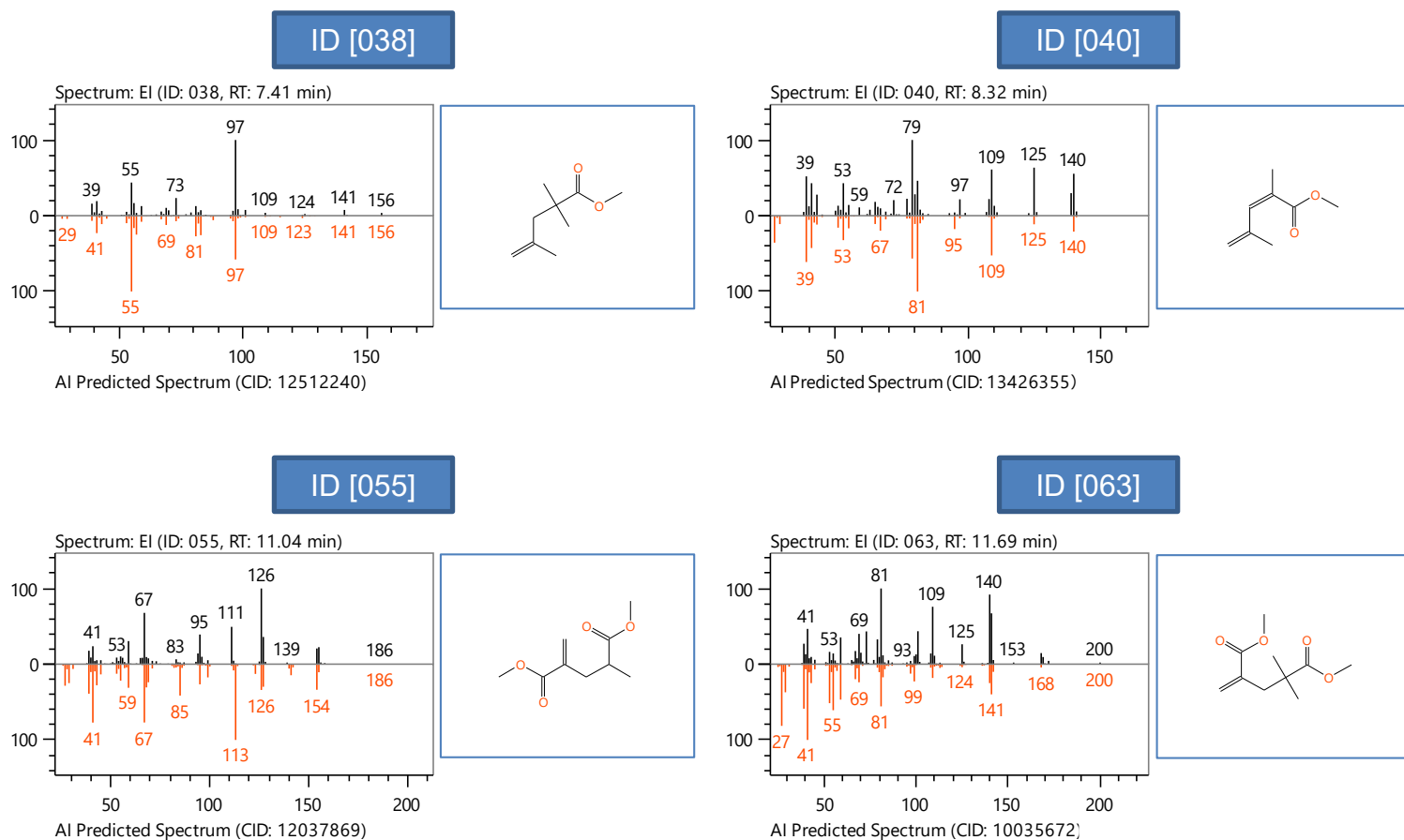
## Results and Discussion

### Comparison of AI structural analysis results and references

Among the observed acrylic resin pyrolysis products, AI structural analysis was performed for four components not registered in the NIST library database and for which structural formulas were proposed in reference [1]. Figure 2 shows the TIC chromatograms obtained from the Py-GC-EI and FI measurements. The peaks with IDs [038], [040], [055], and [063] in Figure 2 are the four components analyzed in this study. Figure 3 shows the measured EI mass spectra for these four components (upper, black), the structural formula proposed in the reference literature (right side of the spectrum), and its predicted EI mass spectrum (lower, red).



**Figure 2: Py-GC-EI and FI TIC chromatograms for an Methyl methacrylate-methyl acrylate copolymer**



**Figure 3: Measured EI mass spectra (upper, black) and predicted EI mass spectra (lower, red) of the proposed structural formula in reference [1] for ID[038], [040], [055], [063] in Figure 2**

AI structural analysis results are shown in Table 2. In the table, the "AI Score" is a score (up to 999) calculated by msFineAnalysis AI that represents the cosine similarity between the measured and predicted EI mass spectra. "Rank" indicates the score rank of the structural formulas listed in Figure 3, and "Total" indicates the number of candidate structural formulas. All four of the components analyzed in this study obtained a score of 750 or higher, indicating a high degree of similarity, and the fragment ions observed in the measured mass spectra and the predicted mass spectra were in good agreement. The number of candidate structural formulae all exceeded 3,000, but in three of the four components, structural formulas proposed in the reference literature were obtained within the top 1% of the candidates.

**Table 2: AI structural analysis results**

Reference [1] data		msFineAnalysis AI result						
Notation	Assignment of Main Peaks	ID	RT(min)	IUPAC name	PubChem CID	AI Score	Rank	Total
d2	C=C(C)-C-C(C)(COOC)-C ?	038	7.41	Methyl 2,2,4-trimethylpent-4-enoate	12512240	872	2	5548
d4	C=C(C)-C=C(COOC)-C ?	040	8.32	Methyl 2,4-dimethylpenta-2,4-dienoate	71327190	865	18	3769
A2'	C=C(COOC)-C-C(COOC)-C ?	055	11.04	Dimethyl 2-methyl-4-methylidenepentanedioate	12037869	753	37	3109
D1	C=C(COOC)-C-C(C)(COOC)-C ?	063	11.69	Dimethyl 2,2-dimethyl-4-methylidenepentanedioate	10035672	825	9	3732

## Conclusion

In this MSTips, we introduced our newly-developed software msFineAnalysis AI, which contains AI structural analysis functionality to enhance qualitative analysis workflow. Additionally, a polymer application using msFineAnalysis AI to identify components of a pyrolyzed acrylic resin was also presented.

Structural analysis using AI was performed on four components not registered in the NIST library database, and results were compared with structural formulae proposed in the reference literature. In spectral pattern comparisons, all cosine similarity scores were over 750, indicating that AI-predicted mass spectra showed a high degree of similarity to measured mass spectra. Even though the number of candidate structural formulae exceeded 3,000 for each of the components, the structural formulae proposed in the reference literature for three of the four components was in the top 1% of candidates. The prediction by AI showed high accuracy, indicating that the method is effective for structural analysis of pyrolysis products.

Qualitative analysis of GC-MS data can be greatly assisted by using EI and SI data together with msFineAnalysis AI, especially when trying to identify unknown compounds in complex samples.

## Reference

[1] Shin Tsuge, Hajime Ohtani, Chuichi Watanabe (2011), Pyrolysis - GC/MS Data Book of Synthetic Polymers, Elsevier

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## Material Evaluation using msFineAnalysis Ver. 3

### —Fast search and analysis of substance in material by two-sample comparison —

Related Product: Mass Spectrometer(MS)

#### Introduction

As polymer materials have become more complex and diverse, the details of their chemical composition have become more critical for the end users. This knowledge allows manufacturers and users to understand the effects of incorporating these polymer materials into their products. Additionally, it is critical to also have tools that can quickly compare two-samples to each other like conventional materials versus alternative materials, new products versus old products, and good products versus defective products.

Gas chromatography-mass spectrometry (GC-MS) is an analytical technique that is widely used for both qualitative and quantitative analysis of volatile compounds in materials. For these types of measurements, GC-MS analyses typically only involve library database searches to identify each analyte. However, it is not so uncommon to measure unknown analytes that are not registered in the database. So for these compounds, it is not possible to identify with the database search method. To address this problem, we developed the msFineAnalysis software in 2018 that uses an "integrated analysis" approach in which the EI fragmentation information is combined with the soft ionization (SI) accurate mass information for the molecular ion to automatically determine the most logical chemical formula for each analyte.

More recently, msFineAnalysis Ver. 3 was introduced in which a differential analysis function was added to the software that uses t-tests to compare two samples to each other, and Retention Index search functionality. In this work, we compared two polypropylene/polyethylene (PP/PE) copolymerized polymers to show the differential analysis capabilities of msFineAnalysis Ver. 3.

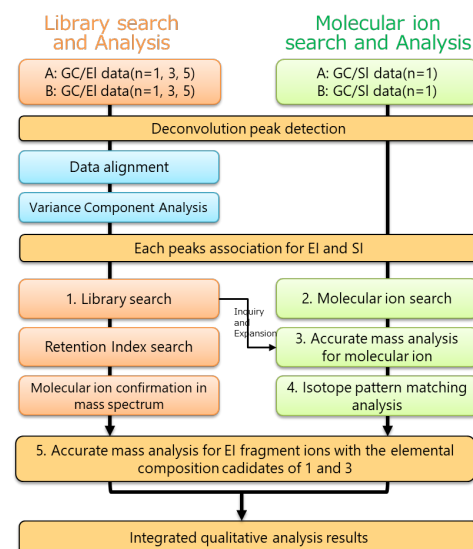
#### Analysis Flow

Fig.1 shows the msFineAnalysis workflow in which the new differential analysis feature is combined with the automatic integrated analysis workflow that was previously discussed in our MS Tips application notes (#275, 280, etc.). The workflow first deconvolves the chromatographic peaks and then performs differential analysis using the EI data for the two samples that are being compared to each other. Data alignment (identity determination) is performed based on the similarity between RT value of chromatographic peaks detected in the EI data and the EI mass spectral pattern. For the compounds obtained through the alignment process, the detected compounds are classified based on the number of occurrences, intensity ratio of the mean area value between the two sample data, and the p-value calculated by t-test.

After classifying the compounds, each chromatographic peak observed in the EI data and SI data are linked to each other based on their retention times and recorded as a single component. Afterwards, the msFineAnalysis is used not only to automatically perform quantitative identification of components registered in the library database but also to determine the most likely elemental composition for unregistered components.

#### Experimental

Two PP/PE copolymers (one "good" sample, one "bad" sample) were used as the samples. Table 1 shows the measurement conditions for the pyrolysis GC-MS measurements. A JMS-T200GC equipped with a Frontier Lab pyrolyzer and the JEOL EI/FI combination ion source was used for the measurements. The sample amounts used for each measurement were 0.2mg for the EI method and 1.0mg for the FI method, respectively. The resulting data was then analyzed by using the msFineAnalysis Ver. 3 integrated workflow (Fig. 1) to compare the two PP/PE copolymers as well as to identify the unique components in each sample.



**Fig. 1 msFineAnalysis Ver.3 workflow for the variance component analysis**

**Table 1. Measurement and analysis conditions**

Pyrolysis conditions		MS conditions	
Pyrolyzer	EGA/PY-3030D(Frontier Lab)	Spectrometer	JMS-T200GC (JEOL Ltd.)
Pyrolysis Temperature	600°C	Ion Source	EI/FI combination ion source
GC conditions		Ionization	EI+:70eV, 300μA
Gas Chromatograph	7890A GC		FI+: -10kV, 40mA/30msec
	(Agilent Technologies)	Mass Range	m/z 29-800
Column	ZB-5MSi (Phenomenex)	Data processing condition	
	30m x 0.25mm, 0.25μm	Software	msFineAnalysis (JEOL Ltd.)
Oven Temperature	40°C(2min)-10°C/min	Library database	NIST17
	-340°C(28min)	Tolerance	±5mDa
Injection Mode	Split mode (100:1)		
Carrier flow	He:1.0mL/min		

## Result

We performed a differential analysis for n=5 sample measurements for Sample A and B that resulted in five characteristic components being uniquely identified in the defective sample (Sample B). The msFineAnalysis Ver. 3 software provides a Volcano Plot where the X axis represents the intensity ratio ( $\text{Log}_2(\text{B/A})$ ) between the 2 samples and the Y axis represents the statistical reproducibility ( $-\text{Log}_{10}(\text{p-value})$ ) to quickly determine the distinguishing components for each sample. Fig. 2 shows the detailed analysis screen for the Volcano Plot in which the area boxed with blue dots shows the characteristic components for Sample A with high reproducibility, while the area boxed with red dots shows the characteristic components for Sample B with high reproducibility. By selecting each dot on the Volcano Plot, a summary for each component is shown that includes the EI and FI mass spectra, results of the integrated analysis, and chromatographic peak area values for Sample A and Sample B.

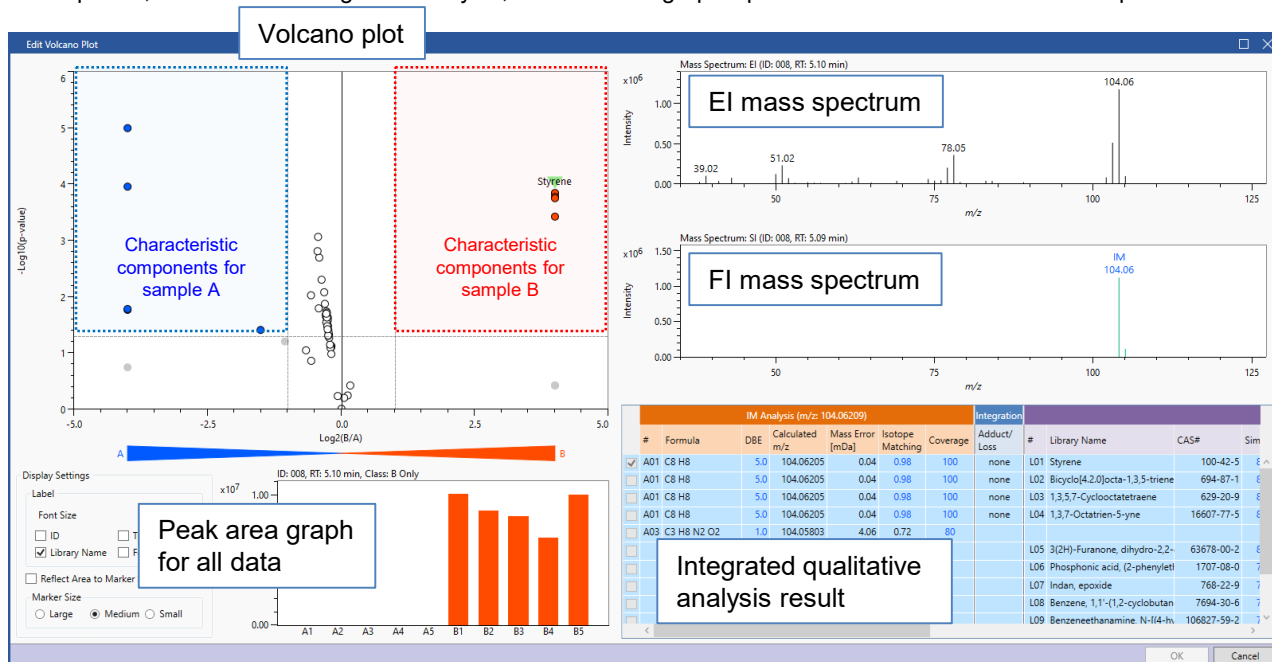


Fig.2 Volcano plot of variance component analysis result

Table 2 shows the integrated analysis results for the five unique components in Sample B. Acrylic nitrile (ID003) and styrene (ID008) were detected with a strong intensity, thus indicating the possibility that the substance in the defective sample (Sample B) is an acrylic nitrile/styrene(AS) copolymerized polymer.

Table 2. Integrated qualitative analysis result for the characteristic components of sample B

General				Variance Component Analysis Result				Total Result									
ID	RT [min]	Data	Height [%]	IM m/z	Class	Log2(B/A)	-Log10(p-value)	Library Name	Similarity	Lib. RI [u]	Formula	DBE	Adduct/Loss	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage
003	1.27	B-EI-5	5.91	53.02651	B Only	4.00	3.75	2-Propenenitrile	711	555	C3 H3 N	3.0	none	53.02600	0.51	0.91	100
008	5.10	B-EI-1	67.44	104.06209	B Only	4.00	3.84	Styrene	894	N/A	C8 H8	5.0	none	104.06205	0.04	0.98	100
018	12.14	B-EI-5	4.31	157.08970	B Only	4.00	3.43	1H-Pyrrole, 1-(phenylmethyl)-	737	N/A	C11 H11 N	7.0	none	157.08860	1.09	0.93	100
026	17.97	B-EI-5	8.66	210.11547	B Only	4.00	3.78	-	-	-	C14 H14 N2	9.0	none	210.11515	0.32	0.79	100
030	21.33	B-EI-5	11.72	261.15223	B Only	4.00	3.85	-	-	-	C19 H19 N	11.0	none	261.15120	1.03	0.82	100

ID018, 26, 30 are all nitrogen-containing compounds. ID018 is a dimer resulting from the thermal decomposition of the AS copolymer. ID026 and ID030 are not registered in the library database, but the elemental compositions from the integrated analysis results correlate to the mixed trimers shown in Fig. 3. These results strongly suggested that the substance in the defective sample (sample B) was AS copolymerized polymer.

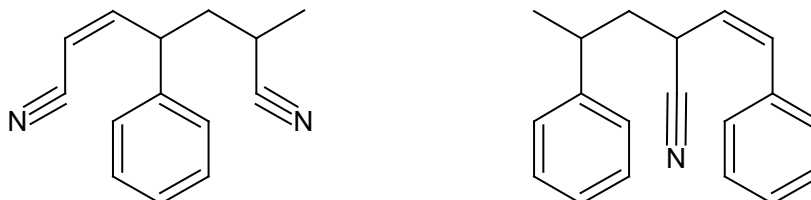


Fig.3 Estimated chemical structures: left: ID026 ( $\text{C}_{14}\text{H}_{14}\text{N}_2$ ), right: ID030 ( $\text{C}_{19}\text{H}_{19}\text{N}$ )

## Conclusions

The msFineAnalysis Ver. 3 software is a powerful tool for determining differences between samples (conventional materials versus alternative materials, new products versus old products, and good products versus defective products) for all component, including those analytes that are not registered in the EI database libraries. More specifically, the latest version of this software statistically extracts analyte differences between samples and performs an integrated analysis for these analytes that is not dependent on the library database search alone. As a result, msFineAnalysis Ver. 3 can quickly distinguish and identify registered and unregistered components that would be difficult, if not impossible to do by traditional GC-MS qualitative analysis involving EI alone.

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## Differential Analysis Function in msFineAnalysis Ver 3 (1): Analysis of Epoxy Resin by using Headspace and Pyrolysis-GC-TOFMS

Related product: Mass spectrometer(MS)

### Introduction

As the performance of mass spectrometers has improved, the demand for differential analysis of trace components in materials has increased. To address this trend, we have added a new differential analysis function to msFineAnalysis, our automated qualitative analysis software specifically designed for GC-HRTOFMS data. This application note describes the workflow used by msFineAnalysis for differential analysis by analyzing epoxy adhesives data measured by headspace(HS)-GC-TOFMS and pyrolysis(Py)-GC-TOFMS.

### Differential Analysis Workflow

The differential analysis workflow is shown at the very top of Figure 1. When measuring samples for a simple comparison ( $n=1$ ), each sample is measured twice: once by GC/EI, once by GC/SI for a total of 4 GC measurements. For statistical analysis ( $n=3, 5$ ), GC/EI measurements are performed for each sample more than once and the GC/SI measurement is performed only once for each (for two samples,  $n=5$ , then the total number of GC measurements would be 12). Afterwards, the GC/EI and GC/SI data are loaded into msFineAnalysis, and then following the GUI instructions, the integrated analysis result are output as a color coded report. The final step requires the analyst to confirm the results.

The msFineAnalysis integrated analysis workflow is shown in the bottom section of Figure 1. The first step for this workflow is chromatogram peak detection (peak deconvolution) for the measured data. During this process, minor peaks are detected that may not be obvious in the TICC. Next, data alignment and variance component analysis are performed for the detected EI peaks based on their retention times (R.T.) as well as the similarity of their mass spectra. The differences are compared using intensity ratios between samples and reproducibility. Afterwards, both the EI and SI data are analyzed by using the integrated analysis workflow used for previous versions of msFineAnalysis. This analysis workflow consists of EI library database searches, molecular ion searches in the SI data, and accurate mass analysis of both EI and SI data. For a detailed explanation of this EI/SI integrated analysis workflow, please see MSTips No. 275. An example of the msFineAnalysis Ver3 differential analysis results will be examined in the following pages.

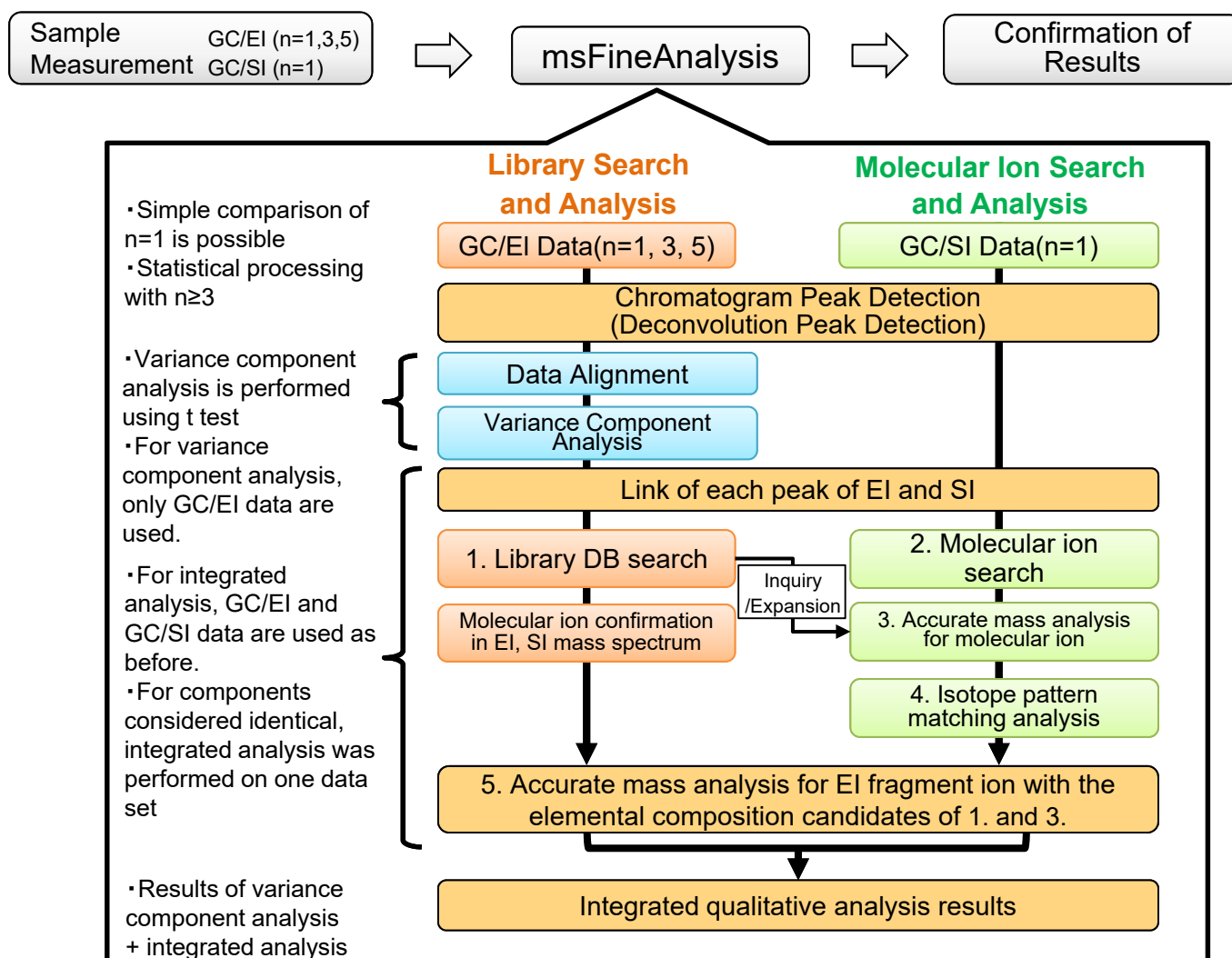


Figure 1. Analysis flow using msFineAnalysis

## Measurement

Two different commercially available epoxy adhesives (A, B) were used as samples. These samples were cured prior to analysis. HS-GC-MS and Py-GC-MS were used for the measurements. For HS-GC-MS, the samples were heated at 50°C, and the thermally-desorbed volatile components were analyzed. For Py-GC-MS, the samples were heated at 600°C and the pyrolysis products were analyzed. The ionization methods used for these measurements were EI and FI (Field Ionization) as hard and soft ionization, respectively. In order to conduct statistical analysis, the GC/EI measurements were performed with n=5. The parameters used to perform differential analysis were the p-value (an index: the smaller the p-value, the higher the statistical reproducibility)  $\leq 5\%$  and fold change (intensity ratio between samples)  $\geq 2$ . The detailed measurement conditions are shown in Table 1.

**Table 1. Measurement and analysis conditions**

HS-GC-MS		Py-GC-MS	
Headspace sampler	MS62070STRAP (JEOL)	Pyrolyzer	EGA/PY-3030D (Frontier Laboratories Ltd)
Sample amount	500mg	Sample amount	0.2mg
Mode	Trap	Mode	Single shot
Sample heating	50°C, 30min	Furnace	600°C
Gas Chromatograph	7890A GC (Agilent Technologies, Inc.)	Gas Chromatograph	7890A GC (Agilent Technologies, Inc.)
Mode	Split20:1	Mode	Split100:1
Column	InertCap-WAX 60m x 0.32mm, 0.5µm (GL Sciences Inc)	Column	ZB-5MSi 30m x 0.25mm, 0.25µm (Phenomenex Inc)
Oven	40°C(3min)→10°C/min →200°C(5min)	Oven	40°C(2min)→10°C/min →320°C(15min)
Carrier gas	He, 1.5mL/min	Carrier gas	He, 1mL/min
TOFMS	JMS-T200GC	TOFMS	JMS-T200GC
Ionization	EI+ : 70eV, 300µA FI+ : -10kV, 40mA	Ionization	EI+ : 70eV, 300µA FI+ : -10kV, 40mA
Monitor ion range	<i>m/z</i> 35-800	Monitor ion range	<i>m/z</i> 35-800
msFineAnalysis	(JEOL)	msFineAnalysis	(JEOL)
Mode	Variance component analysis	Mode	Variance component analysis
Number of data	n=5	Number of data	n=5
p-value	$\leq 5\%$	p-value	$\leq 5\%$
Fold change	$\geq 2$	Fold change	$\geq 2$

## HS-GC-MS Measurement Result

Figure 2 shows a screenshot of the differential analysis results for the headspace samples using msFineAnalysis. The top left of the screen shows the TICC chromatograms as well as the compound peaks detected by deconvolution. The color of the compound peak reflects the result from the difference analysis. The blue color indicates that this particular analyte is strongly associated with Sample A while a red color indicates a strong association with Sample B. The volcano plot at the right top of the screen indicates the intensity difference between samples in the X axis and the statistical reproducibility in the Y axis, enabling comprehensive confirmation of the detected peaks. The right center of the screen shows the classification results, thus allowing for a concrete understanding of the total number of detected peaks as well as a breakdown of how the peaks relate to each sample. The peak list at the bottom shows a color coded table with the integrated analysis results for the detected peaks, thus allowing the analyst to easily correlate which analyte is more strongly associated with a particular sample.

The table at the bottom shows that 15 peaks were detected in total. A breakdown of the peak differences shows that 2 peaks (peak ID [003] butyl ether and [009] butanol) are characteristic of Sample A, 11 peaks are characteristic of Sample B ([001,002] low molecular weight cyclic siloxanes, etc.), and two peaks that have no intensity difference between Sample A and B ([004] toluene and [013] cyclohexasiloxane). Among these differences, the low molecular weight cyclic siloxanes are known to cause problems such as contact faults when used in electric products because of its high volatility and ability to create an oxide insulator film.

### Chromatogram

**Top: GC/EI(TICC/compound peak), Bottom: GI/FI**  
The color of the compound peak reflects the results of difference judgment

- Blue = Strong with sample A
- Red = Strong with sample B
- Yellow = No intensity difference(<2 times)

### Volcano Plot

- X axis: Log2(fold change)      Y axis: -Log10(p-value)
- Blue = Strong with sample A
- Red = Strong with sample B
- White = No intensity difference(<2 times)
- Gray = Low reproducibility



### Peak List

- The color reflects the results of difference analysis
- Blue = Strong with sample A
- Red = Strong with sample B
- White = No intensity difference(<2 times)

### Classification Result

- The ones with high reproducibility are classified into A only, A>B, A=B, A<B, B only.
- The ones with low reproducibility are classified into others.

Figure 2. Screenshot of msFineAnalysis (HS-GC-MS)



## Py-GC-MS Measurement Result

Figure 3 shows a screenshot of the differential analysis results for the pyrolyzed samples using msFineAnalysis. In total, 120 peaks were detected for these samples. A breakdown of the peak differences shows that 28 peaks were characteristic of Sample A (peak ID [044] Dibutylphthalate, etc.), 23 peaks were characteristic of Sample B ([030] p-isopropenylphenol, [048] Bisphenol A, etc.), and 20 peaks that showed no intensity differences between Sample A and Sample B ([018] phenol, etc.). Additionally, there were 49 peaks observed that were judged to have no statistical reproducibility (gray in volcano plot, "other" in classification results). Dibutylphthalate (DBP) is a phthalate ester that is under a RoHS directive. Bisphenol A was detected in both samples and is a base compound for an epoxy adhesive. However, because it was detected in Sample B at two times stronger intensity than Sample A, it was classified as a peak of difference between the samples.

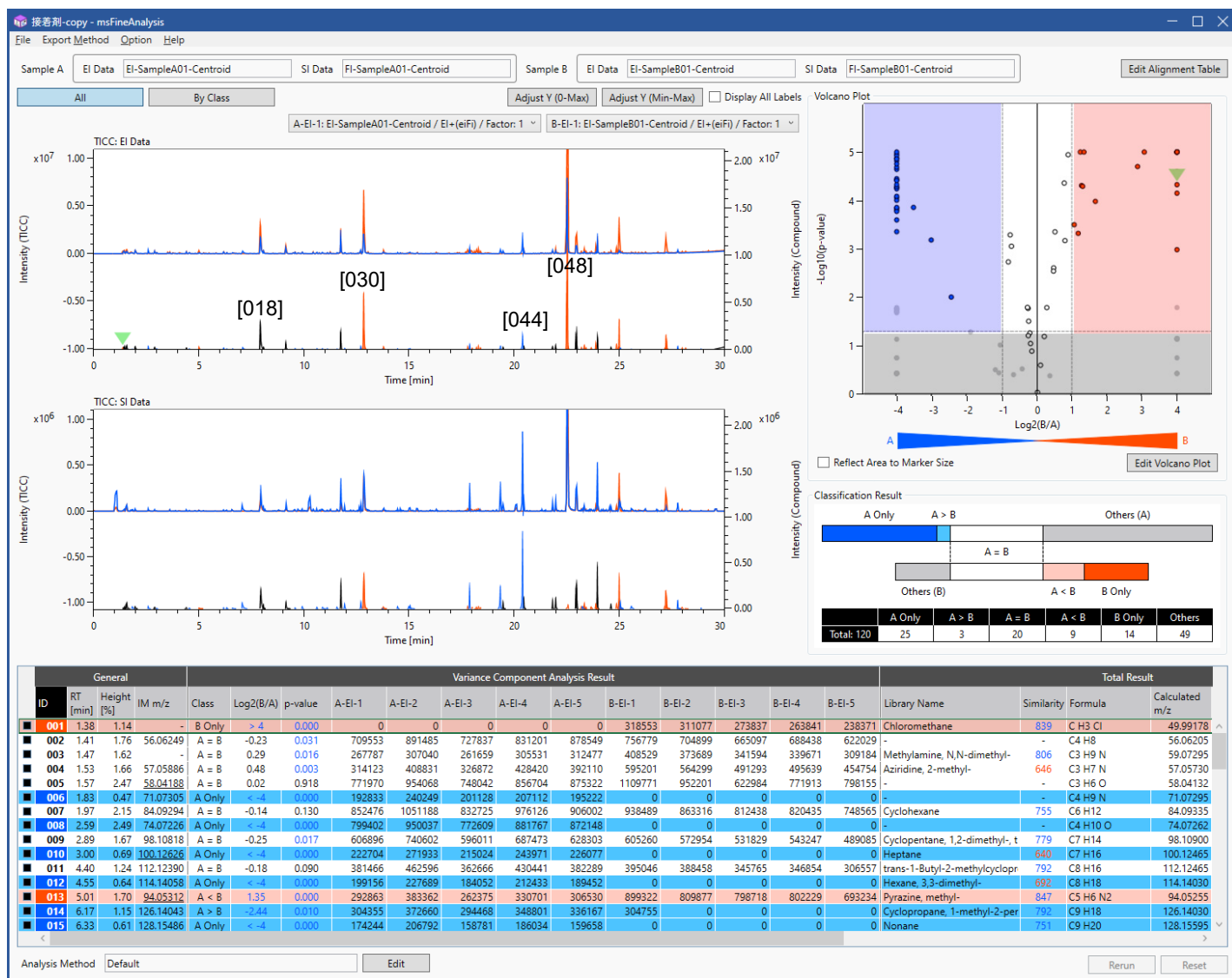


Figure 3. Screenshot of msFineAnalysis (Py-GC-MS)

## Summary

The differential analysis function in MsFineAnalysis Ver3 enabled us to easily acquire information on the difference between two epoxy adhesive samples. Furthermore, these results show that msFineAnalysis enables not only to reduce analysis time due to automation, but also to produce highly-reliable qualitative analysis resulting from peak deconvolution, statistical analysis, and EI/SI integrated analysis.

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## Differential Analysis Function in msFineAnalysis Ver 3 (3): Analysis of Vinyl Acetate Resin by Using Pyrolysis-GC-TOFMS

Related product : Mass Spectrometer(MS)

### Introduction

As the performance of mass spectrometers has improved, the demand for differential analysis of trace components in materials has increased. To address this trend, we have added a new differential analysis function to msFineAnalysis, our automated qualitative analysis software specifically designed for GC-HRTOFMS data. In this work we used msFineAnalysis to compare Vinyl Acetate Resins that were measured by using Pyrolysis (Py)-GC-MS.

### Analysis detail

Two commercially available Vinyl Acetate Resins (adhesives) (A, B) were used as samples. In order to conduct statistical analysis, GC/EI measurements were performed for n=5. As the condition for differential classification, p-value (an index: the smaller the p-value, the higher the statistical reproducibility)  $\leq 5\%$  and fold change (intensity ratio between samples)  $\geq 1.5$  were used to perform differential analysis by using msFineAnalysis. The Table 1 shows the measurements condition details.

**Table 1. Measurement and analysis conditions**

Py-GC-MS			
Pyrolyzer	EGA/PY-3030D (Frontier Laboratories Ltd)	TOFMS	JMS-T200GC (JEOL)
Mode	Single shot	Ionization	EI+:70eV, 300 $\mu$ A FI+: -10kV, 6mA, Carbotec-5 $\mu$ m (CarboTech)
Furnace	600°C	Mass Range	<i>m/z</i> 35-600
Gas Chromatograph	7890A GC (Agilent Technologies, Inc.)	msFineAnalysis	(JEOL)
Mode	Split mode (100:1)	Mode	Variance component analysis
Column	DB-5msUI (Agilent Technologies, Inc.) 15m x 0.25mm, 0.25 $\mu$ m	Number of data	n=5
Oven Temperature	50°C(1min)-30°C/min -330°C(1.7min)	p-value	$\leq 5\%$
Carrier flow	He:1.0mL/min	Fold change	$\geq 1.5$



## Results

Figure 1 shows a screenshot of the differential analysis results for the vinyl acetate resins by using msFineAnalysis. In total, 125 peaks were detected. The breakdown of the differential peaks are: 10 peaks that are characteristic of Sample A (peak ID [024] Diethylene Glycol Dibenzoate, etc.), 15 peaks that are characteristic of Sample B ([016] 2,2,4-Trimethyl-1,3-pentadiol Monoisobutyrate, etc.), and 42 peaks did not show a difference between sample A and B. Additionally, there were 58 peaks that were judged to have no statistical reproducibility (gray in volcano plot, "other" in classification results).

### Chromatogram

Top: GC/EI(TIC/compound peak), Bottom: GI/FI

The color of the compound peak reflects the results of difference judgment

Blue = Strong with Sample A

Red = Strong with Sample B

Yellow = No intensity difference(<2 times)

### Volcano plot

X axis: Log2(fold change) Y axis: -Log10(p-value)

Blue = Strong with Sample A

Red = Strong with Sample B

White = No intensity difference(<2 times)

Gray = Low reproducibility



### Peak List

The color reflects the results of difference judgement

Blue = Strong with Sample A

Red = Strong with Sample B

Note: Only peak of difference are shown.

### Judgement Result

The ones with high reproducibility are classified into

A only, A>B, A=B, A<B, B only.

The ones with low reproducibility are classified into others.

Figure 1. Screenshot of msFineAnalysis

Figure 2 shows a screen shot of individual compound analysis result for peak ID [015]. The first library search candidate (similarity 857) indicated 2,2,4-trimethyl-1,3-pentadioldiisobutyrate ( $C_{16}H_{30}O_4$ ; molecular weight 286). However, since  $m/z$  217 was detected as the base peak in the FI mass spectrum, it was decided that it is more likely the protonated molecule  $[M+H]^+$  for the second candidate (similarity 755) of 2,2,4-trimethyl-1,3-pentadiol Monoisobutyrate ( $C_{12}H_{24}O_3$ ; molecular weight 216). Consequently, the second candidate was selected as the result appropriate choice for the integrated analysis. This example shows that using EI/SI data together, msFineAnalysis makes it possible to obtain highly reliable results.



Figure 2. Screenshot of compound window

## Summary

The differential analysis function of msFineAnalysis Ver3 enabled us to easily obtain the differential information between two Vinyl Acetate samples. Also, because EI and SI data are analyzed together, msFineAnalysis produces highly reliable qualitative analysis results that can be quickly evaluated by the analyst. And finally, this software in combination with GC-HRTOFMS is especially effective for pyrolysis methods in which many of the compounds produced are not registered in library databases.

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## Analyzing a Specific Component using Group Analysis of msFineAnalysis Ver.2 - Integrated Analysis Results of a Vinyl Acetate Resin -

Product: Mass spectrometer (MS)

### [Introduction]

Electron ionization (EI) is a hard ionization method that is commonly used with gas chromatography mass spectrometry (GC-MS). The mass spectral fragmentation patterns produced by EI are used for library database searches to identify compounds. Conversely, soft ionization methods like field ionization (FI) tend to produce clear molecular ions with minimal fragmentation. When high-resolution MS is used with these ionization techniques, the accurate masses for the fragment ions produced by EI and the molecular ions produced by soft ionization provide an additional dimension of information for the analytes. Combining the exact mass information with the results of conventional library search can enhance the accuracy of identification compared to the use of library search alone.

In 2018, we announced the msFineAnalysis software which was designed to automatically integrate two types of data acquired by EI and soft ionization. Recently, we developed msFineAnalysis Version 2, an enhanced version with additional features. msFineAnalysis Version 2 incorporates two new features: Chromatographic Deconvolution and Group Analysis. In this work, we use the group analysis capabilities of the software to evaluate the pyrolysis GC-MS results for a vinyl acetate resin which showed in MSTips No. 275.

### [Software Enhancements]

#### Chromatographic Deconvolution:

The msFineAnalysis Version 2 software supports chromatographic deconvolution to reconstruct mass spectra by using the information (m/z, area) from extracted ion chromatograms (EIC) created using exact mass information. Chromatographic deconvolution is effective in separating coeluting components which are detected as a single peak in the total ion current chromatogram (TICC).

#### Group Analysis:

Group analysis can be used after chromatographic deconvolution to identify compounds that have common substructures. Group analysis is accomplished by creating mass chromatograms from the exact mass data to identify compounds that have the same molecular weight, or that have common fragments or neutral losses. Figure 1 shows the graphical user interface (GUI) for Group analysis.

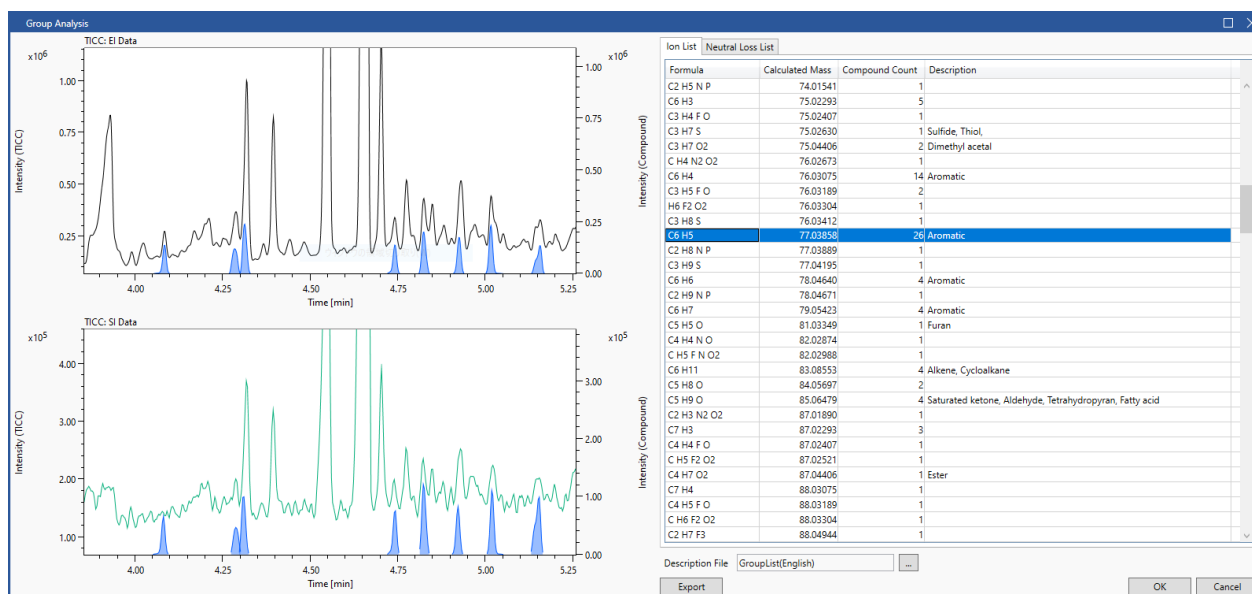


Figure 1. Group Analysis Window

### [Results and Discussion]

Figure 1 shows the  $C_6H_5^+$  fragment ions that were detected in the pyrolysis GC-MS results for the vinyl acetate resin. This fragment ion is characteristic for aromatic compounds. The table on the right shows that there are 26 compounds containing  $C_6H_5^+$ . The view on the left allows the operator to quickly identify where the components containing this ion were detected. The view on the left top shows the GC/EI data with the TICC marked by a solid black line. The bottom left view shows the soft ionization data with the TICC marked by a solid green line. The blue peaks in both views represent the components containing  $C_6H_5^+$  extracted from the chromatographic deconvolution result. The operator can select an ion such as  $C_6H_5^+$  from the table and click the OK button at the bottom right of the GUI to immediately create a  $C_6H_5$  tab, thus allowing for extraction of the components containing that specific fragment (Figure 2).

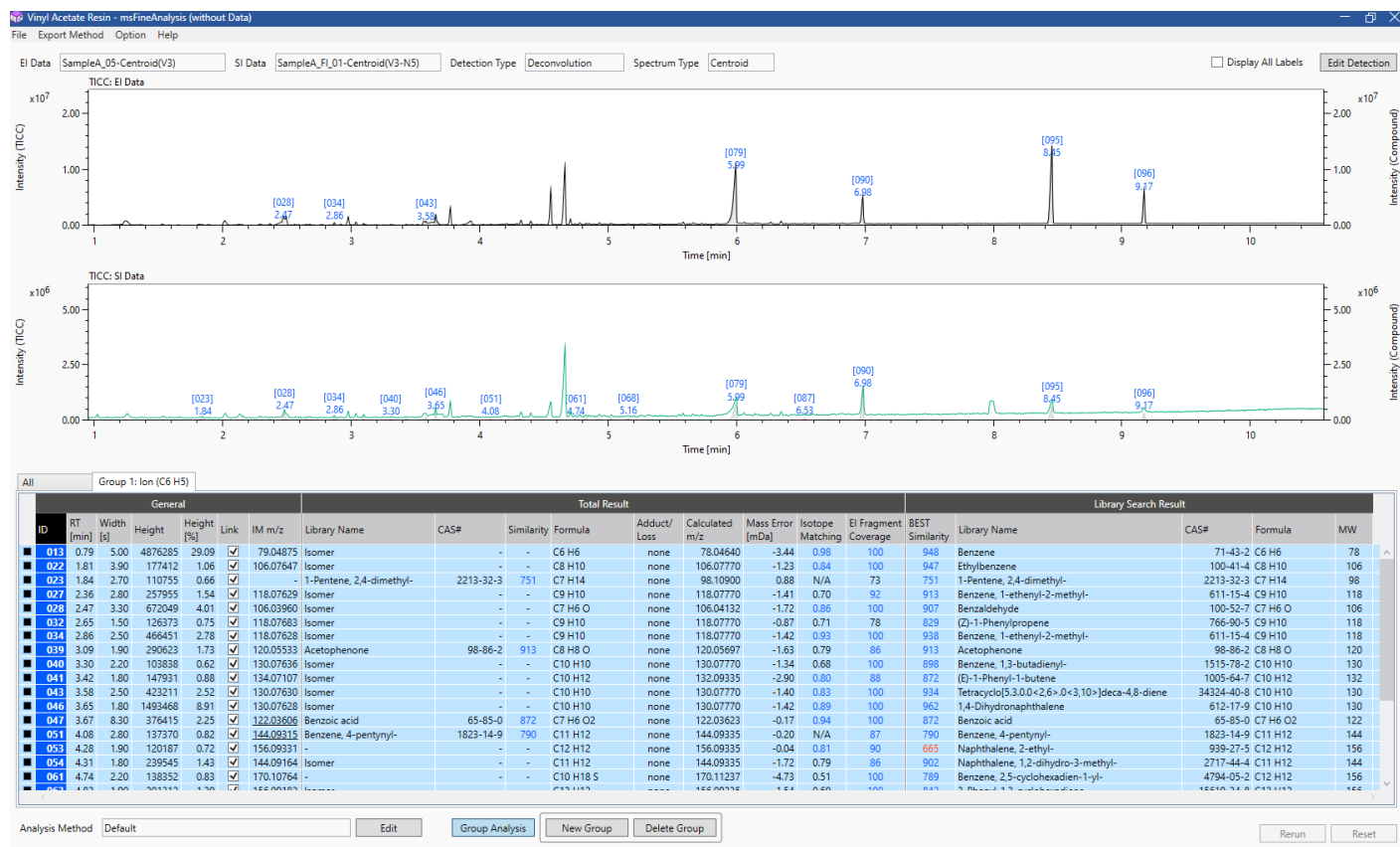
Figure 2. Group analysis results of C<sub>6</sub>H<sub>5</sub><sup>+</sup> ion

Figure 2 shows the extracted results for components containing C<sub>6</sub>H<sub>5</sub><sup>+</sup>. The Group Analysis function displays an “All” tab for the entire analysis results and up to 5 tabs for groups created for ions or neutral losses specified from the exact mass list in Figure 1. For example, the operator can select a fragment ion containing nitrogen, phosphate, or sulfur to find a group of compounds containing the specified elements. The ID and integrated analysis results are then shared between tabs. The results under the C<sub>6</sub>H<sub>5</sub> tab represent a group of aromatic compounds.

## Conclusions

The msFineAnalysis program is designed to run integrated analysis with or without library search. It is a qualitative program based on a new concept that is effective for non-targeted analysis. The basic functions of the program are capable of identifying numerous components for non-targeted analysis. Group Analysis adds the capability to extract specific compounds or families of related compounds in the same manner as target analysis, speeding up the process of their detailed analysis.



## Integrated Analysis of an Acrylic Resin using msFineAnalysis Ver.2

### Product: Mass spectrometer (MS)

#### [General]

Electron ionization (EI) is commonly used in GC-MS systems and produces mass spectra that are characterized by extensive fragmentation. In this case, compounds are typically identified by searching the fragmentation pattern against mass spectral databases. However, molecular ions may be weak or absent in EI mass spectra. Conversely, soft ionization methods such as field ionization (FI), photoionization (PI), and chemical ionization (CI) can provide molecular ions with minimal fragmentation. Furthermore, a high-resolution time-of-flight mass spectrometer (HRTOFMS) can be used to measure the exact masses for both the molecular ions and fragment ions. Combining the exact mass and molecular weight information with the results of a conventional library search can enhance the accuracy of identification when database searches alone are insufficient.

In 2018, msFineAnalysis Ver.1 software was released in which data acquired by EI, soft ionization, and accurate mass measurements were automatically integrated to generate a qualitative report for samples measured by these techniques with GC-MS. Recently, msFineAnalysis Ver.2 was introduced as an enhanced version with additional features. In this work, we will describe the changes in Ver.2, which now includes chromatographic deconvolution, and present applications using the new features.

#### [Software Enhancements]

##### Changes in msFineAnalysis Ver.2:

Version 2 continues to use the integrated analysis work flow (see MS Tips 275) and TICC peak detection developed in Ver.1. Major changes from Version 1 include:

1) Improved graphical user interface (GUI), 2) chromatographic deconvolution, and 3) Group Analysis.

##### 1) Improved GUI:

Version 2 supports two languages: English and Japanese. The GUI was extensively modified to display tabulated integrated analysis results and chromatograms on a single view. Color schemes are now represented by Color Universal Design (CUD) to enhance visibility for people with different kinds of color vision.

##### 2) Chromatographic deconvolution:

Chromatographic deconvolution reconstructs mass spectra by using information ( $m/z$ , area) of peaks detected in extracted ion chromatograms (EIC) using the exact masses of the ions observed. This provides high-quality mass spectra for coeluting components that may appear as a single peak in the total ion current chromatogram (TICC).

##### 3) Group Analysis:

Group analysis identifies related compounds in a complex mixture by creating selected ion chromatograms for compounds that have common fragment ions or common neutral losses. This makes it easier to examine component groups and isomers having a similar partial structure.

#### [Experimental]

A commercial acrylic resin was used as a model sample. A JEOL JMS-T200GC GC-HRTOFMS was used for analysis, and a Frontier Lab pyrolysis inlet was used for sample pretreatment. Additionally, the system was equipped with an EI/FI combination ion source for this work. The resulting data were analyzed by using msFineAnalysis version 2 (JEOL). Table 1 shows the pyrolysis and GC-HRTOFMS analysis conditions.

Table 1. Measuring conditions

<b>[Pyrolysis condition]</b>	
Pyrolyzer	PY-3030D (Frontier Lab)
Pyrolysis Temperature	600°C
<b>[GC Condition]</b>	
Gas Chromatograph	7890A GC (Agilent Technologies)
Column	ZB-5MSi, 30m X 0.25mm, 0.25µm
Oven Temperature	40°C(2min) - 10°C/min - 320°C(15min)
Injection Mode	Split mode (100:1)
<b>[MS condition]</b>	
Spectrometer	JMS-T200GC (JEOL Ltd.)
Ion Source	EI/FI combination ion source
Ionization	EI+ : 70eV, 300µA
	FI+ : -10kV, 40mA/30msec
Mass Range	$m/z$ 35-800
<b>[Data processing condition]</b>	
Software	msFineAnalysis (JEOL Ltd.)
Library database	NIST17
Tolerance	± 5mDa
Electron	Odd
Element set	C:0-50, H: 0-100, O: 0-10



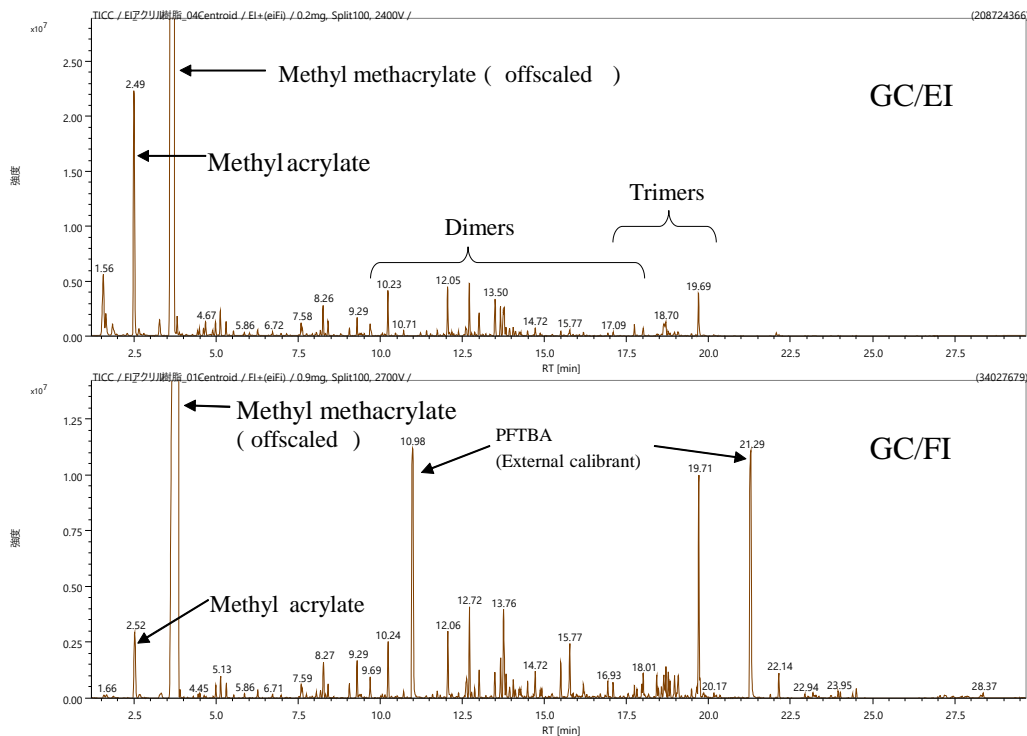


Figure 1. Py-GC/EI and Py-GC/FI total ion current chromatograms of an acrylic resin polymer at 600°C

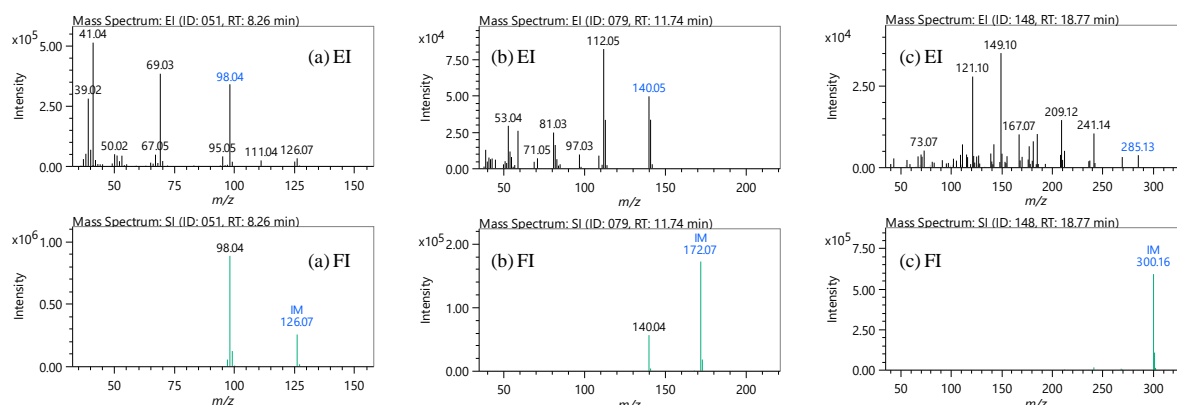


Figure 2. EI and FI mass spectra of related compounds with (a) monomers, (b) dimers, and (c) trimers.

## [Results and Discussion]

Figure 1 shows the TICC data for both GC/EI and GC/FI measurements. Methyl acrylate (MA) and methyl methacrylate (MMA) were detected at high intensity. Dimers and trimers were observed at retention times of 10 min and 18 min, respectively. Figure 2 shows typical mass spectra for the monomers, dimers, and trimers. Molecular ions were detected at high relative intensity in FI mass spectra but were weak or absent in the EI mass spectra. Many of the acrylic resin pyrolysates do not have entries in the library database, making it difficult to identify their components by library search alone. Additionally, soft ionization was essential because EI did not produce molecular ions for many compounds as shown in Figure 2b and 2c.

When the msFineAnalysis Auto Analysis was used on for the GC/EI and GC/FI data, 161 components were automatically detected. Ultimately, molecular formulas of 154 components out of the 161 were uniquely identified. Additionally, the formulas of EI fragment ions, which were obtained from accurate mass data, resulted in structural information for the sample molecules. Next, monomers, dimers, and trimers were examined using Group Analysis—the results are shown in Table 2. Out of the 161 components, 46 were directly related to the monomers, dimers, and trimers. In Group Analysis, molecular ions of a desired repeat unit formula are specified and analyzed, speeding up the analysis process. The results for the Group Analysis can be exported, making it easier to calculate the relative intensities using the sum of the chromatogram peak areas shown in Table 2. Other components detected include pyrolysis products in which alkyl chains are bonded with monomers, dimers, and trimers.

## [Conclusions]

The integrated analysis method produces highly accurate qualitative analysis results from the database entries with high match scores by combining the library search results and molecular formula estimation. Additionally, this analysis makes it possible to determine molecular formulas for unknown components not registered in a library database that cannot be identified by database searching alone. The integrated analysis method made it possible to determine molecular formulas from exact mass results, regardless of the level of match factor score. This narrowed down the candidate compositions, demonstrating the effectiveness of this software for GC/MS qualitative analysis.

Table 2. Integrated qualitative analysis results for monomers, dimers, trimers and their isomers.

Type	Compound	Formula	Mw	Isomer	Sum of chromatogram peak area	Relative Intensity [%]
Monomer	Methyl acrylate (MA)	$C_4H_6O_2$	86	2	55,268,874	5.8
	Methyl methacrylate (MMA)	$C_5H_8O_2$	100	3	837,060,254	88.0
Dimer	MA + MA	$C_8H_{12}O_4$	172	3	1,620,349	0.2
	MA + MMA	$C_9H_{14}O_4$	186	5	11,853,421	1.2
	MMA + MMA	$C_{10}H_{16}O_4$	200	11	23,475,603	2.5
Trimer	MA + MA + MA	$C_{12}H_{18}O_6$	258	3	1,181,635	0.1
	MA + MA + MMA	$C_{13}H_{20}O_6$	272	6	7,004,668	0.7
	MA + MMA + MMA	$C_{14}H_{22}O_6$	286	9	5,205,642	0.5
	MMA + MMA + MMA	$C_{15}H_{24}O_6$	300	4	9,045,242	1.0

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# Comprehensive Analysis + Unknown Component Analysis of Vinyl Acetate Resins Using Pyrolysis GC-MS

## Characteristic Component Extraction by Multiple Classification PCA and Component Identification by High Resolution MS -

Product used : Mass Spectrometer (MS)

### [General]

Advances in mass spectrometry are enabling analysis of micro samples and unknown components that were not observable before. As the volume of information acquired from mass spectrometry increases, researchers are calling for simple techniques to analyze numerous components observed, and as a result, there is a rise in demand for comprehensive analytical techniques including multiple classification analysis.

In this work, we will introduce a new technique for non-target analysis, which combines comprehensive analysis using high resolution GC-TOFMS and unknown component analysis using soft ionization.

### [Method]

As model samples, 6 commercial vinyl acetate resins (adhesives) were used. A gas chromatography time-of-flight mass spectrometer (GC-TOFMS) was used for measurement. Since emulsion samples including adhesives are difficult to analyze without preliminary treatment, the samples were subjected to pyrolysis.

The resulting data was analyzed by AnalyzePro (SpectralWorks) to compare multiple samples by PCA.

### [Results]

A total of 6 vinyl acetate resin samples were analyzed by pyrolysis GC-EI TOFMS ( $n=3$ ), and the resulting data was subjected to PCA by AnalyzerPro. The PCA score plot (Figure 1) shows that sample E was clearly separated at the 1<sup>st</sup> principal component axis and sample B at the 2<sup>nd</sup> principal component axis, respectively. Components contributing to each principal component were easily detected in the loading plot.

Among the components contributing to the separation at the secondary principal component axis (positive side), that is, characteristic components of sample B, the component at R.T. 4.55 min was analyzed in detail (data on the right side of Figure 2).

The NIST library search estimated that the component at R.T. 4.55 min was likely to be 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate (molecular weight 286) with a match factor of 813. However, the FI mass spectrum of this component detected a base peak at  $m/z$  217, and as a result, the molecular weight estimated in NIST library search differed significantly from the molecular weight estimated from the results of FI ionization. While the chemical structure of 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate contains an ester group, FI ionization detected no ion that has an  $m/z$  equal to that. Ester group containing compounds are generally known to produce protonated molecules by FI ionization. Thus, it is likely that the component at R.T. 4.55 min is not the component estimated in NIST library search but is another component having a similar EI spectrum. Figure 3 shows the mass spectra of the component at R.T. 4.55 min acquired by EI and FI. Figure 4 shows the structural formula of 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate. After examining the EI and FI data in detail, it was estimated that the component at R.T. 4.55 min has the structure shown in Figure 5. None of the major libraries provided by NIST included a component equal to this structure.

PCA is an effective and efficient technique for the comprehensive analysis of GC-TOFMS data. Specifically, for multiple sample comparisons, use of score and loading plots makes it possible to examine the similarities between the samples and the characteristic components of each sample. Also, while the NIST library search is a powerful tool for identifying characteristic components of samples, combining NIST library searches with molecular weight information acquired by soft ionization such as FI makes it possible to identify components with a higher level of accuracy, preventing false identifications.

Table 1. Measurement Conditions

### [Py-GC-TOFMS Conditions]

System	JMS-T200GC (JEOL)
Pyrolysis temp.	600°C
Ionization mode	EI+: 70 eV, 300 $\mu$ A FI+: -10 kV, 6 mA (Carbotec 5 $\mu$ m)
GC column	DB-5msUI (Agilent), 15 m x 0.25 mm, 0.25 $\mu$ m
Oven temp.	50°C (1 min)→30°C/min →330°C (1.7 min)
Inlet temperature	300°C
Inlet mode	Split 100:1
He flow	1.0 mL/min (Constant Flow)
$m/z$ range	$m/z$ 35-650
Spectrum recording speed	0.1 sec
Software	AnalyzerPro (SpectralWork)

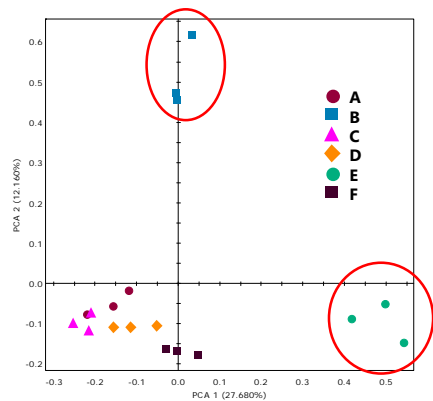


Figure 1. PCA score plot of polyvinyl acetate samples

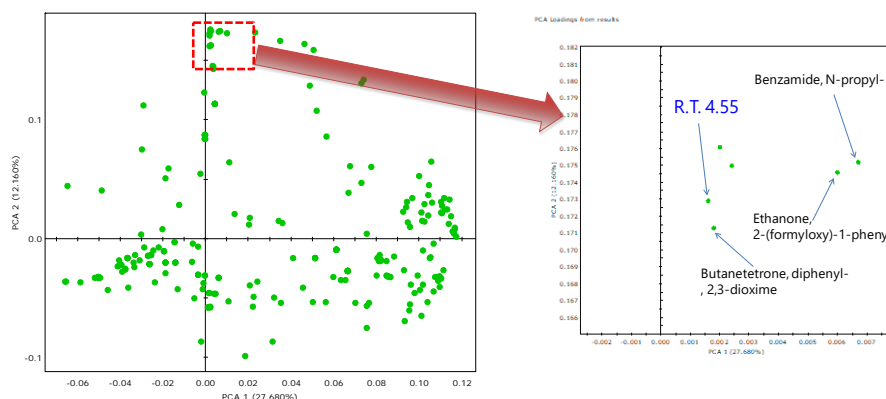
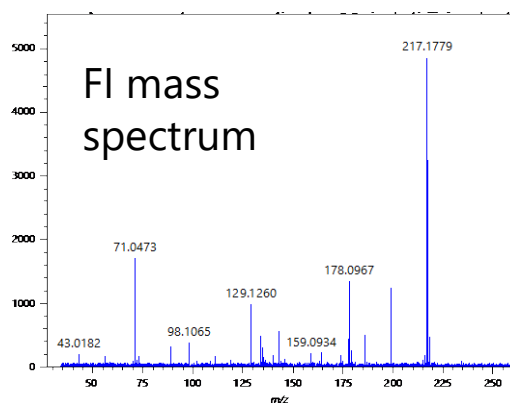
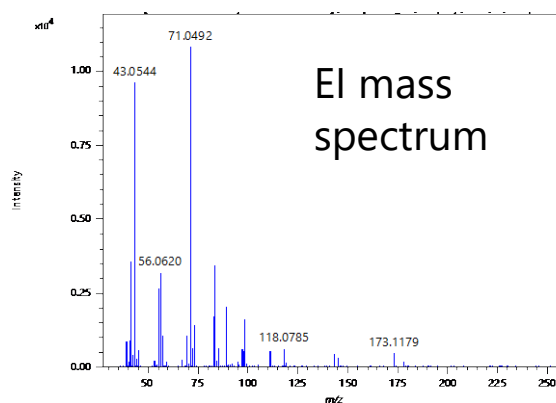


Figure 2. PCA loading plot of polyvinyl acetate samples



Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
217.178	C12 H25 O3	217.1798	-1.8	0.5



Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
43.0544	C3 H7	43.0542	0.2	0.5
56.0622	C4 H8	56.0621	0.1	1.0
71.0493	C4 H7 O	71.0491	0.2	1.5
83.0858	C6 H11	83.0855	0.3	1.5
89.0596	C4 H9 O2	89.0597	-0.1	0.5
98.1091	C7 H14	98.1090	0.1	1.0
111.1177	C8 H15	111.1168	0.9	1.5
143.1096	C8 H15 O2	143.1067	2.9	1.5
145.1246	C8 H17 O2	145.1223	2.3	0.5
173.1189	C9 H17 O3	173.1172	1.7	1.5

Figure 3. EI and FI mass spectra and exact mass analysis results for the unknown component (R.T. 4.55 min) in sample B

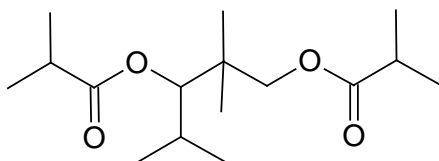


Figure 4. Structural formula of 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

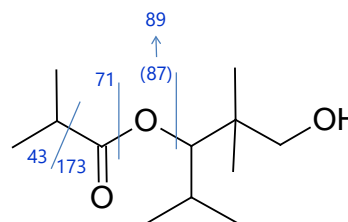


Figure 5. Estimated structural formula for the unknown component (R.T. 4.55 min) in sample B

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## Identification and distribution analysis of additives in a molded nitrile rubber (NBR) by PY/GC×GC/HRTOFMS

Product used : Mass Spectrometer (MS)

### Introduction

The characteristics of polymeric materials vary depending on the additives. Consequently, a variety of additives can be added into the raw polymer resin in order to achieve the required characteristics for the product. GC/MS combined with pyrolyzer system (PY/GC/MS) is used as typical analytical method for polymeric material. However PY/GC/MS is often insufficient chromatographic separation of additives and thermal decomposition compounds. And sometimes it is difficult to assign compound identities because of poor chromatographic separation. The comprehensive two-dimensional gas chromatography/high resolution time-of-flight mass spectrometry (GC×GC/HRTOFMS) is known as the technique that can be take high chromatographic separation by two different polarity GC columns and can be take accurate mass measurements used to estimate elemental compositions. It means that the GC×GC/HRTOFMS combined with PY system has a possibility to take the more detail and accurate information about polymeric materials than conventional PY/GC/MS system.

In this application note, we identified the additives and their distribution within a commercially available molded polymer by using GC×GC/HRTOFMS with pyrolysis (PY/GC×GC/HRTOFMS).

### Experimental

Commercially available X-ring rubber band made of NBR was applied the measurement as test sample. A 0.5mg portion of the X-ring sliced at 1mm thickness was directly measured using PY/GC×GC/HRTOFMS system without any sample preparation. JMS-T200GC "AccuTOF™ GCv 4G" as HRTOFMS, KT2006(ZOEX Corporation) as GC×GC and PY-2020iD(Frontier Laboratories Ltd.) as pyrolyzer are used for the analysis. The details of measurement conditions for each equipment were summarized in Table 1.

Table 1. Measurement Conditions

<b>Instrument</b>	JMS-T100GCV "AccuTOF™ GCv4G" (JEOL Ltd.) KT2006 (GC×GC module , ZOEX corporation) PY-2020iD (Frontier Laboratories Ltd.)
<b>Pyrolysis conditions</b>	
PY temp.	600°C
PY-GC-ITF temp.	350°C
<b>GC×GC conditions</b>	
Inlet temp.	350°C
Inlet mode	Split mode (200 : 1)
1 <sup>st</sup> Column	BPX-5 (30m x 0.25 mm, film thickness 0.25 μm, Trajan SGE)
2 <sup>nd</sup> Column	BPX-50 (2m x 0.1 mm, film thickness 0.1μm, Trajan SGE)
Oven temp. program	50°C (3min) → 5°C/min → 360°C (3min)
Carrier gas flow	1.33mL/min (He, Constant flow)
Modulation period	10 sec
<b>MS conditions</b>	
Ionization mode	EI (+) : 70eV, 300μA, FI (+) : -10kV, Carbon emitter
Interface temp.	300°C
Ion source temp.	EI : 280°C, FI : OFF
Spectrum recording interval	50Hz (0.02sec/spectrum)
<i>m/z</i> range	30 – 600
Drift compensation	<i>m/z</i> 207.0329 (C <sub>7</sub> H <sub>21</sub> O <sub>4</sub> Si <sub>4</sub> )

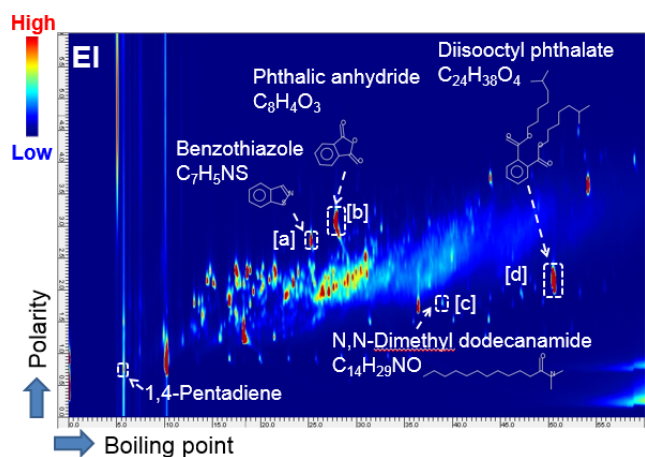


Fig. 1 2D map (EI, TICC) for x-ring

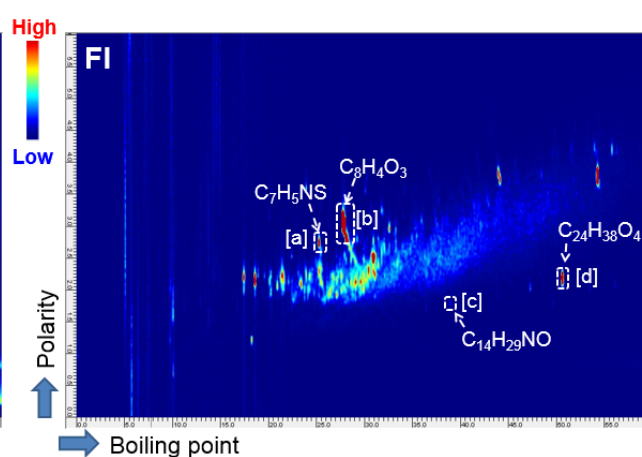


Fig. 2 2D map (FI, TICC) for x-ring

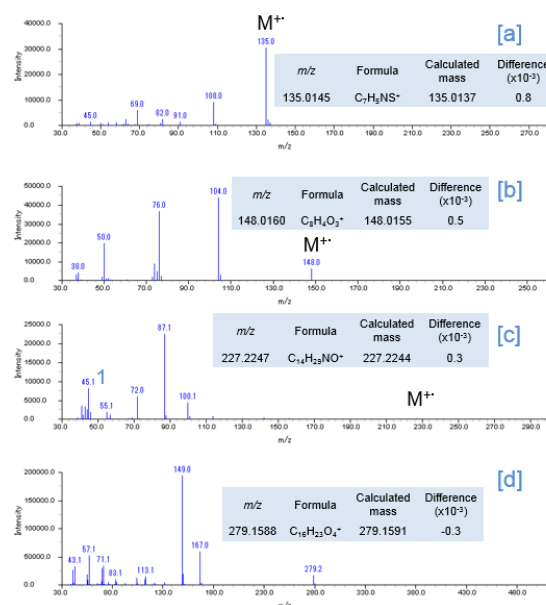


Fig. 3 EI Mass spectra

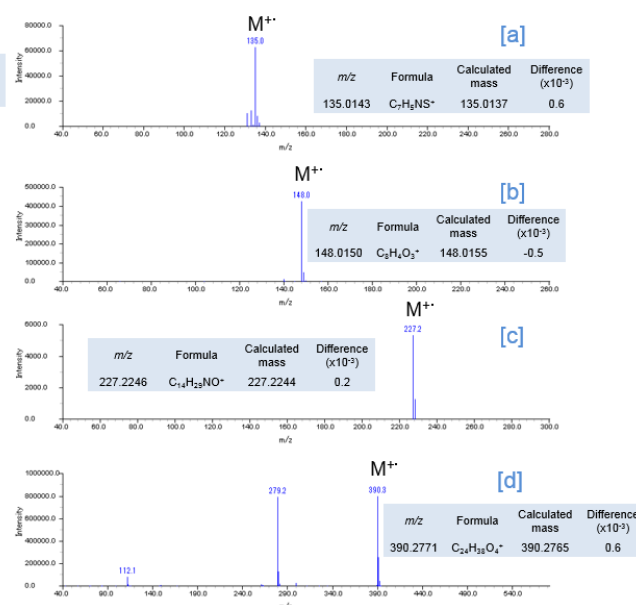


Fig. 4 FI Mass spectra

## Results

The 2D Total ion current chromatogram (TICC) maps of the sample by using EI and FI are shown in Figures 1 and 2, respectively. The horizontal axis indicates boiling point separation and the vertical axis shows polarity chromatographic separation. The mass spectra from the region of [a], [b], [c] and [d] on the each 2D maps were shown in Figure 3 and 4, respectively. The compounds eluted at the region from [a] to [d] were assigned as the additives benzothiazole (Fig. 3 [a]), phthalic anhydride (Fig. 3 [b]), N,N-dimethyl dodecanamide (Fig. 3 [c]) and diisooctyl phthalate (Fig. 3 [d]) in the results by using a NIST library search of the EI spectra. It should be noted here that when a single GC column is used, the identification of benzothiazole is very difficult because this compound completely coelutes with an NBR thermal decomposition compound. To further complicate this situation, the abundance of this compound is very low relative to the interfering thermal decomposition product. However, the benzothiazole was easily separated chromatographically by the addition of a 2nd column (GCxGC conditions). The EI spectrum of diisooctyl phthalate showed only fragment ions (Fig. 3[d]). On the other hand, the FI spectrum showed the molecular ion with a relatively high intensity (Fig. 4[d]) which allowed for the estimation of its elemental composition. The composition result was consistent with the library search result by EI. Furthermore, the results of the elemental composition estimations for the fragment ions by EI were also consistent with the assigned composition of the molecular ion.

## Conclusion

The additives such as benzothiazole in the polymer material were easily separated chromatographically by the GCxGC technique. Verification of library search of the EI mass spectra and the elemental composition estimation for the molecular ion by FI mass spectra were effective for the qualitative identification of the additives. Reliable qualitative analysis for the additives in the polymer material is confirmed by PY/GCxGC/HRTOFMS.



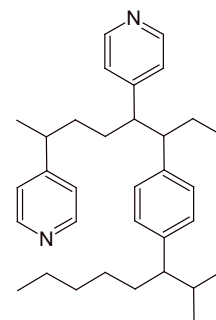
## Ion Exchange Resin Analysis by using Pyrolysis-GCxGC-MS

Product used : Mass Spectrometer (MS)

### 【Introduction】

Recently, we developed a new gas chromatography/high resolution time-of-flight mass spectrometer (GC/HR-TOFMS) system which allows using multiple ionization techniques not only electron ionization (EI) but also field ionization (FI) and photo ionization (PI). PI is a soft ionization technique that provides high sensitivity and molecular ion information for compounds with ionization energies below the maximum practical photon energy (10.8 eV) of the deuterium lamp used in our current design.

In this study, pyrolysis(Py)/GCxGC/HR-TOFMS system was applied to investigate the pyrolysis products of Vinylpyridine and Divinylbenzene copolymer as the ion exchange resin sample.



Vinylpyridine and Divinylbenzene copolymer structure

### 【Result and discussion】

To evaluate the potential of Py/GCxGC technique, we compared the chromatographic peak separation between regular 1DGC and 2DGC. In the 1DGC data, a lot of co-elute components were observed and they were difficult to identify clearly. In 2DGC data, these compounds were separated with 2nd GC dimensions and we observed approximately 600 compounds. Chromatographic peaks of the pyrolysis products were distributed on the TIC chromatogram according to monomer, dimer and trimer regionally.

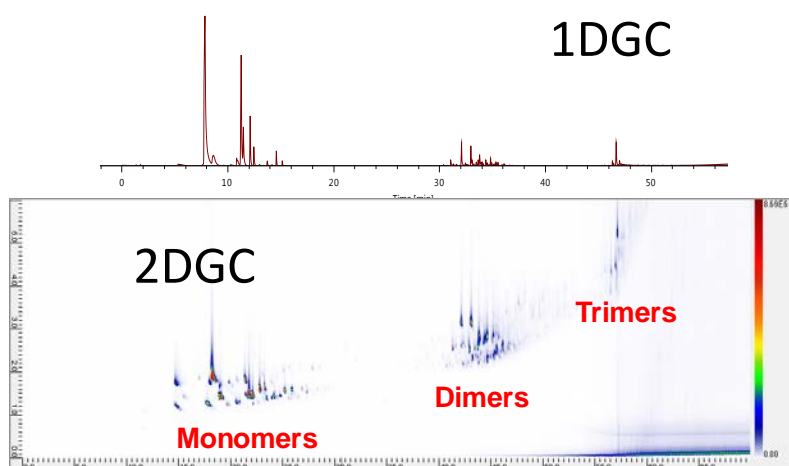


Fig.1 Comparison of the 1DGC and 2DGC TICs

Table 1 Measurement condition

#### 【Pyrolysis condition】

Pyrolysis Temp.: 450 °C

#### 【GCxGC condition】

1st column: Trajan SGE BPX5,  
30m x 0.25mm, 0.25um  
2nd column: Trajan SGE BPX50,  
2m x 0.1mm, 0.1um

Oven temp.:  
50 °C (3 min) -> [5 °C/min]  
-> 320 °C (13 min)

Inj. Temp.: 300 °C  
Inj. Mode: Split mode (200:1)  
Column flow: 1.2 mL/min  
Modulation period: 6 sec

#### 【MS condition】

MS: JEOL, JMS-T200GC  
Ion source: EI/PI combination ion source  
Ionization: EI+, 70 eV, 300 uA  
PI+, D2 lamp: 115-400 nm  
(10.8 eV@115 nm)  
Mass range: *m/z* 40-600



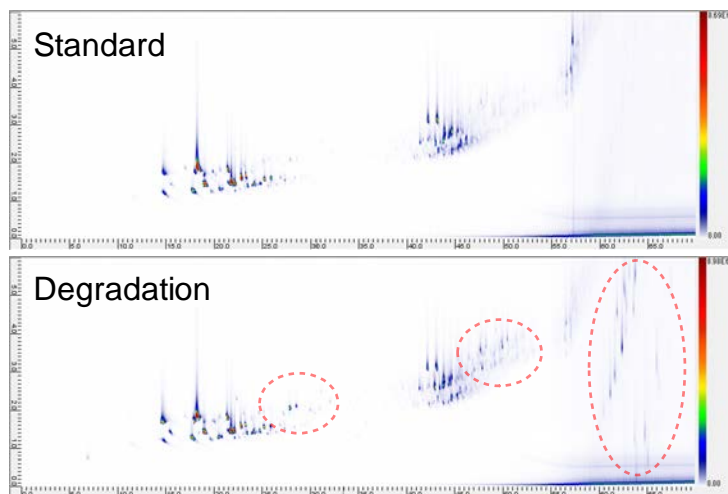


Fig. 2 Comparison of the 2DGC TICCs

In the after degradation sample, many compound were detected higher relative intensity in the longer 1st column retention time. We suspect that un-stable end group copolymers were generated by the thermal degradation under non oxidative condition at 200 °C, and then these compounds were generated from these un-stable end group copolymers.

In the monomer region, we found the Di-alkyl benzene series, Vinyl benzene series and Pyridine series were separated clearly. In the dimer and trimer regions, so many compounds were detected, but they were very difficult to identify by using NIST EI database search only. In this case, we estimated these chemical formulas for the molecular ion detected in PI mass spectra which give molecular ion information mainly as a result of soft ionization technique.

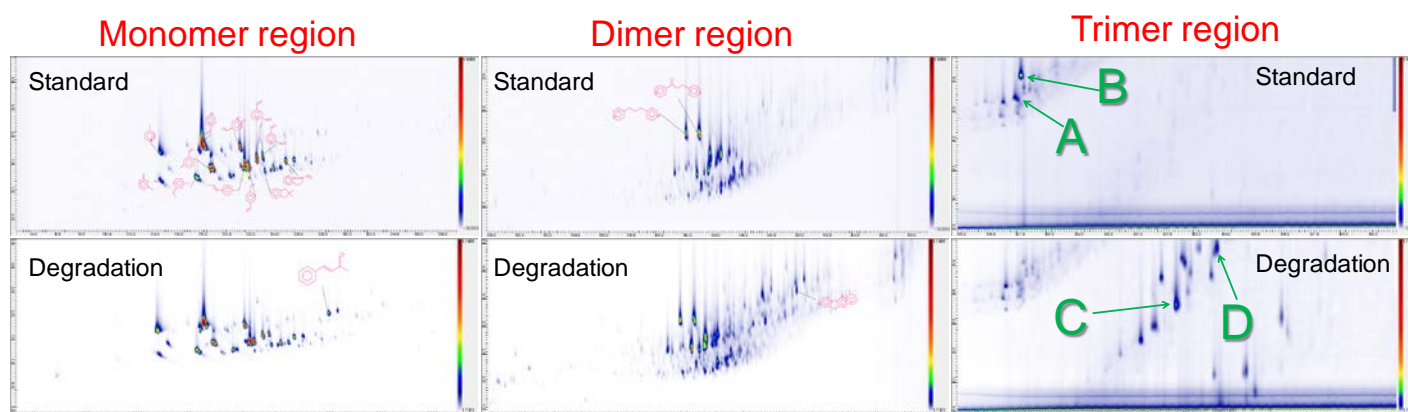


Fig. 3 GCxGC/EI qualitative analysis result

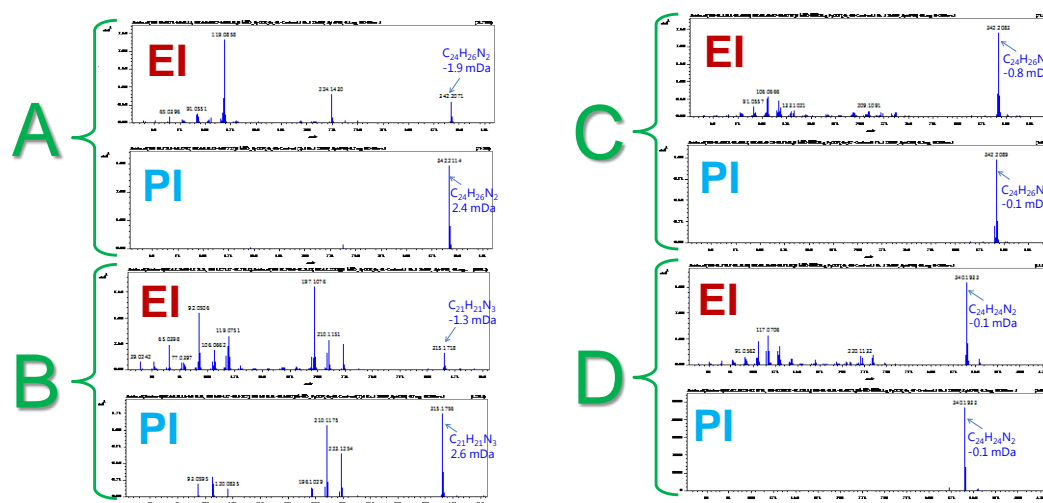


Fig.4 Mass spectra and accurate mass analysis for the compound A, B, C and D on the 2DGC TICC.

## 【Conclusion】

- ❑ GCxGC TIC give an easy interpretation for the differences between standard and degradation sample.
- ❑ EI database search is still first step for the GC/MS qualitative analysis.
- ❑ Soft ionizations and accurate mass analysis is useful for the compound identification.

The combination of PY/GCxGC/HRTOFMS and multiple ionization technique is a quite useful for qualitative analysis of the pyrolysis products of resins.

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## Ethylene Propylene Diene Monomer Rubber Analysis by using Pyrolysis-GCxGC-MS

Product used : Mass Spectrometer (MS)

### 【Introduction】

Recently, we developed a new gas chromatography/high resolution time-of-flight mass spectrometer (GC/HR-TOFMS) system which allows using multiple ionization techniques not only electron ionization (EI) but also field ionization (FI) and photo ionization (PI).

FI is a soft ionization technique that is well suited for hydrocarbons analysis because it generates molecular ions with minimal fragmentation for all compounds, including saturated hydrocarbons. PI is an also soft ionization technique that provides high sensitivity and molecular ion information for compounds with ionization energies below the maximum practical photon energy (10.8 eV) of the deuterium lamp used in our current design.

In this study, pyrolysis(Py)/GCxGC/HR-TOFMS system was applied to investigate the pyrolysis products of Ethylene-propylene–diene rubber (EPDM).

### 【Result and discussion】

To evaluate the potential of Py/GCxGC, we compared the chromatographic peak separation between regular 1DGC and 2DGC (Fig.1) measured by EI. In the 1DGC data, a lot of co-elute components were observed and they were difficult to identify clearly. In the 2DGC data, these compounds were separated with 2nd GC dimensions and we observed approximately 1,023 compounds in the EPDM sample using an automatic peak search function for the GCxGC/EI data.

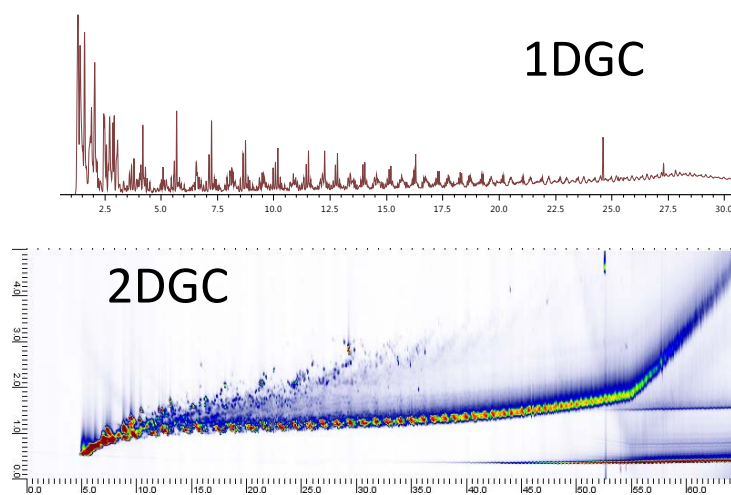


Fig.1 Comparison of the 1DGC and 2DGC TICs

Table 1 Measurement condition

#### 【Pyrolysis condition】

Pyrolysis Temp.: 650 °C

#### 【GCxGC condition】

1<sup>st</sup> column: BPX5(SGE), 30m x 0.25mm, 0.25μm

2<sup>nd</sup> column: BPX50(SGE), 2m x 0.1mm, 0.1μm

Oven temp.: 50 °C (1 min) -> [5 °C/min]

-> 320 °C (10 min)

Inj. Temp.: 300 °C

Inj. Mode: Split mode (100:1)

Column flow: 1.8 mL/min

Modulation period: 5 sec

#### 【MS condition】

Ion source: EI/PI combination ion source

EI/FI combination ion source

Ionization: EI+, 70 eV, 300 uA

PI+, D<sub>2</sub> lamp: 115-400 nm  
(10.8 eV@115 nm)

FI+, -10kV, 8mA/10msec

Mass range: *m/z* 35-650

We got excellent chromatographic separations not only EI method but also soft ionization methods, PI and FI (Fig.2). We identified pyrolysis products using NIST EI database search (Fig.3).

On the other hand, there were many un-known components which cannot be identified using EI database with lower match factor. In this case, we estimated these chemical formulas from the accurate *m/z* values of these molecular ions in FI and PI mass spectra. For example, we showed accurate mass analysis about compound A. We got 6 candidate for the molecule formula. The measured *m/z* and isotopic pattern is most similar with C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>. So, we suspected that this compounds is Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline which is used as **Rubber Antioxidant TMQ**



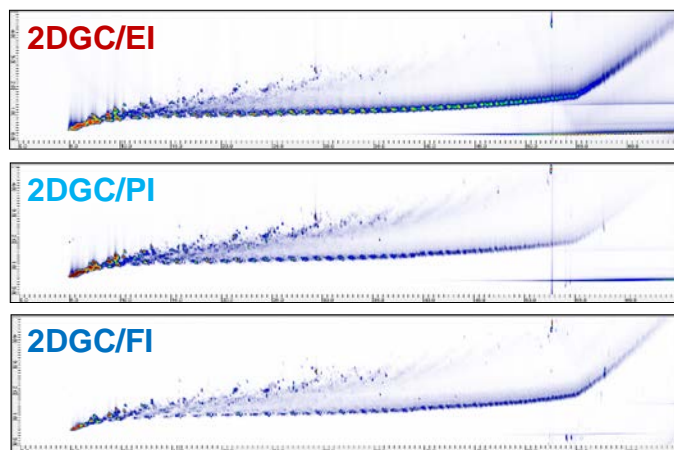


Fig. 2 GCxGC/EI, PI and FI TICCs

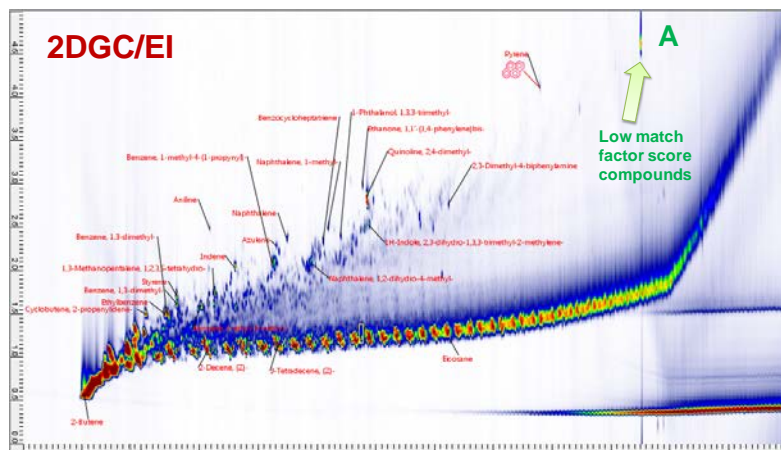


Fig. 3 GCxGC/EI qualitative analysis result

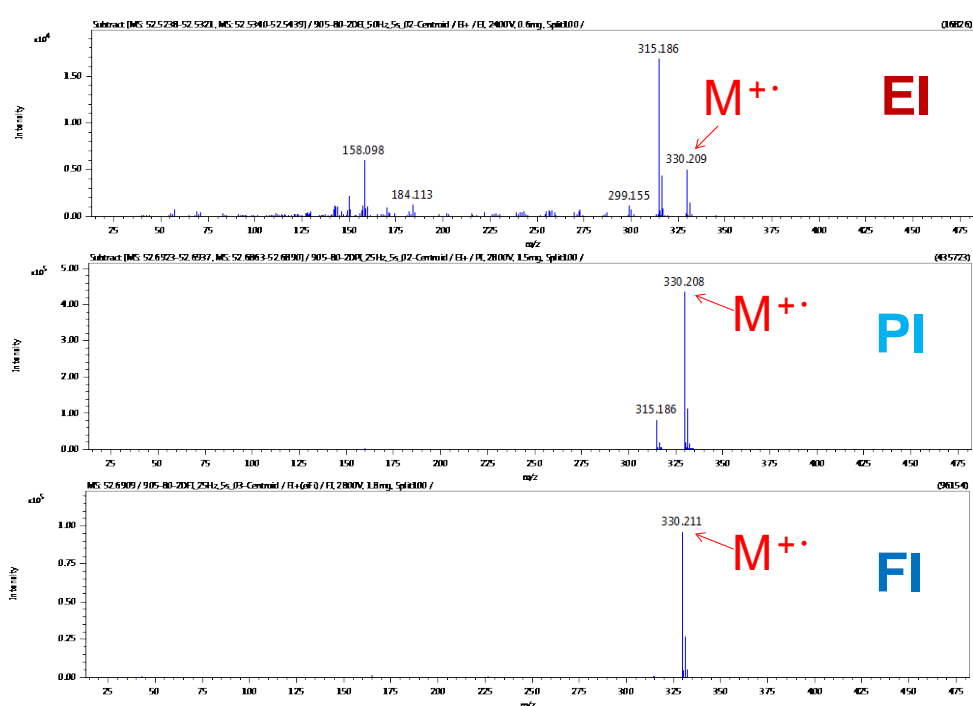


Fig. 4 Mass spectra and accurate mass analysis for the compound A on the 2DGC TICC.

Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
77.0395	C6 H5	77.0386	1.0	4.5
91.0554	C7 H7	91.0542	1.2	4.5
115.0548	C9 H7	115.0542	0.6	6.5
143.0740	C10 H9 N	143.0730	1.0	7
158.0975	C11 H12 N	158.0964	1.1	6.5
184.1133	C13 H14 N	184.1121	1.2	7.5
222.1287	C16 H16 N	222.1277	0.9	9.5
299.1546	C21 H19 N2	299.1543	0.3	13.5
315.1855	C22 H23 N2	315.1856	-0.1	12.5
330.2088	C23 H26 N2	330.2091	-0.3	12

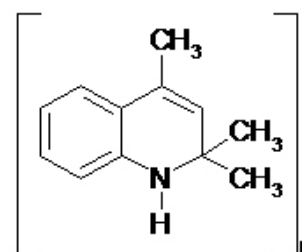
Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
315.1860	C22 H23 N2	315.1856	0.4	12.5
330.2085	C23 H26 N2	330.2091	-0.6	12

Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
330.2111	C23 H26 N2	330.2091	2.1	12

### 【Conclusion】

- We can get excellent GCxGC separations for EI and soft ionizations, PI and FI.
- EI database search is still first step for the GC/MS qualitative analysis.
- Soft ionizations and accurate mass analysis is useful for the compound identification.

The combination of PY/GCxGC/HRTOFMS and multiple ionization technique is a quite useful for qualitative analysis of the pyrolysis products of rubbers.



TMQ



## Natural Polymer Analysis by using Pyrolysis-GCxGC-MS —“Urushi” analysis with GCxGC/EI and GCxGC/PI—

Product used : Mass Spectrometer (MS)

### 【Introduction】

A Japanese lacquer film called “Urushi” is a natural polymer that has been used as a paint and adhesive for living-wares and craft-wares for approximately 8,000 years. “Urushi” has a complex structure that researchers are trying to understand using pyrolysis-gas chromatograph/mass spectrometer (Py/GC/MS) system. Recently, we developed a new gas chromatograph/high resolution time-of-flight mass spectrometer (GC/HR-TOFMS) system that can be used for comprehensive two-dimensional GC (GCxGC) measurements. Additionally, we have developed a unique combination electron ionization/photoionization (EI/PI) ion source that can be used with this GC/HR-TOFMS system. In this work, we measured “Urushi” samples using this unique Py/GCxGC/HR-TOFMS system in combination with our new combination EI/PI ion source.

### 【Result and discussion】

In this study, we initially checked the thermal decomposition temperature for the Japanese lacquer film. Urushiols were observed as the main component in the lacquer film at 400 °C. However, the thermal decomposition components indicating the lacquer film were observed at much higher levels at 500 °C. As a result, we decided to use 500 °C as the decomposition temperature for the GCxGC/EI and GCxGC/PI measurements.

GCxGC is a powerful chromatographic separation technique that provides both boiling point and polar separations simultaneously during a single sample measurement. We detected main components “Urushiols” in both EI and PI data. We also observed approximately 1,000 compounds in the lacquer sample using an automatic peak search function for the GCxGC/EI data. Additionally, this data showed several easily identifiable compound series such as hydrocarbons, carboxylic acids, aromatic ketones, alkyl phenols.

A 2-dimensional extracted ion chromatogram (GCxGC EIC) was constructed for  $m/z$  123.044 ( $C_7H_7O_2$ ), which is a common fragment ion for the alkyl catechols ( $R-C_6H_3(OH)_2$ ). This 2D-EIC allowed us to easily identify two series of compounds that included the Alkyl catechols and Alkyl orcinols. In past research, only the 3-saturated alkyl catechols were focused upon during the analyses as the main thermal decomposition compounds for the lacquer film. The Alkyl orcinols were minor components that would co-elute with the 3-saturated alkyl catechols using a regular 1D GC. These compound series have different polarity characteristics so they are separated by the 2<sup>nd</sup> GC column. Consequently, the GCxGC technique allowed us to easily separate these characteristic compounds from each other.

We also checked PI mass spectra for the main components, i.e., 3-Pentadecyl catechol and 3-Pentadecenyl catechol. The PI mass spectra showed molecular ions for many of the compounds in the sample. PI is a much softer ionization method, so it can be used to obtain molecular ion information for target compound analyses.

1. The Py/GCxGC/HRTOFMS system was easily able to separate Alkyl catechols and Alkyl phenols which are important characteristics components for the lacquer film research by using 2D-EIC with common fragment ions.
2. We detected main components “Urushiols” in both EI and PI data. And we got excellent mass accuracy for those molecular ions in EI/PI data.
3. PI is a soft ionization technique that can be used for hydrocarbons analysis because it generates molecular ions for hydrocarbons

Table 1 Measurement condition

#### 【Py-GCxGC-TOFMS condition】

System	JMS-T200GC (JEOL)
Pyrolysis temp.	500°C
Ionization mode	EI+: 70eV, 300μA PI+: D <sub>2</sub> lamp: 115 - 400 nm (10.8eV@115nm)
GC column	1 <sup>st</sup> : BPX5 (SGE), 30m x 0.25mm, 0.25μm 2 <sup>nd</sup> : BPX50 (SGE), 3m x 0.1mm, 0.1μm
Modulation period	8sec
Oven temp.	50C°(1min)->3C° /min- >300C°(6min)
Inlet temp.	300°C
Inlet mode	Split50:1
He flow	1.5mL/min (Constant Flow)
$m/z$ range	$m/z$ 35-650
Recording interval	EI: 50Hz, PI: 25Hz



**GC-TOFMS:**  
**JMS-T200GC**  
**“AccuTOF™ GCx”**

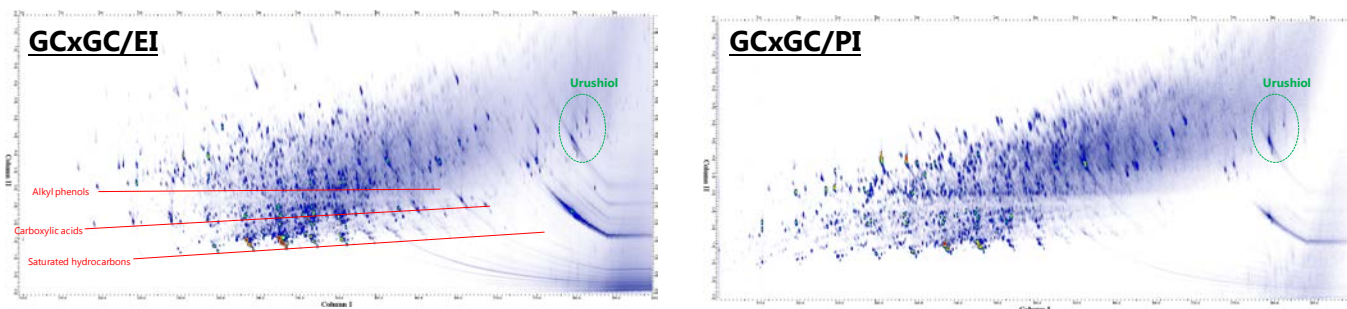


Fig. 1 GCxGC/EI and PI TIC chromatograms

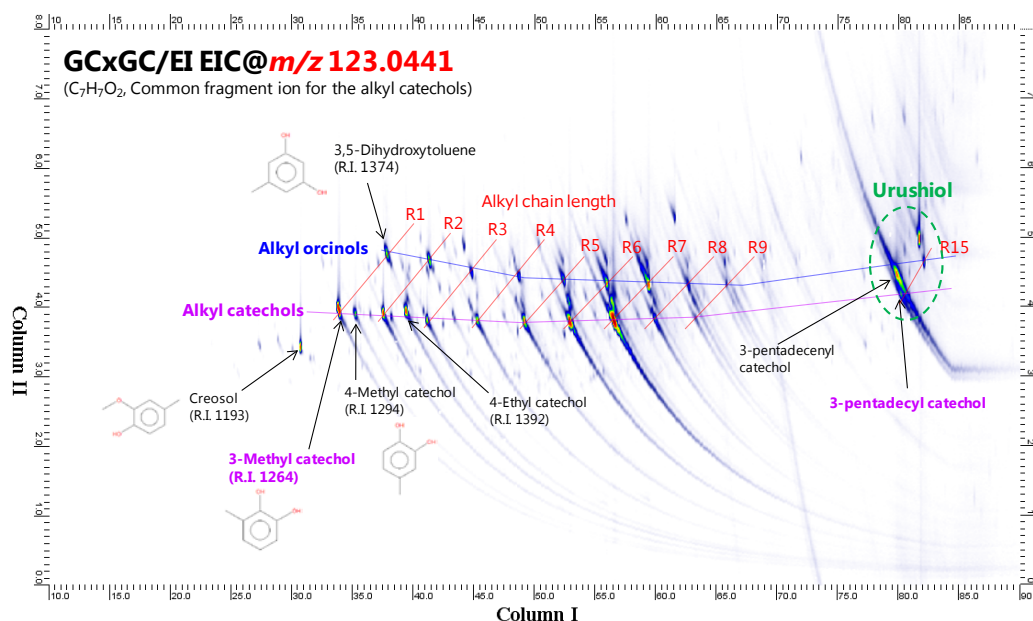
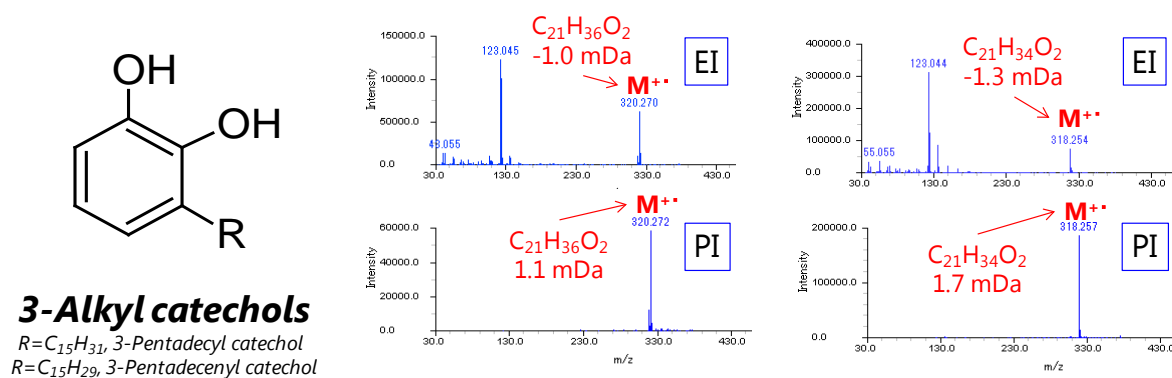
Fig.2 GCxGC/EI EIC chromatogram using  $m/z$  123.0441 ( $C_7H_7O_2$ )  $\pm 0.01$ 

Fig.3 Mass spectra for 3-Pentadecyl catechol (left) and 3-Pentadecenyl catechol (right)

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# Identification of Impurities in an Expired Standard Drug Mixture by Using Multiple Ionization Methods and *msFineAnalysis*

## INTRODUCTION

Gas chromatography combined with high-resolution time-of-flight mass spectrometry (GC-HRTOFMS) is a powerful tool for the analysis of complex mixtures. The AccuTOF GC-Alpha (JMS-T2000GC) mass spectrometer is fast, accurate and sensitive with high mass-resolving power and high mass accuracy.

Data analysis based on database matching alone does not necessarily provide reliable assignments for compounds that have similar electron ionization (EI) mass spectra or compounds that do not have entries in mass spectral databases. JEOL *msFineAnalysis* software provides automated analysis that makes use of all of the information available from a GC-HRTOFMS analysis: elemental composition determination from soft and hard ionization with exact mass measurements and accurate isotope data, database searching, fragment ion coverage, and retention index data.

In this work, GC-MS analysis of a 12-year-old standard drug mixture was carried out with the AccuTOF GC-Alpha (JEOL JMS-T2000GC) mass spectrometer using the combination electron ionization/photoionization (EI/PI) ion source and the chemical ionization (CI) ion source. Data analysis using JEOL *msFineAnalysis* software carried out chromatographic deconvolution and identified the drugs and impurities by combining and integrating all of the information from EI and PI analysis.

## EXPERIMENTAL

The labeled contents of the drug standard mixture (DEA-Exempt Capillary Drug Mix #1, 100 ng mL<sup>-1</sup> in methanol, Alltech PN 01464) are shown in Table 1. Although this standard was kept in the laboratory freezer, it was purchased in 2009 and was frequently used for experiments. The sample is well past its expiration date, so many of the compounds have partially decomposed or reacted, resulting in the loss of potency and the formation of impurities.

The mass spectrometer was auto-tuned and mass-calibrated with perfluorotributylamine (PFTBA) one week prior to the measurements. The sample was measured in EI mode and in PI mode with the combination EI/PI ion source and in CI mode. A mixture of 5% ammonia in methane was used as the CI reagent gas. Although the mass spectrometer was retuned in CI mode with octamethylcyclotetrasiloxane, it was not necessary to repeat the mass calibration. Multiple drift correction was applied using m/z 281.05114 from octamethylcyclotetrasiloxane introduced by opening the reference inlet automatically for 0.25 min at 3.5 minutes and 12.5 minutes. Centroided mass spectra for the drug mixture were processed with chromatographic deconvolution by using the JEOL *msFineAnalysis* software.

Name	Composition	m/z
Caffeine	C <sub>8</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	194.07982
Glutethimide	C <sub>13</sub> H <sub>15</sub> NO <sub>2</sub>	217.109727
Phenobarbital	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	232.084245
Lidocaine	C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O	234.17267
Carbamazepine	C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O	236.094407
Methaqualone	C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O	250.110063
Desipramine	C <sub>18</sub> H <sub>22</sub> N <sub>2</sub>	266.177736
EDDP	C <sub>20</sub> H <sub>23</sub> N	277.182496
Cocaine	C <sub>17</sub> H <sub>21</sub> NO <sub>4</sub>	303.146516
Methadone	C <sub>21</sub> H <sub>27</sub> NO	309.208711

Table 1. Compounds in Capillary Drug Mix #1. The standard was diluted in methanol to a concentration of 10 ng mL<sup>-1</sup> and analyzed using the conditions in Table 2.

graphic deconvolution by using the JEOL *msFineAnalysis* software.

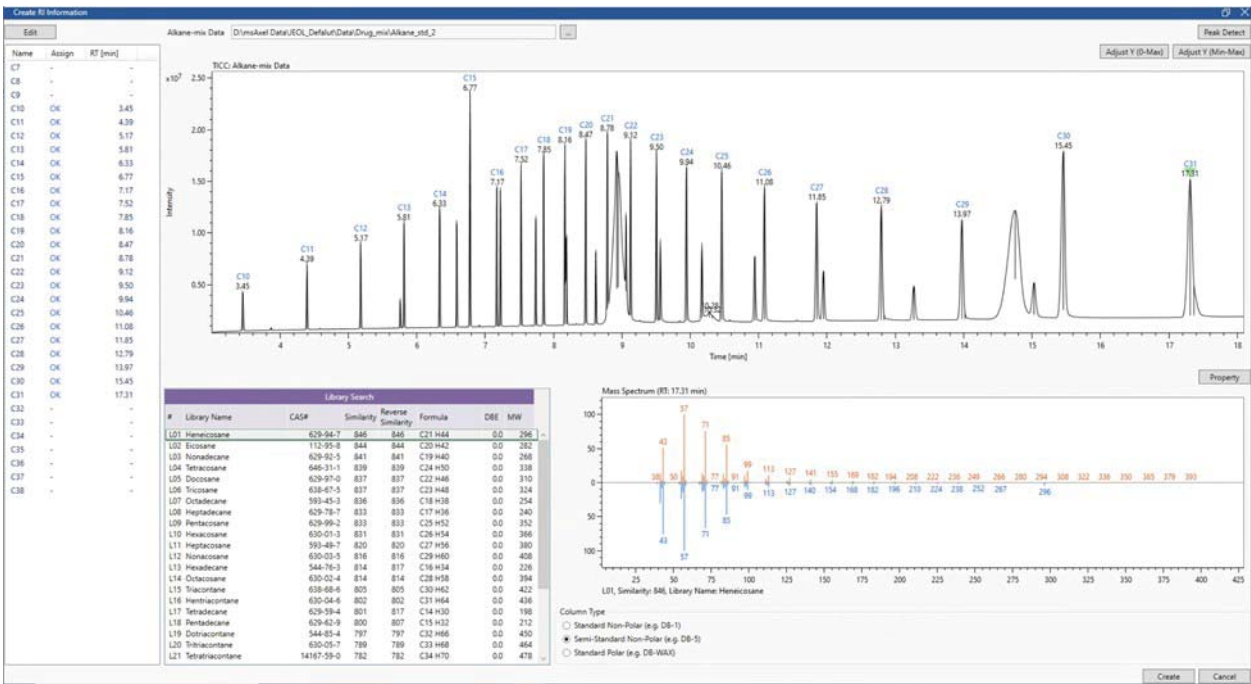
An alkane retention index standard (Qualitative Retention Time Index Standard, Restek Catalog # 31080) was measured using a 1/100 split injection and the GC oven program given in Table 2. The alkane retention index standard was measured in EI mode only.

## RESULTS

JEOL *msFineAnalysis* software was used to create a calibration using the data for the retention time index standard (Figure 1). Clicking on each peak in the total ion current chromatogram displayed a mass spectrum and database search for that peak, making it easy to assign the alkane standards despite the presence of heavy silicone interferences that had been introduced into the vial by previous repeated injections through the silicone seal. The retention index information for the standard was saved to a named file and used to calculate the retention indices for the components in the chromatograms for the drug mixture.

GC	
Autosampler	Agilent 7693A
Column	DB5-MS, 30 m, 0.25 mm ID, 0.25 m film
Flow rate	1 ml/min constant flow
Injection	1.5 µL, splitless, 280°C
Initial Temperature	100°C (1 min.)
Rate:	35°C / min
Final temperature	280°C
Hold time	5 min.
Total time	13.1 min.
MS	
Resolving power	>30,000 (at <i>m/z</i> 614)
Ionization	EI (70 eV), PI (deuterium lamp), and CI (5% ammonia in methane)
<i>m/z</i> range acquired	50-500
Spectral acquisition rate	10 Hz
External mass calibration	PFTP
Drift correction standard	Octamethylcyclotetrasiloxane
Reference valve opened at	3.5 and 12.5 minutes for 0.25 min each

Table 2. Measurement Conditions



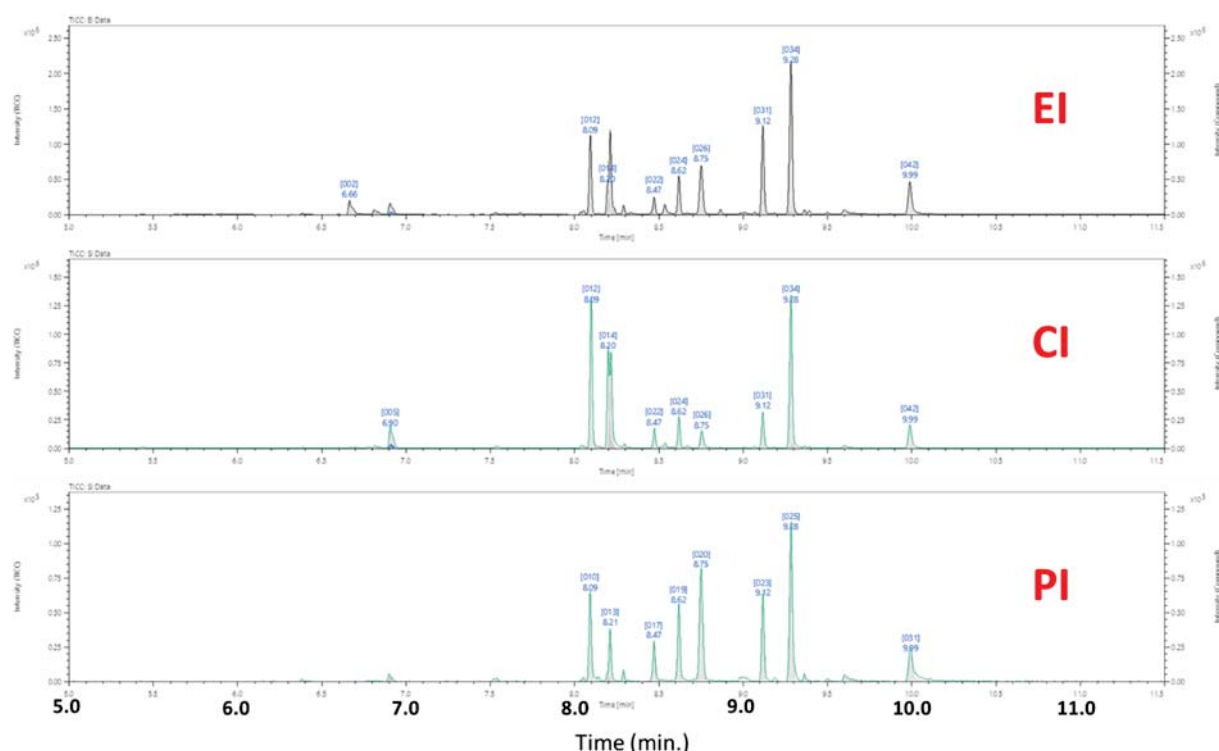


Figure 2. Total ion current chromatograms for analysis of the drug mixture obtained by electron ionization (EI), chemical ionization (CI) and photoionization (PI). Retention times are automatically aligned by *msFineAnalysis*, but compound-dependent response factors can differ for the different ionization modes.

Data analysis was carried out automatically by specifying the names of the hard ionization (EI) and soft ionization (PI or CI) data files. The total ion current chromatograms for each ionization method are shown in Figure 2. The results of the EI/CI analysis are shown in Figure 3 with the chromatograms and chromatographic deconvolution results for the EI data (top) and CI data (bottom) and a tabular summary of the information for each compound. Compound assignments with a high degree of confidence are highlighted in blue in the summary table. Compounds that do not have matching entries in the selected databases are highlighted in white, and compounds with multiple isomers are highlighted in yellow.

The table summarizes results for molecular ion elemental composition determination from exact mass and isotope data from both EI and CI data, database searching, fragment ion coverage, and retention index matching from the EI data. Clicking on the entry for any peak brings up additional windows to view more details of the analysis of that compound. The analyst can review each assignment and approve or interactively interpret the target compound assignments while inspecting the detailed analysis. Decisions about the assignment for isomers with indistinguishable EI mass spectra can be made by examining the retention index data. The analysis repeated by using the EI and PI data gave similar results (not shown).

Chromatographic deconvolution with *msFineAnalysis* is highly effective in separating chromatographically unresolved components as shown in Figure 4. The de-

convolved mass spectra show excellent database matches with no cross-contamination from the overlapping peaks. The database search results are shown in Figures 5 and 6 for glutethimide (similarity = 910) and lidocaine (similarity = 895), respectively.

Despite long-term storage, all of the labeled components (Table 1) could still be detected. Many of the impurities related to specific components in the mixture were also detected. For example, methyl ecgonidine and methyl ecgonine are impurities that can be present in cocaine. Iminodibenzyl and iminostilbene are impurities that may be present in carbamazepine. Desimpramine and imipramine only differ by the presence of an N-methyl group. Methyl palmitate and methyl stearate have many sources, and could have been introduced from a variety of sources over the 12-year period in which the sample was stored. Table 3 summarizes the results for 19 compounds that are identified with high certainty and 4 low-level compounds with fair-to-poor database similarities, but with good agreement for elemental compositions and retention indices for the database matches.

Group analysis can also be carried out with *msFineAnalysis* to identify compounds having similar structures that result in common fragment ions or common neutral losses. Figure 7 shows the identification of the tricyclic antidepressants (imipramine, desipramine and carbamazepine) and a characteristic impurity (iminostilbene).

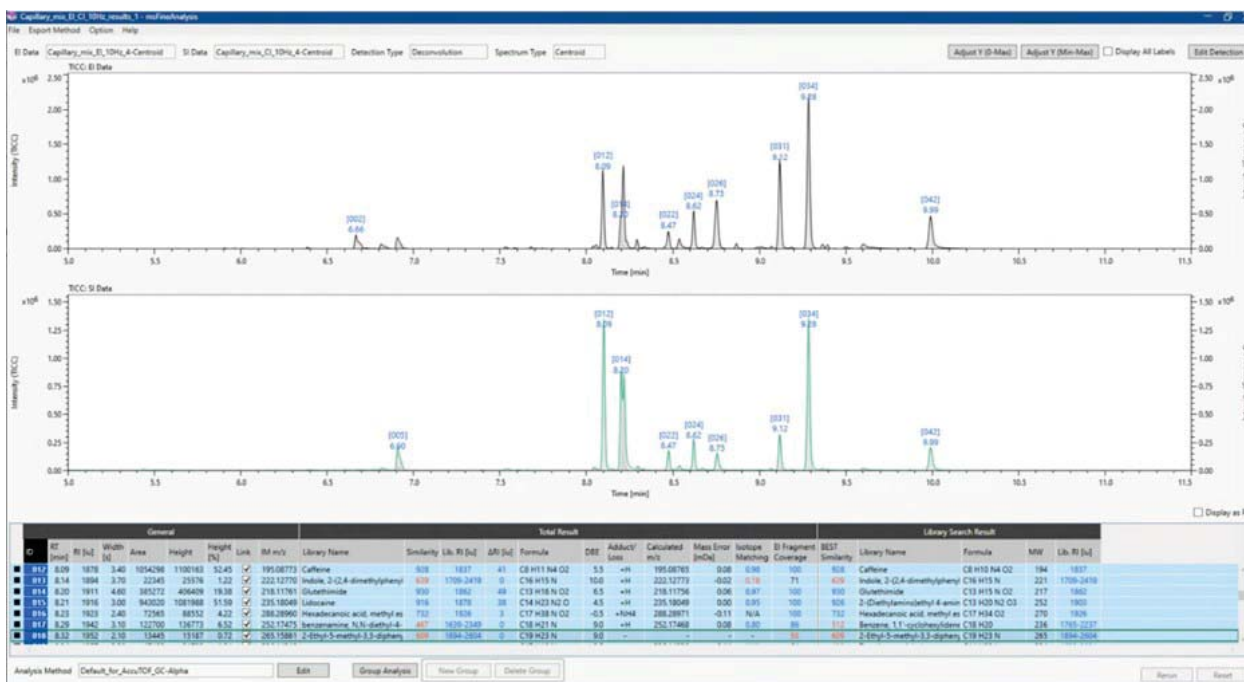


Figure 3. Results of the EI/CI data analysis by *msFineAnalysis*

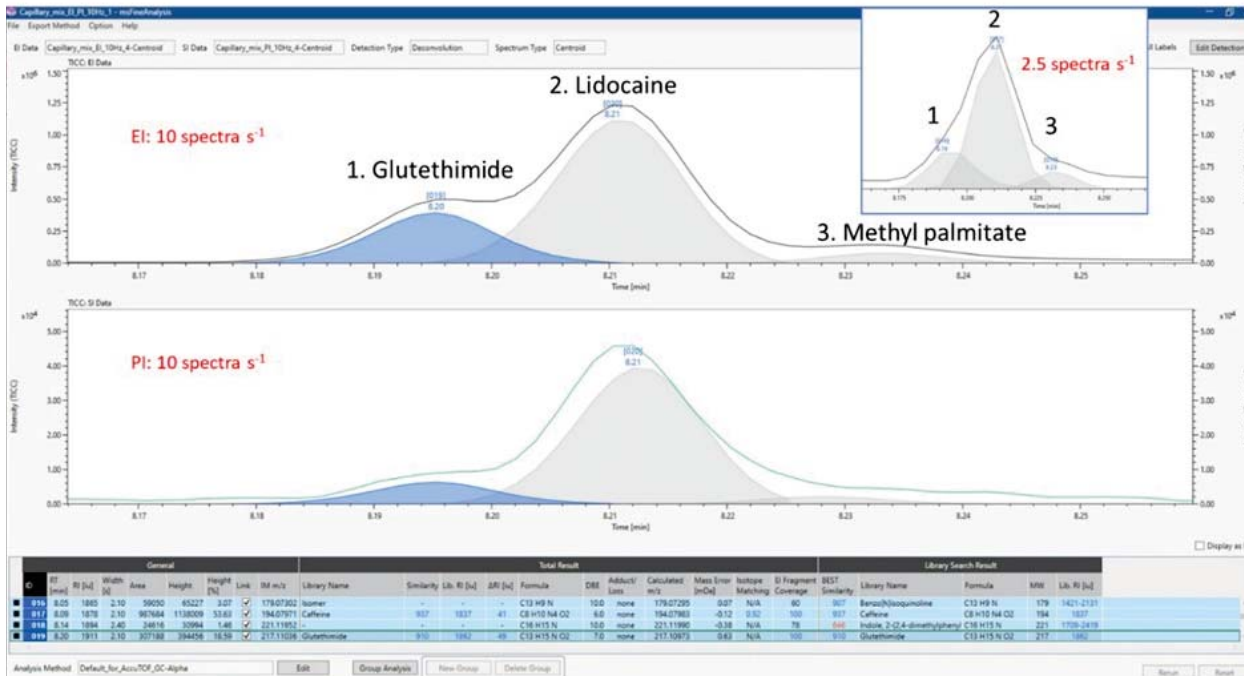
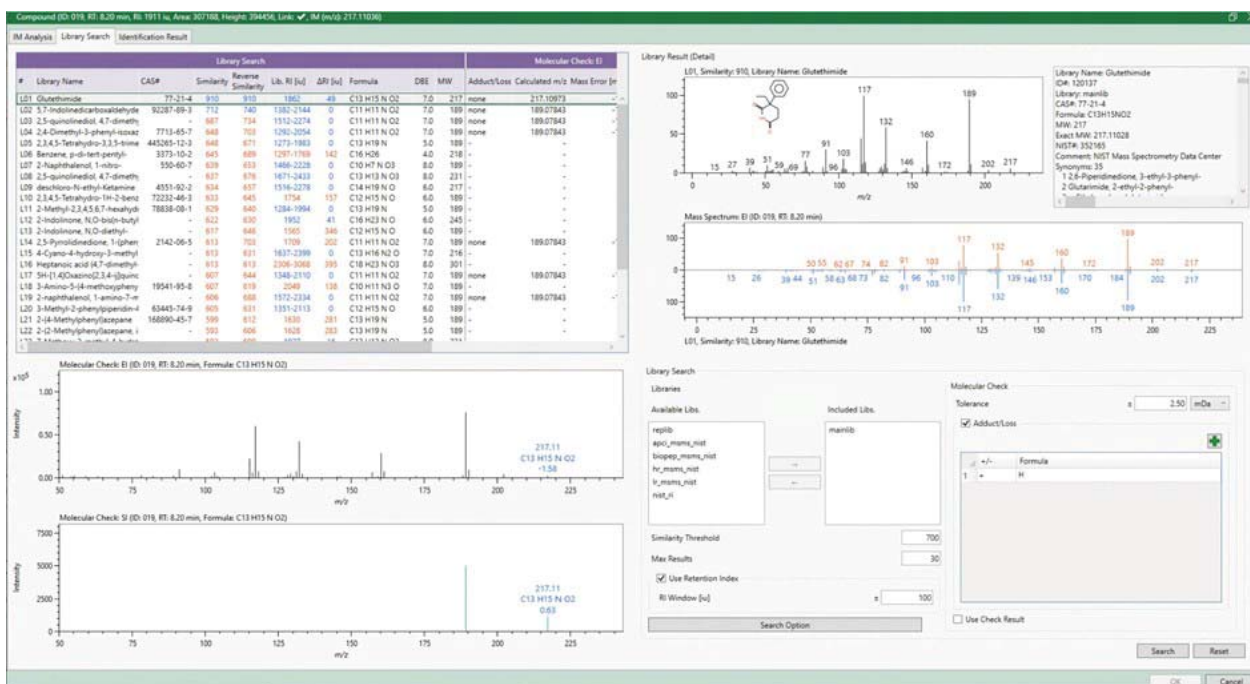


Figure 4. Chromatographic deconvolution of data acquired at 10 spectra  $s^{-1}$  showing separation of glutethimide (8.20 min), lidocaine (8.21 min) and methyl stearate impurity (8.23 min). The inset shows that deconvolution is still effective at separating these components even with a slower spectral acquisition rate (0.25 spectra  $s^{-1}$ ) and poor GC separation.





RT [min]	Area	Library Name	Similarity	Formula	Adduct/Loss	Mass Error [mDa]	Note
6.38	19274	Methyl ecgonidine	804	C10 H16 N O2	+H	0.15	Cocaine impurity
6.81	89326	Methyl ecgonine	647	C10 H17 N O3	+H	0.10	Cocaine impurity
6.82	42678	1,4-Benzenedicarboxylic acid, dimethyl ester	849	C10 H10 O4	none (EI)	-1.40	
6.90	193228	Benzoic acid, 4-ethoxy-, ethyl ester	907	C11 H15 O3	+H	0.13	
8.09	1054298	Caffeine	928	C8 H11 N4 O2	+H	0.08	Stimulant
8.14	22345	Indole, 2-(2,4-dimethylphenyl)-	639	C16 H15 N	+H	-0.02	
8.20	385272	Glutethimide	930	C13 H16 N O2	+H	0.06	Barbiturate
8.21	943020	Lidocaine	916	C14 H23 N2 O	+H	0.00	Local anesthetic
8.23	72565	Methyl palmitate	732	C17 H38 N O2	+NH4	-0.11	
8.29	122700	Benzenamine, N,N-diethyl-4-(1-phenylethenyl)-	467	C18 H21 N	+H	0.08	
8.45	22186	EMDP	758	C19 H22 N	+H	0.05	Opiate
8.47	245177	Iminodibenzyl	915	C14 H14 N	+H	0.09	Tricyclic
8.53	199582	Phenobarbital	826	C12 H13 N2 O3	+H	0.06	Barbiturate
8.62	527459	Iminostilbene	920	C14 H12 N	+H	0.05	Carbamazepine
8.75	942815	EDDP	929	C20 H24 N	+H	-0.17	Opiate
8.86	68646	Methyl stearate	812	C19 H39 O2	+H	-0.30	
9.12	1232363	Methadone	945	C21 H28 N O	+H	-0.34	Opiate
9.28	2305038	Methaqualone	957	C16 H15 N2 O	+H	-0.10	Hypnotic
9.39	66183	Cocaine	797	C17 H22 N O4	+H	-0.36	Cocaine
9.50	49806	Imipramine	794	C19 H24 N2	none (PI)	0.18	Tricyclic
9.60	139382	Desipramine	781	C18 H23 N2	+H	-0.31	Tricyclic
9.87	15276	Octadecanoic acid, butyl ester	511	C22 H44 O2	+H	-0.60	
9.99	786912	Carbamazepine	901	C15 H13 N2 O	+H	0.01	Tricyclic

Table 3. A summary extracted from the *msFineAnalysis* reports. The 10 drugs in Table 1 are highlighted in bold. The root-mean-square mass accuracy for all 23 compounds is 0.36 mDa.

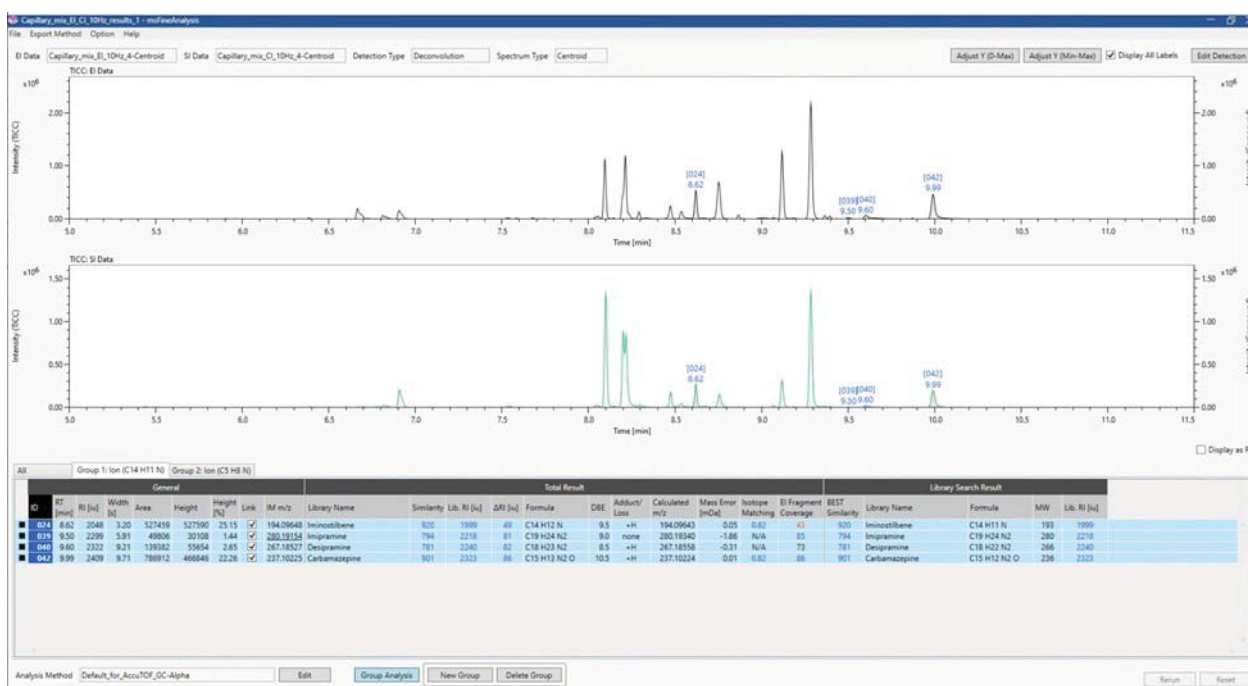


Figure 7. Group analysis for the common fragment ion  $C_4H_{11}N^+$  identifies related tricyclic compounds.

## CONCLUSION

The AccuTOF-GC Alpha provided high-resolution accurate-mass data for all detected compounds in both EI, CI, and PI modes. The root-mean-square mass accuracy for the identified components was 0.00036 u (0.36 mDa) for 24 components that exhibited molecular ions in the EI, CI, or PI mass spectra. Two low-level contaminants did not show clear peaks for the protonated molecules in the CI mass spectra, but molecular ions were observed in their EI or PI mass spectra (see Table 3).

Although some low-level components did not have entries in the mass spectral database, all ten of the listed drugs were detected, together with several impurities or degradation products. Assignments were confirmed by *msFineAnalysis* software using a combination of exact-mass and accurate-isotope data from both soft and hard ionization, database searching, fragment ion coverage and retention index matching.



JMS-T2000GC AccuTOF™ GC-Alpha GC-MS System



# Integrated Analysis of High Resolution GC-MS Data Using Hard and Soft Ionization to Identify Trace Impurities

Author: Robert Cody, Principal Scientist, JEOL USA, Inc.

## OVERVIEW

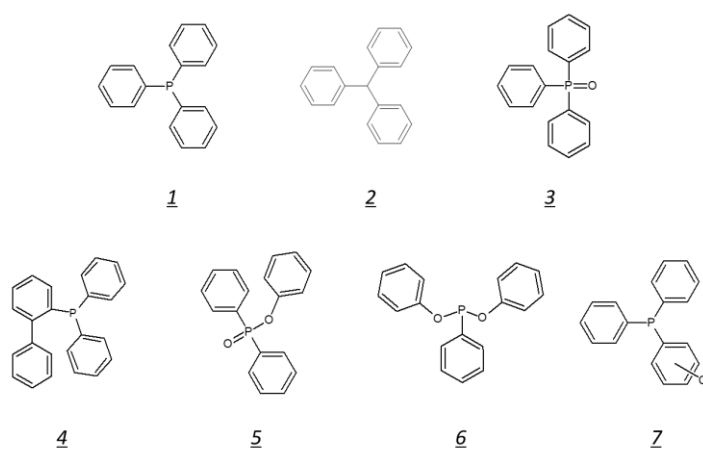
Non-targeted analysis of complex mixtures by GC-HRMS should make use of all of the available data to identify unknowns. An automated data analysis software package combining chromatographic deconvolution with integrated analysis of high-resolution mass spectra for electron ionization (EI) and soft ionization measurements is applied to the identification of trace impurities in a fine chemical (triphenylphosphine).

## INTRODUCTION

Gas chromatography combined with mass spectrometry (GC-MS) is well known as a powerful analytical tool for non-targeted analysis of complex mixtures such as environmental samples, quality control for feedstocks and fine chemicals, contaminants and impurities in commercial products, and metabolomic studies. GC-MS with a pyrolysis inlet is also widely used for materials characterization.

Interpretation of GC-MS data is heavily reliant upon searching electron ionization (EI) mass spectra against databases such as the NIST and Wiley mass spectral databases. Problems arise if the molecular ion is weak or absent, making it difficult to discriminate between compounds with different compositions, but similar mass spectra. A further complication is that many compounds do not have an entry in the databases.

A high-resolution time-of-flight mass spectrometer (HRTOFMS) is ideal for non-targeted analysis because it provides accurate mass and isotope data and is compatible with fast chromatography. Soft ionization methods<sup>[1]</sup> such as chemical ionization (CI), field ionization (FI) and photoionization (PI) provide molecular weight and elemental composition data to complement the database search results for electron ionization. Manual interpretation of the data is time-consuming. Here, we present a simple example of how an automated data interpretation program ("*msFineAnalysis*") combines all of the information from the high-resolution mass spectra for both electron ionization and chemical ionization mass spectra<sup>[2]</sup> to identify trace impurities in triphenylphosphine (**1**), a fine chemical used as a reagent for organic synthesis.



## EXPERIMENTAL

A sample of triphenylphosphine from our chemical stockroom was dissolved in dichloromethane at a concentration of 250 ng  $\mu\text{L}^{-1}$  and analyzed by GC with a 20:1 split injection. Mass spectra were acquired using a JEOL AccuTOF-GCX Plus mass spectrometer. Separate injections were made for EI and CI measurements. The chemical ionization reagent was 5% ammonia in methane and perfluorotributylamine was used as an external mass calibration standard. Column bleed peaks were used as a drift correction for GC-MS accurate mass measurements. The measurement conditions are summarized in Table 1.

### GC

- Agilent 7890B
- Column: 30 m DB-5ms
- Split injection (25:1)
- Oven temperature program:
  - Initial temperature = 100°C (hold 1 min)
  - Heat to 300°C at 15°C min<sup>-1</sup> (hold 20 min)

### MS

- Separate EI and CI measurements
  - EI, 70 eV, 300  $\mu\text{A}$
  - CI: 5% ammonia in methane
- Resolving power = 10,000
- m/z 35-800 at a spectrum s<sup>-1</sup>
- Solvent delay: 1.8 minutes

Table 1. Measurement Conditions

The results were analyzed by using JEOL *msFineAnalysis* version 2 software. The chromatographic deconvolution function detected low-level peaks that were not immediately evident from the total ion chromatograms (TIC) for the EI and CI data. Each detected peak in the EI data was searched against the NIST

2020 mass spectral database. Molecular weight and elemental composition information in the CI data was correlated with the EI database matches, using both accurate masses and isotopic abundances. A fragment coverage score was calculated for the EI mass spectra by determining elemental compositions for all fragments assuming the elemental composition for the candidate molecule. Compounds that have high database search scores with confirming elemental compositions and high fragment coverage are color-coded in pale blue to indicate reliable assignments. Data analysis is fully automated, with the results presented in a summary table. Using a color-blind friendly palette, compounds that have multiple matches are color-coded in pale orange, and compounds that do not have any reliable assignments are color-coded in white. Clicking on any entry brings up details of the analysis for that peak: database search results, molecular weight and elemental composition information from the soft ionization measurement, and a table summarizing all of the data for that peak assignment. A list of fragment ion compositions and a list of neutral losses is created from all detected peaks. This list can be used to perform group analysis to identify “families” of related compounds that have common fragments or neutral losses.

## RESULTS

### *Compound identification using multiple pieces of information*

To look for impurities, a high concentration of triphenylphosphine was injected with a 25:1 split ratio. Because the peak for triphenylphosphine eluting at 11.17 minutes is off scale, the mass spectrum is clipped, distorting the spectral pattern. The top database match is (2-Carboxyethyl)-triphenylphosphonium bromide which has the composition  $C_{21}H_{12}BrO_2P$  and a molecular weight of 414. However, the CI data identify the correct formula as  $C_{18}H_{15}P$  consistent with the second-best database match, triphenylphosphine. Although Br was not included in the list of elements used to calculate elemental compositions, the program used “feedback” from the database search matches to ensure that all elements in the database matches are considered for the elemental composition calculation. The two impurities with the highest relative abundances are readily identified as triphenylmethane (**2**) at 10.12 minutes and triphenylphosphine oxide (**3**) at 13.14 minutes. (Figure 1).

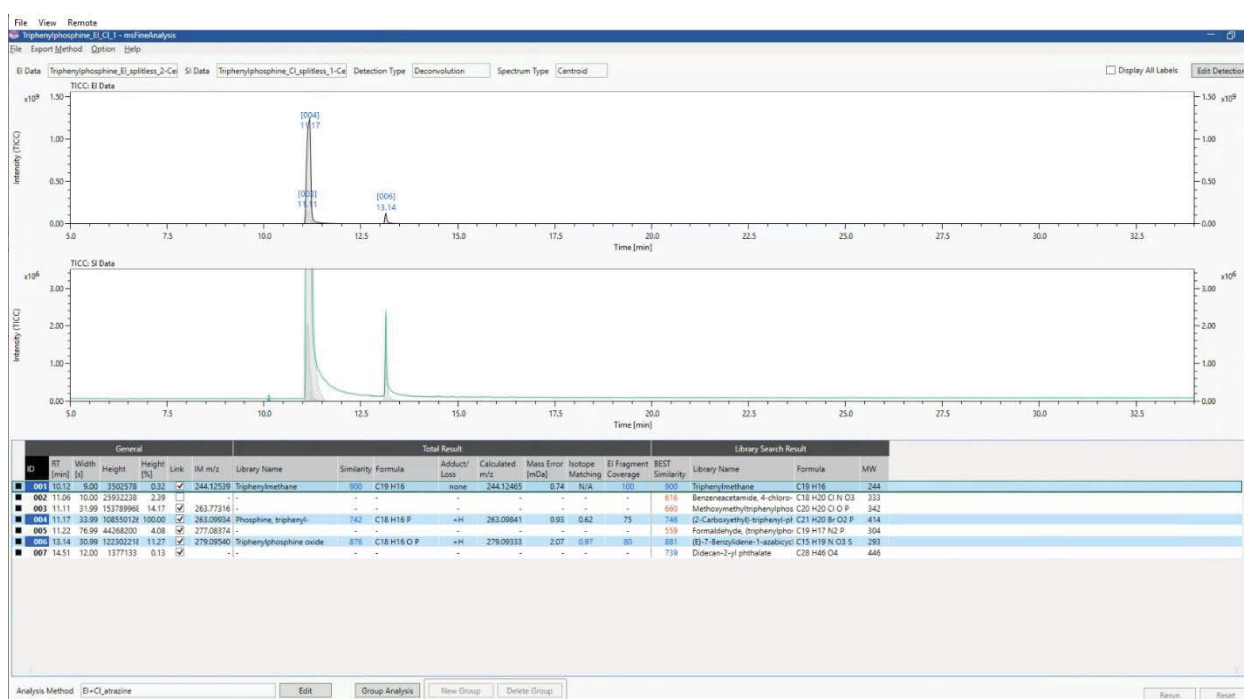


Figure 1. Assignments for the three most abundant peaks in the chromatogram



The triphenylphosphine oxide assignment will be used as an example to show of how the information is used by the program. The highest-scoring database match the peak eluting at 13.14

minute is not triphenylphosphine oxide - the oxide is the second-best match (Figure 2).

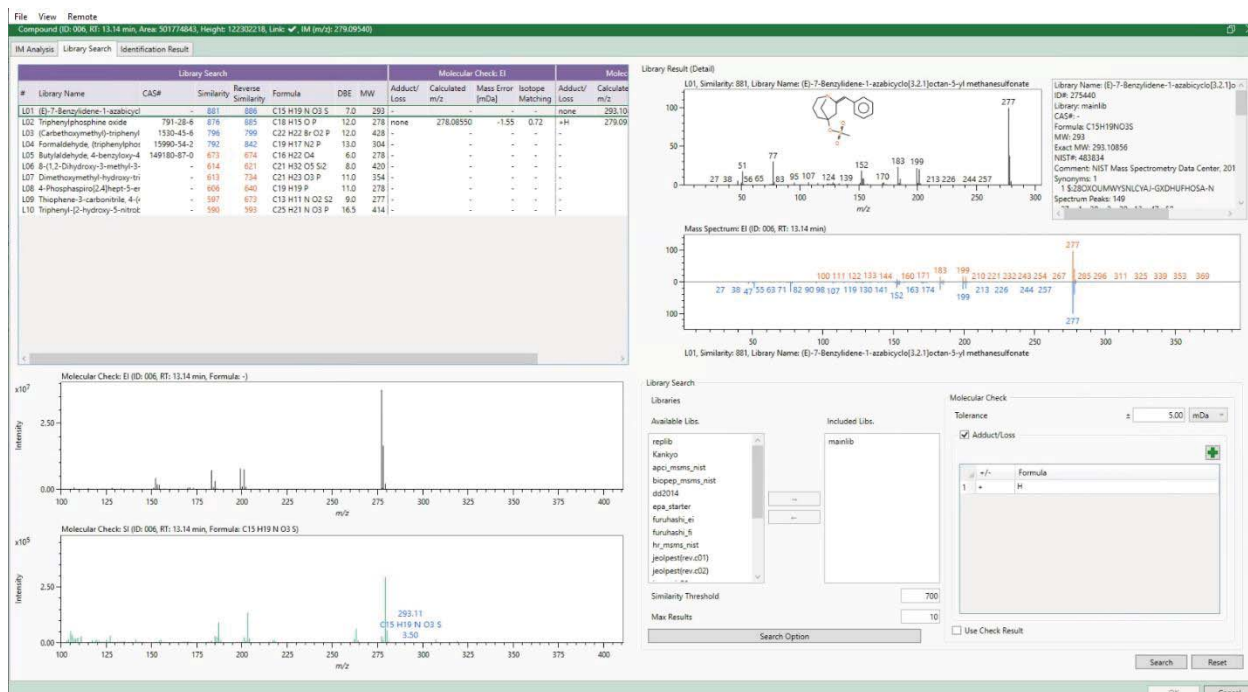


Figure 2. Database search results for the peak eluting at 13.14 minutes

However, from the CI data, we know the protonated molecule is detected at  $m/z$  279.095. One of the calculated elemental compositions is  $C_{18}H_{16}OP$ , which is consistent with the second-

highest scoring database match, triphenylphosphine oxide (Figure 3).

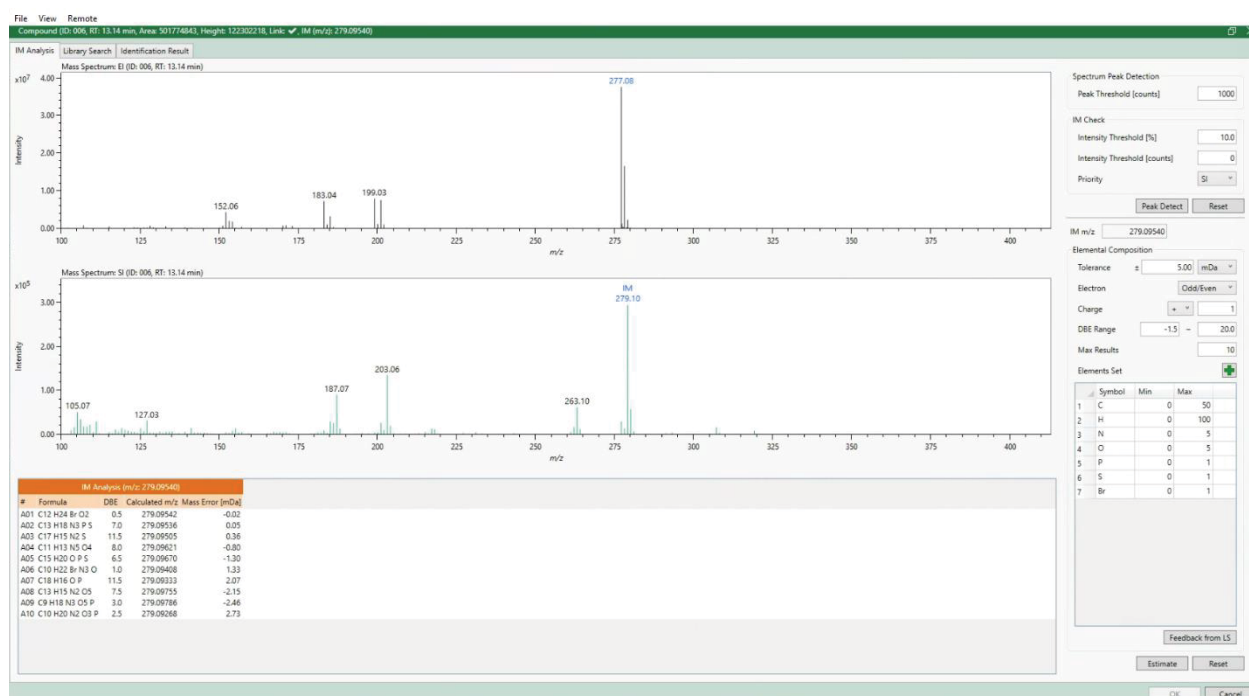


Figure 3. Elemental compositions from the CI mass spectrum for the peak at 13.14 minutes



Triphenylphosphine oxide is the only assignment that has correlated data for all of the information at that retention time: high database match scores, accurate mass and isotope data in the CI mass spectrum with a consistent elemental composition, and high fragment ion coverage (Figure 4). Therefore,

msFineAnalysis reports triphenyl phosphine oxide as the correct assignment. The presence of triphenylphosphine oxide is not surprising, given that triphenylphosphine undergoes slow oxidation in air.

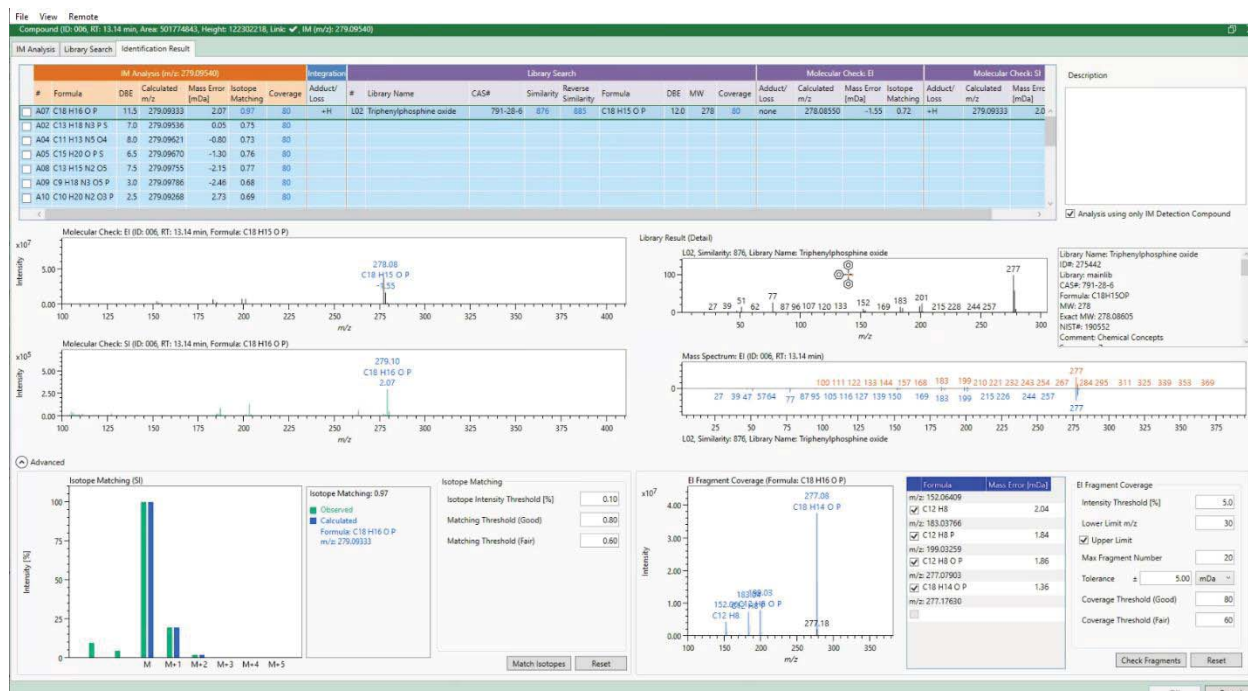


Figure 4. Summary page showing details of triphenylphosphine oxide assignment.

Another compound eluting at 12.64 minutes is identified as C<sub>18</sub>H<sub>15</sub>O<sub>2</sub>P. The highest-scoring database match is diphenylphosphinic acid, phenyl ester (5) although the second-best match phosphonous acid, phenyl-, diphenyl ester (6) has a nearly identical mass spectrum and cannot be ruled out without a standard sample.

#### Using Group Analysis to find related compounds

We can use the group analysis functions to look for families of related compounds. From the list of fragment ions (Figure 5), we can see that 4 compounds have a diphenyl fragment C<sub>12</sub>H<sub>8</sub><sup>+</sup>.

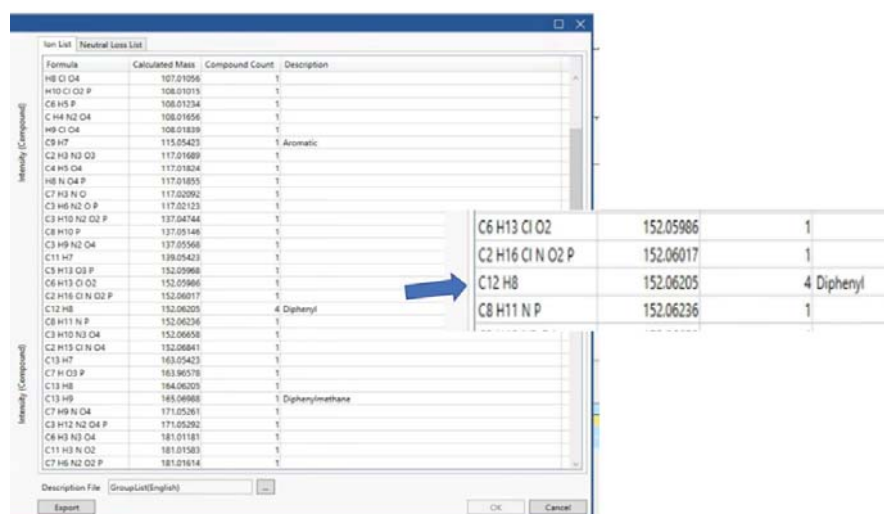


Figure 5. Group Analysis tab showing fragment ions detected in the dataset

Triphenylmethane and triphenylphosphine oxide are identified with high confidence in this group along with 2 (Diphenylphosphino)-biphenyl (**4**), which elutes at 13.99 minutes. A small peak eluting at 12.07 minutes is highlighted in

yellow (Figure 6) because it does not have a confirmed composition with matching database entries and elemental composition.

General						Total Result										Library Search Result			
ID	RT [min]	Width [s]	Height	Height [%]	Link	IM m/z	Library Name	Similarity	Formula	Adduct/ Loss	Calculated m/z	Mass Error [mDa]	Isotope Matching	EI Fragment Coverage	BEST Similarity	Library Name	Formula	MW	
003	10.12	9.00	3902774	0.29	✓	244.12539	Isomer	-	C19 H16	none	244.12465	0.74	N/A	100	916	Triphenylmethane	C19 H16	244	
013	12.07	11.00	538759	0.04	✓	296.05237	-	-	Multi Hits	-	-	-	-	-	513	erythro-8-(1,2-Dibromo-2-ph	C16 H16 Br2 N4 C	454	
019	13.14	30.99	14315900	10.55	✓	279.09540	Triphenylphosphine oxide	910	C18 H16 O P	+H	279.09333	2.07	0.97	86	920	(E)-7-Benzylidene-1-azabicycl	C15 H19 N O3 S	293	
024	13.99	18.00	1176418	0.09	✓	339.13194	2-(Diphenylphosphino)-biphe	900	C24 H20 P	+H	339.12971	2.22	N/A	100	900	2-(Diphenylphosphino)-biphe	C24 H19 P	338	

Figure 6. Compounds detected with a  $C_{12}H_8^+$  fragment

Double-clicking on this entry brings up detailed information from this analysis. The molecular ion occurs at nominal  $m/z$  296 which is confirmed by the  $m/z$  297 peak for the protonated molecule in the CI mass spectrum. From the accurate mass and isotope data and fragment coverage (Figure 7), it is clear that the elemental composition is  $C_{18}H_{14}ClP$  or (2,3, or 4-chlorophenyl) diphenylphosphine (**7**). Although database

searching did not return a match because there is no entry in the NIST or Wiley databases for any compounds with this elemental composition, the accurate mass and isotope data allowed us to assign a composition, and the fragment ion elemental compositions are consistent with the proposed structure.

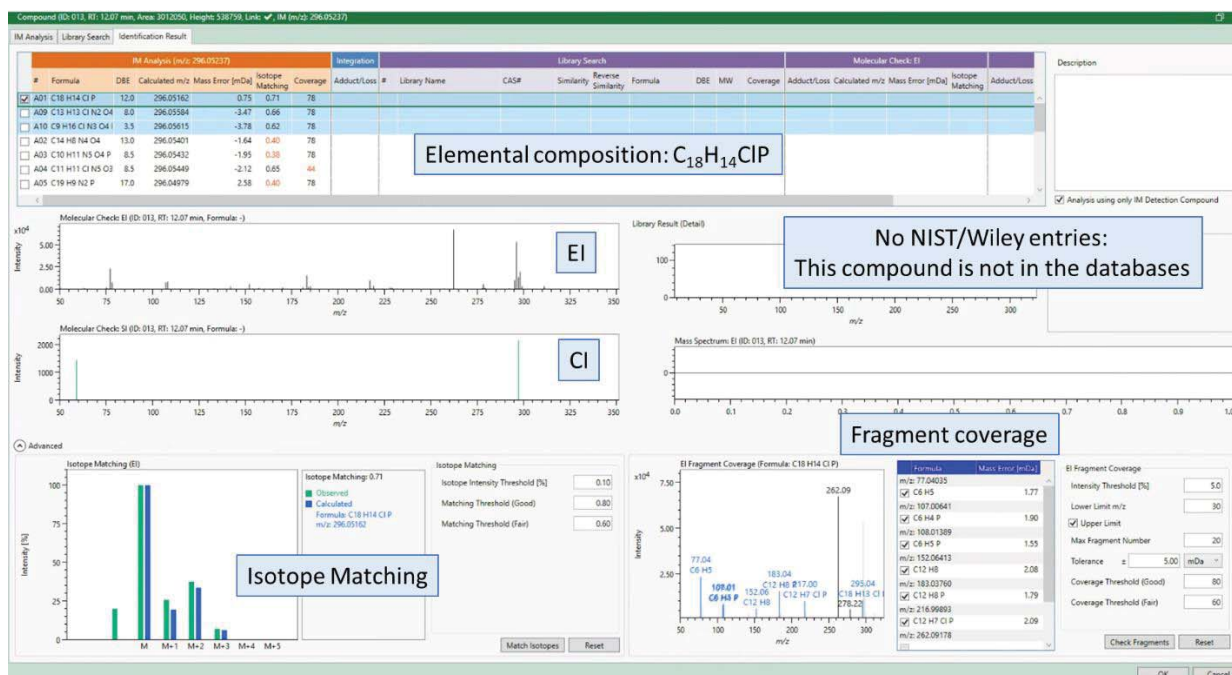


Figure 7. Summary page for identification of  $C_{18}H_{14}ClP$

## Conclusions

The AccuTOF-GCX Plus GC-HRTOFMS system is shown to be a useful method for identifying trace impurities. The msFineAnalysis version 2 software combines chromatographic deconvolution with integrated data analysis of both soft (EI) and hard (CI) ionization measurements, including accurate mass and isotope data. The resulting report assigns high confidence to compounds that have high-scoring database search matches and accurate mass/isotope data that support the search result. High-resolution mass spectral data is summarized to aid in interpreting mass spectra for compounds that do not have database entries. Although a simple example was shown here,

the method is valuable for more complex mixtures, as shown in the examples in references 2 and 3.<sup>[2, 3]</sup>

## References

1. T. Furuhashi, K. Okuda. Application of GC/MS Soft Ionization for Isomeric Biological Compound Analysis. *Critical Reviews in Analytical Chemistry*, 2017, 1.
2. M. Ubukata, A. Kubo, K. Nagatomo, T. Hizume, H. Ishioka, A. J. Dane, R. B. Cody, Y. Ueda. Integrated qualitative analysis of polymer sample by pyrolysis-gas chromatography combined with high-resolution mass spectrometry: Using accurate mass measurement results from both electron ionization and soft ionization. *Rapid Communications in Mass Spectrometry*, 2020, 34, e8820.
3. R. B. Cody. Analysis and Identification of Mezcal and Tequila Aromas by Ambient Ionisation MS, GC-MS, and GCxGC-MS. *Chromatography Today*, Aug-Sep 2020.

## Integrated Analysis of Fatty Acid Methyl Esters using msFineAnalysis Version 2

### - Molecular Ion Detection by FI -

Product: Mass spectrometer (MS)

#### [Introduction]

Electron ionization (EI) is a hard ionization method that is commonly used with gas chromatography mass spectrometry (GC-MS). The mass spectral fragmentation patterns produced by EI are used for library database searches to identify compounds. Conversely, soft ionization methods like field ionization (FI) tend to produce clear molecular ions with minimal fragmentation. When high-resolution MS is used with these ionization techniques, the accurate masses for the fragment ions produced by EI and the molecular ions produced by soft ionization provide an additional dimension of information for the analytes. Combining the exact mass information with the results of conventional library search can enhance the accuracy of identification compared to the use of library search alone.

Fatty acid methyl esters (FAMES) are crucial for determining the fat content in food. Being environmentally friendly, they are also increasingly used as bio-diesel fuels. Many of the FAMES are unsaturated with double bonds in the alkyl chains. As the number of double bonds increases (more unsaturation), the EI measurements tend to lack molecular ions. In this work, we measured a standard sample containing multiple FAMES using EI and FI to detect their molecular ions. The resulting data was further examined by using msFineAnalysis to produce an integrated report for these compounds in which the library database search was combined with the molecular ion exact mass analysis to produce a qualitative identification of these compounds.

#### [Experimental]

A commercial 37-component FAME standard mixture (Restek, 200-600 ng/ $\mu$ L) was used as a sample. Table 1 shows the measurement conditions used for the GC/EI and GC/FI analyses.

#### [Results and Discussion]

Figure 1 shows the TICC for the GC/EI and GC/FI measurements. While the sample contains 37 components, there were only 36 peaks observed in each chromatogram. The *cis*-4,7,10,13,16,19-docosahexaenoic acid methyl ester ( $C_{23}H_{34}O_2$ ) and the heneicosanoic acid methyl ester ( $C_{22}H_{44}O_2$ ) coelute with exactly the same retention time (RT) at 38.8 min. However, the FI mass spectrum for this peak showed the molecular ions for each component (Figure 2). Because the JMS-T200GC is always measuring high-resolution mass spectra, these components, which are not quite separated in the chromatogram, can be identified by mass separation.

Table 1. Measurement conditions

#### [GC Conditions]

GC system: 7890A (Agilent Technologies)  
 Column: DB-5msUI, 30 m x 0.25 mm, 0.25  $\mu$ m  
 Oven temperature: 50°C (1 min)  $\rightarrow$  10°C/min  $\rightarrow$  140°C  $\rightarrow$  3°C/min  $\rightarrow$  260°C (5 min)  
 Injection mode: Split mode (50:1)

#### [TOFMS Conditions]

MS system: JMS-T200GC (JEOL Ltd.)  
 Ion source: EI/FI combined ion source  
 Ionization: EI+, 70 eV, 300  $\mu$ A  
 FI+, -10 kV, 50 mA (slope mode)  
 Mass range:  $m/z$  35-600

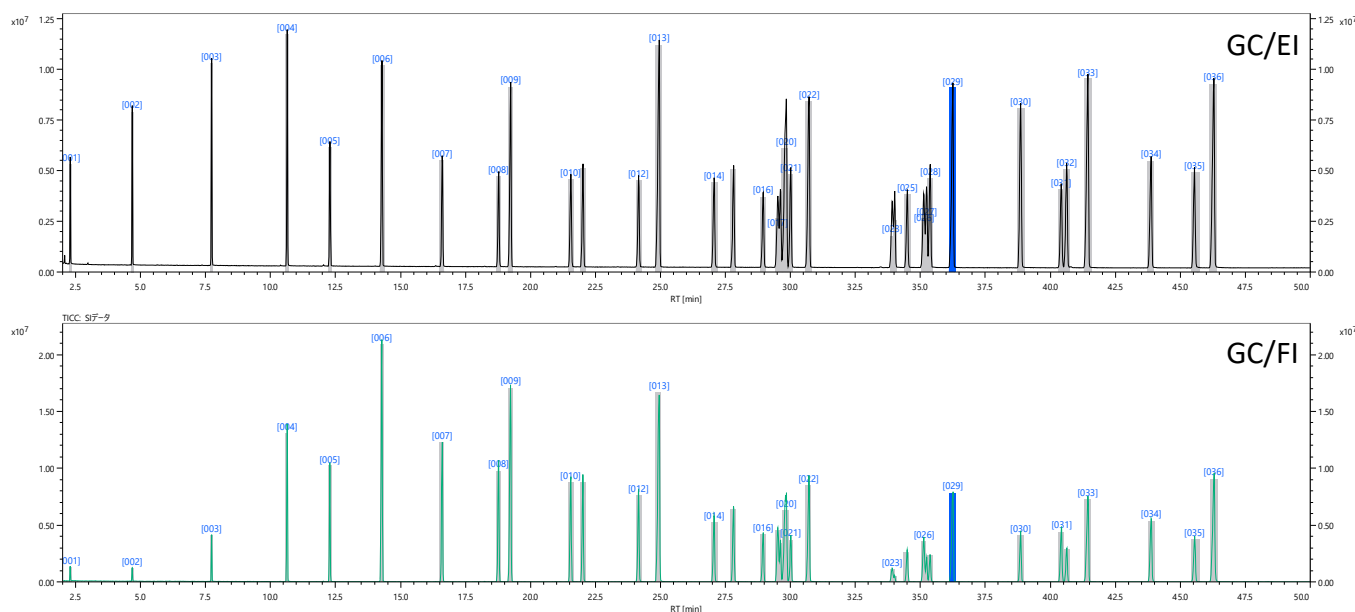


Figure 1. GC/EI and GC/FI total ion current chromatograms for the 37 FAME mixture

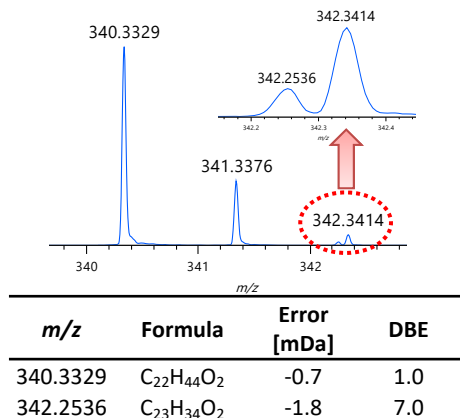


Figure 2. FI mass spectrum (enlarged) at RT 38.8 min and exact mass analysis results

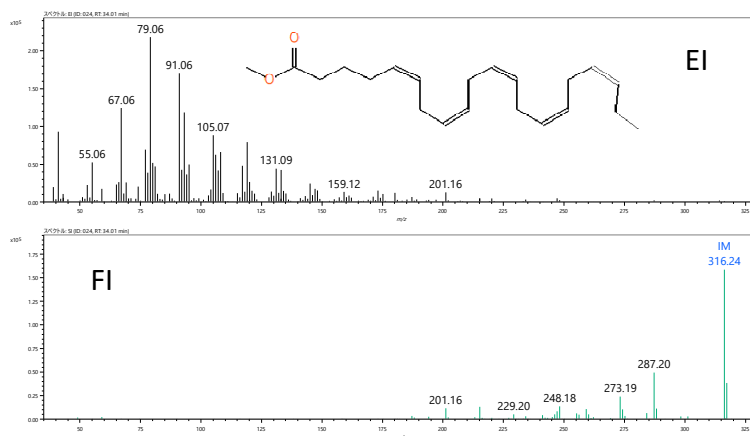


Figure 3. EI and FI mass spectra of 5, 8, 11, 14, 17-eicosapentaenoic acid methyl ester (all-Z)-

The FI mass spectra show molecular ions for all 37 FAMES in the mixture. Additionally, these molecular ions are the base peak in each FI mass spectrum except for the 15-tetracosenoic acid methyl ester (Z)-, which is detected at a relative intensity of >80%. All of these results demonstrate that FI ionizes FAMES softly and efficiently. As an example, Figure 3 shows the EI and FI mass spectra for 5,8,11,14,17-eicosapentaenoic acid methyl ester (all-Z)-, which has 5 double bonds and an alkyl group. In this example, the molecular ion was not observed in the EI mass spectrum, but the molecular ion is the base peak in the FI mass spectrum. Figure 4 shows the FI mass spectra and chemical formulas for 6 components that all have a carbon number of 20 (minus the ester bond) and have 0 to 5 double bonds. Lastly, Table 2 shows the integrated analysis report generated by msFineAnalysis. In each case, the FI molecular ion accurate masses were automatically used to determine the molecular formula for each component in the FAMES mixture to help identify the correct match from the EI library database search.

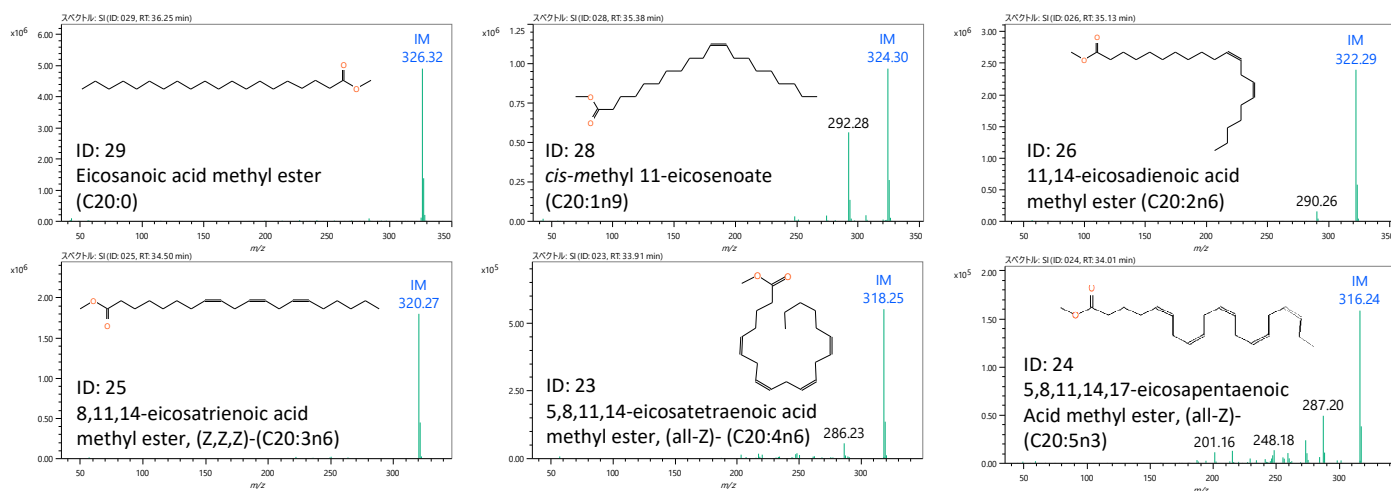


Figure 4. FI mass spectra for the C20 FAMES.

## [Conclusions]

The msFineAnalysis integrated analysis method produces highly accurate qualitative analysis results for the FAMES by combining the library search results and molecular formula estimation. This combination of using GC/EI and GC/FI measurements together for qualitative analysis is particularly important for FAMES as these types of compounds do not produce molecular ions for EI, making it difficult to use database searches alone for identification.

Table 2. Integrated qualitative analysis results report using msFineAnalysis

General					Total Result						Library Search Result				
ID	RT [min]	Area	Area [%]	IM m/z	Library Name	CAS#	Similarity	Formula	Calculated m/z	Mass Error [mDa]	BEST Similarity	Library Name	CAS#	Formula	MW
001	2.29	7,802,029	14.13	102.06850	Butanoic acid, methyl ester	623-42-7	902	C5 H10 O2	102.06753	0.97	902	Butanoic acid, methyl ester	623-42-7	C5 H10 O2	102
002	4.68	12,509,365	22.65	130.09965	Hexanoic acid, methyl ester	106-70-7	954	C7 H14 O2	130.09883	0.82	954	Hexanoic acid, methyl ester	106-70-7	C7 H14 O2	130
003	7.74	17,836,754	32.30	158.13091	Octanoic acid, methyl ester	111-11-5	921	C9 H18 O2	158.13013	0.78	921	Octanoic acid, methyl ester	111-11-5	C9 H18 O2	158
004	10.64	22,872,875	41.42	186.16241	Decanoic acid, methyl ester	110-42-9	951	C11 H22 O2	186.16143	0.98	951	Decanoic acid, methyl ester	110-42-9	C11 H22 O2	186
005	12.28	13,873,023	25.12	200.17785	Undecanoic acid, methyl ester	1731-86-8	947	C12 H24 O2	200.17708	0.77	947	Undecanoic acid, methyl ester	1731-86-8	C12 H24 O2	200
006	14.29	28,637,881	51.86	214.19378	Dodecanoic acid, methyl ester	111-82-0	924	C13 H26 O2	214.19273	1.05	924	Dodecanoic acid, methyl ester	111-82-0	C13 H26 O2	214
007	16.61	16,639,305	30.13	228.20907	Tridecanoic acid, methyl ester	1731-88-0	962	C14 H28 O2	228.20838	0.68	962	Tridecanoic acid, methyl ester	1731-88-0	C14 H28 O2	228
008	18.78	15,928,565	28.84	240.20818	Methyl myristoleate	56219-06-8	951	C15 H28 O2	240.20838	-0.20	951	Methyl myristoleate	56219-06-8	C15 H28 O2	240
009	19.24	33,711,996	61.05	242.22503	Methyl tetradecanoate	124-10-7	956	C15 H30 O2	242.22403	1.00	956	Methyl tetradecanoate	124-10-7	C15 H30 O2	242
010	21.55	16,820,354	30.46	254.22386	Methyl (Z)-10-pentadecenoate	-	928	C16 H30 O2	254.22403	-0.18	928	Methyl (Z)-10-pentadecenoate	-	C16 H30 O2	254
011	22.02	18,711,161	33.88	256.24022	Pentadecanoic acid, methyl ester	7132-64-1	949	C16 H32 O2	256.23968	0.54	949	Pentadecanoic acid, methyl ester	7132-64-1	C16 H32 O2	256
012	24.16	17,805,851	32.24	268.23913	9-Hexadecenoic acid, methyl ester, (Z)-	1120-25-8	942	C17 H32 O2	268.23968	-0.55	942	9-Hexadecenoic acid, methyl ester, (Z)-	1120-25-8	C17 H32 O2	268
013	24.95	55,221,475	100.00	270.25537	Hexadecanoic acid, methyl ester	112-39-0	946	C17 H34 O2	270.25533	0.04	946	Hexadecanoic acid, methyl ester	112-39-0	C17 H34 O2	270
014	27.07	18,586,681	33.66	282.25402	cis-10-Heptadecenoic acid, methyl ester	-	943	C18 H34 O2	282.25533	-1.32	943	cis-10-Heptadecenoic acid, methyl ester	-	C18 H34 O2	282
015	27.82	20,566,515	37.24	284.27051	Heptadecanoic acid, methyl ester	1731-92-6	933	C18 H36 O2	284.27098	-0.47	933	Heptadecanoic acid, methyl ester	1731-92-6	C18 H36 O2	284
016	28.96	15,344,971	27.79	292.23830	Methyl γ-linolenate	16326-32-2	945	C19 H32 O2	292.23968	-1.38	945	Methyl γ-linolenate	16326-32-2	C19 H32 O2	292
017	29.52	8,858,244	16.04	294.25444	9,12-Octadecadienoic acid, methyl ester, (E,E)-	2566-97-4	835	C19 H34 O2	294.25533	-0.89	877	11,14-Octadecadienoic acid, methyl ester	56554-61-1	C19 H34 O2	294
018	29.62	8,877,607	16.08	292.23851	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	301-00-8	918	C19 H32 O2	292.23968	-1.17	918	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	301-00-8	C19 H32 O2	292
019	29.79	18,365,132	33.26	294.25465	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	112-63-0	866	C19 H34 O2	294.25533	-0.68	866	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	112-63-0	C19 H34 O2	294
020	29.84	32,367,534	58.61	296.26984	9-Octadecenoic acid (Z)-, methyl ester	112-62-9	894	C19 H36 O2	296.27098	-1.14	894	9-Octadecenoic acid (Z)-, methyl ester	112-62-9	C19 H36 O2	296
021	30.02	19,095,805	34.58	296.27036	9-Octadecenoic acid, methyl ester, (E)-	1937-62-8	927	C19 H36 O2	296.27098	-0.62	941	trans-13-Octadecenoic acid, methyl ester	-	C19 H36 O2	296
022	30.72	41,648,466	75.42	298.28652	Methyl stearate	112-61-8	939	C19 H38 O2	298.28663	0.11	939	Methyl stearate	112-61-8	C19 H38 O2	298
023	33.91	6,037,723	10.93	318.25265	5,8,11,14-Eicosatetraenoic acid, methyl ester, (all-Z)-	2566-89-4	909	C21 H34 O2	318.25533	-2.68	909	5,8,11,14-Eicosatetraenoic acid, methyl ester, (all-Z)-	2566-89-4	C21 H34 O2	318
024	34.01	6,574,800	11.91	316.23636	5,8,11,14,17-Eicosapentaenoic acid, methyl ester, (all-Z)-	2734-47-6	945	C21 H32 O2	316.23968	-3.32	945	5,8,11,14,17-Eicosapentaenoic acid, methyl ester, (all-Z)-	2734-47-6	C21 H32 O2	316
025	34.50	16,559,406	29.99	320.26864	8,11,14-Eicosatrienoic acid, methyl ester, (Z,Z,Z)-	21061-10-9	937	C21 H36 O2	320.27098	-2.34	937	8,11,14-Eicosatrienoic acid, methyl ester, (Z,Z,Z)-	21061-10-9	C21 H36 O2	320
026	35.13	10,403,767	18.84	322.28535	11,14-Eicosadienoic acid, methyl ester	2463-02-7	820	C21 H38 O2	322.28663	-1.28	902	cis-11,14-Eicosadienoic acid, methyl ester	-	C21 H38 O2	322
027	35.25	9,642,111	17.46	320.26997	11,14,17-Eicosatrienoic acid, methyl ester	55682-88-7	861	C21 H36 O2	320.27098	-1.01	861	11,14,17-Eicosatrienoic acid, methyl ester	55682-88-7	C21 H36 O2	320
028	35.38	18,118,358	32.81	324.30086	cis-Methyl 11-eicosenoate	2390-09-2	948	C21 H40 O2	324.30228	-1.42	948	cis-Methyl 11-eicosenoate	2390-09-2	C21 H40 O2	324
029	36.25	45,036,437	81.56	326.31784	Eicosanoic acid, methyl ester	1120-28-1	895	C21 H42 O2	326.31793	-0.10	936	Methyl 18-methylnonadecanoate	-	C21 H42 O2	326
030	38.86	36,312,501	65.76	340.33291	Heneicosanoic acid, methyl ester	6064-90-0	781	C22 H44 O2	340.33358	-0.67	781	Heneicosanoic acid, methyl ester	6064-90-0	C22 H44 O2	340
031	40.42	18,929,601	34.28	350.31571	cis-13,16-Docosadienoic acid, methyl ester	-	947	C23 H42 O2	350.31793	-2.22	947	cis-13,16-Docosadienoic acid, methyl ester	-	C23 H42 O2	350
032	40.63	22,206,388	40.21	352.33120	13-Docosenoic acid, methyl ester, (Z)-	1120-34-9	881	C23 H44 O2	352.33358	-2.38	912	Methyl 11-docosenoate	-	C23 H44 O2	352
033	41.44	48,576,846	87.97	354.34851	Docosanoic acid, methyl ester	929-77-1	940	C23 H46 O2	354.34923	-0.73	940	Docosanoic acid, methyl ester	929-77-1	C23 H46 O2	354
034	43.88	25,785,457	46.69	368.36379	Tricosanoic acid, methyl ester	2433-97-8	947	C24 H48 O2	368.36488	-1.09	947	Tricosanoic acid, methyl ester	2433-97-8	C24 H48 O2	368
035	45.55	23,274,202	42.15	380.36207	15-Tetracosenoic acid, methyl ester, (Z)-	2733-88-2	871	C25 H48 O2	380.36488	-2.81	876	15-Tetracosenoic acid, methyl ester	56554-33-7	C25 H48 O2	380
036	46.29	51,225,970	92.76	382.37968	Tetracosanoic acid, methyl ester	2442-49-1	922	C25 H50 O2	382.38053	-0.85	922	Tetracosanoic acid, methyl ester	2442-49-1	C25 H50 O2	382

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*JMS-T100GC Application Data*

## Analysis of polydimethylsiloxanes by GC/TOFMS

### Introduction

Three polydimethylsiloxane compounds; octamethylcyclotetrasiloxane (sample No. 1), decamethylcyclopentasiloxane (No. 2) and octa(dimethylsiloxo)silsesquioxane (No. 3), were analyzed using JMS-T100GC. The samples No. 1 and No. 2 were relatively small molecules with molecular weights of 296 and 370 respectively and could be introduced through the mass reference sample inlet (reservoir.) They can be used as internal mass references for accurate mass measurement. The sample No. 3 has a molecular weight of 1,016 and was difficult to be introduced through the reservoir. Sample No. 3 was analyzed by GC/MS.

### Methods

- Samples**
1. Octamethylcyclotetrasiloxane,  $C_8H_{24}O_4Si_4$ , Neat
  2. Decamethylcyclopentasiloxane,  $C_{10}H_{30}O_5Si_5$ , Neat
  3. Octa(dimethylsiloxo)silsesquioxane,  $C_{16}H_{56}O_{20}Si_{16}$ , 2 mg/ml in acetone

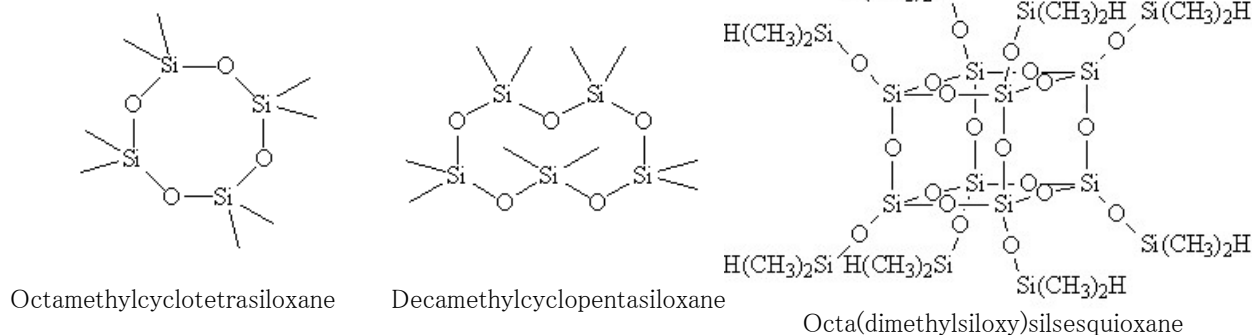


Fig.1 Structural formulae of the samples.

### GC conditions

Column:	ZB-5ms, 30 m x 0.25 mm, 0.25 $\mu$ m
Injector:	320 °C, 1 mL/min (constant flow mode,) split mode (50:1)
Oven:	50 °C (1 min) $\rightarrow$ 20 °C/min $\rightarrow$ 320 °C (5.5 min)

### MS conditions

Mass spectrometer:	JMS-T100GC "AccuTOF GC"
El ionization:	Electron energy: 70 eV      Ionization current: 300 $\mu$ A
FI ionization:	Cathode potential: -10 kV
	Emitter current: 7 mA for 20 msec between spectra
Temperatures:	Ion source: 280 °C      GC-ITF: 280 °C      Reservoir: 100 °C
Acquired mass range:	$m/z$ 35 – 1,400
Spectral recording interval:	0.4 sec

## Results and discussion

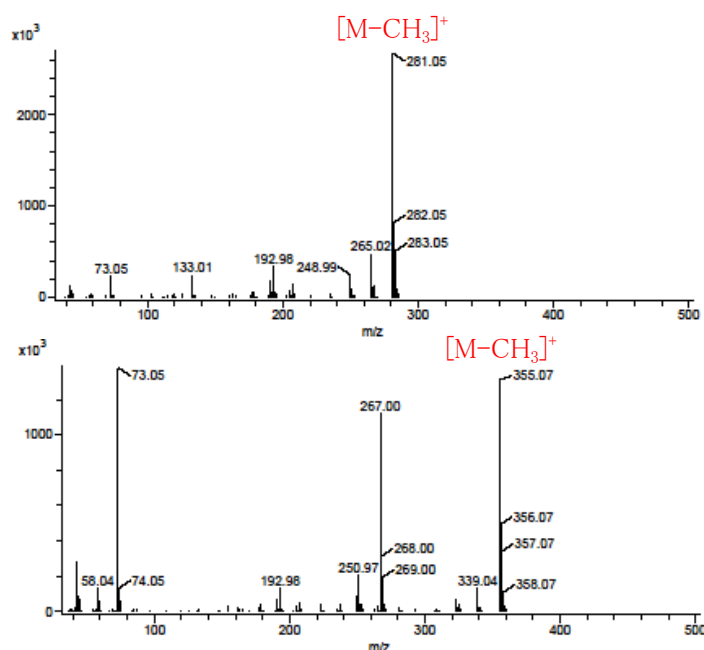


Fig.2 Mass spectra of Octamethylcyclotetrasiloxane (upper) and Decamethylcyclopentasiloxane (lower) by EI.

Table1 Information of calculated exact mass for each ions .

	Calculated exact mass	Fomula
Octamethylcyclo tetrasiloxane	73.04735	C <sub>3</sub> H <sub>9</sub> Si
	248.98909	C <sub>5</sub> H <sub>13</sub> O <sub>4</sub> Si <sub>4</sub>
	265.02039	C <sub>6</sub> H <sub>17</sub> O <sub>4</sub> Si <sub>4</sub>
	281.05169	C <sub>7</sub> H <sub>21</sub> O <sub>4</sub> Si <sub>4</sub>
Decamethylcyclo pentasiloxane	73.04735	C <sub>3</sub> H <sub>9</sub> Si
	266.99965	C <sub>5</sub> H <sub>15</sub> O <sub>5</sub> Si <sub>4</sub>
	355.07048	C <sub>9</sub> H <sub>27</sub> O <sub>5</sub> Si <sub>5</sub>
Octa(dimethylsiloxy) silsesquioxane	1000.94384	C <sub>15</sub> H <sub>53</sub> O <sub>20</sub> Si <sub>16</sub>
	1014.95949	C <sub>16</sub> H <sub>55</sub> O <sub>20</sub> Si <sub>16</sub>

The acquired mass spectra for sample 1 and 2 are shown in Fig. 2. For both compounds, the base peaks were those of  $[M-CH_3]^+$  ions, whereas the molecular ions were not detected. The major peaks, as documented in Table 1, can be used as internal mass references for accurate mass measurement. If these compounds are analyzed by field ionization (FI,) the base peaks would be those of  $[M-CH_3]^+$  ions; virtually no molecular ions or fragment ions would be detected (cf. MS Tips No. 96.)

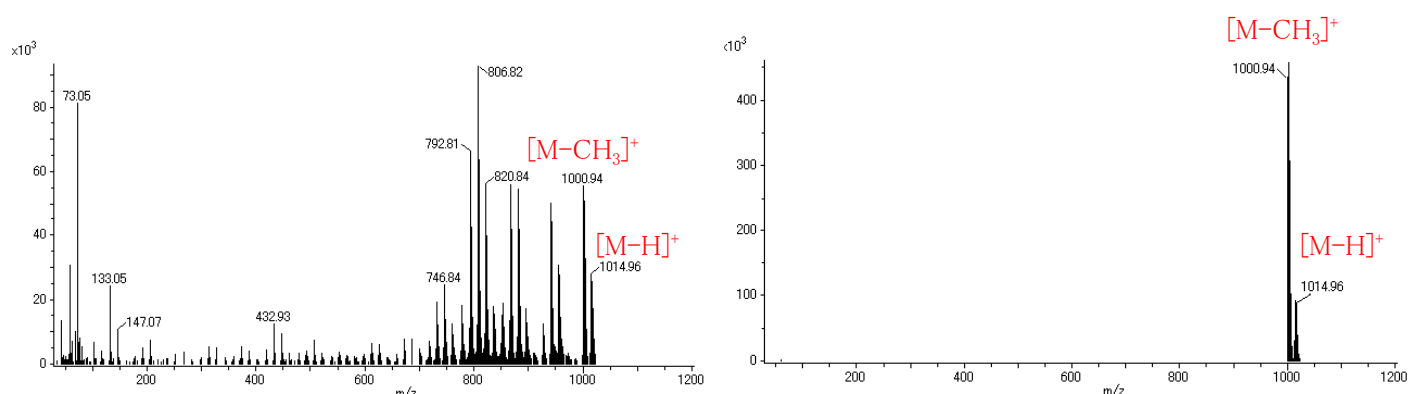


Fig.3 Mass spectrum of Octa(dimethylsiloxy)silsesquioxane by EI (left) and FI (right).

The mass spectrum of octa(dimethylsiloxy)silsesquioxane is shown in Fig. 3. Characteristic ions such as  $[M-H]^+$  at  $m/z$  1014.96 and  $[M-CH_3]^+$  at  $m/z$  1000.94 were observed in both electron ionization (EI) and FI. In EI, fragment ions that are common to sample 1 and 2, including that at  $m/z$  73.05, were detected whereas no fragment ions other than those at  $m/z$  1014.96 and  $m/z$  1000.94 were detected in FI. Polydimethylsiloxanes are found to generate strong  $[M-CH_3]^+$  ions in both EI and FI but detection of the molecular ions are found to be difficult even in FI.

## Acknowledgement

The author would like to thank Mr. Junji Takaie of Showa Denko K.K. for his generous gift of the samples.

## GC/TOFMS analysis of high boiling point compounds ~ cholesterol and Irganox® 1010 ~

### Introduction

As examples of GC/MS analyses of high boiling point compounds, cholesterol and Irganox® 1010, an anti-oxidant additive for polymers, were analyzed. The analyses were performed with electron ionization (EI) and field ionization (FI,) which is a soft ionization method.

### Methods

<u>Samples</u>	cholesterol	1 mg/mL (in methanol)
	Irganox® 1010	1 mg/mL (in methanol)

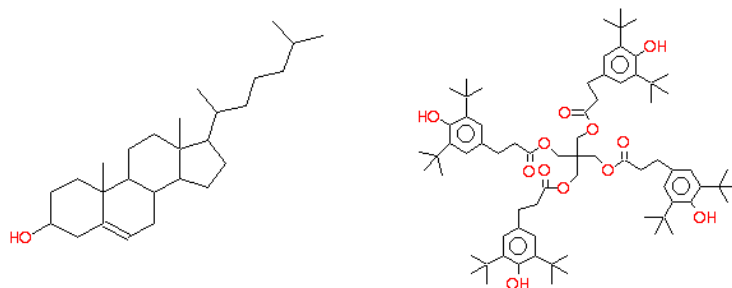


Fig.1 Structural formulas of Cholesterol (left) and Irganox® 1010 (right)

### GC conditions

Column:	DB-1HT, 7 m x 0.25 mm, 0.10 µm
Injector:	380 °C, 2 mL/min (constant flow mode)
Injection mode:	EI: split (80:1), FI: split (10:1)
Oven:	120 °C (1 min) → 30 °C/min → 380 °C (10.33 min)

### MS conditions

Mass spectrometer:	JMS-T100GC "AccuTOF GC"		
Ionization mode: EI:	Electron energy:	70 eV	
	Ionization current:	300 μA	
	Ion source temperature:	300 °C	
FI:	Cathode potential:	-10 kV	
	Emitter current:	35 mA for 30 msec between spectra	
	Ion source temperature:	250 °C	
GC interface temperature:	350 °C		
Acquired mass range:	<i>m/z</i> 35 – 1,400		
Spectral recording interval:	0.4 sec		

## Results and Discussion

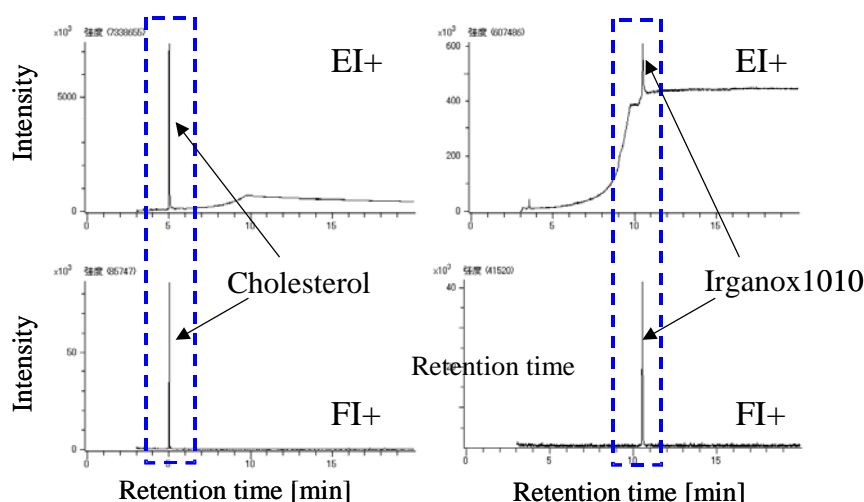


Fig.2 RTICCs of Cholesterol (left) and Irganox® 1010 (right)

Reconstructed total ion current chromatograms are shown on Fig. 2. In GC/EI analyses, ions derived from GC column bleed (e.g.,  $m/z$  207, 281) were strongly observed. As a result, the baseline of RTICC went up as GC oven temperature was programmed up. Since cholesterol eluted at around 240 °C, the base line rise was not so significant and the chromatographic peak was easily seen. Irganox® 1010 peak eluted at 380 °C (i.e., at the final oven temperature,) was on a high baseline.

In GC/FI analyses, the GC column bleed was hardly ionized and the RTICC baseline was flat. Both cholesterol and Irganox® 1010 peaks were easily detectable on RTICCs.

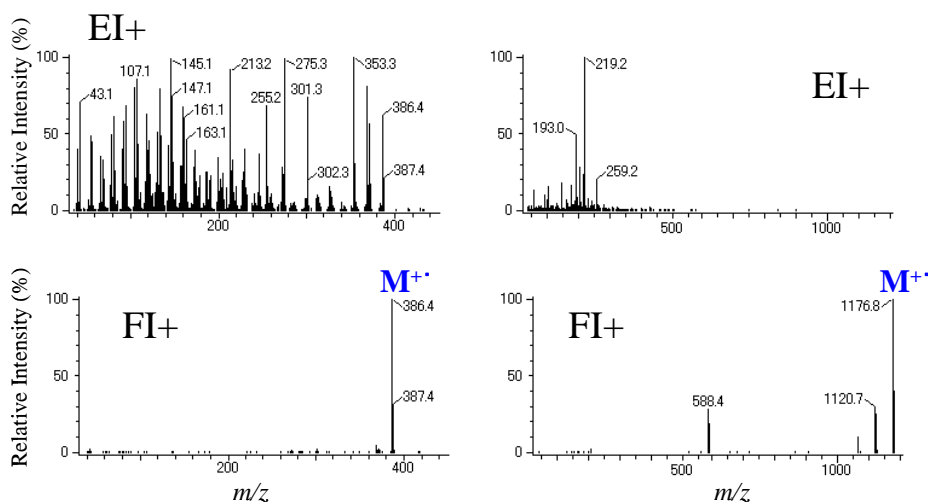


Fig.3 Mass spectra of Cholesterol (left) and Irganox® 1010 (right)

The mass spectra observed are shown on Fig. 3. In EI mass spectra, a lot of fragment ion peaks and no molecular ion peak from Irganox® 1010 were observed. In contrast, there were only a few fragment ion peaks in FI mass spectra and the molecular ion peaks were observed as base peaks for both compounds.

The JMS-T100GC “AccuTOF GC” is capable of performing GC/MS analyses of very high boiling point compounds, such as Irganox® 1010. The ionization method can be chosen from EI, FI, and chemical ionization (CI.) By combining FI, with which you can observe molecular ion from most analytes, and EI, a hard ionization method, more accurate and confident qualitative analyses become possible. (U – JT)

## Analysis of photo polymerization initiator in UV light curing adhesives by GC/TOFMS

A UV and visible light curing adhesive is a liquid composed of monomer, oligomer, initiator and additives. It cures layers in a short period of time under the influence of light.

In this report, a photo polymerization initiator in a UV light curing adhesive was analyzed by electron ionization (EI) and field ionization (FI).

### <Sample and measurement conditions>

Sample UV light curing adhesive

#### GC condition

GC: Agilent 6890N  
Column: ZB-5ms, 30m×0.25mm I.D., 0.25μm  
Oven Temp: 40°C (1min)→10°C/min→280°C(5min)  
Injection Temp.: 280°C  
Injection mode: Split (50:1) [for EI+], Splitless [for FI+]  
Injection volume: 1.0μL  
Carrier gas: He (1.0mL/min: constant flow mode)

#### MS conditions

MS: JMS-T100GC "AccuTOF GC"

Ionization mode : EI+ and FI+

For EI(+): Ionization voltage: 70V  
Ionization current: 300μA  
Chamber Temp.: 280°C  
For FI(+): Cathode voltage : -10kV  
Emitter current : 0 mA

Acquired m/z range: m/z 35—500

Recording interval: 0.6sec

### <Result>

The TIC is shown in Fig.1. Many components are observed in the TIC in both EI+ and FI+.

The unreacted photo polymerization initiator (R.T. 27.9 min.) was determined by using accurate mass measurement conditions in EI and FI.

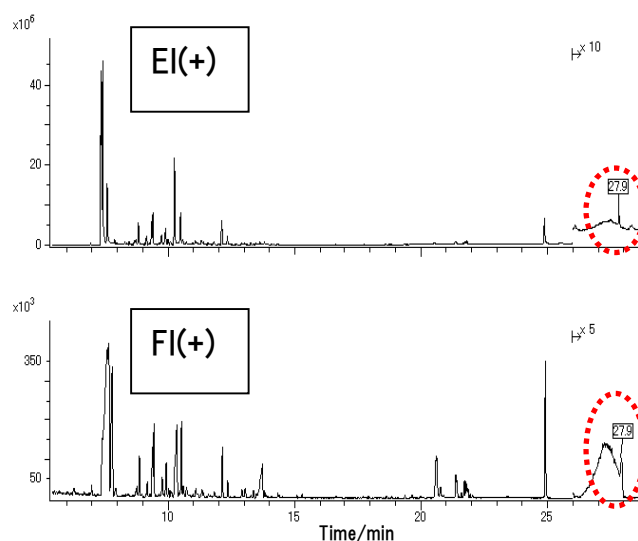


Fig.1 TIC <Upper: EI(+), Lower: FI+>

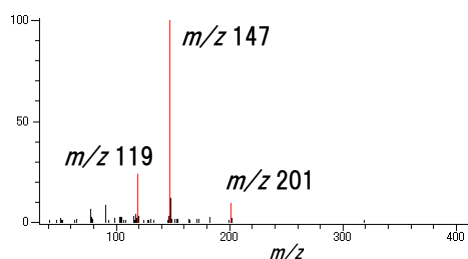


Fig.2 EI+ mass spectrum

Table1 Elemental composition determination by EI+

Observed m/z	Calculated m/z	Error (mDa)	Estimated mormula	U.S.
119.08526	119.08608	-0.82	12C9 1H11	4.5
147.08013	147.08099	-0.86	12C10 1H11 16O	5.5
201.04750	201.04693	0.58	12C12 1H10 16O 31P	9.5
	201.04920	-1.70	12C2 1H21 16O2 32P4	-1.5

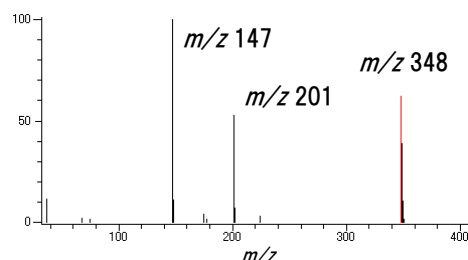


Fig.3 FI+ mass spectrum

Table2 Elemental composition determination by FI+

Observed m/z	Calculated m/z	Error (mDa)	Estimated mormula	U.S.
348.12829	348.12792	0.37	12C22 1H21 16O2 31P	14.0
	348.13019	-1.90	12C12 1H32 16O3 31P4	3.0
	348.12555	2.74	12C15 1H26 16O5 31P2	6.0
	348.13256	-4.27	12C19 1H27 32P3	11.0

An EI mass spectrum and a FI+ mass spectrum are shown in Fig.2 and Fig.3. The indicated ions (red) are selected for elemental composition determination. The results for each spectrum are shown in Table 1 and Table 2.

Ions with  $m/z$  119, 147 and 201 are mainly observed by EI+. The result of the elemental composition determination for these ions, shows that only one ion formula can be estimated for  $m/z$  119 and 147. On the other hand, 2 different ion formula are estimated for  $m/z$  201. Finally, ion formula for  $m/z$  201 could be estimated as  $C_{12}H_{10}OP$  according to the mass difference, the elements present and its number of elements. Also, the ion at  $m/z$  201 was a fragment ion because the unsaturation number is half-integer.

Ions at  $m/z$  147, 201 and 348 are mainly observed in FI+. Since ions at  $m/z$  147 and 201 are the same in EI+, an elemental composition for ion at  $m/z$  348 was estimated. There are 4 candidates within 5 mDa of mass difference but  $C_{22}H_{21}O_2P$  was estimated, based on the mass difference and the number of phosphor and oxygen atoms. The unsaturation number of this formula is integer so, this ion is determined as molecular ion. Since the unsaturation number is 14, it's possible to consider more than 2 benzene rings are included in the structure. The final estimated structure is shown in Fig.4.

JMS-T100GC "AccuTOF GC" obtains accurate  $m/z$  values very easily in EI+ and also in FI+. This capability is very helpful for structure analysis for unknown compounds.

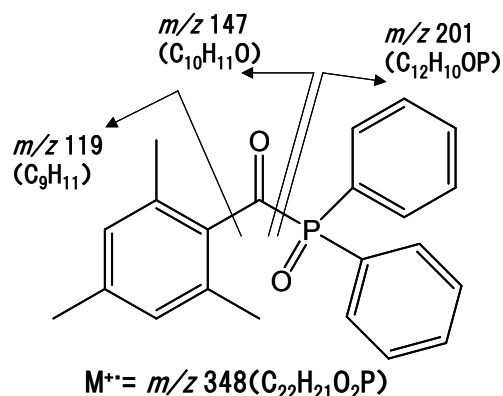


Fig.4 Estimated structure



## Analysis of advanced materials by FD/FI using “AccuTOF GC” Part I

**~ analysis of polymer building blocks with isocyanate and pilazole groups ~**

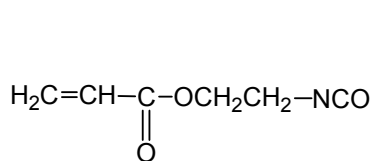
## Introduction

Field Ionization (FI) is a soft ionization method which ionizes analytes by electron tunneling from analyte molecules to a solid surface (emitter) in a high electric field. Vaporized analyte molecules are introduced to the proximity of the emitter.

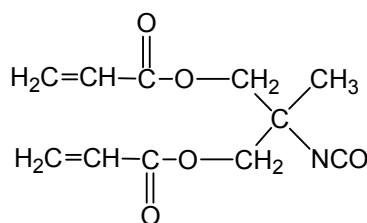
We have analyzed functional monomers (building blocks for functional polymers) by GC/El and GC/Fl methods and compared the obtained mass spectra.

## Methods

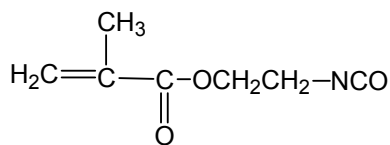
Samples: functional monomers with isocyanate and pilazole groups (Showa Denko K.K.)



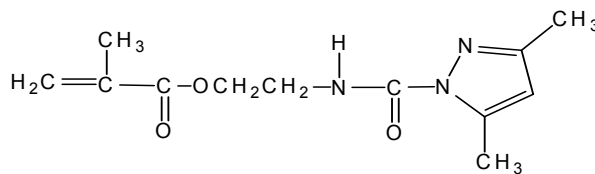
(1) Karenz AOI® ( $C_6H_7NO_3$ )



(3) Karenz BEI® ( $C_{11}H_{13}NO_5$ )



(2) Karenz MOI® ( $C_7H_9NO_3$ )



(4) Karenz MOI-BP® (C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>)

### GC conditions

Column: ZB-5ms, 30 m x 0.25 mm, film thickness: 0.25  $\mu$ m  
Carrier gas: Helium, 1.0 mL/min (constant flow rate mode)  
Oven: 40  $^{\circ}$ C (2 min)  $\rightarrow$  30  $^{\circ}$ C/min  $\rightarrow$  280  $^{\circ}$ C (12 min)

## MS conditions

Mass spectrometer: JMS-T100GC “AccuTOF GC”  
 Ionization mode: EI: Electron energy: 70 eV, Ionization current: 300  $\mu$ A  
 FI: Cathode potential: -10 kV, Emitter current: 0 mA  
 Acquired mass range:  $m/z$  35 – 550  
 Spectral recording interval: 0.4 sec

## Results and Discussion

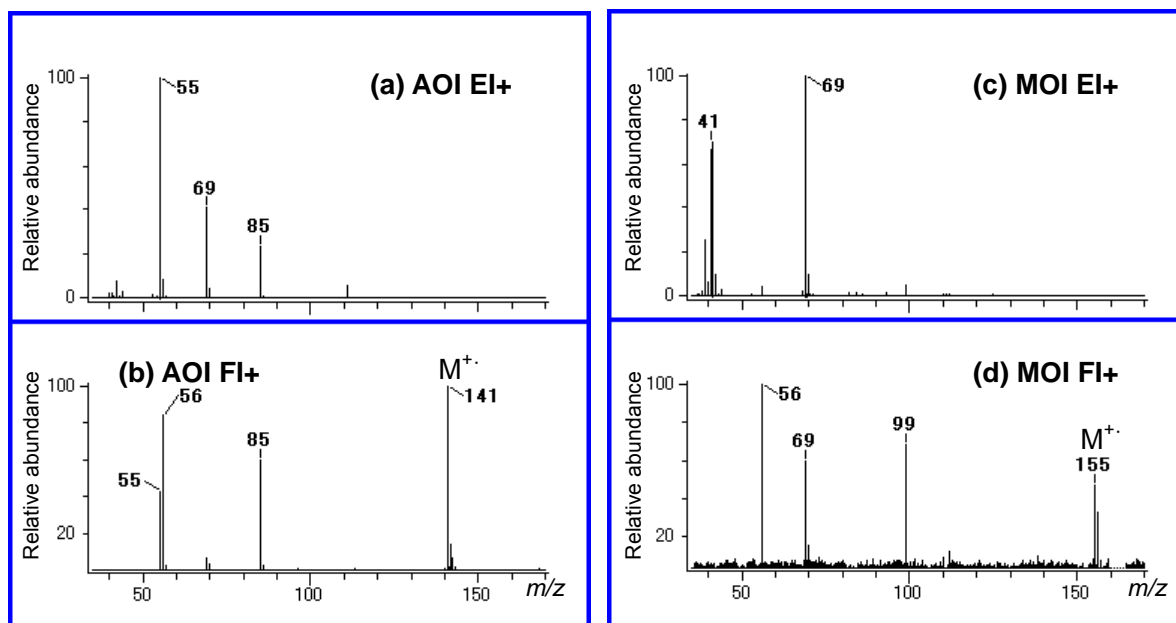


Fig. 1 Mass spectra of Karenz AOI®; (a) EI+, (b) FI+  
Mass spectra of Karenz MOI®; (c) EI+, (d) FI+

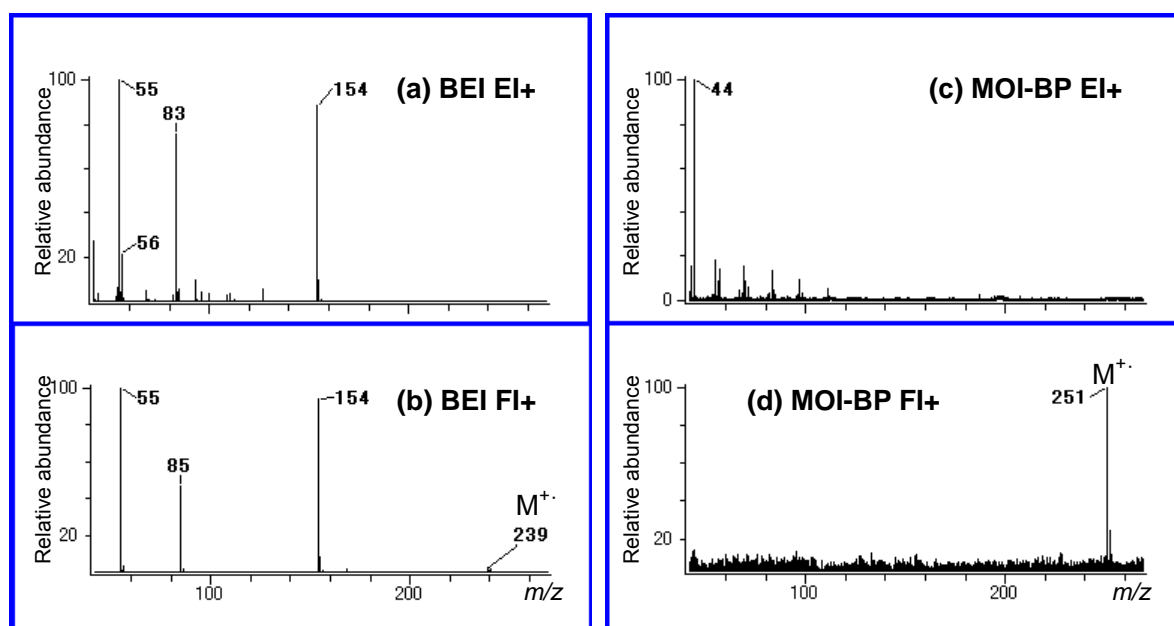


Fig. 2 Mass spectra of Karenz BEI®; (a) EI+, (b) FI+  
Mass spectra of Karenz MOI-BP®; (c) EI+, (d) FI+

Karenz AOI®, MOI®, BEI® have isocyanate groups, and MOI-BP® has a pyrazole group. Observation of molecular ions is difficult for these types of compounds. (Refer (a) and (c) in Figs. 1 and 2 respectively). It was possible to observe molecular ions from all samples by using FI method. FI method was found suitable for the analysis of highly reactive compounds such as the ones above.

## Acknowledgement

We acknowledge the generous offer of the samples by Fine Chemicals Group, Specialty Chemicals Department, Chemicals Division, SHOWA DENKO K.K.

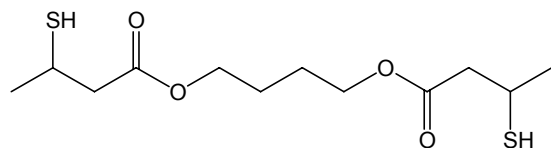
**Analysis of advanced materials by FD/FI using “AccuTOF GC” Part II****~ analysis of multifunctional thiols, curing agents for functional polymers ~****Introduction**

Field Ionization (FI) is a soft ionization method which ionizes analytes by electron tunneling from analyte molecules to a solid surface (emitter) in a high electric field. Vaporized analyte molecules are introduced to the proximity of the emitter.

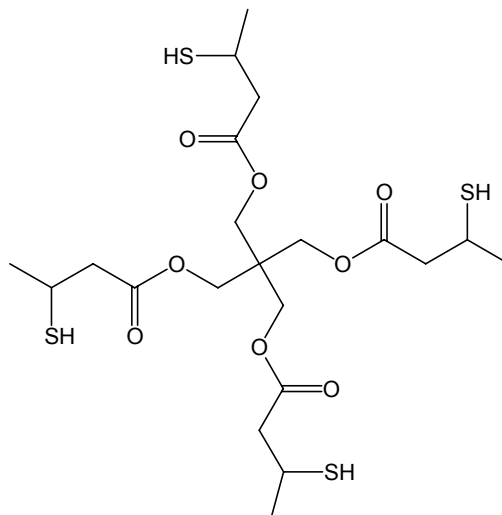
We have analyzed multifunctional thiols, curing agents for functional polymers, by GC/EI and GC/FI methods and compared the mass spectra obtained.

**Methods**

Samples: multifunctional thiols (Showa Denko K.K.)



(1) Karenz MT® BD1 ( $C_{12}H_{22}O_4S_2$ )



(2) Karenz MT® PE1 ( $C_{21}H_{36}O_8S_4$ )

**GC conditions**

Column: ZB-5ms, 30 m x 0.25 mm, film thickness: 0.25  $\mu$ m  
 Carrier gas: Helium, 1.0 mL/min (constant flow rate mode)  
 Oven: 40 °C (2 min)  $\rightarrow$  30 °C/min  $\rightarrow$  280 °C (12 min)

**MS conditions**

Mass spectrometer: JMS-T100GC “AccuTOF GC”  
 Ionization mode: EI: Electron energy: 70 eV, Ionization current: 300  $\mu$ A  
                           FI: Cathode potential: -10 kV, Emitter current: 0 mA  
 Acquired mass range:  $m/z$  35 – 550  
 Spectral recording interval: 0.4 sec

## Results and Discussion

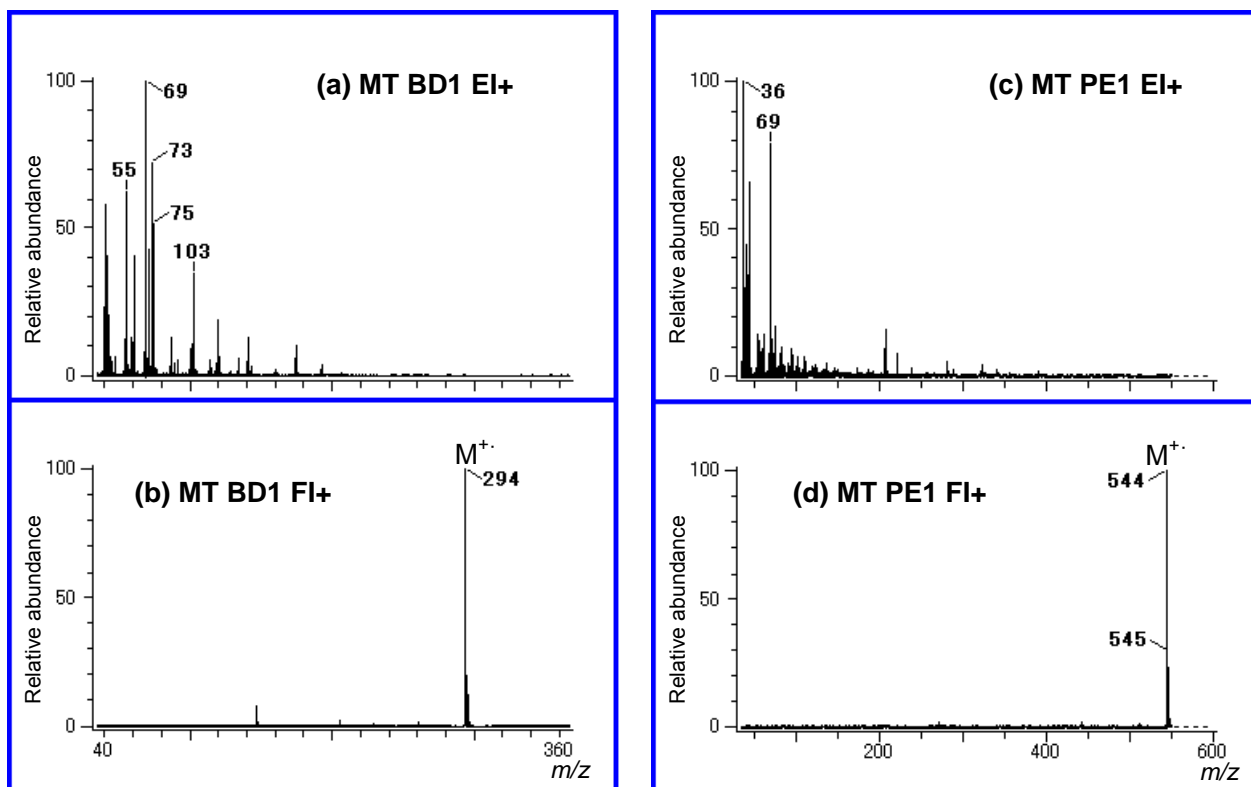


Fig. 1 Mass spectra of Karenz MT® BD1; (a) EI+, (b) FI+  
Mass spectra of Karenz MT® PE1; (c) EI+, (d) FI+

For both Karenz MT® BD1 and PE1, which are multifunctional thiols, many fragment ions were observed with EI method while molecular ions were not observed at all. Molecular ions were very clearly observed by FI method for both samples while only a few fragment ions were observed, as shown in (b) and (d) of Fig. 1. The FI method was found suitable for analyzing multifunctional thiol compounds.

## Acknowledgement

We acknowledge the generous offer of the samples by Fine Chemicals Group, Specialty Chemicals Department, Chemicals Division, SHOWA DENKO K.K.

## Detection of molecular ions of fluorine compounds by GC/FI-TOFMS

Chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) have been used extensively as solvent, cleaning agent and foaming agent. Unfortunately CFC and HCFC have negative effects on the environment like ozone depletion and global warming. For this reason, CFC's substitutes, such a hydrofluorocarbon (HFC) and hydrofluorocarbon ether (HFE), have been developed.

In general, fluorine compounds are analyzed by gas chromatography (GC) / mass spectrometry (MS). However, molecular ions of these compounds are often not observed with electron ionization (EI) and chemical ionization (CI). Therefore, molecular weight determination is often difficult for unknown compounds when they are present as by-product or impurity.

On the other hand, field ionization (FI) is a very soft ionization technique capable to observe the molecular ion of volatile compounds. This application note shows that FI is a suitable technique to determine the molecular weight of compounds which are not producing molecular ions in EI or CI.

### 【Measurement Conditions】

Mass Spectrometer: JEOL JMS-T100GC

Gas Chromatograph: Agilent 6890N

Sample:

Fluorinated ether (MW174) and AK225 (Mixture)

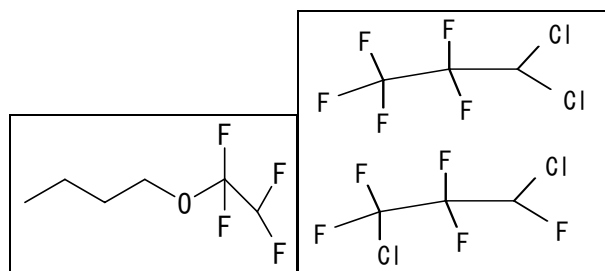


Fig.1 Structure of fluorinated ether (Left) and AK225 (Right)

GC	
Carrier Gas	He
Flow rate	0.8 ml/min (const. flow)
Temperature (Injection)	200 degree C
Injection mode	Split (10:1)
Oven temperature	40C (2min) - <5C/min> - 60C - <15C/min> - 200C
MS	
Ionization mode	FI+
Acquired m/z range	35 -450
Spectrum recording interval	0.4 sec

### 【Result】

Each TIC and FI mass spectrum of 2 samples are shown in Fig.2 and Fig.3. Although the molecular ion of these compounds are not observed by EI or CI, FI works well and produces the molecular ion of each compound clearly.

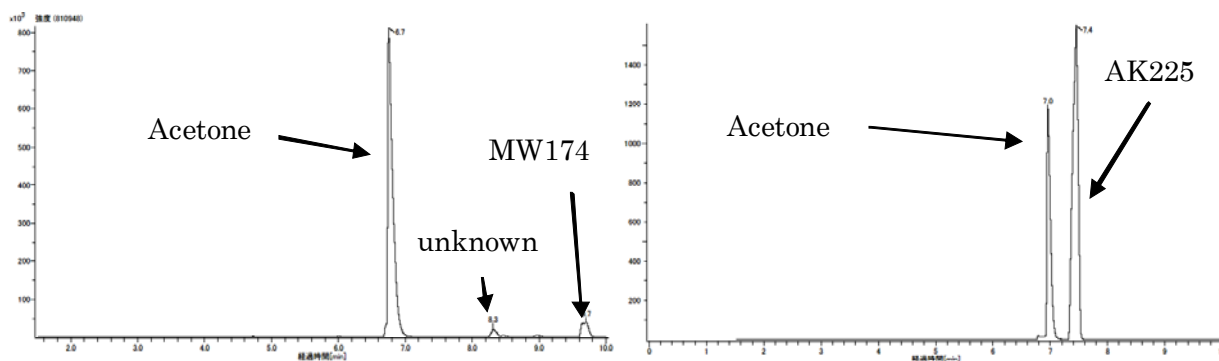


Fig.2 TIC of fluorinated ether (left) and AK225 (right)

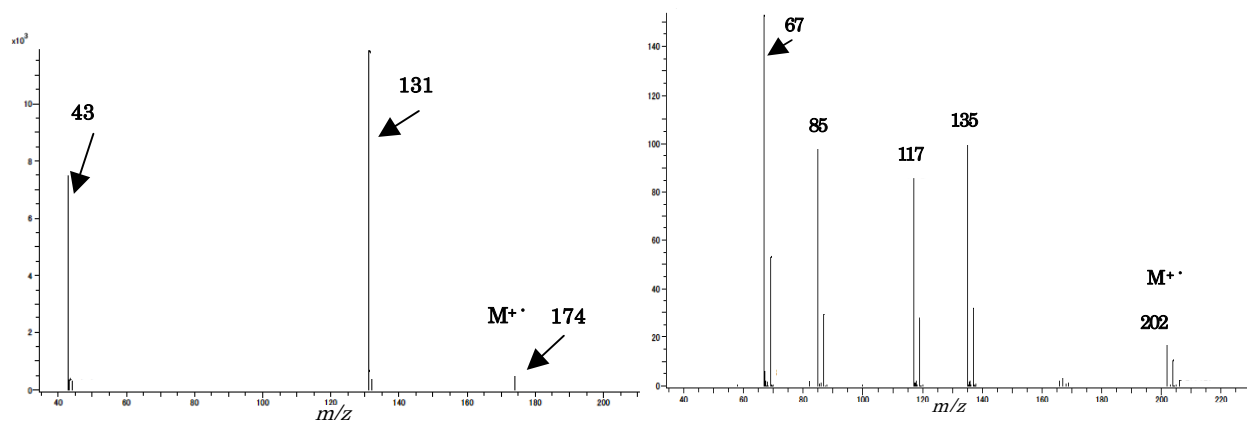


Fig.3 FI spectra of fluorinated ether (left) and AK225 (right)

Both compounds produce not only fragment ions but also the molecular ion with FI. It is very clear to confirm the molecular weight of compounds in comparison with EI and CI. In addition, the elemental composition of the molecular ion and fragment ions were determined with accurate mass. This result is very useful to identify the unknown compound.

Table 2 Result of elemental composition determination for fluorinated ether (left) and AK225 (right)

Observed	Calculated	Diff.(mDa)	Formula
43.05632	43.05478	1.55	C <sub>3</sub> F <sub>7</sub>
131.01407	131.01200	2.07	C <sub>3</sub> H <sub>3</sub> F <sub>4</sub> O
	131.01086	3.21	C <sub>6</sub> H <sub>2</sub> F <sub>3</sub>
174.06348	174.06678	-3.29	C <sub>6</sub> H <sub>10</sub> F <sub>4</sub> O

Observed	Calculated	Diff.(mDa)	Formula
66.97379	66.97508	-1.29	CHClF
84.96424	84.96566	-1.42	CClF <sub>2</sub>
116.97270	116.97189	0.81	C <sub>2</sub> HClF <sub>3</sub>
134.96324	134.96347	0.78	C <sub>2</sub> ClF <sub>4</sub>
201.93481	201.93755	-2.74	C <sub>3</sub> HCl <sub>2</sub> F <sub>5</sub>

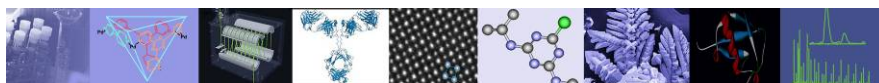
#### 【Acknowledgement】

We gratefully acknowledge Dr. Yoji Nakajima of Asahi Glass Co., Ltd. for providing the fluorinated compounds.

#### 【Reference】

T. Isemura, R. Kakita, A. Tamaoki, S. Yonemori, J. Fluor. Chem., 80(1996)81-85




**JEOL**

## AccuTOF-GCv Series

### The Power of Exact Mass Measurement: An Example of Unknown Compound Identification

#### Introduction

Recently, JEOL introduced the AccuTOF-GC, an innovative GC/time-of-flight mass spectrometer (TOF MS) that is capable of both high data acquisition rates and easy exact mass measurements. The exact mass measurements can then be used to generate lists of possible elemental compositions, which is a powerful tool for identifying unknown compounds. Additionally, this information can be combined with the fragmentation information to help confirm the identity of an unknown compound.

In this work, the AccuTOF-GC system was used to identify an unknown compound in a liquid crystal extract.

#### Experimental

The system used for this work was the JEOL AccuTOF-GC TOF MS. Liquid crystal from a pocket calculator display was dissolved in hexane. Afterwards, the sample was injected onto a DB-5 GC column (0.18mm x 10m, 0.18 $\mu$ m film thickness). The oven temperature was held at 40°C for 1 min and then increased to 300°C at 50°C/min rate. The TOF MS was tuned to achieve a resolution of 5,000 (FWHM) at  $m/z$  293 (Perfluorokerosene). 2,4,6-tris(trifluoromethyl)-1,3,5-triazine was used as an internal standard for the exact mass measurements in both EI and CI modes. The CI reagent gas was isobutane. The NIST mass spectral database (2002) was used for the EI spectrum searches.

#### Results

Figure 1 shows the total ion chromatograms (TIC) for the liquid crystal extract in both EI and CI modes. All of the peaks in the TIC were identified by the NIST library search using their EI spectra except the last peak (marked with an asterisk). Both the EI and CI spectra for this compound are shown in Figure 2. The base peak at  $m/z$  334 ( $[M+H]^+$ ) was observed in the CI spectra which correlated with the small peak at  $m/z$  333 ( $[M]^+$ ) in the EI spectra, thus indicating that the molecular weight for this compound is 333. The NIST library search for the EI spectrum yielded a very low matching score and none of the matches had a molecular weight of 333. It is likely that this compound

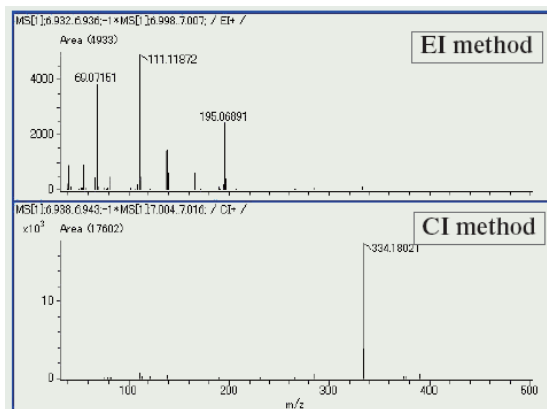


Fig. 1 TIC of liquid crystal extract in both EI and CI modes

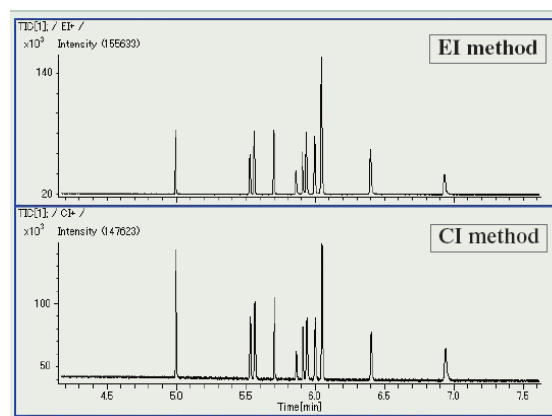
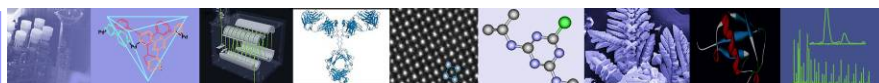


Fig. 2 Mass spectra for the unknown compound marked with an asterisk (\*) in Fig. 1

is not in the current version of the NIST library database. To identify this unknown compound, we used the exact mass measurement to generate a list of the possible elemental compositions for each ion. Based on the typical liquid crystal compound structures listed in the book "Liquid Crystal Compound Glossary" (1), only C, H, O, N, and F were included in the elemental composition calculation. The AccuTOF-GC can measure masses with errors smaller than 2 mmu. All possible compositions for each ion within a 2 mmu tolerance are listed in Table 1.



Candidate	Measured m/z	Theoretical m/z	Error (mmu)	Estimated formula	Unsaturation number
No.1	334.18021	334.18070	-0.49	C <sub>22</sub> H <sub>24</sub> NO <sub>2</sub>	11.5
No.2		334.18185	-1.64	C <sub>19</sub> H <sub>25</sub> FNO <sub>3</sub>	7.5

Ion	Measured m/z	Theoretical m/z	Error (mmu)	Estimated formula	Unsaturation number
m/z 333	333.17432	333.17288	1.44	C <sub>22</sub> H <sub>23</sub> NO <sub>2</sub>	12
m/z 195	195.06891	195.06841	0.5	C <sub>13</sub> H <sub>9</sub> NO	10
m/z 111	111.11872	111.11738	1.34	C <sub>8</sub> H <sub>15</sub>	1.5
m/z 69	69.07042	69.07042	1.09	C <sub>6</sub> H <sub>9</sub>	1.5

Table 1. Results of exact mass measurement and elemental composition determination

Let us first consider the No.2 composition C<sub>19</sub>H<sub>25</sub>FNO<sub>3</sub> as the [M+H]<sup>+</sup> ion. Compounds having three oxygen atoms are limited to azoxy compounds and p-cyano-phenyl-ester compounds with p-alkyl substitution of a benzoic acid. However, none of these compounds containing a fluorine atom have been previously reported as a possible liquid crystal composition (1). As a result, the elemental composition was assigned as the first composition, C<sub>22</sub>H<sub>24</sub>NO<sub>2</sub>. It is known that there are no liquid crystal compound that contain -NH<sub>2</sub> or -NO<sub>2</sub> groups (1). Therefore, one nitrogen atom in this composition has to be in the form of -CN. The first composition also has two oxygen atoms, which were assigned as an ester. In addition, the unsaturation number for [M+H]<sup>+</sup> is 11.5. There must be at least one or two benzene rings in the structure. Based on all of these estimations and the typical liquid crystal compounds listed in "Liquid Crystal Compound Glossary" (1), two structures for this compound were possible, as shown in Figure 3.

To determine which structure is most probable, the 3 major fragment ions, m/z 69, 111, and 195 were

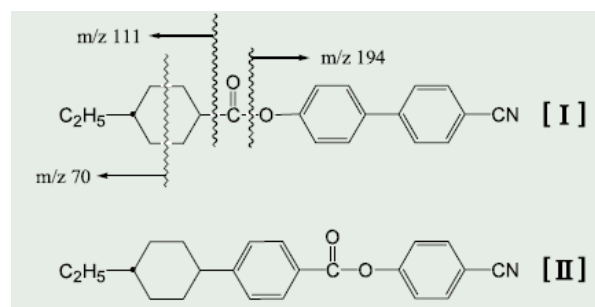


Fig. 3 Possible structures for unknown liquid crystal compound

considered in the EI spectra. The ion at m/z 111 is likely formed by a simple cleavage of an alkyl group and the m/z 69 is formed by a cleavage in the cyclohexane ring with a hydrogen transfer. These two fragment ions can be formed from both structures I and II. However, m/z 195 can only be formed by a simple cleavage of the alkoxy group with hydrogen transfer in structure I. Thus, the most likely structure for this unknown compound is structure I.

### Conclusion

Using a list of possible liquid crystal candidates, the exact mass measurements for the molecular ions and fragment ions were used to determine the structure of an unknown compound that was not identified by the NIST library search.

### Reference

(1) Liquid Crystal Compound Glossary, ed. Japan Society for the Promotion of Science, Baifukan Co., Ltd, Tokyo

# Confirmation of the chemical formula of heat/light sensitive compounds using field desorption coupled with high-resolution mass spectrometry

Related product: Mass spectrometer (MS)

## Introduction

Field desorption (FD) is a soft ionization technique useful for producing molecular ions in an MS ion source. The combination of high-resolution time-of-flight mass spectrometry (HRTOFMS) and FD is useful for direct MS measurement of a sample, and provides information for identifying the chemical formula of synthetic compounds and confirming the molecular weight. Since FD-HRMS vaporizes and ionizes a sample rapidly in a vacuum, and does not use a gas chromatograph, it has advantages for measuring unstable compounds, such as those sensitive to heat and light.

The FD emitter consists of carbon whiskers on a tungsten wire, and is inserted into the ion source using a probe. After coating the emitter with a sample solution and installing the probe to MS, FD measurement is performed by turning on the high voltage in the mass spectrometer. The most common method for coating the FD emitter is using a micro-syringe. This application note reports the syringe sampling procedure, and measurement results of example compounds that are sensitive to heat and light.

## Measurement

Two bis(diazo) compounds sensitive to heat and light were measured. The corresponding chemical structures are shown in Figure 1. The sample was dissolved in tetrahydrofuran to concentration of 10 mg/mL (Sample solution).

Table 1 shows the details of the measurement conditions for FD-HRMS analysis. The sampling procedure and tools are illustrated in Figure 2.

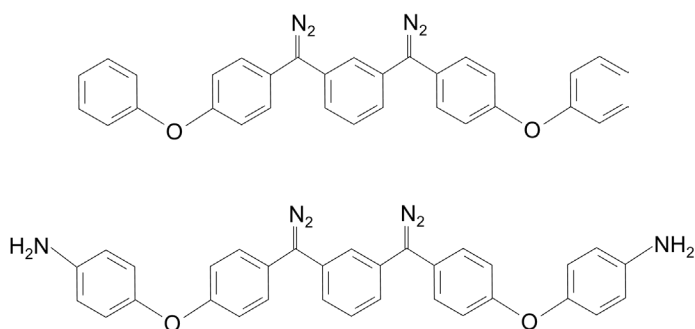


Figure 1. Chemical structures

Table 2. The features of syringe sampling with tool

Sampling operability	Requires familiarity with sampling
Sample volume	Approx. 4 $\mu$ L/measurement
Merits	<ul style="list-style-type: none"> <li>Requires smaller sample volume</li> <li>Good for analytes in solvents with low boiling temperatures</li> </ul>

Table 1. Measurement and analysis conditions

HRMS	
Sampling method	Syringe
Sample volume	4 $\mu$ L
TOFMS	JMS-T2000GC (JEOL)
Ionization	FD+: -10 kV, 40 mA
Cathode voltage	-10 kV
Emitter current program	0 mA $\rightarrow$ 25.6 mA/min $\rightarrow$ 40 mA
Monitor ion range	$m/z$ 35-1600

## Sampling Procedure

1. Set the probe on the probe stand.
2. Pull up 4  $\mu$ L of sample solution using the micro-syringe, and set the micro-syringe on the syringe stand.
3. Move the tip of the micro-syringe close to the emitter.
4. Push the plunger to make droplet of sample solution, then coat the emitter with the sample droplet.

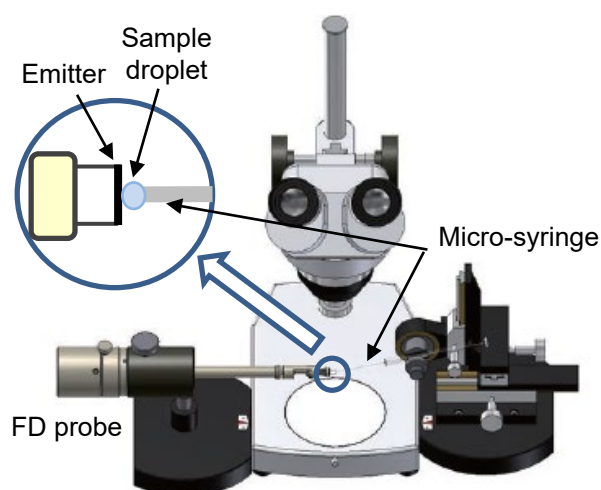
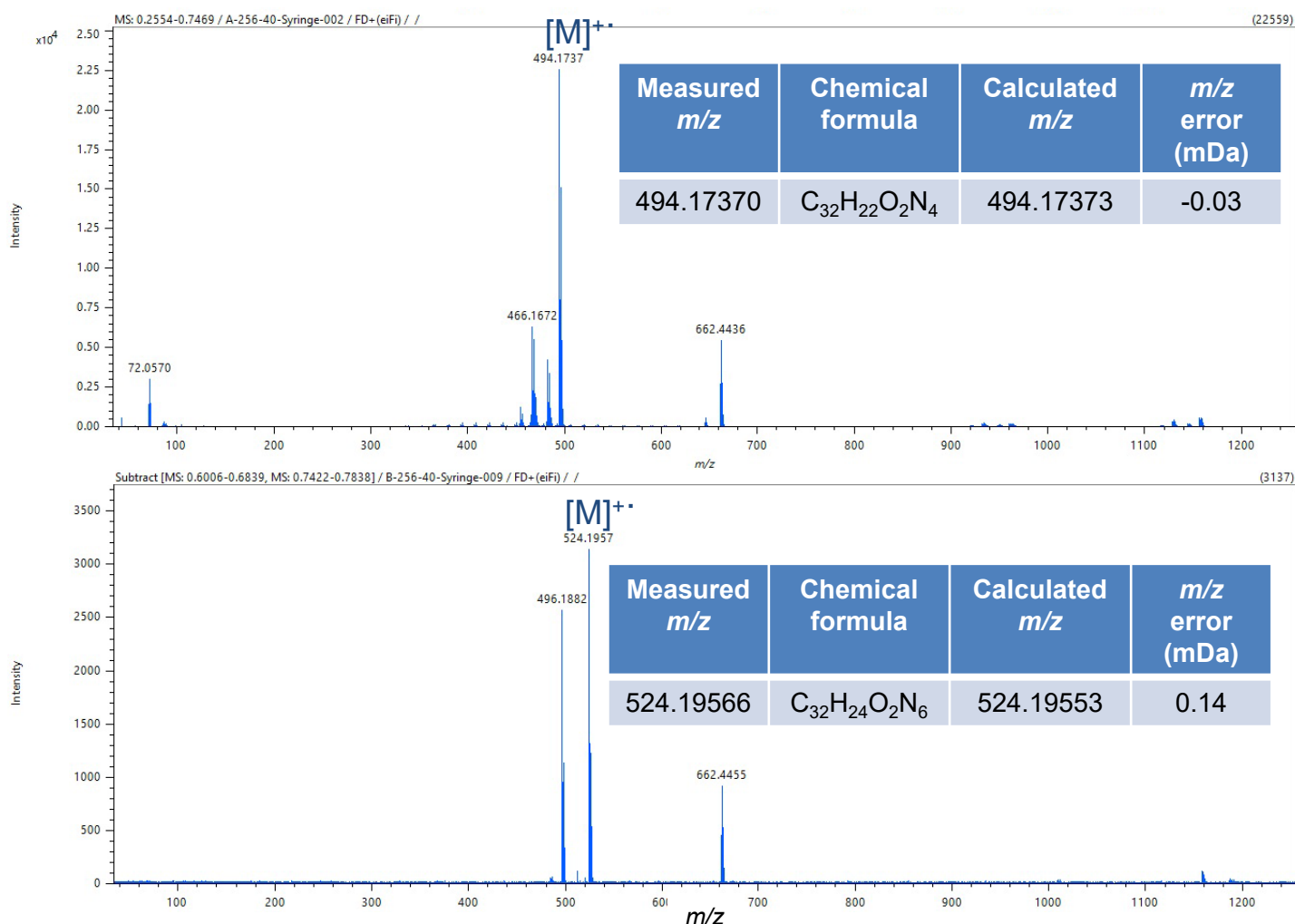


Figure 2. Scheme of syringe sampling tool

## Result

FD-HRMS mass spectra were shown in Figure 3. The molecular ion  $[M]^{+•}$  was primary component detected from each sample. Some impurities or reacted compounds were also detected, though peak intensity was notably less than the molecular ion peak. The accuracy of the  $m/z$  measured for both molecular ions was less than 1 mDa of error.



**Figure 3. FD mass spectra and estimated chemical formulae calculated from the exact mass of the molecular ions**

The advantages of the syringe-sampling method are shown in Table 2. Although the method requires some familiarity with the sampling operation, only a small sample volume is required, because it can be dispensed with a micro-syringe. The method can also result in less contamination at the emitter, because the sample is applied only to the emitter wire. It is also possible to get a higher concentration of sample on the emitter by repeatedly applying the sample solution. Using an air tight micro-syringe for sampling is advantageous when using highly volatile solvents.

## Summary

In this application note, we reported the FD-HRMS measurement results of two heat/light sensitive compounds using a micro-syringe sampling method. Since FD measurement takes only 1 to 3 minutes from applying sample to completion of measurement, it is a useful analytical method that can help rapidly determine the chemical composition and molecular weight of sample compounds, even if the target compounds are sensitive to heat and light.

## Acknowledgement

The author would like to thank Dr. Xiaosong Liu (刘晓松博士) at Oxford Suzhou Center for Advanced Research for providing the sample and for agreeing to use the data.

## Additive analysis in lubricating oil by FD method using JMS-T2000GC AccuTOF™ GC-Alpha

Related products: Mass spectrometer (MS)

### Introduction

JMS-T2000GC AccuTOF™ GC-Alpha provides advanced analysis results with high throughput by high-resolution TOFMS, multi-ionization mode, and automatic analysis software msFineAnalysis. In MSTips No. 355, the effectiveness of the FD method in additive analysis was shown using an analysis example of bromine flame retardant in polypropylene products. In this report, we introduce an analysis example of molybdenum dithiocarbamate (MoDTC), which is a friction reducing agent for lubricating oil.

### Experiment

Table 1 shows the details of the measurement conditions in this experiment. Two commercially available engine oil additives were used as samples. Sample A is 100% MoDTC, and Sample B is a product containing MoDTC.

**Table 1. Measurement conditions**

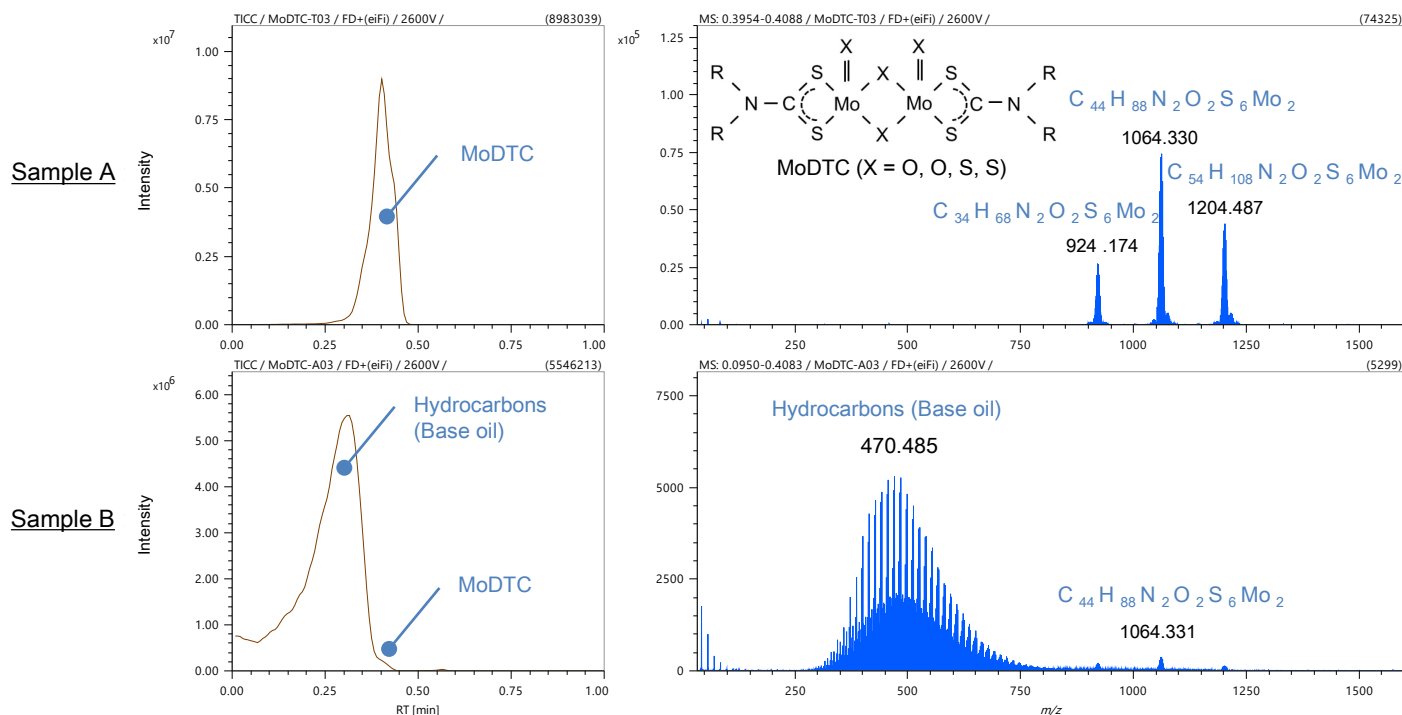
Sample	Engine oil additive (Sample A : 100% MoDTC, Sample B : contains MoDTC)
Preprocessing	Dilute 1mg sample with 1mL chloroform
MS	JMS-T2000GC AccuTOF™ GC-Alpha (JEOL)
Ion source	EI / FI / FD combination ion source
Ionization	FD method, Cathode voltage -10kV, Emitter current 0 → 51.2mA / min → 40mA
Mass range	$m/z$ 50 to 1,600

### Result

From sample A, three types of MoDTC peaks with different numbers of CH were observed. From sample B, these MoDTC peaks and peaks of hydrocarbon compounds derived from the base oil were observed.

**TIC chromatograms**

**Mass spectra**



**Figure 1. TIC chromatograms and mass spectra by FD method**

Figure 2 shows the measured and simulated spectra of  $C_{44}H_{88}N_2O_2S_6Mo_2$ . The mass error in the monoisotopic ion (about 2mDa) and the isotope pattern matching were good.

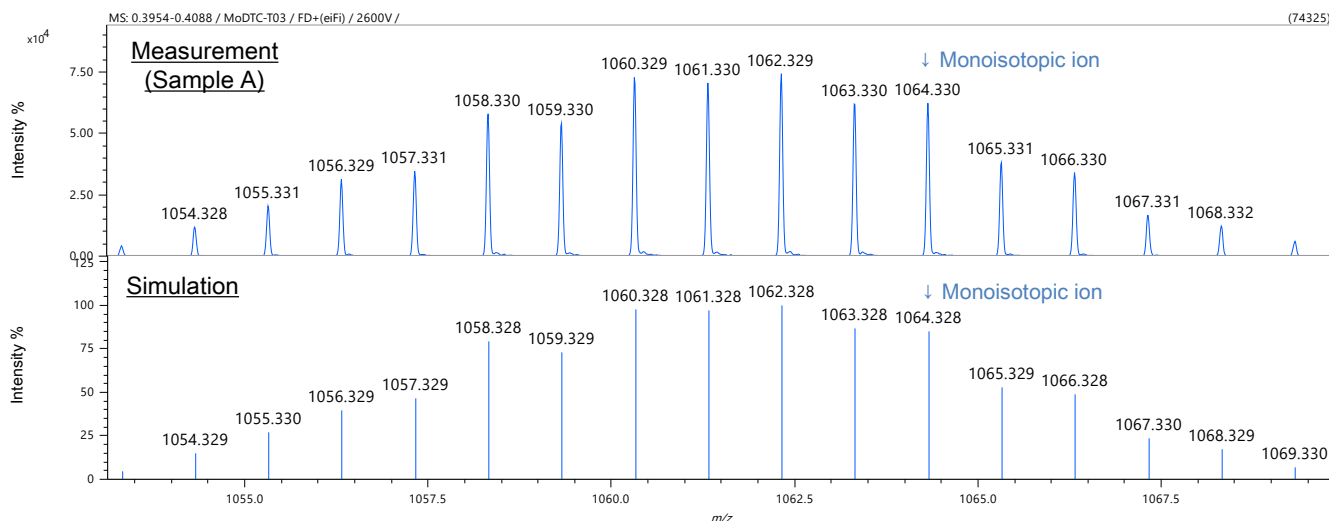


Figure 2. Mass spectra of MoDTC ( $C_{44}H_{88}N_2O_2S_6Mo_2$ )

Figure 3 shows the KMD plot of sample B created by msRepeatFinder. By using the KMD plot, it is possible to visualize and confirm the peaks of hydrocarbon compounds and MoDTC.

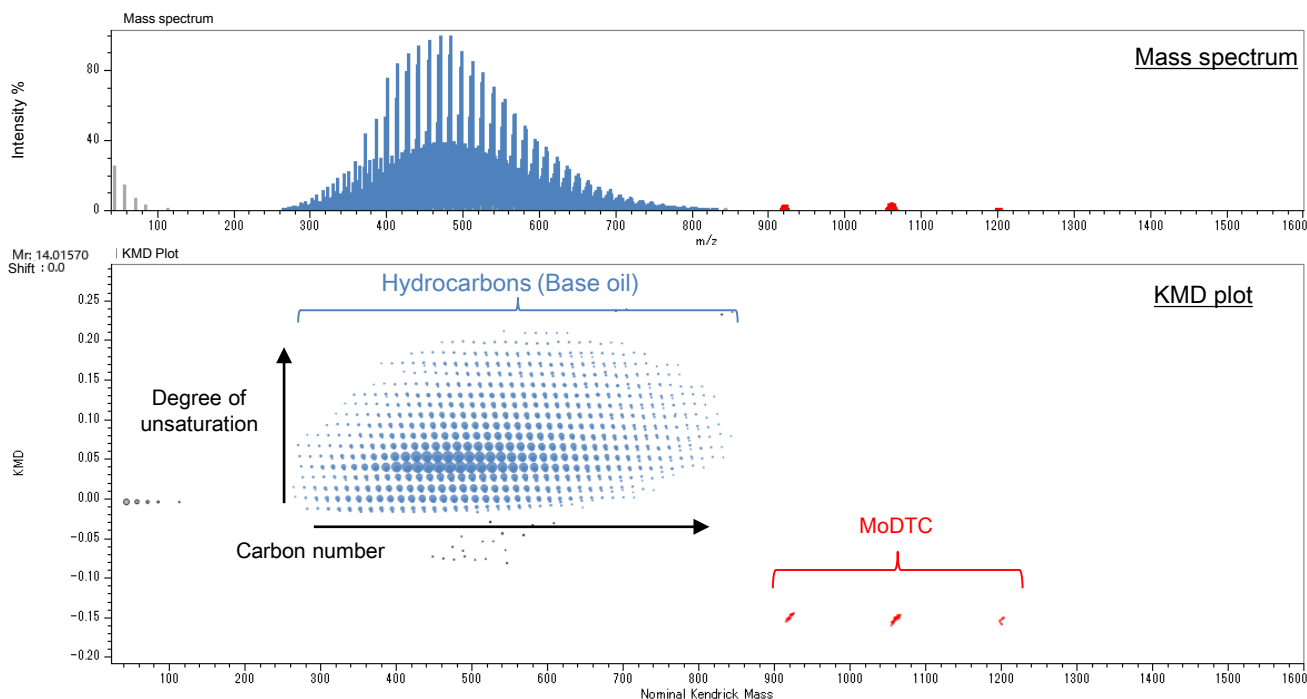


Figure 3. Mass Spectrum and KMD plot of Sample B

### Summary

The FD method of JMS-T2000GC AccuTOF™ GC-Alpha can easily detect high mass components such as MoDTC. Since the FD method does not have chromatogram separation, weak peak may be overlooked in the mixture sample, but it can be visualized and confirmed by using the KMD plot of msRepeatFinder.





## Analysis of brominated flame retardants in polypropylene products by FD method using JMS-T2000GC AccuTOF™ GC-Alpha

Related products: Mass spectrometer (MS)

### Introduction

JMS-T2000GC AccuTOF™ GC-Alpha provides advanced analysis results with high throughput by high-resolution TOFMS, multi-ionization mode and automatic analysis software msFineAnalysis. Pyrolysis-GC-MS method is widely used in material analysis using GC-MS, in MSTips No. 330, the result of difference analysis between the non-defective product and the defective product in the PP / PE copolymer product was shown. On the other hand, in the analysis of additives in materials, there are high boiling point components that are difficult to pyrolyze and cannot pass through the column, and components that are difficult to estimate the previous structure after pyrolysis. The FD method is effective for these components. This report shows the result of analysis for two types of polypropylene (PP) products. The difference between sample was not found by the pyrolysis method, but a brominated flame retardants was found as a difference by the FD method.

### Overview of FD method

Figure 1 shows a schematic diagram of the FD method. In the FD method, the sample is diluted with a solvent and then dropped onto an emitter probe to be introduced into an ion source. At this time, the sample does not need to be completely dissolved in the solvent. In this case, it is possible to analyze only the additives in the solvent. Since it is a direct sample injection method without using a column, high boiling point (high mass) components can be measured. Since it is soft ionization, molecular ions can be detected. By using the EI/FI/FD combination ion source, it is possible to continuously measure the pyrolysis method and the FD method without releasing the vacuum and exchanging the ion source.

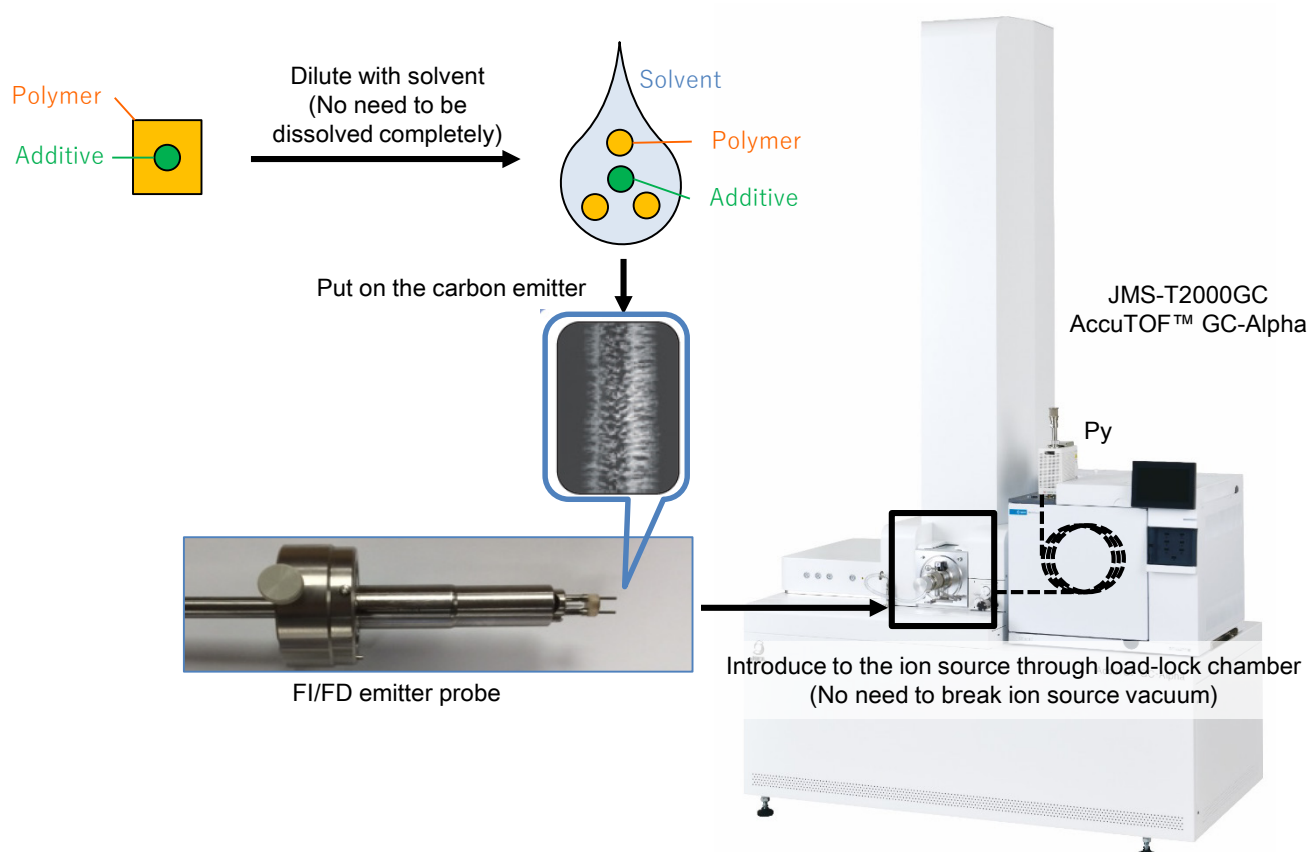


Figure 1. Schematic diagram of the FD method

## Experiment

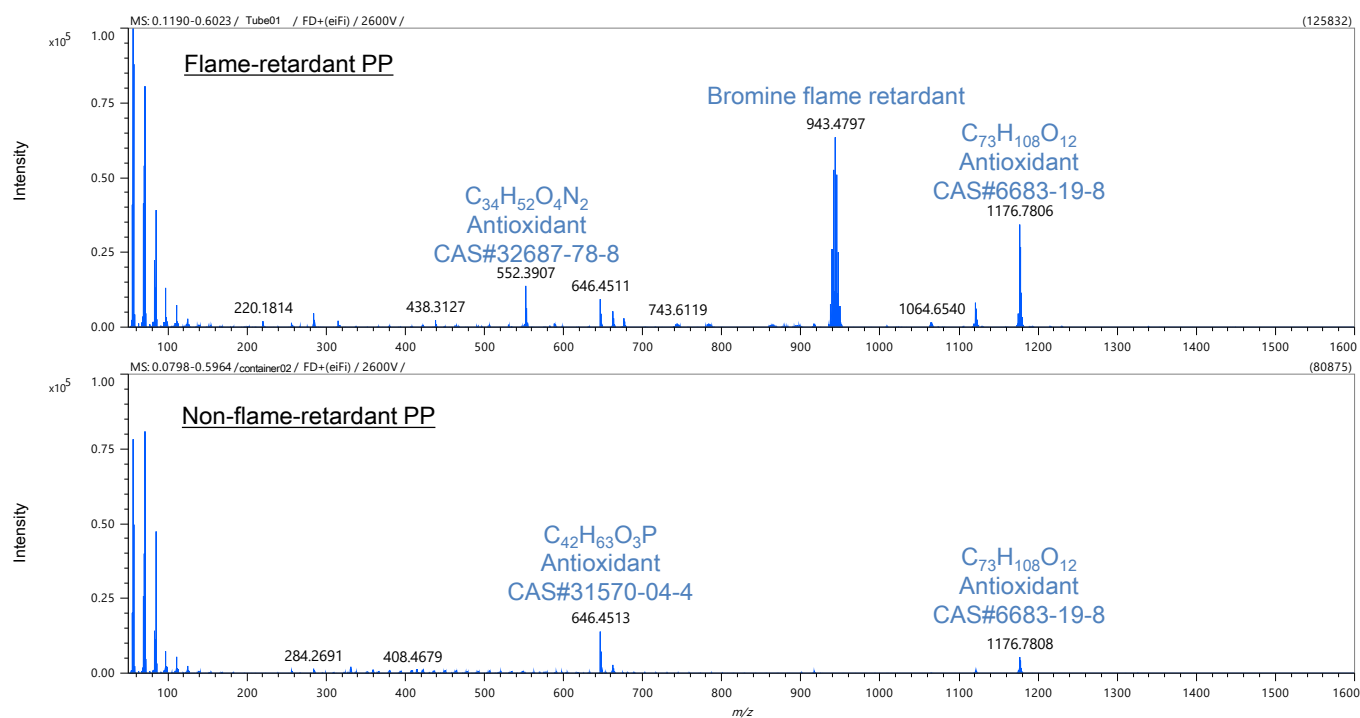
Table 1 shows the details of the measurement conditions in this experiment. Two types of commercially available PP products (flame-retardant and non-flame-retardant) were used as samples. The flame retardant was not detected as a different component between samples in the pyrolysis method. The measurement by the FD method is as short as 1 minute per sample. A high voltage of -10 kV is applied to the emitter, which extracts electrons from the sample molecule and soft-ionizes them. After the start of measurement, the emitter current is gradually increased to assist ionization, and finally the residue is burned out at a high temperature. Therefore, the conditioning operation is not required after the measurement, and the next sample can be measured immediately.

**Table 1. Measurement conditions**

Sample	2 types polypropylene products (Flame-retardant, non-flame-retardant)
Preprocessing	Dilute 1mg sample with acetone after freezing and grinding
MS	JMS-T2000GC AccuTOF™ GC-Alpha
Ion source	EI/FI/FD combination ion source
Ionization	FD method, Cathode voltage -10kV, Emitter current 0→51.2mA/min→40mA,
Mass range	$m/z$ 50~1,600

## Results

Figure 2 shows the mass spectra of the FD measurement results. A clear difference peak was detected at  $m/z$  943.4797 from the flame-retardant PP. It was estimated to be a brominated flame retardant by isotope pattern analysis and composition estimation. Furthermore, analysis was performed using the analysis software Mass Mountaineer (RBC Software). This software automatically performs peak assignment and composition estimation from the mass spectrum. The screening analysis of various components is possible using the composition formula list. In this results, some antioxidants were hit from the composition formula list of additives.



**Figure 2. Mass spectra by FD method**

## Conclusion

FD method of JMS-T2000GC AccuTOF™ GC-Alpha can detect additives that may be missed by the pyrolysis method. Since both method have high affinity, they are expected to be a new analysis flow in material analysis.

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## JMS-T100GCV Application Data

## Analysis of polymer additives using DIP-EI and FD

**[Introduction]**

This report shows the result of the ionization of phenolic polymer antioxidants analyzed by electron ionization (EI) with direct insertion probe (DIP) and field desorption (FD).

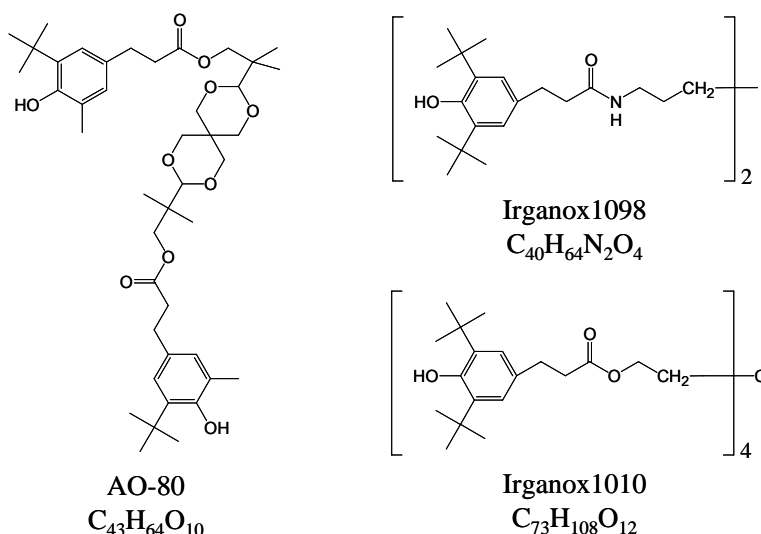
**[Method]**Samples

Phenolic antioxidant

AO-80 (1mg/mL in methanol)

Irganox1098 (1mg/mL in methanol)

Irganox1010 (1mg/mL in methanol)

Measurement conditions

See table 1.

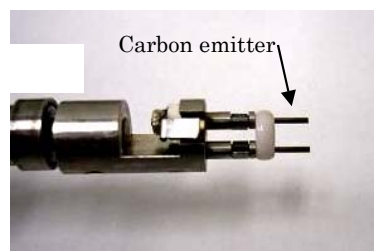
Fig.1 Structural formula of sample compounds

Table 1 Measurement conditions.

Instrument	JMS-T100GCV (JEOL Ltd.)
Direct probe	DIP
Ionization mode	EI+ (70eV, 300μA)
Probe condition	50°C → 64°C/min → 400°C
Ion source temp.	280°C
<i>m/z</i> range	<i>m/z</i> 50-1500
Spectrum recording time	1.0sec
Direct probe	FDP
Ionization mode	FD+ (Cathode volt.: -10kV)
Probe condition	0mA → 51.2mA/min → 40mA
Ion source temp.	Heater OFF
<i>m/z</i> range	<i>m/z</i> 50-1500
Spectrum recording time	0.5sec



(a) DIP (Direct Insertion Probe)



(b) FDP (Field Desorption Probe)

Fig.2 Picture of direct probes.

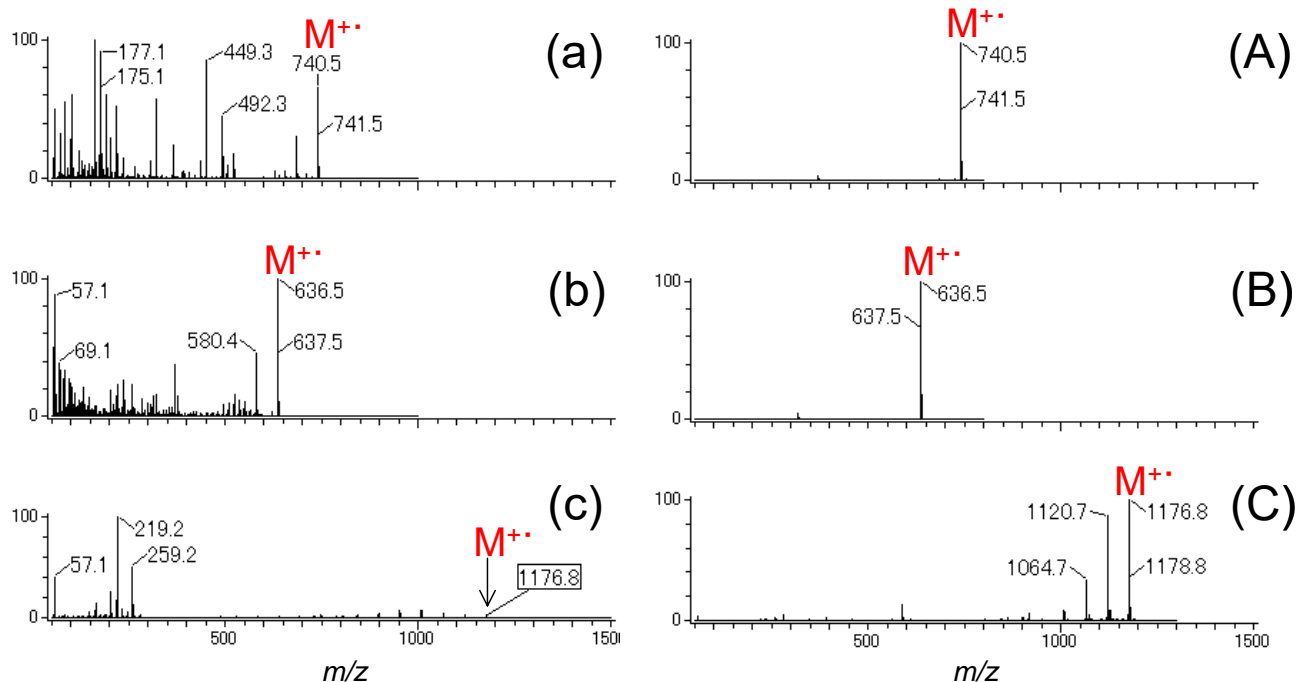


Fig.3 : Mass spectra of phenolic antioxidant by DIP-EI and FD.

EI mass spectra: (a) AO-80, (b) Irganox1098, (c) Irganox1010

FD mass spectra: (A) AO-80, (B) Irganox1098, (C) Irganox1010

### [Result and discussion]

The analysis time was about 5 minutes by DIP-EI and about 1 minute by FD when measurement condition in Table 1 was used.

The observed mass spectra are shown in Fig. 3. The molecular ion was observed in all mass spectra. However, the ion intensity of the molecular ion of Irganox1010 by using DIP-EI was remarkably lower than the ion intensity of other fragment ions. On the other hand, the molecular ion was observed as base peak in all mass spectra by using FD.

The JMS-T100GCV is capable to analyze antioxidants simply and quickly by using a direct injection method. This report shows that the JMS-T100GCV can be used for classic GC/MS but also for DI/MS as very useful tool for qualitative analysis.

## Analysis of organogermanium compounds by field desorption (FD) ionization using JMS-T100GC "AccuTOF GC"

### Introduction

Organogermanium compounds are organometallic compounds containing a carbon to germanium chemical bond. Germanium shares group 14 in the periodic table with silicon, tin and lead and the chemistry of organogermanium is somewhat similar to that of organosilicon compounds and organotin compounds. While metallic germanium is widely used in semiconductor devices, infrared light sensors, etc., organogermanium is advocated as a non-toxic alternative to many toxic organotin reagents.

Here we report the analyses of organogermanium compounds using JMS-T100GC "AccuTOF GC" time-of-flight mass spectrometer.

### Methods

#### Samples

Three organogermanium compounds

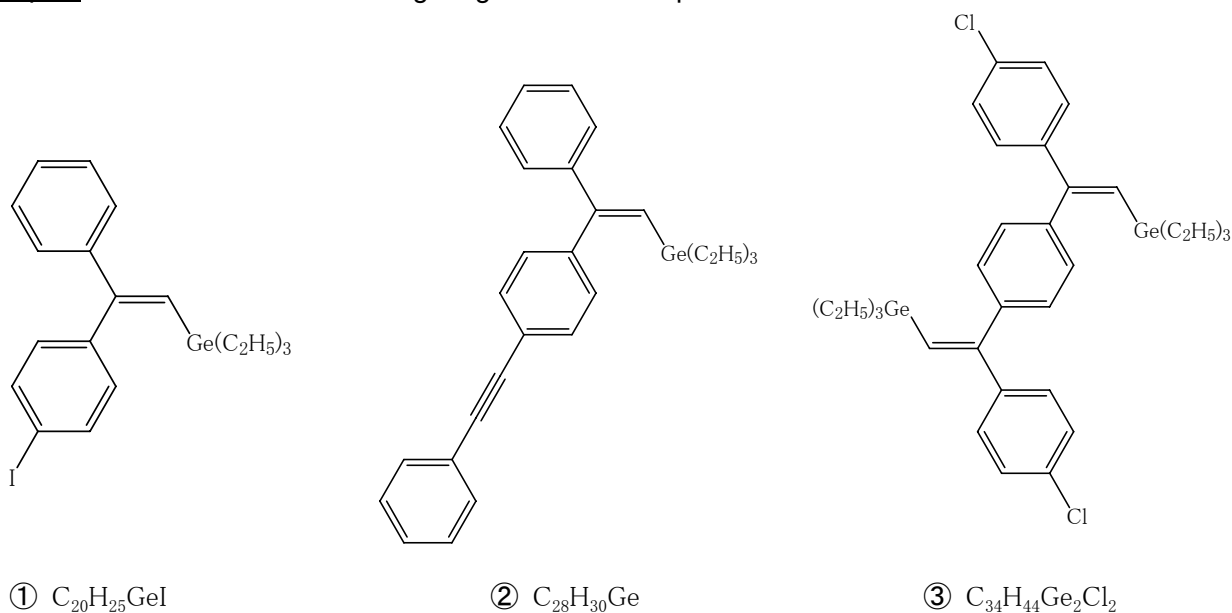


Fig.1 Structural formulae of the samples

#### MS conditions

Mass spectrometer:	JMS-T100GC "AccuTOF GC"
Ionization mode:	FD(+)
Cathode potential:	-10 kV
Emitter current:	0 mA $\rightarrow$ 51.2 mA/min $\rightarrow$ 35 mA
Acquired mass range:	$m/z$ 35 – 800
Spectral recording interval:	1.0 sec

## Results and discussion

Acquired FD mass spectra, comparisons between observed and simulated isotope clusters, and measured accurate mass of the monoisotopic peaks are shown in Fig. 1.

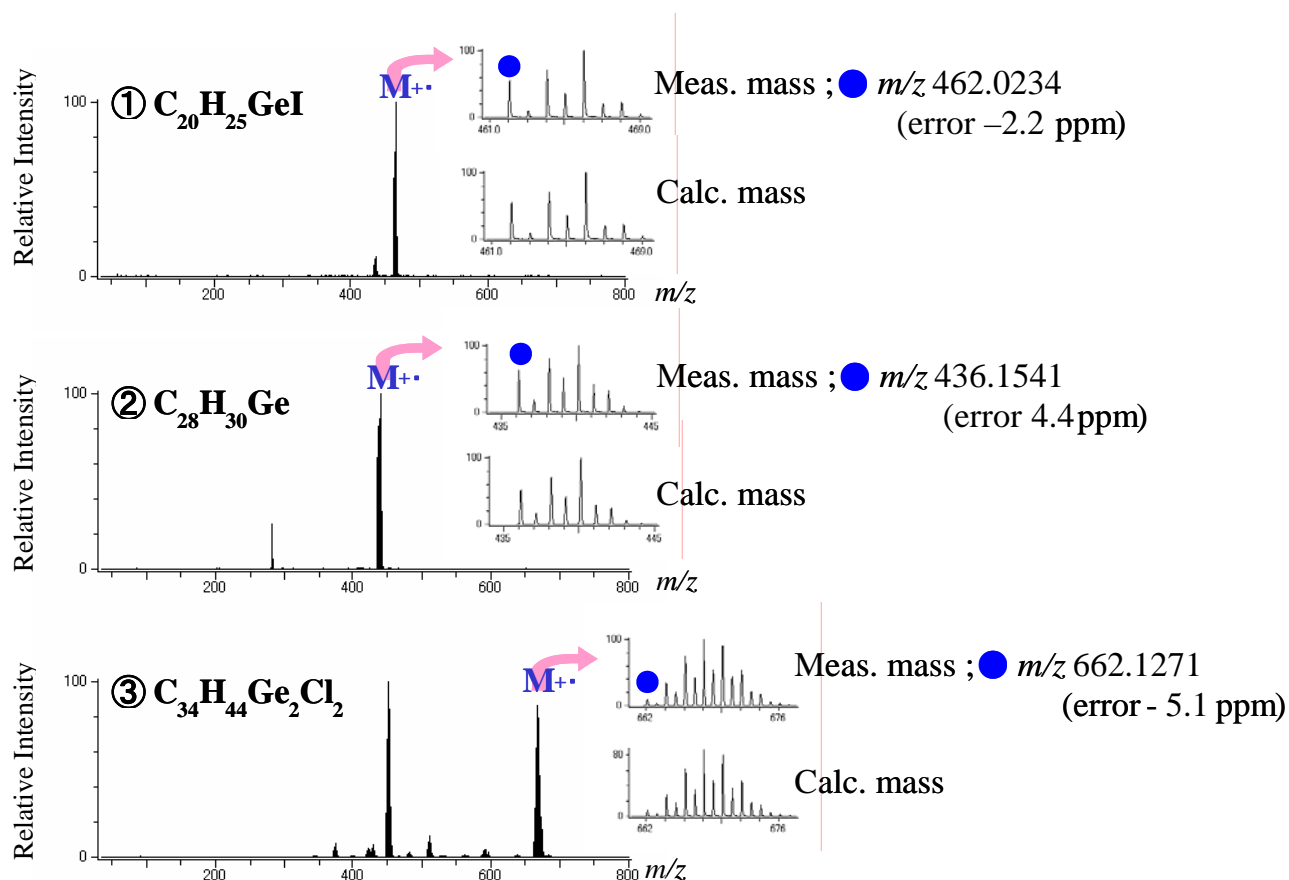


Fig.1 FD mass spectra, comparisons between observed and simulated isotope clusters, and accurate mass measurement results for the organogermanium compounds.

By using FD, the molecular ions are clearly observed for all the organogermanium compounds analyzed. The observed isotope cluster patterns, which were rather complex and typical for organometallic compounds, agreed very well with those simulated from the literature values. The measured accurate masses of the monoisotopic peaks were within 5 ppm of the calculated exact masses.

Field desorption (FD) on JMS-T100GC "AccuTOF GC" time-of-flight mass spectrometer is an invaluable technique for analyzing organometallics. Quick and confident identification is possible by observing molecular ions, comparing isotope cluster patterns with simulated ones, and from accurate mass measurements, as exemplified by the analyses of organogermanium compounds reported above. (U-JT)

## Reference

T. Kataishi, H. Oku, M. Ubukata, Y. Takahashi, T. Nakano et al, Appl. Organometal. Chem., to be submitted.

## Acknowledgement

The author would like to thank Prof. Taichi Nakano of the Graduate School of Science and Technology, Tokai University for providing valuable samples.



## Analysis of ionic liquid by field desorption (FD) ionization using JMS-T100GC "AccuTOF GC"

### Introduction

Ionic liquids are liquids comprised predominantly of ions and ion-pairs. Recently, it has come to be used for salts that are in liquid state at room temperature. Ionic liquids are electrically conductive and have extremely low vapor pressure. Many have low combustibility and excellent thermal stability. They are expected to find many applications as functional materials.

Here we report the analysis of a commercially available ionic liquid by field desorption (FD) ionization using JMS-T100GC "AccuTOF GC" time-of-flight mass spectrometer.

### Methods

#### Sample

1-Butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide (14654 Aldrich)

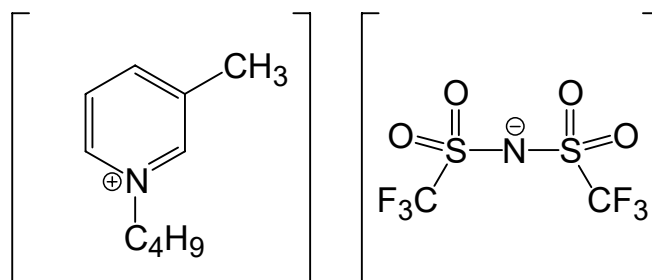


Fig. 1 Structural formula of the sample

#### MS conditions

Mass spectrometer:	JMS-T100GC "AccuTOF GC"
Ionization mode:	FD(+)
	Cathode potential: -10 kV
	Emitter current: 0 mA → 51.2 mA/min → 35 mA
Acquired mass range:	$m/z$ 35 – 800
Spectral recording interval:	1.0 sec

### Results and discussion

FD ionization is usually set up to observe positive ions, the intact cation (C) is readily detected. On the other hand, detecting the intact anion (A) alone is difficult<sup>1), 2)</sup>. For ionic compounds, single-charge cluster ions of the (C<sub>n+1</sub>A<sub>n</sub>) are readily observed but neutral species such as (CA) are not observed<sup>2)</sup>. The acquired FD mass spectrum is shown in Fig. 2.

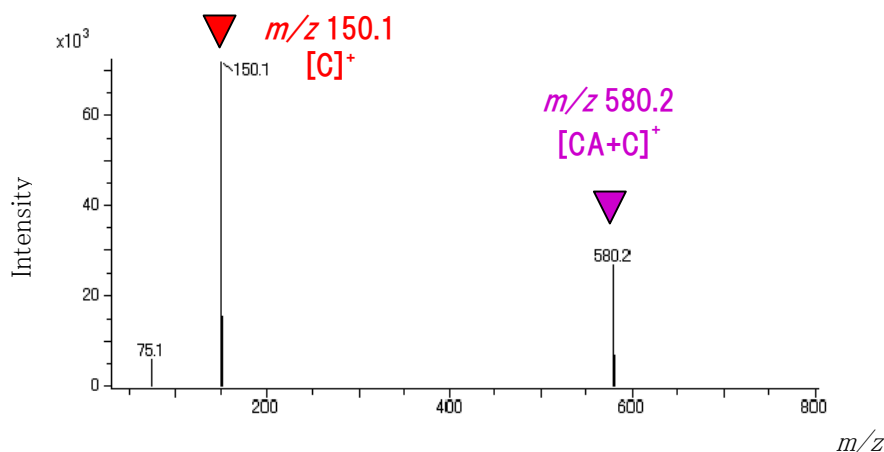


Fig. 2 FD mass spectrum of the sample

The base peak was observed at  $m/z$  150.1 and the second most abundant peak was observed at  $m/z$  580.2. The former corresponds to the intact cation (C) whereas the later corresponds to a cluster ion (CA+C). The results of accurate mass measurements of the ions are shown in Table 1.

Table 1 Measured accurate masses and calculated compositions of the ions.

Ionic species	Measured accurate mass	Calculated exact mass	Error ( $10^{-3}$ u)	Estimated formulae
<b>C</b>	150.1289	150.1283	0.6	$C_{10}H_{16}N$
<b>CA+C</b>	580.1766	580.1738	2.80	$C_{22}H_{32}F_6N_3O_4S_2$

Since the elemental compositions of C and CA+C have been elucidated, the elemental composition of A can be derived:

$$(CA+C) - 2 \times C = A$$

$$A = (C_{22}H_{32}F_6N_3O_4S_2) - 2 \times (C_{10}H_{16}N) = C_2F_6NO_4S_2$$

By analyzing ionic compounds by FD, the intact cation can be readily detected and the mass of the intact anion can be readily elucidated from the masses of the cluster ions. By measuring accurate masses of the intact cation and the cluster ions, the elemental compositions of both anion and cation can be elucidated.

## References

- 1) J. H. Gross, "Mass Spectrometry", Springer-Verlag Berlin Heidelberg, Germany (2004).
- 2) J. H. Gross, *J. Am. Soc. Mass Spectrom.*, **18**, 2254 (2007).
- 3) MS Tips / Application Note for DART No.D031 (<http://www.jeol.co.jp>)

## Analysis of block copolymer by field desorption (FD) using JMS-T100GC "AccuTOF GC"

### Introduction

A commercially available PO (polyoxypropylene) - EO (polyoxyethylene) block copolymer was analyzed by field desorption (FD) on JMS-T100GC "AccuTOF GC" and group-type analysis was performed on the obtained mass spectrum.

### Methods

**Sample** Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)  
(Aldrich 435406; BASF Pluronic® L-31),  $M_n = 1,100$ , 50 mg/mL in THF

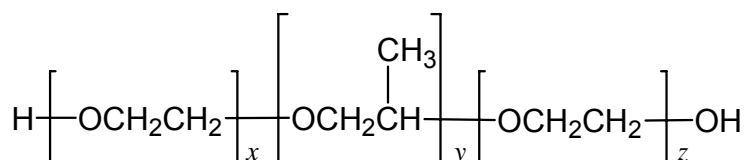


Fig.1 Structural formula of the sample

### MS conditions

Mass spectrometer: JMS-T100GC "AccuTOF GC"  
Ionization mode: FD (+)  
Cathode potential: -10 kV  
Emitter current: 0 mA → 51.2 mA/min → 40 mA  
Acquired mass range:  $m/z$  35 – 1,600  
Spectral recording interval: 1.0 sec

### Results and discussion

The obtained FD mass spectrum is shown in Fig.2.

The base peak was observed at  $m/z$  1,005.7. Other significant peaks were observed with 58 interval (corresponds to  $\text{C}_3\text{H}_6\text{O}$ ) at  $m/z$  947.7,  $m/z$  889.7, etc. These ions correspond to the structure shown in Fig. 1 with  $x = 0$ ,  $y = 15$ , 16, 17, and  $z = 0$ .

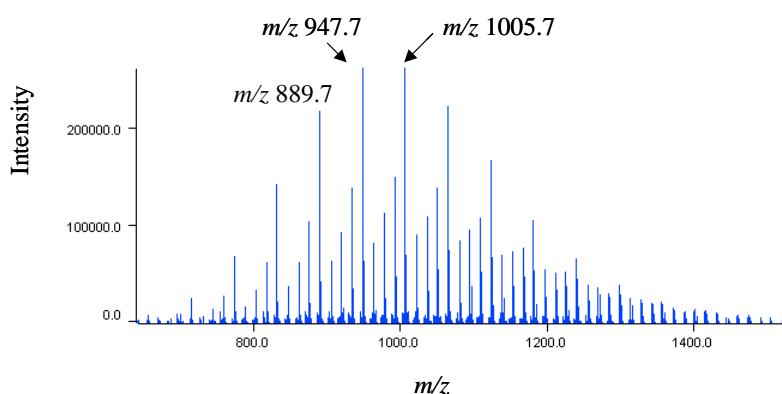


Fig.2 FD mass spectrum

For group-type analysis, the following parameters were used. Even though the sample was an EO-PO-EO triblock copolymer, only two repeat units, PO and EO, were specified since two of the three blocks were EO.

Group-type analysis parameters

Software	Polymerix™ (Sierra Analytics)
Repeat unit A:	C <sub>3</sub> H <sub>6</sub> O
Repeat unit B:	C <sub>2</sub> H <sub>4</sub> O
α end group:	H
ω end group:	OH
Adduct:	H
Match tolerance:	± 0.05 u

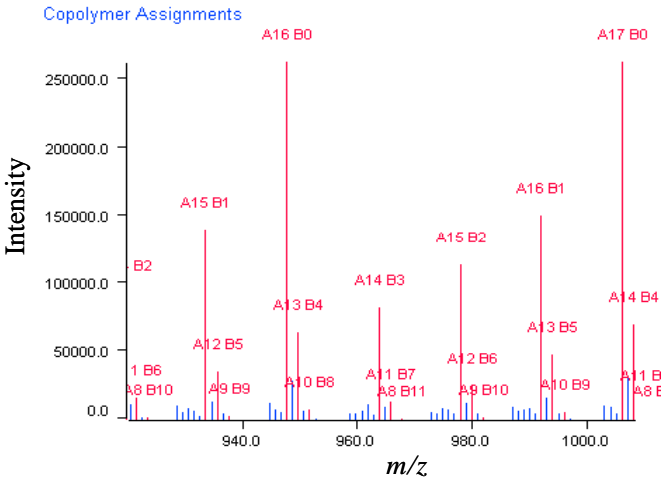


Fig.3 Type analysis assignments (*m/z* 920–1020)

Some of the assignments made by the software with the parameters settings from above are shown in Fig. 3; “A” means C<sub>3</sub>H<sub>6</sub>O, “B” means C<sub>2</sub>H<sub>4</sub>O, and the number following “A” or “B” means the number of the repeat. In Fig. 3, the peaks that correspond to A = 12 to 17 and B = 0 to 10 are assigned. The distribution of the numbers of the repeat units, A (PO) and B (EO,) are shown in Fig. 4 and the average molecular weights and other metrics derived from the group-type analysis are shown in Table 1.

		Copolymer Distribution												
		Repeat B												
		0	1	2	3	4	5	6	7	8	9	10	11	
Repeat A	6													
	7													
	8													
	9					1.08	1.66	1.27	1.33	1.61				
	10			1.63	2.17	4.19	4.24	3.04	2.26	2.58	1.72			
	11	2.65	3.42	5.09	6.17	8.20	7.60	5.81	4.63	4.34	2.42			
	12	9.58	10.37	12.54	14.00	15.99	13.09	9.23	5.62	4.32	3.27	2.19	1.40	
	13	25.98	23.80	23.46	24.20	23.93	17.79	12.39	7.36	6.81	3.56	2.24	1.22	
	14	54.36	39.41	35.20	31.16	26.41	20.61	13.98	9.37	7.03	4.81	2.82	1.11	
	15	83.18	52.75	43.08	34.49	28.19	19.84	14.31	9.97	6.35	2.97	2.14	1.09	
	16	99.99	56.93	41.44	32.28	25.35	18.00	12.60	8.69	6.50	3.50			
	17	100.00	52.72	36.53	26.54	20.38	14.20	10.73	6.67	3.61				
	18	84.89	41.17	27.92	20.53	16.96	9.92	7.72	4.55	3.09	1.37			
	19	63.64	29.20	19.25	14.66	10.89	7.26	4.05	3.16	1.73				
	20	40.33	19.86	13.74	9.46	6.85	4.96	1.56	1.69					
	21	25.17	11.41	8.93	5.77	4.50	3.04	2.11						
	22	14.63	7.35	3.67	3.55	2.94								
	23	7.94	4.08	1.86										
	24	4.44	2.56											
	25	1.69												
	26													

Fig.4 Copolymer distribution

Table 1 Type analysis result

	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	<i>M<sub>z</sub></i>	PD
(H[C <sub>3</sub> H <sub>6</sub> O] <sub>n</sub> [C <sub>2</sub> H <sub>4</sub> O] <sub>m</sub> OH) + H <sup>+</sup>	1053.2	1077.1	1100.9	1.03

By analyzing the FD mass spectrum of triblock copolymer with a suitable group-type analysis software, metrics such as ratios and distribution among constituents, number average molecular weight (*M<sub>n</sub>*), weight average molecular weight (*M<sub>w</sub>*), Z average molecular weight (*M<sub>z</sub>*), polydispersity (PD,) were easily obtained.

## Analysis of advanced materials by FD/FI using "AccuTOF GC" Part III

### ~ analysis of organic borates, photoinitiators for polymerization ~

#### Introduction

Field desorption (FD) is an ionization method utilizing electron tunneling effect in a high electric field near the emitter surface or whisker tip. Sample is applied on the emitter and heated by applying an electric current through the emitter for desorption and ionization.

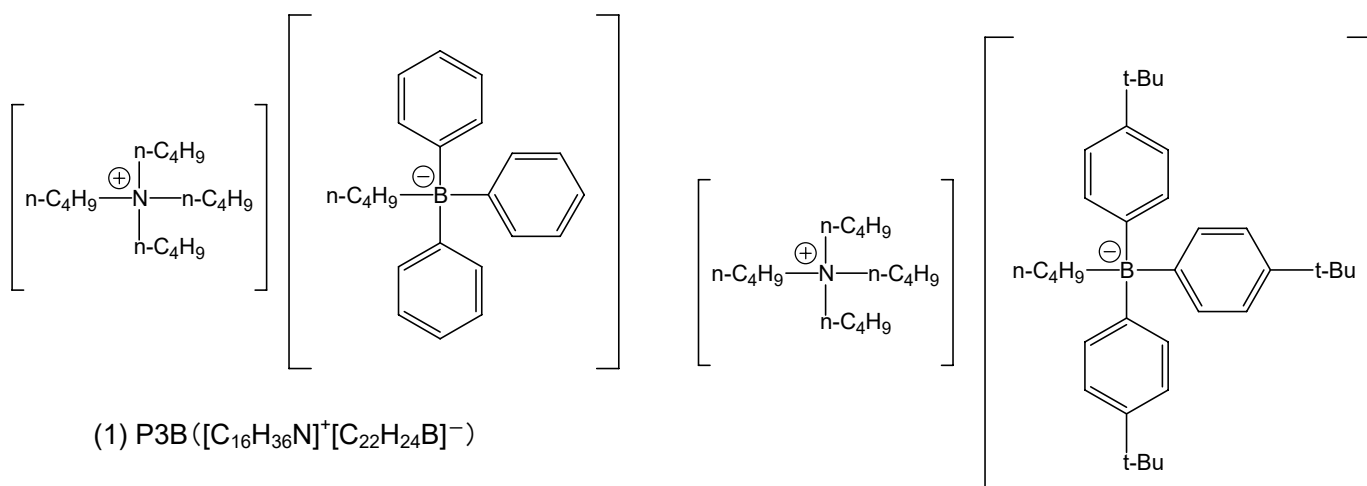
FD has been used to analyze nonvolatile compounds, polymers, etc. as soft ionization method, which yields intact molecular ions with very few fragment ions in most cases.

We have analyzed some quaternary borate ammonium salts that are designed as photoinitiators for the polymerization of functional polymers by FD.

#### Methods

##### Samples

Quaternary borate ammonium salts (Showa Denko K.K.)



(1) P3B ( $[C_{16}H_{36}N]^+[C_{22}H_{24}B]^-$ )

(2) BP3B ( $[C_{16}H_{36}N]^+[C_{34}H_{48}B]^-$ )

##### MS conditions

Mass spectrometer: JMS-T100GC "AccuTOF GC"

Acquired mass range:  $m/z$  30 – 900

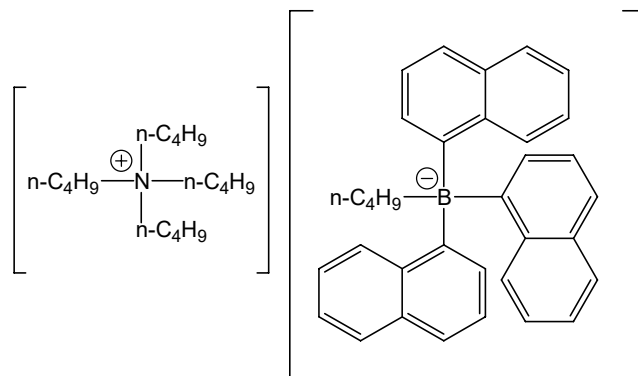
Spectral recording interval: 0.3 sec

Ionization mode: FD+

Cathode potential: -10 kV

Emitter current program:

0 mA  $\rightarrow$  51.2 mA/min  $\rightarrow$  40 mA



(3) N3B ( $[C_{16}H_{36}N]^+[C_{34}H_{30}B]^-$ )

## Results and discussion

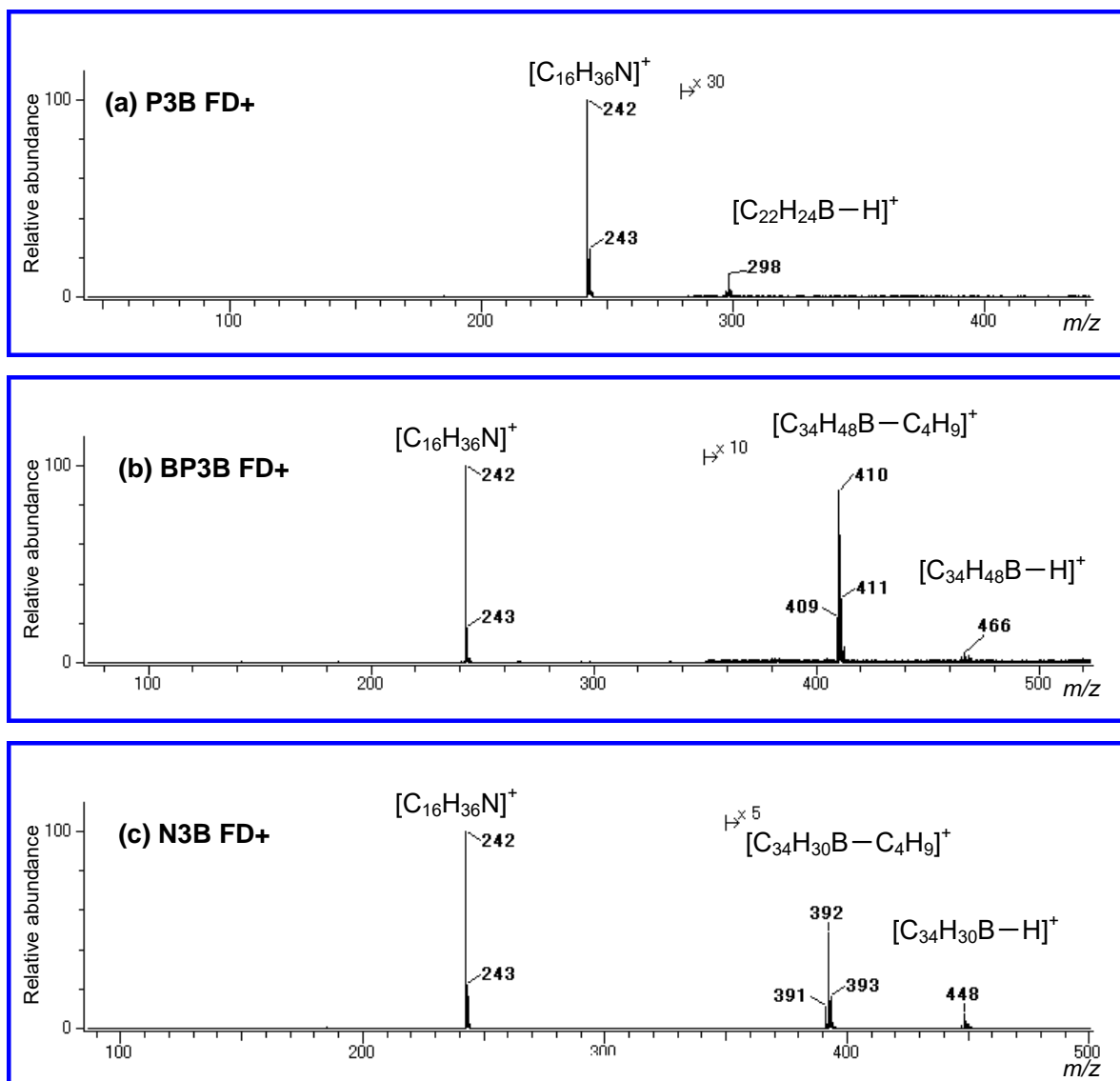


Fig. 1 FD+ mass spectra of organic borate ammonium salts

Molecular ions  $[(Anion)(Cation)]^+$  were not detected for all three quaternary borate ammonium salts. The quaternary ammonium cation at  $m/z$  242 ( $[C_{16}H_{36}N]^+$ ) was observed as the base peak for all samples. The ions that correspond to  $[(Anion) - H]^+$  were observed for all samples, though they are relatively weak. For BP3B and N3B, ions that correspond to  $[(Anion) - C_4H_9]^+$  at  $m/z$  401 and at  $m/z$  392 respectively, were also observed.

With FD, the cation part of salts can be clearly detected. For the quaternary borate salts analyzed here, we found that the anion part of the salts can be detected as de-protonated cations.

## Acknowledgement

We acknowledge the generous offer of the samples by Fine Chemicals Group, Specialty Chemicals Department, Chemicals Division, SHOWA DENKO K.K.



**Analysis of advanced materials by FD/FI using “AccuTOF GC” Part IV**  
**~ analysis of NIR-photosensitive dyes ~****Introduction**

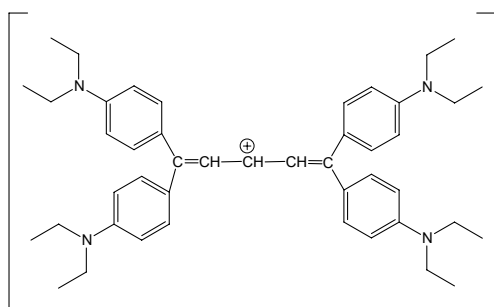
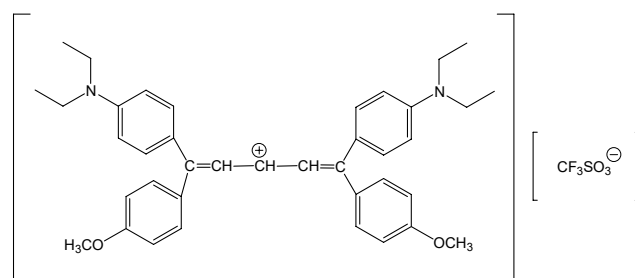
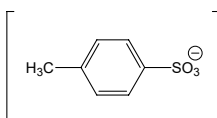
Field desorption (FD) is an ionization method utilizing electron tunneling effect in a high electric field near the emitter surface or whisker tip. Sample is applied on the emitter and heated by applying an electric current through the emitter for desorption and ionization.

FD has been used to analyze nonvolatile compounds, polymers, etc. as soft ionization method, which yields intact molecular ions with very few fragment ions in most cases.

We have analyzed near infrared ray (NIR) photosensitive dyes that are designed as photoinitiators for the polymerization of functional polymers by FD.

**Methods**● Samples

NIR photosensitive dyes (Showa Denko K.K.)

(1) IRT ( $[\text{C}_{45}\text{H}_{59}\text{N}_4]^+[\text{C}_7\text{H}_7\text{SO}_3]^-$ )(2) IR13F ( $[\text{C}_{39}\text{H}_{45}\text{O}_2\text{N}_2]^+[\text{CF}_3\text{SO}_3]^-$ )MS conditions

Mass spectrometer:	JMS-T100GC “AccuTOF GC”
Acquired mass range:	$m/z$ 30 – 900
Spectral recording interval:	0.3 sec
Ionization mode:	FD+
Cathode potential:	-10 kV
Emitter current program:	0 mA → 51.2 mA/min → 40mA

## Results and discussion

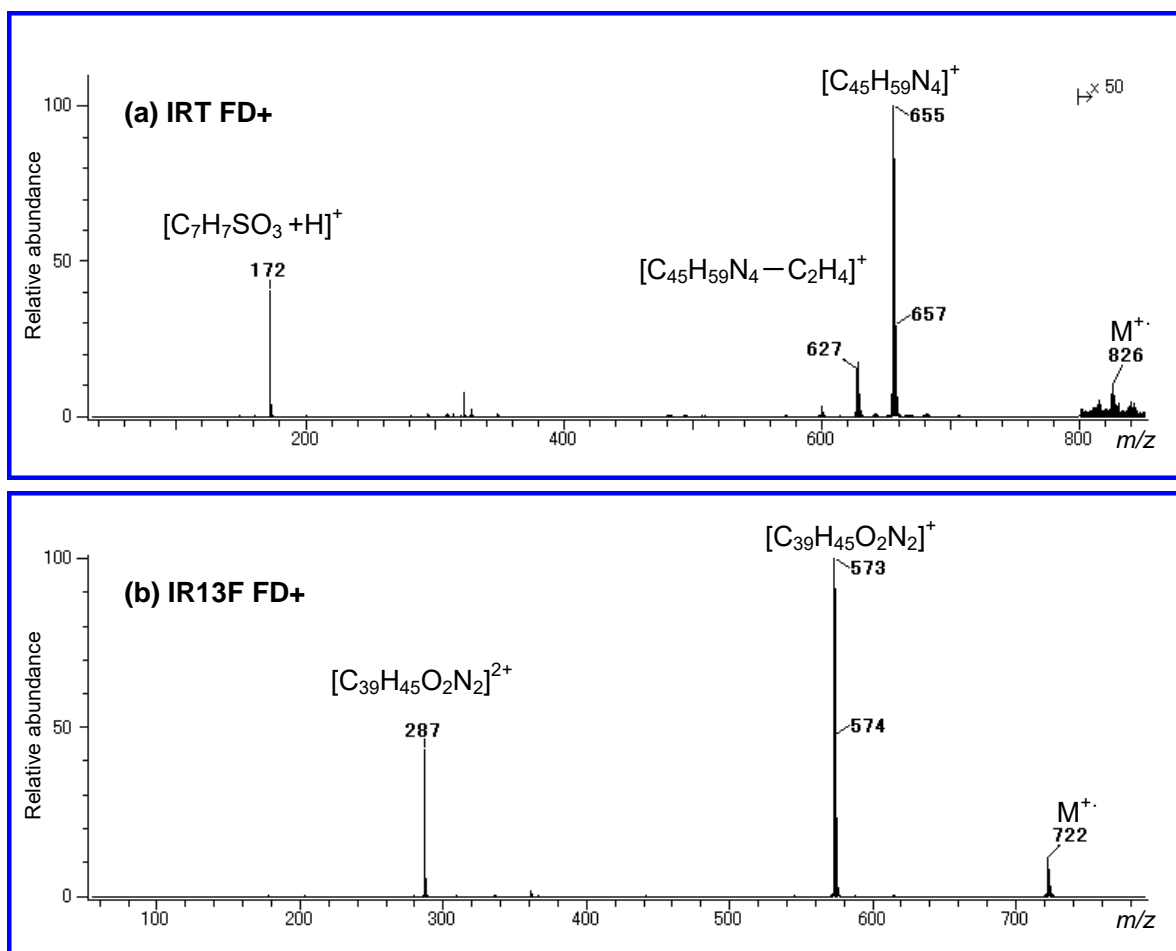


Fig. 1 FD+ mass spectra of NIR photosensitive dyes

Molecular ions  $[(Anion)(Cation)]^{+}$  were observed for both samples by using FD.

For the sample IRT, the cation part of the salt was detected as the base peak at  $m/z$  655 as shown in Fig. 1 (a) above. In addition,  $[(Cation) - C_2H_4]^+$  at  $m/z$  627 and  $[(Anion) + H]^+$  at  $m/z$  172 were observed.

For the sample IR13F, the cation part of the salt was detected as the base peak at  $m/z$  573 and the molecular ion at  $m/z$  722 was relatively strong. As a characteristic ion of this sample,  $m/z$  287 which is double-charge ion of the cation of the salt, has been observed.

For the analysis of salts, FD was found effective in detecting cation of the salt with good sensitivity.

## Acknowledgement

We acknowledge the generous offer of the samples by Fine Chemicals Group, Specialty Chemicals Department, Chemicals Division, SHOWA DENKO K.K.

## Detection of molecular ions from OLED material using AccuTOF GC

## Introduction

Organic electroluminescence, (Organic EL, Organic Light Emitting Diode, OLED, we use "Organic EL" hereafter) is a light emitting phenomenon by exciton generated by recombination of electron holes and electrons which were injected in organic substance. Application to displays and illuminations is expected. At the moment, it has been commercialized for small displays, such as a sub-display of a mobile phone, and its research has been on-going for practical applications comparable to those of a liquid crystal display and a plasma display.

Field desorption (FD) is an ionization method utilizing electron tunneling effect in high an electric field near the emitter whisker tip and is known as a very soft ionization method. It gives very simple mass spectra with little fragmentation and, therefore, interpretation of a mass spectrum from a mixture is easy. Since no sample vaporization is required, it is suitable for the analysis of thermally labile compounds. We have analyzed an organic EL material by FD using AccuTOF GC time-of-flight mass spectrometer.

## Methods

**Mass spectrometer** JMS-T100GC  
**Sample** Bis-(2-methyl-8-quinolinolate)-  
 4-(phenylphenolate)aluminium (BAIq)  
 (Luminescence Technology Corp.)

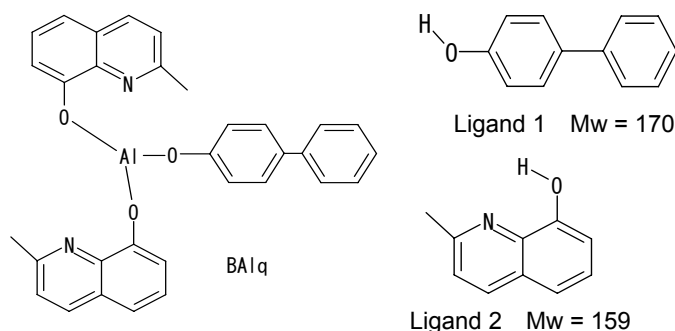


Fig. 1 Organic EL material and its ligands

## Results and discussion

As shown in Fig. 2, the molecular ion was observed as the base peak at  $m/z$  512. Two peaks observed in the low mass region are those from the ligands. The peak at  $m/z$  501 is that from a complex consists from three Ligand 2 molecules and Al. The structure of an organic EL material, an aluminum complex, was readily confirmed using soft FD ionization.

FD Probe Condition	
Emitter	10 $\mu$ m (Carbotec)
Rising Current Rate	51.2mA/min
Maximum Current V	50 mA
Sample Concentration	0.3 mg/ml
Sample Volume	1 $\mu$ L
MS Analysis Condition	
Ionization Mode	FD(positive)
Countercurrent Electrode Voltage	-10 kV
Analysis Time	1.2 min
Mass Range	$m/z$ 3-1500
Spectrum Recording Interval	0.4 sec

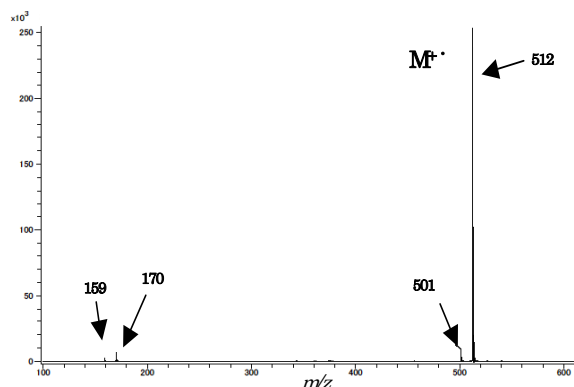


Fig. 2 FD mass spectrum of BAIq



## Analysis of organic pigments using a direct exposure probe on JMS-T100GC "AccuTOF GC"

### Introduction

With the direct exposure probe (DEP), the analyte solution (or suspension) is placed on a coiled platinum filament at the end of the probe (Fig. 3). The probe is introduced into the ion source and the analyte is rapidly heated and vaporized by passing an electric current through the filament. Since the analyte is vaporized by rapid heating with DEP, it is efficient and suitable for the analysis of high boiling point and thermally labile compounds. When used with electron ionization (EI), the method may be called desorption electron ionization (DEI). When used with chemical ionization (CI), the method may be called desorption chemical ionization (DCI).

Commercially available organic pigments, which are widely used in paints, inks, or plastic coloring, are analyzed by DEI.

### Methods

Sample commercial organic pigments (Pigment Yellow 83 and Pigment Red 144)

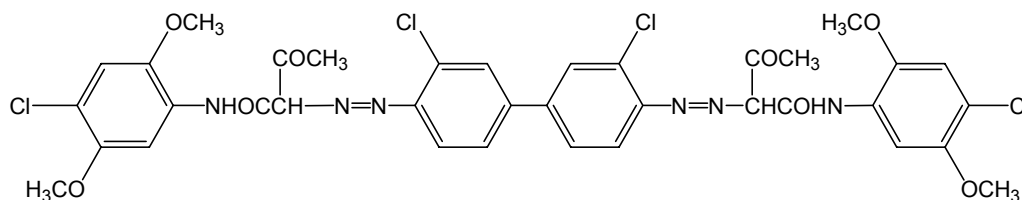


Fig. 1 Pigment Yellow 83 ( $C_{36}H_{32}Cl_4N_6O_8$ )

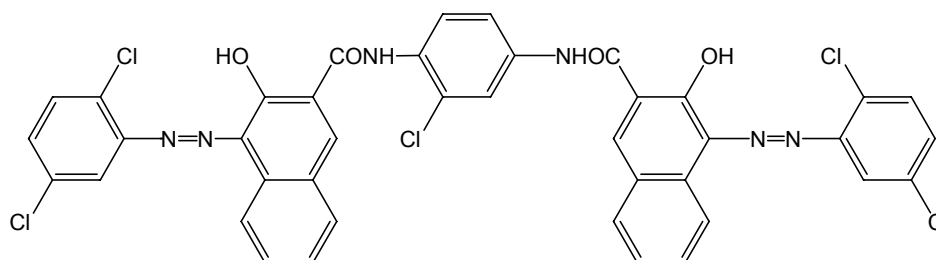


Fig. 2 Pigment Red 144 ( $C_{40}H_{23}Cl_5N_6O_4$ )

DEI conditions	EI conditions:	70 eV, 300μA
	DEP conditions:	0 A → 5.12 A/min → 1.0A
Ion source temperature:		250 °C
Acquired mass range:		m/z 35 – 900
Spectral recording interval:		0.3 sec



Fig. 3 DEP tip

## Results and discussion

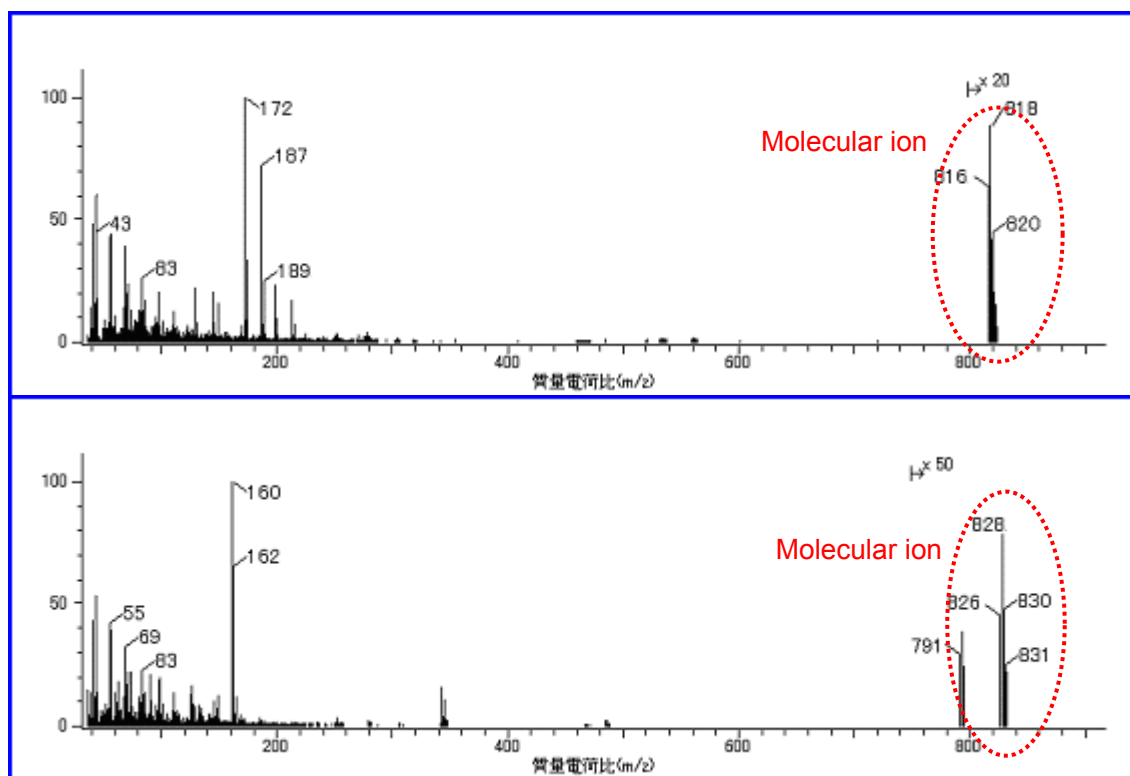


Fig. 4 Mass spectra (top: Pigment Yellow 83, bottom: Pigment Red 144)

As shown in Fig. 4, the mass spectra for the organic pigments were obtained and the molecular ions of both analytes were detected. By applying one of the analytes and 2, 4, 6-tris(pentadecafluoroheptyl) - 1, 3, 5-triazine (the triazine hereafter) to the filament and perform the analysis, the accurate mass of the molecular ions were obtained. A fragment ion from the triazine,  $C_{18}F_{32}N_3$  ( $m/z$  865.95812) was used as an internal mass reference for single point drift correction. The results of the accurate mass measurements are shown below.

Table 1 Accurate mass measurement results

Sample	Measured accurate mass	Calculated exact mass	Error (ppm)	Elucidated composition	Unsaturation
Pigment Yellow 83	816.10205	816.10357	-1.86	$C_{36}H_{32}Cl_4N_6O_8$	22
Pigment Red 144	826.02515	826.02234	3.40	$C_{40}H_{23}Cl_5N_6O_4$	30

The JMS-T100GC “AccuTOF GC” has high mass accuracy as it has very low inherent systematic mass error. Only a single mass reference ion peak is required to perform an accurate mass measurement. Even for DEI, accurate mass can be readily measured by applying the analyte and a mass reference sample to the probe simultaneously and highly reliable structural elucidation is possible.

### Acknowledgement

The author would like to thank Mr. Haruo Yoshiya of YBE Scientific Analysis Laboratory, Inc. for his generous gift of the samples.

## Analysis of organic EL material by JMS-T100GC "AccuTOF GC"

## ~ comparison of FD and DEI methods ~

## Introduction

Field desorption (FD) is an ionization method utilizing electron tunneling effect in high electric field near the emitter surface or whisker tip. Sample is applied on an emitter and heated up by applying an electric current through the emitter inducing desorption and ionization.

FD has been used to analyze nonvolatile compounds, polymers, etc. as soft ionization method, generating an intact molecular ion and very few fragment ions in most cases.

We have compared FD and desorption electron ionization (DEI), which are both direct sample introduction methods, for the analysis of an organic electroluminescence material with many aromatic rings.

<b>Methods</b>	Sample:	4,4'-Bis(2,2-diphenyl-ethen-1-yl)biphenyl (DPVBi) (Luminescence Technology Corp.)
	FD conditions:	Cathode potential: -10 kV Emitter current program: 0 mA → 51.2 mA/min → 40 mA
	DEI conditions:	EI conditions: 70 eV, 300 $\mu$ A DEP conditions: 0 A → 5.12 A/min → 1.0A
	Acquired mass range:	m/z 35 – 600
	Spectral recording interval:	0.5 sec

## Results and discussion

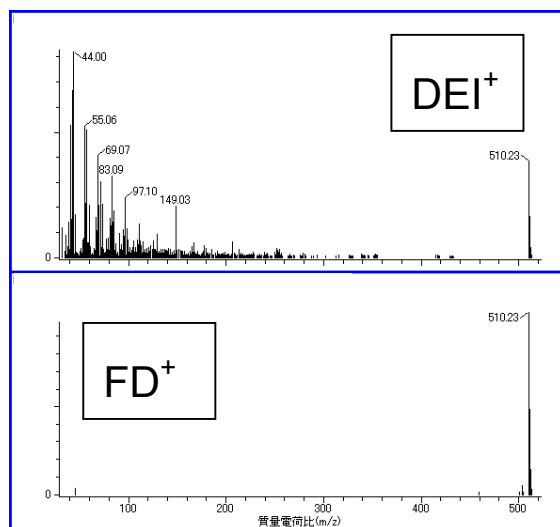


Fig. 1 Mass spectra of DPVBi

Table 1 Accurate mass measurement result

Mass	Intensity	Calc. Mass	Mass Diff. (mmu)	Formula	Unsaturation
510.23378	217546.53	510.23475	-0.97	$C_{24}H_{20}$	26.0

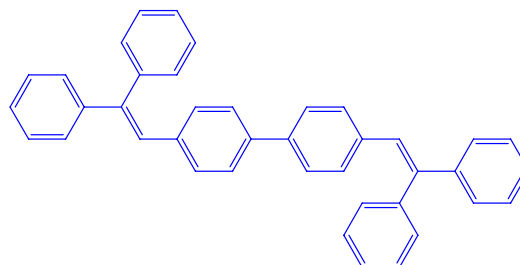


Fig. 2 Structure of DPVBi

As shown in Fig. 1, a lot of fragment ions were observed in addition to the molecular ion with the DEI method. With the FD method, confirmation of molecular weight was very straightforward as only the molecular ion was observed. Moreover, AccuTOF GC is capable of performing accurate mass measurement with FD, as shown in Table 1, and the molecular formula of DPVBi was readily confirmed.





## Analysis of calcium oxalate and polystyrene in oxidizing atmosphere using high-resolution TG-TOFMS

Related products: Mass spectrometer (MS)

### Introduction

Thermogravimetric-mass spectrometry (TG-MS) is a measurement technique for obtaining weight change and qualitative information of evolved gas during heating. It is used to evaluate resins and synthetic rubber products. Usually, the inert gas such as helium and nitrogen are used as the TG atmosphere gas. On the other hand, oxidizing atmosphere measurement such as the air will be effective for product development and quality control. However, the electron ionization (EI) method, which is a standard ionization method, is difficult to analyze for a long time under oxygen due to deterioration of the filament. We have developed an oxygen-resistant filament to solve this issue. We have introduced the oxygen-resistant filament application note for QMS in MSTips No. 320. In this MSTips, we introduce anti-oxygen filament application data for high-resolution TOFMS.

### Measurement

STA2500 Regulus (NETZSCH) was used as TG. It can also be used for differential thermal analysis (DTA). JMS-T2000GC equipped with an oxygen-resistant filament was used as the MS (Figure 1). The calcium oxalate (①) and Polystyrene (②) were used as test samples. Helium or oxidizing gas (helium : oxygen = 4 : 1 mixed) was used as the TG atmosphere gas, and we have compared these results from two types of the atmosphere gases. Table 1 shows the TG-MS measurement conditions.

**Table 1. Measurement conditions**

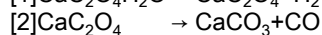
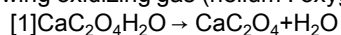
Sample	①Calcium oxalate 20mg
	②Polystyrene 5mg
TG	STA 2500 Regulus (NETZSCH)
Furnace temp.	①60°C→20°C/min→1,000°C
	②60°C→20°C/min→600°C
Transfer-line temp.	300°C
Transfer-line column	Blank capillary tube, 3m, I.D.0.32mm
Atmosphere	Pure He, 100mL/min
	Oxidizing (He:O <sub>2</sub> = 4:1), 100mL/min
Split ratio	30:1
MS	JMS-T2000GC (JEOL)
Ionization	EI, Ionization Energy 70eV, 100μA
Mass range	<i>m/z</i> 10~800
Ion source temp.	300°C
GC-ITF temp.	300°C



**Figure 1. JMS-T2000GC with TG**

## Results - ① calcium oxalate

Figure 2 shows the TG curves of calcium oxalate. The black line in each graph is showing pure helium data, and the red line is showing oxidizing gas (helium : oxygen = 4 : 1) data. The reaction formula for each weight loss in a pure helium is as follows.



In oxidizing gas, reaction of [2] also produces  $\text{CO}_2$ .

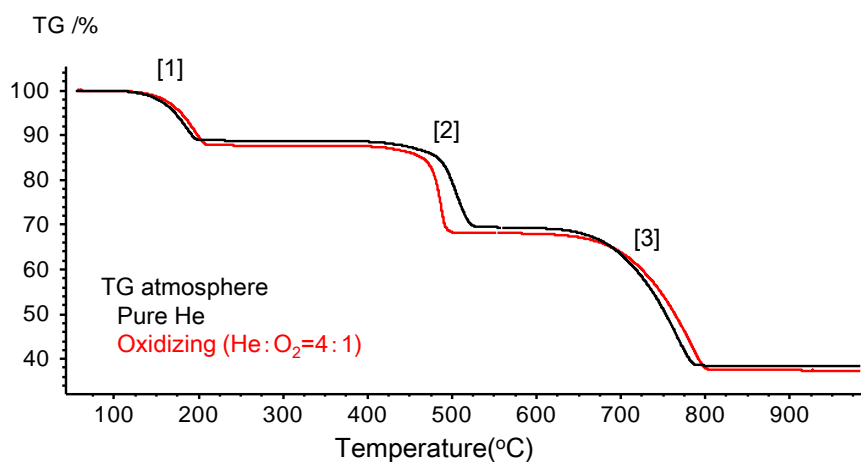
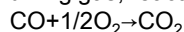


Figure 2. TG curves of Calcium oxalate

Figure 3 shows the DTA curves. It was confirmed that the reaction of [2] became exothermic in oxidizing gas.

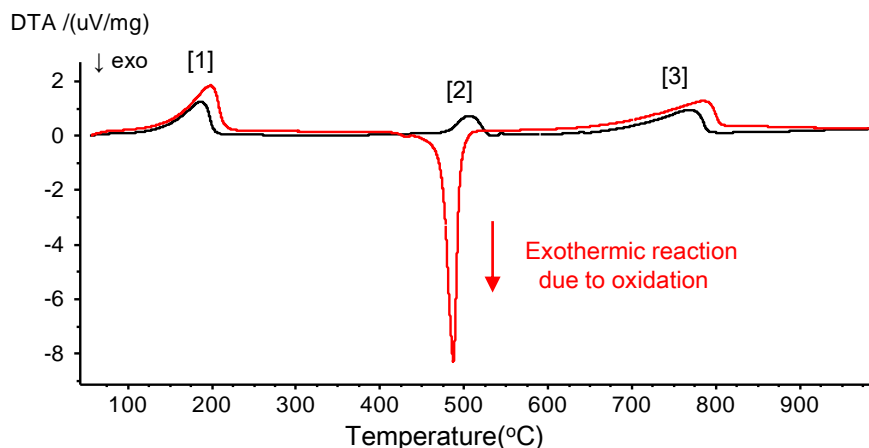


Figure 3. DTA curves of Calcium oxalate

Figure 4 shows the TIC chromatograms. A change in peak shape was observed.

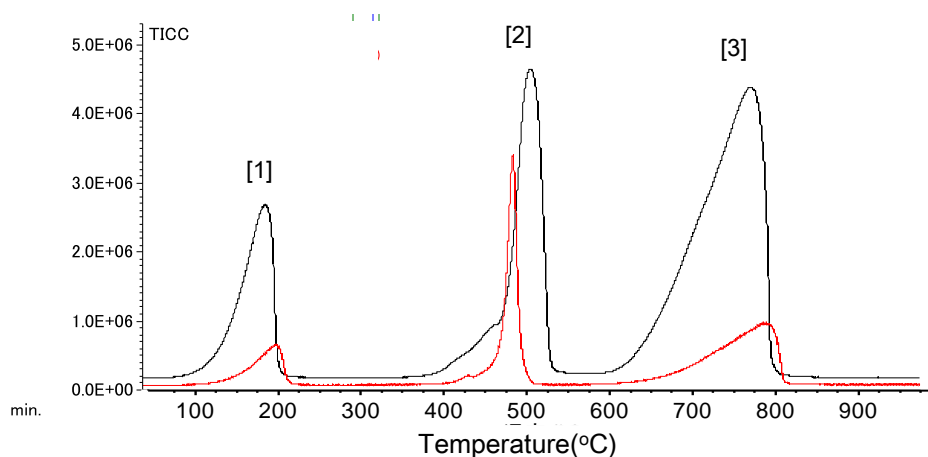


Figure 4. TIC chromatograms of Calcium oxalate

Figure 5 shows the mass spectra of peaks [1] to [3] of calcium oxalate. In the oxidizing atmosphere, the CO signal decreased and the CO<sub>2</sub> signal increased due to the reaction  $2\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ .

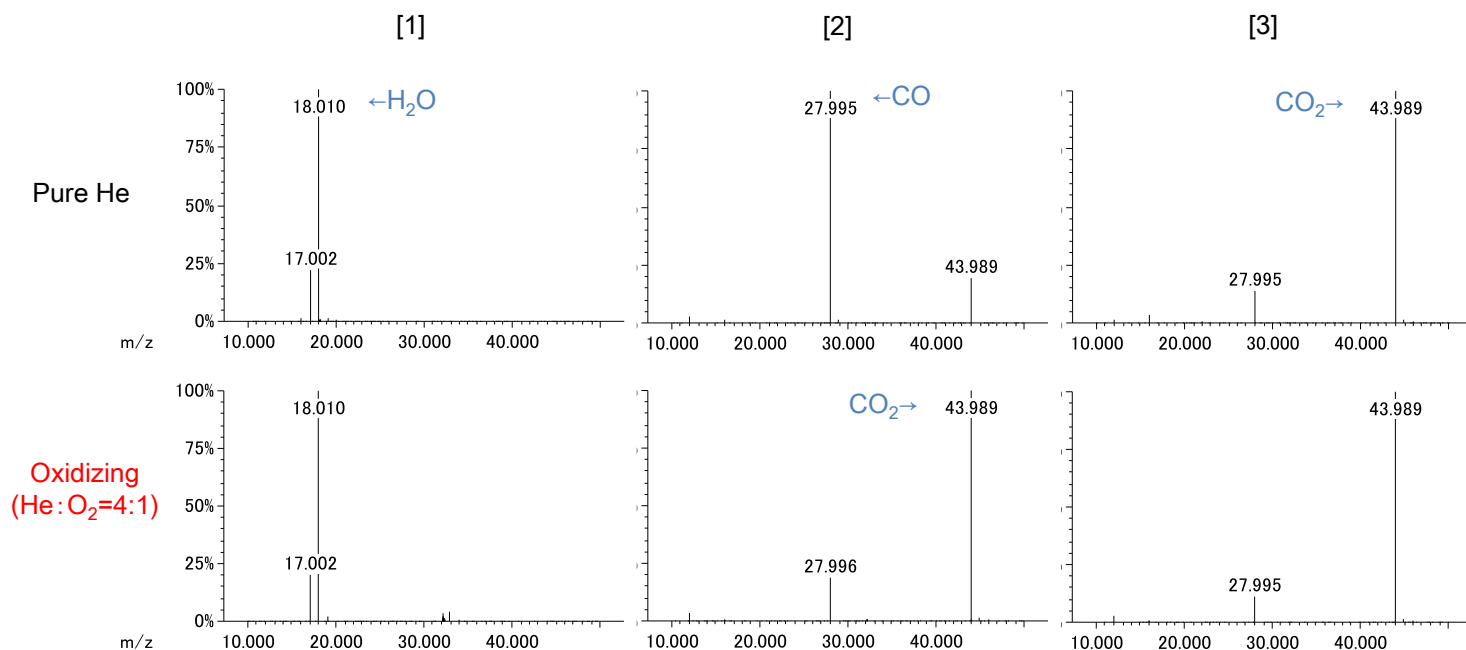


Figure 5. Mass spectra of Calcium oxalate

#### Results - ② polystyrene

Figure 6 shows the TG curve of polystyrene and Figure 7 shows the TIC chromatogram. The starting temperature of the reaction was lower in the oxidizing atmosphere.

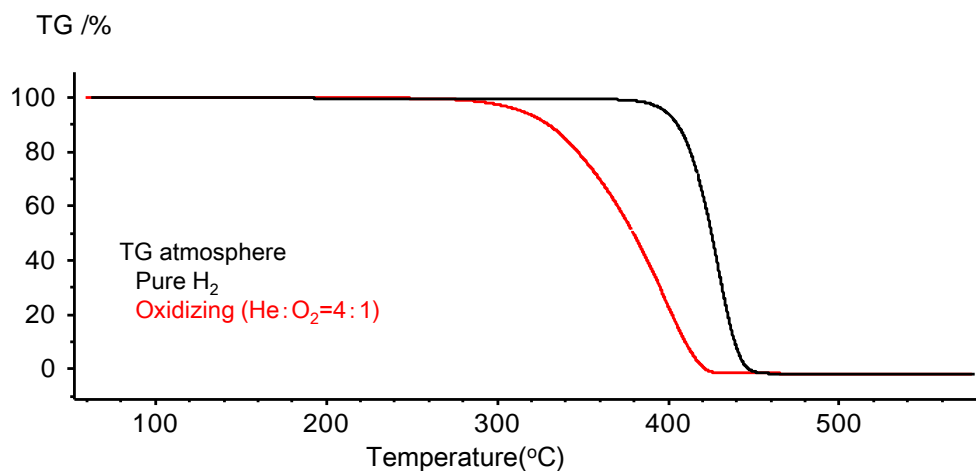


Figure 6. TG curve

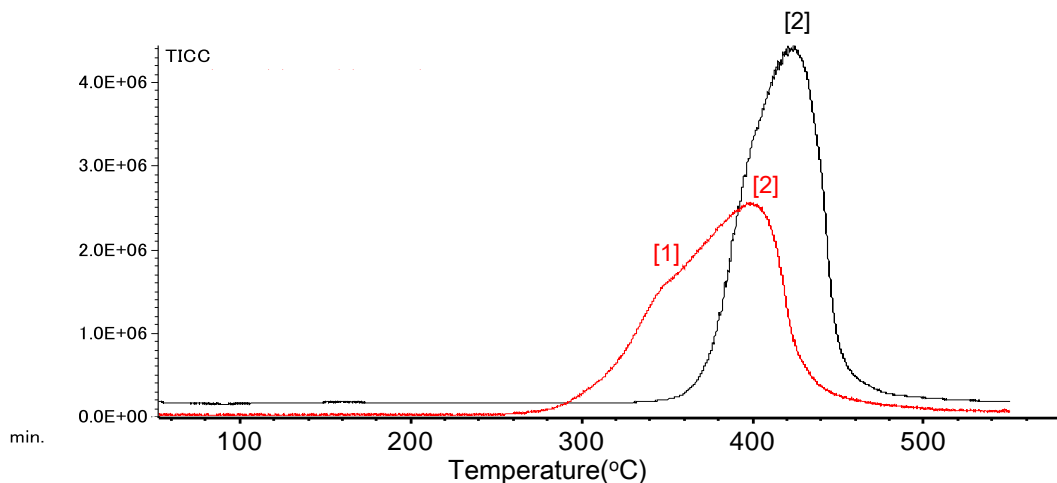


Figure 7. TIC chromatograms of Polystyrene

Figure 8 shows the mass spectra of polystyrene peaks [1] and [2]. In the pure helium atmosphere, major pyrolysis products of polystyrene such as toluene, styrene and styrene dimer were observed. In the front peak [1] of oxidizing atmosphere, the peaks of styrene oxide (= benzaldehyde) and styrene dimer oxide were observed. In the rear peak [2], toluene, styrene, styrene dimer were observed as in the pure helium atmosphere.

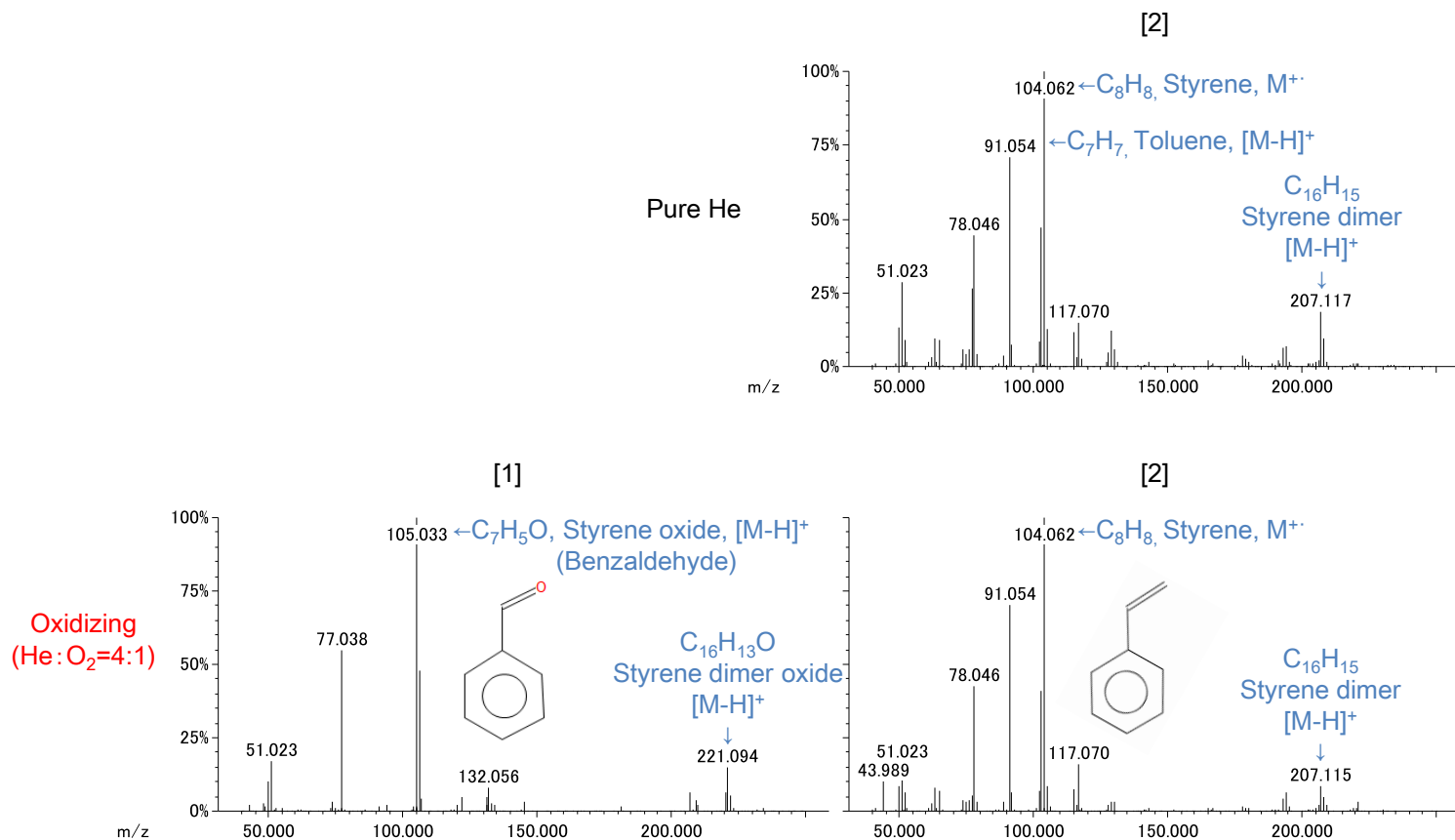


Figure 8. Mass spectra of Polystyrene

Figure 9 shows the TIC chromatogram and the extracted ion chromatogram (EIC) for the base ions of benzaldehyde ( $m/z$  105.03) and styrene ( $m/z$  104.06) in the oxidizing atmosphere. Benzaldehyde was produced in the front (low temperature) and styrene in the rear (high temperature).

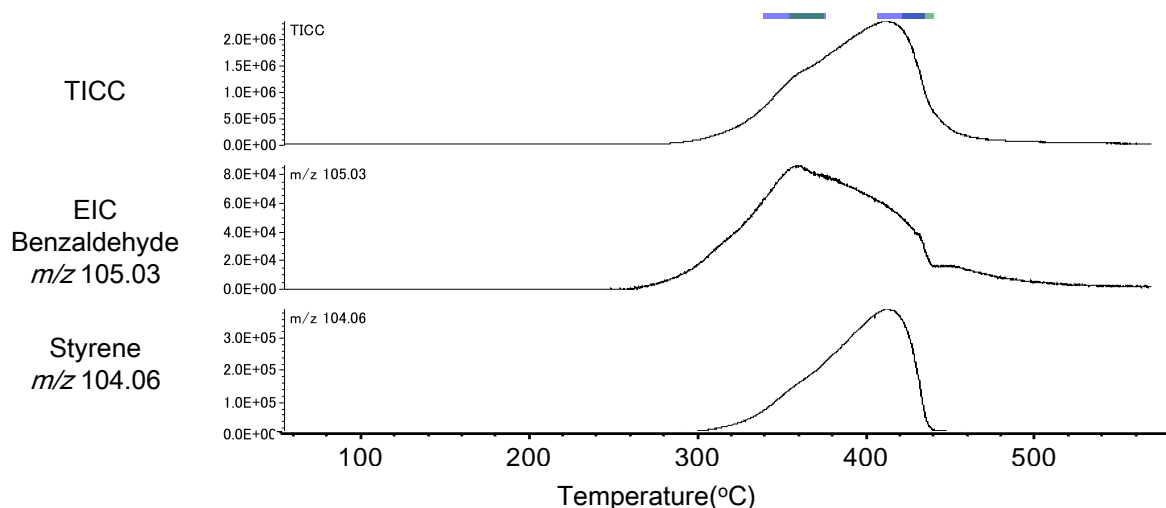


Figure 9. TIC chromatogram and EIC of Polystyrene in oxidizing atmosphere

## Conclusion

Measurements were performed in an oxidizing atmosphere with a JMS-T2000GC equipped with an oxygen-resistant filament. As a result, the oxidation reaction of calcium oxalate and polystyrene were observed. In these measurements, the life-time of the filament in an oxidizing atmosphere was more than 50 hours, and it was confirmed that there was no problem with durability. Analysis under an oxidizing atmosphere using this TG-MS system is effective for analysis of various resins and synthetic rubbers, and can be used in product development and quality control.

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## Thermal decomposition analysis of antioxidant additive by TG-MS

### — Accurate mass measurement with TG-TOFMS system—

Product used : Mass Spectrometer (MS)

#### 【Introduction】

Thermogravimetry (TG) is a thermal analysis technique that measures sample weight changes during sample heating and provides sample thermophysical properties. Combining a TG with a mass spectrometer (MS) makes it possible to perform the qualitative analysis of organic compounds that are evolved as the sample weight changes. Typically, a general purpose quadrupole MS is used for these types of analyses. However, since the measurable  $m/z$  value of a quadrupole MS is nominal mass, this detector provides limited capabilities for the qualitative analysis of synthetic polymers, additives and unknown compounds. Alternatively, a time-of-flight mass spectrometer (TOFMS) can be used in combination with the TG to provide accurate mass measurement capability to identify the detected compounds. In this work, we measured an antioxidant additive by using a TG-TOFMS system.

#### 【Measurement condition】

A fluorocarbon polymer was analyzed by using a JMS-T200GC "AccuTOF™ GC" (JEOL Ltd.), gas chromatograph / high-resolution time-of-flight mass spectrometer equipped with a STA2500 TG system (NETZSCH Co., Ltd.) as shown in Fig. 1. The measurement conditions are shown in Table 1. The GC was used as a thermostatic oven with a fixed temperature of 350 °C with blank capillary tube (3m X 0.25mm I.D.).

#### 【Result】

The TG-EI-TOFMS measurement result for the antioxidant additive is shown in Fig. 2. A broad peak was observed around 38 minutes on the TIC chromatogram where the TG temperature was ~350 to 450 °C. This peak showed that the thermal decomposition of the antioxidant occurred in this temperature range.

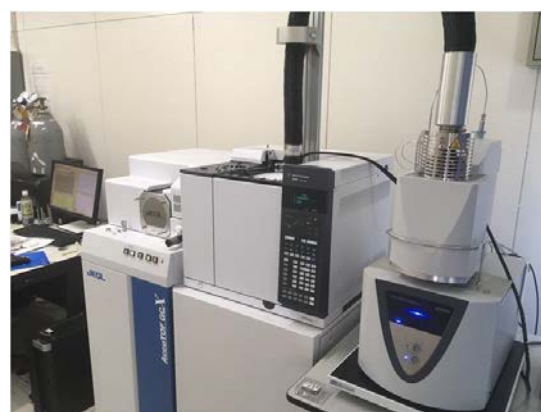
Next, the sample was pyrolyzed for qualitative analysis of the generated compounds. The EI mass spectrum is shown in the lower part of Fig. 2. Since the TG-MS data does not include chromatographic separation, multiple components are simultaneously ionized all at once. And, because EI is a hard ionization method, a large number of fragment ions along with their molecular ions are observed in the mass spectrum, all at once. As a result, it was very difficult to identify the thermal decomposition products using the EI data. Therefore, it was necessary to try PI (Photo Ionization), which is a soft ionization method, to look at the antioxidant thermal decomposition products, in which fragment ions are fewer than EI method and molecular ions are easily observed. The results of TG-PI-TOFMS measurement are shown in Fig. 3.

The PI mass spectrum was much simpler and had less fragment ions than the EI mass spectrum. Table 2 shows the accurate mass measurement results for three of the high intensity ions (★ mark in Fig. 3) observed in the PI mass spectrum --  $m/z$  166, 222, and 278. These ions were estimated to consist of C, H and O, with an unsaturation number of 5. Based on these results, it is expected that these ions will have similar antioxidant core structures. The expected structural formulas for each are shown in Fig. 4.

The TG/DTA curve of the antioxidant and the EIC chromatogram of  $m/z$  166, 222, and 278 observed in the PI mass spectrum are shown in Fig. 5. The peak maximum for the  $m/z$  166 EICC was observed at 420.6 °C,  $m/z$  222 was observed at 399.7 °C, and  $m/z$  278 was observed at 382.1 °C. These results show that the larger antioxidant was detected at lower temperatures while the smaller antioxidant was detected at a higher temperature.

#### 【Summary】

The qualitative analysis of multiple components observed at the same time can be performed by using a soft ionization method with TOFMS accurate mass measurements. TG-TOFMS is a powerful analytical tool for the detailed thermal analysis of synthetic polymer and additives.



JMS-T200GC

STA2500Regulus

Fig.1 TG-TOFMS system

Table 1 Measurement condition

#### 【TG-TOFMS condition】

System	JMS-T200GC (JEOL) STA2500Regulus(NETZSCH)
Furnace temp.	50°C→10°C/min→ 650°C
Transfer line temp.	400°C
Atmosphere gas flow	He, 100mL/min (open-split system)
Ionization mode	EI+: 70eV, 300μA
	PI+: D <sub>2</sub> lamp: 115 - 400 nm (10.8eV@115nm)
$m/z$ range	$m/z$ 35-1,200

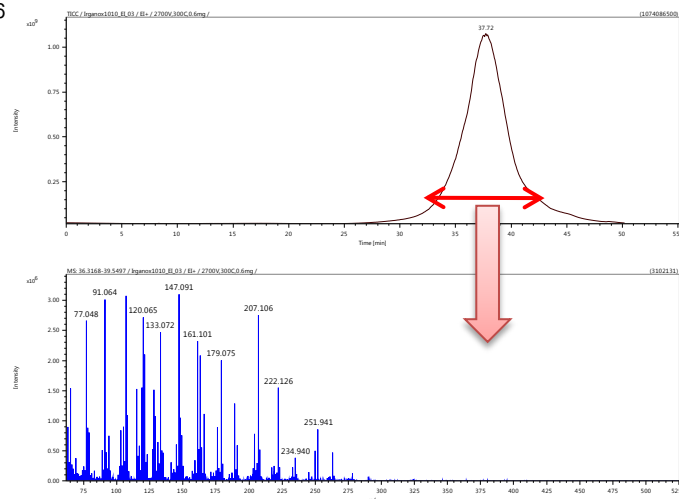


Fig. 2 TG-EI-TOFMS data:  
TIC chromatogram and EI mass spectrum

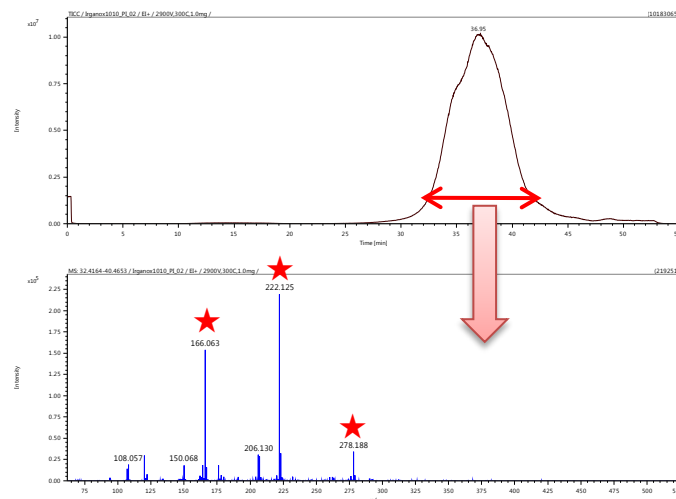


Fig. 3 TG-PI-TOFMS data:  
TIC chromatogram and PI mass spectrum

Table 2 PI Accurate mass analysis result

Mass	Formula	Calculated Mass	Mass Difference [mDa]	DBE
166.0625	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	166.0625	0.1	5
222.1250	C <sub>13</sub> H <sub>18</sub> O <sub>3</sub>	222.1251	-0.1	5
278.1875	C <sub>17</sub> H <sub>26</sub> O <sub>3</sub>	278.1877	-0.1	5

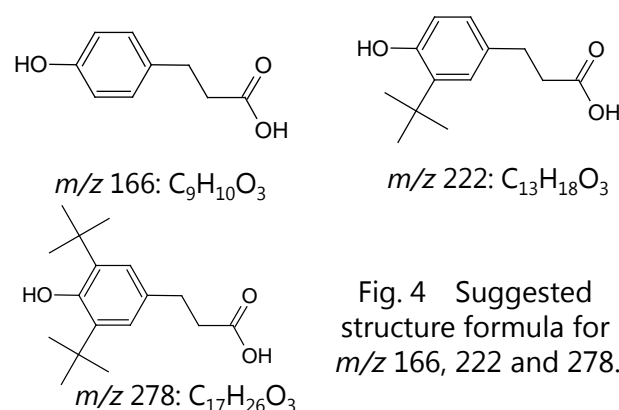


Fig. 4 Suggested  
structure formula for  
 $m/z$  166, 222 and 278.

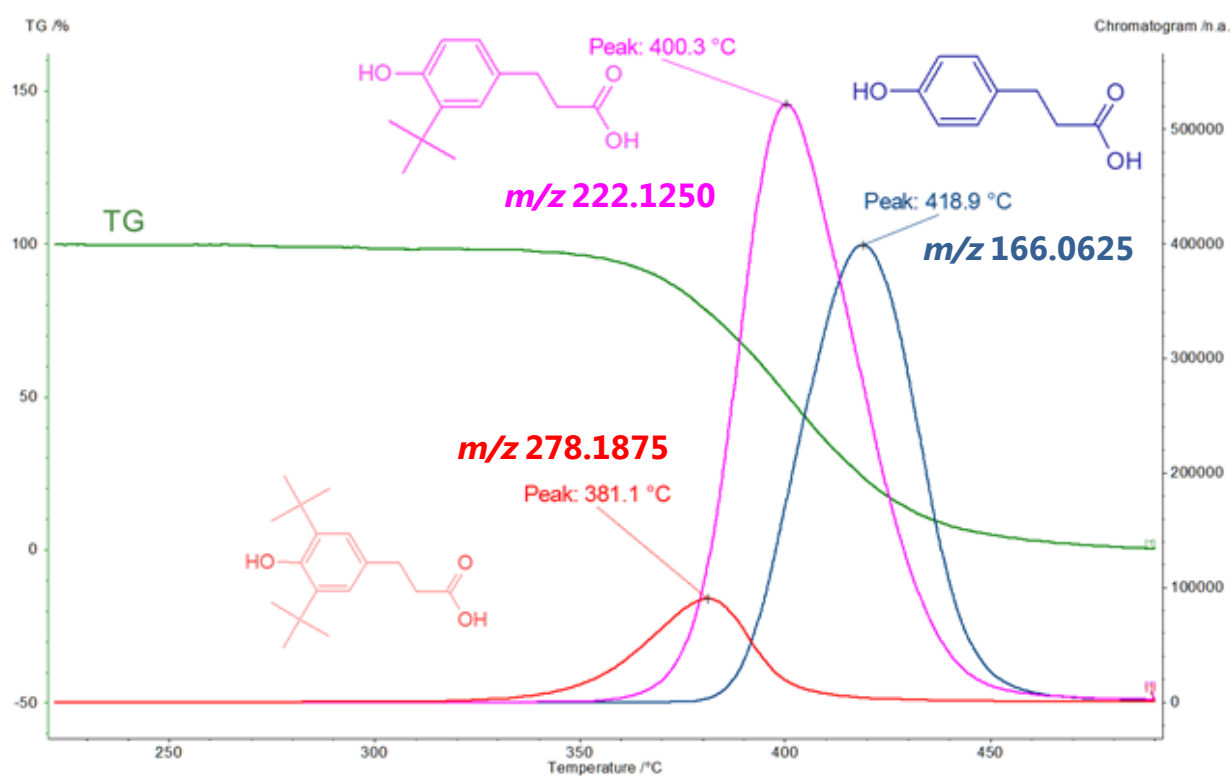


Fig. 5 TG/DTA curves and EIC chromatograms for three ions in PI mass spectrum (Fig.3,★)

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## Fluorocarbon polymers analysis by TG-MS -High $m/z$ range measurement using TG-TOFMS system-

Product used : Mass Spectrometer (MS)

### 【Introduction】

Thermogravimetry (TG) is a thermal analysis technique that measures sample weight changes during sample heating and provides sample thermophysical properties. Combining a TG with a mass spectrometer (MS) makes it possible to perform the qualitative analysis of organic compounds that are evolved as the sample weight changes. Typically, a general purpose quadrupole MS is used for these types of analyses. However, since the measurable  $m/z$  range limitation of a quadrupole MS is about  $m/z$  1,000, this detector provides limited capabilities for the analysis of synthetic polymers and high molecular weight compounds. Alternatively, a time-of-flight mass spectrometer (TOFMS) can be used in combination with the TG to provide a wider measurable  $m/z$  range (greater than  $m/z$  6000). In this work, we measured a fluorocarbon polymer by using a TG-TOFMS system.

### 【Measurement condition】

The fluorocarbon polymer was analyzed by using a JMS-T200GC "AccuTOF™ GC" (JEOL Ltd.), gas chromatograph / high-resolution time-of-flight mass spectrometer equipped with a STA2500 TG system (NETZSCH Co., Ltd.) as shown in Fig. 1. The measurement conditions are shown in Table 1. The GC was used as a thermostatic oven with a fixed temperature of 350 °C with blank capillary tube (3m X 0.25mm I.D.).

### 【Result】

The TG-TOFMS measurement result for 5 mg of fluorocarbon polymer is shown in Fig. 2. The TG curve showed that the weight reduction started around 500 °C and stopped at 600 °C. An EI mass spectrum around 550 °C is shown in Fig. 3. A number of high mass ions with specific repeat units were observed around  $m/z$  2,500 that were indicative of the fluorocarbon polymer thermal decomposition.

The  $m/z$  1,531; 1,831; 2,031; 2,393 and 2,543 EIC chromatograms are also shown in Fig. 2. The maximum for each EIC chromatographic peak was consistent with the weight reduction indicated by the TG curve. This data shows that the thermal decomposition reaction for the fluorocarbon polymer occurred between 500 °C and 600 °C, as detected by the TOFMS.

An enlarged EI mass spectrum around  $m/z$  1,600 is shown in the lower part of Fig. 3. Ions were observed at repeating units of  $\text{CF}_2$  (50 Da), and another minor series corresponding to mass difference of  $\text{F}_2$  (38 Da) was also observed with the main series peaks.

### 【Summary】

The TG-TOFMS data showed that the measurable  $m/z$  range greater than 1000Da which is wider than ordinary TG-QMS and can be used for the measurement of synthetic polymers in the oligomer region.



Fig. 1 TG-TOFMS system

Table 1 Measurement conditions

#### 【TG-TOFMS condition】

System	JMS-T200GC (JEOL) STA2500Regulus(NETZSCH)
Furnace temp.	50°C→10°C/min→ 650°C
Transfer line temp.	400°C
Atmosphere gas flow	He, 100mL/min (open-split system)
Ionization mode	EI+: 70eV, 300μA
$m/z$ range	$m/z$ 35-3,200

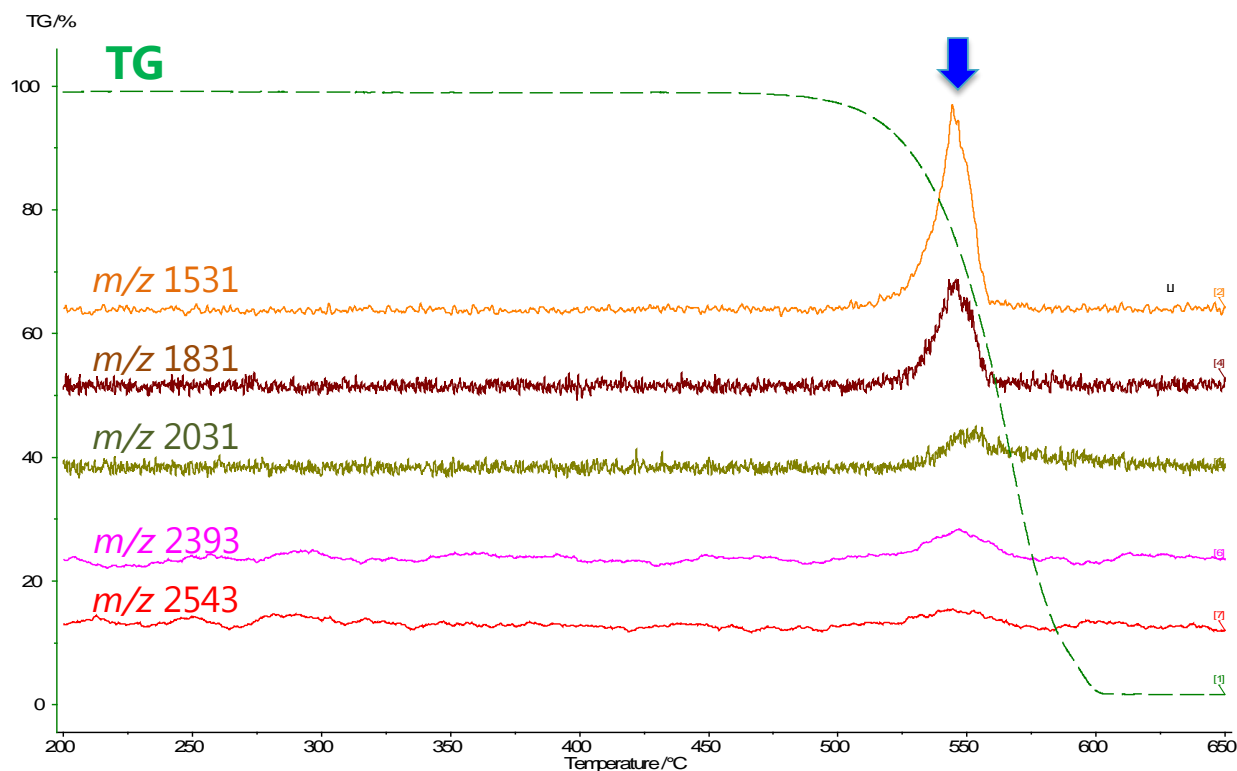
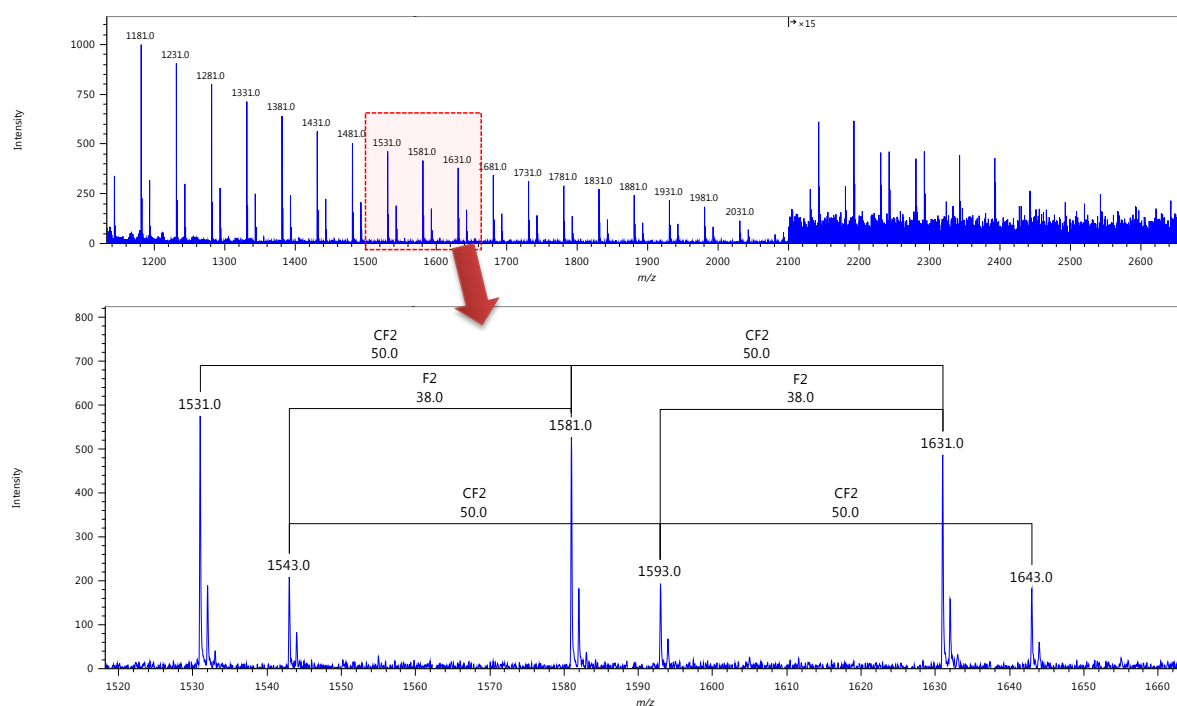
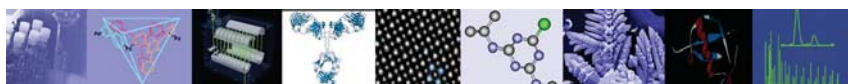
Fig. 2 TG curve and EIC chromatograms for high  $m/z$  ions

Fig. 3 EI mass spectrum at 550°C

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## Evolved gas monitoring from PA66 by using PY-GC-HRTOFMS

### Introduction

Compounds which are generated upon heating polymer materials include monomers, additives and fragments characteristic of the polymer materials. Low molecular weight compounds generated by pyrolysis and/or locally desorption are observed. The relationship between the behavior of evolved gas compounds and the heating temperature is important for understanding the chemical characteristics of polymer materials. A gas chromatograph (GC) - mass spectrometer (MS) with thermogravimetric / differential thermal analyzer (TG/DTA) or pyrolyzer (Py) is generally used to identify the thermally evolved gas compounds from polymer materials. However, GC with a low-resolution MS such as quadrupole MS (QMS) may have difficulty monitoring low molecular-weight compounds generated by heating, since the GC is not used to provide chromatographic separation and QMS has poor mass spectrometric separation in the low mass region. (For example,  $N_2^+$ ,  $CO^+$  and  $C_2H_4^+$  are detected as the same signal of nominal mass  $m/z$  28.)

We report the use of Py - GC - high resolution time-of-flight MS (HRTOFMS) for monitoring the low-molecular weight compounds generated upon heating the polymer materials. This report focuses on the generation of low molecular weight compounds near  $m/z$  18, 28, 4 and 4.

	Conventional method	This application method
	Py/GC/QMS	Py/GC/HRTOFMS
Identification technique	Library searching	Library searching and <u>determination of chemical formula from accurate mass</u>
Monitoring of low-molecular weight compounds	Very difficult without chromatographic separation	<u>Possible by high resolution</u>

### Experimental

A small piece of commercial PA66 (Nylon 66) 0.28mg was measured without further sample preparation by using PY/GC/HRTOFMS, using the JMS-T200GC "AccuTOF GCx-plus" coupled with a PY-2020iD. Measurement conditions were shown in Table 1. To detect evolved gases by heating, we used a low filament current.

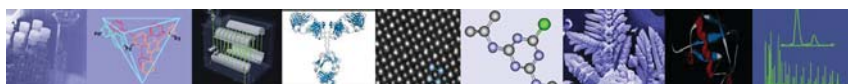
Table 1. Measurement Conditions

<b>Instruments</b>	JMS-T200GC "AccuTOF GCx-plus" (JEOL Ltd.) PY-2020iD (Frontier laboratories Ltd.)
<b>Py conditions</b>	
Furnace temp. program	60°C -> 20°C/min -> 700°C (1min)
Py-GC-ITF temp.	350°C
<b>GC conditions</b>	
Inlet temp.	350°C
Inlet mode	Split 50 :1
Column	Blank tube (5 m x 0.25 mm)
Oven temp. program	350°C (33 min)
Carrier gas flow rate	1 mL/min (He, Constant flow)
<b>MS conditions</b>	
Ionization method	El(+); 25 V, 200 $\mu$ A
GC-MS ITF temp.	350°C
Ion source temp.	250°C
Recording interval	2.5 Hz (0.4 sec/spectrum)
$m/z$ range	10 ~ 800
Drift compensation	$m/z$ 28.0056 ( $N_2^+$ )



Table 2 Assignment Results

Measured $m/z$	Chemical Formula	Calculated mass	Error ( $\times 10^{-3}$ u)
18.0104	$H_2O^+$	18.0100	0.4
18.0344	$NH_4^+$	18.0338	0.6
27.9950	$CO^+$	27.9944	0.6
28.0180	$CH_2N^+$	28.0182	-0.2
28.0308	$C_2H_4^+$	28.0308	-0.0
43.9884	$CO_2^+$	43.9893	-0.9
44.0491	$C_2H_6N^+$	44.0495	-0.4



## Results

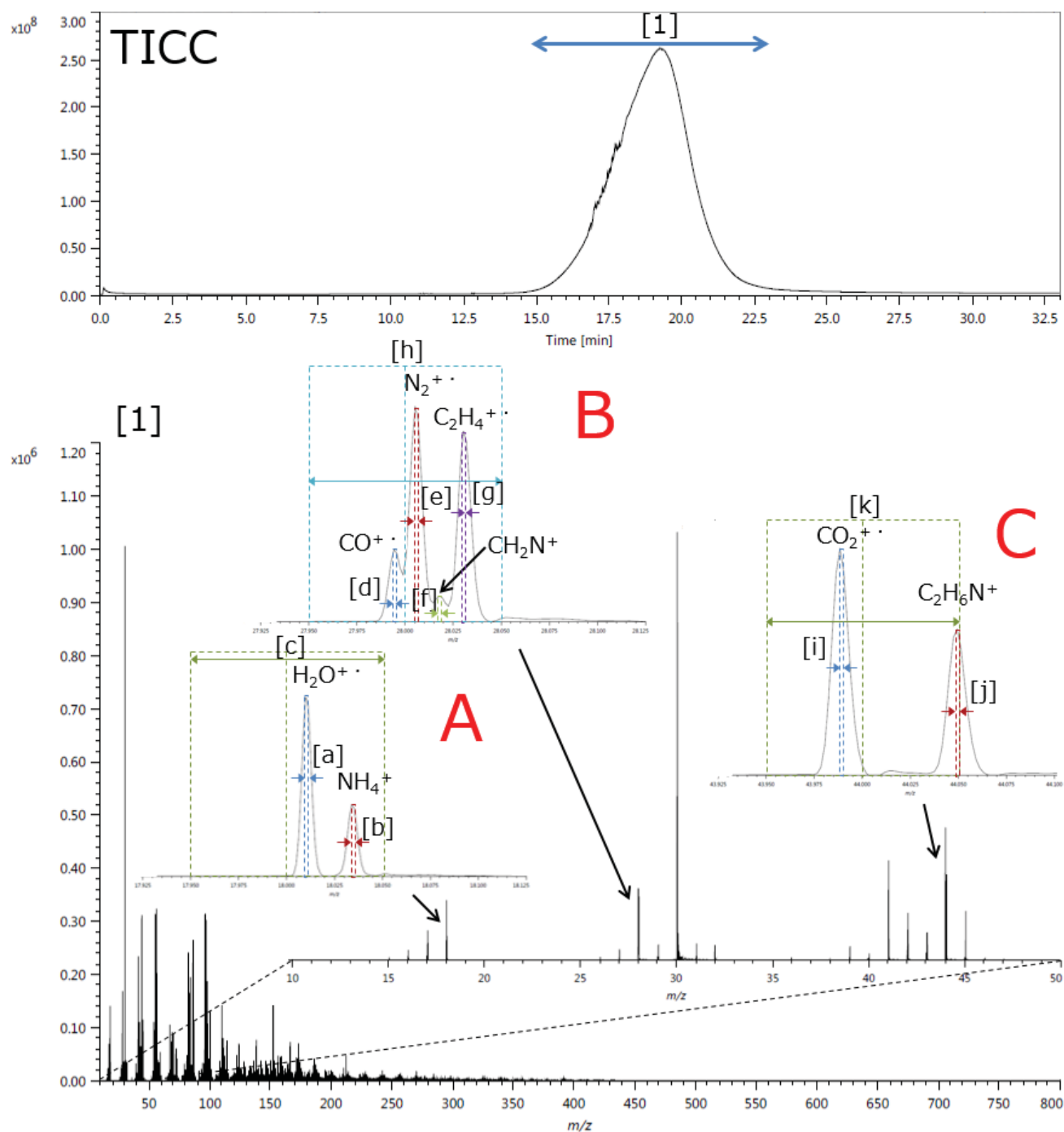


Figure 1. EGA thermogram and average mass spectrum

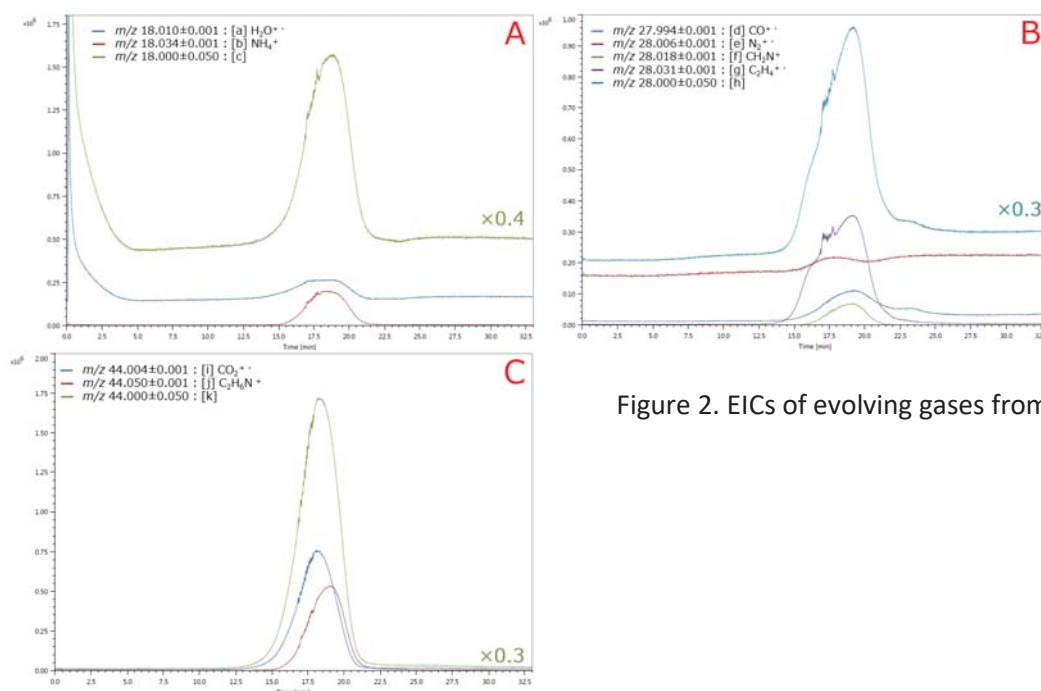


Figure 2. EICs of evolving gases from PA66

The average mass spectrum and the EGA thermogram are shown in Fig.1. In the average mass spectrum, two peaks were detected near  $m/z$  18, four peaks were detected near  $m/z$  28 and two peaks were detected near  $m/z$  44 respectively. Table 2 shows the formulas for each compound. Figure 2 shows the extracted ion chromatogram (EIC) for the calculated  $m/z$  value  $\pm 0.001$  u. To compare the EIC created using exact  $m/z$  value with the EIC created using the nominal  $m/z$  value, figure 2 also shows the EIC created with nominal  $m/z$  value  $\pm 0.050$  u. The EIC of Fig. 2A shows no big difference from the behavior of each  $\text{H}_2\text{O}^+$  (EIC [a]) and  $\text{NH}_4^+$  (EIC [b]). On the other hand, in the EIC of Fig. 2B shows slightly different behavior of each EIC [d], [e], [f], and [g]. The baseline intensity of EIC [e] includes contaminating  $\text{N}_2$  in the He carrier gas cylinder and  $\text{N}_2$  from a slight leak in the system. Although this level is originally high, generated  $\text{N}_2$  due to thermal decomposition is shown near  $410^\circ\text{C}$ . In contrast, EIC [h] which assumes measurement with low-resolution MS looks like the integrated EICs of [d], [e], [f], and [g]. Likewise, EIC C in Fig. 2, the behavior of  $\text{CO}_2^+$  (EIC [i]) and  $\text{C}_2\text{H}_6\text{N}^+$  (EIC [j]) can be distinguished, and it was possible to clearly observe a slight difference in the behaviors of each compound.

## Conclusion

A HRTOFMS can separate low molecular ions composed from carbon, hydrogen, nitrogen and oxygen. The Chemical formula of evolved gases can be determined with high accuracy. Py/GC/HRTOFMS results also permit monitoring the time- and temperature dependence of evolved gases with high accuracy from the measured exact masses. Consequently, PY/GC/HRTOFMS system is possible to monitor the behavior of low molecular weight compounds generated upon heating the polymer materials by high mass resolution.







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