**Applications note**
High Performance Gas Chromatograph -
Time-of-Flight Mass Spectrometer

Solutions for Innovation

## AccuTOF GC series

# Applications Notebook

Edition April 2016

JEOL Ltd.

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# New Gas Chromatography/ High Resolution Time-of-Flight Mass Spectrometer JMS-T200GC "AccuTOF GCx"

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## General

As mass spectrometry (MS) is used in a wide range of scientific fields today, different types of MS systems are available to meet different research objectives and applications. Compared to other scientific instruments, the most powerful feature of MS is its high sensitivity. Some of the commercial MS systems can easily detect and analyze ultra trace components in the fg ($10^{-15}$ g) order. Time-of-flight MS (TOFMS) and magnetic sector MS systems, capable of acquiring high resolution (HR) and high mass accuracy data, make it possible to determine elemental compositions from the exact mass data of the detected ions. Thus, MS is being used in a variety of fields as a powerful analytical instrument for qualitative and quantitative examination of ultra trace components.

In the fall of 2004, JEOL announced the JMS-T100GC AccuTOF GC, the first gas chromatography/high resolution time-of-flight mass spectrometer (GC/HR-TOFMS) developed in Japan. The system has been received well by many users. JEOL has recently completed the 4th generation GC/HR-TOFMS, JMS-T200GC AccuTOF GCx, featuring higher sensitivity and higher mass resolution. In this article, we will provide an overview of the AccuTOF GCx, and describe its advantages in comparison to the original system.

## System Overview

**Figure 1** shows an external view of the system. The AccuTOF GCx supports the same ionization techniques as the original system, that is, electron ionization (EI), chemical ionization (CI), field ionization (FI), as well as desorption electron ionization (DEI), desorption chemical ionization (DCI), and field desorption (FD) ionization using specialized direct sample inlet probes.

**Figure 2** shows the low acceleration ion transfer and orthogonal acceleration (oa)-TOFMS systems. The low acceleration ion transfer system, using a split lens and the potential difference of deflectors, eliminates 99% or more of the helium ions from the GC carrier gas before the oa-TOFMS system. This feature maximizes detector lifetime. The oa-TOFMS system incorporates an ion accelerating mechanism and reflectron. The ion beam is spatially focused by the ion accelerating mechanism, and is further time-focused by the reflectron to accomplish high resolution mass analysis at all times. While the oa-TOFMS remains nearly identical to the original system, the parameters were reviewed and optimized to achieve higher mass resolution. An isolation valve between the ion source-ion transfer unit and the oa-TOFMS makes it possible to bring the ion source and ion transfer unit to atmospheric pressure while maintaining a high vacuum in the oa-TOFMS.

The ion detector and electric circuits of the detector system were also modified and optimized to achieve higher resolution and higher sensitivity, simultaneously. The data detection system uses an ADC 4 GHz-digitizer to acquire mass spectral data with ample data points. The system enhances the reproducibility of the mass accuracy (horizontal axis of mass spectrum) and the intensity (vertical axis of mass spectrum) of the ion peaks detected.

The AccuTOF GCx achieves a sensitivity level 3 times higher and a mass accuracy level twice higher than the original system, while the dimensions of the system remain unchanged from the older models.

## Basic Performance

The basic performance of the AccuTOF GCx is as follows:

- Ionization mode: EI, CI, FI, DEI, DCI and FD
- GC/EI sensitivity: OFN 1 pg, S/N>300
- Mass resolution: >10,000 (FWHM)
- Mass accuracy: <1.5 mDa or 4 ppm (RMS)
- Mass range: *m/z* 4 to 6,000
- Spectrum recording speed: Up to 50 spectra/sec

The GC/EI sensitivity is specified as S/N 300 or higher for 1 pg of octafluoronaphthalene (OFN). **Figure 3** shows the extracted ion chromatogram (EIC) of the molecular ion at *m/z* 271.9867 and EI mass spectrum when 1 pg of OFN was analyzed. Both the EIC and EI mass spectrum demonstrate a high S/N ratio. **Figure 4** shows the EIC of the molecular ion acquired from 100 fg of OFN that was analyzed continuously

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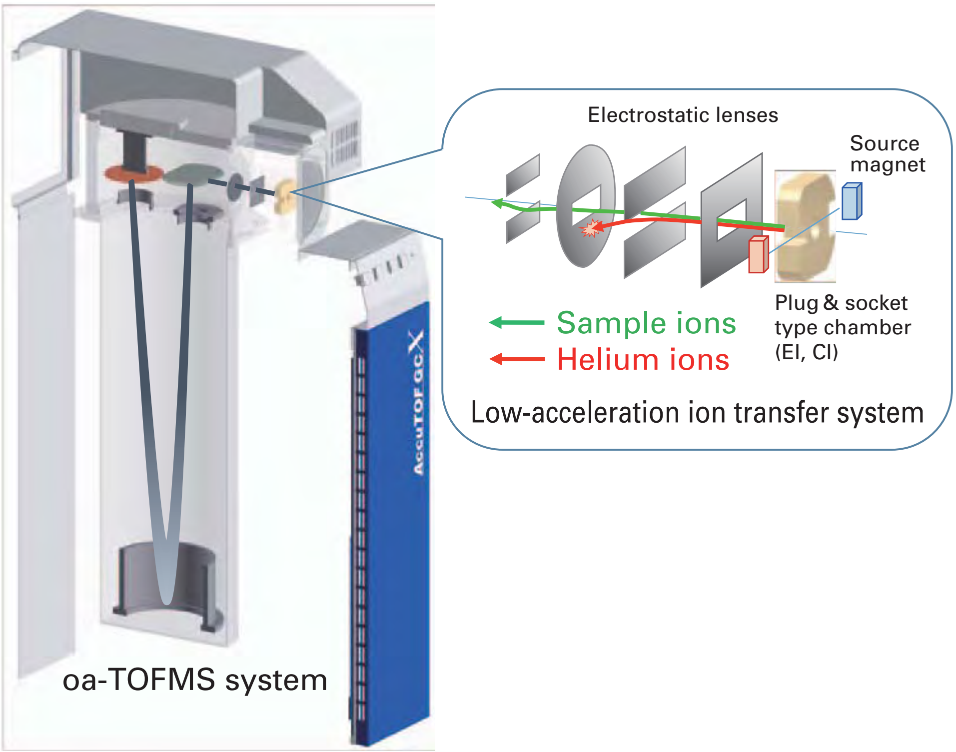
Fig. 1 JMS-T200GC "AccuTOF GCx"

Fig. 2 Low-acceleration ion transfer system and oa-TOFMS system



8 times. The figure also shows the peak area, the relative standard deviation, and the instrument detection limit (IDL) calculated from these data. Despite the ultra micro amount of 100 fg, the relative standard deviation was 5.2%, demonstrating high stability. The IDL, which was statistically calculated from the repeated accuracy of the peak areas with a given level of reliability, was 16 fg. As the data above demonstrates, the AccuTOF GCx is a GC/MS system that combines high sensitivity and high stability in ultra micro analysis.

**Figure 5** compares the data acquired by the AccuTOF GCx and the conventional system, showing the peaks of $C_6F_{11}^+$, a fragment ion of perfluorokerosene, which is used widely as a mass calibration sample for GC/MS, and $C_7H_{21}O_4Si_4^+$ observed as a background ion from the GC column. These ions, being extremely close in exact mass, were not completely separated in the original system (bottom of Fig. 5; mass resolution: 5,105; peak FWHM: 55 mDa). The AccuTOF GCx, with a specified resolution of 10,000, separated these peaks completely (top of

**Fig. 3 OFN 1 pg: EIC of *m/z* 271.9867 and EI mass spectrum**

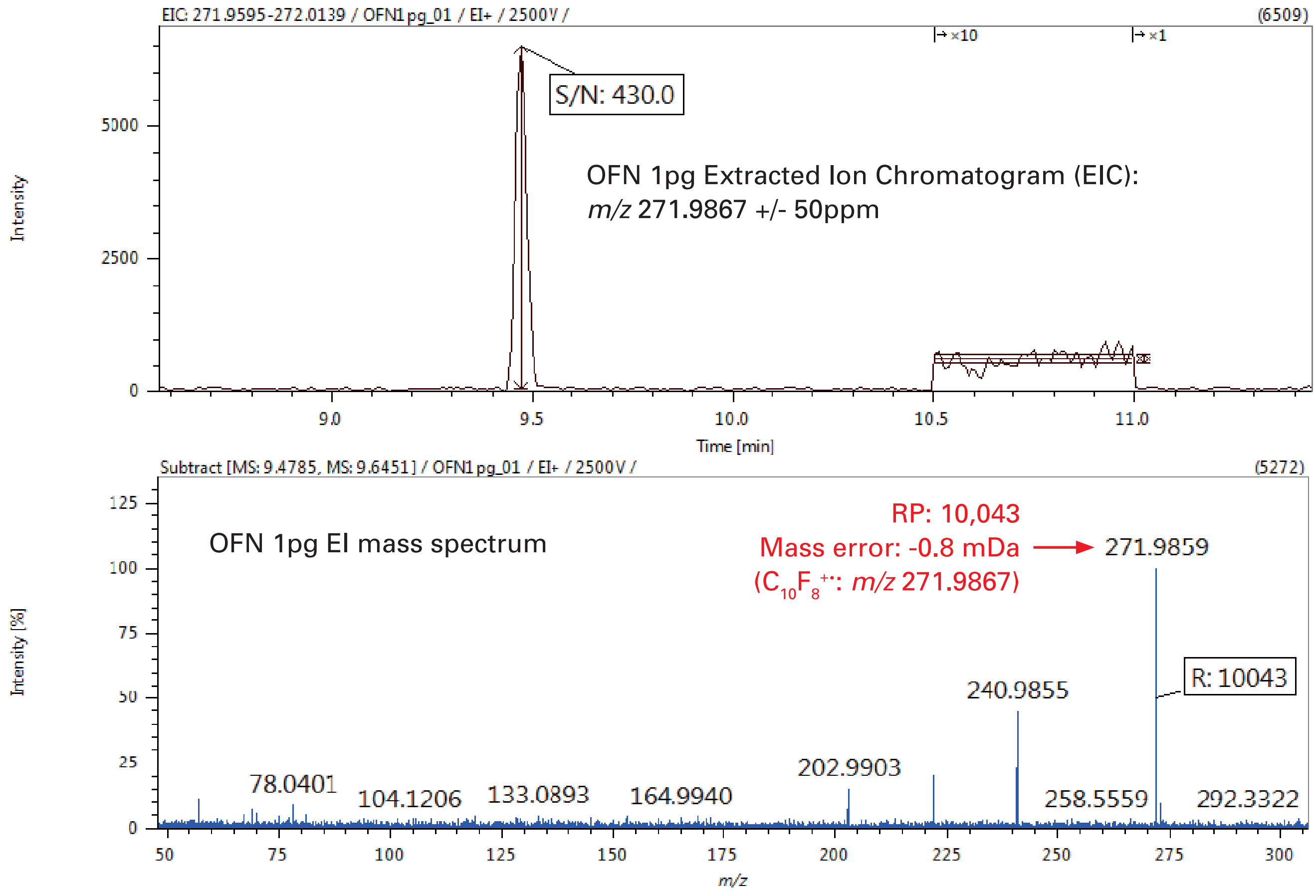
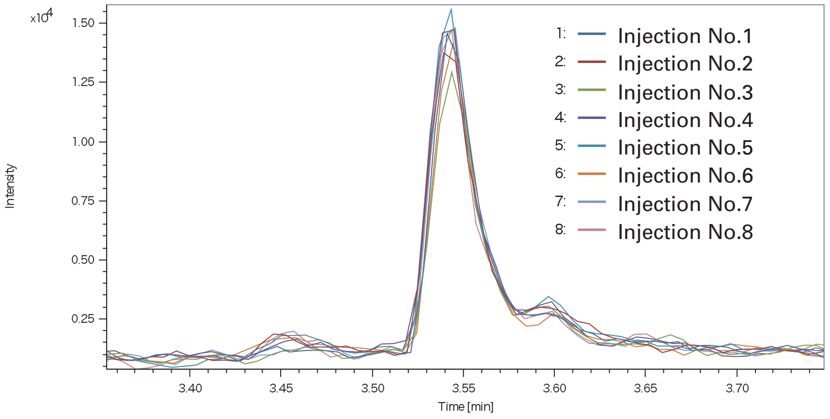


**Fig. 4 OFN 100 fg: EICs of *m/z* 271.9867 and IDL**



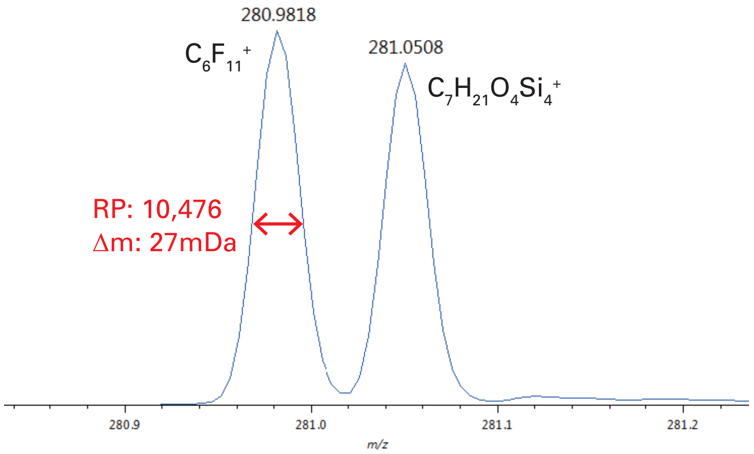
| Injection No. | Peak Area |
|---|---|
| 1 | 65745 |
| 2 | 67212 |
| 3 | 58394 |
| 4 | 70698 |
| 5 | 65897 |
| 6 | 65604 |
| 7 | 65994 |
| 8 | 65230 |

| | |
|---|---|
| Relative Standard Deviation (%) | 5.2 |
| IDL (fg) | 16 |

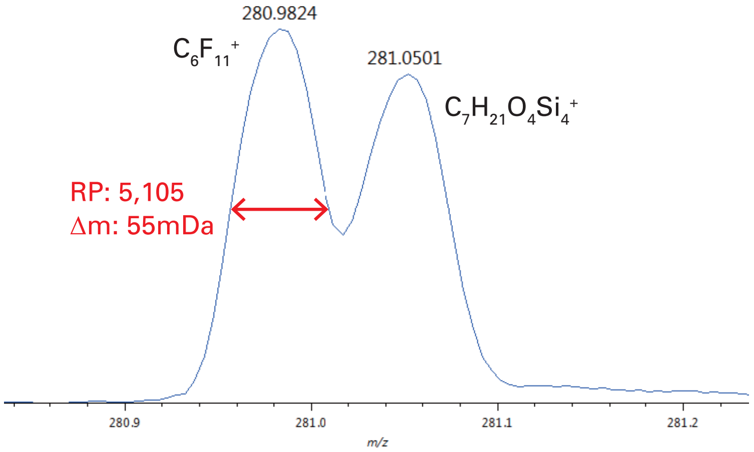
Fig. 5; mass resolution: 10,476; peak FWHM: 27 mDa).

As the mass resolution is improved, so is the mass accuracy, which is specified at 1.5 mDa or 4 ppm or less. The system easily acquires mass spectral data featuring a high level of mass accuracy in all ionization techniques. This allows the user to determine the molecular formula of a target compound from the accurate mass data of the molecular ions and protonated molecules observed by soft ionization techniques such as CI and FI, and the structural formula of a target compound from the accurate mass data of fragment ions observed by hard ionization such as EI. **Figure 6** shows the EI and FI mass spectra of allyl(tert-butyl)dimethylsilane and the elemental

## Fig. 5 Comparison of mass resolution and ion peak shape

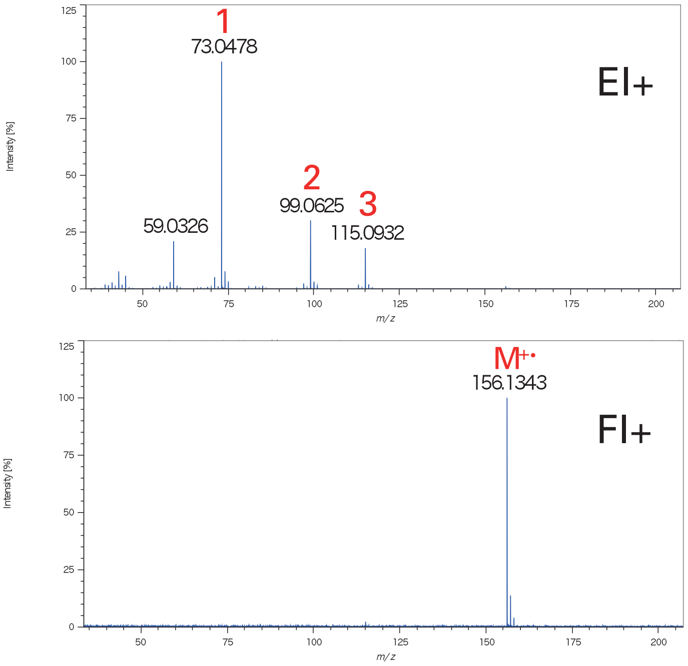


JMS-T200GC AccuTOF GCx (4th model)

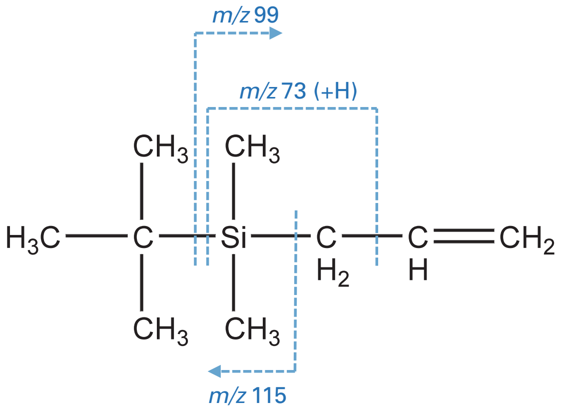


JMS-T100GC AccuTOF GC (1st model)

## Fig. 6 EI and FI mass spectra of Allyl(tert-butyl)dimethylsilane



| Mode | Ion | Obs. *m/z* | Error (mDa) | Formula |
|---|---|---|---|---|
| EI+ | 1 | 73.0478 | 1.0 | $C_3H_9Si$ |
|  | 2 | 99.0625 | 0.0 | $C_5H_{11}Si$ |
|  | 3 | 115.0932 | -0.6 | $C_6H_{15}Si$ |
| FI+ | $M^{+\bullet}$ | 156.1343 | 1.5 | $C_9H_{20}Si$ |



composition of the ions detected. While a small molecular ion was observed at *m/z* 156 in the EI mass spectrum, its intensity was extremely low. EI, being the hardest ionization technique, can detect many fragment ions other than molecular ions. However, it can often fail to detect the molecular ions. When analyzing an unknown sample, it is extremely difficult to determine from the EI spectrum alone if the ion with the highest mass is a molecular ion or a fragment ion. On the other hand, FI is capable of detecting molecular ions most easily, compared to other soft ionization techniques. In the FI mass spectrum of allyl(tert-butyl)dimethylsilane, the molecular ion at *m/z* 156 was detected with the highest intensity in the mass spectrum. From the accurate mass data of the molecular ion at *m/z* 156 in the FI mass spectrum, the elemental composition of this ion was identified as $C_9H_{20}Si$, the same molecular formula as allyl(tert-butyl)dimethylsilane. Also, the accurate mass data for the fragment ions observed in the EI mass spectrum provided the elemental composition data that indicated a segment of the structural formula of allyl(tert-butyl)dimethylsilane. Thus, combining the elemental composition data acquired by multiple ionization techniques, the AccuTOF GCx is capable of highly reliable qualitative analysis.

Another powerful feature of the AccuTOF GCx is a wide mass range from *m/z* 4 to 6,000. Typical GC/MS analysis, especially with EI, uses a mass range up to *m/z* 600. Meanwhile, FD is often used for samples having relatively large masses such as synthetic polymers and organic metal complexes. The mass range of the AccuTOF GCx up to *m/z* 6,000 enables analysis of these samples (**Fig. 7**). FD is one of the direct MS techniques using a specific direct sample inlet probe. While typical GC/MS systems are almost exclusively designed for GC/MS analysis, the AccuTOF GCx also supports two additional direct sample inlet probes (Direct Exposure Probe, Direct Insertion Probe).

The AccuTOF GCx features a spectrum recording speed of up to 50 spectra/sec. This makes the AccuTOF GCx a powerful tool for any applications that require extremely fast data acquisition such as high speed gas chromatography (Fast GC) and comprehensive 2D gas chromatography (GCxGC).

The AccuTOF GCx is a next generation GC/MS system that combines high sensitivity, high mass resolution, high mass accuracy, wide mass range, and high speed spectrum recording.

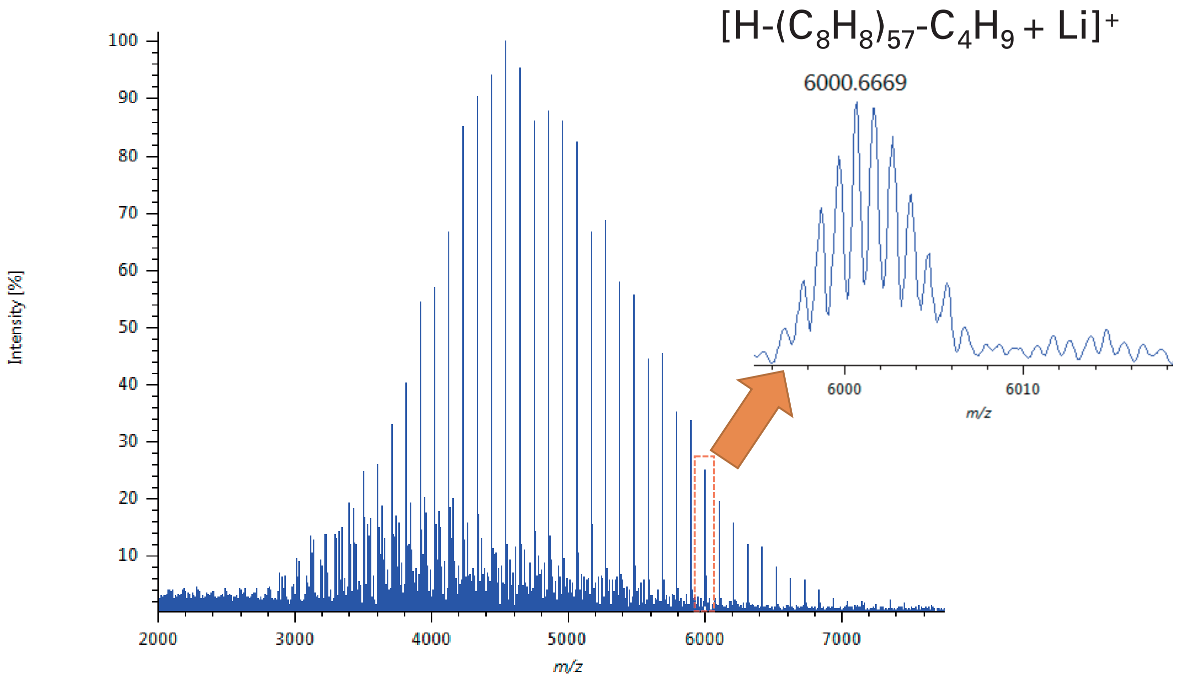
## EI/FI/FD combination ion source

The EI/FI/FD combination ion source is an optional accessory for the AccTOF GCx, a single ion source that supports sample analysis using 3 different ionization techniques (GC/EI, GC/FI, FD). An ionization mode is selected by replacing the probe. Probes can be changed while keeping the ion source in high vacuum, minimizing system downtime for an ionization mode switch. The effectiveness of this unique EI/FI/FD combination ion source has been valued by many users since it was first incorporated in the second generation system, the AccuTOF GCv. As discussed above, because the TOFMS base unit accomplishes high sensitivity and high mass resolution, the EI/FI/FD combination ion source acquires mass spectral data that features higher sensitivity and higher resolution.

## New software "msAxel"

The AccuTOF GCx is accompanied by a new software package, msAxel, for system control and data analysis (**Fig .8**). msAxel has an intuitive user interface in which each view is designed to facilitate access to all necessary information. msAxel also includes a Tuning Assistant, one of the features of the previous software, to optimize the system conditions. Tuning

**Fig. 7 Polystyrene 5200 FD mass spectrum**



Assistant is supported in all ionization modes.

The most powerful feature of msAxel is that it enables speedy setup of data processing conditions from a single view. The system accomplishes the steps listed below, which are essential in mass data analysis, under the preset conditions, as it acquires the mass spectrum.

1. Detect ion peaks
2. Determine the center point of ion peak
3. Calculate the exact mass, ion peak intensity/area
4. Create an ion peak list based on the data above

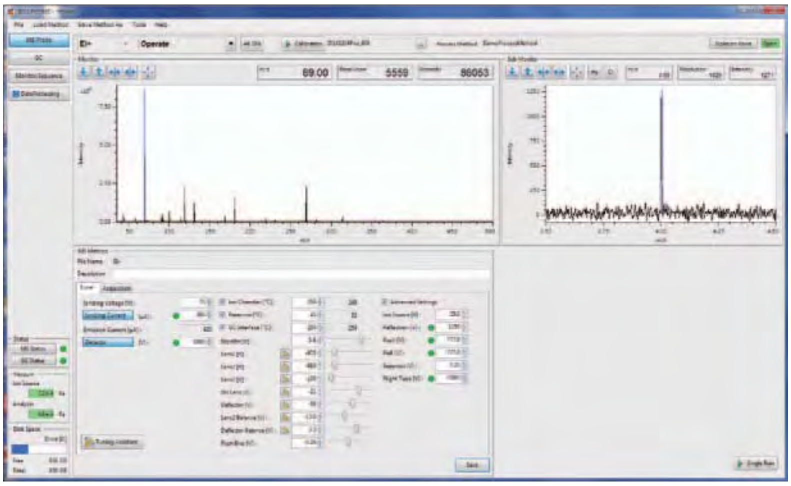
Furthermore, unlike the original software, msAxel can search the NIST library database and determine elemental compositions based on the peak list created in the process above. Accomplishing these steps while maintaining the profile mass spectrum, msAxel simplifies the data analysis process, and also allows the user to process the data while examining ion peaks that have similar exact masses.

## Summary

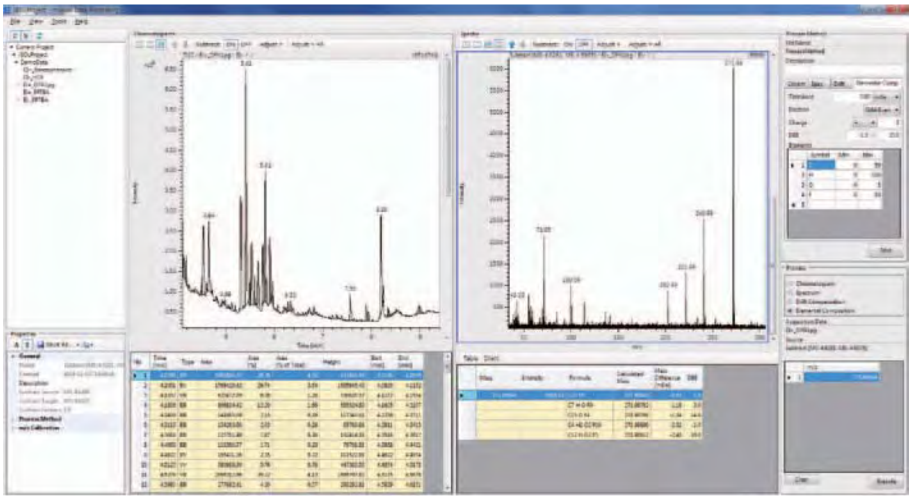
The AccuTOF GC series has been appreciated by many users since the 1st generation AccuTOF GC system was introduced in 2004. The 4th generation AccuTOF GCx is JEOL's latest GC/HR-TOFMS system that combines the most advanced hardware and software components. It is a powerful and versatile system that is effective as a TOFMS for elemental composition determination, as a tool for advanced gas chromatography techniques such as Fast GC and GCxGC, and as a direct MS system that uses direct sample inlet probes. We expect that the AccuTOF GCx will be fully utilized in a wide range of applications, thus contributing to the advancement of science and technology.

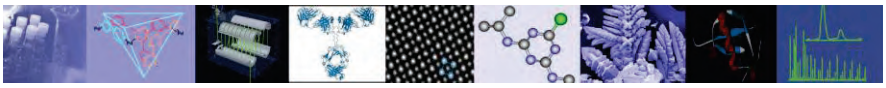
**Fig. 8 msAxel: Main and Data Processing Views**

msAxel Main view



msAxel Data Processing view





Applications Note

# AccuTOF-GCx Series

## Introduction of latest GC/HR-TOFMS system:JMS-T200GC AccuTOF-GCx - High Mass Accuracy and Stability

### Introduction

JEOL has recently announced a 4th-generation GC/HR-TOFMS system, the JMS-T200GC AccuTOF-GCx, in 2015. The AccuTOF-GCx offers high sensitivity, high mass resolving power, high mass accuracy, and a wide dynamic range in combination with high-speed data acquisition.

In this application note, we show high mass accuracy and *m/z* stability using this latest GC/HR-TOFMS system.

### Results and Discussion

We made 100 replicate splitless injections of 1 µL of a 100fg/µL solution of octafluoronaphthalene (OFN) and acquired the mass spectra in electron ionization (EI) mode. All data were mass-calibrated with a one-point drift compensation by using a background column-bleed ion from the capillary column (*m/z* 281.05114: $C_7H_{21}O_4Si_4^+$) as a lock mass.

We obtained excellent reproducibility for the mass accuracy for the OFN molecular ion ($C_{10}F_8^+$, *m/z* 271.9867 ) . All 100 measurements were within +/- 1 mDa using the column-bleed drift compensation (Figure 2).

*Figure 1. 4th-generation of the JEOL GC/HR-TOFMS system JMS-T200GC AccuTOF-GCx*

### Conclusion

The AccuTOF-GCx system provides high mass accuracy and stability by using a simple one-point drift compensation.

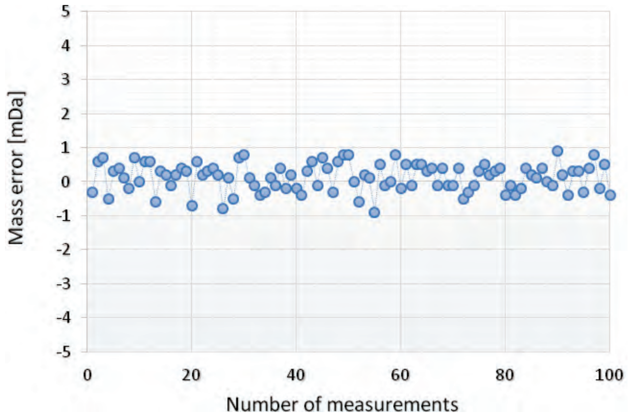


*Figure 2. Mass error of the OFN 100fg molecular ion (C10F8+, m/z 271.9867 ) during 100 replicate measurements*

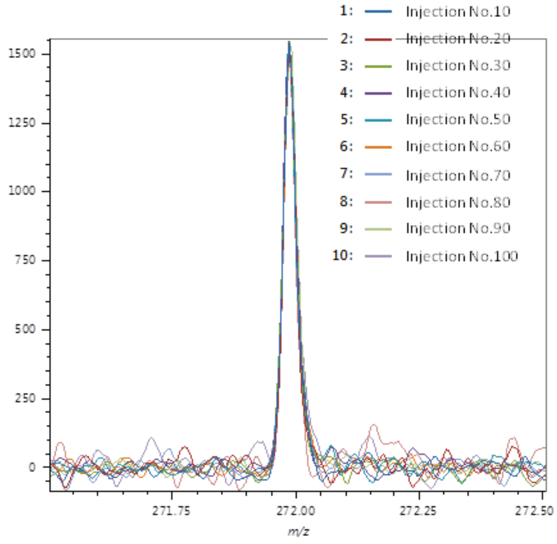


*Figure 3. Overlay chart of the OFN molecular ion peaks*

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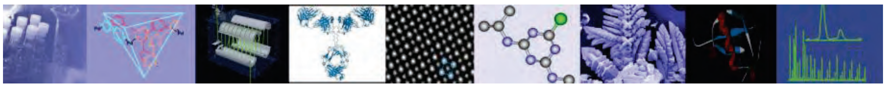

Applications Note

# AccuTOF-GCx Series

## Introduction of latest GC/HR-TOFMS system: JMS-T200GC AccuTOF GCx - High Mass Resolution

### Introduction

JEOL has recently announced a 4th-generation GC/HR-TOFMS system, the JMS-T200GC AccuTOF GCx, in 2015. The AccuTOF-GCx offers high sensitivity, high mass resolving power, high mass accuracy, and a wide dynamic range in combination with high-speed data acquisition.

In this application note, we show the high mass resolution that can be obtained with this latest GC/HR-TOFMS system.

### Results and Discussion

We measured perfluorotributylamine (PFTBA) introduced through the reservoir of the heated volatiles inlet. A resolving power of 10,000 was easily obtained for the *m/z* 614 peak (Figure 2).

Next, we checked the mass separation for a doublet comprised of the peaks corresponding to $C_6F_{11}^+$ (PFK) and $C_7H_{21}O_4Si_4^+$ (GC column background). In comparison with the original 1st-generation model, the “AccuTOF GC” (with only a mass resolving power of 5,000), the 4th-generation model “AccuTOF GCX” has over 10,000 mass resolving power (Figure 3).

*Figure 1. 4th-generation of the JEOL GC/HR-TOFMS system JMS-T200GC AccuTOF GCx*

### Conclusion

The AccuTOF GCX system has a mass resolving power of >10,000 that can easily be obtained for all GC/MS and direct MS measurements.

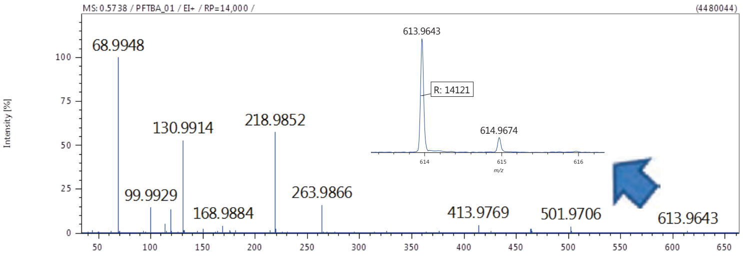

*Figure 2. PFTBA EI mass spectrum*

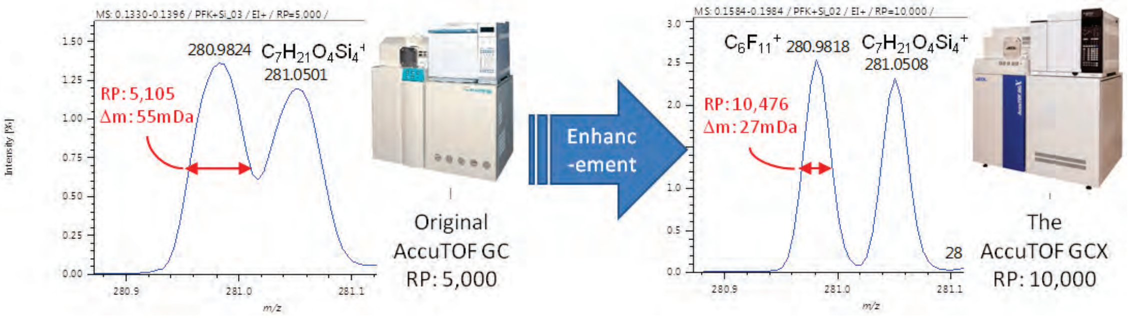

*Figure 3. Evolution of mass resolving power from the 1st-generation AccuTOF-GC to the 4th-generation AccuTOF-GCx*

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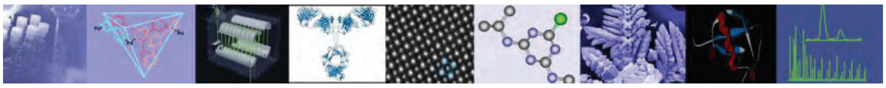


# AccuTOF-GCx Series

## Introduction of latest GC/HR-TOFMS system: JMS-T200GC AccuTOF GCx - High Sensitivity Measurement

**Introduction**

JEOL has recently announced a 4th-generation GC/HR-TOFMS system, the JMS-T200GC AccuTOF-GCx, in 2015. The AccuTOF-GCx offers high sensitivity, high mass resolving power, high mass accuracy, and a wide dynamic range in combination with high-speed data acquisition.

In this application note, we show the high sensitivity measurement capability using this latest GC/HR-TOFMS system.

**Experimental**

We checked the system sensitivity by measuring a standard sample of octafluoronaphthalene (OFN) and standard dioxin samples. Mass spectra were acquired at a spectral acquisition rate of 0.3 seconds per spectrum. Splitless GC injections were used for all measurements reported here.

**Results**

*OFN measurement result*

We measured a 1pg/µL standard solution of OFN by injecting 1µL of the solution into the AccuTOF-GCx system. We observed a signal-to-noise ratio of 443 by creating a high-selectivity extracted ion chromatogram (EIC) with a narrow *m/z* range for the molecular ion of OFN (Figure 2a). The EI mass spectrum gave a mass accuracy of -0.8 mDa with a mass resolving power of 10,043 for the OFN molecular ion *m/z* 271.9859 (Figure 2b).

*Dioxin measurement result*

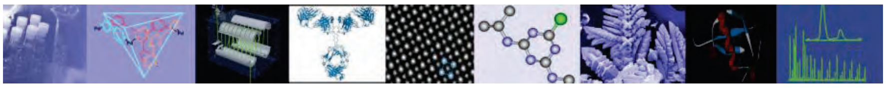
We measured standard dioxin solutions at concentrations of 50, 100 and 1000 fg/µL in order to evaluate the sensitivity and linearity of the calibration curve for 2,3,7,8-tetrachlorodibenzodioxin (TeCDD). The EICs for each sample are shown in Figure 4. The calibration curve created from the EIC data shows excellent linearity.

*Figure 1. 4th-generation of the JEOL GC/HR-TOFMS system JMS-T200GC "AccuTOF GCx"*

Figure 5 shows the data for a 50 fg/µL injection. At the 50 fg/µL level, we can observe many interferences in the standard solution. However, the high-resolution EIC's created from the AccuTOF-GCx system showed complete separation between the isotopic peaks corresponding to the molecular ions of 2,3,7,8-TeCDD ($C_{12}H_4O_2Cl_4$: *m/z* 321.8931 and *m/z* 319.8960) and the peaks resulting from the low-level contaminants.

**Conclusion**

The JMS-T200GC AccuTOF-GCx is high-sensitivity and high-resolution GC/MS system. It is suitable not only for qualitative analysis but also for quantitative analysis. The 4th-generation model from the JEOL AccuTOF-GC series provides detection limits with good sensitivity for femtogram concentration levels.



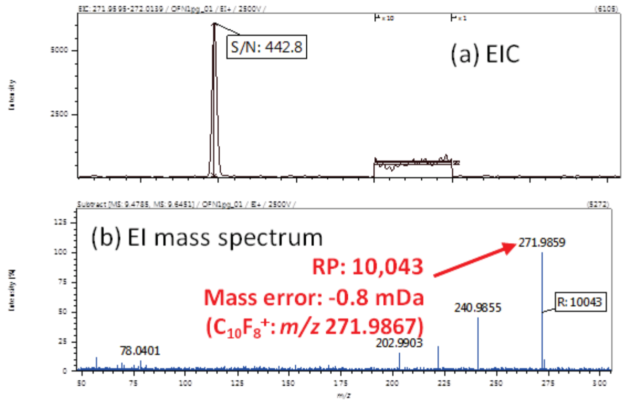


Figure 2. OFN 1pg/μL data,
(a) EIC: m/z 271.9867 +/- 50ppm, (b) EI mass spectrum

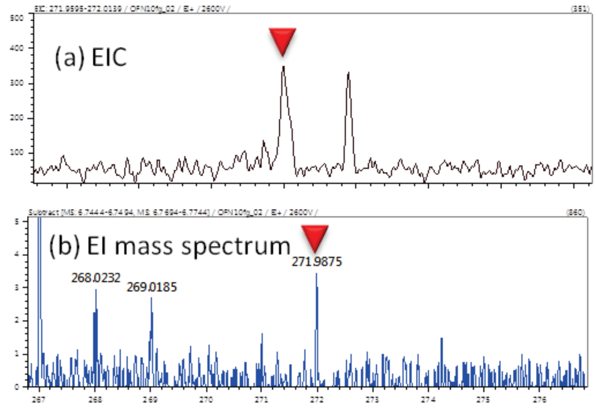
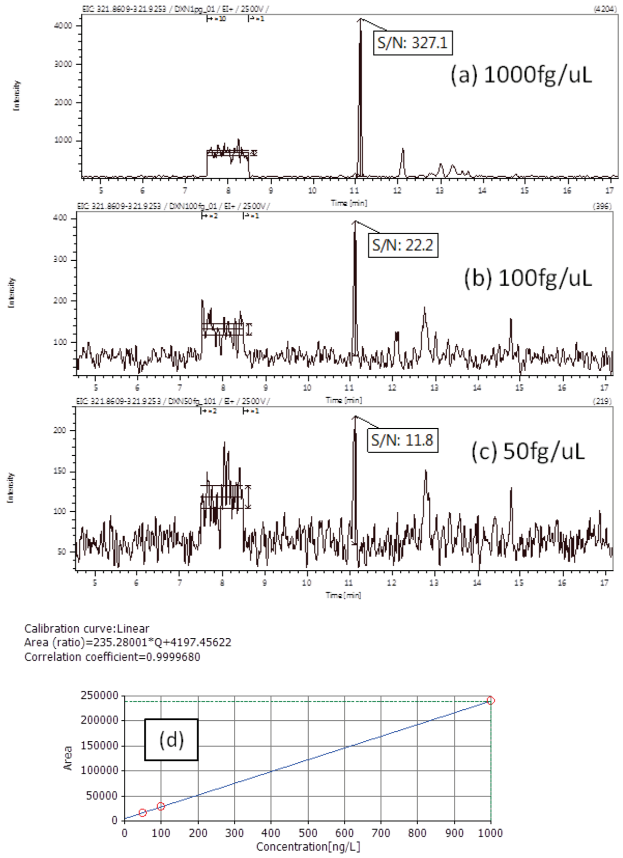


Figure 3. OFN 10fg/μL data, (a) EIC: m/z 271.9867 +/- 50ppm, (b) EI mass spectrum (enlarged)



Calibration curve:Linear
Area (ratio)=235.28001*Q+4197.45622
Correlation coefficient=0.9999680

Figure 4. 2,3,7,8-TeCDD EIC: m/z 321.8931 +/- 50ppm, (a) 1000fg/μL, (b) 100fg/μL, (c) 50fg/μL
(d) Calibration curve

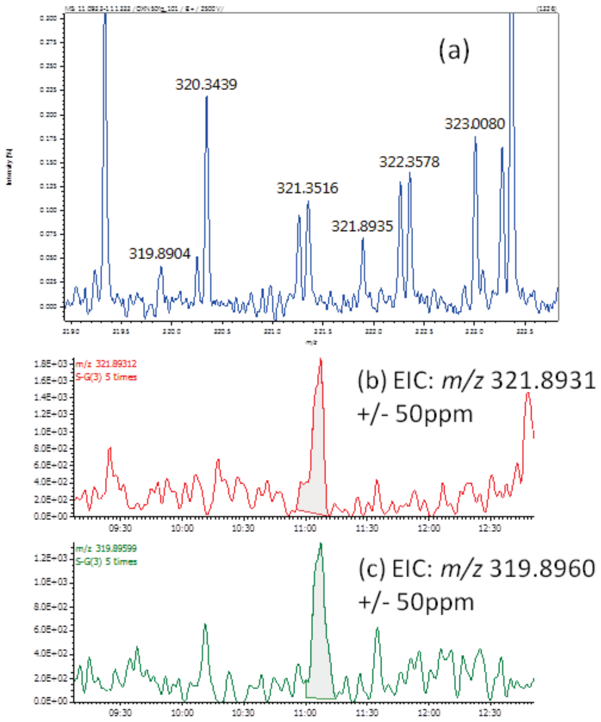


Figure 5. 2,3,7,8-TeCDD 50 fg/μL data
(a) EI mass spectrum (enlarged),
(b) EIC: m/z 321.8931 +/- 50ppm,
(c) EIC: m/z 319.8960 +/- 50ppm

# Features and Applications of Newly-Developed GC-TOFMS “The AccuTOF GC”

*Note: This article was based on the first-generation JEOL AccuTOF GC so it does not reflect the improved performance and new fetaures of the fourth-generation AccuTOF GCx. However, the article explains the important concepts behind the design and applications of these systems and is included for your information.*

**Masaaki Ubukata**

**Analytical Instrument Division, JEOL Ltd.**

## Introduction

A gas-chromatograph mass spectrometer (GC-MS) is a combined analyzer that has superior ability in analyzing organic compounds qualitatively and quantitatively. The first part, gas chromatograph, separates the compounds included in a sample (mixture), then the second part, mass spectrometer, obtains mass spectra of the compounds to carry out qualitative analysis. Quantitative analysis can be carried out as well from the peak area of the mass chromatogram of the compound.

As a mass spectrometer of a GC-MS system, several types of mass spectrometers are on the market, such as magnetic field, quadrupole (QMS), ion trap (ITD), and time-of-flight (TOF). Each mass spectrometer has its own features and applications.

By the way, “fast GC”, one of the GC methods, has become to attract attention recently. The fast GC method can shorten the analysis time remarkably while keeping a good separation ability equal to the conventional GC methods, by using a narrow and short column of about 0.1 mm inside diameter and 10 m long. The fast GC method, adopted in a GC-MS system, has the ability to improve the system throughput. However, it requires a fast spectrum-acquisition speed to the mass spectrometer, because the chromatograph peaks are narrower in time than a conventional GC. TOFMS only has the ability to satisfy the demand for fast spectrum-acquisition speed at the present time, but the existing GC-TOFMS systems are not satisfactory by either of the following reasons: it can follow the fast speed of the fast GC, but its mass resolution is too low to measure accurate mass, or, on the inverse, it has a mass resolution high enough to measure accurate masses but cannot follow the fast speed of the fast GC.

JEOL has developed and announced an innovative GC-TOFMS instrument, JMS-T100GC “The AccuTOF GC” in September of 2004, which satisfies both demands for high speed responding to the fast GC method, and for obtaining accurate mass easily.

The AccuTOF GC inherits the features of high resolution, accurate mass measurement with simple operation, and high sensitivity from its sister instrument, JMS-T100LC “The AccuTOF.” The AccuTOF series contains a continuous averager in the data acquisition system that offers a wider dynamic range when compared to the time-to-digital converter (TDC) used in a conventional GC-TOFMS. In addition to this, the AccuTOF GC supports the fast GC/MS measurement, and is the first instrument that realizes these features in one instrument, which was impossible for the conventional instruments.

We have reported the principal features and the basic performances of the AccuTOF GC in the preceding 2003 MS Users Meeting. Here, we discuss the applications of the AccuTOF GC, in addition to the features and the basic performances.

## Overview

### Basic configuration

The basic configuration of the AccuTOF GC is as follows:

- TOFMS main unit
  (EI ion source is the standard)
- GC (Agilent 6890N)
- Personal computer
- Printer

Options include:

- Direct Injection Probe
  (Direct Exposure Probe (DEP))
- GC Automatic Sampler
  (injector + 100 sample trays)
- CI Ion Source
- FD/FI Ion Source
- EZChrom
  (software for quantitative analysis)

A plug-and-socket ion chamber is provided for both the standard EI ion source and the optional CI ion source, which allows cleaning of the easily contaminated ion chamber only, and makes replacing the filament easy.

An isolation valve is provided between the ion transfer system and the analyzer. Closing it keeps the analyzer in a high vacuum even during the following occasions: replacing the column and maintenance of the ion source, when a large quantity of solvent flows from the GC during measurement, and in emergency such as power failure.

The direct injection probe is a DEP type; the sample is initially dissolved in a solvent, and is applied to the platinum filament of the probe using a syringe.

### External view

**Figure 1** shows the external view of the AccuTOF GC. The AccuTOF GC is an on-floor type and has casters at the bottom to facilitate transport of the system.
(Note: In order to prevent damage to the turbomolecular pump, the system cannot be moved while in operation.)

The AccuTOF GC has integrated a turbomolecular pump and a rotary pump into the main unit, resulting in an effective footprint equal to or smaller than a typical bench-top system.

## Features of the Instrument

**Figure 2** shows the diagram of the AccuTOF GC. It comprises depending on the functions:

- Ion source and ion transfer system
- Analyzer
- Detector
- Data acquisition system
- Data system (personal computer)

### Ion source and ion transfer system

**Figure 3** shows a plan-view sectioned diagram of the ion source and ion transfer system. The role of this system is to ionize the sample introduced from the GC, and to transfer the ions to the analyzer at a low kinetic energy of about 30 eV.

The plug-and-socket ion chamber, shown at the top left of Fig. 3, has two gas inlets. One at the upper right in the photo is the gas inlet from the GC, and another one at the lower right is the gas inlet from the sample-heating device for the standard sample and others. The plug-in structure facilitates easy maintenance.

In a GC-MS system, a large quantity of helium gas, used as the GC carrier gas, is introduced to the ion source. The helium gas is ionized and transferred to the analyzer together with the sample. The helium gas, because of its overwhelming volume, causes a serious space-charge effect including charging-up of the surrounding parts. Because the AccuTOF GC is an orthogonal accelerating time-of-flight mass spectrometer (oa-TOF MS), the ions

Fig. 1 External view of the AccuTOF GC (Includes an optional automatic sampler).

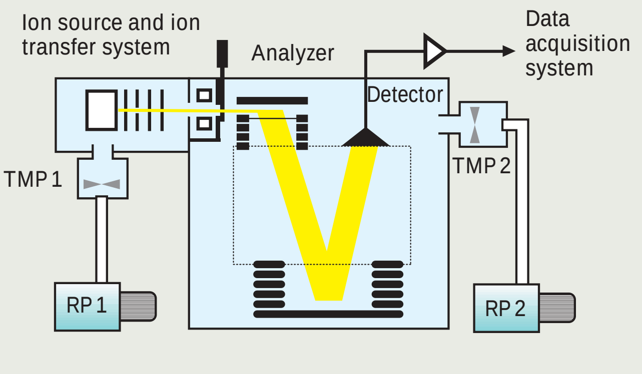


Fig. 2 Diagram of the AccuTOF GC.

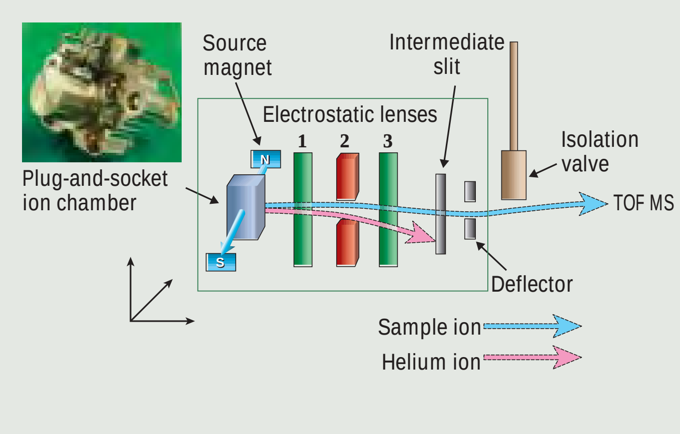


Fig. 3 Ion transfer system diagram.

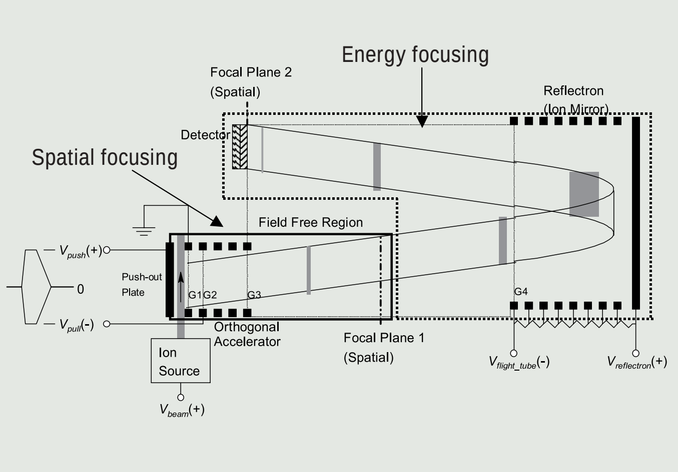


Fig. 4 Analyzer diagram.

must be transferred at a low kinetic energy of about 30 eV to the analyzer. Therefore, the ions are highly susceptible to the space-charge effect. Moreover, as all the ions, including helium ions, introduced to the analyzer reach the detector, the large quantity of helium ions might lead to a failure of the detector. To avoid the problem, the AccuTOF GC specifically developed an ion-transfer system that can remove more than 99% of helium ions before the ions enter the analyzer. The ion transfer system has the following three structural features:

- The electrostatic lens 2 is separated into two parts.
- An intermediate slit is installed.
- A deflector behind the intermediate slit.

In the EI ion source, a source magnet is placed to prevent dispersion of the electron beam emitted from the filament. By arranging the source magnet in a horizontal plane, an ionized ion accepts a force so that it is deflected downward, in case of a positive ion, while moving toward the analyzer. The extent of deflection differs according to the mass; the smaller the mass-to-charge ratio, the larger the deflection. The AccuTOF GC, making use of this mass selection ability of the source magnet, succeeded in colliding the helium ions with the plate of the intermediate slit and remove them, by optimizing the balance of the voltages of the upper and lower parts of the electrostatic lens 2. The intermediate slit also assists the differential evacuation between the ion source and the analyzer. The ions passed through the intermediate slit are introduced to the analyzer with good efficiency due to the optimized deflector voltage.

In addition, the AccuTOF GC incorporates an isolation valve that isolates the ion transfer system from the analyzer. The isolation valve makes it possible to vent the ion source and carry out maintenance of it without venting the analyzer. Furthermore, it isolates the analyzer automatically in an emergency such as an unexpected stop of the evacuation system, which prevents the detector from degrading.

## Analyzer

The analyzer of the AccuTOF GC is an orthogonal accelerating time-of-flight mass spectrometer (oa-TOF MS) incorporating two-stage acceleration and a single-stage reflectron. It achieves high resolution owing to the spatial focusing by the two-stage acceleration and the energy focusing by the single-stage reflectron.

The diagram of analyzer of the AccuTOF GC is shown in **Fig. 4**. The sample is ionized in the ion source continuously, arranged in a parallel ion beam, and introduced to the space between the push-out plate and the grid 1 (G 1) in the orthogonal accelerator. To accelerate ions to the orthogonal direction, pulse voltages, $V_{push}$ and $V_{pull}$, are applied at the push-out plate and the grid 2 (G 2) respectively. A negative high voltage, $V_{flight\text{-}tube}$, is applied at the grid 3 (G 3) and the shield surrounding the field free region all the time, in case of analyzing positive ions. A positive voltage, $V_{reflectron}$, is always applied at the end of the reflectron.

## Detector

As we will see in the section " Data acquisition system," when a time-to-digital converter (TDC) is used as the data acquisition system, the quality of a mass spectrum is hardly affected by the characteristics of the data acquisition system. But the TDC system is difficult to handle because it requires statistical correction of the acquired signal, and the mass accuracy depends on the accuracy of the parameter for the statistical correction. On the other hand, when a high-speed analog-to-digital converter (ADC) in combination with a continuous averager is used as the data acquisition system, the quality of a mass spectrum, such as mass resolution and peak shape, is directly affected by the characteristics of the data acquisition system, but this system has a merit that it does not require the statistical correction essentially. The AccuTOF GC adopts the ADC-with-continuous averager method, and a device to minimize the signal distortion is installed.

The detector is mainly comprised of a micro channel plate (MCP) and an anode. The MCP is a glass plate approximately 0.6 mm thick having channels, that are honeycomb holes with an inside diameter of 10 µm at intervals of 12 µm (between channel centers). Both surfaces of the MCP are metal coated, serving as electrodes. A voltage applied between the electrodes will produce an electric-field gradient inside the channel.

When an electron hits the inner wall of the channel near the entrance, multiple secondary electrons will be emitted. These electrons will be accelerated by the electric-field gradient inside the channel, hitting the wall on the opposite side and emitting secondary electrons again. Thus, the electrons advance to the exit while hitting the inner wall of the channel repeatedly, resulting in a flow of electrons exponentially multiplied.

The electrons will be captured by the anode to produce an electrical signal. The amplification factor of the MCP (the number of electrons emitted from the exit when one ion is introduced to the entrance) is several thousands at maximum. Since TOF MS requires a detector having an amplification factor of $10^6$, it usually uses two MCPs layered (dual MCP).

## Data acquisition system

The data acquisition system digitizes electrical signals from the detector, arranges them into a format compatible with the data system, and transfers them to the data system. The data acquisition system of an oa-TOF MS system must meet the following severe requirements.

### Acquiring data with extremely high time resolution

When the AccuTOF GC achieves a mass resolution of 5,000 (FWHM; full width at half maximum) with the molecular ion of octafluronaphthalene (m/z 272), the time of FWHM of the peak is 3 ns. To specify the peak position (= flight time = mass) as accurately as possible, it is said that at least 10 data points are necessary in the FWHM. Accordingly a time resolution of 300 ps is required for the data acquisition system of the AccuTOF GC.

### Acquiring data continuously

The system needs to begin acquiring data for the next ion flight as soon as one ion flight is completed. If there is a time lag between flights, the ion utilization ratio will decline because the ions that have passed through between the push-out plate and the grid 1 are wasted and not detected, resulting in poor sensitivity.

### Accumulating spectra in real time

The flight times of any ions will be shorter than 200 ms. When the m/z range to measure is less than 1,000, the flight time of ions will be shorter than 55 ms. Therefore, when ion flights are repeated with this time intervals, ion flights of approximately 18,000 times per a second are counted. However, it is meaningless to try to get each flight data as an independent spectrum due to the following two reasons: First, each flight data is poor in S/N to be analyzed because the number of ions generated in the ion chamber in 1/18,000 second is small. Second, saving data of 18,000 spectra per second on a hard disk is utterly impractical in terms of data transfer speed and data capacity. Therefore, the data acquisition system acquires and accumulates multiple spectra for a specified period of time and forwards the accumulated data to the data system.

Two types of data acquisition systems meet these basic requirements, TDC and the ADC-with-continuous averager.

TDC (time-to-digital converter) is a kind of high-speed and high-accuracy stopwatch. It judges if any pulse of ions having a height exceeding a certain threshold level is detected or not in a specified measurement interval, resulting data of 1 (detected) or 0 (not detected). Even if multiple pulses are detected in one measurement interval, the later pulses are not counted, resulting in data of 1 (dead time loss). Thus, the TDC method requires a statistical correction, resulting in a low dynamic range as low as $10^3$, which is one of the demerits.

On the other hand, the ADC-with-continuous averager converts a signal from the amplifier with its high speed 8-bit analog-to-digital

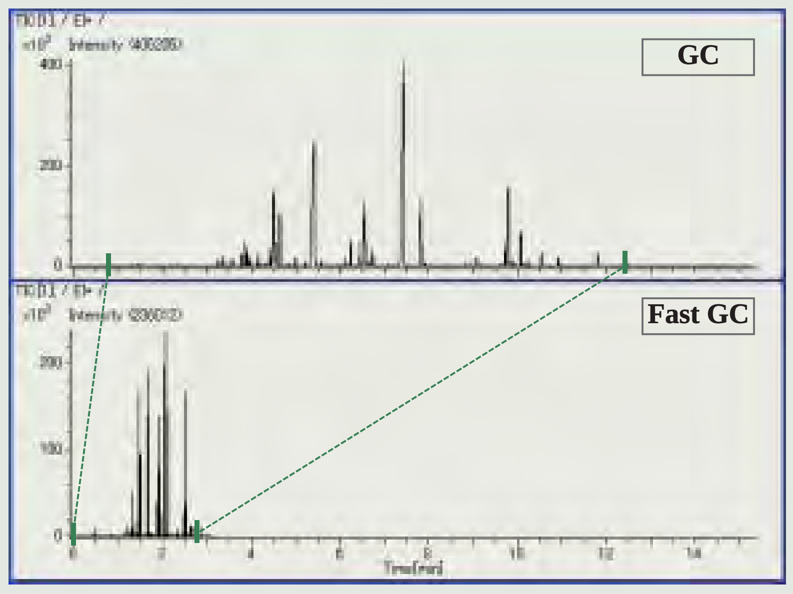


Fig. 5 Comparison of total ion chromatograms using conventional GC and fast GC methods (upper: conventional GC, lower: fast GC).

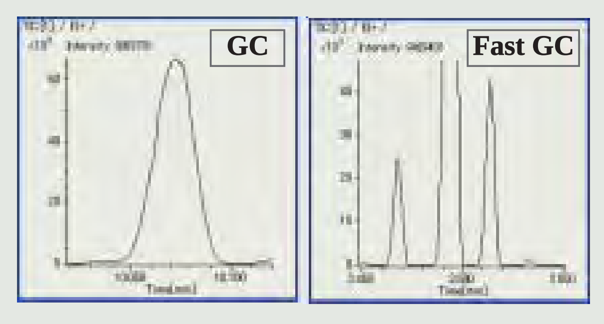


Fig. 6 Chromatogram peaks of β-farnesene measured using GC (left) and fast GC (right) methods (time range for both TIC is 0.1 minute).

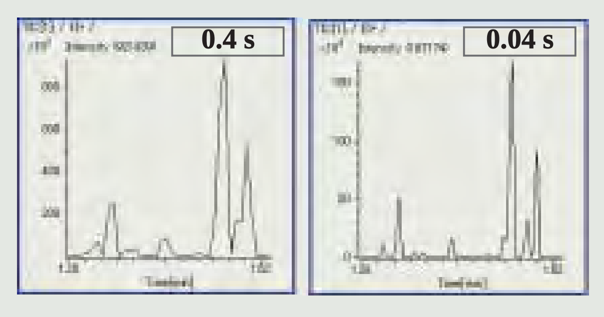


Fig. 7 Difference of chromatogram peaks with different spectrum-acquisition speeds (acquisition intervals) in fast GC method (left: 0.4 s, right: 0.04 s; both are data of AccuTOF GC).

converter (ADC) to a digital value of 0 to 255 (= $2^8$-1), and the data are accumulated in the summing memory. Therefore, the ADC-with-continuous averager basically does not need a statistical correction.

The AccuTOF GC adopts an ADC-with-continuous averager in the data acquisition system.

## Basic Performance

The basic performance of the AccuTOF GC is as follows.

- Resolution: 5,000 or more
  (FWHM, PFK m/z293)
- Mass range: 4 to 2,000
- Sensitivity
  EI$^+$ mode: S/N⩾100,
  Octafluoronaphthalene, 1 pg
  (mass chromatogram of m/z 272, RMS)
  CI$^+$ mode: S/N⩾150, Benzophenone, 100 pg
  (mass chromatogram of m/z 183, RMS)
  Isobutane: 0.1 mL/min
  CI$^-$ mode: S/N⩾20,
  Hexachlorobenzene, 100 fg
  (mass chromatogram of m/z 284, RMS)
  Methane: 1.0 mL/min
  GC conditions:
  Column: Agilent Technologies, DB-5ms
  0.25 mm (inside diameter) × 30 m
  (length), 0.25 µm (film thickness)
  Flow rate: Helium 1.0 mL/min
  (constant flow)
- Spectrum-acquisition speed: 0.04 s or longer
  (25 spectra/s or smaller)
- Mass accuracy: 2 mmu or 5 ppm
  (RMS, internal standard)

The AccuTOF GC has the features of high resolution, accurate mass measurement with easy operation, and high sensitivity as same as its sister instrument, JMS-T100LC "The AccuTOF." The AccuTOF GC furthermore attains a high spectrum-acquisition speed of 25 spectra per second, and fully corresponds to the fast GC/MS measurement.

We show data regarding the basic performance below, that are: fast GC/MS measurement, accurate mass measurement, stability, and dynamic range.

### Fast GC/MS measurement

As an example of the fast GC/MS measurement, an essential oil of lavender is measured. Here, we discuss the differences between the conventional GC and the fast GC methods, and the high spectrum-acquisition speed required for the fast GC/MS method. These two points are described briefly.

### What is fast GC method?

The fast GC method uses a narrow and short column, which shortens the analysis time while retaining a high-separation ability equivalent to a conventional GC method.

An essential oil of lavender is measured using the AccuTOF GC with the conventional GC method, and also with the fast GC method, and the results are compared.

#### ■ GC parameters

- Sample injection: Split (1:500)
- Sample injection volume: 0.2 µL
- Oven program:70°C (0.5 min) →<ramp rate: 10 °C/min> → 250°C (3 min)
- Column: DB-5ms, 0.25 mm (inside diameter) × 30 m (length), 0.25 µm (film thickness)

#### ■ Fast GC parameters

- Sample injection: Split (1:500)
- Sample injection volume: 0.2 µL
- Oven program: 70°C (0.5 min)→<ramp rate: 60°C/min> → 250 °C (3 min)
- Column:BPX-5, 0.1 mm (inside diameter) × 10 m (length), 0.1 µm (film thickness)

#### ■ MS parameters

- Mass measurement range: m/z 35 to 300
- Spectrum-acquisition speed: 0.04 s
  (25 spectra/s)

The parameters for GC and the fast GC differs in two points; column type and oven-temperature ramp rate. The fast GC uses a narrow and short column of 0.1 mm inside diameter and 10 m long, and the oven-temperature ramp

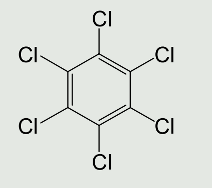


Fig. 8 Structural diagram of hexachlorobenzene ($C_6Cl_6$).

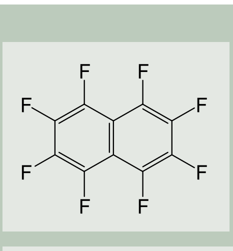


Fig. 10 Structural diagram of octafluoronaphthalene ($C_{10}F_8$).

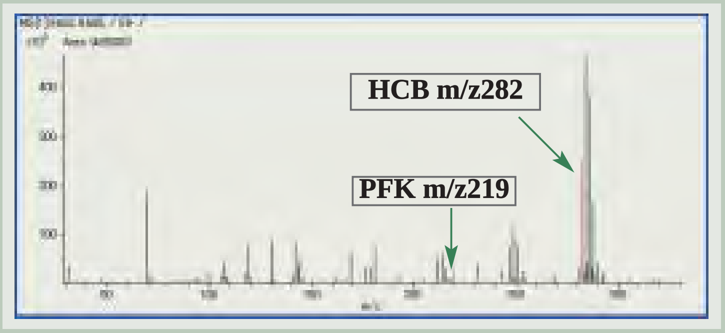


Fig. 9 Mass spectrum of mixture of PFK and hexachlorobenzene (2 ng).

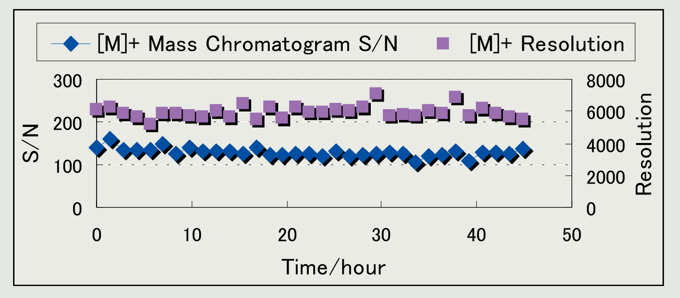


Fig. 11 Stability of sensitivity and resolution during the 45-hour continuous measurement. Sample: octafluoronaphthalene.

Table 1 Measured masses of hexachlorobenzene with different concentrations are compared with the theoretical mass.

| Sample concentration | Theoretical m/z | Measured m/z | Error (mmu) |
|---|---|---|---|
| 3pg | 281.81312 | 281.81233 | – 0.79 |
| 10pg | | 281.81180 | – 1.32 |
| 30pg | | 281.81196 | – 1.16 |
| 100pg | | 281.81211 | – 1.01 |
| 300pg | | 281.81160 | – 1.52 |
| 1ng | | 281.81153 | – 1.59 |
| 2ng | | 281.81214 | – 0.98 |

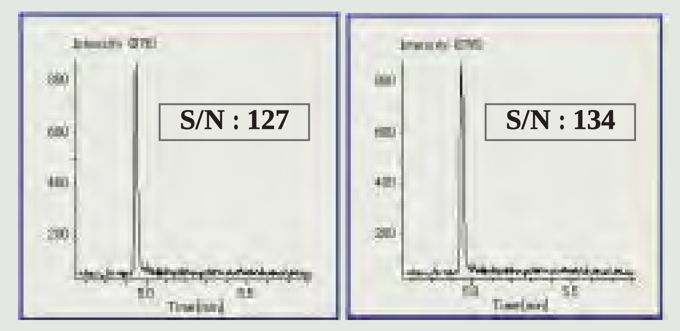


Fig. 12 Mass chromatograms of m/z 272 when starting (left) and 45 hours later (right).

rate is rapid as 60°C/min. If the rapid oven-temperature ramp rate of 60°C/min was applied to the conventional thick and long column, the peaks will overlap resulting in a poor resolution. To shorten the measurement time, it is necessary to raise the oven temperature rapidly and separate the sample rapidly. A narrow and short column satisfies this requirement.

The upper chromatogram in **Fig. 5** shows a TIC taken using a conventional GC, which takes about 12 minutes, whereas, the lower chromatogram, using the fast GC, takes about 3 minutes, which is one fourth of the conventional GC. The throughput has improved four times concerning only the measurement time, excluding the preparation and data processing times. The fast GC method provides a high throughput GC/MS.

### *Fast spectrum-acquisition speed required for fast GC/MS measurement*

The fast GC method uses a narrow and short column. For that reason, chromatogram peaks in the fast GC/MS measurement are very sharp having widths of about 0.5 to 1 second, compared to 2 to 3 seconds using the conventional GC method (**Fig. 6**).

If a QMS, which is widely used in a GC-MS system, or a magnetic-field type MS, which is used for measurements such as dioxin to check for conformity with environmental regulations, is combined with a fast GC, it will not be able to acquire sufficient number of data points needed for each peak, because its spectrum-acquisition speed (scan speed) is 0.2 to 0.4 second. On the other hand, the AccuTOF GC can measure the total mass range in 0.04 second (25 spectra/s) and can follow the high-speed of the fast GC without losing the separation ability of the chromatograph and also, with high sensitivity.

**Fig. 7** shows the results of the AccuTOF GC with different spectrum-acquisition speeds using the fast GC method.

The left chromatogram is measured with a spectrum-acquisition speed of 0.4 s, which is equal to the conventional magnetic-field MS and QMS, and the right is measured at a spectrum-acquisition speed of 0.04 s, the maximum speed of the AccuTOF GC. The difference between the two is quite obvious; for example at the retention time near 1.5 min, two sharp peaks are observed in the 0.04 s data, whereas the data of 0.4 s cannot separate the peaks because of the lack of data points.

As shown above, a fast spectrum-acquisition speed is necessary for the fast GC/MS measurement. The conventional magnetic-field and QMS mass spectrometers can not meet the high-speed requirement, but the AccuTOF GC can.

## Accurate mass measurement (one-point calibration)

The AccuTOF GC essentially has a high mass accuracy and therefore, calibration can be carried out correctly using the one-point calibration method. That is, the AccuTOF GC needs only one ion whose exact mass is known (internal standard ion) to measure accurate masses, whereas a magnetic-field mass spectrometer needs two or more internal standard ions of known masses before and after the unknown peak. For example, hexachlorobenzene was analyzed as an unknown sample with PFK (m/z 219) as an internal standard for mass calibration (**Fig. 9**).

### ■ Sample

- Sample: Hexachlorobenzene (**Fig. 8**)
- Sample concentration: 3 pg/µ L to 2 ng/µ L (solvent : hexane)
- Internal standard for mass calibration: PFK

### ■ GC parameters

- Sample injection: Splitless
- Sample injection volume: 1.0 µL
- Oven program: 40°C (1 min) → <ramp rate: 20°C/min> → 280°C (3 min)
- Column: DB-5ms, 0.25 mm (inside diameter) × 30 m (length), 0.25 µm (film thickness)

### ■ MS parameters

- Mass measurement range: m/z 30 to 350
- Spectrum-acquisition speed: 0.2 s (5 spectra/s)

**Table 1** shows measured masses of hexachlorobenzene with different concentrations. It shows such good mass accuracy that each mass error is smaller than –1.59 mmu.

Although we used m/z 219 of PFK in the measurement above as the mass calibration ion, m/z 207, 281 or others brought by column breed when using a polydimethylsiloxane-bonded column can be used as the one-point calibration ion. That is, when an ion of known mass, originated in the column, is detected in the measured data, the ion can be used to calculate the accurate mass without using a standard sample.

## Stability

Good stability when measuring continuously is one of the features of the AccuTOF GC. This comes from the stability of the newly-developed low-acceleration ion transfer system, in addition to the stability of the analyzer

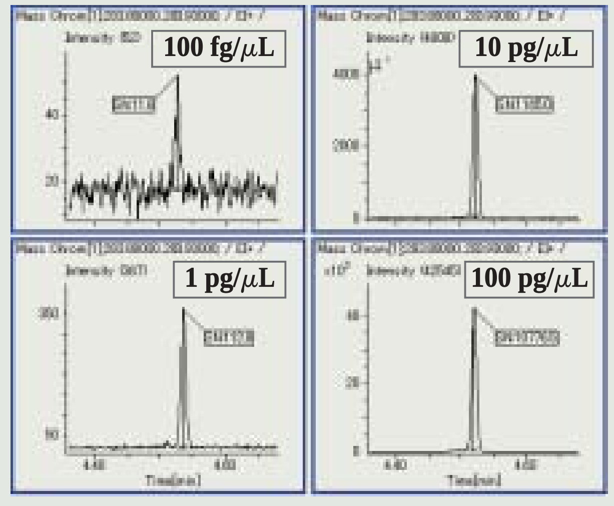


Fig. 13 Mass chromatograms of hexachlorobenzene (100 fg/µL, 1 pg/µL, 10 pg/µL, and 100 pg/µL).

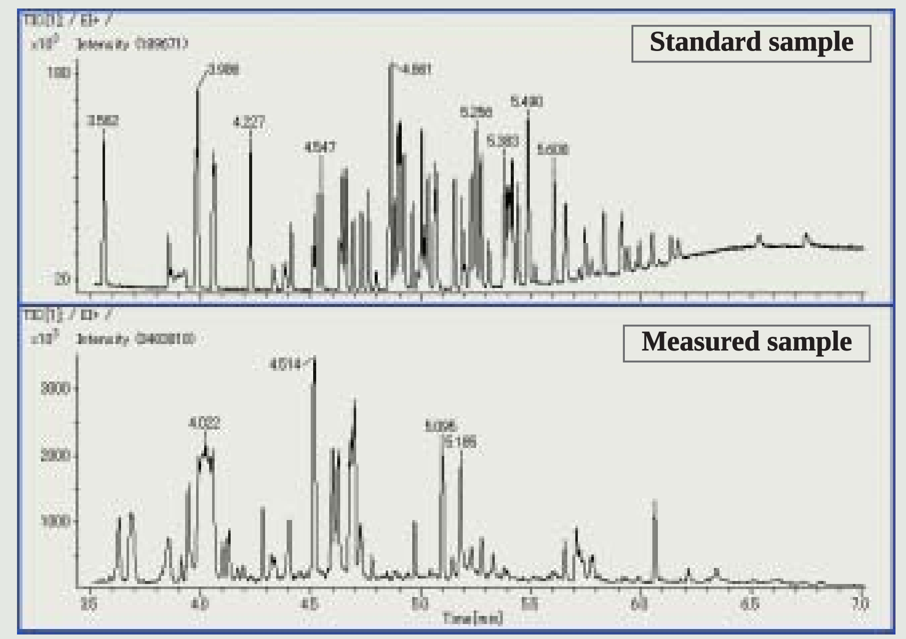


Fig. 14 Results of fast GC/MS measurements for standard sample (upper) and measured sample (lower).

already achieved by the AccuTOF. Stability is tested by measuring 1 pg of octafluoronaphthalene for 45 hours continuously (**Fig.11**). Octafluoronaphthalene is the sample used for specifying the sensitivity of EI positive mode.

### ■ Sample

- Sample: Octafluoronaphthalene (**Fig. 10**)
- Sample concentration: 1 pg/μL (solvent: hexane)

### ■ GC parameters

- Sample injection: Splitless
- Sample injection volume: 1.0 μL
- Oven program: 40°C (1 min) → <ramp rate: 20°C/min> → 280°C (3 min)
- Column: DB-5ms, 0.25 mm (inside diameter) × 30 m (length), 0.25 μm (film thickness)

### ■ MS parameters

- Mass measurement range: m/z 30 to 300
- Spectrum-acquisition speed: 0.2 s (5 spectra/s)

At every measurement, the S/Ns of the chromatogram of m/z 272 were more than 100, and the mass resolutions at m/z 272 were more than 5,000. The sensitivity was very stable during the measurement time of 45 hours (approximately two days); the S/N was 127 at the start and 134 at 45 hours later (**Fig. 12**).

## Dynamic range

In order to demonstrate the dynamic range, hexachlorobenzene was analyzed at various concentrations ranging from 100 fg/μL to 100 pg/μL (100 fg/μL, 1 pg/μL, 10 pg/μL and 100 pg/μL) (**Fig. 13**).

The AccuTOF GC has a wider dynamic range than a conventional GC-TOFMS, realizing a dynamic range of $10^3$ or more.

# Application Data

Here, we introduce the application data that demonstrate the features of the AccuTOF GC: fast GC/MS measurement, improvement of selection ability using high-resolution mass chromatogram, and identifying unknown components by accurate mass measurement using CI method.

## Improvement of selection ability using high-resolution mass chromatogram

A magnetic field mass spectrometer can carry out quantitative and qualitative analysis with accuracy even when the sample contains many foreign materials (impurities), by taking advantage of its high-resolution analysis capability. In recent years, the high-resolution magnetic field mass spectrometers are playing an active part in the field of environmental analysis such as dioxin. Since the AccuTOF GC always operates at a high resolution with high sensitivity, it is expected to be applied to qualitative analysis of very small quantity compounds.

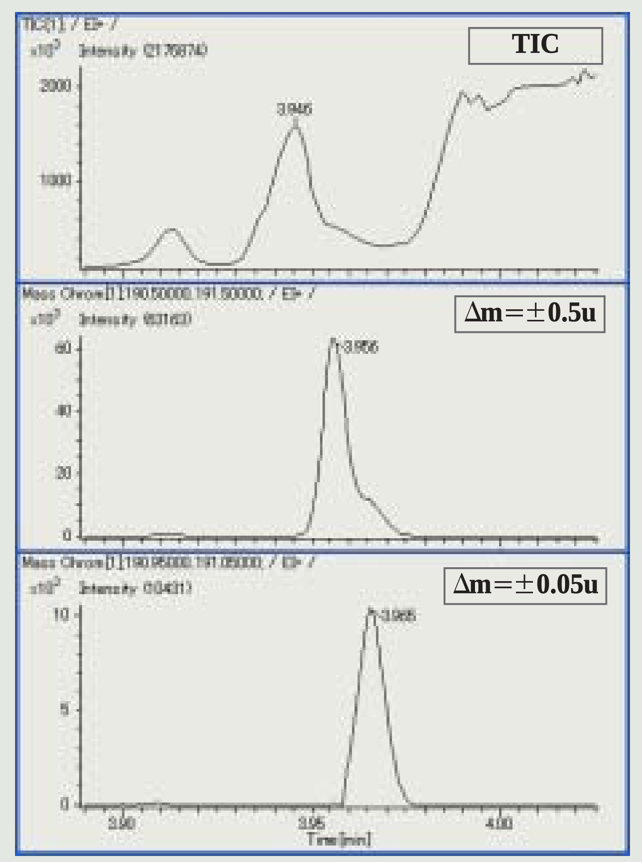


Fig. 15 TIC of the measured sample (top), and mass chromatograms of m/z 191 with Δm = ±0.5 u (middle) and ±0.05 u (bottom).

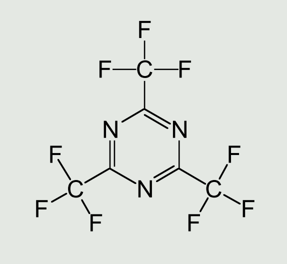


Fig. 16 Structural diagram of TTT ($C_6N_3F_9$).

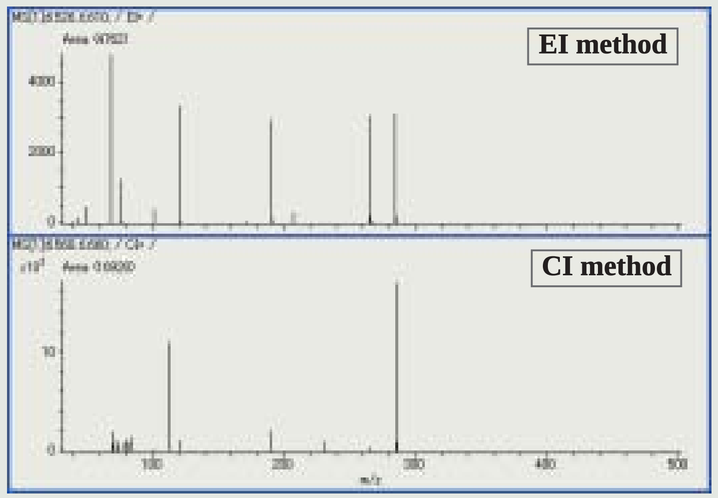


Fig. 17 Mass spectra of TTT (upper: EI method, lower: CI method).

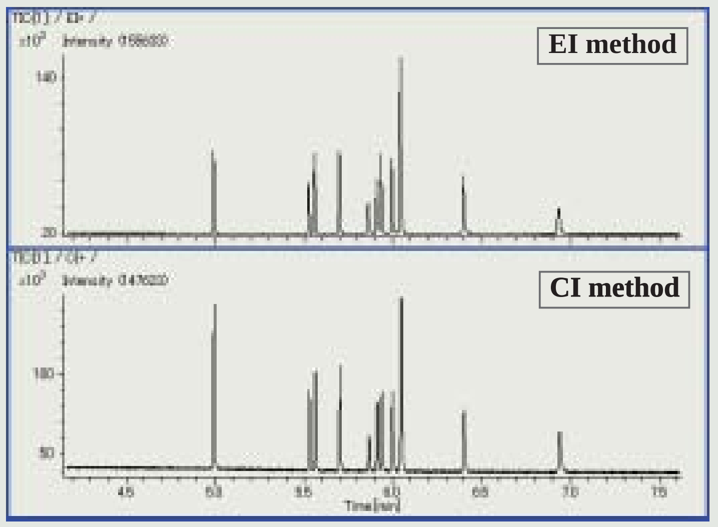


Fig. 18 TIC of liquid crystal (upper: EI method, lower: CI method).

In order to verify mass separation of a target compound from a sample containing many foreign materials using a high-resolution mass chromatogram, we added a standard sample, which includes 68 pesticides, into the extract from food, and verified that the compounds can be detected as a peak in a mass chromatogram. Measurement conditions and results are presented below.

## ■ Sample

- Standard sample: Includes 68 pesticides.
- Standard sample concentration: 50 pg/μ L (solvent: hexane)
- Measured sample: Blank (extract from food) + standard sample

## ■ Fast GC parameters

- Sample injection: Splitless
- Sample injection volume: 1.0 μL
- Oven program: 40°C (1 min) → <ramp rate: 50°C/min> → 300°C (1 min)
- Column: DB-5, 0.18 mm (inside diameter) × 10 m (length) × 0.18 μ m (film thickness)

## ■ MS parameters

- Mass measurement range: m/z 30 to 500
- Spectrum-acquisition speed: 0.04 s (25 spectra/s)

**Figure14** shows the TICs of the standard sample (upper) and the measured sample (lower). The measured sample is prepared by spiking 50 pg of standard sample into the blank (extract from food). The standard sample (upper) is clearly separated, and we could identify each pesticide even in the TIC. However, it is difficult to identify the standard sample in the TIC of the measured sample (lower), because the measured sample contains many foreign materials.

In the AccuTOF GC, when you create a mass chromatogram from measured data, a mass range (window width) must be specified. That is, if a wide mass range is specified, a low-resolution mass chromatogram equivalent to the conventional low-resolution measurement is obtained. On the other hand, if a narrow mass range is specified, a high-resolution mass chromatogram is obtained.

We examined what kind of mass chromatograms are obtained when we give two window width values, Δm = ±0.5 u and ±0.05 u, to the base peak of Chloroneb, $[M\text{-}CH_3]^+$ (m/z 191), which is one of the 68 pesticides (**Fig. 15**).

In the TIC (top), the intense background is observed, and the chromatogram is broad and dull. In the mass chromatogram with the window width Δm = ±0.5 u (middle), a peak was observed at a retention time of 3.956 minutes. However, searching for this spectrum using the NIST library database identified that the compound is most possibly 2, 4-Di-tert-butylphenol, a different material from the spiked 68 pesticides. Next, in the mass chromatogram with the window width Δm = ±0.05 u (bottom), a peak was observed at a retention time of 3.965 minutes. This peak was identified to be chloroneb using the NIST library database.

Thus, when we create a low-resolution mass chromatogram (Δm = ±0.5 u, equivalent to QMS), it was difficult to find the compounds buried in the foreign materials; however, the high-resolution mass chromatogram (Δm = ±0.05 u) enabled the identification of the com-

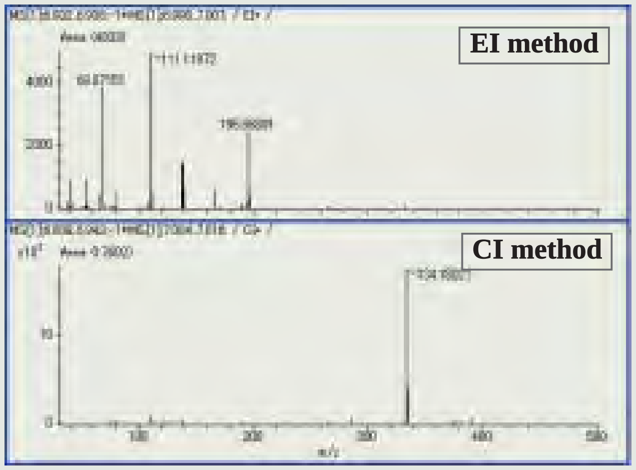


Fig. 19 Mass spectra of compound A (upper: EI method, lower: CI method).

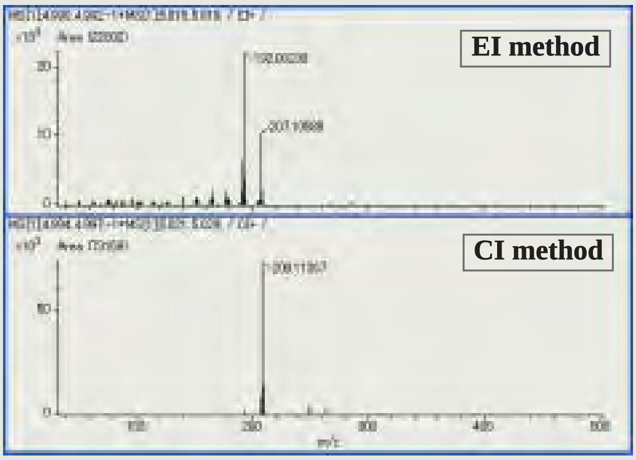


Fig. 20 Mass spectra of compound B (upper: EI method, lower: CI method).

Table 2 Calculated accurate mass of each ion.

| Ionization method | Ion | Theoretical m/z | Measured m/z | Error (mmu) |
|---|---|---|---|---|
| EI method | $[M-CH_3]^+$ | 192.08132 | 192.08230 | 0.98 |
| | $[M]^+$ | 207.10480 | 207.10589 | 1.09 |
| CI method | $[M+H]^+$ | 208.11262 | 208.11367 | 1.05 |

Table 3 Composition estimation result of $[M+H]^+$ in compound B.

| Candidate | Measured m/z | Theoretical m/z | Error (mmu) | Estimated formula | Unsaturation number |
|---|---|---|---|---|---|
| No.1 | 334.18021 | 334.18070 | −0.49 | $C_{22}H_{24}NO_2$ | 11.5 |
| No.2 | | 334.18185 | −1.64 | $C_{19}H_{25}FNO_3$ | 7.5 |

Table 4 Estimated formula for each ion of compound B observed by EI method.

| Ion | Measured m/z | Theoretical m/z | Error (mmu) | Estimated formula | Unsaturation number |
|---|---|---|---|---|---|
| m/z 333 | 333.17432 | 333.17288 | 1.44 | $C_{22}H_{23}NO_2$ | 12 |
| m/z 195 | 195.06891 | 195.06841 | 0.5 | $C_{13}H_9NO$ | 10 |
| m/z 111 | 111.11872 | 111.11738 | 1.34 | $C_8H_{15}$ | 1.5 |
| m/z 69 | 69.07042 | 69.07042 | 1.09 | $C_6H_9$ | 1.5 |

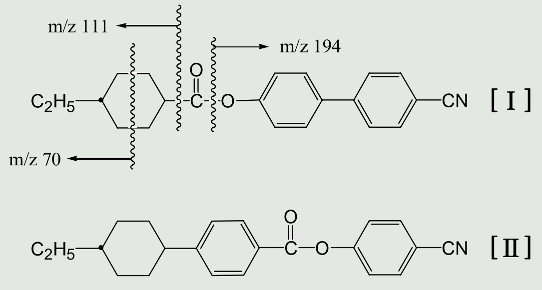


Fig. 21 Estimated structure of compound B.

pound.

In addition, we mention that the fast GC/MS measurement took only about six minutes to detect the 68 pesticides. It will take about thirty minutes for a conventional GC/MS measurement, demonstrating improvement of the throughput about five times.

## Identifying unknown compounds by accurate mass measurement using CI method

The process of the CI method is as follows: First, the reagent gas, for example, methane or isobutene, is introduced into a closed ionization chamber, and the reagent gas is ionized by the EI method. Next, the sample is introduced from the sample injection section (a GC or standard-sample injection section) into the ionization chamber. There, an ion-molecule reaction takes place between the reagent gas ions and the sample molecules resulting in the ionization of the sample.

The CI method is a soft ionization method compared to the EI method, and offers useful information for determining the molecular mass of unknown sample. As the reagent gas, methane, isobutene or ammonia is mainly used. Ions $[M+H]^+$ are mainly observed when using the former two gases, and $[M+NH_4]^+$ ions when using ammonia gas.

In the present experiment, we carried out a measurement that combines the CI method and “simple and accurate mass measurement”, one of the features of the AccuTOF GC.

### ■ Sample

- Sample: Liquid crystal in a commercially available pocket calculator was dissolved in a solvent (hexane).
- Internal standard compound: 2, 4, 6-Tris (trifluoromethyl)-1, 3, 5-triazine (abbreviated to TTT, **Fig. 16**)

### ■ Fast GC parameters

- Sample injection: Split (1:400 (EI method), 1:200 (CI method)
- Sample injection volume:1.0 μ L
- Oven program: 40°C (1 min) → <ramp rate: 50°C /min> → 300°C (1 min)
- Column: DB-5, 0.18 mm (inside diameter) × 10 m (length) × 0.18 μ m (film thickness)

### ■ MS parameters

- Measurement mass range: m/z 70 to 500
- Spectrum-acquisition speed: 0.04 s (25 spectra/s)

### ■ CI parameters

- CI reagent gas: Isobutane
- Flow rate of CI reagent gas: 0.1 mL/min (controlled by mass-flow controller)

**Figure 17** shows the mass spectra of TTT, the internal standard compound, obtained using EI (upper) and CI (lower) methods.

The TTT can be ionized by the CI method since it contains many nitrogen atoms, as well as by the EI method. Figure 17 indicates that $[M]^+$ is obtained by the EI method and $[M+H]^+$ by the CI method with good sensitivity. The accurate masses are calculated by one-point calibration using these ions. The measured data are shown below.

**Figure 18** shows very sharp peaks since the injection method “split” is used in both EI and CI methods. To show an example of identification analysis, we selected the first peak A (compound A) at the retention time around 5.0 min and the last peak B (compound B) at the retention time around 7.0 min.

On the upper mass spectrum in **Fig. 19**, compound A by EI method, m/z 192 is observed as the base peak and the next intense peak is m/z 207. The lower mass spectrum in the figure, compound A by CI method, shows base peak of m/z 208. Therefore, it is inferred that m/z 207 ion observed using the EI method is the molecular ion of the compound A. The mass spectrum obtained by the EI method is searched for using the NIST library database, resulting in a compound with molecular mass of 207 as the first candidate (match: 912), that is, (1, 1’-Biphenyl)-4-carbonitrile, 4’-ethyl- ($C_{15}H_{13}N$). As the next step, one-point calibration is carried out to calculate the accurate mass of it using TTT, the internal standard compound.

Accurate masses are calculated from the predicted structures of each ion (**Table 2**). As a result, measured values have mass errors of about 1 mmu from the theoretical values, showing very good accuracy. Thus, the compound A is determined to be (1, 1’-Biphenyl)-4-carbonitrile, 4’-ethyl- using the NIST library database search and the calculated accurate masses by using the EI and CI methods.

Next, the compound B is analyzed and discussed below. The obtained mass spectra are shown in **Fig. 20**.

On the upper mass spectrum in Fig. 20, compound B by EI method, m/z 111 is observed as the base peak, and m/z 69 and 195 as successive peaks. The lower mass spectrum in the figure (compound B by CI method) shows base peak of m/z 334. In the upper mass spectrum by EI, a small peak is observed at m/z 333. Therefore, it is inferred that m/z 333 is the molecular ion of the compound B. However, when we searched for the mass spectrum obtained by the EI method using the NIST library database, even the spectrum pattern of the first-candidate compound could not agree (match: 557). In addition, its molecular mass was not 333. Furthermore, other candidates did not have a molecular mass of 333. Thus, from the viewpoints of spectrum pattern and molecular mass, it is considered that there is a high possibility that this compound is not registered in the NIST library database. In order to find this unknown compound, we calculated accurate masses of each ion and estimated the composition.

Since the molecular mass of this compound is estimated to be 333, an odd number, it is considered, from the nitrogen rule, that the number of nitrogen atoms contained is odd. In the present study, estimation was carried out by aiming and estimating element species and their numbers, taking the representative liquid-crystal families into account [1]. **Table 3** shows the result of the composition estimation by deducing from the accurate mass of m/z 334 in the mass spectrum obtained by the CI method. In estimating composition, the calculation was carried out with an error of 2 mmu or less.

When we consider the composition of candidate No. 2 from the compounds of the representative liquid-crystal families, compounds having three oxygen atoms are narrowed down to azoxy compounds and p-cyano-phenyl-ester compounds of p-alkyl substitution benzoic acid. But, among these compounds, not one containing a fluorine atom has been reported [1]. From these facts, the composition of compound B is possibly and surely must be No. 1. We estimated the structure from the composition formula of No. 1 ($C_{22}H_{24}NO_2$) and the fragment pattern obtained by the EI method.

First, we estimated the composition formula from the accurate masses of the ions obtained by the EI method. **Table 4** shows the results.

The candidate No. 1 contains one nitrogen atom, but it is known that there is no compound having an amino group ($-NH_2$) or a nitro group ($-NO_2$) in the liquid-crystal families. From this fact, it is estimated that the nitrogen atom in the candidate No. 1 exists in the form of a cyano group (-CN). The candidate No. 1 also includes two oxygen atoms and they are estimated to form an ester. In addition, since the unsaturation number of $[M]^+$ is twelve, it is estimated that at least one or two benzene nuclei are included. As a result, two structures are deduced and shown in **Fig. 21**, that are p-cyanophenylester and cyclohexanecarboxylic acid aryl ester substitution product.

It is considered that m/z 111 is formed by a simple cleavage of an alkyl group, and m/z 69 is formed accompanying hydrogen transfer in a cyclohexane ring. These two ions can be generated from either structures [I] and [II]. However the ion m/z 195 is difficult to create from structure [II], and is deduced to arise from a simple cleavage of an alkoxy group accompanying hydrogen transfer in structure [I]. As a conclusion, the structure of the compound B is suggested to be structure [I] from the fragment ions obtained by the EI method.

## Conclusion

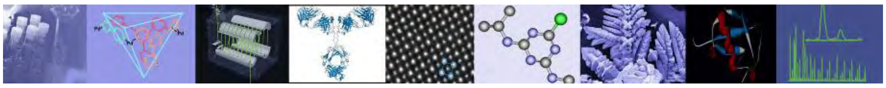
In the present paper, we introduced the features of the AccuTOF GC and its applications, including fast GC/MS measurement, accurate mass measurement, and improvement of selection ability using high-resolution mass chromatogram. In particular, it was demonstrated that measuring accurate masses using the EI and CI methods allows structural and qualitative analysis of the target compound with high reliability.

JMS-T100GC, the AccuTOF GC, is an innovative GC-MS that succeeds in obtaining the features that were impossible to attain simultaneously using conventional instruments. The features are: fast spectrum-acquisition speed that deals the fast GC/MS data, accurate mass measurement with simple operation, and stable, high sensitivity.

We hope the AccuTOF GC will help you in your research and studies.

## References

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



# 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 conditions 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,<br>45 mA<br>(30 msec refresh between every stored spectrum) | -10 kV,<br>0 mA → 51.2 mA/min →<br>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 conditions.

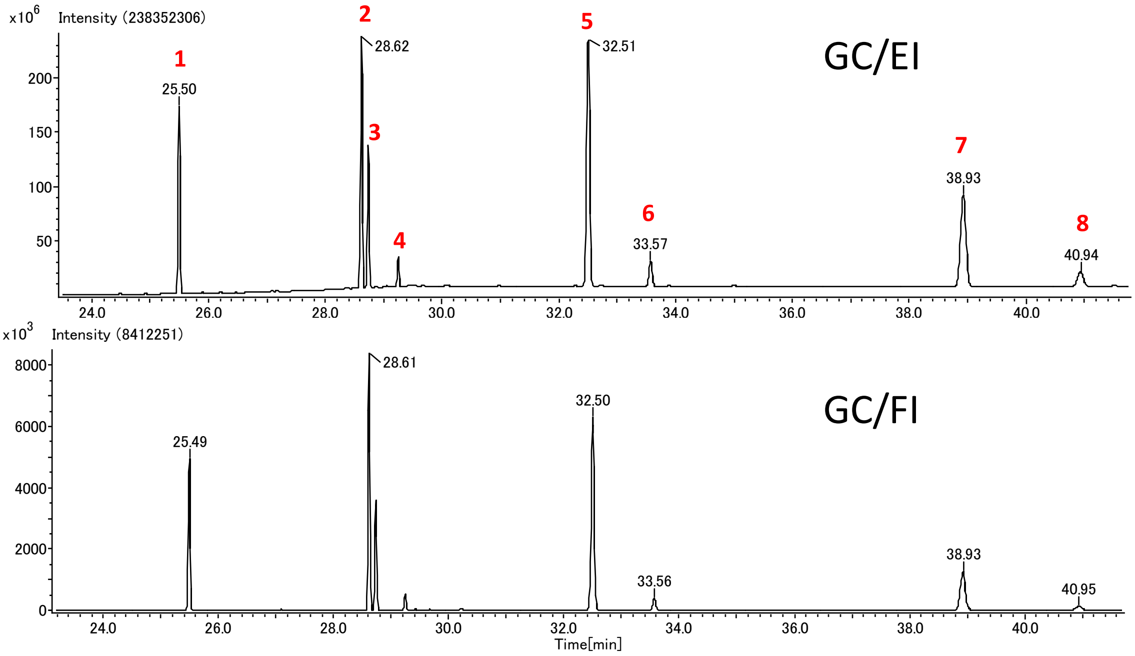


Figure 1. The TICs for GC/EI and GC/FI

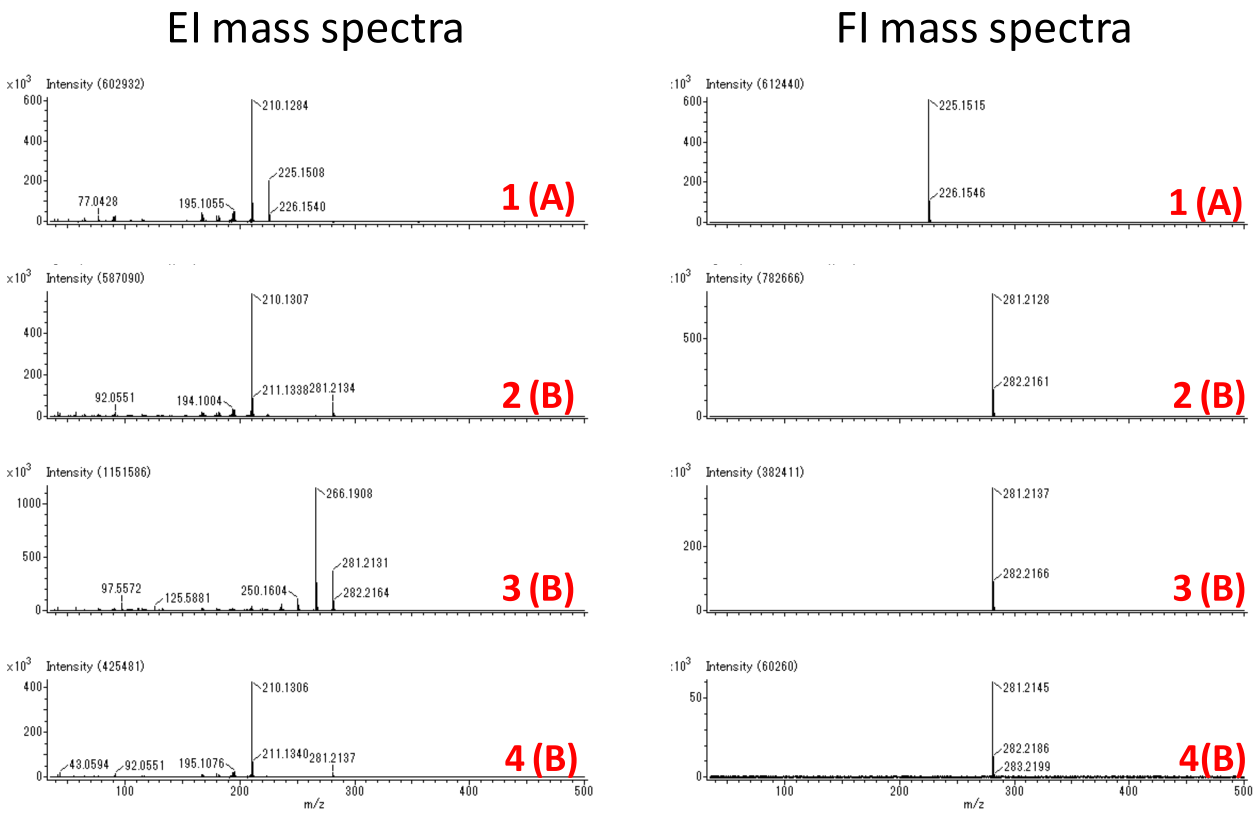


Figure 2. Mass spectra of component1-4, left: EI mass spectra, right: FI mass spectra (A,B: Isomer group)

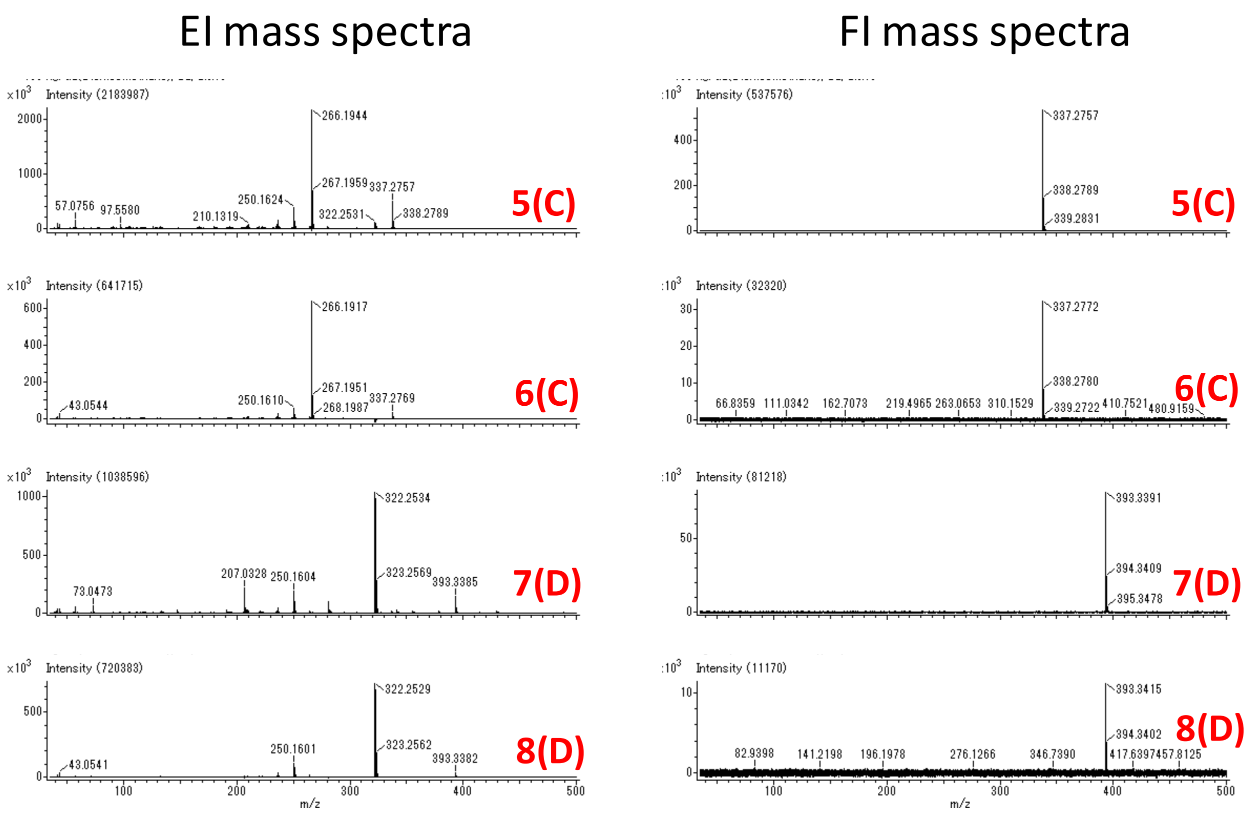
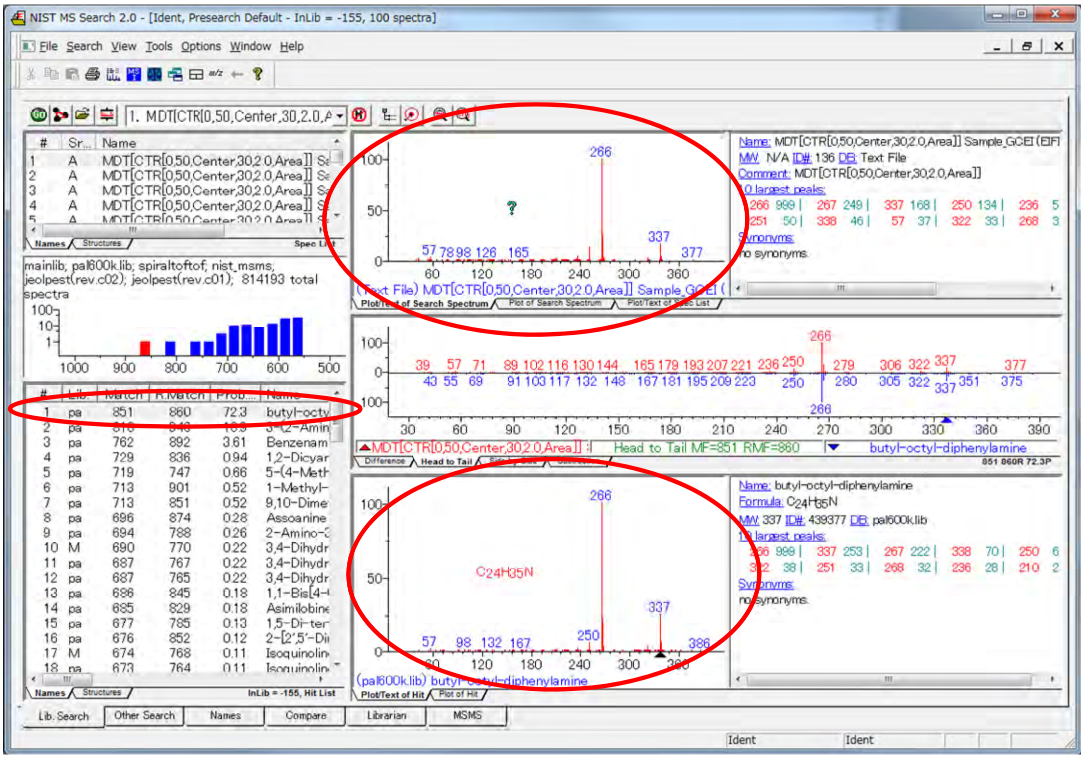


Figure 3. Mass spectra of component5-8, left: EI mass spectra, right: FI mass spectra (C,D: Isomer group)

| Component (Isomer group) | Ionization mode | Obs. $m/z$ | Theo. $m/z$ | Error (mDa) | Fomula |
|---|---|---|---|---|---|
| 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 | 393.3391 | 393.3396 | −0.5 | $C_{28}H_{43}N$ |

Table 2. Accurate mass measurement results



NIST MS Search 2.0 - [Ident, Presearch Default - InLib = -155, 100 spectra]

1. MDT[CTR[0,50,Center,30,2.0,A

| # | Sr... | Name |
|---|---|---|
| 1 | A | MDT[CTR[0,50,Center,30,2.0,Area]] Sa |
| 2 | A | MDT[CTR[0,50,Center,30,2.0,Area]] Sa |
| 3 | A | MDT[CTR[0,50,Center,30,2.0,Area]] Sa |
| 4 | A | MDT[CTR[0,50,Center,30,2.0,Area]] Sa |
| 5 | A | MDT[CTR[0,50,Center,30,2.0,Area]] Sa |

mainlib; pal600k.lib; spiraltoftof; nist_msms; jeolpest(rev.c02); jeolpest(rev.c01); 814193 total spectra

| # | Lib. | Match | R.Match | Prob... | Name |
|---|---|---|---|---|---|
| 1 | pa | 851 | 860 | 72.3 | butyl-octy |
| 2 | pa | [illegible] | [illegible] | [illegible] | 3-(2-Amin |
| 3 | pa | 762 | 892 | 3.61 | Benzenam |
| 4 | pa | 729 | 836 | 0.94 | 1,2-Dicyar |
| 5 | pa | 719 | 747 | 0.66 | 5-(4-Meth |
| 6 | pa | 713 | 901 | 0.52 | 1-Methyl- |
| 7 | pa | 713 | 851 | 0.52 | 9,10-Dime |
| 8 | pa | 696 | 874 | 0.28 | Assoanine |
| 9 | pa | 694 | 788 | 0.26 | 2-Amino-3 |
| 10 | M | 690 | 770 | 0.22 | 3,4-Dihydr |
| 11 | pa | 687 | 767 | 0.22 | 3,4-Dihydr |
| 12 | pa | 687 | 765 | 0.22 | 3,4-Dihydr |
| 13 | pa | 686 | 845 | 0.18 | 1,1-Bis[4- |
| 14 | pa | 685 | 829 | 0.18 | Asimilobine |
| 15 | pa | 677 | 785 | 0.13 | 1,5-Di-ter |
| 16 | pa | 676 | 852 | 0.12 | 2-[2',5'-Di |
| 17 | M | 674 | 768 | 0.11 | Isoquinolin |
| 18 | pa | 673 | 764 | 0.11 | Isoquinolin |

InLib = -155, Hit List

(Text File) MDT[CTR[0,50,Center,30,2.0,Area]] Sample_GCEI (

Name: MDT[CTR[0,50,Center,30,2.0,Area]] Sample_GCEI (EI/FI
MW: N/A ID#: 136 DB: Text File
Comment: MDT[CTR[0,50,Center,30,2.0,Area]]
10 largest peaks:
266 999 | 267 249 | 337 168 | 250 134 | 236 5
251 50 | 338 46 | 57 37 | 322 33 | 268 3
Synonyms:
no synonyms.

MDT[CTR[0,50,Center,30,2.0,Area]] Head to Tail MF=851 RMF=860 butyl-octyl-diphenylamine
851 860R 72.3P

(pal600k.lib) butyl-octyl-diphenylamine

Name: butyl-octyl-diphenylamine
Formula: $C_{24}H_{35}N$
MW: 337 ID#: 439377 DB: pal600k.lib
10 largest peaks:
266 999 | 337 253 | 267 222 | 338 70 | 250 6
322 38 | 251 33 | 268 32 | 236 28 | 210 2
Synonyms:
no synonyms.

Figure 4. NIST search for component 5.

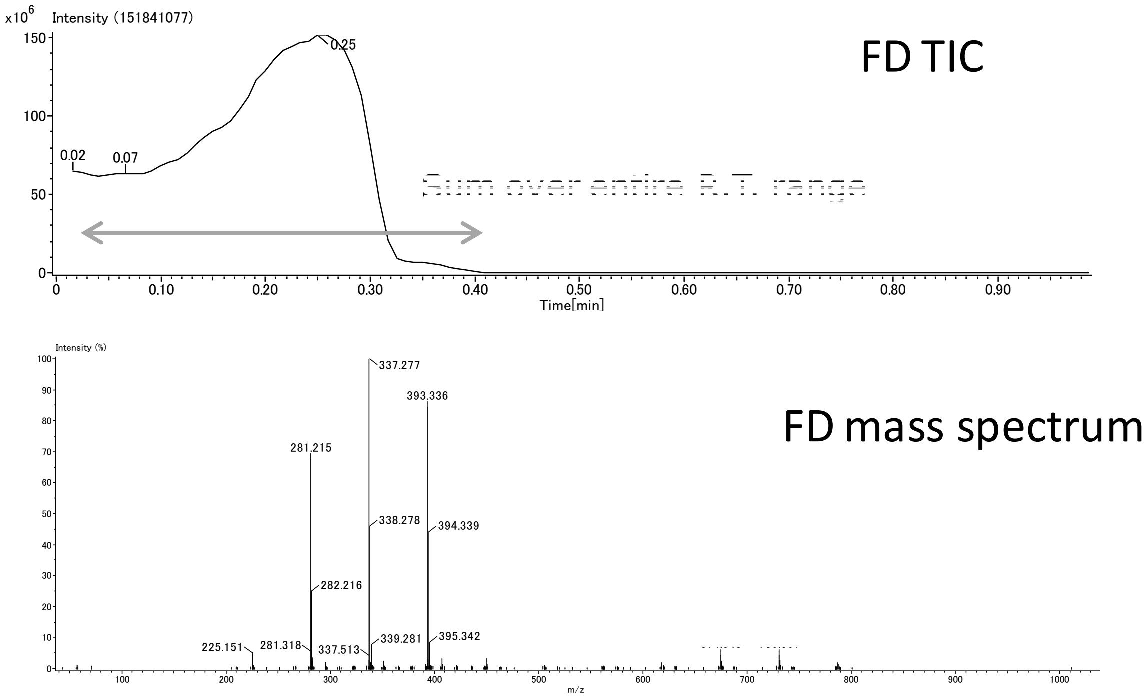


Figure 5. FD measurement result

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.

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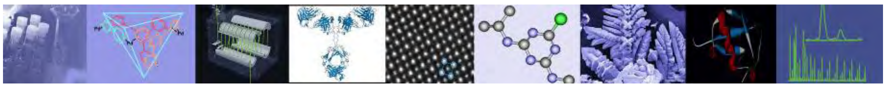


# AccuTOF-GCv Series

## 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 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, 0.18µm 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.

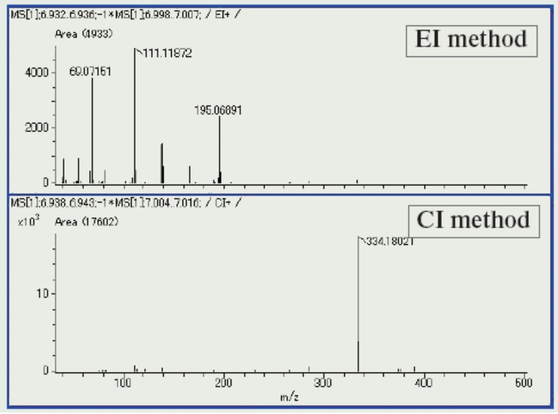


*Fig. 1 TIC of liquid crystal extract in both EI and CI modes*

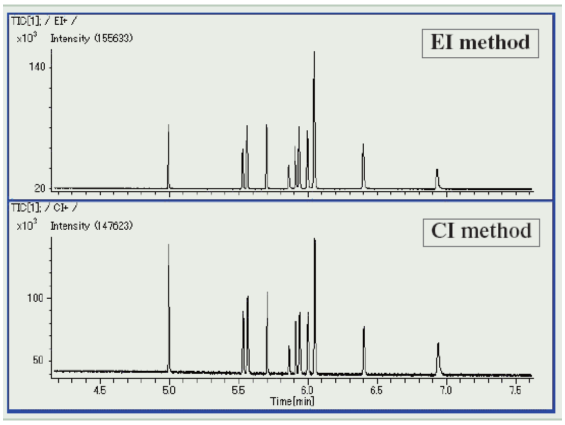
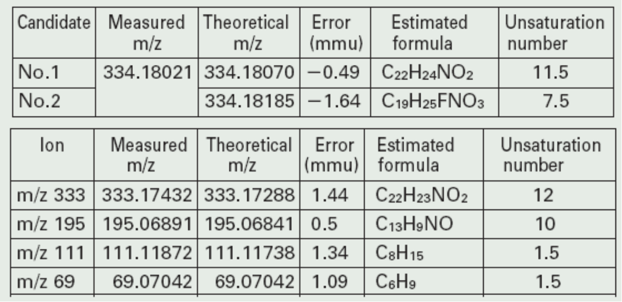


*Fig. 2 Mass spectra for the unknown compound marked with an asterisk (*) in Fig. 1*

### 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 ($[M]^{+\bullet}$) 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 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 | $C_{22}H_{24}NO_2$ | 11.5 |
| No.2 | | 334.18185 | −1.64 | $C_{19}H_{25}FNO_3$ | 7.5 |

| Ion | Measured m/z | Theoretical m/z | Error (mmu) | Estimated formula | Unsaturation number |
|---|---|---|---|---|---|
| m/z 333 | 333.17432 | 333.17288 | 1.44 | $C_{22}H_{23}NO_2$ | 12 |
| m/z 195 | 195.06891 | 195.06841 | 0.5 | $C_{13}H_9NO$ | 10 |
| m/z 111 | 111.11872 | 111.11738 | 1.34 | $C_8H_{15}$ | 1.5 |
| m/z 69 | 69.07042 | 69.07042 | 1.09 | $C_6H_9$ | 1.5 |

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

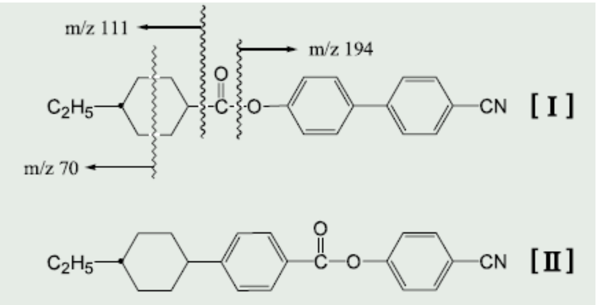


*Fig. 3 Possible structures for unknown liquid crystal compound*

Let us first consider the No.2 composition $C_{19}H_{25}FNO_3$ as the $[M+H]^+$ 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, $C_{22}H_{24}NO_2$. It is known that there are no liquid crystal compound that contain $–NH_2$ or $–NO_2$ 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 $[M+H]^+$ 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 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

*JEOL MS Data Sheet*

**MS Tips**

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

*No.088*

*AccuTOF GC ( JMS-T100GC ) Application Note*

# 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)

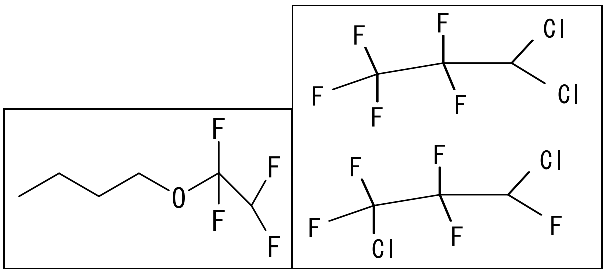


Fig.1 Structure of fluorinated ether (Left) and AK225 (Right)

| GC | |
|---|---|
| Carrier Gas | He |
| Flow rate | 0.8 ml/min (const. flow) |
| Temerature (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.

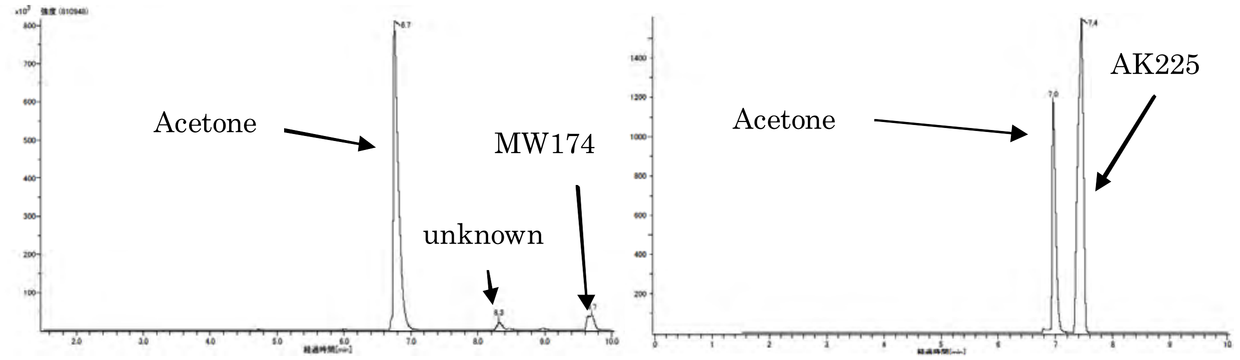


Fig.2 TIC of fluorinated ether (left) and AK225 (right)

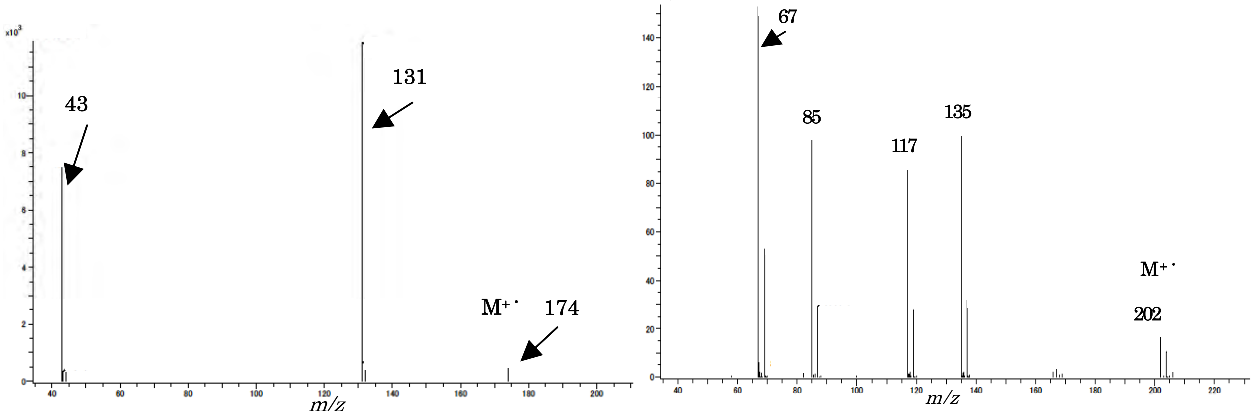


Fig.3 FI spectra of fluorinated ether (left) and AK225 (right)

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 AK255 (right)

| Observed | Calculated | Diff.(mDa) | Formula |
|---|---|---|---|
| 43.05632 | 43.05478 | 1.55 | $C_3F_7$ |
| 131.01407 | 131.01200 | 2.07 | $C_3H_3F_4O$ |
| | 131.01086 | 3.21 | $C_6H_2F_3$ |
| 174.06348 | 174.06678 | −3.29 | $C_6H_{10}F_4O$ |

| Observed | Calculated | Diff.(mDa) | Formula |
|---|---|---|---|
| 66.97379 | 66.97508 | −1.29 | CHClF |
| 84.96424 | 84.96566 | −1.42 | $CClF_2$ |
| 116.97270 | 116.97189 | 0.81 | $C_2HClF_3$ |
| 134.96324 | 134.96347 | 0.78 | $C_2ClF_4$ |
| 201.93481 | 201.93755 | −2.74 | $C_3HCl_2F_5$ |

【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 MS Data Sheet*

**MS Tips**

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

*No.089*

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

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

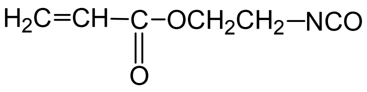
### Introduction

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/EI and GC/FI methods and compared the obtained mass spectra.

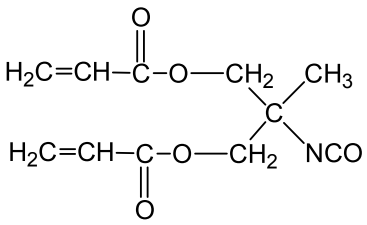
### Methods

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

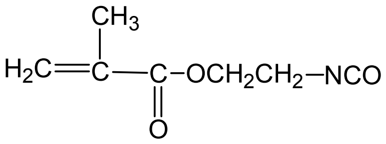


$H_2C{=}CH{-}C({=}O){-}OCH_2CH_2{-}NCO$

(1) Karenz AOI®（$C_6H_7NO_3$）

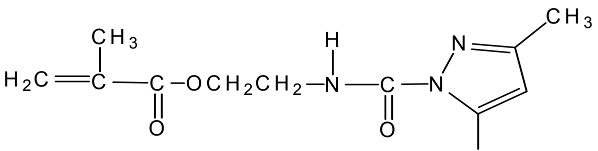


(3) Karenz BEI®（$C_{11}H_{13}NO_5$）



$H_2C{=}C(CH_3){-}C({=}O){-}OCH_2CH_2{-}NCO$

(2) Karenz MOI®（$C_7H_9NO_3$）



(4) Karenz MOI-BP®（$C_{12}H_{17}N_3O_3$）

GC conditions

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

MS conditions

Mass spectrometer: JMS-T100GC “AccuTOF GC”
Ionization mode: EI: Electron energy: 70 eV, Ionization current: 300 μA
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

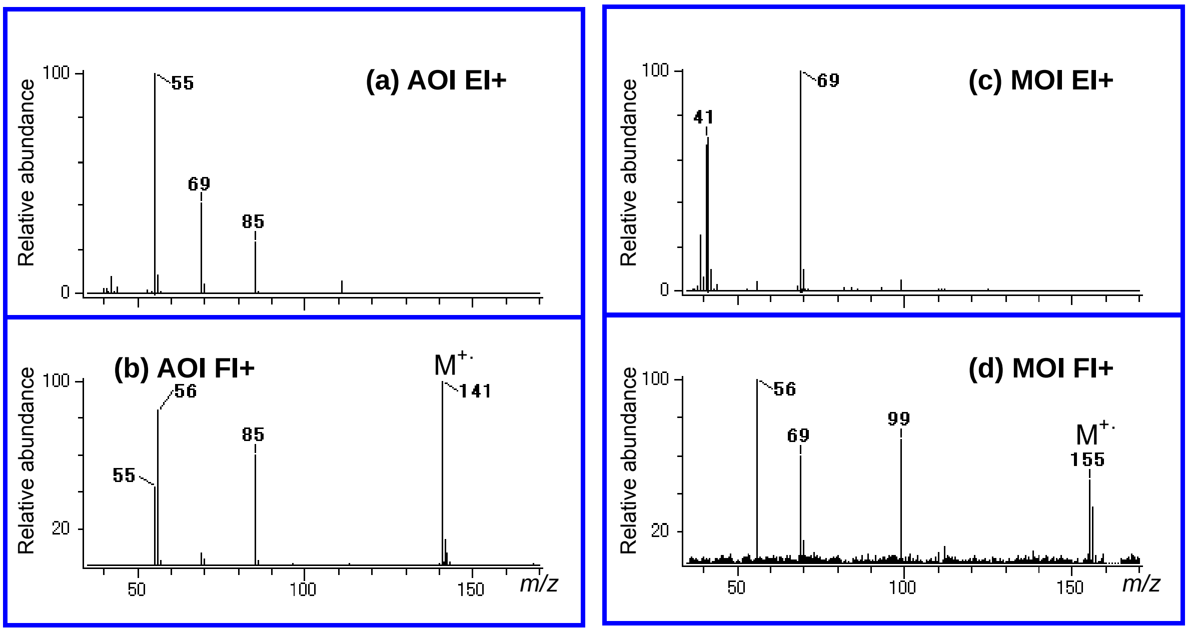


Fig. 1 Mass spectra of Karenz AOI®; (a) EI+, (b) FI+

Mass spectra of Karenz MOI®; (c) EI+, (d) FI+

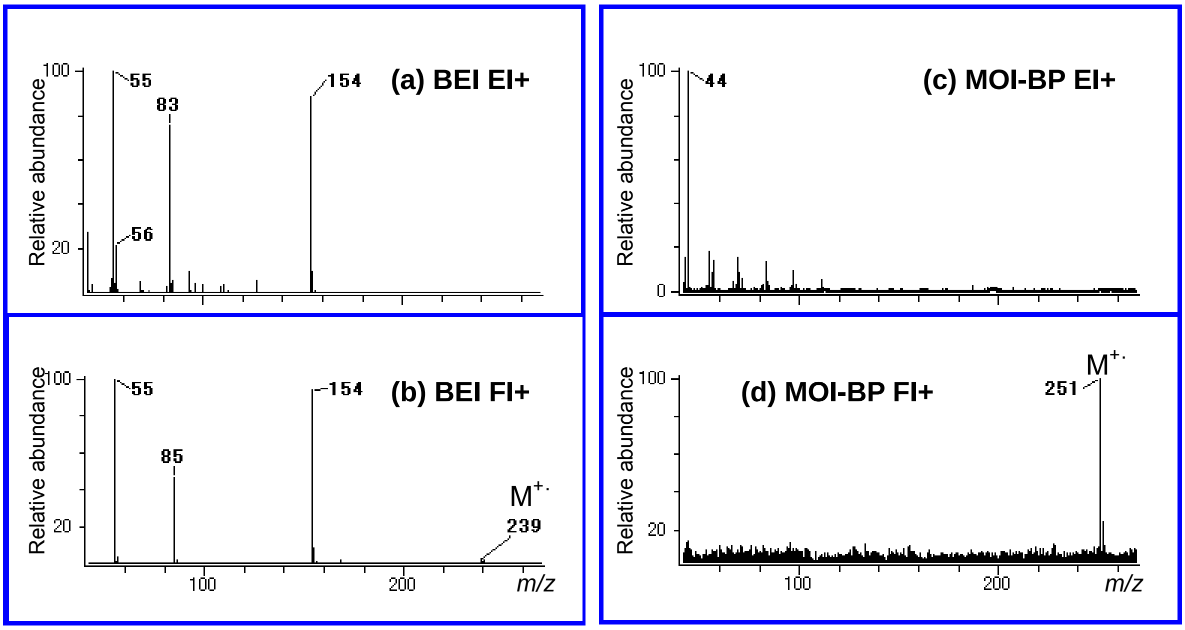


Fig. 2 Mass spectra of Karenz BEI®; (a) EI+, (b) FI+

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.

*JEOL MS Data Sheet*

**MS Tips**

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

*No.090*

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

## ~ analysis of multifunctional thiols, curing agents for functional polymers ~

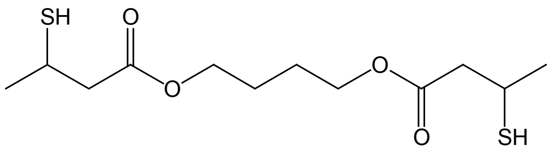
### Introduction

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.

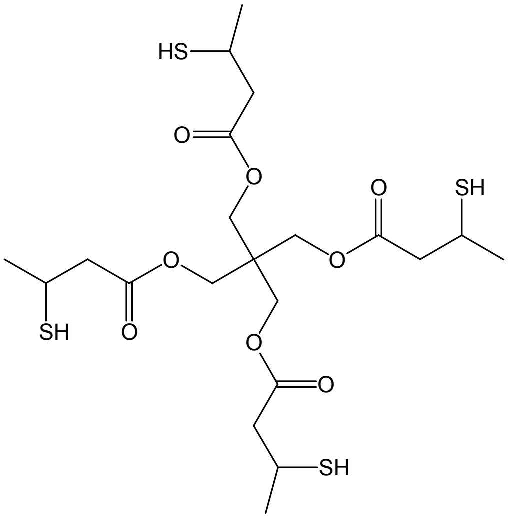
We have analyzed multifunctional thiols, curing agents for functional polymers, by GC/EI and GC/FI methods and compared the mass spectra obtained.

### 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 μm
Carrier gas: Helium, 1.0 mL/min (constant flow rate mode)
Oven: 40 °C (2 min) → 30 °C/min → 280 °C (12 min)

MS conditions

Mass spectrometer: JMS-T100GC “AccuTOF GC”
Ionization mode: EI: Electron energy: 70 eV, Ionization current: 300 μA
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

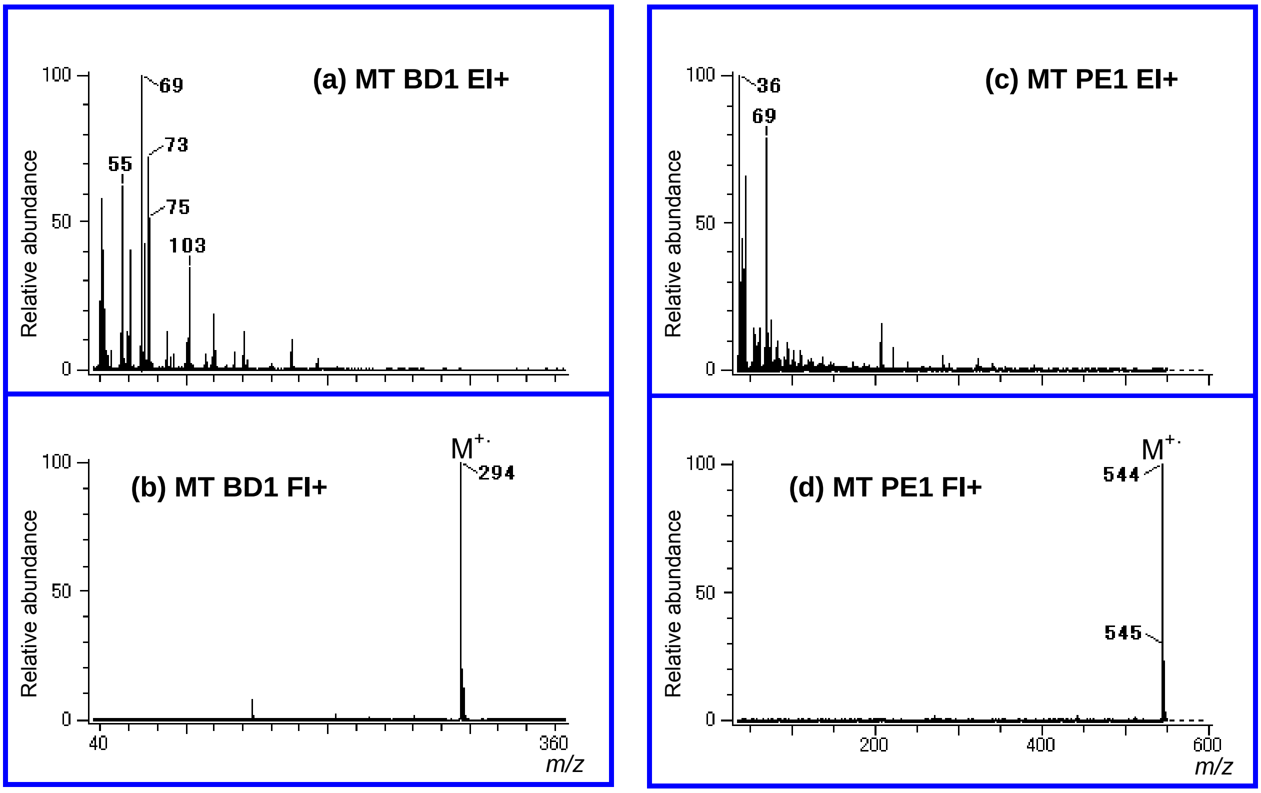


Fig. 1 Mass spectra of Karenz MT® BD1; (a) EI+, (b) FI+
Mass spectra of Karenz MT® PE1; (c) EI+, (d) FI+

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.

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.108

# 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℃（1min）→10℃/min→280℃(5min) |
| Injection Temp.: | | 280℃ |
| 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℃ |
| 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.

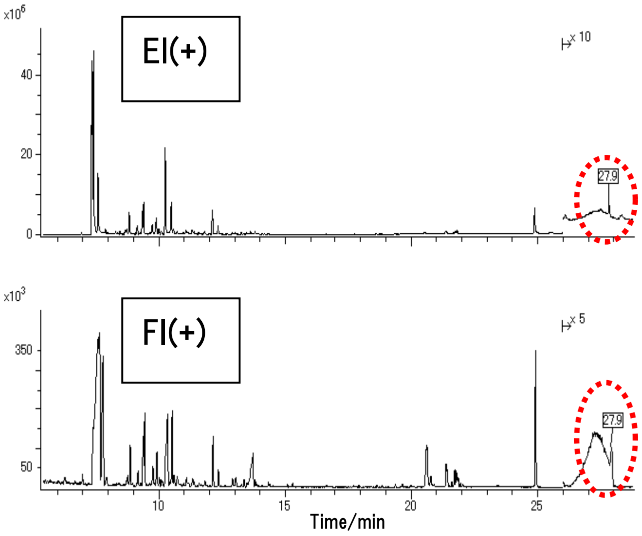


Fig.1 TIC <Upper: EI(+), Lower: FI+>

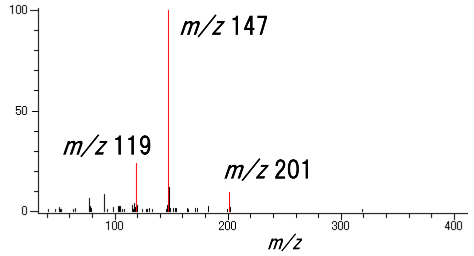


Fig.2 EI+ mass spectrum

Table1 Elemental composition determination by EI+

| Observed m/z | Calcurated 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 |

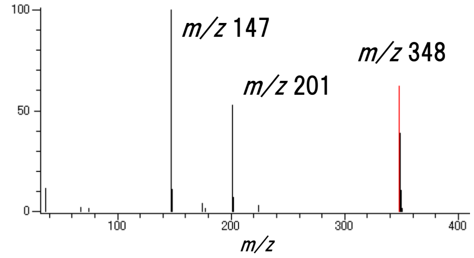


Fig.3 FI+ mass spectrum

Table2 Elemental composition determination by FI+

| Observed m/z | Calcurated 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.

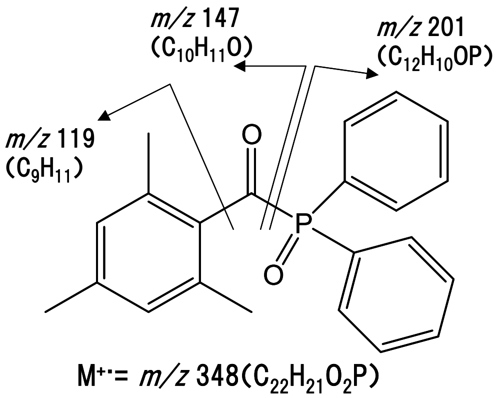


Fig.4 Estimated structure

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MS Tips
No.123

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

# 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>

| | | |
|---|---|---|
| Samples | cholesterol | 1 mg/mL (in methanol) |
| | Irganox® 1010 | 1 mg/mL (in methanol) |

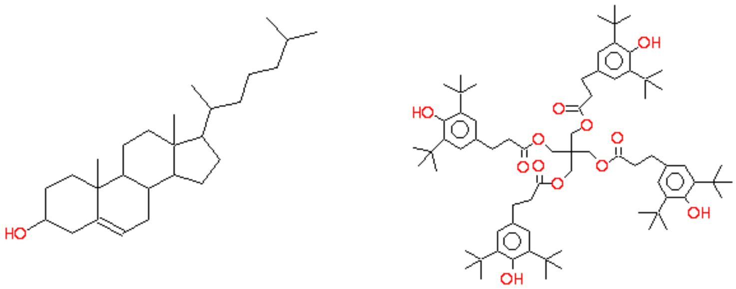

Fig.1 Structural formulas of Cholesterol (left) and Irganox® 1010 (right)

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: *m/z* 35 – 1,400
Spectral recording interval: 0.4 sec

## Results and Discussion

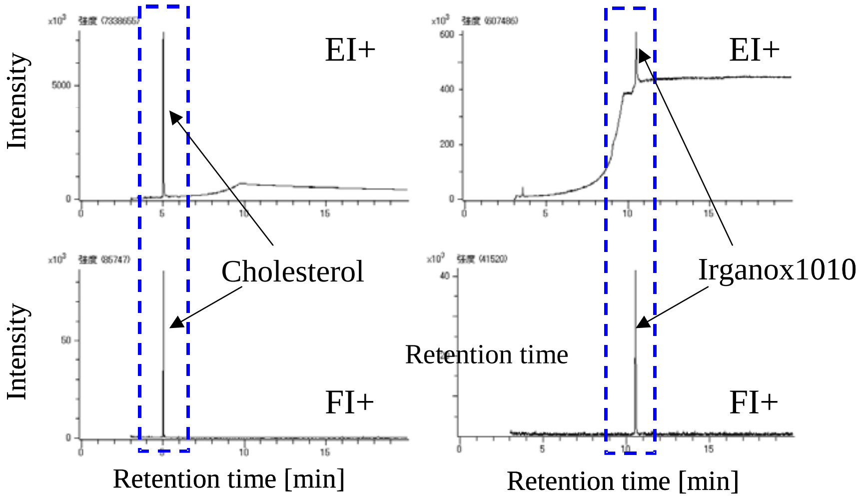

Fig.2 RTICCs of Cholesterol (left) and Irganox® 1010 (right)

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.

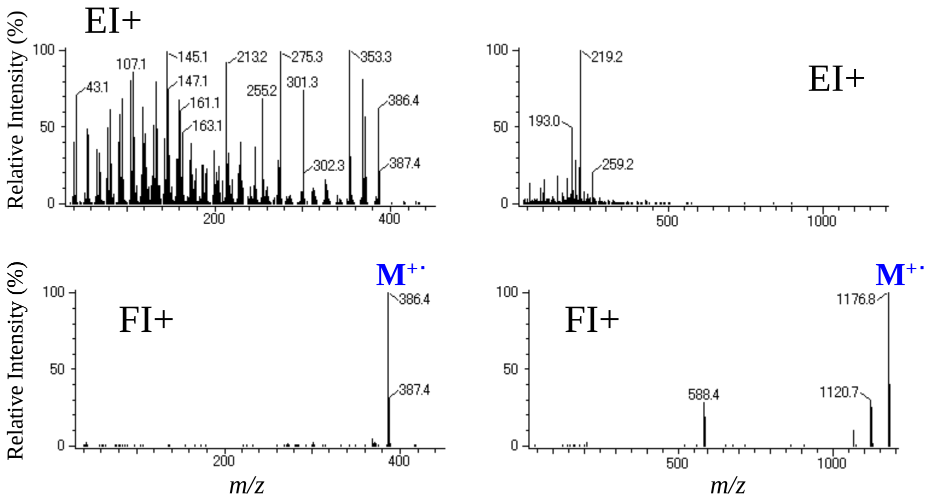

Fig.3 Mass spectra of Cholesterol (left) and Irganox® 1010 (right)

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)

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MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.131

JMS-T100GC Application Data

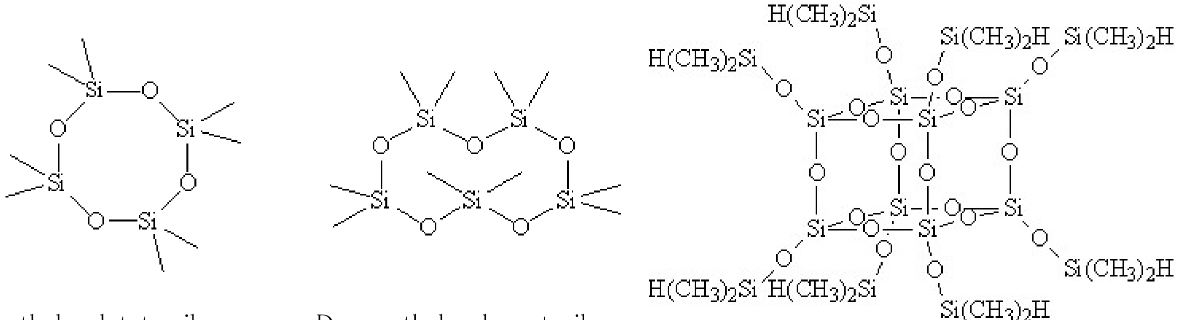
# Analysis of polydimethylsiloxanes by GC/TOFMS

## Introduction

Three polydimethylsiloxane compounds; octamethylcyclotetrasiloxane (sample No. 1), decamethylcyclopentasiloxane (No. 2) and octa(dimethylsiloxy)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(dimethylsiloxy)silsesquioxane, $C_{16}H_{56}O_{20}Si_{16}$, 2 mg/ml in acetone



Octamethylcyclotetrasiloxane    Decamethylcyclopentasiloxane    Octa(dimethylsiloxy)silsesquioxane

Fig.1 Structural formulae of the samples.

GC conditions

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

MS conditions

Mass spectrometer: JMS-T100GC “AccuTOF GC”
EI ionization: Electron energy: 70 eV  Ionization current: 300 µA
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

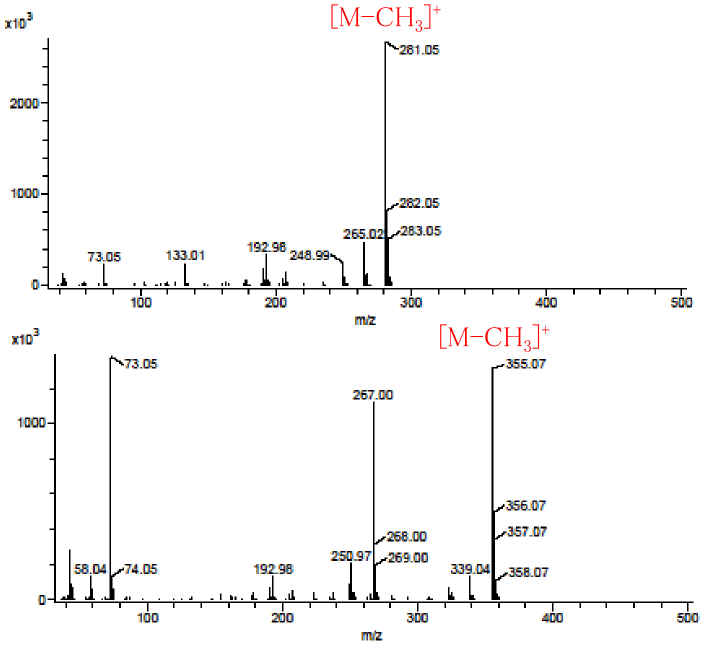


Fig.2 Mass spectra of Octamethylcyclotetrasiloxane (upper) and Decamethylcyclopentasiloxane (lower) by EI.

Table1 Information of calculated exact mass for each ions .

| | Calculated exact mass | Fomula |
|---|---|---|
| Octamethylcyclo tetrasiloxane | 73.04735 | $C_3H_9Si$ |
| | 248.98909 | $C_5H_{13}O_4Si_4$ |
| | 265.02039 | $C_6H_{17}O_4Si_4$ |
| | 281.05169 | $C_7H_{21}O_4Si_4$ |
| Decamethylcyclo pentasiloxane | 73.04735 | $C_3H_9Si$ |
| | 266.99965 | $C_5H_{15}O_5Si_4$ |
| | 355.07048 | $C_9H_{27}O_5Si_5$ |
| Octa(dimethylsiloxy) silsesquioxane | 1000.94384 | $C_{15}H_{53}O_{20}Si_{16}$ |
| | 1014.95949 | $C_{16}H_{55}O_{20}Si_{16}$ |

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.)

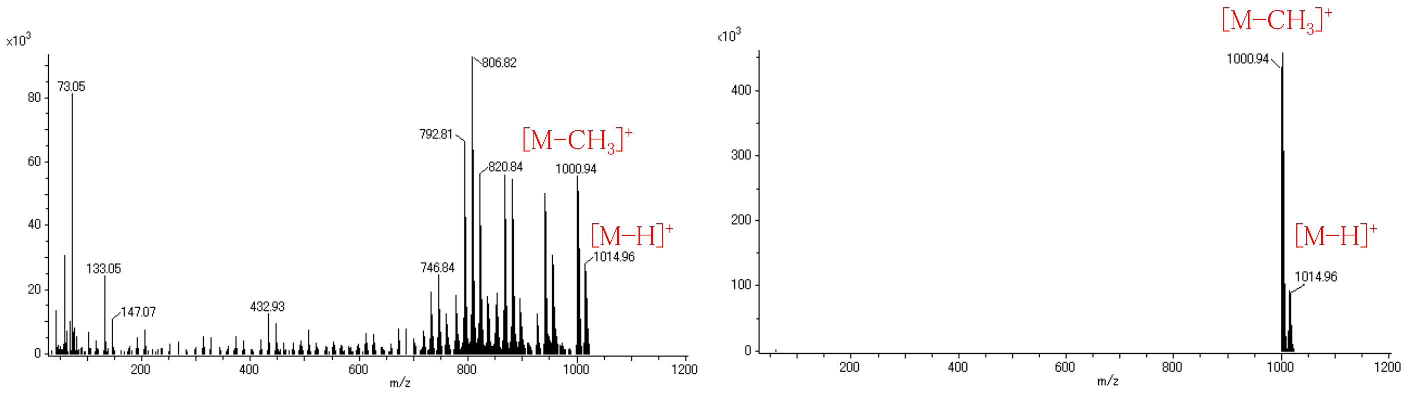


Fig.3 Mass spectrum of Octa(dimethylsiloxy)silsesquioxane by EI (left) and FI (right).

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.

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.101

# Analysis of acrylic resin by pyrolysis GC-TOFMS

Pyrolysis gas chromatography / mass spectrometry (PyGC/MS) is widely used for the analysis of synthetic polymers. As the sample is decomposed instantaneously, the thermal decomposition process is reproducible.

We have performed pyrolysis GC/MS analysis with high sensitivity, high resolution, and high mass accuracy by using Frontier Lab's PY2020D pyrolyzer and JMS-T100GC gas chromatograph – time-of-flight mass spectrometer (GC-TOFMS). The sample was a commercially available acrylic resin.

## Methods

| | |
|---|---|
| Mass spectrometer | JMS-T100GC (JEOL) |
| Pyrolyzer | PY2020D (Frontier Lab.) |
| Gas chromatograph | 6890N (Agilent) |
| Sample | acrylic resin (0.5 mg) |

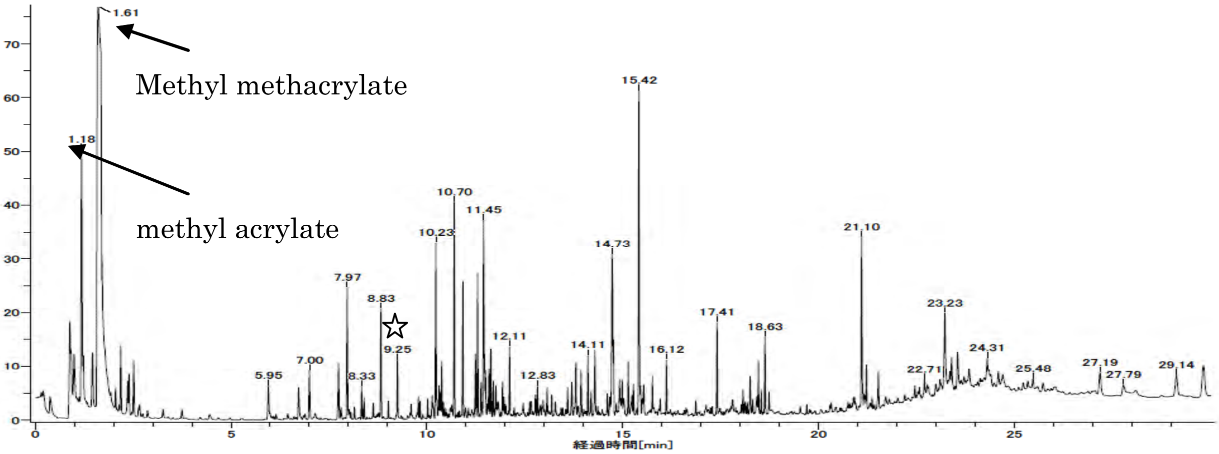
## Results and discussion

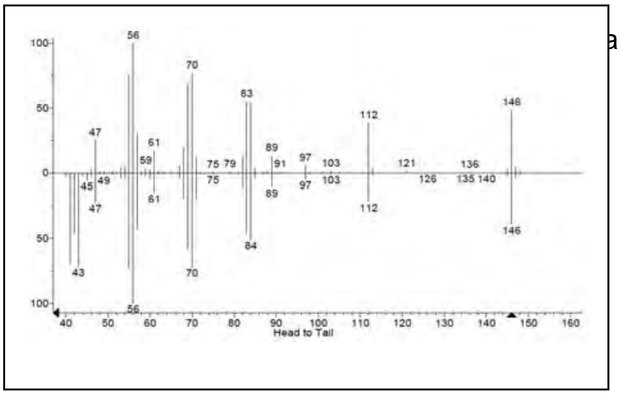
The reconstructed total ion current chromatogram (RTICC) is shown in Fig. 1. Most major peaks on the RTICC were identified by mass spectral library search. Methyl methacrylate, methyl acrylate, and many of their analogs were identified.

The peak at 9.25 min (☆) was identified as 1-ocanethiol by library search. While the result was supported by both Match Factor and Probability, the existence of sulfur was confirmed from measured accurate mass.

Table 1 Analysis Parameters

| Pyrolysis GC | |
|---|---|
| Pyrolysis temp. | 550 °C |
| Interface temp. | 300 °C |
| Carrier gas flow | 1.0 mL/min |
| Split ratio | 50:1 |
| GC column | DB-5MS, 30 m x 0.25 mm I.D.<br>film thickness: 0.25μm |
| GC oven temp. | 50 °C – 15 °C/min – 325 °C |
| **MS** | |
| Ion source temp. | 250 °C |
| Interface temp. | 320 °C |
| Detector voltage | 2200 V |
| Acquisition range | *m/z* 45 – 800 |
| Acquisition rate | 0.5 s/spectrum |





| No. | DB | MF | RMF | Prob. | compound |
|---|---|---|---|---|---|
| 1 | R | 923 | 925R | 80.7P | 1-Octanethiol |
| 2 | M | 780 | 917R | 2.54P | Cyclooctane |
| 3 | M | 780 | 893R | 2.54P | Octane, 1-methoxy- |
| 4 | M | 764 | 877R | 1.46P | Formic acid, octyl ester |
| 5 | M | 763 | 916R | 1.41P | cis-1-Butyl-2-methylcyclopropane |
| 6 | M | 760 | 895R | 1.24P | Cyclopropane, pentyl- |
| 7 | R | 758 | 898R | 1.14P | Octane, 4-chloro- |
| 8 | M | 756 | 910R | 1.06P | trans-1-Butyl-2-methylcyclopropane |
| 9 | R | 754 | 873R | 0.97P | 1-Octanol |
| 10 | M | 750 | 871R | 0.82P | Octane, 3-chloro- |

Fig. 2 Library search results (right,) acquired (top left) and library (bottom left) spectra

The elemental compositions of the major peaks in the mass spectrum (marked red in Fig. 3) are determined with errors less than 1 mmu. For the molecular ion at m/z 146, there were two possibilities, $C_8H_{18}S$ and $C_{11}H_{14}$ within 5 mmu tolerance range. Considering the mass accuracy achieved on other peaks and library search result, $C_8H_{18}S$ seems reasonable. The isotopic cluster pattern of the molecular ion in the observed mass spectrum matched well with that calculated from the elemental composition $C_8H_{18}S$. We concluded that the compound detected at 9.25 min is indeed 1-octanethiol based on library search, accurate mass measurement, and isotope cluster pattern.

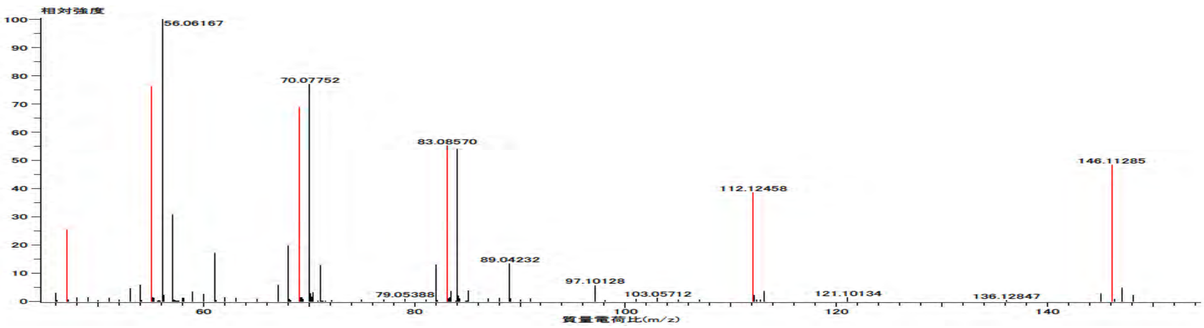
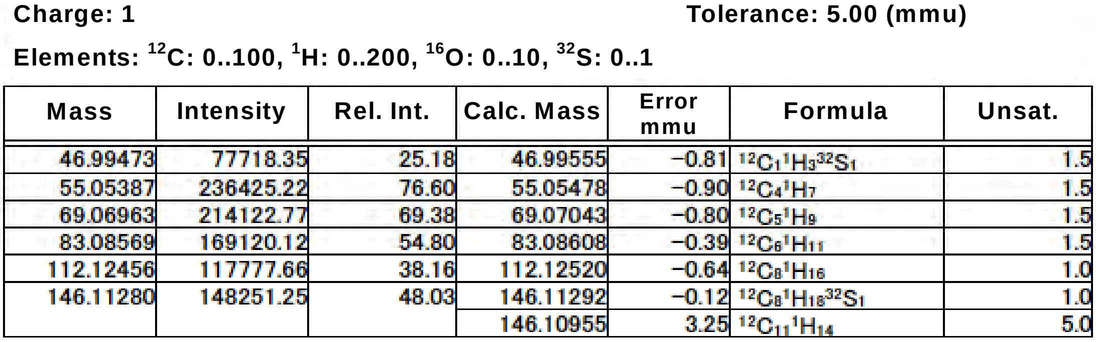


Fig. 3 Observed mass spectrum at 9.25 min and peaks whose elemental compositions were determined

## Conclusion

Table 2 Determined elemental compositions


**Charge: 1** **Tolerance: 5.00 (mmu)**

**Elements: $^{12}C$: 0..100, $^{1}H$: 0..200, $^{16}O$: 0..10, $^{32}S$: 0..1**

| Mass | Intensity | Rel. Int. | Calc. Mass | Error mmu | Formula | Unsat. |
|---|---|---|---|---|---|---|
| 46.99473 | 77718.35 | 25.18 | 46.99555 | −0.81 | $^{12}C_1{}^1H_3{}^{32}S_1$ | 1.5 |
| 55.05387 | 236425.22 | 76.60 | 55.05478 | −0.90 | $^{12}C_4{}^1H_7$ | 1.5 |
| 69.06963 | 214122.77 | 69.38 | 69.07043 | −0.80 | $^{12}C_5{}^1H_9$ | 1.5 |
| 83.08569 | 169120.12 | 54.80 | 83.08608 | −0.39 | $^{12}C_6{}^1H_{11}$ | 1.5 |
| 112.12456 | 117777.66 | 38.16 | 112.12520 | −0.64 | $^{12}C_8{}^1H_{16}$ | 1.0 |
| 146.11280 | 148251.25 | 48.03 | 146.11292 | −0.12 | $^{12}C_8{}^1H_{18}{}^{32}S_1$ | 1.0 |
| | | | 146.10955 | 3.25 | $^{12}C_{11}{}^1H_{14}$ | 5.0 |

In PyGC/MS analyses, many of the detected compounds are often left unidentified since there are not many mass spectra of pyrolysis products in mass spectral libraries. The JMS-T100GC GC-TOFMS, with its easy accurate mass measurement capability, not only ensures the library search results but also is effective in identifying compounds whose spectra are not in the libraries. Its ability to acquire accurate isotope cluster pattern further aids in identifying unknown molecules.

Frontier Laboratories' pyrolyzer system is provided and supported through Frontier Laboratories' sales and support network and may not be available in your territory. Contact your local JEOL representative for detail.

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.138 (U: 02/'09)

*JMS-T100GCV* **Application Data**

# Analysis of additives in plastic by thermal desorption (TD) GC-TOFMS

## ~ accurate mass measurement and isotope pattern matching ~

### Introduction

Among various methods for characterizing plastics, qualitative and quantitative analyses using pyrolysis (Py) GC/MS and thermal desorption (TD) GC/MS are widely used. These are simple techniques, but provide detailed information.

In this application note, we report the analysis of additives in plastic by thermal desorption GC-TOFMS using a thermal desorption system and JEOL JMS-T100GCV "AccuTOF GCv" GC-TOFMS. Identification of the analytes was accomplished by library search and accurate mass measurement. Isotope cluster pattern matching was performed using the software "Mass Spec Tools™."

### Methods

Sample: Plastic (0.4 mg)

Thermal desorption

Instrument: PY-2020iD (Frontier Laboratories Ltd., Fukushima, Japan)
Temperature: 150 °C → 10 °C/min → 350 °C (20 minutes total)

GC

Instrument: 6890N (Agilent)
Column: DB1-HT, 8 m x 0.25 mm x 0.1 µm

MS

Instrument: JMS-T100GCV (JEOL)
Ionization mode: EI(+): Electron energy: 70 eV
Ionization current: 300 µA
Acquired mass range: *m/z* 35 – 1,400
Spectral recording interval: 0.4 sec

Software: Mass Spec Tools™ (ChemSW, Inc., Fairfield, CA, U.S.A.)

## Results and discussion

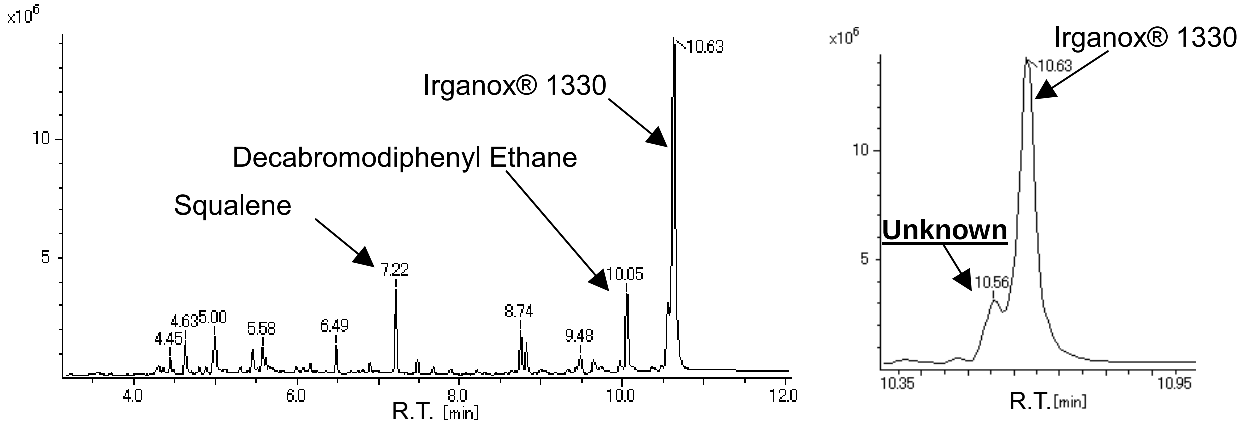


Fig.1 TIC chromatogram

The TIC chromatogram is shown in Fig. 1. Some of the peaks identified by searching NIST mass spectral library include squalene, decabromodiphenyl ethane, a brominated flame retardant, and Irganox® 1330, an antioxidant. The expansion of the TICC from 10.35 min to 10.95 min is shown in the inset of Fig. 1. There found an “unknown” component that could not be identified by the library search at the left of the Irganox® 1330 peak. The mass spectrum of this “unknown” component was analyzed by the “Elcomp™,” a part of “Mass Spec Tools™.”

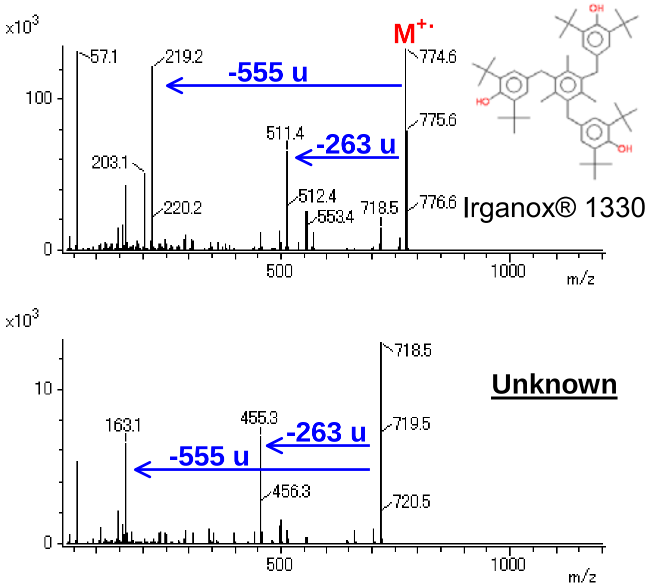
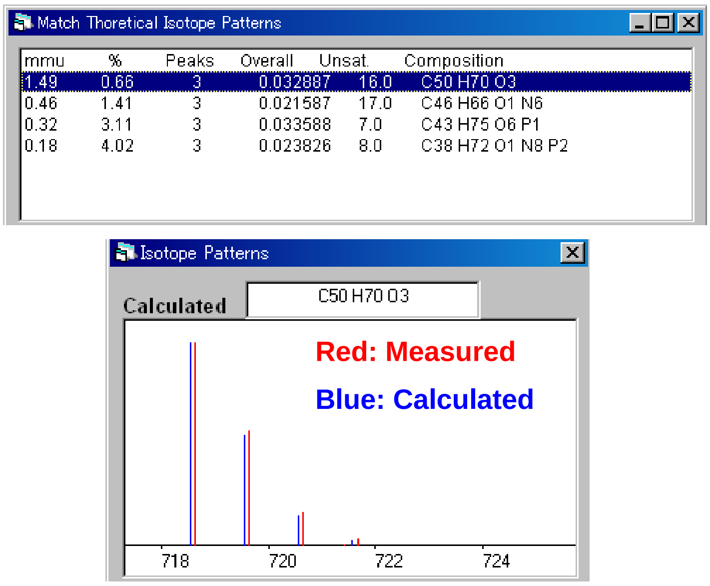


Fig.2 Mass spectra of Irganox® 1330 (upper) and unknown component (lower).


Match Thoretical Isotope Patterns

| mmu | % | Peaks | Overall | Unsat. | Composition |
|---|---|---|---|---|---|
| 1.49 | 0.66 | 3 | 0.032887 | 16.0 | C50 H70 O3 |
| 0.46 | 1.41 | 3 | 0.021587 | 17.0 | C46 H66 O1 N6 |
| 0.32 | 3.11 | 3 | 0.033588 | 7.0 | C43 H75 O6 P1 |
| 0.18 | 4.02 | 3 | 0.023826 | 8.0 | C38 H72 O1 N8 P2 |

Isotope Patterns

Calculated: C50 H70 O3

Fig.3 Analysis results table (upper) and isotope patterns (lower)

The mass spectra of Irganox® 1330 and the unknown component are shown in Fig. 2. Although *m/z* values of the major peaks in the spectra are different, the fragmentations are very similar, suggesting that they are similar in their structures. The elemental composition of the unknown was elucidated from the combinations of C, H, O, N, and P, although the spectral similarity suggests that it likely consists from C, H, and O. 21 candidates were found within the error range of ± 5 mmu. By using isotope pattern matching, they were narrowed down to 4, as shown in the top portion of Fig. 3. Among them, $C_{50}H_{70}O_3$ had the smallest matching error (the smaller the “%” in Fig. 3, the better the matching) and the matching was indeed excellent, as shown in the bottom of Fig. 3. The structure of the unknown was elucidated as an analog of Irganox® 1330 with one of the t-butyl group being substituted by H.

*JEOL MS Data Sheet*

**MS Tips**

Mass Spectrometry Application Group
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*No.078*

# 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.

**Methods** 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 μA
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

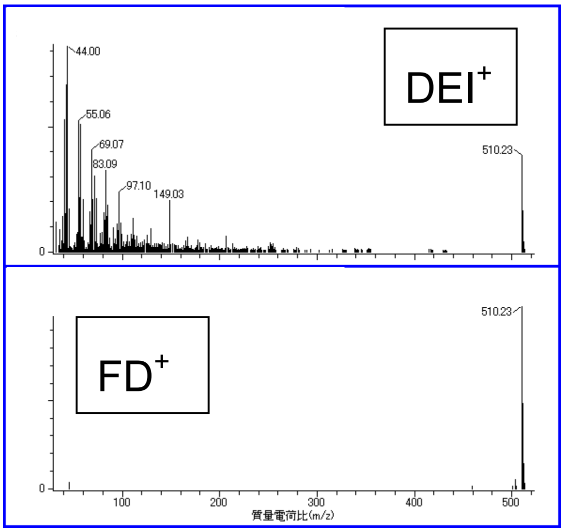

Fig. 1 Mass spectra of DPVBi

Table 1 Accurate mass measurement result

| Mass | Intensity | Calc. Mass | Mass Diff. (mmu) | Formula | Unsaturation |
|---|---|---|---|---|---|
| 510.23378 | 217546.53 | 510.23475 | -0.97 | 12C40 1H30 | 26.0 |

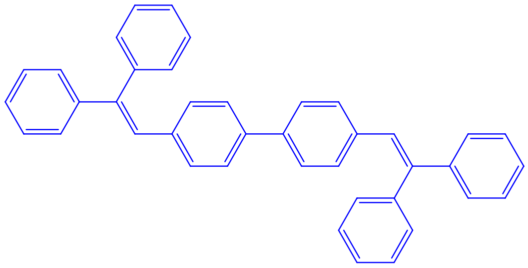

Fig. 2 Structure of DPVBi

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.

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JEOL MS Data Sheet

MS Tips

No.085

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# 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 though 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)

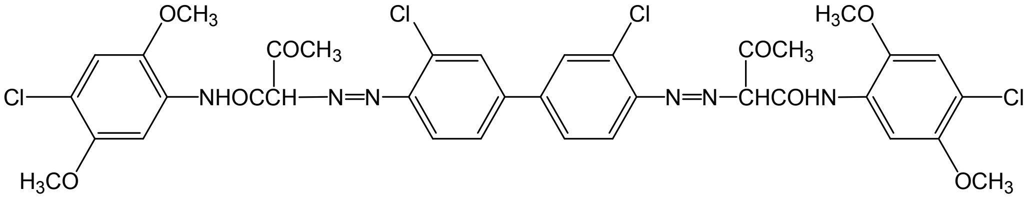

Fig. 1 Pigment Yellow 83 ($C_{36}H_{32}Cl_4N_6O_8$)

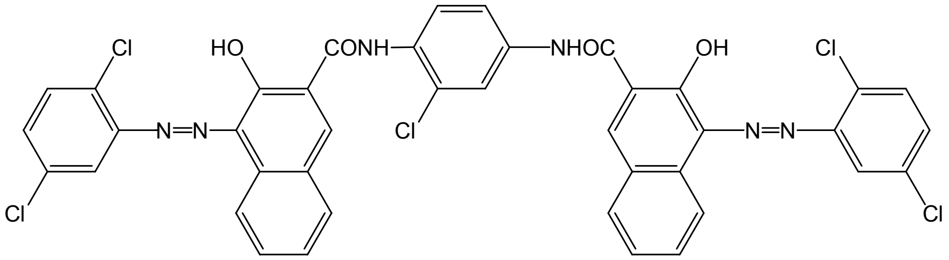

Fig. 2 Pigment Read 144 ($C_{40}H_{23}Cl_5N_6O_4$)

| | | |
|---|---|---|
| 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

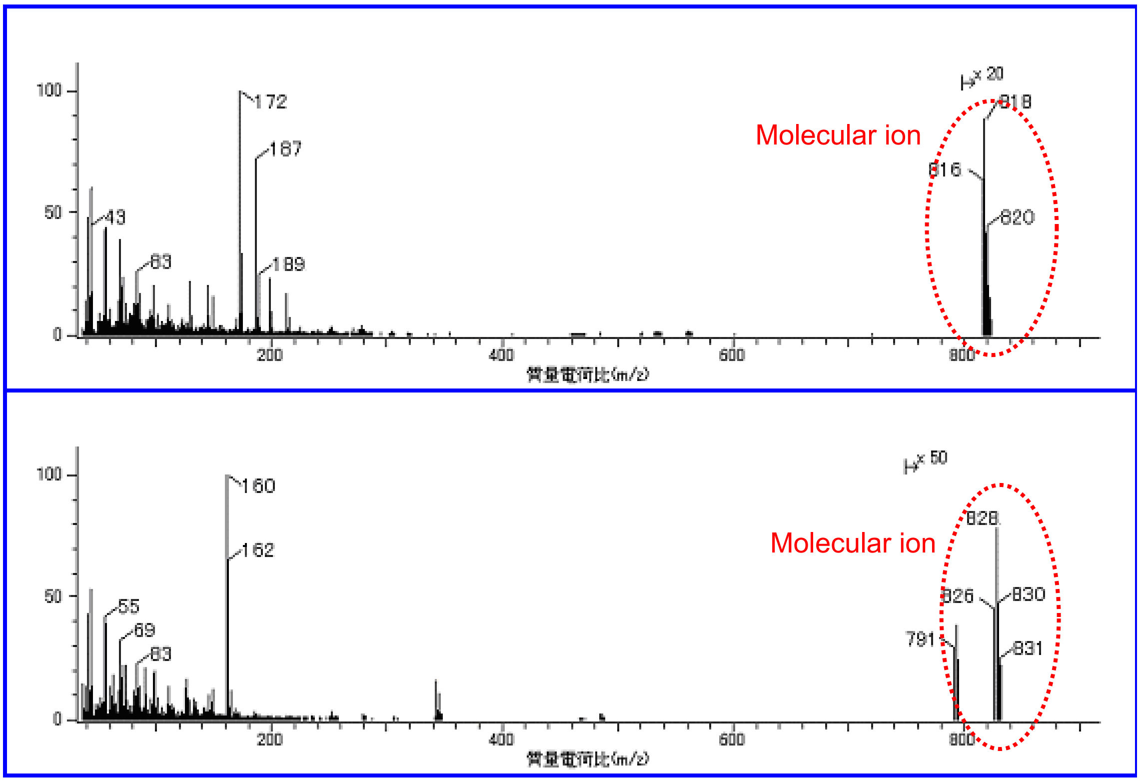

Fig. 4 Mass spectra (top: Pigment Yellow 83, bottom: Pigment Red 144)

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.

**JEOL MS Data Sheet**

# MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

**No.087**

# 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 (BAlq)
(Luminescence Technology Corp.)

| FD Probe Condition | |
|---|---|
| Emitter | 10 µm (Carbotec) |
| Rising Current Rate | 51.2mA/min |
| Maximum Current V | 50 mA |
| Sample Concentration | 0.3 mg/ml |
| Sample Volume | 1 µL |
| 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 |

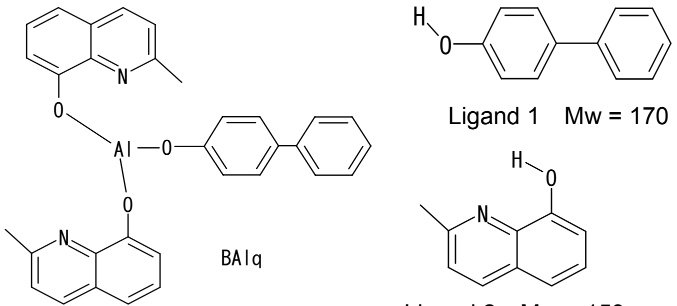

Fig. 1 Organic EL material and its ligands

## 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.

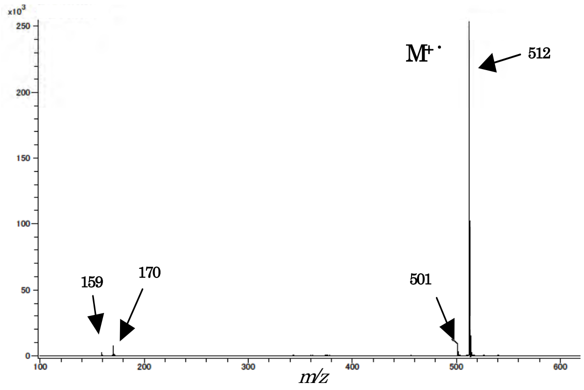

Fig. 2 FD mass spectrum of BAlq

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JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.091

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

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

### Introduction

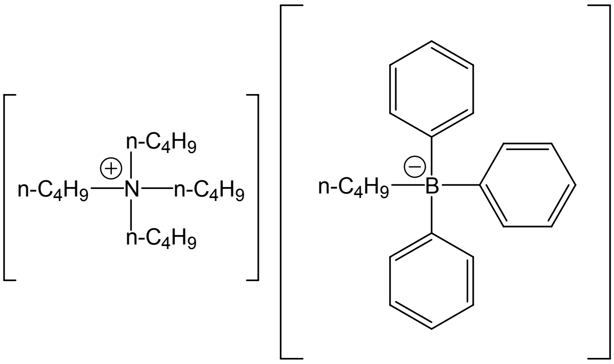
Field desorption (FD) is an ionization method utilizing electron tunneling effect in a high electric field near the emitter surface or whisker tip. Sample is applied on the emitter and heated by applying an electric current through the emitter for desorption and ionization.

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.

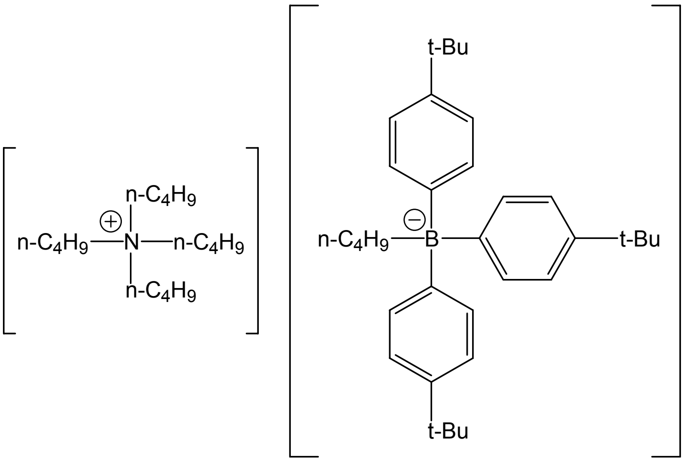
We have analyzed some quaternary borate ammonium salts that are designed as photoinitiators for the polymerization of functional polymers by FD.

### 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

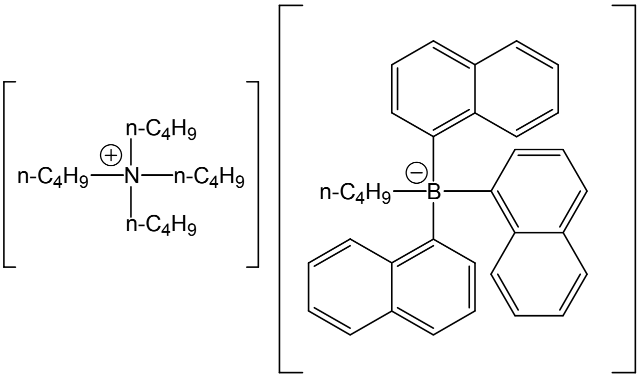
Spectral recording interval: 0.3 sec

Ionization mode: FD+

Cathode potential: -10 kV

Emitter current program:

0 mA → 51.2 mA/min → 40 mA



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

## Results and discussion

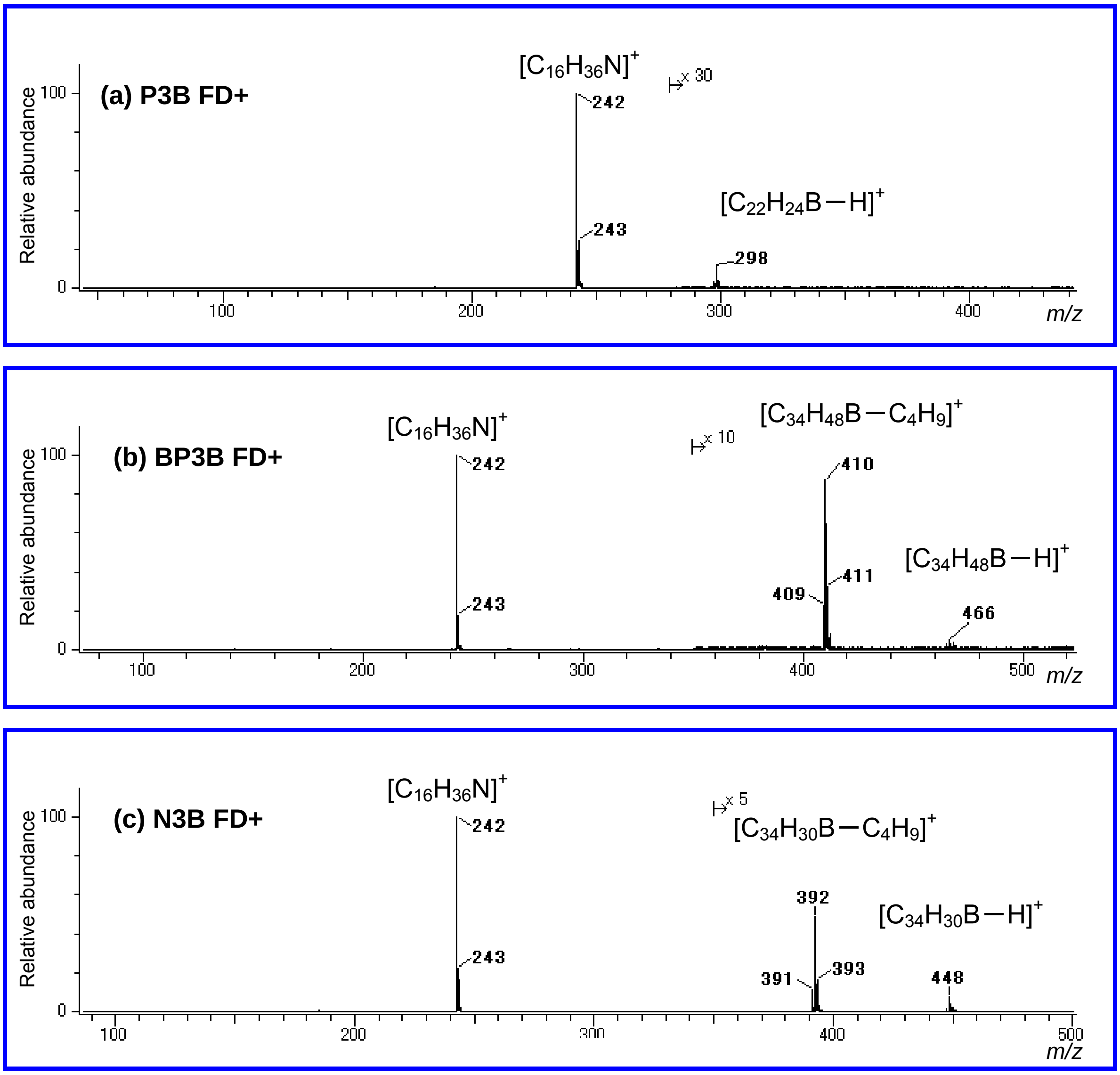


Fig. 1 FD+ mass spectra of organic borate ammonium salts

Molecular ions $[(\text{Anion})(\text{Cation})]^{+\cdot}$ 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 $[(\text{Anion}) - \text{H}]^+$ were observed for all samples, though they are relatively weak. For BP3B and N3B, ions that correspond to $[(\text{Anion}) - C_4H_9]^+$ 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.

JEOL MS Data Sheet

**MS Tips**

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.092

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

## ~ analysis of NIR-photosensitive dyes ~

### Introduction

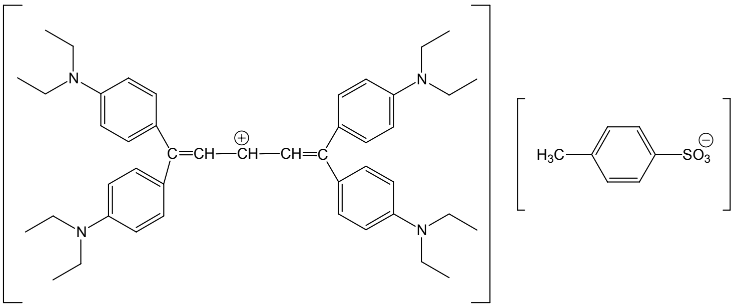
Field desorption (FD) is an ionization method utilizing electron tunneling effect in a high electric field near the emitter surface or whisker tip. Sample is applied on the emitter and heated by applying an electric current through the emitter for desorption and ionization.

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.

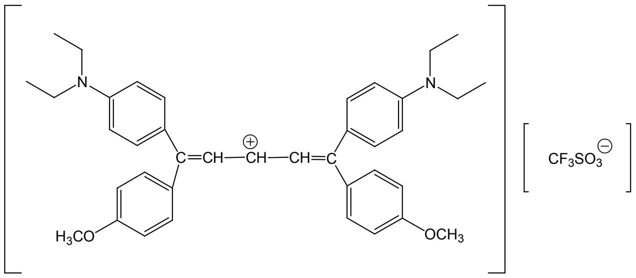
We have analyzed near infrared ray (NIR) photosensitive dyes that are designed as photoinitiators for the polymerization of functional polymers by FD.

### Methods

- Samples NIR photosensitive dyes (Showa Denko K.K.)



(1) IRT（$[C_{45}H_{59}N_4]^+[C_7H_7SO_3]^-$）



(2) IR13F（$[C_{39}H_{45}O_2N_2]^+[CF_3SO_3]^-$）

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

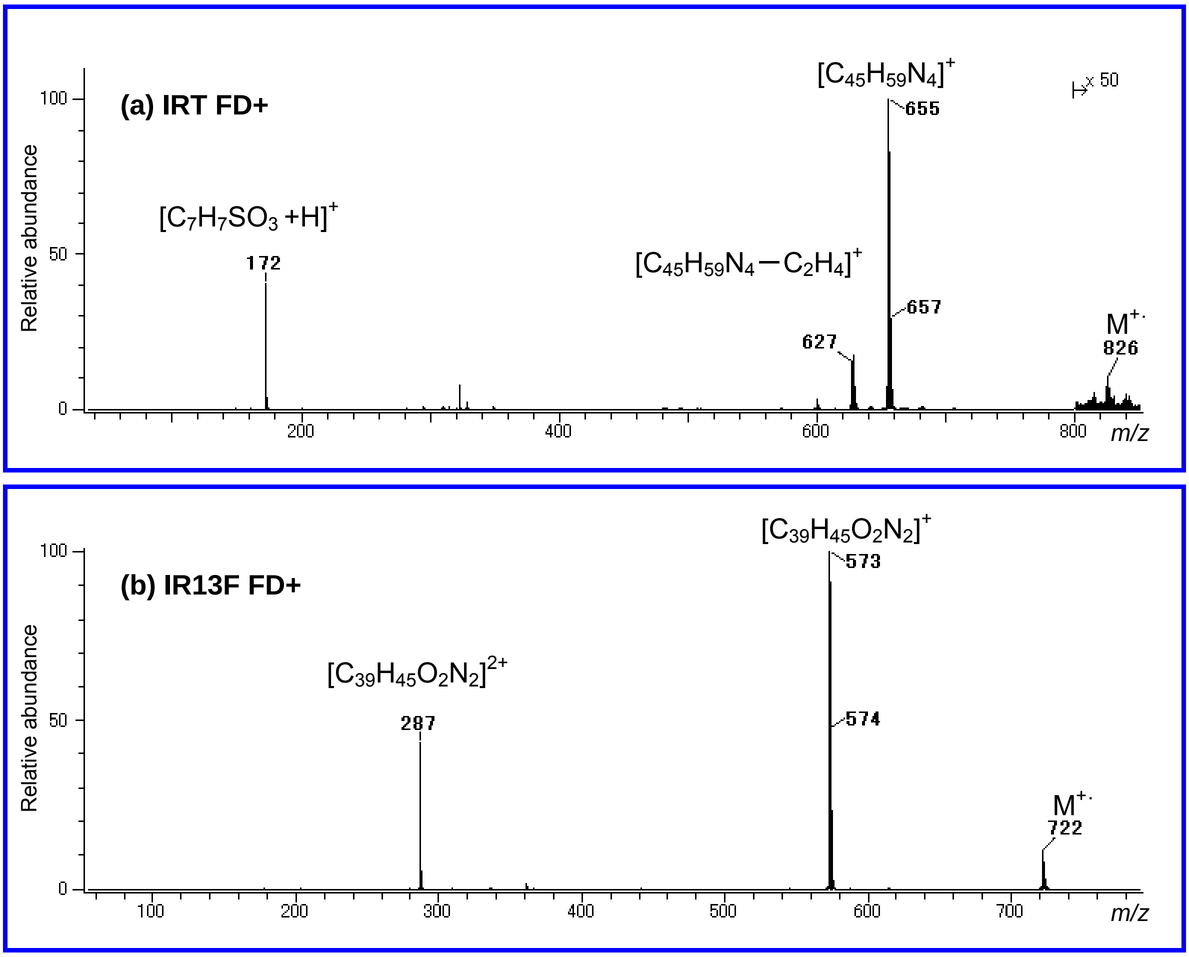


Fig. 1 FD+ mass spectra of NIR photosensitive dyes

Molecular ions [(Anion)(Cation)]$^{+\cdot}$ 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$_2$H$_4$]$^+$ 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.

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.110

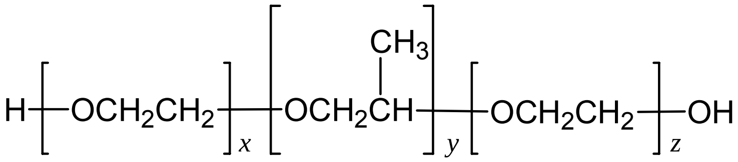
# Analysis of block copolymer by field desorption (FD) using JMS-T100GC "AccuTOF GC"

## 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



$H{-}[OCH_2CH_2]_x{-}[OCH_2\overset{CH_3}{CH}]_y{-}[OCH_2CH_2]_z{-}OH$

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 $C_3H_6O$) 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.

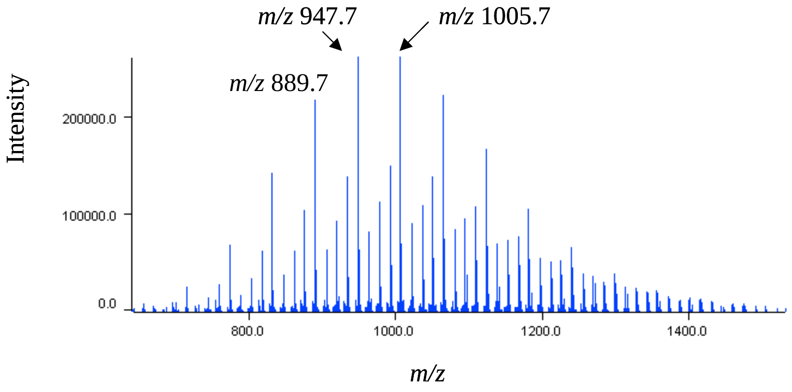


Fig.2 FD mass spectrum

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™<br>(Sierra Analytics) |
| Repeat unit A: | $C_3H_6O$ |
| Repeat unit B: | $C_2H_4O$ |
| α end group: | H |
| ω end group: | OH |
| Adduct: | H |
| Match tolerance: | ± 0.05 u |

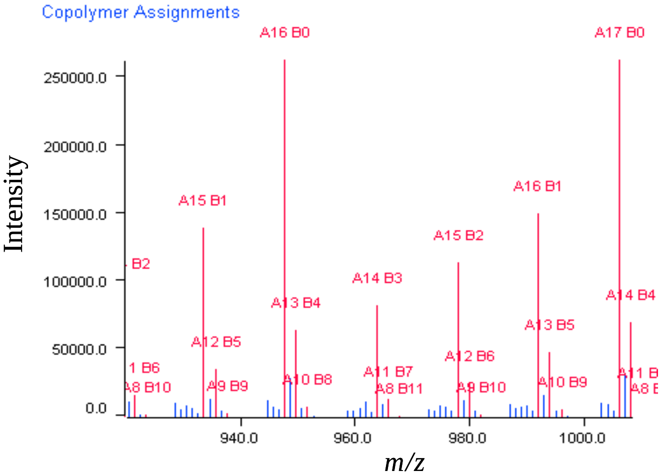
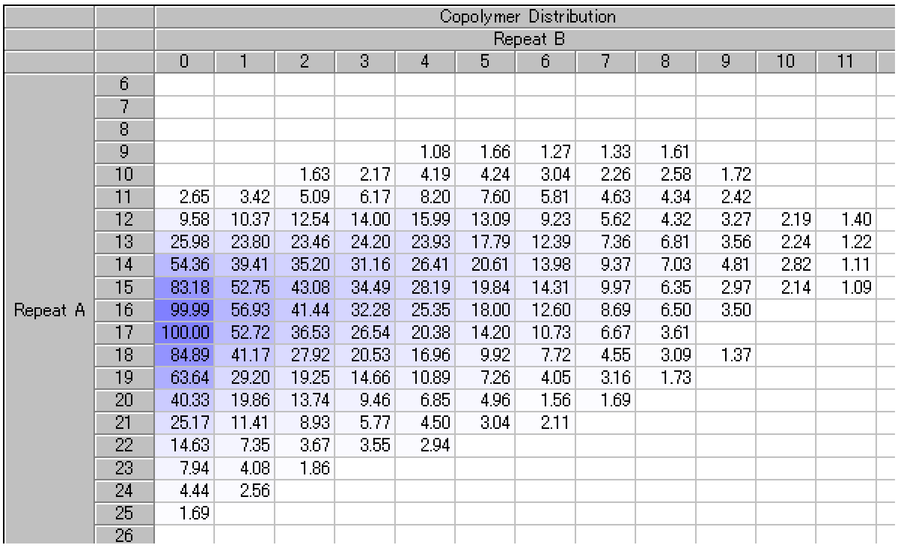


Fig.3 Type analysis assignments ($m/z$ 920–1020)

Some of the assignments made by the software with the parameters settings from above are shown in Fig. 3; "A" means C3H6O, "B" means C2H4O, 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

| | $M_n$ | $M_w$ | $M_z$ | PD |
|---|---|---|---|---|
| $(H[C_3H_6O]_n[C_2H_4O]_mOH)+H^+$ | 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 ($M_w$,) weight average molecular weight ($M_w$,) Z average molecular weight ($M_z$,) polydispersity (PD,) were easily obtained.

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
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No.113

# 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(trifluormethylsulfonyl)imide (14654 Aldrich)

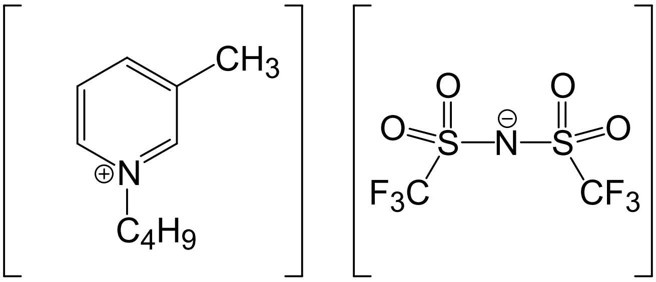

Fig. 1 Structural formula of the sample

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 difficult1), 2). For ionic compounds, single-charge cluster ions of the ($C_{n+1}A_n$) are readily observed but neutral species such as (CA) are not observed2). The acquired FD mass spectrum is shown in Fig. 2.

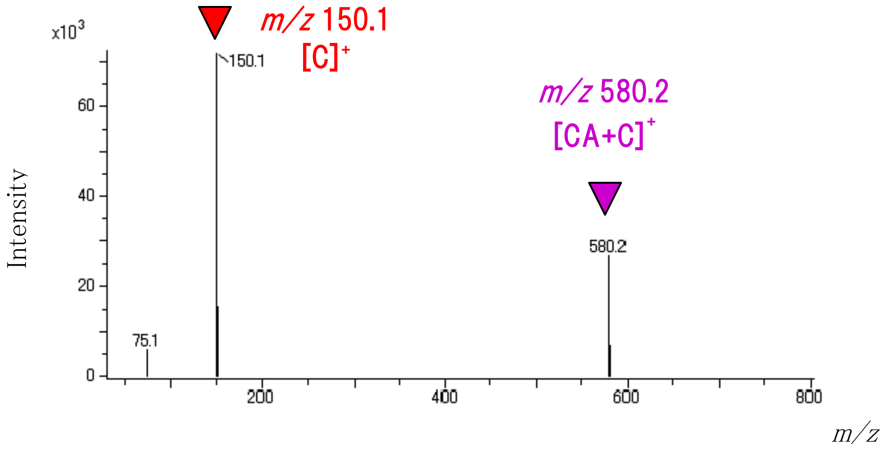

Fig. 2 FD mass spectrum of the sample

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 |
|---|---|---|---|---|
| C | 150.1289 | 150.1283 | 0.6 | $C_{10}H_{16}N$ |
| CA+C | 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 x 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)

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
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No.121

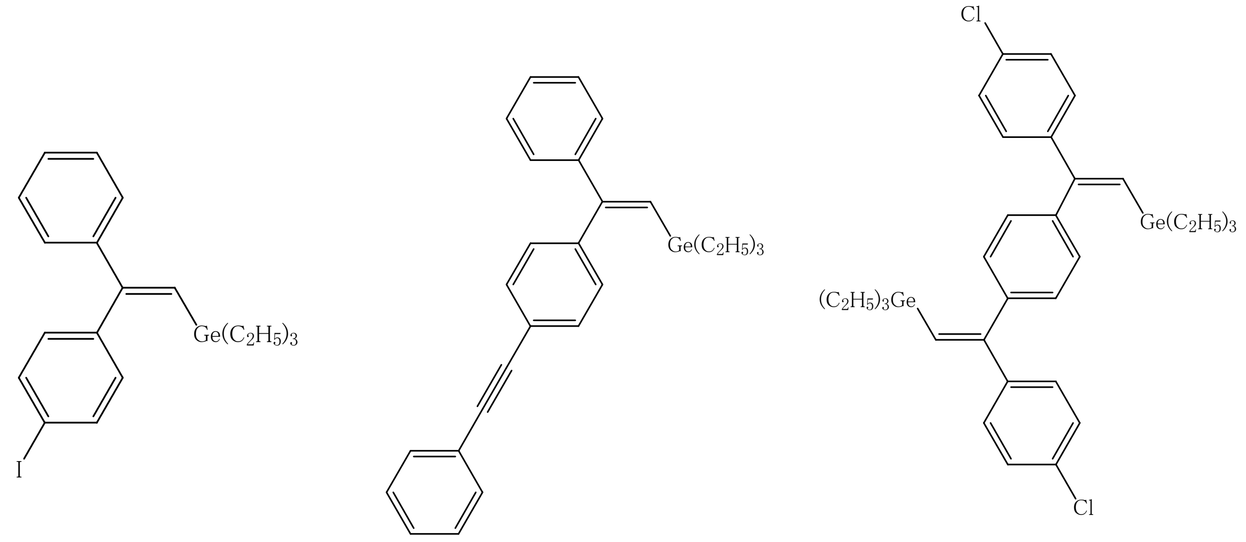
# Analysis of organogermanium compounds by field desorption (FD) ionization using JMS-T100GC “AccuTOF GC”

## 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



① $C_{20}H_{25}GeI$ ② $C_{28}H_{30}Ge$ ③ $C_{34}H_{44}Ge_2Cl_2$

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 → 51.2 mA/min → 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.

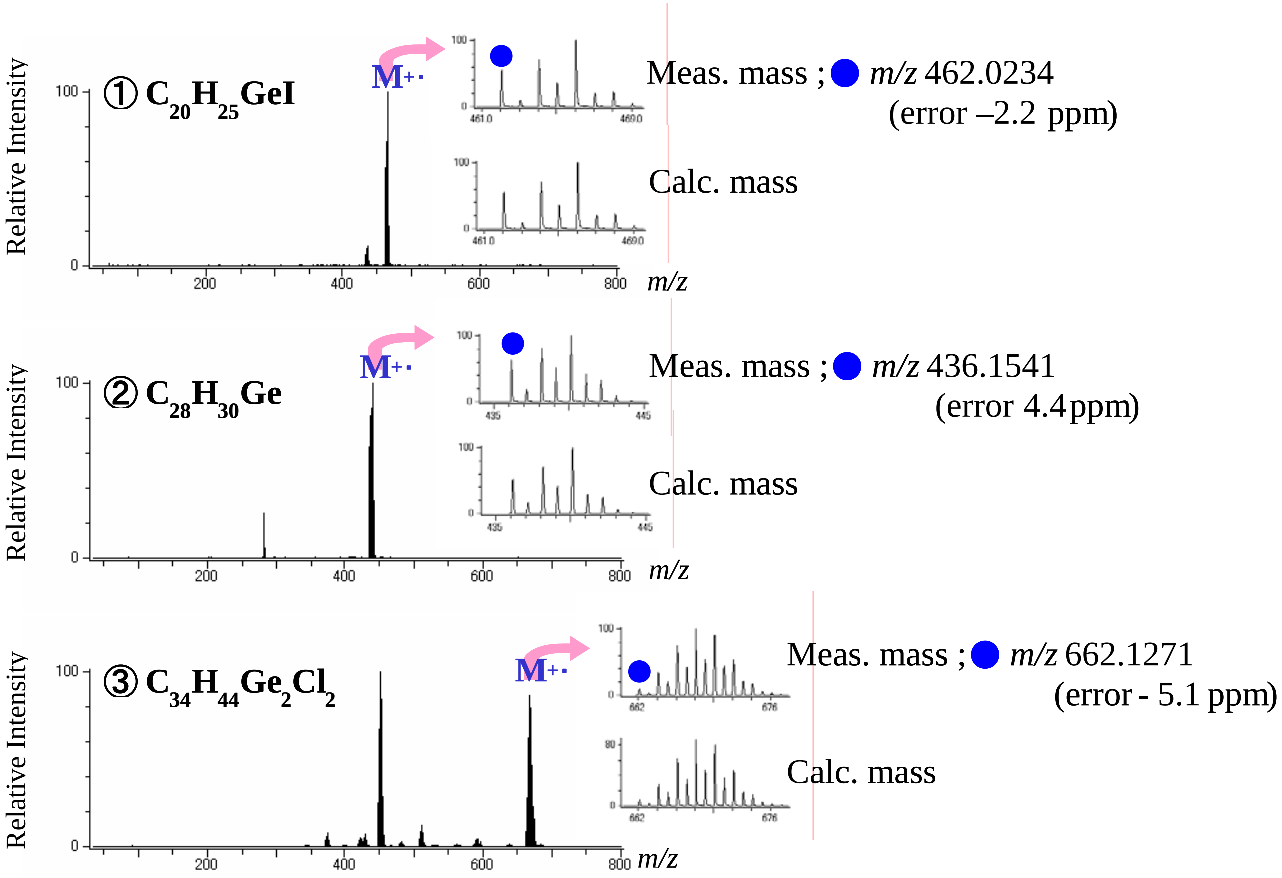


Fig.1 FD mass spectra, comparisons between observed and simulated isotope clusters, and accurate mass measurement results for the organogermanium compounds.

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 patters 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.

*JEOL MS Data Sheet*

**MS Tips**

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

*No.151*

***JMS-T100GCV Application Data***

# Analysis of polymer additives using DIP-EI and FD

## [Introduction]

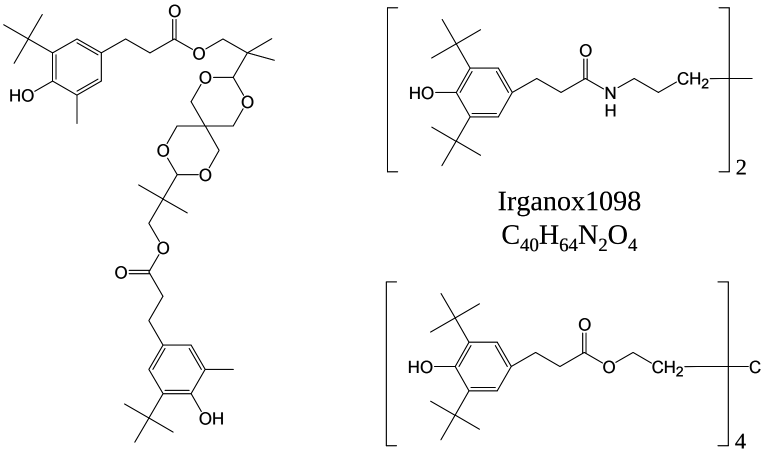
This report shows the result of the ionization of phenolic polymer antioxidants analyzed by electron ionization (EI) with direct insertion probe（DIP）and field desorption (FD）.

## [Method]

Samples

Phenolic antioxidant

AO-80 (1mg/mL in methanol)
Irganox1098 (1mg/mL in methanol)
Irganox1010 (1mg/mL in methanol)



AO-80
$C_{43}H_{64}O_{10}$

Irganox1098
$C_{40}H_{64}N_2O_4$

Irganox1010
$C_{73}H_{108}O_{12}$

Fig.1 Structural formula of sample compounds

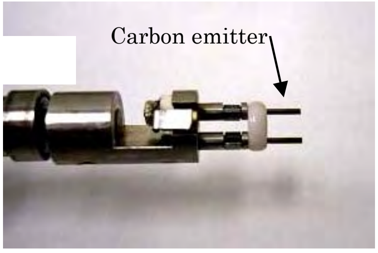
Measurement conditions

See table 1.

Table 1 Measurement conditions.

| | |
|---|---|
| Instrument | JMS-T100GCV (JEOL Ltd.) |
| Direct probe | DIP |
| Ionization mode | EI+ (70eV, 300μA) |
| Probe condition | 50℃ → 64℃/min → 400℃ |
| Ion source temp. | 280℃ |
| *m/z* range | *m/z* 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 |
| *m/z* range | *m/z* 50-1500 |
| Spectrum recording time | 0.5sec |

(a) DIP（Direct Insertion Probe）



(b) FDP（Field Desorption Probe）

Fig.2 Picture of direct probes.

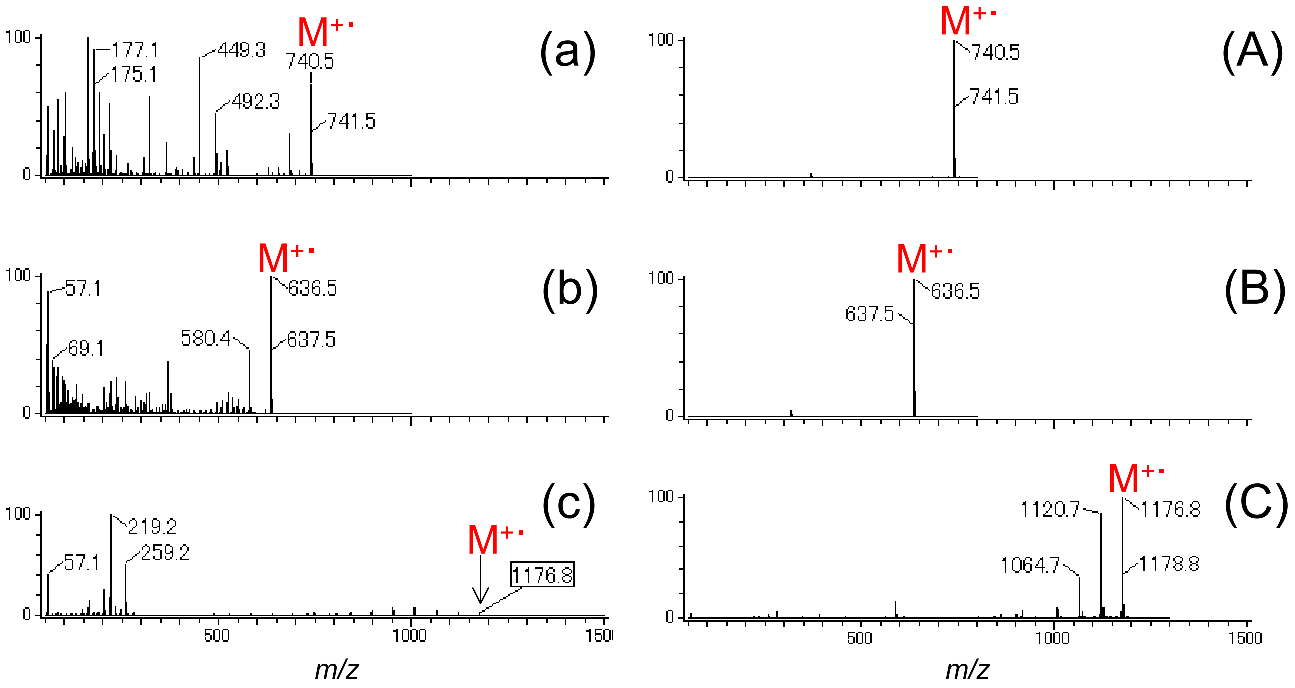


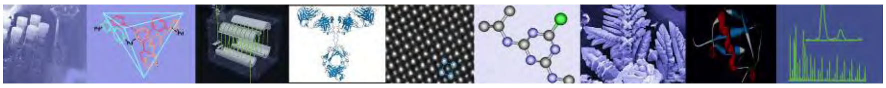
Fig.3 : Mass spectra of phenolic antioxidant by DIP-EI and FD.
EI mass spectra: (a) AO-80, (b) Irganox1098, (c) Irganox1010
FD mass spectra: (A) AO-80, (B) Irganox1098, (C) Irganox1010

## [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.



Applications Note

# 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 2nd 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 conditions 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-5SilMS, 30 m x 0.25 mm, 0.25 um | |
| 2nd column | Rxi-17SilMS, 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 Conditions.

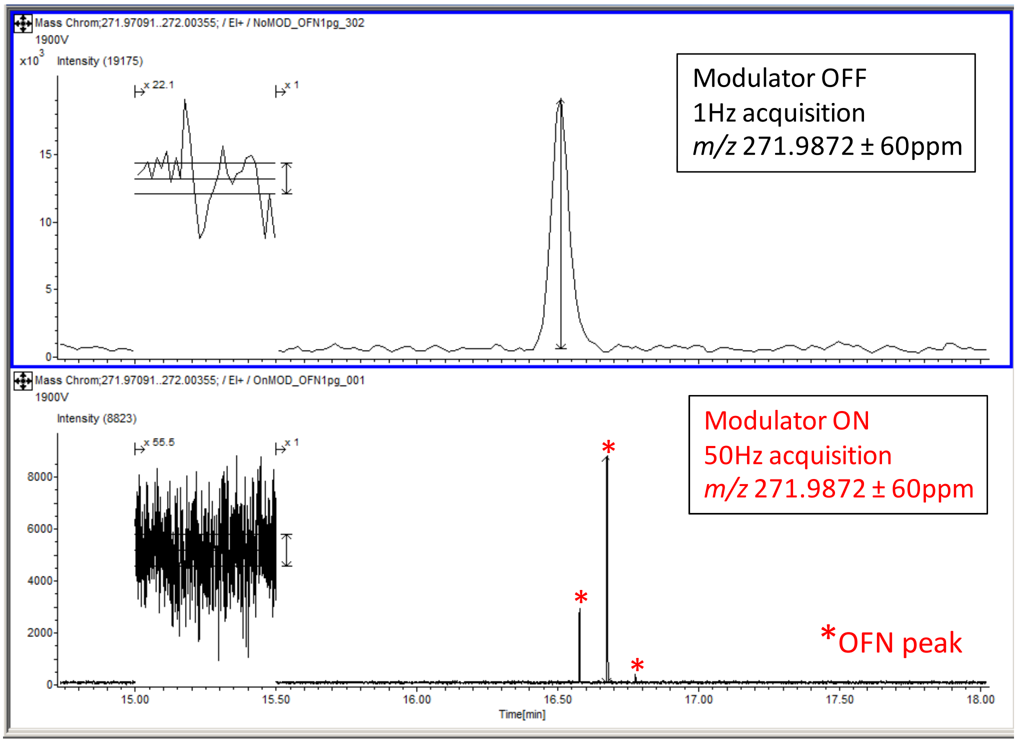
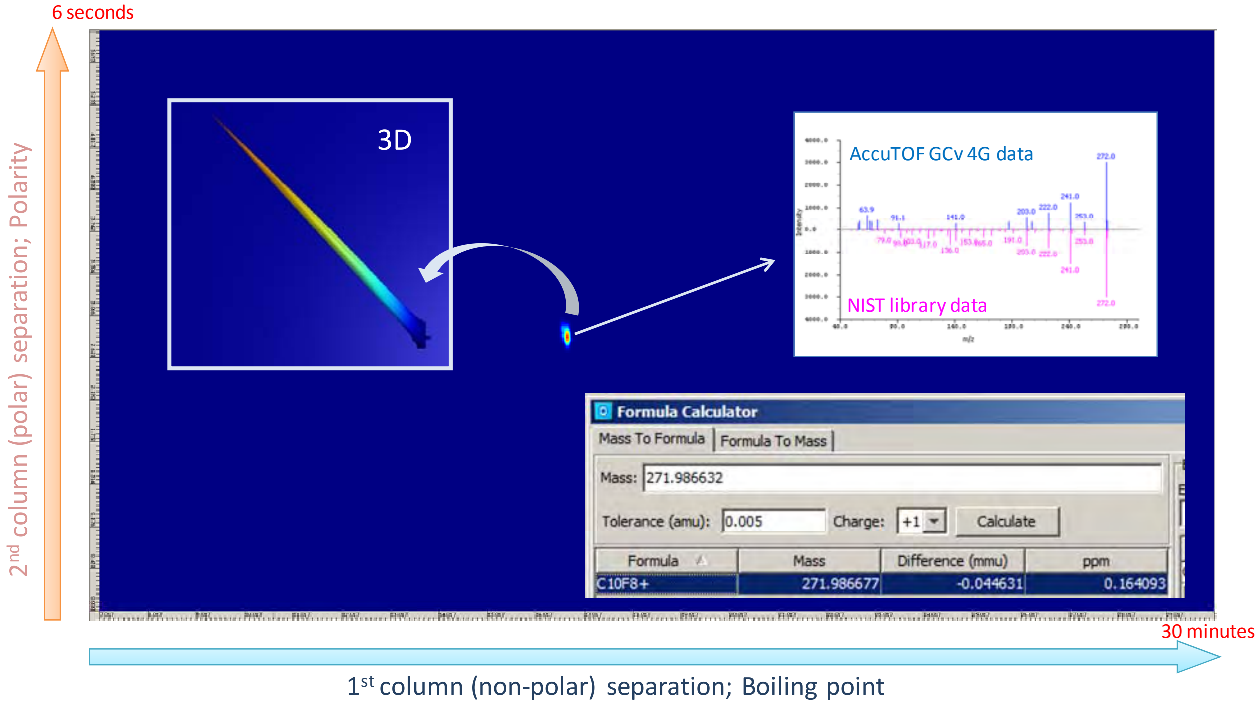


Figure 1. Mass chromatograms of OFN 1pg, Raw data, Mass windows: *m/z* 271.9872 ± 60ppm
Upper: modulator OFF, 1 Hz acquisition,
Lower: modulator ON, 50 Hz acquisition



Mass: 271.986632

Tolerance (amu): 0.005 Charge: +1

| Formula | Mass | Difference (mmu) | ppm |
|---|---|---|---|
| C10F8+ | 271.986677 | -0.044631 | 0.164093 |

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

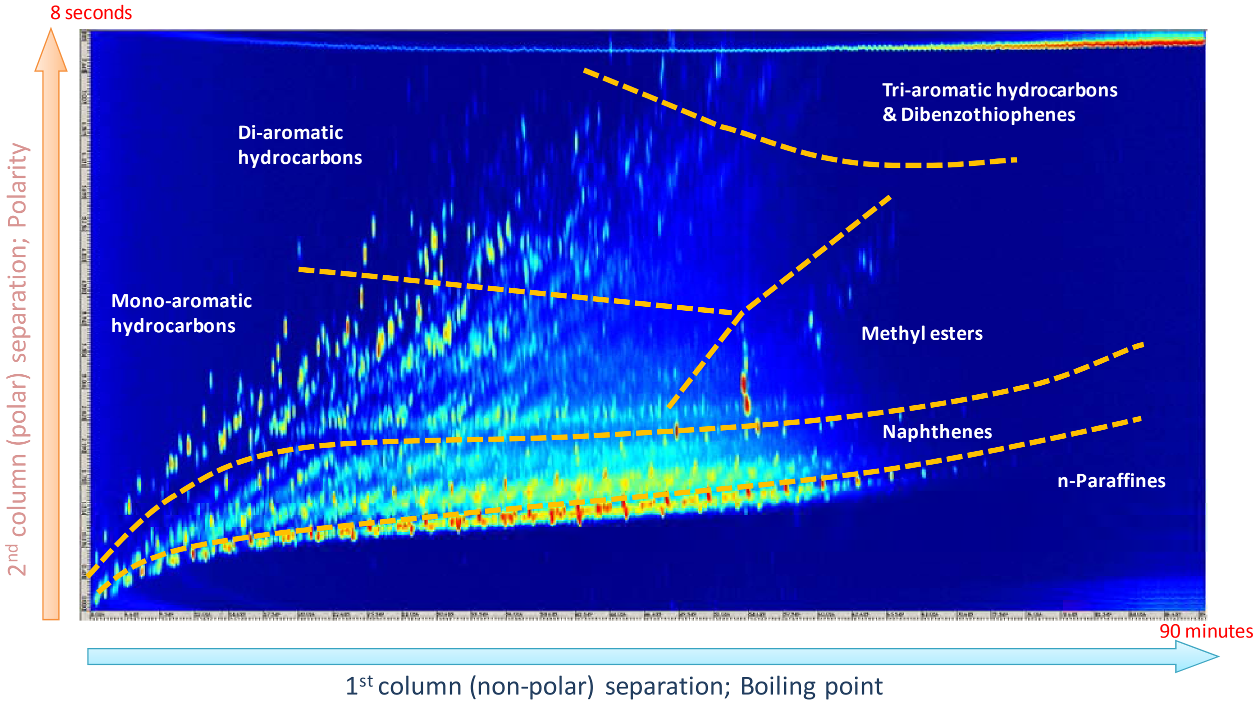


Figure 3. 2-dimensional TIC chromatogram for diesel fuel (50 Hz data acquisition).

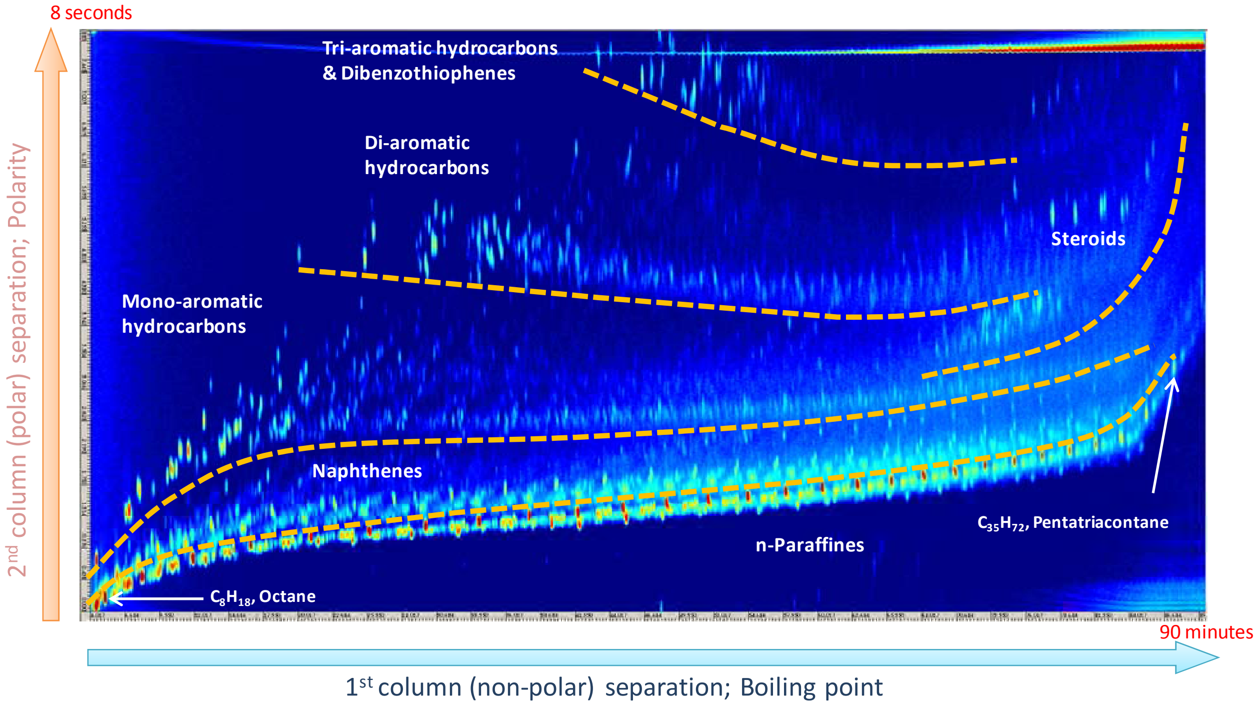


Figure 4. 2-dimensional TIC chromatogram for crude oil (50 Hz data acquisition).

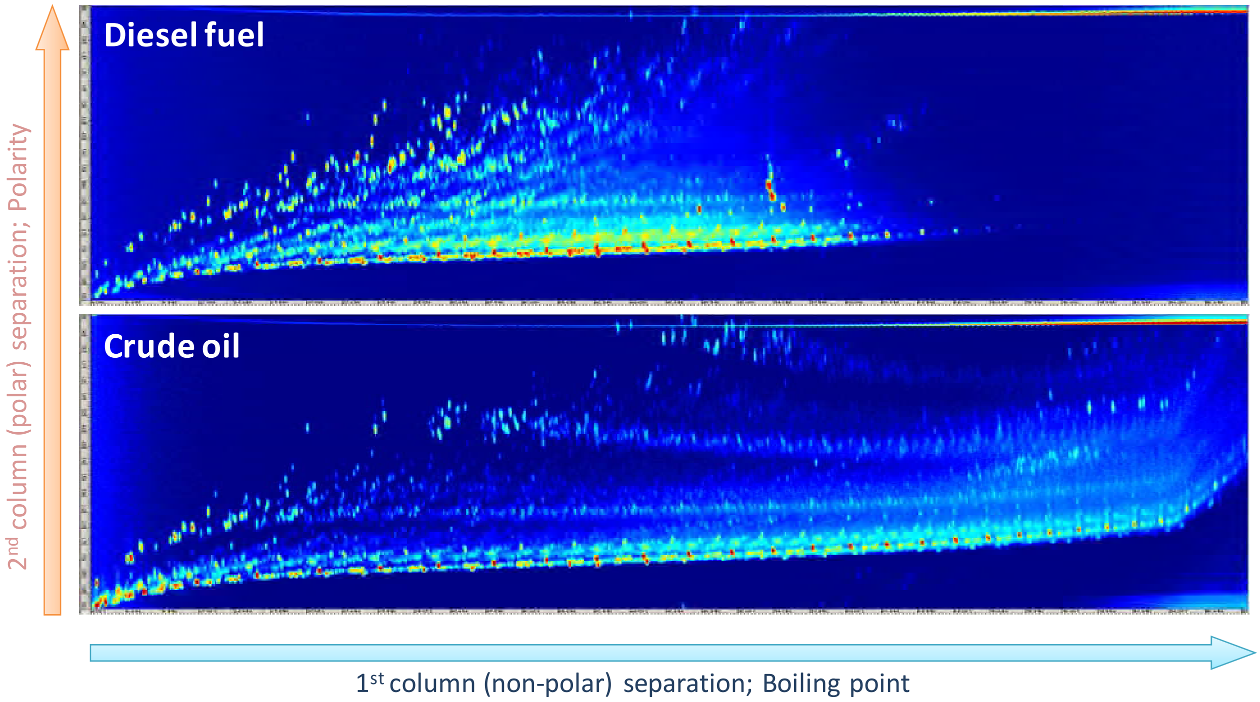


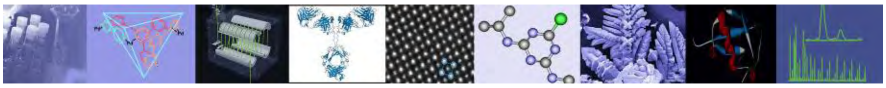
Figure 5. Comparing the 2-dimensional TIC chromatograms for diesel fuel and crude oil.

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.



Applications Note

# AccuTOF-GCv Series

## GC x GC/EI and GC x GC/FI Measurements Using the EI/FI Combination Ion Source

### Introduction

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

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. Also JEOL has developed a unique EI/FI combination ion source for this system which provides the capabilities of GC/EI and GC/FI 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.

In this work, we measured diesel fuel using both the GC x GC/EI and GC x GC/FI techniques on the AccuTOF GCv 4G.

### Experimental

Sample information and measurement conditions are shown in Table 1.

### Results

The GC x GC/EI and GC x GC/FI total ion chromatograms (TICs) for the diesel fuel sample are shown in Figures 1 and 2, respectively. Both chromatograms showed the presence of a wide variety of components in the sample.

Several EI and FI mass spectra for this sample are shown in Figure 3. The FI mass spectra (Right side) showed that the molecular ions were the dominant peaks observed in the mass spectra. Additionally, the mass accuracy was less than 2 mDa for the molecular ions measured by both EI and FI using the external one-point calibration method.

| Condition | GC x GC/EI | GC x GC/FI |
|---|---|---|
| Sample | Diesel Fuel | |
| Concentration | 1/100 (Hexane) | |
| GCxGC system | ZX2 thermal modulator (ZOEX) | |
| 1st column | Rxi-5SilMS, 30 m x 0.25 mm, 0.25 um | |
| 2nd column | Rxi-17SilMS, 2 m x 0.15 mm, 0.15 um | |
| Modulator | Deactivated fused silica, 1.5 m x 0.15 mm | |
| Modulator period | 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 | Split 10:1 | Splitless |
| Oven temp. | 5 0C(1 min) -> 3 C/min -> 300 C(6 min) | |
| GC-TOFMS system | AccuTOF GCv 4G (JEOL) | |
| Ion source | EI/FI combination | |
| Ionization mode | EI+ | FI+ |
| $m/z$ range | $m/z$ 35-500 | |
| Acquisition speed | 50Hz | 33Hz |
| External calibrant | $m/z$ 207.0329<br>($C_5H_{15}O_3Si_3^+$) | $m/z$ 226.2661<br>($C_{16}H_{34}^+$) |

Table 1. Measurement Conditions

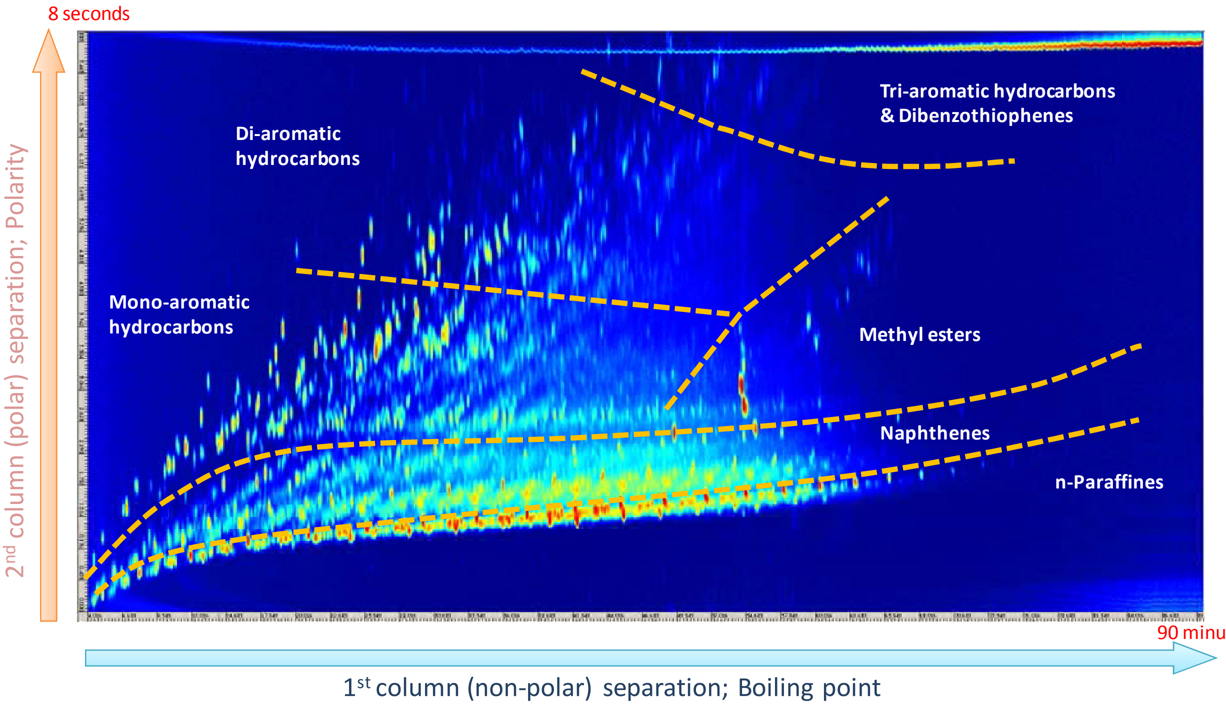


Figure 1. GCxGC/EI TIC for diesel fuel

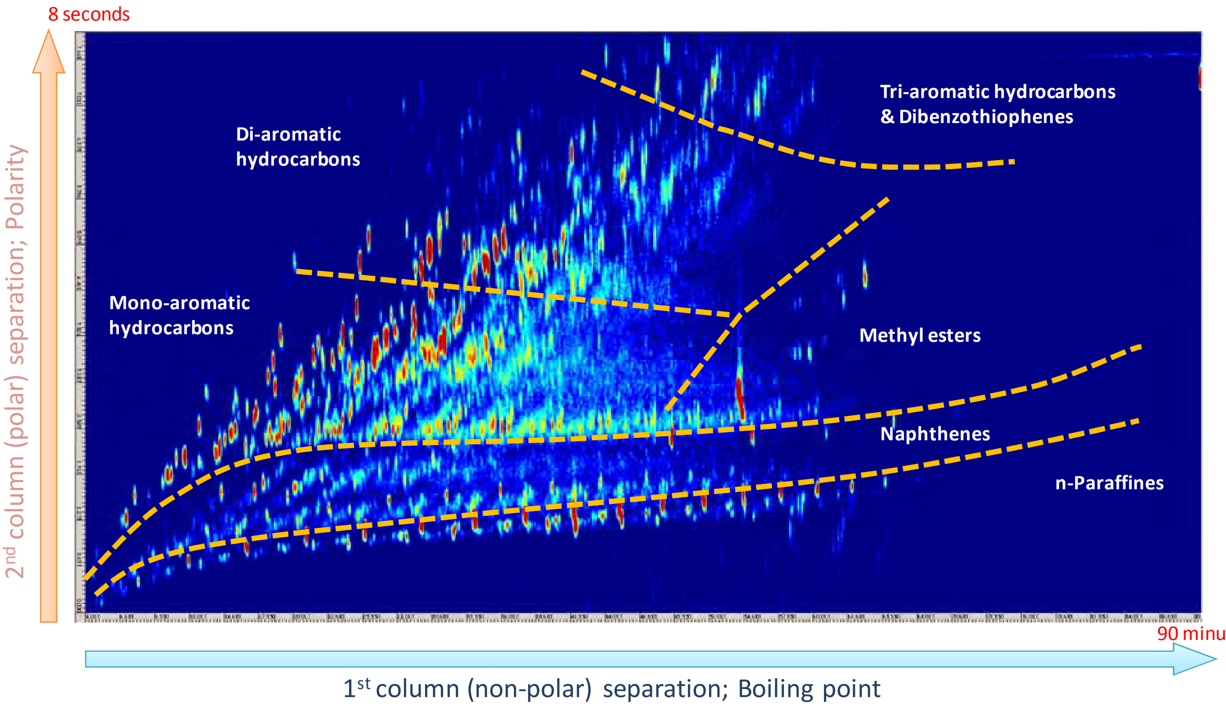
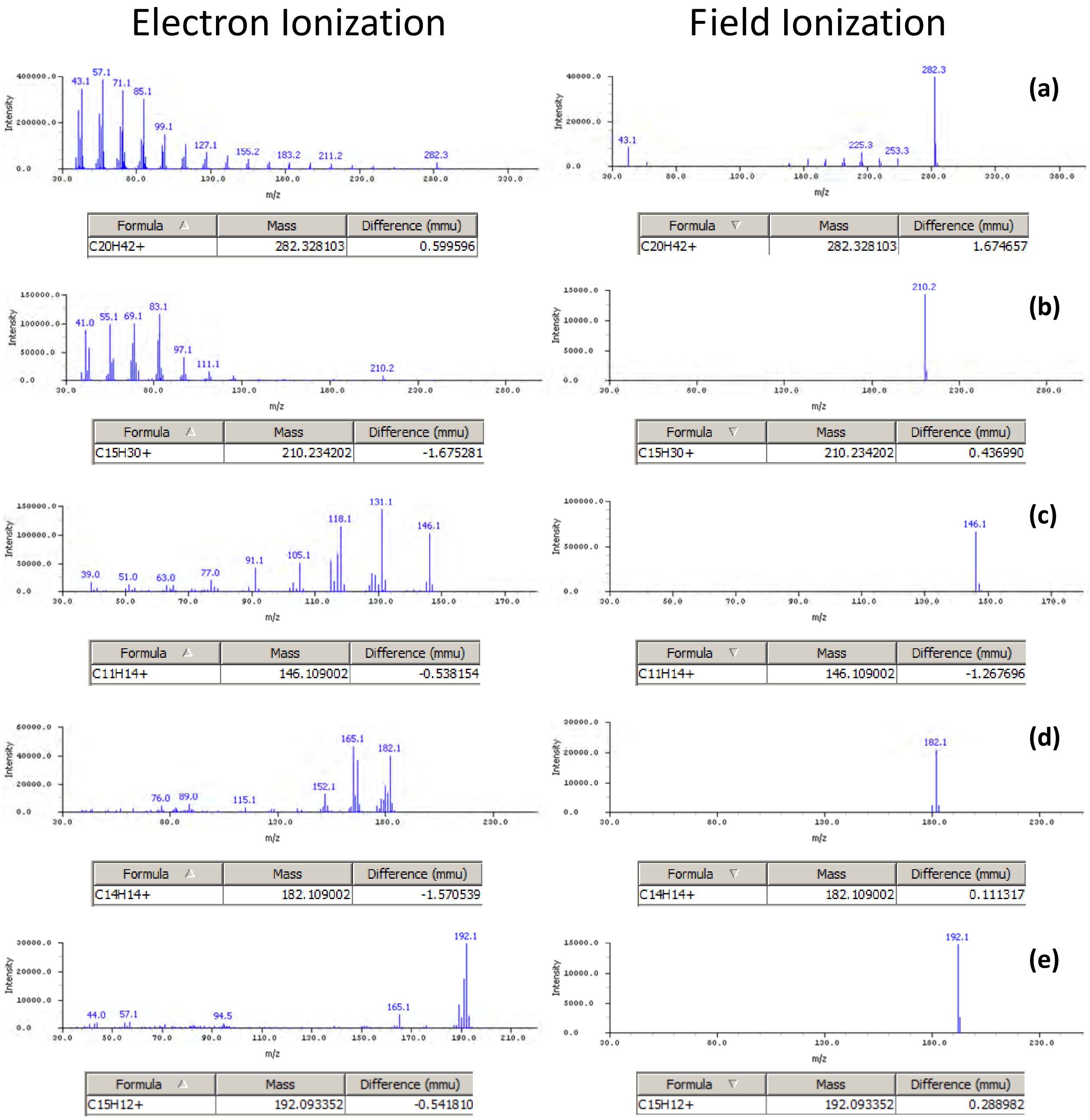


Figure 2. GCxGC/FI TIC for diesel fuel



| Formula | Mass | Difference (mmu) |
|---|---|---|
| C20H42+ | 282.328103 | 0.599596 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C20H42+ | 282.328103 | 1.674657 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C15H30+ | 210.234202 | -1.675281 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C15H30+ | 210.234202 | 0.436990 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C11H14+ | 146.109002 | -0.538154 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C11H14+ | 146.109002 | -1.267696 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C14H14+ | 182.109002 | -1.570539 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C14H14+ | 182.109002 | 0.111317 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C15H12+ | 192.093352 | -0.541810 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C15H12+ | 192.093352 | 0.288982 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C19H38O2+ | 298.286632 | -1.465507 |

| Formula | Mass | Difference (mmu) |
|---|---|---|
| C19H38O2+ | 298.286632 | 1.709336 |

Figure 3. EI and FI mass spectra for **(a)** n-parafin ($C_{20}H_{42}$), **(b)** naphthene ($C_{15}H_{30}$), **(c)** monoaromatic hydrocarbon ($C_{11}H_{14}$), **(d)** diaromatic hydrocarbon ($C_{14}H_{14}$), **(e)** triaromatic hydrocarbon ($C_{15}H_{12}$), **(f)** ethyl esters ($C_{19}H_{38}O_2$).

## Conclusion

The AccuTOF GCv 4G has a unique EI/FI combination ion source which does not require breaking vacuum in order to switch between each ionization mode. Consequently, this system was able to easily measure the GC x GC/EI and GC x GC/FI data for diesel fuel. The resulting data provided structural information for the chemical components using EI (hard ionization) and accurate mass molecular weight information using FI (soft ionization). The AccuTOF GCv 4G is a powerful tool for measuring both GC x GC/EI and GC x GC/FI mass spectra for very complex samples.

JEOL MS Data Sheet
MS Tips
Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.
No.055

# Qualitative analysis by comprehensive 2D GC / TOFMS [1]
## - Comparison of kerosene and diesel oil -

Comprehensive two-dimensional gas chromatography (GC x GC) is a kind of a continuous hard-cut GC system. Two different types of columns are connected via a modulator in the same GC oven. The GC x GC technique has a very high separating power compared to single GC. GC x GC systems requires a fast acquiring detection system, because the peak width in the GC chromatogram is very narrow. This requirement of very fast data acquisition is fully met in the AccuTOF-GC. Since the maximum spectrum recording interval on JEOL AccuTOF-GC is 25Hz (0.04sec), the system can successfully be used as detection system in combination with a GC x GC system.
This application note shows the results of kerosene and diesel oil by GC x GC-TOFMS.

<Sample and measurement conditions>

| | | |
|---|---|---|
| Sample | | kerosene and diesel oil |
| Measurement conditions | | |
| For GC×GC | | |
| | System: | Agilent 6890GC<br>ZOEX KT2004 |
| | Column: | 1$^{st}$: HP-1ms (30m × 0.25mm I.D., 0.25μm)<br>2$^{nd}$: DB-17 (2m × 0.1mm I.D., 0.1μm) |
| | Oven temp.: | 50C（1min） → 5C/min → 280C（6min） |
| | Injection temp.: | 280C |
| | Injection volume: | 0.5μl [Split mode (1:200)] |
| | Carrier gas: | He (Const. pressure: 680kPa) |
| | Trapping interval: | 6 sec |
| For MS | | |
| | MS: | JMS-T100GC “AccuTOF GC” |
| | Ionization method: | EI+（70eV, 300μA） |
| | Acquired m/z range: | m/z 35－500 |
| | Spectrum recording interval: | 0.04 sec (25Hz) |

<Results and discussion>

All the chromatograms were created by using GC Image software (ZOEX). The GC x GC chromatograms of kerosene and diesel oil are shown on Fig.1. The X axis corresponds with the separation by the 1$^{st}$ column on differences in boiling point and the Y axis corresponds with the separation by the 2$^{nd}$ column of differences in polarity. Also, the color in the chromatograms show the intensity of each peak. The intensity increases from light blue to yellow and red. Red color shows that the compound intensity is over the setting value of maximum intensity.

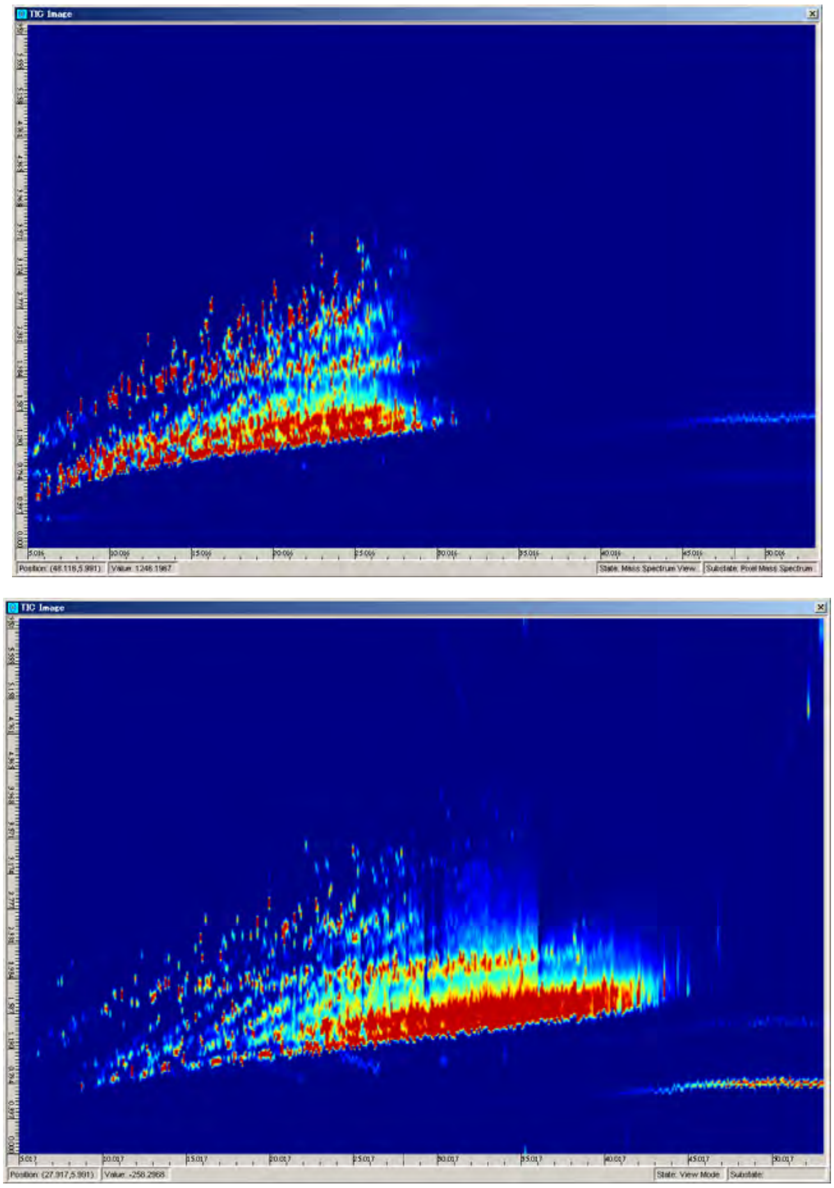


Fig.1 TICC by GC x GC (Top: kerosene, Bottom: diesel oil)

In general, kerosene is a mixture of C9 - C15 hydrocarbons and diesel oil is a mixture of C11 - C15 hydrocarbons. GC x GC chromatograms show that kerosene includes more low-boiling point compounds and diesel oil includes more high-boiling point compounds. In addition, GC x GC separates saturated hydrocarbons, unsaturated hydrocarbons, and aromatic hydrocarbons and so on by the difference of polarity.

The AccuTOF-GC has the capability of high speed spectrum recording to combine with GC x GC system. Furthermore, it is possible to have a good reliability with high sensitivity with high mass resolving power.

<Acknowledge>

This analysis was supported by Ms. Ieda and Dr. Ochiai, Gerstel K.K.

JEOL MS Data Sheet

MS Tips

No.056

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
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# Qualitative analysis by comprehensive 2D GC / TOFMS [2]

## - Analysis of polycyclic aromatic hydrocarbons in kerosene -

Comprehensive two-dimensional gas chromatography (GC x GC) is a kind of a continuous hard-cut GC system. Two different types of columns are connected via a modulator in the same GC oven. The GC x GC technique has a very high separating power compared to single GC. GC x GC systems requires a fast acquiring detection system, because the peak width in the GC chromatogram is very narrow. This requirement of very fast data acquisition is fully met in the AccuTOF-GC. Since the maximum spectrum recording interval on JEOL AccuTOF-GC is 25Hz (0.04sec), the system can successfully be used as detection system in combination with a GC x GC system.

This application note shows the results of the qualitative analysis for polycyclic aromatic hydrocarbons in kerosene by GC x GC-TOFMS.

<Sample and measurement conditions>

Sample kerosene

Measurement conditions

For GC×GC

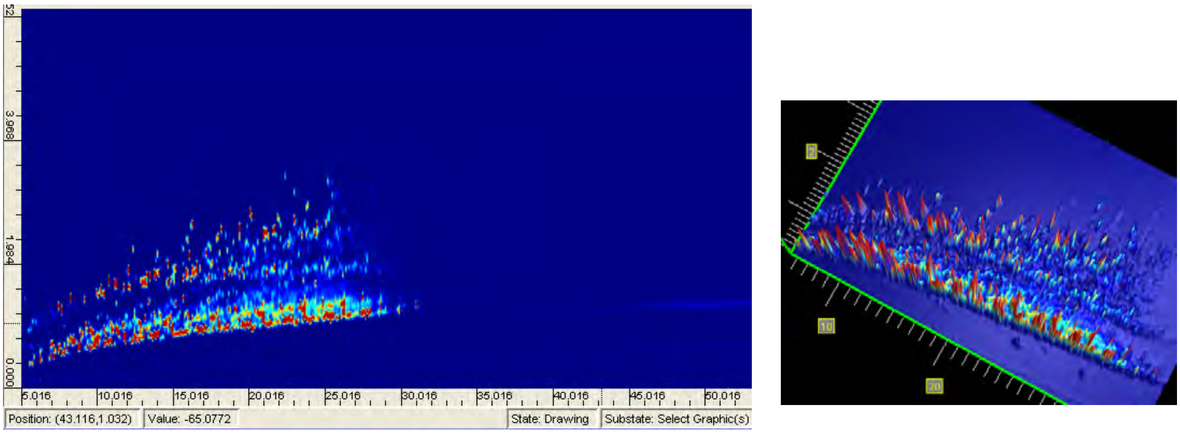
System: Agilent 6890GC
ZOEX KT2004
Column: 1st: HP-1ms (30m × 0.25mm I.D., 0.25μm)
2nd: DB-17 (2m × 0.1mm I.D., 0.1μm)
Oven temp.: 50C（1min） → 5C/min → 280C（6min）
Injection temp.: 280C
Injection volume: 0.5μl [Split mode (1:200)]
Carrier gas: He (Const. pressure: 680kPa)
Trapping interval: 6 sec

For MS

MS: JMS-T100GC “AccuTOF GC”
Ionization method: EI+（70eV, 300μA）
Acquired m/z range: m/z 35－500
Spectrum recording interval: 0.04 sec (25Hz)

<Results and discussion>

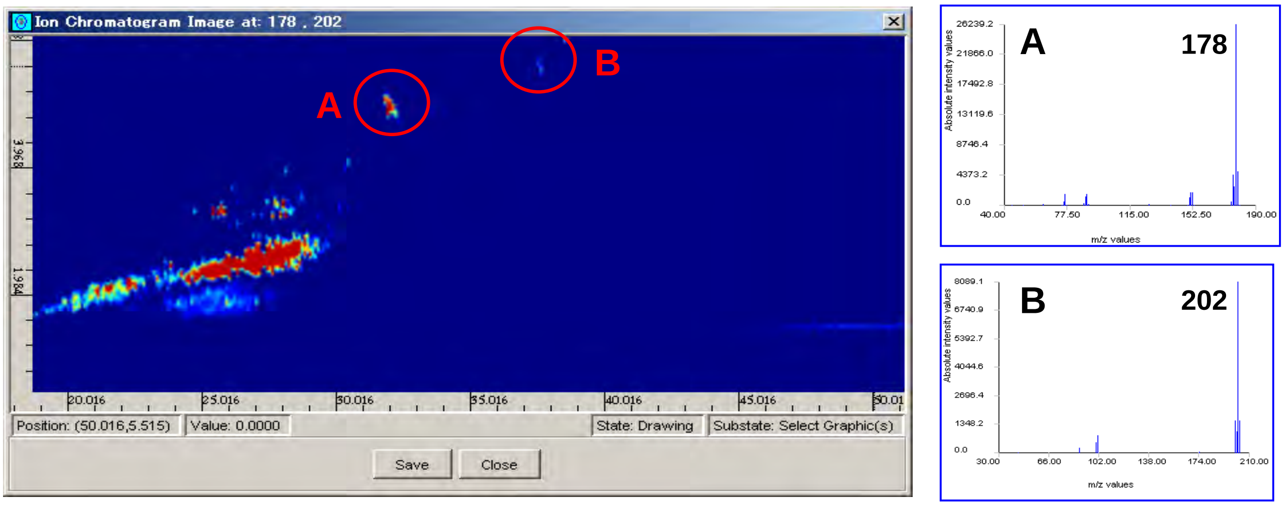
All the chromatograms were created by using GC Image software (ZOEX). The GC x GC chromatograms of kerosene and diesel oil are shown on Fig.1. The X axis corresponds with the separation by the 1st column on differences in boiling point and the Y axis corresponds with the separation by the 2nd column on differences in polarity. Also, the color in the chromatograms show the intensity of each peak The intensity increases from light blue to yellow and red. Red color shows that the compound intensity is over the setting value of maximum intensity.



Position: (43.116,1.032) Value: -65.0772 State: Drawing Substate: Select Graphic(s)

Fig.1 TICC of kerosene by GC x GC (Left: 2D image, Right: 3D image)

GC x GC can classify all of compounds in a series of saturated and unsaturated hydrocarbons. Fig.2 shows a GC x GC mass chromatogram of m/z 178 and 202 to identify tri-cyclic and tetra-cyclic aromatic hydrocarbons. Also, mass spectra of compound A and B are shown in Fig.2. Each spectrum is detected as anthracene (compound A) and pyrene (compound B).


Ion Chromatogram Image at: 178 , 202

Position: (50.016,5.515) Value: 0.0000 State: Drawing Substate: Select Graphic(s)

Fig.2 : GC x GC mass chromatogram of m/z 178 and 202 for polycyclic aromatic hydrocarbons and mass spectra of tri- and tetra-cyclic aromatic hydrocarbons.

The AccuTOF-GC has the capability of high speed spectrum recording to combine with GC x GC system. Furthermore, it is possible to have a good reliability with high sensitivity with high mass resolving power. Also GC x GC-AccuTOF can obtain very useful information of substances in more complicated samples such as petroleum products, perfume and environmental pollutant.

<Acknowledge>

This analysis was supported by Ms. Ieda and Dr. Ochiai, Gerstel K.K.

Zoex’s GC x GC system is provided and supported through Zoex’s sales and support network and may not be available in your territory. Contact your local JEOL representative for detail.

JEOL MS Data Sheet

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# MS Tips

No.057

# Qualitative analysis by comprehensive 2D GC / TOFMS [3]
## - Analysis of sulfur-contained substances in diesel oil -

Comprehensive two-dimensional gas chromatography (GC x GC) is a kind of a continuous hard-cut GC system. Two different types of columns are connected via a modulator in the same GC oven. The GC x GC technique has a very high separating power compared to single GC. GC x GC systems requires a fast acquiring detection system, because the peak width in the GC chromatogram is very narrow. This requirement of very fast data acquisition is fully met in the AccuTOF-GC. Since the maximum spectrum recording interval on JEOL AccuTOF-GC is 25Hz (0.04sec), the system can successfully be used as detection system in combination with a GC x GC system.

This application note shows the results of the qualitative analysis for sulfur-containing substances in diesel oil by GC x GC-TOFMS.

<Sample and measurement conditions>

| | |
|---|---|
| Sample | diesel oil |

Measurement conditions

For GC×GC

| | |
|---|---|
| System: | Agilent 6890GC<br>ZOEX KT2004 |
| Column: | 1st: HP-1ms (30m × 0.25mm I.D., 0.25μm)<br>2nd: DB-17 (2m × 0.1mm I.D., 0.1μm) |
| Oven temp.: | 50C（1min） → 5C/min → 280C（6min） |
| Injection temp.: | 280C |
| Injection volume: | 0.5μl [Split mode (1:200)] |
| Carrier gas: | He (Const. pressure: 680kPa) |
| Trapping interval: | 6 sec |

For MS

| | |
|---|---|
| MS: | JMS-T100GC “AccuTOF GC” |
| Ionization method: | EI+（70eV, 300μA） |
| Acquired m/z range: | m/z 35－500 |
| Spectrum recording interval: | 0.04 sec (25Hz) |

<Results and discussion>

GC x GC mass chromatogram of m/z 184, 198 and 212 shown in Fig 1, which are the molecular ions of dibenzothiphenes are created by ZOEX GC Image software. In addition, mass spectra for compound A, B and C are shown in Fig.2.

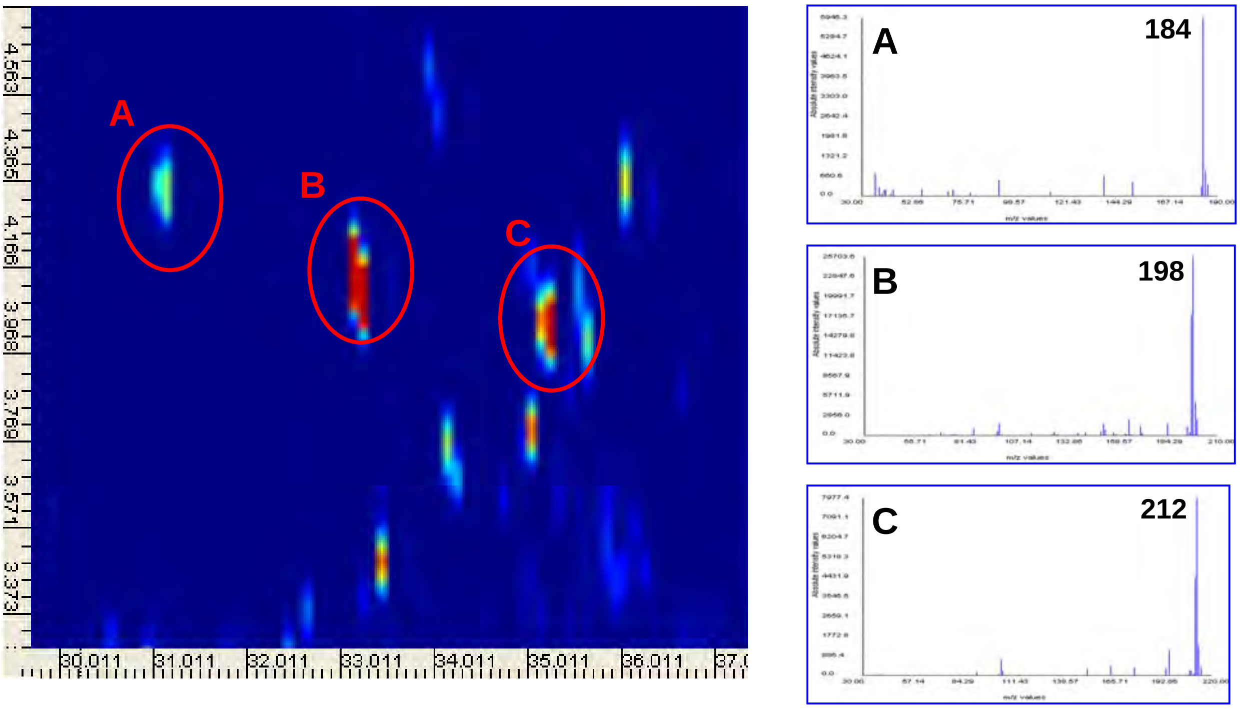

Fig.1 GC x GC mass chromatogram of m/z 184, 198 and 212 (Left) and mass spectra for compound A, B and C (Right)

Compound A, B and C are confirmed as sulfur-containing substances due to the isotopic pattern. The elemental composition of those ions is determined by accurate mass by using 1 point internal calibration using anthracene ($M^+$: m/z178.0783) present in the sample. Each estimated elemental composition is shown in Table.1.

Table 1 The result of elemental composition determination for M+ and ion of m/z152

| Substance | Cal. mass | Obs. mass | Diff. (mDa) | Formula |
|---|---|---|---|---|
| Dibenzothiophene | 184.0347 | 184.0343 | -0.4 | $C_{12}H_8S$ |
| | 152.0626 | 152.0619 | -0.7 | $C_{12}H_8$ |
| 3-Methyldibenzothiophene | 198.0503 | 198.0495 | -0.8 | $C_{13}H_{10}S$ |
| | 152.0626 | 152.0620 | -0.6 | $C_{12}H_8$ |
| 2,8-Dimethyldibenzothiophene | 212.0660 | 212.0654 | -0.6 | $C_{14}H_{12}S$ |
| | 152.0626 | 152.0622 | -0.4 | $C_{12}H_8$ |

The proposed formula is the same as the formula of dibenzothiophens and the mass difference of the molecular ion and the fragment ions from the exact mass, is within 1 mDa.

The AccuTOF GC has the capability of high speed spectrum recording to combine with a GC x GC system. In this way, GC x GC-AccuTOF GC can perform very reliable qualitative analysis.

<Acknowledge>

This analysis was supported by Ms. Ieda and Dr. Ochiai, Gerstel K.K..

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JEOL MS Data Sheet

MS Tips

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No.154

*JMS-T100GCV Application Data*

# Analysis of diesel oil by using GC x GC-HRTOFMS (FI) with 2 different sets of column combinations

## [Introduction]

Comprehensive two-dimensional gas chromatography (GC x GC) is a kind of a continuous hard-cut GC system. Two different types of columns are connected via a modulator in the same GC oven. GC x GC shows a very high separating power compared to single GC.

This report shows the difference of separation result for diesel oil when 2 different sets of combined columns are used with GCxGC-HRTOFMS (FI).

## [Sample and method]

Sample: diesel oil
Method: see Table 1

## [Result and discussion]

Fig.1 shows 2 TIC chromatograms. Upper TICC is the result by using a normal column set (1st column: non-polar column, 2nd column: polar column) for general GCxGC analysis. Lower TIC is the result by using reverse column set (1st column: polar column, 2nd column: non-polar column).

Some of components such as n-paraffins, naphthenes and aromatic hydrocarbons could be separated based on a different polarity because 2nd column in normal column set was a polar column. However, since the polarity between monocyclic and polycyclic naphthenes is not so different, the separation of these compounds was not enough due to the use of a very short 2nd column (ca. 2m).

On the other hand, when the reverse column set was used, some of components such as n-paraffins, monocyclic and polycyclic naphthenes, monocyclic and polycyclic hydrocarbons could be separated by the difference in boiling point because non-polar column was used as 2nd column. The reverse column set had a better performance to separate monocyclic and polycyclic naphthenes compared to the normal column set because of the differences in boiling point. This result shows that the normal column set is suitable to separate aromatic compounds and the reverse column set is suitable to separate naphthenes.

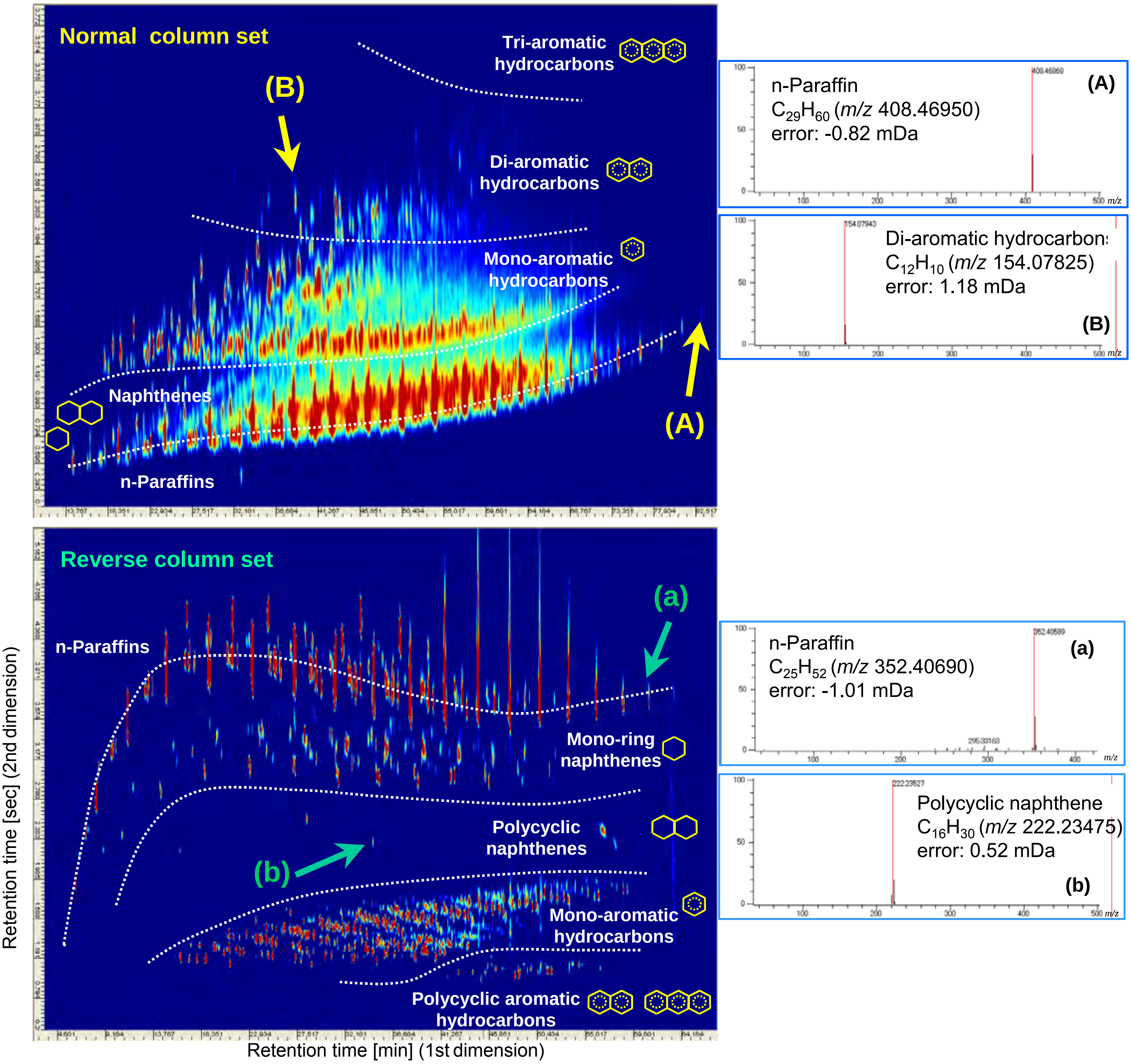

Fig.1 2-dimentional TIC chromatograms and FI mass spectra

In addition, only molecular ions were observed in mass spectra due to use of FI. It is sometimes difficult to confirm molecular ions of hydrocarbons by EI. But, it was very easy to confirm molecular ions of hydrocarbons.with FI. The mass accuracy of molecular ions was less than 1.2 mDa.

As this report shows, FI could be used with the GC x GC method on the JMS-T100GCV due to both high sensitivity and high speed acquisition. Also, it is possible to do highly-detailed qualitative analysis by using high mass accuracy with GC x GC separation.

## [Acknowledgement]

This analysis was supported by Ms. T. Ieda of GERSTEL K.K., Japan.

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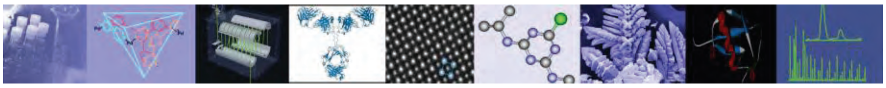


Applications Note

# AccuTOF-GCv Series

## Diesel Fuel Classification Analysis Using GC x GC/FI and Kendrick Mass Defect Plots

### Introduction

Comprehensive two-dimensional gas chromatography (GC x GC) in combination with high-resolution mass spectrometry is a powerful tool for the analysis of complex mixtures.

In this work, we analyzed a diesel fuel sample by using GC x GC in combination with a new high-resolution time-of-flight mass spectrometer (HR-TOFMS) . Field ionization (FI) produced molecular ions for all components and exact mass measurements were used to obtain elemental compositions. A traditional Kendrick Mass Defect (KMD) plot was used to identify hydrocarbon groups in the diesel fuel sample.

### Experimental

A commercially available diesel fuel sample was analyzed with the JEOL JMS-T100GCV "AccuTOF GCv 4G" equipped with a Zoex ZX2 thermal modulator and experimental GC Image software (version 2.5.0a2).

*Figure 1. JMS-T100GCV "AccuTOF GCv 4G" GC x GC/HR-TOFMS system*

| Condition | GC x GC/FI |
|---|---|
| Sample | Diesel Fuel |
| Concentration | 1/100 (Hexane) |
| GCxGC system | ZX2 thermal modulator (ZOEX) |
| 1st column | Rxi-5SilMS, 30 m x 0.25 mm, 0.25 µm |
| 2nd column | Rxi-17SilMS, 2 m x 0.15 mm, 0.15 µm |
| Modulation loop | Deactivated fused silica, 1.5 m x 0.15 mm |
| Modulation period | 10 sec |
| Hot jet temp. | 270 °C |
| Inlet pressure | 200 kPa at Oven temp. 50 °C<br>(Constant flow mode) |
| Inlet temp. | 280 °C |
| Inlet mode | Splitless |
| Oven temp. | 50 °C (1 min) -> 3 °C/min -> 280 °C (0.3 min) |
| GC-TOFMS system | AccuTOF GCv 4G (JEOL) |
| Ion source | EI/FI/FD combination |
| Ionization mode | FI+ |
| *m/z* range | *m/z* 35-500 |
| Acquisition speed | 33 spectra/sec |
| Software | GC Image$^{TM}$ Version 2.5.0a2 |

*Table 1. Measurement conditions.*

### Results

The Kendrick mass scale that defines the mass of $CH_2$ as exactly 14.0000 is used to identify families of compounds that differ only by the length of alkyl substituents. The Kendrick mass is calculated as follows:

***Kendrick Mass = IUPAC mass x (14.00000/14.01565)***

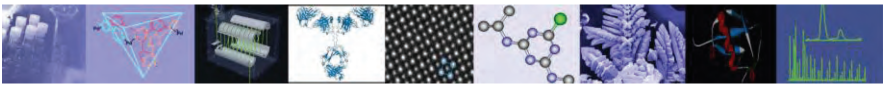
The Kendrick Mass Defect (KMD) is the difference between nominal Kendrick mass and exact Kendrick mass. The KMD is defined as follows on the GC Image software:

***Kendrick Mass Defect (KMD) = Kendrick Mass - nominal Kendrick Mass***

In a KMD plot, the Kendrick mass is used for the X-axis and KMD is used for the Y-axis. From left-to-right, the numbers of $CH_2$units in the observed ions increase. From top-to-bottom, the differences in chemical formula such as the degree of unsaturation, oxidation, etc., increase. Families of homologous compounds are easily recognized in the KMD plot. A KMD plot was created for the composite mass spectrum created by summing all mass spectra in the GC x GC/FI analysis of the diesel fuel sample (Figure 2). Selected ion current chromatograms (Figure 3) were created for compound families shown in Figure 2c.

In conclusion, Kendrick Mass Defect plots are a powerful tool for data analysis when combined with GC x GC/FI and high-resolution mass spectra measured with the JEOL AccuTOF GCv 4G system.

MS-040814



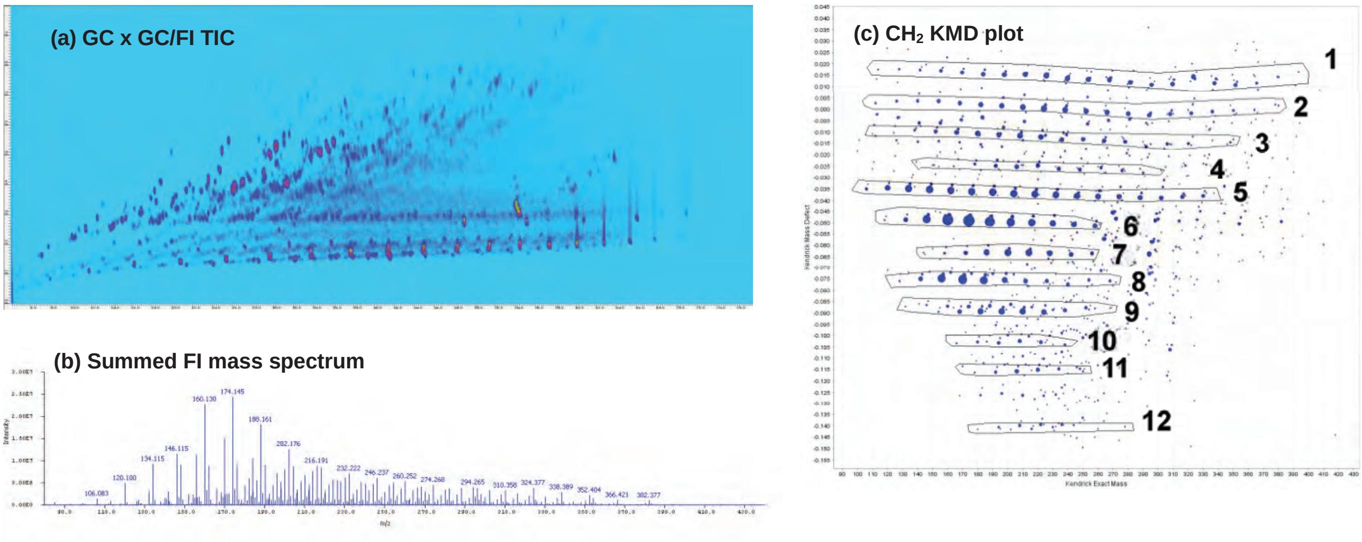


*Figure 2. (a) 2-dimensional TIC chromatogram of the diesel sample, (b) the summed FI mass spectrum for the entire retention time region, (c) $CH_2$ Kendrick Mass Defect plot for the summed FI mass spectrum*

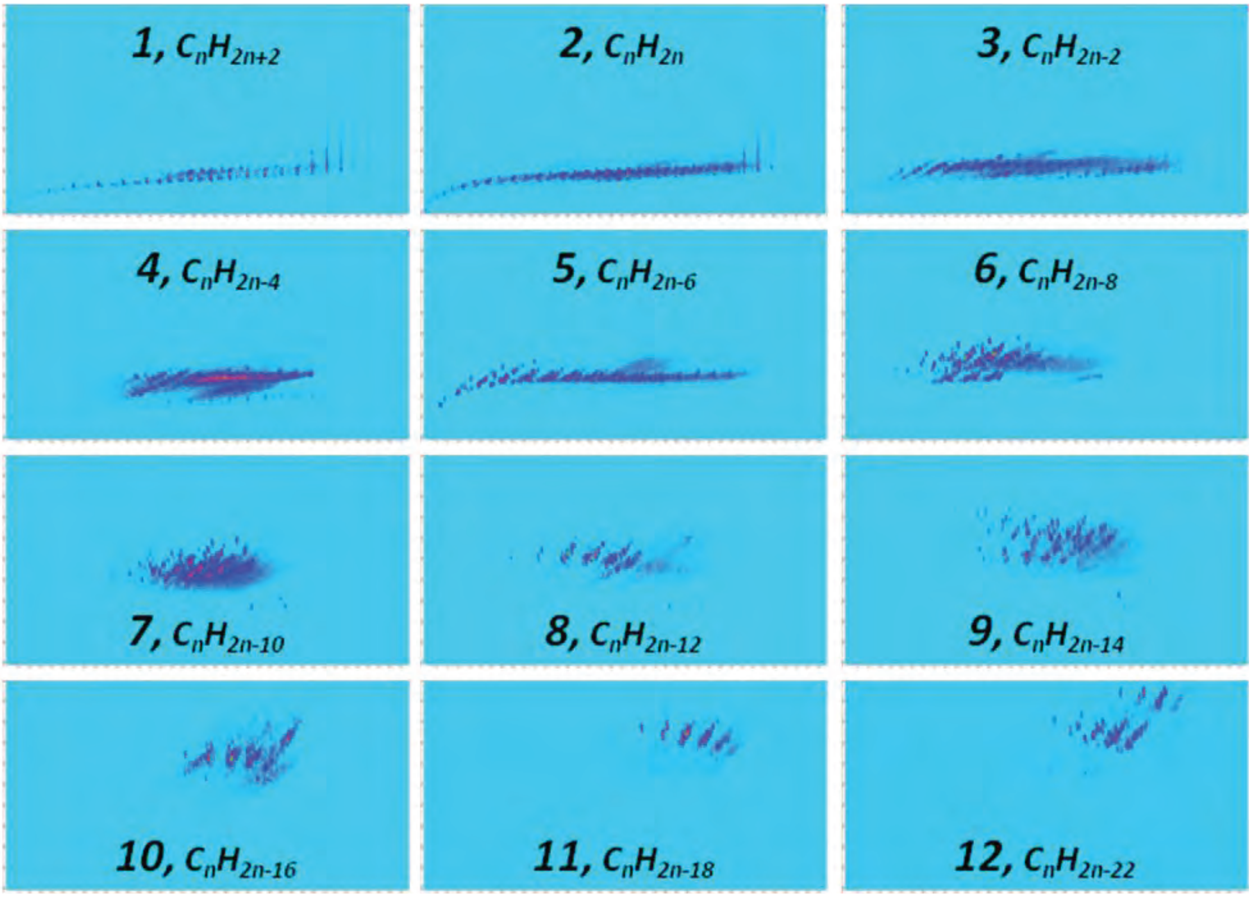


*Figure 3. 2-dimensional SIC chromatograms using Kendrick m/z (in Figure 2) ± 0.015u*

*JEOL MS Data Sheet*

**MS Tips**

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

**No.058**

# Accurate mass measurement of lube oil by GC/FI-TOFMS

FD (Field Desorption) and FI (Field Ionization) are ionization techniques based on the tunneling effect that is induced in high electric potential fields. When a sample is applied on the emitter in advance, it is called FD. On the other hand, it is called FI when a vaporized sample is introduced to the emitter.

FD and FI produces molecular ions easily and very few fragment ions. For this reason, FI is a very useful ionization method for samples which hardly produce molecular ions by EI (Electron Ionization), such as oil.

This application note shows the result of a commercial lube oil by GC/FI and the elemental composition determination by FI.

## <Sample and measurement conditions>

Sample lube oil

Measurement conditions

For GC

| | |
|---|---|
| GC: | Agilent 6890N |
| Column: | DB-5 (30m x 0.32 mm I.D., 0.25μm) |
| Oven temp.: | 50C → 15C/min → 320C (2min) |
| Injection temp.: | 280C |
| Injection amount: | 1.0 μL [Split mode (1:200)] |
| Carrier gas: | He (Const. flow mode: 1mL/min) |

For MS

| | |
|---|---|
| MS: | JMS-T100GC “AccuTOF GC” |
| Ionization method: | FI (Cathode volt.: -10kV, Emitter current: 0mA) |
| Spectrum recording interval: | 0.4 sec |

## <Result and discussion>

This sample was analyzed by GC/EI and hydrocarbons and fatty acid esters were determined.

Fig.1 shows TICC of lube oil by GC/FI. Hydrocarbons and fatty acid esters were observed in this TICC.

As an example, a mass spectrum of C13 hydrocarbon is shown in Fig.1. Only molecular ions are produced by FI. Since an exact mass of this molecular ion is known as 184.2191 ($C_{13}H_{28}$), this ion was used as internal calibrant in order to determine the elemental composition of other ions (peak1, 2, 3 and 4). The result of the elemental composition determination for other ions is shown in Table 1.

The accurate mass for all of molecular ions of peak 1, 2, 3 and 4 is within 2mDa from the exact mass.

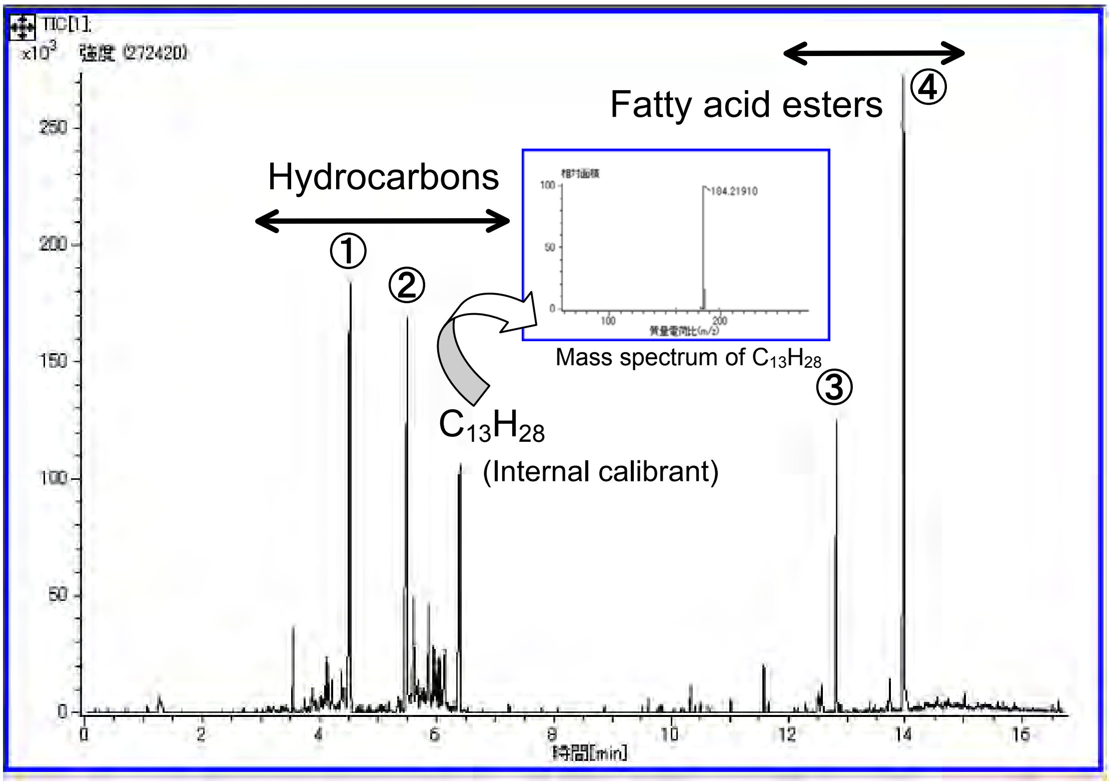


Fig.1 TICC of lube oil

Table 1 The result of elemental composition determination by GC/FI

| | Cal. m/z | Obs. m/z | Diff.(mDa) | Formula |
|---|---|---|---|---|
| 1 | 156.1878 | 156.1868 | -1.0 | $C_{11}H_{24}$ |
| 2 | 170.2034 | 170.2030 | -0.4 | $C_{12}H_{26}$ |
| 3 | 312.3028 | 312.3046 | +1.8 | $C_{20}H_{40}O_2$ |
| 4 | 340.3341 | 340.3356 | +1.5 | $C_{22}H_{44}O_2$ |

JMS-T100GC “AccuTOF GC” has essentially capabilities of high mass accuracy and very small systematic mass error. For this reason, AccuTOF GC can get accurate mass with single point internal calibrant by any kind of ionization method even by FI. Therefore, it is possible to perform elemental composition analysis with high reliability.

JEOL MS Data Sheet
MS Tips
Mass Spectrometry Application Group
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No.071

# Group-type analysis of Crude Oil using GC/FI-TOFMS 1

## ~Determination of average molecular weights by group-type analysis~

### Introduction

Field Desorption (FD) and Field Ionization (FI) are ionizing analytes by electron tunneling from analyte molecules to the solid surface (emitter) in a high electric field. In case of FD, the sample is applied on the emitter and heated by applying an electric current through the emitter for desorption and ionization. In the case of FI, vaporized analyte molecules are introduced to the proximity of the emitter.

FI is a soft ionization method that yields intact molecular ions and in most cases, with very few fragment ions. It was used to ionize analytes that are easy to fragment and where molecular ions are difficult to be detected, such as hydrocarbons in crude oil.

For complex mixtures such as crude oil or synthetic polymers, molar mass distributions and average molecular weights are important chemical properties. By analyzing a FI mass spectrum, mostly consisting of molecular ions of complex hydrocarbon mixture, and using a group-type analysis software, one can obtain molar mass distributions and average molecular weights of the various hydrocarbon types (e.g., paraffin, naphthene, olefin, aromatics) in the mixture.

We have analyzed a crude oil sample by GC/FI method using JMS-T100GC "AccuTOF GC" and processed the obtained data using a group-type analysis software.

### Methods

Sample Crude Oil
(Refer Fig. 1 for preparation)

Analysis conditions

GC conditions

| | |
|---|---|
| GC: | Agilent 6890N |
| Column: | DB-5ms<br>30 m x 0.25 mm I.D., 0.25 μm |
| Oven: | 50°C→15°C/min→280°C (5 min) |
| Injection port: | 280 °C, Split (1:200) |
| Injection volume: | 1.0 μl |
| Career gas: | He (1 mL/min, constant flow mode) |

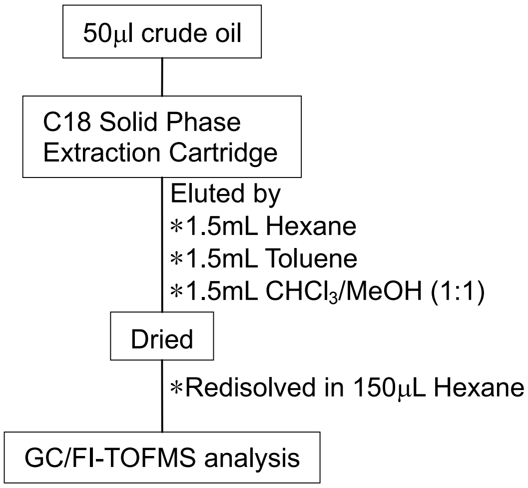


Fig. 1 Sample preparation flow

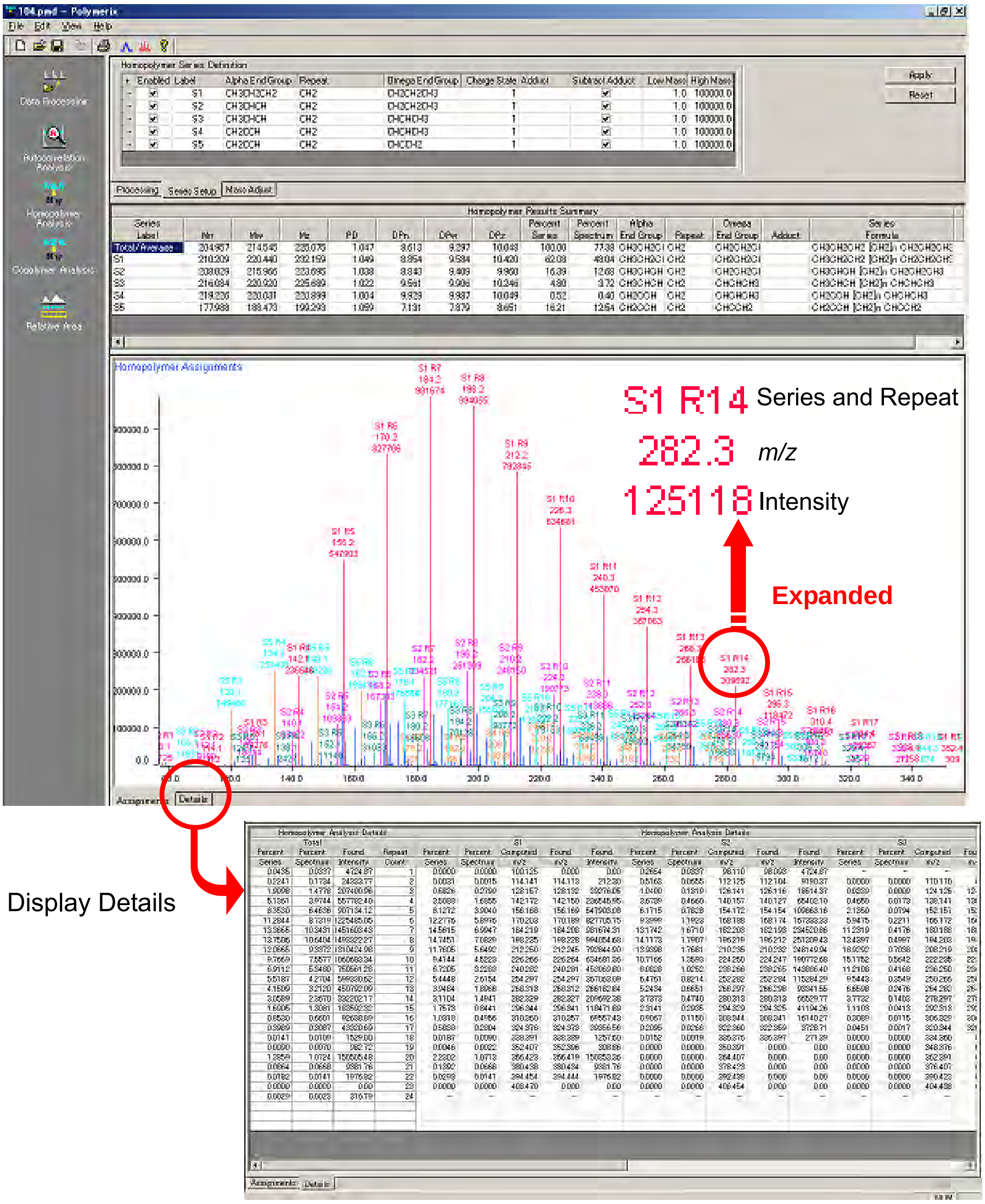
MS conditions

| | |
|---|---|
| MS: | JMS-T100GC "AccuTOF GC" |
| Ionization: | FI+ (Cathode voltage: -10 kV, Emitter current: 0 mA) |
| Mass range: | *m/z* 35 - 500 |
| Acquisition rate: | 0.3 s/spectrum |

Software Polymerix™ (Sierra Analytics, Inc.)

## Results and Discussion

The output from the group-type analysis software Polymerix™ (Sierra Analytics, Inc., http://massspec.com/) is shown in Fig. 2.



Homopolymer Series Definition

| + | Enabled | Label | Alpha End Group | Repeat | Omega End Group | Charge State | Adduct | Subtract Adduct | Low Mass | High Mass |
|---|---|---|---|---|---|---|---|---|---|---|
| - | ☑ | S1 | CH3CH2CH2 | CH2 | CH2CH2CH3 | 1 | | ☑ | 1.0 | 100000.0 |
| - | ☑ | S2 | CH3CHCH | CH2 | CH2CH2CH3 | 1 | | ☑ | 1.0 | 100000.0 |
| - | ☑ | S3 | CH3CHCH | CH2 | CHCHCH3 | 1 | | ☑ | 1.0 | 100000.0 |
| - | ☑ | S4 | CH2CCH | CH2 | CHCHCH3 | 1 | | ☑ | 1.0 | 100000.0 |
| - | ☑ | S5 | CH2CCH | CH2 | CHCCH2 | 1 | | ☑ | 1.0 | 100000.0 |

Homopolymer Results Summary

| Series Label | Mn | Mw | Mz | PD | DPn | DPw | DPz | Percent Series | Percent Spectrum | Alpha End Group | Repeat | Omega End Group | Adduct | Series Formula |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Total/Average | 204.957 | 214.545 | 225.075 | 1.047 | 8.613 | 9.297 | 10.048 | 100.00 | 77.38 | CH3CH2C | CH2 | CH2CH2C | | CH3CH2CH2 [CH2]n CH2CH2C |
| S1 | 210.209 | 220.440 | 232.159 | 1.049 | 8.954 | 9.584 | 10.420 | 62.08 | 48.04 | CH3CH2C | CH2 | CH2CH2C | | CH3CH2CH2 [CH2]n CH2CH2C |
| S2 | 208.029 | 215.966 | 223.695 | 1.038 | 8.840 | 9.409 | 9.960 | 16.39 | 12.68 | CH3CHCH | CH2 | CH2CH2C | | CH3CHCH [CH2]n CH2CH2CH3 |
| S3 | 216.084 | 220.920 | 225.689 | 1.022 | 9.561 | 9.906 | 10.246 | 4.80 | 3.72 | CH3CHCH | CH2 | CHCHCH3 | | CH3CHCH [CH2]n CHCHCH3 |
| S4 | 219.236 | 220.031 | 220.899 | 1.004 | 9.929 | 9.987 | 10.049 | 0.52 | 0.40 | CH2CCH | CH2 | CHCHCH3 | | CH2CCH [CH2]n CHCHCH3 |
| S5 | 177.988 | 188.473 | 199.293 | 1.059 | 7.131 | 7.879 | 8.651 | 16.21 | 12.54 | CH2CCH | CH2 | CHCCH2 | | CH2CCH [CH2]n CHCCH2 |

- Specify α and γ end groups and repeating unit.
- Perform group-type analysis.
- Results such as $M_n$, $M_w$, $M_z$, and polydispersity for each series are displayed.
- Mass spectral peaks are color coded based on the series to which they belong.

Fig. 2 The group-type analysis results of the Crude Oil

The data acquired by the AccuTOF GC was directly read into the Polymerix™ software. All the mass spectra acquired during the retention time range of the sample were summed to form a single mass spectrum and then processed. Properties such as number average molecular weight ($M_n$), weight average molecular weight ($M_w$), z average molecular weight ($M_z$), and polydispersity (PD) were calculated for 5 hydrocarbon types with the degree of unsaturation from 0 to 4 and for the total/average of the 5 types.

Group-type analysis of complex hydrocarbon mixtures such as crude oil can be easily performed by using GC/FI method on the AccuTOF GC and Polymerix™ group-type analysis software.

*JEOL MS Data Sheet*

**MS Tips**

Mass Spectrometry Application Group
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*No.072*

# Group-type analysis of Crude Oil using GC/FI-TOFMS 2

## ~Reproducibility of group-type analysis results~

## Introduction

Field Desorption (FD) and Field Ionization (FI) are ionizing analytes by electron tunneling from analyte molecules to the solid surface (emitter) in a high electric field. In case of FD, the sample is applied on the emitter and heated by applying an electric current through the emitter for desorption and ionization. In the case of FI, vaporized analyte molecules are introduced to the proximity of the emitter.

FI is a soft ionization method that yields intact molecular ions and in most cases, with very few fragment ions. It was used to ionize analytes that are easy to fragment and were molecular ions are difficult to be detected, such as hydrocarbons in crude oil.

For complex mixtures such as crude oil or synthetic polymers, molar mass distributions and average molecular weights are important chemical properties. By analyzing a FI mass spectrum, mostly consisting of molecular ions of complex hydrocarbon mixture, and using a group-type analysis software, one can obtain molar mass distributions and average molecular weights of the various hydrocarbon types (e.g., paraffin, naphthene, olefin, aromatics) in the mixture.

We have analyzed a crude oil sample by GC/FI method using JMS-T100GC “AccuTOF GC” and processed the obtained data using a group-type analysis software.

## Methods

<ins>Sample</ins> Crude Oil

(Refer Fig. 1 for preparation)

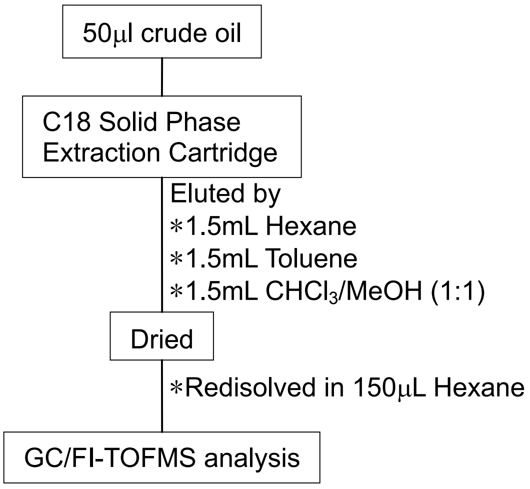

Fig. 1 Sample preparation flow

### Analysis conditions

GC conditions

GC: Agilent 6890N
Column: DB-5ms
30 m x 0.25 mm I.D., 0.25 μm
Oven: 50°C→15°C/min→280°C (5 min)
Injection port: 280 °C, Split (1:200)
Injection volume: 1.0 μl
Career gas: He (1 mL/min, constant flow mode)

MS conditions

MS: JMS-T100GC “AccuTOF GC”
Ionization: FI+ (Cathode voltage: -10 kV, Emitter current: 0 mA)
Mass range: *m/z* 35 - 500
Acquisition rate: 0.3 s/spectrum

Software Polymerix™ (Sierra Analytics, Inc.)

## Results and Discussion

Group-type analysis for 5 hydrocarbon types with an unsaturation degree from 0 to 4 and for the total/average of the 5 types was performed. (Refer MS Tips No. 71 for details.)

The table below shows the properties calculated for the total/average of the 5 hydrocarbon types for 10 repeated analyses and their statistics.

Table 1 Results of the group-type analysis of the crude oil (Total/Average)

| Total/Average | $M_n$ | $M_w$ | $M_z$ | PD | $DP_n$ | $DP_w$ | $DP_z$ |
|---|---|---|---|---|---|---|---|
| 1 | 206.188 | 217.016 | 229.273 | 1.053 | 8.699 | 9.471 | 10.346 |
| 2 | 204.957 | 214.545 | 225.075 | 1.047 | 8.854 | 9.297 | 10.048 |
| 3 | 200.606 | 211.629 | 225.105 | 1.055 | 8.298 | 9.085 | 10.046 |
| 4 | 205.978 | 215.44 | 225.597 | 1.046 | 8.685 | 9.36 | 10.085 |
| 5 | 200.029 | 208.101 | 216.649 | 1.041 | 8.261 | 8.837 | 9.447 |
| 6 | 205.491 | 215.402 | 226.173 | 1.049 | 8.654 | 9.361 | 10.13 |
| 7 | 206.532 | 217.31 | 229.255 | 1.052 | 8.723 | 9.492 | 10.344 |
| 8 | 205.573 | 215.814 | 227.008 | 1.05 | 8.656 | 9.387 | 10.185 |
| 9 | 209.459 | 220.152 | 231.519 | 1.051 | 8.937 | 9.7 | 10.511 |
| 10 | 209.18 | 220.678 | 233.522 | 1.055 | 8.907 | 9.728 | 10.644 |
| Average | 205.399 | 215.609 | 226.918 | 1.050 | 8.667 | 9.372 | 10.179 |
| Std. Dev. | 3.074 | 3.722 | 4.598 | 0.004 | 0.229 | 0.265 | 0.327 |
| **C.V. (%)** | **1.50** | **1.73** | **2.03** | **0.42** | **2.64** | **2.83** | **3.21** |

$M_n$: number average molecular weight

$M_w$: weight average molecular weight

$M_z$: z average molecular weight

PD: polydispersity

$DP_n$: $M_n/R$

$DP_w$: $M_w/R$

$DP_z$: $M_z/R$

(R: mass of repeating unit)

(DP: degree of polymerization)

The coefficients of variation are very good and around or below 3% for all properties calculated. Especially, the coefficient of variation for PD is excellent at 0.42%.

Group-type analysis of a crude oil using GC/FI method on the AccuTOF GC and Polymerix™ group-type analysis software is confirmed to have excellent reproducibility.

JEOL MS Data Sheet
MS Tips
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No.111

# Rapid analysis using inactivated fused silica tube (a.k.a. "guard column") as a sample inlet (1)

## Introduction

Average molecular weight is an important reference for evaluating samples with molecular weight distributions, such as crude oils, which are complex mixtures, or synthetic polymers. Almost all the ions observed in field desorption (FD) and field ionization (FI) mass spectra are molecular ions since these are soft ionization methods. Average molecular weight of the sample can be calculated directly from the masses (or "*m/z*") and intensities of all ions observed by FD or FI. By applying group-type analysis, the components can be classified into types based on their functional groups and/or unsaturations. Average molecular weight, polydispersity index, or relative abundance of each type can be obtained.

A diesel fuel was analyzed on JMS-T100GC "AccuTOF GC" with 3 sample introduction methods and the results were compared:

- Capillary GC / FI
- Rapid FD in which the analysis time was shorten by ramping the emitter current much faster than that on conventional analyses on double-focusing mass spectrometers
- Blank tube inlet / FI in which a fused silica tube was used to connect the GC injector and the ion source

## Methods

Blank tube inlet / FI

The schematics of the sample inlets are shown in Fig. 1. The specifications of the GC column and the fused silica tube used in the experiments are also shown in Fig. 1.

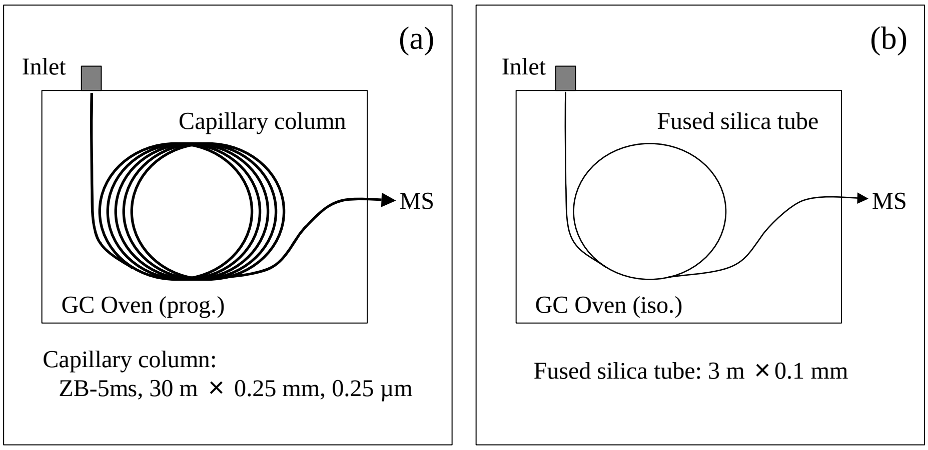

Fig.1 Schematic diagrams of sample introduction system by using GC, (a) capillary GC/FI. (b) blank tube inlet/FI.

In ordinary GC/MS analysis, a mixture is separated by a GC column and then detected by MS. When performing group-type analysis from GC/MS data, however, all acquired spectra are summed into a single spectrum. Component separation or individual spectra in the data are not really necessary.

In blank tube inlet / FI, a sample is introduced from the GC injection port through a short fused silica tube ("guard column"), held in the isothermal GC oven, to the ion source. The advantages are:

- Short analysis time
- Loss of low boiling point components are minimized compared with probe based methods, such as FD, DEI, and DCI, in which the sample is put on the probe at ambient pressure. However, low boiling point components are evaporated as the probe is introduced into the vacuum.
- Loss of high boiling point and trace components is minimized compared to the GC/MS method since there are no interaction with a GC stationary phase.
- GC conditions are not critical; no need to worry about separation.
- Lager amount of sample can be injected than in the GC/MS method; no GC column overloading.

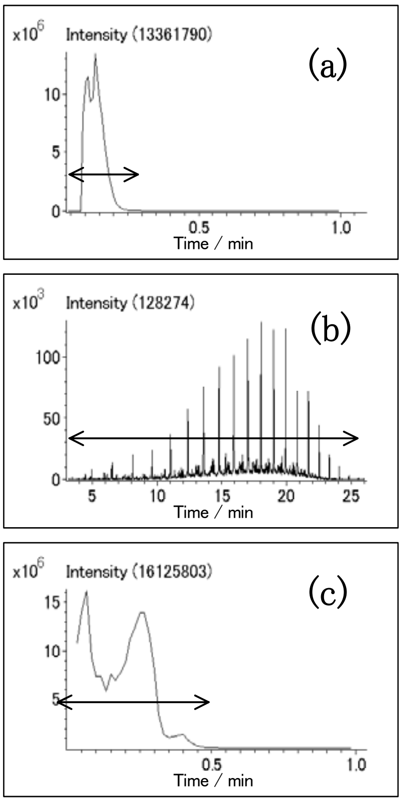

Fig.2 TICs of diesel oil
(a) blank tube inlet/FI,
(b) capillary GC/FI, (c) FD

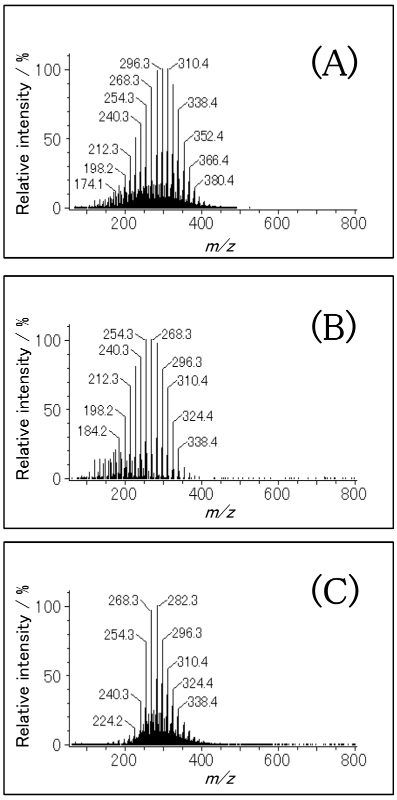

Fig.3 Mass spectra of diesel oil
(A) blank tube inlet/FI,
(B) capillary GC/FI, (C) FD

## Results and discussion

The results are shown on Fig. 2 and 3. The spectra on Fig. 3 were generated by summing the spectra in the time ranges shown by the arrows in Fig. 2.

With GC/FI, the analysis took 25 minutes although each component can be examined in detail due to the separation. FD and blank tube inlet / FI do not provide separation but the analysis times were very short; both within 1 minute.

By comparing the spectra from 3 methods, blank tube inlet / FI detected 1) low boiling point components (n-$C_{18}H_{38}$ (*m/z* 254) and smaller) that were missing in FD 2) high boiling point and trace components that were missing in GC/FI.

For group-type analysis in which parameters such as relative abundance and average molecular weight for each type are obtained, *m/z*'s and summed intensities of all the detected ions are used; no separation is required. The blank tube inlet / FI method is well suited for the group-type analysis of petrochemicals because of short analysis time, better detectability of low boiling point components than FD, better detectability of high boiling point and trace components than GC/FI. It can handle larger amount of sample injection than GC; well suited with FI whose ionization efficiency is lower than EI.

## Reference

M. Ubukata et al., *J. Mass Spectrom. Soc. Jpn.,* **56**, 13-19 (2008).

JEOL MS Data Sheet

# MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.112

# Rapid analysis using inactivated fused silica tube (a.k.a. “guard column”) as a sample inlet (2)

## Introduction

Average molecular weight is an important reference for evaluating samples with molecular weight distributions, such as crude oils, which are complex mixtures, or synthetic polymers. Almost all the ions observed in field desorption (FD) and field ionization (FI) mass spectra are molecular ions since these are soft ionization methods. Average molecular weight of the sample can be calculated directly from the masses (or “*m/z*”) and intensities of all ions observed by FD or FI. By applying group-type analysis, the components can be classified into types based on their functional groups and/or unsaturations. Average molecular weight, polydispersity index, or relative abundance of each type can be obtained.

In MS Tips No. 111, the details of the “blank tube inlet / FI” method was discussed. In this application note, crude oil, diesel fuel, and kerosene were analyzed by blank tube inlet / FI, capillary GC/FI, and FD and the results were compared and discussed.

## Methods

The samples were commercially available kerosene, commercially available diesel fuel, and crude oil from Middle East. The parameters used in the analyses are summarized in Table 1.

Table 1 Operating conditions for blank tube inlet/FI, capillary GC/FI and FD.

| | Blank tube inlet/FI | Capillary GC/FI | FD |
|---|---|---|---|
| GC parameter | | | |
| Injection mode | Split(100:1) | Split(500:1) | — |
| Inlet temp. / ℃ | 280 | 280 | — |
| Column | — | ZB-5ms, 30 m × 0.25 mm, 0.25 μm | — |
| Fused silica tube | 3 m × 0.1mm | — | — |
| Oven temp. / ℃ [hold time / min] | 280 [1] | 40[1]-300[1] | — |
| Oven temp. ramp rate/ ℃ min$^{-1}$ | — | 10 | — |
| Sample Volume / μL | 1 | 1 | — |
| He Carrier gas flow rate / mL min$^{-1}$ | 0.1 | 1 | — |
| TOFMS parameter | | | |
| Ionization mode | FI(+) | FI(+) | FD(+) |
| Emitter wire diameter / μm | 5 | 5 | 10 |
| Emitter current / mA | 5 | 5 | 0-50 |
| Emitter current ramp rate / mA min$^{-1}$ | — | — | 51.2 |
| Flush time after recording spectrum / ms | 50 | 50 | — |
| Cathode voltage / V | -10000 | -10000 | -10000 |
| Transfer line temp. / ℃ | 280 | 280 | — |
| Acquired *m/z* range / m z$^{-1}$ | 35-800 | 35-800 | 35-800 |
| Spectrum redording time / s | 0.5 | 0.5 | 1 |

## Results and discussion

The reconstructed total ion current chromatograms (RTICCs,) the mass spectra, and the summary of the type-group analysis results are shown in Fig. 1, Fig. 2, and Table 2 respectively.

With GC/FI, the analyses took 20 min, 25 min, and 30 min for kerosene, diesel fuel, and crude oil respectively, although each component can be examined in detail due to the separation. FD and blank tube inlet / FI do not provide separation but the analysis times were very short; within 1 minute in both methods and for all 3 samples.

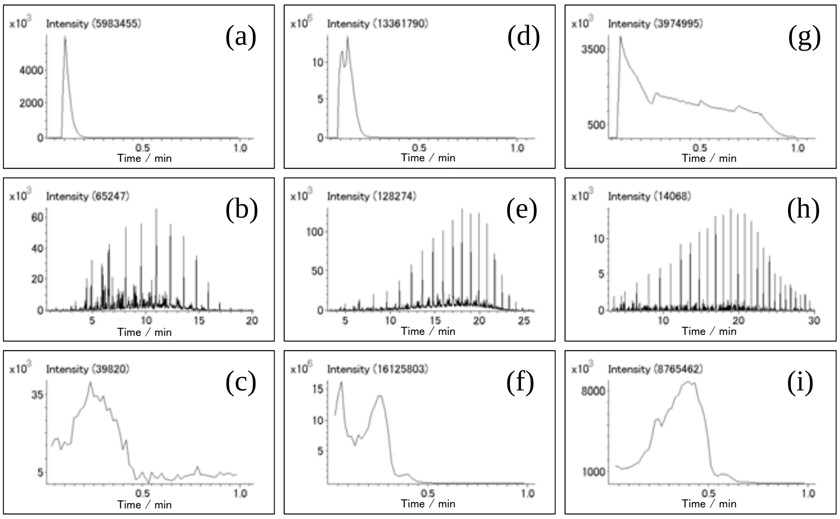

Fig. 1 Comparison of TICs of kerosene, diesel oil and crude oil by using differ methods; (a) kerosene by blank tube inlet/FI. (b) kerosene by capillary GC/FI. (c) kerosene by FD. (d) diesel oil by blank tube inlet/FI. (e) diesel oil by capillary GC/FI. (f) diesel oil by FD. (g) crude oil by blank tube inlet/FI. (h) crude oil by capillary GC/FI. (i) crude oil by FD.

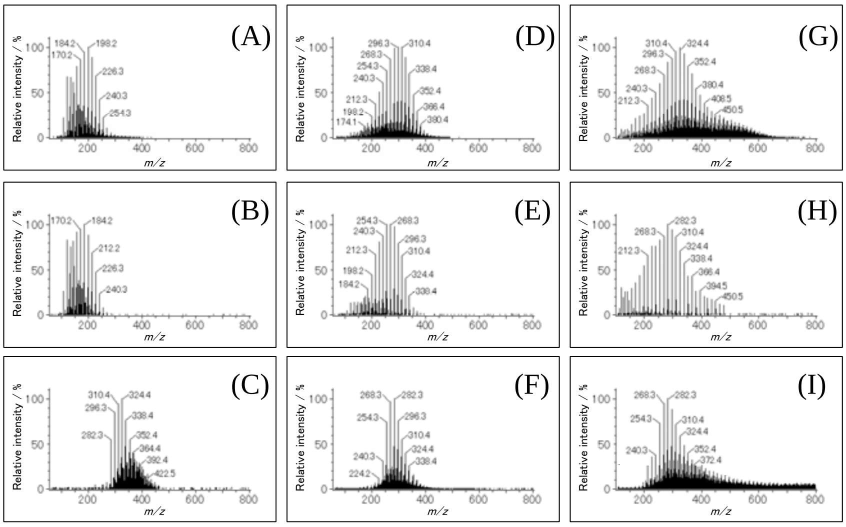

Fig. 2 Comparison of averaged mass spectra of kerosene, diesel oil and crude oil by using differ methods; (A) kerosene by blank tube inlet/FI. (B) kerosene by capillary GC/FI. (C) kerosene by FD. (D) diesel oil by blank tube inlet/FI. (E) diesel oil by capillary GC/FI. (F) diesel oil by FD. (G) crude oil by blank tube inlet/FI. (H) crude oil by capillary GC/FI. (I) crude oil by FD.

As was discussed in MS Tips No. 111, the blank tube inlet / FI has a number of advantages. Unlike FD, it did not miss low boiling point components or over-emphasize high boiling point components. The analysis time was very short and high boiling point components of up to *m/z* 600 and trace components were detected. For group-type analysis in which parameters such as relative abundance and average molecular weight for each type are obtained, *m/z*'s and summed intensities of all the detected ions are used; no separation is required. The blank tube inlet / FI method is well suited for the group-type analysis of petrochemicals because of short analysis time, better detectability of low boiling point components than FD, better detectability of high boiling point and trace components than GC/FI. It can handle larger amount of sample injection than GC; well suited with FI whose ionization efficiency is lower than EI.

Table 2 Summary of type analysis results.

| | | Blank tube inlet/FI | Capillary GC/FI | FD |
|---|---|---|---|---|
| Kerocene | | | | |
| | Measuring time / min | 0.2 | 18 | 0.5 |
| | $M_n$ | 179.2 | 165.3 | 348.9 |
| | PD | 1.04 | 1.03 | 1.02 |
| | Base peak | $C_{14}H_{30}$ | $C_{13}H_{28}$ | $C_{23}H_{48}$ |
| Diesel oil | | | | |
| | Measuring time / min | 0.3 | 25 | 0.5 |
| | $M_n$ | 282.6 | 247.6 | 299.4 |
| | PD | 1.04 | 1.04 | 1.02 |
| | Base peak | $C_{22}H_{46}$ | $C_{20}H_{42}$ | $C_{20}H_{42}$ |
| Crude oil | | | | |
| | Measuring time / min | 1.0 | >30 | 0.7 |
| | $M_n$ | 365.7 | 264.6 | 403.0 |
| | PD | 1.09 | 1.10 | 1.12 |
| | Base peak | $C_{23}H_{48}$ | $C_{20}H_{42}$ | $C_{20}H_{42}$ |

$n = 3$; $M_n$: number-average molecular weight; PD: polydispersity

## References

M. Ubukata et al., *J. Mass Spectrom. Soc. Jpn.*, **56**, 13-19 (2008).

JEOL MS Data Sheet

MS Tips

No. 098

Mass Spectrometry Application Group
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# Degradation of rotary vacuum pump oil determined by field desorption (FD) - TOFMS and group-type analysis software

## Introduction

Field desorption (FD) is an ionization method in which an electron of the analyte molecule is extracted by tunneling effect under very strong electric field at the surface or at the tips of the “whiskers” grown from the emitter. The analyte is applied as a thin film directly to the emitter and heated by passing a current through the emitter.

FD has been used for the analysis of nonvolatile compounds, synthetic polymers, etc., as a soft ionization method to produce molecular ions with little or no fragmentations.

New and used oil for rotary vane vacuum pump (RP hereafter) were analyzed and the change in their compositions was determined by performing group-type analysis on the FD mass spectra.

## Methods

Samples

RP oil (new and used)

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: 0.5 sec

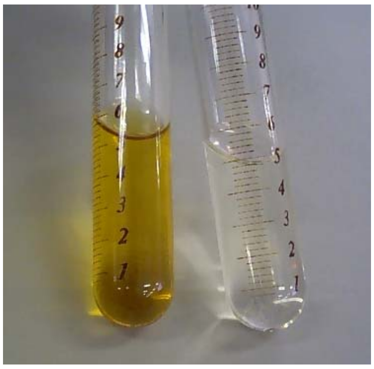

Fig. 1 RP oil (left: used, right: new)

## Results and discussion

The acquired FD mass spectra are shown below.

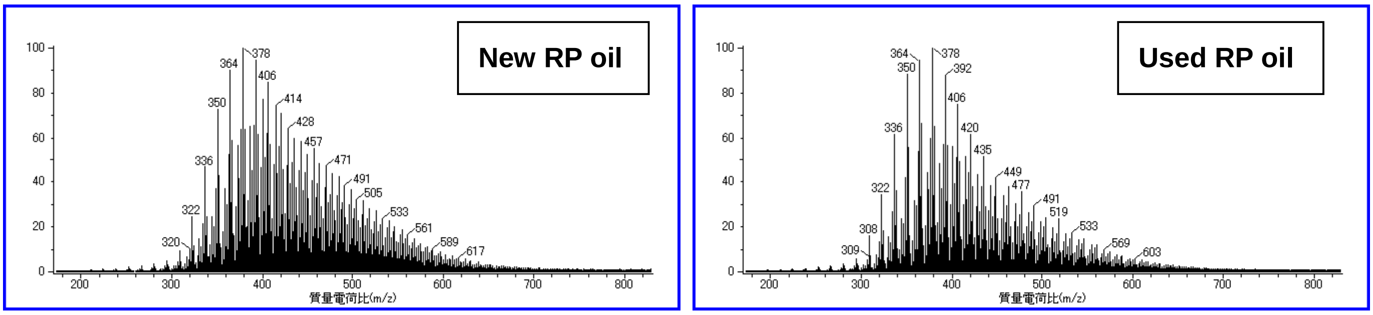

Fig. 2 Acquired FD mass spectra

As shown in Fig. 2, typical FD mass spectra for hydrocarbon mixture were obtained. Since the difference was rather subtle (more peaks were observed for the new oil at around *m/z* 500,) group-type analysis was performed to determine the differences in their composition. The results are shown below.

Table 1 Type analysis result of new RP oil

| Series Label | Mn | Mw | Mz | PD | DPn | DPw | DPz | Percent Series |
|---|---|---|---|---|---|---|---|---|
| Total/Average | 453.82 | 483.97 | 531.27 | 1.07 | 25.57 | 27.73 | 31.10 | 100.00 |
| $C_nH_{2n+2}$ | 447.44 | 479.98 | 533.06 | 1.07 | 24.78 | 27.10 | 30.89 | 15.47 |
| $C_nH_{2n}$ | 435.82 | 462.47 | 504.05 | 1.06 | 24.10 | 26.00 | 28.96 | 23.19 |
| $C_nH_{2n-2}$ | 451.28 | 482.02 | 530.39 | 1.07 | 25.34 | 27.54 | 30.99 | 16.70 |
| $C_nH_{2n-4}$ | 464.22 | 498.14 | 551.19 | 1.07 | 26.41 | 28.83 | 32.61 | 12.69 |
| $C_nH_{2n-6}$ | 459.36 | 486.90 | 529.76 | 1.06 | 26.21 | 28.17 | 31.23 | 18.90 |
| $C_nH_{2n-8}$ | 478.50 | 511.38 | 561.52 | 1.07 | 27.72 | 30.06 | 33.64 | 13.06 |

Table 2 Type analysis result of used RP oil

| Series Label | Mn | Mw | Mz | PD | DPn | DPw | DPz | Percent Series |
|---|---|---|---|---|---|---|---|---|
| Total/Average | 446.82 | 483.77 | 546.99 | 1.08 | 25.05 | 27.68 | 32.20 | 100.00 |
| $C_nH_{2n+2}$ | 434.74 | 473.54 | 544.08 | 1.09 | 23.88 | 26.64 | 31.68 | 16.76 |
| $C_nH_{2n}$ | 425.93 | 455.81 | 507.39 | 1.07 | 23.39 | 25.52 | 29.20 | 26.43 |
| $C_nH_{2n-2}$ | 444.90 | 481.25 | 543.39 | 1.08 | 24.89 | 27.48 | 31.91 | 17.57 |
| $C_nH_{2n-4}$ | 461.91 | 506.41 | 581.41 | 1.10 | 26.24 | 29.42 | 34.77 | 12.03 |
| $C_nH_{2n-6}$ | 458.94 | 494.97 | 555.72 | 1.08 | 26.18 | 28.75 | 33.08 | 16.65 |
| $C_nH_{2n-8}$ | 485.15 | 530.63 | 603.67 | 1.09 | 28.19 | 31.44 | 36.65 | 10.58 |

Hydrocarbon types with different degrees of unsaturation were used. The hydrocarbon types used were $C_nH_{2n+2}$, $C_nH_{2n}$, $C_nH_{2n-2}$, $C_nH_{2n-4}$, $C_nH_{2n-6}$, and $C_nH_{2n-8}$. The difference in hydrocarbon compositions is shown below.

Table 3 Difference in hydrocarbon compositions

| Series Label | New Percent Series |  | Used Percent Series |
|---|---|---|---|
| Total/Average | 100.00 |  | 100.00 |
| $C_nH_{2n+2}$ | 15.47 | – increase → | 16.76 |
| $C_nH_{2n}$ | 23.19 | – increase → | 26.43 |
| $C_nH_{2n-2}$ | 16.70 | – increase → | 17.57 |
| $C_nH_{2n-4}$ | 12.69 | – decrease → | 12.03 |
| $C_nH_{2n-6}$ | 18.90 | – decrease → | 16.65 |
| $C_nH_{2n-8}$ | 13.06 | – decrease → | 10.58 |

As shown in Table 3, fraction of highly unsaturated hydrocarbons, i.e., $C_nH_{2n-4}$, $C_nH_{2n-6}$, and $C_nH_{2n-8}$, decreased while fraction of moderately unsaturated and saturated hydrocarbons, i.e., $C_nH_{2n-2}$, $C_nH_{2n}$, and $C_nH_{2n+2}$ increased in used RP oil. This suggests either opening of ring structures or hydrogenation of double bonds or triple bonds in $C_nH_{2n-4}$, $C_nH_{2n-6}$, and $C_nH_{2n-8}$.

Another possibility is oxidative degradation of unsaturated hydrocarbons. The exact masses of an oxidation product and its hydrocarbon isobar are very close and can not be mass-resolved with the analysis conditions used. However, the apparent increase of saturated and moderately unsaturated hydrocarbons and decrease of highly unsaturated hydrocarbons could be partly due to the oxidation products.

The difference in compositions of new and used RP oil was clearly revealed by group-type analysis.

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**No. 100**

# Type Analysis of Micro Crystalline Wax (Petroleum Wax)

[Introduction]

Petroleum waxes are a class of hydrocarbons that are solid at room temperature and are classified by the Japan Industrial Standards (JIS K2235) into 3 types: paraffin wax, micro crystalline wax, and petrolatum. A typical micro crystalline wax contains hydrocarbons having a carbon number of 30 to 60 and molecular weights between 500 and 800. These waxes also include large quantities of isoparaffins and cycloparaffins in addition to the paraffins.

Field desorption (FD) is an ionization technique that utilizes the tunneling effect of electrons in the presence of a high electric field. The sample is applied directly onto an FD emitter filament and then an electric current is applied to the filament to produce a high electric field across the emitter surface (including the whisker tips) to desorb and ionize the samples. As a soft ionization technique that minimizes fragmentation and acquires information on molecular ions, FD has been used for analyzing refractory compounds and high molecular weight polymers.

In this work we ionized a micro crystalline wax by using a JMS-T100GC AccuTOF GC with FD ionization to do a sample type analysis that was based on the mass and intensity of the resulting ions.

[Experimental]

Sample: Commercial micro crystalline wax product (10 mg/ml, chloroform solvent)

MS: JMS-T100GC AccuTOF GC
Ionization mode: FD(+)
Cathode voltage: -10 kV
Emitter current: 0 mA → 6.4 mA/min → 45 mA
Mass range: *m/z* 20 to 1600
Recording interval: 3.2 s

[Results]

In the mass range under *m/z* 450, saturated hydrocarbon compounds were detected, while unsaturated hydrocarbon compounds were detected in the range over *m/z* 450. A type analysis was conducted using the unsaturated hydrocarbon compounds. A total of 6 hydrocarbon compounds were used: $C_nH_{2n+2}$(S1), $C_nH_{2n}$(S2), $C_nH_{2n-2}$(S3), $C_nH_{2n-4}$(S4), $C_nH_{2n-6}$(S5), and $C_nH_{2n-8}$(S6). The table below shows the results for each series of hydrocarbons.

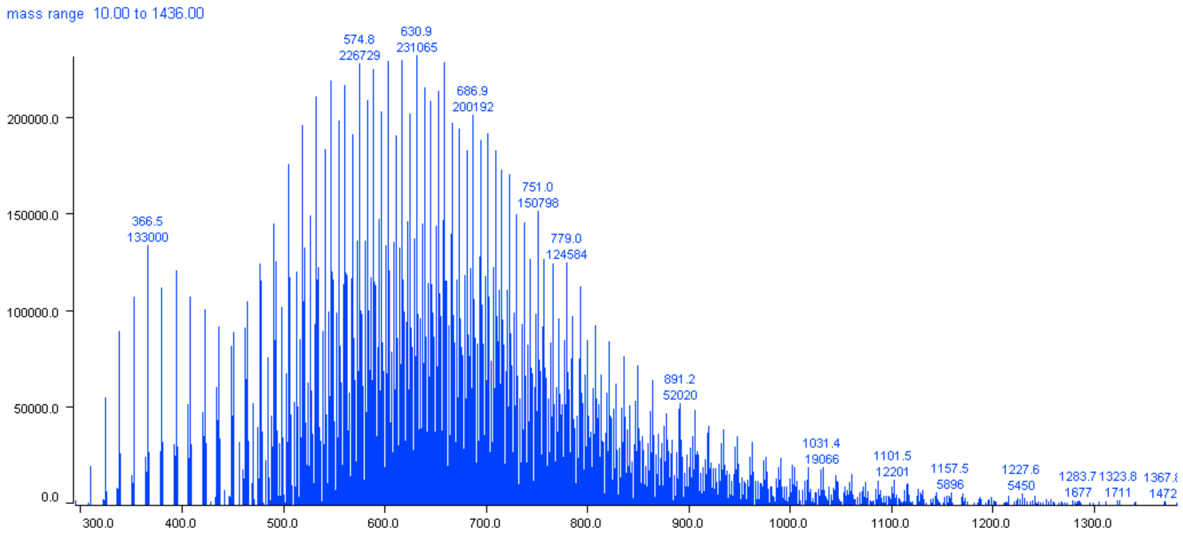

Figure 1. FD mass spectrum of micro crystalline wax

Table 1. Type analysis of microcrystalline wax

| Series Label | | Mn | Mw | Mz | PD | DPn | DPw | DPz | Percet Series | Percent Spectrum |
|---|---|---|---|---|---|---|---|---|---|---|
| Total/Average | | 657.0 | 686.9 | 718.9 | 1.0 | 40.1 | 42.2 | 44.5 | 100.0 | 64.1 |
| S1 | $C_nH_{2n+2}$ | 571.1 | 617.3 | 665.3 | 1.1 | 33.6 | 36.9 | 40.3 | 17.3 | 11.1 |
| S2 | $C_nH_{2n}$ | 529.7 | 655.0 | 680.8 | 1.0 | 37.9 | 39.7 | 41.6 | 24.2 | 15.5 |
| S3 | $C_nH_{2n-2}$ | 670.5 | 692.3 | 715.6 | 1.0 | 41.0 | 42.5 | 44.2 | 13.1 | 8.4 |
| S4 | $C_nH_{2n-4}$ | 715.6 | 739.0 | 764.7 | 1.0 | 44.3 | 46.0 | 47.8 | 8.4 | 5.4 |
| S5 | $C_nH_{2n-6}$ | 688.3 | 717.9 | 751.1 | 1.0 | 42.5 | 44.7 | 47.0 | 22.5 | 14.5 |
| S6 | $C_nH_{2n-8}$ | 710.0 | 739.6 | 772.8 | 1.0 | 44.2 | 46.3 | 48.7 | 14.5 | 9.3 |

Mn: Average molecular weight
Mw: Weight-average molecular weight
Mz: Z-average molecular weight
PD: Polydispersity

DPn: Mn/R
DPw: Mw/R
DPz: Mz/R
(R: Mass of repeat unit)

The content of $C_nH_{2n}$ was the highest at 24.2% among the 6 hydrocarbons series shown in the table. This hydrocarbon series was followed by $C_nH_{2n-6}$ at 22.5% and $C_nH_{2n+2}$ at 17.3%. The micro crystalline wax contained large amounts of isoparaffins (equal to S1) and cycloparaffins (equal to S2), and the content of ion species in these series tended to be higher than observed for the other hydrocarbon types.

## [Conclusions]

These results demonstrate that by using the AccuTOF-GC with FD ionization, a solid wax can be analyzed at room temperature to produce high resolution mass spectra that provide detailed information about the sample, including the hydrocarbon types present in the samples, their average molecular weight information, and their compositional ratios relative to each other.

## [Acknowledgment]

We wish to express our thanks to Dr. Seiichi Kawahara, Associate Professor, Nagaoka University of Technology, for providing the sample.

AccuTOF™

# A new method for pesticides identification: fast GC/time-of-flight mass spectrometry

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## Introduction

Pesticides have been widely used all over the world. Although the use of pesticides is strictly regulated in many countries, laboratories still monitor their residues due to their toxicity and highly persistent nature. The most common method for pesticides identification is GC/MS with select ion monitoring (SIM).  Since most of samples contain many different components, a long GC separation is generally needed when a low-resolution SIM MS is used. This is very time-consuming. Fast GC has been available for several years; however, the combination of fast GC with mass spectrometry had not been commercially available until high acquisition rate time-of-flight mass spectrometry was introduced. Here, we describe a new method by using fast GC/time-of-flight MS to identify 67 pesticides. The high resolution time-of-flight MS always yields high quality library searchable spectrums without compromising the sensitivity. The method is simple, fast, and reliable.

## Experimental

All solvents used were of HPLC grade. The pesticide standards used are listed in Table 1. They were prepared in ethyl acetate with concentration of 100 ppb.

An Agilent 6890N gas chromatograph was used. Samples were injected onto an HP-5MS capillary column (10 x 0.18 mm, 0.18 μm film thickness) with splitless injection mode. Helium was used as the carrier gas and set at 0.6 mL/min. The injector temperature was set at 200 °C. The oven temperature was held at 40 °C for 1 min and then increased to 300 °C at a rate of 50 °C/min.

| Pesticide | Formula | Pesticide | Formula | Pesticide | Formula |
|---|---|---|---|---|---|
| Simazine | C7H12ClN5 | Thiobencarb | C12H16ClNOS | Isoxathion | C13H16NO4PS |
| Diazinon | C12H21N2O3PS | Fenitrothion | C9H12NO5PS | Isoprothiolane | C12H18N4S2 |
| Chlorothalonil | C8Cl4N2 | Propyzamide | C12H11Cl2NO | Dichlorvos | C4H7Cl2O4P |
| Fenobcarb | C12H17NO2 | Chlornitrofen | C12H6Cl3NO3 | CNP-amino | C12H8Cl3NO |
| Iprobenfos | C13H21O3PS | EPN | C14H14NO4PS | Isofenphos | C15H24NO4PS |
| Chlorpyrifos | C9H11Cl3NO3PS | Pyridafenthion | C14H17N2O4PS | Iprodione | C13H13Cl2N3O3 |
| Etridiazole | C5H5Cl3N2OS | Captan | C9H8Cl3NO2S | Chloroneb | C8H8Cl2O2 |
| Tolclofos-methyl | C9H11Cl2O3PS | Flutolanil | C17H16F3NO2 | Pencycuron | C19H21ClN2O |
| Metalaxyl | C15H21NO4 | Mepronil | C17H19NO2 | Dithiopyr | C15H16F5NO2S2 |
| Terbucarb | C17H27NO2 | Napropamide | C17H21NO2 | Pyributicarb | C18H22N2O2S |
| Butamifos | C13H21N2O4PS | Benfluralin | C13H16F3N3O4 | Pendimethalin | C13H19N3O4 |
| Methyldymron | C17H20N2O | Alachlor | C14H20ClNO2 | Edifenphos | C14H15O2PS2 |
| Pyroquilon | C11H11NO | Phthalide | C8H2Cl4O2 | Mefenacet | C16H14N2O2S |
| Pretilachlor | C17H26ClNO2 | Isoprocarb | C11H15NO2 | Thenylchlor | C16H18ClNO2S |
| Methidathion | C6H11N2O4PS3 | Bromobutide | C15H22BrNO | Molinate | C9H17NOS |
| Procymidone | C13H11Cl2NO2 | Anilofos | C13H19ClNO3PS2 | Atrazine | C18H14ClN5 |
| Dichlobenil | C7H2Cl2N | Dimethoate | C5H12NO3PS2 | Endosulphan | C9H6Cl6O3S |
| Etofenprox | C25H28O3 | Fenthion | C10H15O3PS2 | Malathion | C10H19O6PS2 |
| Simetryne | C8H15N5S | Dimepiperate | C15H21NOS | Phenthoate | C12H17O4PS2 |
| Buprofezin | C16H23N3OS | Ethyl thiometon | C8H19O2PS3 | Esprocarb | 85785-20-2 |
| Bifenox | C14H9Cl2NO5 | Piperophos | C14H28NO3PS2 | Dimethametryn | C11H21N5S |
| Propiconazole | C15H17Cl2N3O2 | Pyriproxyfen | C20H19NO3 | Trifluralin | C13H16F3N3O4 |
| Cafenstrole | C16H22N4O3S | | | | |

*Table 1. List of 67 pesticides*

The mass spectrometer system consisted of JEOL AccuTOF-GC™ time-of-flight mass spectrometer with EI source and JEOL MassCenter™ workstation. The source and transfer line temperature were set at 250°C, respectively. The detector voltage was set at 2500V. The acquisition range is from m/z 35 to 500 with spectrum recoding interval of 0.05 s. The system was tuned with PFK to achieve a resolution of 6,000 (FWHM) at m/z 292.9824.

## Results

Figure 1 shows the TICs of 67 pesticides separated by the AccuTOF™ GC/MS system.  The high acquisition rate of this GC/MS system makes fast GC separation possible. The running time is only 6.5 min.

In order to determine the data quality for the unresolved chromatographic peaks, we chose tolclofos-methyl and alachlor. Their retention times have only 0.008 min difference. Since time-of flight mass spectrometer always runs at high resolution and full mass range without compromising the sensitivity, a full mass-range spectrum can be obtained for each pesticide.

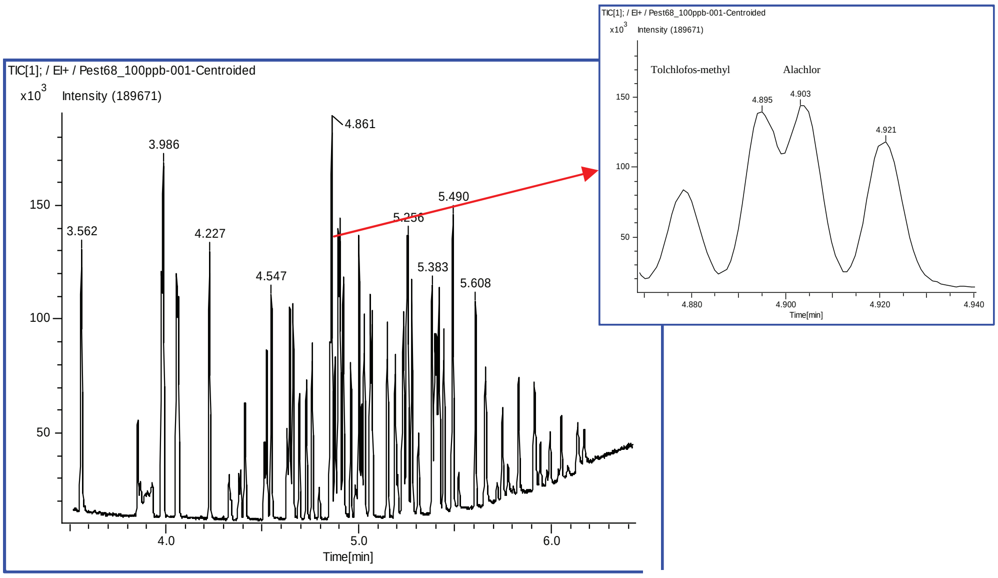


*Fig 1. Total ion chromatogram of 67 pesticides.*

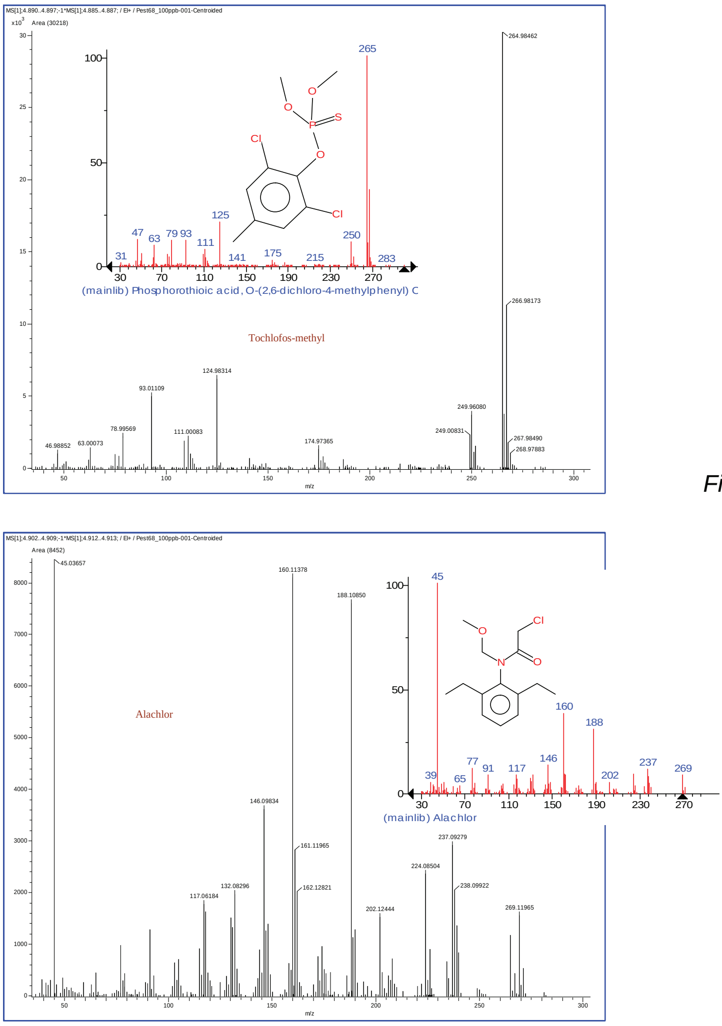
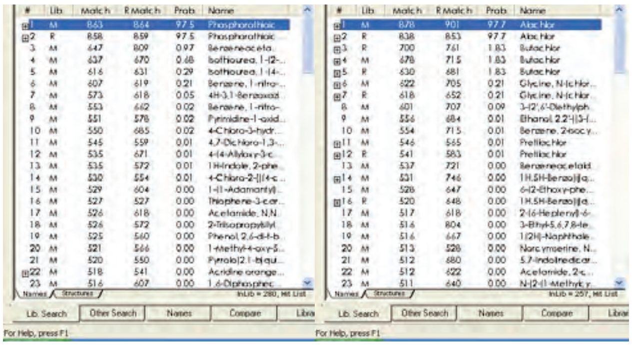


*Fig. 2 Mass spectra for selected two pesticides*

Figure 2 shows the mass spectra for these two pesticides in the sample and their corresponding spectra in the NIST library. An excellent library search was obtained and the results are shown in Figure 3. The probability index for both pesticides is greater than 97%, showing a strong confidence for identification results.

In addition, the high-resolution time-of-flight MS system has the capability for exact mass measurement. Possible elemental compositions for each pesticide and its fragments are ready obtained. The exact mass measurement results for two selected pesticides are listed in Table 2. The errors for all selected ions are less than 2 mmu.

The elemental composition estimation combined with full mass range spectrum make the identification unambiguous.



| # | Lib. | Match | R.Match | Prob. | Name |
|---|---|---|---|---|---|
| 1 | M | 863 | 864 | 97.5 | Phosphorothioic |
| 2 | R | 858 | 859 | 97.5 | Phosphorothioic |
| 3 | M | 647 | 809 | 0.97 | Benzeneaceta |
| 4 | M | 637 | 670 | 0.68 | Isothiourea, 1-(2-... |
| 5 | M | 616 | 631 | 0.29 | Isothiourea, 1-(4-... |
| 6 | M | 607 | 619 | 0.21 | Benzene, 1-nitro-... |
| 7 | M | 573 | 618 | 0.05 | 4H-3,1-Benzoxazi... |
| 8 | M | 553 | 662 | 0.02 | Benzene, 1-nitro- |
| 9 | M | 551 | 578 | 0.02 | Pyrimidine-1-oxid... |
| 10 | M | 550 | 685 | 0.02 | 4-Chloro-3-hydr... |
| 11 | M | 545 | 559 | 0.01 | 4,7-Dichloro-1,3-... |
| 12 | M | 535 | 671 | 0.01 | 4-(4-Allyloxy-3-c |
| 13 | M | 535 | 572 | 0.01 | 1H-Indole, 2-phe... |
| 14 | M | 530 | 554 | 0.01 | 4-Chloro-2-[(4-c... |
| 15 | M | 529 | 604 | 0.00 | 1-(1-Adamantyl)... |
| 16 | M | 527 | 527 | 0.00 | Thiophene-3-car... |
| 17 | M | 526 | 618 | 0.00 | Acetamide, N,N |
| 18 | M | 526 | 572 | 0.00 | 2-Triisopropylsilyl |
| 19 | M | 525 | 560 | 0.00 | Phenol, 2,6-di-t-b... |
| 20 | M | 521 | 566 | 0.00 | 1-Methyl-4-oxy-5... |
| 21 | M | 520 | 550 | 0.00 | Pyrrolo[2,1-b]qui... |
| 22 | M | 518 | 541 | 0.00 | Acridine orange... |
| 23 | M | 516 | 607 | 0.00 | 1,6-Diphosphec... |

InLib = 280, Hit List

| # | Lib. | Match | R.Match | Prob. | Name |
|---|---|---|---|---|---|
| 1 | M | 878 | 901 | 97.7 | Alachlor |
| 2 | R | 838 | 853 | 97.7 | Alachlor |
| 3 | R | 700 | 761 | 1.83 | Butachlor |
| 4 | M | 678 | 715 | 1.83 | Butachlor |
| 5 | R | 630 | 681 | 1.83 | Butachlor |
| 6 | M | 622 | 705 | 0.21 | Glycine, N-(chlor... |
| 7 | R | 618 | 652 | 0.21 | Glycine, N-(chlor... |
| 8 | M | 601 | 707 | 0.09 | 3-(2',6'-Diethylph... |
| 9 | M | 556 | 684 | 0.01 | Ethanol, 2,2'-[(3-(... |
| 10 | M | 554 | 715 | 0.01 | Benzene, 2-isocy... |
| 11 | M | 546 | 565 | 0.01 | Pretilachlor |
| 12 | R | 541 | 583 | 0.01 | Pretilachlor |
| 13 | M | 537 | 721 | 0.00 | Benzeneacetald |
| 14 | M | 531 | 746 | 0.00 | 1H,5H-Benzo[ij]q... |
| 15 | M | 528 | 647 | 0.00 | 6-(2-Ethoxy-phe... |
| 16 | R | 520 | 648 | 0.00 | 1H,5H-Benzo[ij]q... |
| 17 | M | 517 | 618 | 0.00 | 2-(6-Heptenyl)-6- |
| 18 | M | 516 | 804 | 0.00 | 3-Ethyl-5,6,7,8-te... |
| 19 | M | 516 | 667 | 0.00 | 1(2H)-Naphthale... |
| 20 | M | 513 | 528 | 0.00 | Norcymserine, N... |
| 21 | M | 512 | 680 | 0.00 | 5,7-Indolinedicar... |
| 22 | M | 512 | 622 | 0.00 | Acetamide, 2-c... |
| 23 | M | 511 | 640 | 0.00 | N-[2-(1-Methylc... |

InLib = 257, Hit List

*Fig 3. NIST library research.*

| Tolclofos-methyl | | | |
|---|---|---|---|
| Measured m/z | Calc. m/z | Error (mmu) | Formula |
| 124.9831 | 124.9826 | 0.5 | $C_2H_6O_2PS$ |
| 174.9737 | 174.9717 | 2.0 | $C_7H_5Cl_2O$ |
| 249.9608 | 249.9620 | -1.2 | $C_8H_8ClO_3PS$ |
| 264.9846 | 264.9855 | -0.9 | $C_9H_{11}ClO_3PS$ |
| Alachlor | | | |
| 146.0983 | 146.0970 | 1.3 | $C_{10}H_{13}N$-H |
| 160.1138 | 160.1126 | 1.2 | $C_{11}H_{15}N$-H |
| 174.0925 | 174.0919 | 0.6 | $C_{11}H_{13}NO$-H |
| 188.1085 | 188.1075 | 1.0 | $C_{12}H_{15}NO$-H |
| 202.1244 | 202.1232 | 1.2 | $C_{13}H_{17}NO$-H |
| 224.0850 | 224.0842 | 0.8 | $C_{12}H_{15}ClNO$ |
| 237.0928 | 237.0920 | 0.8 | $C_{13}H_{17}ClNO$ |
| 269.1197 | 269.1183 | 1.4 | $C_{14}H_{20}ClNO_2$ |

*Table 2. Exact mass measurement results for major fragment ions for two selected pesticides.*

## Conclusion

Fast GC/time-of-flight mass spectrometry was used to identify 67 pesticides in 6.5 minutes. Full mass range spectrum and exact mass measurement provide positive identification.

## References

1. Lehotay SJ. *Journal of AOAC International.* 83(3):680-97, 2000 May-Jun.
2. http://www.leco.org/customersupport/apps/separationscience/-227.pdf

***JEOL MS Data Sheet***

# MS Tips

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No. 130

***JMS-T100GC Application Data***

## Examining Selectivity using High Resolution Extracted Ion Current Chromatograms (EICC)

### [Introduction]

Transformer oil containing no PCBs was diluted 10000 times, and then this solution was spiked with a mixture of commercially available PCBs (KC-500). The resulting sample was analyzed by using the JEOL AccuTOF-GC with FastGC/MS conditions. Afterwards, the data was examined by varying the mass range window (called "window width" in EICC generation) used for the PCB extracted ion current chromatograms (EICC) to determine if the effect of the background interference can be eliminated so that the analyte peaks are easily observed in the resulting data.

### [Samples and Measuring Conditions]

| | | |
|---|---|---|
| Sample | KC-500 (0.1 ppm), transformer oil (diluted 10000 times) | |
| GC conditions | Sample inlet: | Splitless, 280°C |
| | Column: | DB-5, 10 m x 0.18 mm, 0.18 um |
| | He flow rate: | 0.5 ml/min (fixed flow rate) |
| | Oven: | 50°C (2 min) → 60°C/min → 280°C (2 min) |
| MS conditions: | MS: | JMS-T100GC AccuTOF GC |
| | Ionization mode: | EI+ (ionization voltage: 70 eV, current: 300 µA) |
| | Mass range: | *m/z* 30 to 550 |
| | Recording interval: | 0.1 s (10 Hz) |
| | Temperature: | Ion source: 280°C, GC-ITF: 280°C |

### [Result and Discussion]

The window width for the EICC generation was varied to see if the chromatographic effect of the background interferences can be eliminated. Figure 1 shows the EICCs generated under low resolution (top) and high resolution (bottom) conditions. "Low resolution" and "high resolution" do not refer to the resolving power of the instrument, but instead refer to the different window widths used for the *m/z* 352.88 EICCs. The mass resolution levels calculated with the

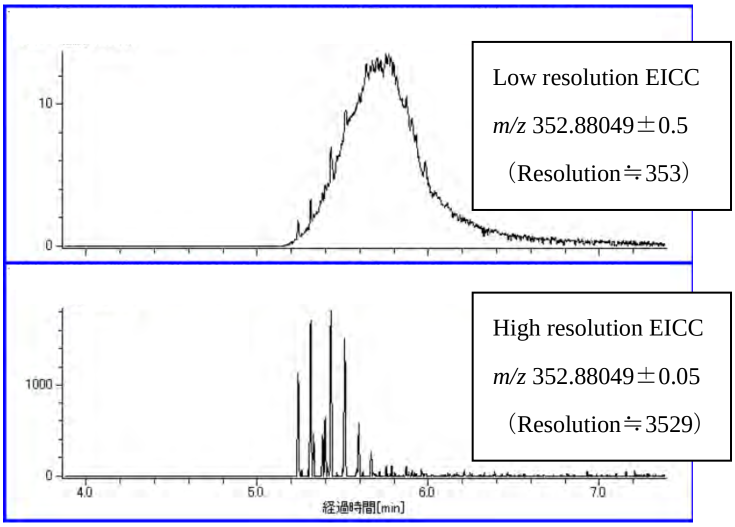

Figure 1. Comparison of mass chromatograms
for penta-chlorinated PCBs in oil

different window widths are shown in Figure 1. The actual resolution for the data acquired by the AccuTOF GC during these sample measurements was R≧5000 @ *m/z* 293. As Figure 1 shows, the low resolution EICC (*m/z* 352.88049 ± 0.5, analogous to a quadrupole MS analysis) showed a wide, unresolved sample envelope that was caused by the transformer oil. Meanwhile, the high resolution EICC (*m/z* 352.88049 ± 0.05) eliminated the effect of the oil background, and extracted only the peaks for the penta-chlorinated PCBs.

## [Conclusions]

These results demonstrate that the AccuTOF GC, a high resolution GC-TOFMS system, is a powerful tool for analyzing complex real-world samples that contain high levels of interfering impurities.

*JEOL MS Data Sheet*

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*No.147*

***JMS-T100GCV Application Data***

# Qualitative analysis of pyrazole pesticides in tea leaf by using FastGC-HRTOFMS

## [Introduction]

FastGC method is a very useful technique for rapid GC analysis. On the other hand, GC-TOFMS has the capability of very fast data acquisition in comparison with other types of mass spectrometers. Therefore, TOFMS is most suitable to combine with the FastGC technique. In combination with the high resolution capability (HR-TOFMS) we can obtain very accurate spectra with exact m/z determination.

In this application note, we describe the qualitative and quantitative analysis by FastGC/HRTOFMS of pyrazole pesticides (Fipronil, Ethiprole, Pyraflufen ethyl and Tebfenpyrad) in tea leaf. We confirm that rapid analysis with high sensitivity is easy to perform and very useful for fast screening.

## [Sample and method]

Measurement conditions are shown in Table 1. Tea leaf (5g) was prepared using the multiresidue method for agricultural chemicals by GC/MS published by Ministry of Health, Labour and Welfare, Japan. Pyrozole pesticides were added to make 0.01, 0.05 and 0.1ppm solution in the prepared solution from tea leaf. These concentrations in solution are equivalent to 4, 20 and 40ppb in tea leaf. Each sample was analyzed 3 times to check the reproducibility.

Table 1 GC/MS measurement conditions.

| | |
|---|---|
| Instrument | JMS-T100GCV (JEOL) |
| Quantitative software | Escrime (JEOL) |
| Injection mode | Splitless |
| Injection temp. | 250℃ |
| Oven temp. program | 40℃(1min) → 50℃/min → 300℃(3.8min) |
| Injection volume | 1μL |
| Column | DB-5, 10m x 0.18mm, 0.18μm |
| Carrier gas | He, 0.7mL/min, Const. flow |
| Ionization mode | EI+, 70eV, 300μA |
| Ion source temp. | 250℃ |
| m/z range | m/z 35 - 500 |
| Spectrum recording time | 0.1sec |

## [Results and discussion]

Fig.1 shows TIC chromatogram and mass chromatograms of each pesticide. Pyrazole pesticides are detected within 6 minutes by using the FastGC method. Expanded mass chromatogram of Fipronil is shown in the right side of Fig.1. The peak width becomes very narrow in the FastGC methods.

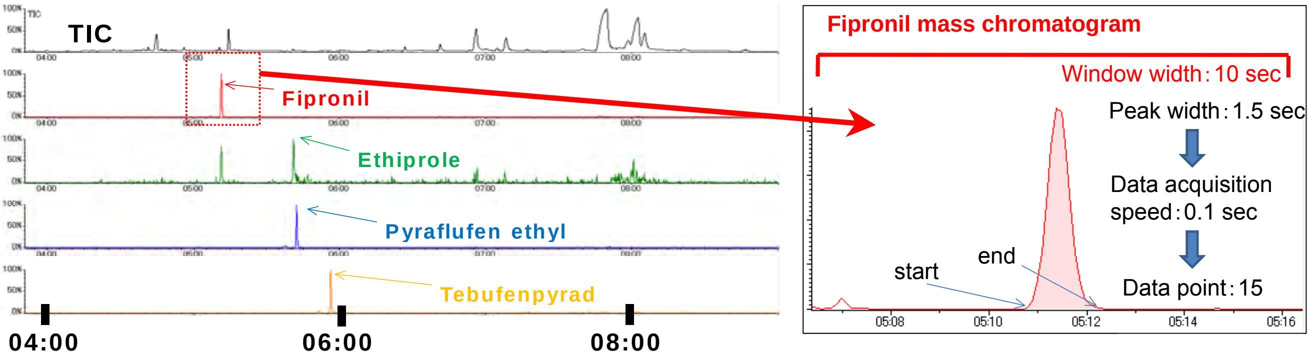

Fig.1 TIC chromatograms and Mass chromatograms

Now, the maximum recording interval on JMS-T100GCV is 0.04 seconds/spectrum (25Hz). When 0.1 seconds/spectrum (10Hz) of recording interval is used in this analysis, about 15 data points are acquired per chromatographic peak and this is enough to get good peak profile.

Mass spectrum of Fipronil is shown in Fig.2. Chemical backgrounds from tea leafs are observed prominently even at very low concentrated solution. However, characteristic ions of Fipronil such as *m/z* 350.95, 366.94 and 419.94 are observe and Fipronil is identified as first choice using NIST database search even in 0.01 ppm sample solution (4 ppb in tea leaf). In addition, mass accuracy for *m/z* 350.95, 366.94 and 419.94 is within 2.0x10$^{-3}$u. Table 2 shows the mass accuracy for characteristic ions of each pyrazole pesticide at different concentrations.

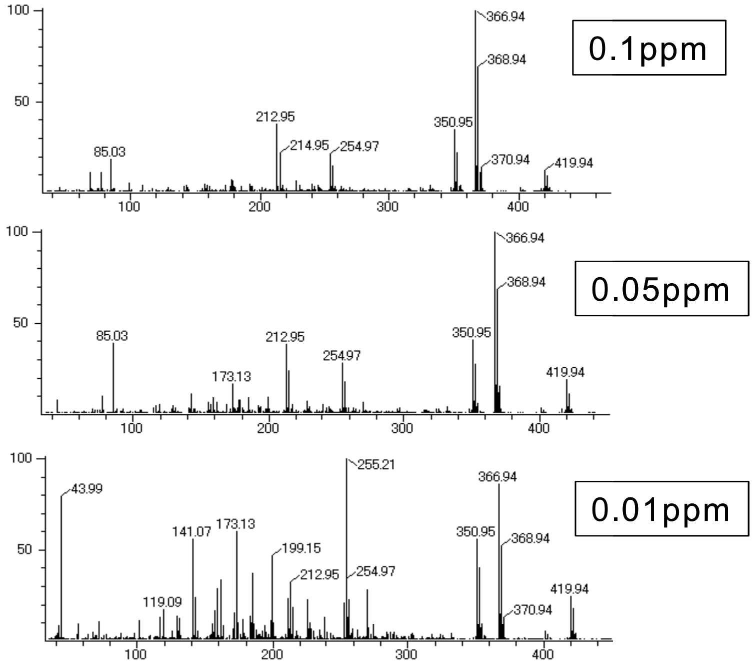

Fig.2 Mass spectra of Fipronil.

JMS-T100GCV can easily obtain good data with high spectrum sensitivity and high mass accuracy even if sample includes chemical contaminants. Identification using accurate mass is very useful in addition to the database search.

Table 2 Results of exact mass measurements.

**Fipronil**

| ion | $C_{11}H_4Cl_2F_3N_4S$ | $C_{11}H_4Cl_2F_3N_4OS$ | $C_{12}H_4Cl_2F_6N_4S$ |
|---|---|---|---|
| Calc. exact mass | 350.9486 | 366.9435 | 419.9438 |

| ppm | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) |
|---|---|---|---|---|---|---|
| **0.1** | 350.9473 | −1.3 | 366.9417 | −1.8 | 419.9435 | −0.3 |
| **0.05** | 350.9472 | −1.4 | 366.9423 | −1.2 | 419.9425 | −1.3 |
| **0.01** | 350.9474 | −1.2 | 366.9431 | −0.4 | 419.9449 | 1.1 |

**Pyraflufen ethyl**

| ion | $C_{12}H_8Cl_2F_3N_2O_2$ | $C_{13}H_9ClF_3N_2O_4$ | $C_{15}H_{13}Cl_2F_3N_2O_4$ |
|---|---|---|---|
| Calc. exact mass | 338.9915 | 349.0203 | 412.0205 |

| ppm | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) |
|---|---|---|---|---|---|---|
| **0.1** | 338.9917 | 0.2 | 349.0194 | −0.9 | 412.0212 | 0.7 |
| **0.05** | 338.9911 | −0.4 | 349.0184 | −1.9 | 412.0207 | 0.2 |
| **0.01** | 338.9914 | −0.1 | 349.0191 | −1.2 | 412.0201 | −0.4 |

**Ethiprole**

| ion | $C_8H_4Cl_2F_3N_2$ | $C_{11}H_5Cl_2F_3N_4S$ | $C_{13}H_9Cl_2F_3N_4S$ |
|---|---|---|---|
| Calc. exact mass | 254.9704 | 351.9564 | 379.9877 |

| ppm | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) |
|---|---|---|---|---|---|---|
| **0.1** | 254.9722 | 1.8 | 351.9577 | 1.3 | 379.9894 | 1.7 |
| **0.05** | 254.9721 | 1.7 | 351.9547 | −1.8 | 379.9885 | 0.8 |
| **0.01** | 254.9767 | 6.4 | 351.9563 | −0.1 | 379.9897 | 2.0 |

**Tebufenpyrad**

| ion | $C_7H_8ClN_2O$ | $C_{17}H_{21}ClN_3O$ | $C_{18}H_{24}ClN_3O$ |
|---|---|---|---|
| Calc. exact mass | 171.0325 | 318.1373 | 333.1608 |

| ppm | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) | Meas. exact mass | Error ($10^{-3}$u) |
|---|---|---|---|---|---|---|
| **0.1** | 171.0343 | 1.8 | 318.1379 | 0.6 | 333.1617 | 0.9 |
| **0.05** | 171.0335 | 1.0 | 318.1383 | 1.0 | 333.1614 | 1.7 |
| **0.01** | 171.0333 | 0.8 | 318.1388 | 1.5 | 333.1616 | 0.8 |

## [Reference]

M. Ubukata et al., Abstract of the 97th conference of the Japanese Society for Food Hygiene and Safety, page 20 (2009)

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd.

No.148

*JMS-T100GCV Application Data*

# Quantitative analysis of pyrazole pesticides in tea leaf using FastGC-HRTOFMS

## [Introduction]

FastGC method is a very useful technique for rapid GC analysis. On the other hand, GC-TOFMS has the capability to acquire data very fast in comparison with other types of mass spectrometer. Therefore, TOFMS is most suitable mass spectrometer to combine with FastGC method. In combination with the high resolution capability (HR-TOFMS) we can obtain very accurate spectra with exact m/z determination.

In this application note, we describe the qualitative and quantitative analysis by FastGC/HRTOFMS of pyrazole pesticides (Fipronil, Ethiprole, Pyraflufen ethyl and Tebfenpyrad) in tea leaf. We confirm that rapid analysis with high sensitivity is easy to perform and very useful for fast screening.

## [Sample and method]

Measurement conditions are shown in Table 1. Tea leaf (5g) was prepared using the multiresidue method for agricultural chemicals by GC/MS published by Ministry of Health, Labour and Welfare, Japan. Pyrozole pesticides were added to make 0.01, 0.05 and 0.1ppm solution in the prepared solution from tea leaf. These concentrations in solution are equivalent to 4, 20 and 40ppb in tea leaf. Each sample was analyzed 3 times to check the reproducibility.

Table 1 GC/MS measurement conditions.

| | |
|---|---|
| Instrument | JMS-T100GCV (JEOL) |
| Quantitative software | Escrime (JEOL) |
| Injection mode | Splitless |
| Injection temp. | 250℃ |
| Oven temp. program | 40℃(1min) → 50℃/min → 300℃(3.8min) |
| Injection volume | 1μL |
| Column | DB-5, 10m x 0.18mm, 0.18μm |
| Carrier gas | He, 0.7mL/min, Const. flow |
| Ionization mode | EI+, 70eV, 300μA |
| Ion source temp. | 250℃ |
| m/z range | m/z 35 - 500 |
| Spectrum recording time | 0.1sec |

## [Results and discussion]

Fig.1 shows an expanded mass spectrum of a 0.01ppm sample solution (4ppb in tea leaf) of Fipronil. This spectrum shows the *m/z* 254.97 ion produced by Fipronil and the ion of m/z 255.21 produced by a contaminant. When low-resolution MS such as QMS is used, these ions can not be separated. However, as Fig.1 shows, HR-TOFMS can separate each ion easily.

Therefore, it is possible to create high-resolution mass chromatogram with narrow m/z window (±0.05 Da) in order to eliminate the influence of chemical background.

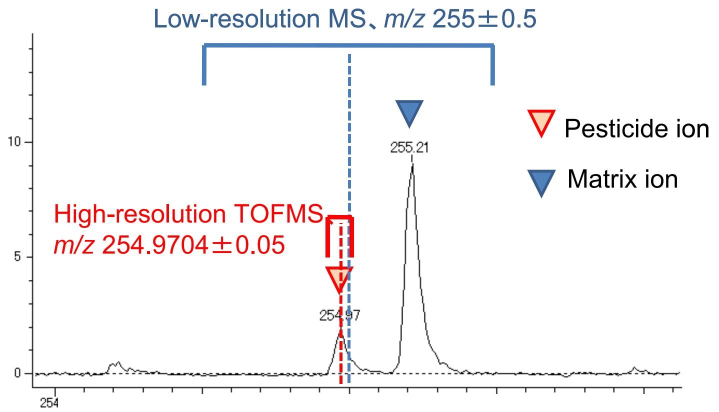

Fig.1 Mass spectrum of Fipronil.

Fig.2 shows high-resolution the mass chromatograms for each pesticide in a 0.01ppm sample solution.

Fig.3 shows the calibration curves and Table 2 shows the reproducibility (n=3) for each pesticide. Japanese default maximum regulated residues level (MRLs) for Fipronil is 2ppb and for Pyraflufen ethyl is 10ppb. The averaged S/N for each chromatographic peak in a 0.01 ppm sample solution (4ppb in tea leaf) is shown in Fig.2. For both Fipronil and Pyraflufen ethyl, this is almost 300. This S/N is enough to analyze them even if these concentrations are around the MRL value. Furthermore, the correlation coefficient for each pesticide is more than 0.997 and it shows very good linearity. The reproducibility (n=3) is shown in Table2. The variation coefficient C.V. (%), of about 10% for each pesticide at each concentration, demonstrates good reproducibility.

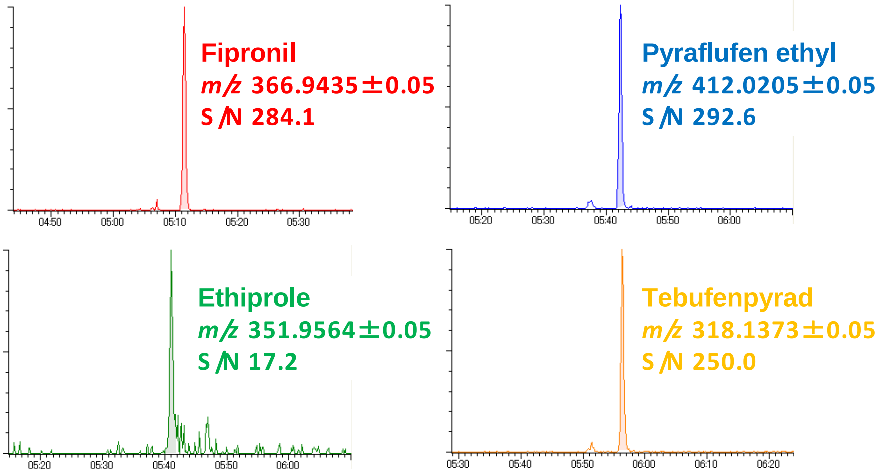

Fig.2 High-resolution Mass chromatograms of 0.01ppm

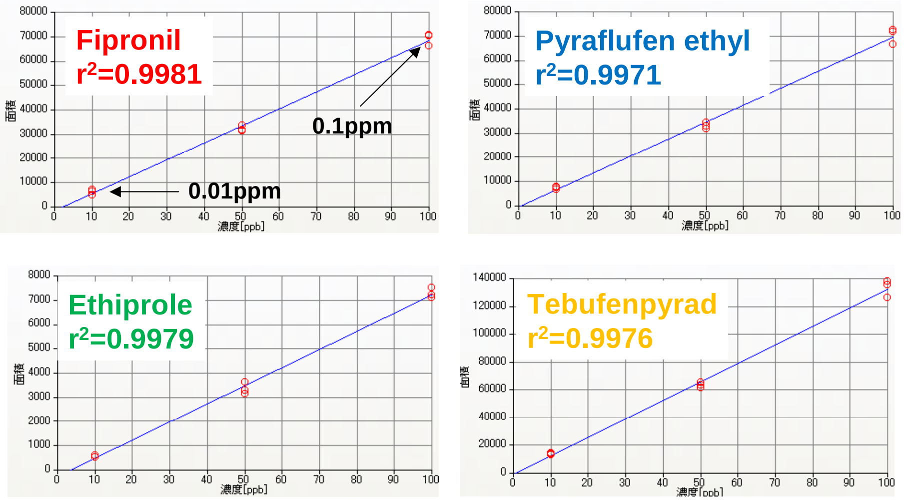

Fig.3 Calibration curves

Table 2 Results of quantitative analysis.

| ppm | No. | Fipronil | Ethiprole | Pyraflufen ethyl | Tebufenpyrad |
|---|---|---|---|---|---|
| 0.01 | 1 | 9.39 | 10.51 | 10.47 | 10.58 |
| | 2 | 11.37 | 10.51 | 11.49 | 11.26 |
| | 3 | 11.81 | 11.85 | 11.65 | 10.8 |
| | Ave. | 10.86 | 10.96 | 11.20 | 10.88 |
| | C.V.(%) | 11.87 | 7.06 | 5.71 | 3.19 |
| 0.05 | 1 | 49.73 | 47.36 | 49.57 | 49.84 |
| | 2 | 46.78 | 45.64 | 46.1 | 47.06 |
| | 3 | 47.37 | 51.84 | 49.57 | 48.35 |
| | Ave. | 47.96 | 48.28 | 48.41 | 48.42 |
| | C.V.(%) | 3.25 | 6.63 | 4.14 | 2.87 |
| 0.1 | 1 | 101.06 | 99.98 | 104.01 | 102.29 |
| | 2 | 95.44 | 98.32 | 95.63 | 95.43 |
| | 3 | 101.66 | 104 | 103.25 | 104.39 |
| | Ave. | 99.39 | 100.77 | 100.96 | 100.70 |
| | C.V.(%) | 3.45 | 2.90 | 4.59 | 4.65 |

This result shows that the JMS-T100GCV can easily obtain good quantitative result with high spectrum sensitivity, high mass accuracy and high resolution even if sample including chemical contaminants.

## [Reference]

M. Ubukata et al., Abstract of the 97th conference of the Japanese Society for Food Hygiene and Safety, page 20 (2009)

JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
JEOL Ltd. www.jeol.com

No.167 (U , 06/'10)

*JMS-T100GCV Application Data*

# Fast GC/TOFMS Analysis of Organophosphorus Pesticides

## Introduction

With this MSTips, we examined the Fast GC analysis of organophosphorus pesticides by using gas chromatograph – high resolution time-of-flight mass spectrometer (GC-HRTOFMS) JMS-T100GCV which enables high speed data acquisition. Our findings on the analysis of pesticide residues in food using GC-HRTOFMS based on this examination are reported.

## Sample and analysis conditions

Extract of frozen pumpkin was used to simulate food matrix. Water (5 g) and acetonitrile (10 mL) was added to 10 g of frozen pumpkin and homogenized. The extraction procedure according to "QuEChERS" method was then performed. The extract (in acetonitrile) was purified according to the "Simultaneous Test Methods for Agrochemicals by GC/MS (Agricultural Products)". The resulted residue was dissolved in 2 mL of acetone/hexane = 1/1. Finally, the standard pesticide mixture was added to the concentration equivalent to 0.01 ppm (per each analyte) in the original frozen pumpkin.

*Table 1 GC-HRTOFMS analysis conditions.*

| | |
|---|---|
| Instrument | JMS-T100GCV (JEOL Ltd.) |
| Quantitative software | Escrime (JEOL Ltd.) |
| Injection mode | Pulsed Splitless (250 kPa, 1.1 min) |
| Injection temp. | 250℃ |
| Oven temp. program | 50℃(0.5min)→45℃/min→125℃<br>→20℃/min→300℃(5min) |
| Injection volume | 1μL |
| GC column | ZB-5ms, 20m × 0.18mm、0.18μm |
| Carrier gas | He, 0.7mL/min (Constant flow mode) |
| Ionization mode | EI+ (70eV, 300μA) |
| m/z range | *m/z* 40-450 |
| Data acquisition speed | 0.1 sec (10 Hz) |

The analysis conditions are shown in Table 1. The Fast GC condition was optimized by referring to the "GC Condition (example 2)" in the Office Memo of the Ministry of Health, Labour, and Welfare "Test Method for Organophosphorus Pesticide Residues in Foods" dated March 7, 2008(1).

## Results and Discussion

Under the Fast GC condition shown above, the retention times of methamidophos, the first eluting analyte, and coumaphos, the last eluting analyte, were 3.64 min and 10.87 min respectively. The total analysis time was shortened to 16 min; approximately half of 31.5 min under conventional GC condition.

The reproducibility of 5 repetitive analyses of the sample is summarized on Table 2. The mass chromatogram for quantitation was generated with the m/z window of (calculated exact m/z) ± 0.025 for each analyte. The C.V. % of the mass chromatogram peak areas for 5 analyses for each analyte was 7.7 % or less, showing that the limit of quantitation (LOQ) is well below 0.01 ppm in frozen pumpkin for all analytes. The average error of measured accurate *m/z* of the quantitation ion is below 2 mDa for most analytes, showing that the confirmation of all analytes based on measured accurate *m/z* is possible.

## Reference

1） Test Method for Organophosphorus Pesticide Residues in Foods, M.H.L.W, March 7, 2008.
2） Ubukata, M., et al., Abstract of The 32nd Workshop for Pesticide Residue Analysis, P217-225 (2009).

*Table 2 Results of quantitative analysis with Fast GC technique.*

| No. | Pesticides | Retention time (min) | Qualitative ion (*m/z*) | Average mass error (n=5) (mDa) | Mass chromatogram peak area C.V. (n=5) (%) |
|---|---|---|---|---|---|
| 1 | Methamidophos | 3.64 | 94.0058 | 1.3 | 3.2 |
| 2 | Dichlorvos | 3.73 | 109.0055 | 0.9 | 2.2 |
| 3 | Acephate | 4.77 | 136.0164 | 1.1 | 3.5 |
| 4 | Omethoate | 5.68 | 156.0010 | 0.8 | 3.1 |
| 5 | Ethoprophos | 5.93 | 157.9625 | 1.1 | 6.1 |
| 6 | Cadusafos | 6.21 | 158.9703 | 0.3 | 2.1 |
| 7 | Monocrotophos | 6.14 | 127.0160 | 1.2 | 3.4 |
| 8 | Salithion | 6.14 | 216.0010 | 0.6 | 4.7 |
| 9 | Phorate | 6.26 | 75.0269 | 1.4 | 3.2 |
| 10 | Thiometon | 6.39 | 88.0347 | 1.3 | 4.5 |
| 11 | Dimethoate | 6.44 | 87.0158 | 1.0 | 3.8 |
| 12 | Terbufos | 6.70 | 230.9737 | 1.1 | 6.5 |
| 13 | Diazinon | 6.74 | 137.0715 | 0.4 | 4.4 |
| 14 | Cyanophos | 6.69 | 243.0119 | 0.5 | 3.1 |
| 15 | Ethylthiometon | 6.87 | 88.0347 | 0.8 | 5.5 |
| 16 | Etrimfos | 6.91 | 292.0647 | 0.8 | 2.6 |
| 17 | Iprobenfos | 7.03 | 91.0566 | 0.6 | 3.6 |
| 18 | Formothion | 7.08 | 124.9826 | 0.9 | 4.5 |
| 19 | Dichlofenthion | 7.18 | 279.0012 | 1.4 | 3.4 |
| 20 | Chlorpyrifos-methyl | 7.24 | 285.9261 | 0.8 | 2.2 |
| 21 | Tolclophos-methyl | 7.32 | 264.9855 | 0.8 | 3.7 |
| 22 | Pirimiphos-methyl | 7.52 | 290.0728 | 1.1 | 5.3 |
| 23 | Fenitrothion | 7.56 | 124.9826 | 1.4 | 4.3 |
| 24 | Dimethylvinphos-E | 7.59 | 294.9694 | 1.1 | 1.8 |
| 25 | Malathion | 7.63 | 124.9826 | 1.0 | 4.2 |
| 26 | Chlorpyrifos | 7.71 | 196.9202 | 0.9 | 1.3 |
| 27 | Dimethylvinphos-Z | 7.73 | 294.9694 | 0.9 | 0.6 |
| 28 | Fenthion | 7.76 | 278.0200 | 0.9 | 2.1 |
| 29 | Fosthiazate-1 | 7.95 | 195.0119 | 1.4 | 6.3 |
| 30 | Chlorfenvinphos-E | 8.03 | 266.9381 | 0.9 | 1.9 |
| 31 | Fosthiazate-2 | 7.98 | 195.0119 | 1.0 | 3.3 |
| 32 | Isofenphos | 8.12 | 213.0317 | 0.9 | 4.9 |
| 33 | Chlorfenvinphos-Z | 8.13 | 266.9381 | 1.3 | 1.0 |
| 34 | Phenthoate | 8.20 | 273.9887 | 1.1 | 1.0 |
| 35 | Quinalphos | 8.21 | 146.0480 | 1.6 | 2.3 |
| 36 | Bromophos (Bromophos-methyl) | 8.34 | 358.9070 | 0.9 | 3.4 |
| 37 | Propaphos | 8.35 | 219.9959 | 1.3 | 0.8 |
| 38 | Methidathion | 8.35 | 145.0072 | 1.3 | 3.1 |
| 39 | Vamidothion | 8.41 | 145.0561 | 1.3 | 5.1 |
| 40 | Butamifos | 8.51 | 286.1031 | 2.3 | 5.9 |
| 41 | Phenamiphos | 8.53 | 303.1058 | 1.1 | 1.3 |
| 42 | Prothiofos | 8.62 | 266.9470 | 1.8 | 4.8 |
| 43 | Profenofos | 8.66 | 207.9112 | 0.5 | 2.0 |
| 44 | Isoxathion | 8.88 | 105.0340 | 0.7 | 7.7 |
| 45 | Fensulfothion | 9.03 | 292.0351 | 1.1 | 2.6 |
| 46 | Ethion | 9.10 | 230.9737 | 1.5 | 4.6 |
| 47 | Sulprofos | 9.26 | 322.0285 | 1.7 | 4.4 |
| 48 | Cyanofenphos | 9.37 | 156.9877 | 0.4 | 4.0 |
| 49 | Edifenphos | 9.40 | 109.0123 | 0.5 | 2.1 |
| 50 | Pyridaphenthion | 9.82 | 340.0647 | 1.1 | 5.7 |
| 51 | EPN | 9.92 | 156.9877 | 0.4 | 2.2 |
| 52 | Phosmet | 9.91 | 160.0434 | 0.7 | 3.2 |
| 53 | Phosalone | 10.24 | 182.0009 | 0.8 | 4.1 |
| 54 | Azinphos-methyl | 10.29 | 132.0449 | 1.0 | 2.9 |
| 55 | Azinphos-ethyl | 10.58 | 132.0449 | 1.2 | 7.2 |
| 56 | Pyraclofos | 10.64 | 360.0464 | 2.8 | 4.5 |
| 57 | Coumaphos | 10.87 | 362.0145 | 2.3 | 5.4 |

# Determination of Triazolam by AccuTOF™ GC/Time-of-Flight Mass Spectrometry

**Zhanpin Wu, JEOL USA, Inc.**

## Introduction

Triazolam is a benzodiazepine with a very short elimination half-life. The range is reported to be 1.5 to 5.5 hours[1]. Due to its frequent use as a sedative and its potential to affect human activities such as driving, an unambiguous and sensitive analysis method is needed for its identification and quantitation. Generally, for determination of triazolam, screen tests are performed in biological samples followed by confirmation and quantitation with GC/MS [2]. Here, we demonstrate the feasibility by using the JEOL AccuTOF™ GC, time-of-flight mass spectrometer with accurate mass measurement and negative ion chemical ionization (NCI) capabilities for triazolam determination. $D_4$-triazolam was used as internal standard. The mass accuracy without internal reference is smaller than 2 mmu. The limit of detection is 5 ng/mL. The quantitation standard curve can be linear from 5 ng/mL to 1000 ng/mL with $R^2$ of 0.9992. To the best of our knowledge, this is the first time that triazolam has been detected by GC/time-of-flight mass spectrometry with accurate mass measurement.

## Experimental

### 1. Solvents and standards

All solvents used were of HPLC grade. Triazolam and $d_4$-triazolam standard solutions were purchased from Cerilliant (Round Rock, TX). A series of triazolam standard solutions, with concentrations from 5 ng/mL to 1000 ng/mL, was prepared in methanol. A stock solution of $d_4$-triazolam with 100 ng/mL was also prepared in methanol.

### 2. Sample preparation

An aliquot of 100 µL of sample was transferred into a small silanized glass tube, and then 100 µL of the internal standard was added. The solvent was evaporated under a gentle stream of nitrogen gas. Fifty microliters of ethyl acetate followed by 50 µL BSA/TMCS (5/1) were added to the tube. All tubes were heated at 80 °C for 30 min. The liquid was transferred to an autosampler vial for injection.

### 3. GC/MS analysis

The system included a JEOL AccuTOF™ GC time-of-flight mass spectrometry system set at NCI mode and an Agilent 6890 N GC. The system was controlled by a JEOL MassCenter™ workstation. The GC column was a DB5-MS capillary column (30 m, 0.25 mm i.d., 0.25µm). The initial oven temperature of 60 °C was held for 1 min, and then increased to 325 °C at the rate of 25 °C/min and held at the final temperature for 3 min. The carrier gas was helium with a constant flow rate of 1 mL/min. The temperatures for injection port, transfer line and ion source were 275 °C, 250 °C, and 200 °C, respectively. The reagent gas was methane with a flow rate of 0.83 mL/min. The ionizing voltage and current were 200 V and 300 μA, respectively. The MCP detector was set at 2,500 V. One microliter sample was injected onto the column with splitless mode.

## Results and Discussion

Triazolam has very short elimination half-time. It is metabolized via hepatic microsomal oxidation. The hydroxylated metabolites, which are inactive, are excreted primarily in the urine as conjugated glucuronides. The level of parent drug in the biological fluid is usually very low after a few hours administration. It is generally known that negative-ion chemical ionization (NCI) provides very high sensitivity for analyzing compounds containing halogen atoms. Triazolam contains 2 chlorine atoms, making it possible to obtain very high sensitivity under NCI detection. Treatment with BSA/TMCS (5/1) improved the peak shapes of triazolam. Theoretically, only its hydroxylated metabolites – not the drug itself - should form TMS derivatives. However, TMS may enhance the chromatography for triazolam by either associating with the drug or by deactivating the GC column [3]. We first tested the detection limit under the current experimental conditions. An average signal-to-noise ratio of 70 was achieved when 5 ng/mL triazolam was injected. The error for mass accuracy is less than 2 mmu. Bigger than 3 mmu mass accuracy error was obtained if lower than 5 ng/mL samples were injected. Figure1 shows the high-resolution mass chromatogram ($\Delta m = 0.01$) and mass spectrum for m/z 306, $[M\text{-}Cl\text{-}H]^-$, in the standard solution with 5 ng/mL triazolam and 100 ng/mL internal standard.

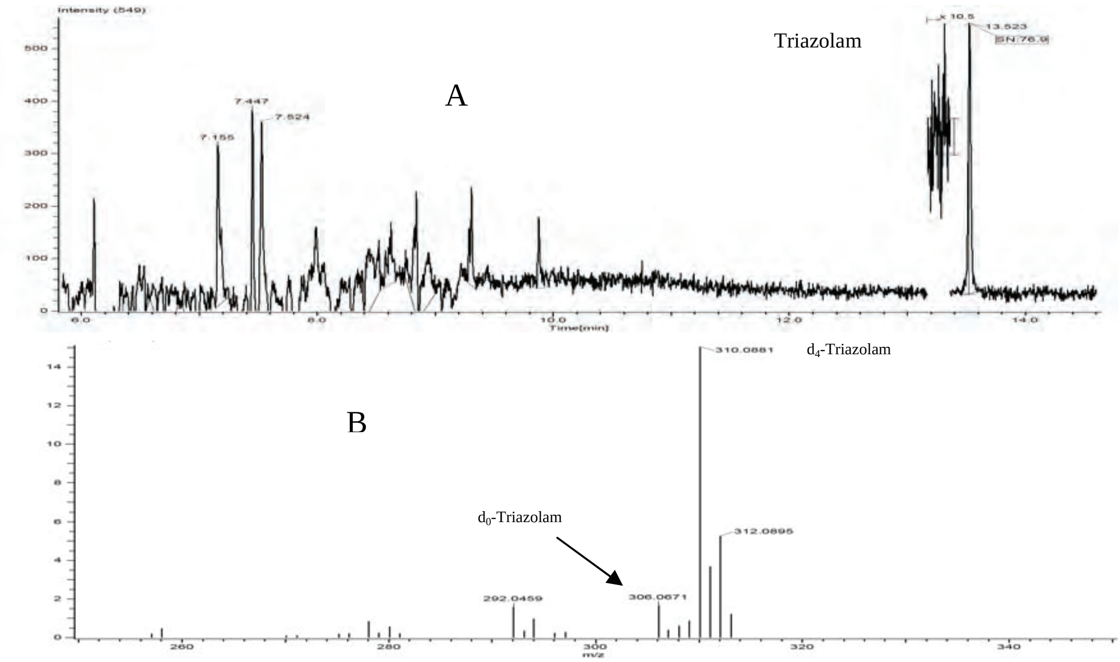

Fig.1 (A) Mass chromatogram of triazolam (m +/- 0.01) with concentration of 5 ng/mL. (B) Mass spectrum of traizolam with concentration of 5 ng/mL

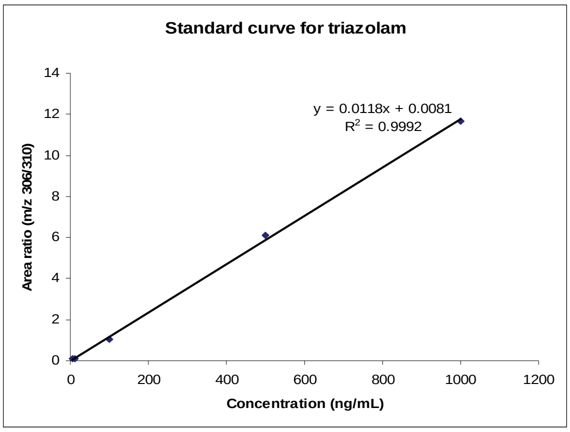

Fig. 2 Standard curve for triazolam from 5 ng/mL to 1000 ng/mL with d4-triazolam as the internal standard.

| Concentration (ng/mL) | Precision % CV | Mass Accuracy (mmu) |
|---|---|---|
| 5 | 16.2 | 1.44 |
| 10 | 3.2 | 1.12 |

Table 1. Precision and mass accuracy for two different concentrations of triazolam ( n = 5 )

Peak-area ratios ($d_0/d_4$) from high-resolution mass chromatograms were calculated for each standard and plotted against the known concentrations of the standard. Correlation coefficient ($R^2$) is 0.9992. The standard curve is shown in Figure 2.

The method precision was determined by analyzing two different concentrations of standard solution. The samples were analyzed five times in duplicate. The percent coefficient of variation (CV) is 3.2% for the 10 ng/mL sample and 16.2% for the 5 ng/mL sample. Higher than 20% CV was obtained if samples lower than 5 ng/mL were injected. Therefore, the quantitation limit for the assay is 5 ng/mL. The results are listed in Table 1.

## Conclusion

To the best of our knowledge, this is the first time the feasibility of using GC/time-of-flight mass spectrometry to determine triazolam has been evaluated. The accurate mass measurement capability of a high-resolution time-of-flight mass spectrometer makes the determination unambiguous even in very low concentrations. The method was sensitive, precise and simple. In order to apply this method for biological samples, additional method development including sample extraction and validation may be required.

## References

1. http://www.mentalhealth.com/drug/p30-h01.html
2. Hold, KM, Forensic Science International, 84(1997), 201-209
3. Hold, KM, J. Mass Spectrometry, 31(1996), 1033-1038

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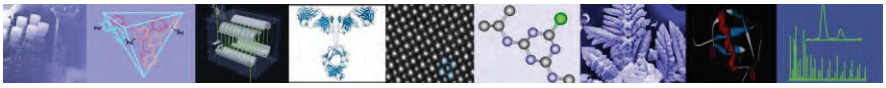


# AccuTOF-GCv Series

## Analyzing Polycyclic Aromatic Hydrocarbons in Diesel Particulate Matter using GC×GC-HRTOFMS

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) refer to aromatic hydrocarbons that have at least 2 benzene rings, such as naphthalene and anthracene which feature 2 and 3 benzene rings, respectively. PAHs are found in crude oil and are often released into the environment (water, atmosphere, etc.) when crude oil and oil products such as heating oil and light gas oil are burned. As it turns out most PAHs are carcinogenic with some of them identified as highly carcinogenic. Therefore, it is critical to determine the levels of PAHs present in the environment. In this work, we analyzed PAHs in diesel particulate matter using GCxGC-HRTOFMS, a technique that combines a JMS-T100GCV with comprehensive 2DGC (GCxGC).

### Experimental

A commercial sample (2975 Diesel Particulate Matter, NIST) was mixed with chloroform (weight ratio 1:10) and heated at 100°C for 5 hours to accomplish solvent extraction. The extract was then centrifugally separated from the particulate material, and the resulting supernatant liquid was concentrated for measurement. Table 1 shows the instrument measurement conditions used for the analysis.

| | |
|---|---|
| Instrument | JMS-T100GCV (JEOL Ltd.)<br>KT2004 (Zoex Corporation) |
| Injection mode | Split 20:1 |
| Injection temp. | 300°C |
| Oven temp. program | 50°C (1min)→5°C/min→280°C (13min) |
| Injection volume | 0.2μL |
| Column | 1st:DB-1ms, 30m × 0.25mm, 0.25μm<br>2nd:DB-17, 2m × 0.1mm, 0.1μm |
| Carrier gas | He, 2.0 mL/min, Constant flow |
| Modulation | Period:6sec, Releasing:0.3sec |
| Ionization mode | EI+, 70eV, 300μA |
| Ion source temp. | 280°C |
| m/z range | *m/z* 29—800 |
| Data acquisition speed | 0.04 sec (25 Hz) |

*Table 1. GCxGCHRTOF-MS measurement conditions*

### Results and Discussion

Figure 1 shows the GCxGC TIC chromatogram acquired from the sample. The X axis represents analyte separation by the 1st column, DB-1ms, in which the components

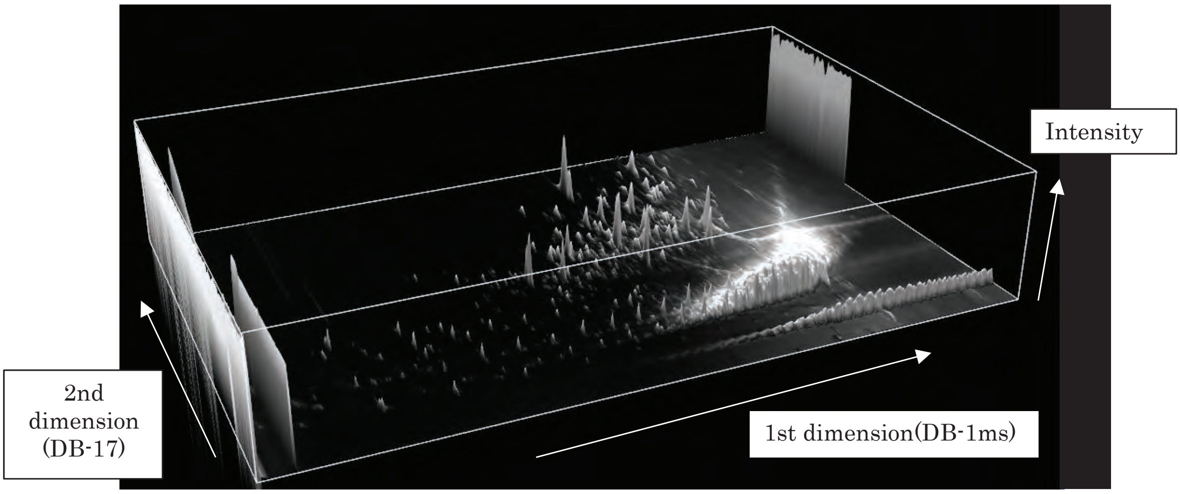
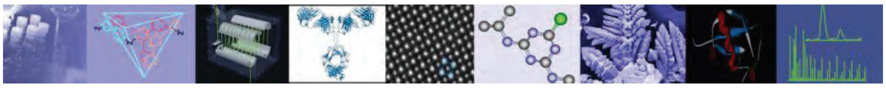


*Figure 1. GCxGC TIC chromatogram (3D)*



were separated according to their boiling points. The Y axis represents the separation in the 2nd column, DB-17, in which the components were separated according to their polarities. The Z axis represents the peak intensity of the ions in the TIC. Although the sample preparation consisted of a simple solvent extraction of the commercial sample, a wide variety of components were observed in the TIC (Figure 1).

Next, several mass chromatograms for $C_{18}H_{12}$, which contains 4 fused benzene rings, were compared to examine the selective detection of PAHs. The wide *m/z* window GCxGC mass chromatogram in Figure 2 (a) shows a number of impurities in addition to the PAHs. However, in the narrow *m/z* window GCxGC mass chromatogram in Figure 2 (b), only the PAHs were selectively detected. Figure 3 shows the mass spectrum for the PAHs detected in Figure 2. The mass spectrum shows that $C_{18}H_{12}$ (*m/z* 228.0930), a molecular ion of PAHs, was detected with high mass accuracy (0.3 mDa).

**Conclusions**

The results show that the GCxGC/HRTOFMS enhances the resolution of the GCxGC and the selectivity of HRTOFMS. Furthermore, combining these techniques is a powerful tool for analyzing complex samples that consist of many components and impurities.

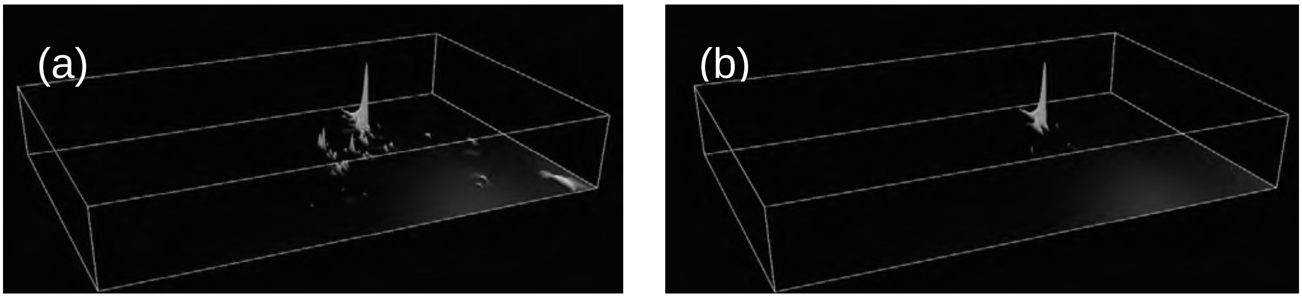
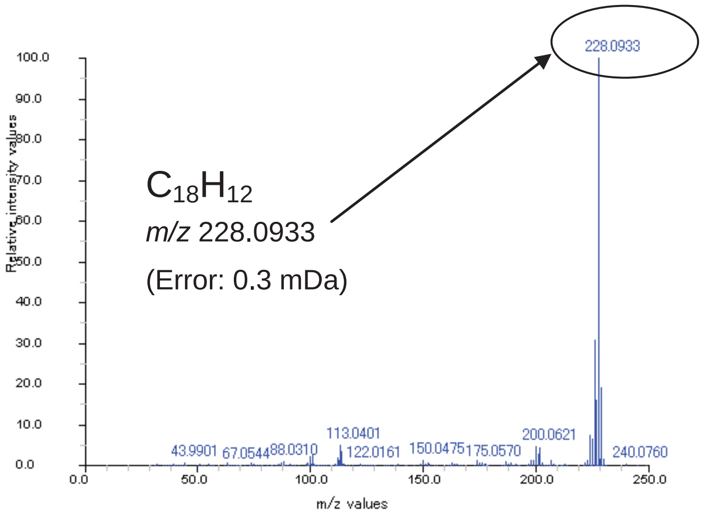
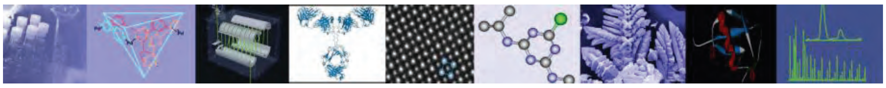


*Figure 2. GCxGC chromatograms (3D)*
*(a) m/z 228±0.5 (b) 228.0930±0.01*



$C_{18}H_{12}$
*m/z* 228.0933
(Error: 0.3 mDa)

*Figure 3. EI mass spectrum for $C_{18}H_{12}$ in Figure 2 (a) and (b)*



# AccuTOF-GC Series

## Analysis of Electronics Waste by GCxGC Combined with High-resolution Mass Spectrometry: Using Accurate Mass Information and Mass Defect Analysis to Explore the Data [1]

**Introduction**

Comprehensive two-dimensional gas chromatography (GCxGC) in combination with high-resolution mass spectrometry (HRMS) is a powerful tool for the analysis of complex mixtures. However, new software tools are required to facilitate the interpretation of the rich information content in GCxGC/HRMS data sets. In this work, we analyzed a dust sample collected from an electronics recycling facility by using GCxGC in combination with a new high-resolution time-of-flight (TOF) mass spectrometer. Nontraditional Kendrick Mass Defect (KMD) plots were used to identify halogenated contaminants in an electronics waste sample. Database search results combined with elemental composition determinations from exact-mass data were used to identify (potential) persistent organic pollutants (POPs).

**Sample and Instrument**

A dust sample was collected from an electronics recycling facility. Then, 1 gram of this sample was used for extraction into hexane. Afterwards, the hexane solution was analyzed with the JEOL JMS-T100GCV "AccuTOF GCv 4G" equipped with a Zoex ZX2 thermal modulator (Figure 1) and a high-resolution version of the GC Image software (version 2.5.0a2). Table 1 shows the measurement conditions used for the analysis.

**Result and Discussion**

Figure 2a shows the GCxGC/EI TIC for the sample. Afterwards, a composite mass spectrum was created by summing the mass spectra for all components in the GC x GC/HRMS analysis (Figure 2b). Halogenated contaminants are readily recognized by their mass defects [2]. The next step then was to then create nontraditional KMD plots by converting the measured IUPAC *m/z* to H/Cl mass scales corresponding to the mass of a chlorine atom minus the mass of a hydrogen atom. Afterwards, the nominal mass was plotted vs. the corresponding mass defect for each peak (Figure 2c).

*H/Cl mass = IUPAC mass x (34/33.96102)*

The resulting mass defect plot facilitated the rapid identification of families of compounds that differ by the number of chlorine substituents. The KMD plots for H/Cl and H/Br are nearly identical, allowing us to view both Cl and Br substitutions in one plot.

1. We found chlorinated and brominated compounds immediately, easily and visually by using H/Cl KMD plots. We then used this information to make the 2D mass chromatograms (Figure 3).
2. Additionally, we obtained NIST library search results and accurate mass measurement results from the data acquired in EI mode (Figure 3).
3. We showed a good example for the analysis of a complex sample using GCxGC, high-resolution MS and the KMD method. The combination of these techniques is a very powerful and useful tool for detailed qualitative analysis.
4. We also performed NICI measurements with GCxGC and KMD analysis (Figure 4). We observed similar results to the EI data for several compounds. However, some compounds showed abundant $Cl^-$ and $Br^-$ peaks instead of molecular ions so their 2D mass chromatograms were plotted as well (Figure 5). The NICI method is a good ionization technique for low-concentration samples and quantitative analysis.

*Figure 1. JMS-T100GCV AccuTOF GCv 4G GCxGC/HR-TOFMS system*

<table>
<tr><th>Condition</th><th>GC x GC/EI</th><th>GC x GC/NICI</th></tr>
<tr><td>Sample</td><td colspan="2">Dust sample<br>collected from an electronics recycling facility</td></tr>
<tr><td>GC x GC system</td><td colspan="2">ZX2 thermal modulator (ZOEX)</td></tr>
<tr><td>1st column</td><td colspan="2">Rxi-5SilMS, 30 m x 0.25 mm, 0.25 µm</td></tr>
<tr><td>2nd column</td><td colspan="2">Rxi-17SilMS, 2 m x 0.15 mm, 0.15 µm</td></tr>
<tr><td>Modulation loop</td><td colspan="2">Deactivated fused silica, 1.5 m x 0.15 mm</td></tr>
<tr><td>Modulation period</td><td colspan="2">8 sec</td></tr>
<tr><td>Modulation duration</td><td colspan="2">400 msec</td></tr>
<tr><td>Inlet pressure</td><td colspan="2">200 kPa at Oven temp. 50 °C (Constant flow mode)</td></tr>
<tr><td>Inlet mode</td><td colspan="2">Splitless</td></tr>
<tr><td>Oven temp.</td><td colspan="2">50 °C (1 min) -> 5 °C/min -> 320 °C (5 min)</td></tr>
<tr><td>GC-TOFMS system</td><td colspan="2">AccuTOF GCv 4G (JEOL)</td></tr>
<tr><td>Ionization mode</td><td>EI+</td><td>CI-</td></tr>
<tr><td>Ionization voltage</td><td>70 V</td><td>150 V</td></tr>
<tr><td>Ionization current</td><td>300 µA</td><td>300 µA</td></tr>
<tr><td>CI gas</td><td></td><td>Ammonia/Methane<br>0.5 mL/min</td></tr>
<tr><td>Ion source temp.</td><td>250 °C</td><td>200 °C</td></tr>
<tr><td>GC-ITF temp.</td><td colspan="2">280 °C</td></tr>
<tr><td>*m/z* range</td><td>*m/z* 45-800</td><td>*m/z* 30-800</td></tr>
<tr><td>Acquisition time</td><td colspan="2">20 msec (50 Hz)</td></tr>
<tr><td>Sampling time</td><td colspan="2">0.25 nsec (4 GHz)</td></tr>
<tr><td>External calibrant</td><td>*m/z* 207.0329 ($C_5H_{15}O_3Si_3^+$)</td><td>*m/z* 234.9405 ($ReO_3^-$)</td></tr>
<tr><td>Software</td><td colspan="2">GC Image™ Version 2.5.0a2</td></tr>
</table>

*Table 1.Measurement Conditions*

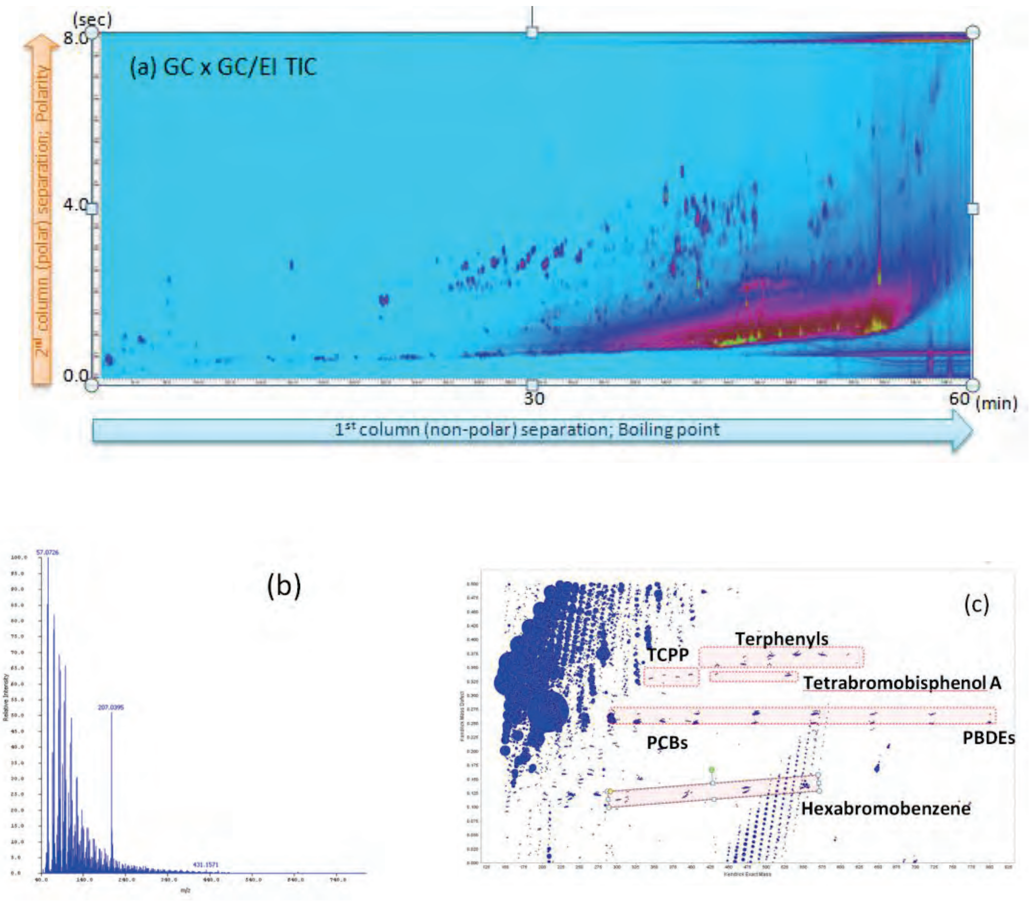


*Figure 2. (a) GCxGC/EI TIC chromatogram of the dust sample, (b) Averaged mass spectrum for the whole retention time region, (c) H/Cl mass defect plot for the averaged mass spectrum.*

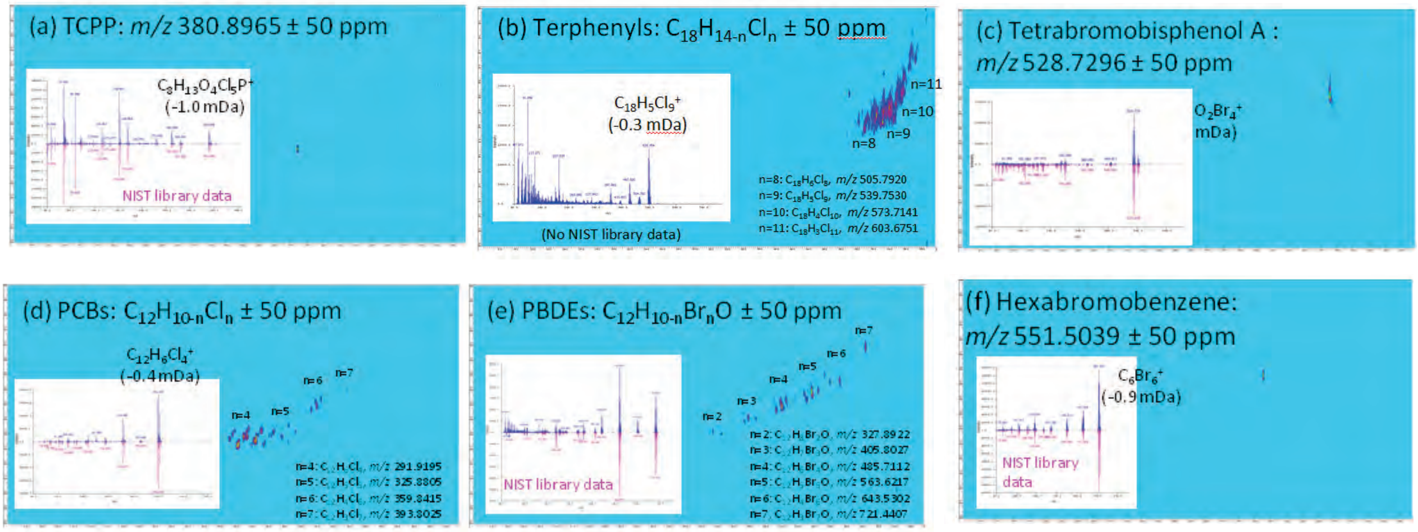


*Figure 3. 2D mass chromatogram using mass of the most abundant isotope ion ± 50 ppm (a) TCPP, (b) Terphenyls, (c) Tetrabromobisphenol A, (d) PCBs, (e) PBDEs, (f) Hexabromobenzene*

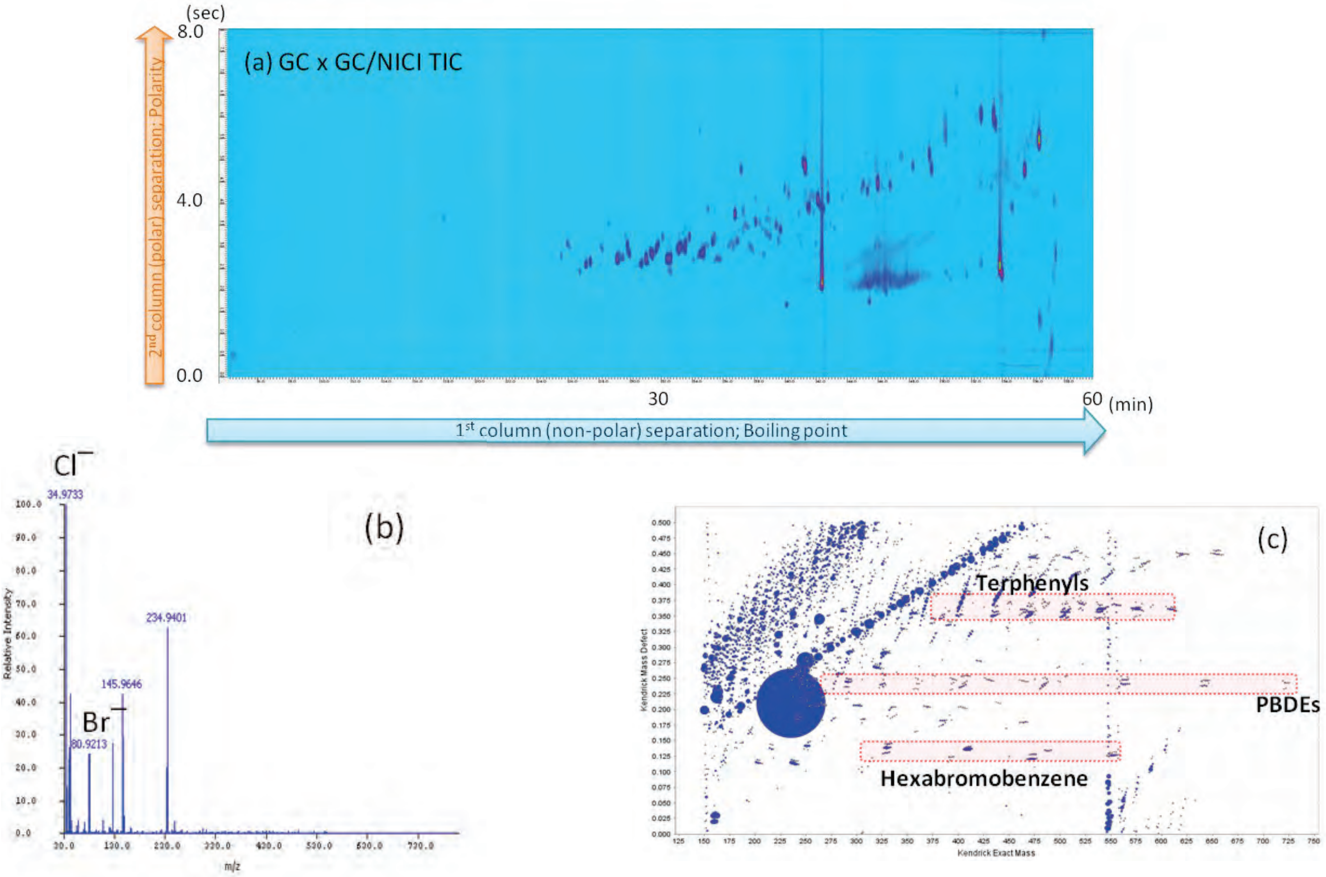


*Figure 4. (a) GCxGC/NICI TIC chromatogram of the dust sample, (b) Averaged mass spectrum for the whole retention time region, (c) H/Cl mass defect plot for the averaged mass spectrum.*

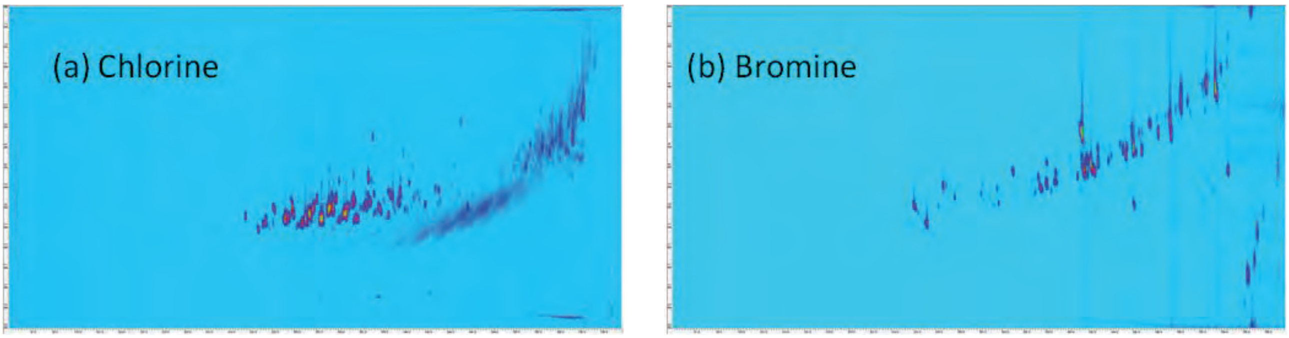


*Figure 5. 2D mass chromatogram using mass of the most abundant isotope ion ± 0.02 u for (a) Chlorine (m/z 34.9689), and (b) Bromine (m/z 78.9183)*

**Reference**

[1] M. Ubukata, K. J. Jobst, E. J. Reiner, S. E. Reichenbach, Q. Tao, J. Hang, Z. Wu, A. J. Dane, R. B. Cody. Non-targeted analysis of electronics waste by comprehensive two-dimensional gas chromatography combined with high-resolution mass spectrometry: using accurate mass information and mass defect analysis to explore the data. *Journal of Chromatography A*, **2015**. doi:10.1016/j.chroma.2015.03.050

[2] K. J. Jobst, L. Shen, E. J. Reiner, V. Y. Taguchi, P. A. Helm, R. McCrindle, S. Backus. The use of mass defect plots for the identification of (novel) halogenated contaminants in the environment, *Anal Bioanal Chem (2013)* 405:3289–3297

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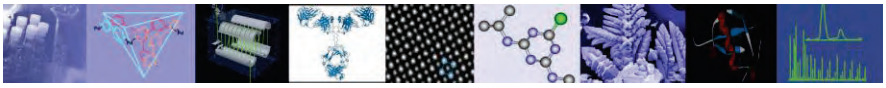


# AccuTOF-GCv Series

## Aroma Oil Analysis using GCxGC-HRTOFMS Performance Test for AccuTOF GCv 4G

### Introduction

The AccuTOF GCv 4G is JEOL's third generation high resolution GC-TOFMS. New, enhanced features of the system include:

1) Recording speed: up to 50 spectra/sec
2) Mass resolution: 8,000 or more (*m/z* 614, FWHM)
3) Mass accuracy: 1.5 mmu or 4 ppm
4) Mass range: *m/z* 4 to 5,000

Comprehensive 2D GC (GCxGC) is a chromatographic separations technique that uses 2 columns with different polarities arranged in a series. Featuring higher resolution than conventional capillary GC analysis, it is a powerful tool for the measurement of multiple components in a complex mixture. However, because there is a cryo-trap before the 2nd column, the resulting peaks in the chromatograms are extremely narrow. As a result, the system requires a detector capable of high speed data recording. The TOFMS is an ideal detector for the 2D GC system.

In this work, we analyzed aroma oil using a GCxGC-HRTOFMS system, in which the AccuTOF GCv 4G was used with a Zoex GCxGC system to examine the spectrum recording speed and mass accuracy.

| | |
|---|---|
| Instrument | JMS-T100GCV 4G (JEOL Ltd.)<br>KT2004 (Zoex Corporation ) |
| Injection mode | Split 200 : 1 |
| Injection temp. | 270 °C |
| Oven temp. | 50 °C(3min) → 5 °C/min → 270 °C(8min hold) |
| Injection volume | 0.2 μL |
| Column set | 1st: BPX-5 ( 30 m x 0.25 mm, 0.25 μm )<br>2nd: BPX-50 ( 2 m x 0.1 mm, 0.1 μm ) |
| Modulation period | 6 sec |
| Ionization mode | EI+: 70 eV, 300 μA |
| Ion source temp. | 270 °C |
| m/z range | *m/z* 35 - 500 |
| Data acquisition | 0.02 sec (50 Hz) |

*Table 1. Measurement conditions*

### Experimental

For the sample, a commercial product of tea tree oil, a type of aroma oil, was used without treatment. Table 1 shows the measurement conditions used for the analysis. GC Image (Zoex) was used for processing of the GCxGC data.

### Results and Discussion

Figure 1 shows a 2D map created from the aroma oil TIC. The compounds identified from each EI mass spectrum

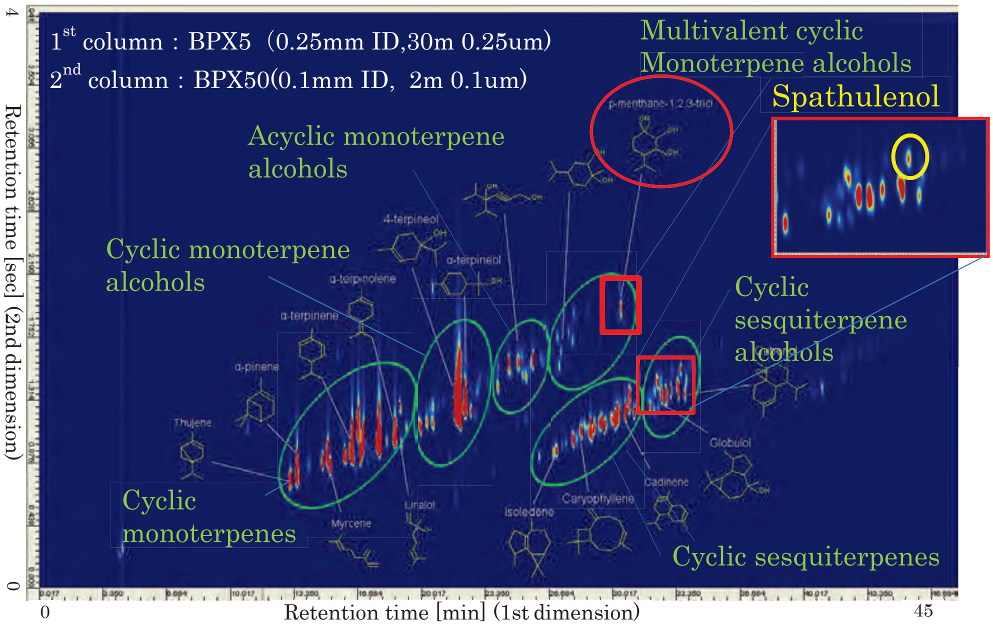


*Figure 1. 2D map of tea tree oil sample analyzed by GCxGC-HRTOFMS*

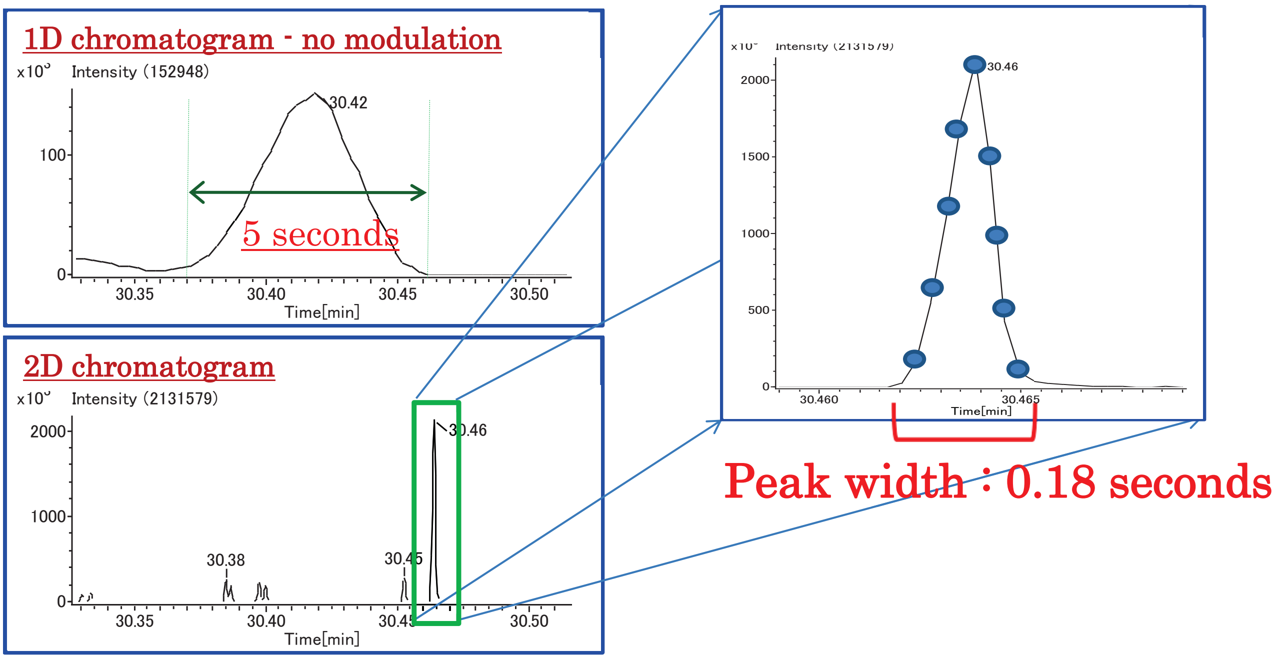


*Figure 2. Magnified peak of p-menthane-1,2,3-triol*

and their corresponding structures are marked on the 2D map.

Because the column set used for the analysis had a nonpolar 1st column and a polar 2nd column, the components were eluted with reference to their boiling point in the horizontal axis and their polarity in the vertical axis. Figure 1 shows cyclic and acyclic monoterpenes and monoterpene alcohols in groups from 12 to 30 minutes in the horizontal axis. The cyclic sesquiterpenes and cyclic sesquiterpene alcohols were observed between 25 and 35 minutes in the 1$^{st}$ dimension.

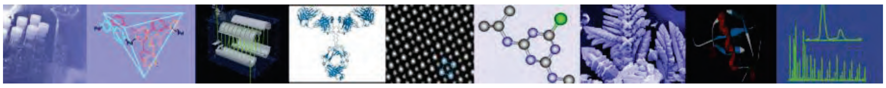
**Recording speed**

The recording speed was examined using the peak width in the chromatogram of p-menthane-1,2,3-triol that was eluted at approximately 30 minutes in Figure 1. Figure 2 shows the 1D and 2D chromatograms of p-menthane-1,2,3-triol at the elution time with and without modulation on the same column set. The figure also shows a magnified chromatogram of the p-menthane-1,2,3-triol peak in the 2D chromatogram.

In the 1D chromatogram without modulation, the peak with p-menthane-1,2,3-triol as its major component had a peak width of approximately 5 sec. Meanwhile, in the 2D chromatogram, the p-menthane-1,2,3–triol had an extremely narrow peak width of approximately 0.18 sec. This demonstrates that at the recording speed at 50 Hz, the system was able to acquire sufficient data points on the chromatogram, 9 points as shown in the magnified view in Figure 2, compared to the recording speed at 2.5 to 10 Hz that is typically used in 1D GC-MS data acquisition.

**Exact mass accuracy**

Next, the mass accuracy was examined using the mass spectrum of spathulenol ($C_{15}H_{24}O$, exact mass: 220.18271), a cyclic sesquiterpene that eluted at approximately 33 min in Figure 1. Figure 3 shows the measured mass spectrum for this compound. Table 2 shows the error (mDa) between the measured exact mass and the expected exact mass for the molecular ion when the same sample was analyzed 5 different times. The error ranged from 0.46 to 0.78 mDa, showing extremely high levels of accuracy and stability. These results demonstrate that the system is capable of estimating the composition with high precision during the high speed data acquisition that is required for GCxGC analyses.



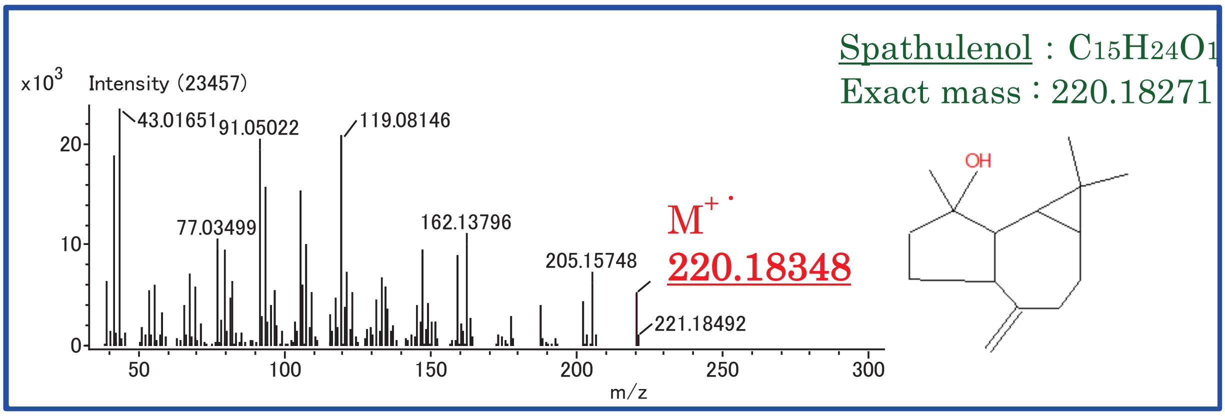


*Figure 3. Mass spectrum of spathulenol*

| No. | Accurate mass (Da) | Error (mDa) |
|---|---|---|
| 1 | 220.18348 | 0.77 |
| 2 | 220.18337 | 0.65 |
| 3 | 220.18326 | 0.55 |
| 4 | 220.18349 | 0.78 |
| 5 | 220.18318 | 0.46 |

*Table 2. Errors between exact mass and accurate mass of spathulenol*

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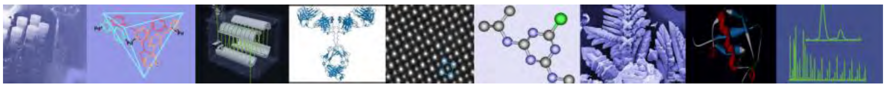


# AccuTOF-GCv Series

## SPME-GCxGC/HRTOFMS Analysis of Tequila

### Introduction

The JEOL "AccuTOF GCv 4G" is a third generation GC/HRTOFMS system with high speed data acquisition capabilities of up to 50Hz which makes it well suited as the detector for comprehensive 2-dimensional GC (GCxGC) measurements. Along with the high speed data acquisition, this MS system also provides high mass resolution, accurate mass measurements, and high sensitivity, all simultaneously. Consequently, this GCxGC/HRTOFMS system is a powerful tool for the qualitative analysis of complicated samples.

In this work, we measured commercially available tequila samples using GCxGC/HRTOFMS combined with solid-phase micro-extraction (SPME) preparation.

### Experimental

Sample information and measurement conditions are shown in Figure 2 and Table 1.

*Fig. 1. GCxGC/HRTOFMS system.*

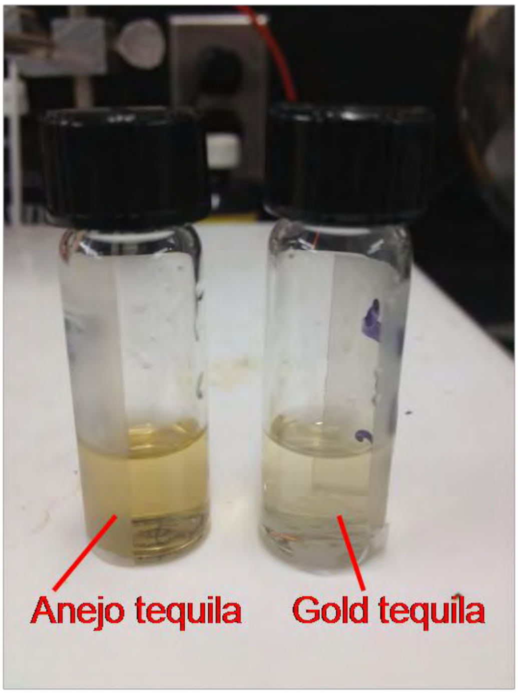


*Fig. 2. Tequila samples.*

| Condition | SPME-GCxGC-EI |
|---|---|
| Sample | 1. Anejo tequila<br>2. Gold tequila |
| SPME | 50/30 um DVB/CAR/PDMS (SUPELCO) |
| SPME condition | 10 min at room temparature |
| GCxGC system | ZX2 thermal modulator (ZOEX) |
| 1st column | Rxi-5SilMS, 30 m x 0.25 mm, 0.25 um |
| 2nd column | Rxi-17SilMS, 2 m x 0.15 mm, 0.15 um |
| Modulator loop | Deactivated fused silica, 1.5 m x 0.15 mm |
| Modulator period | 10 sec |
| Modulator duration | 400 msec |
| Inlet pressure | 200 kPa |
| Inlet mode | Split 10:1 |
| Oven temp. | 50 C (1 min) -> 3 C/min -> 250 C |
| GC-TOFMS system | AccuTOF GCv 4G (JEOL) |
| Ionization mode | EI+ |
| Ionization condition | Ionization voltage: 70 V<br>Ionization current: 300 uA |
| Ion source temp. | 250 C |
| GC-ITF temp. | 280 C |
| *m/z* range | *m/z* 35-500 |
| Acquisition time | 20 msec (50 Hz) |
| Sampling time | 0.25 nsec (4 GHz) |
| External calibrant | *m/z* 207.0329 (column background) |

*Table 1. Measurement conditions.*

We analyzed two tequila samples (Figure 2), anejo and gold tequila. The anejo tequila is an aged tequila that is more expensive than the typical gold tequila. The SPME sample preparation step consisted of immersing the SPME fiber in the pure tequila for 10 minutes at room temperature. Afterwards, the SPME sample was measured using GCxGC/EI method (Table 1).

## Results

The 2-dimensional total ion chromatograms (2D TICs) for each tequila sample are shown in Figures 3 and 4, respectively. Both TICs showed the presence of a wide variety of components in the sample.

The red circles in each 2D TIC, referred to as "Blobs," show the detected chemical components and include

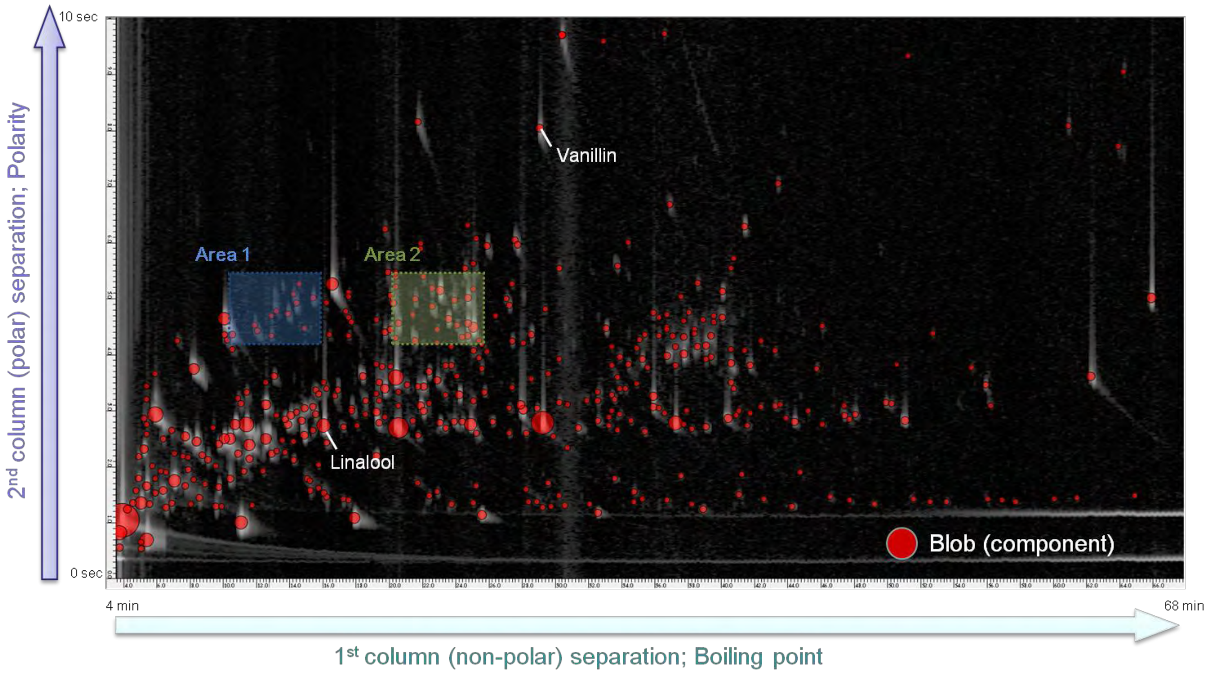


*Fig. 3. GCxGC/EI TIC chromatogram of an anejo tequila.*

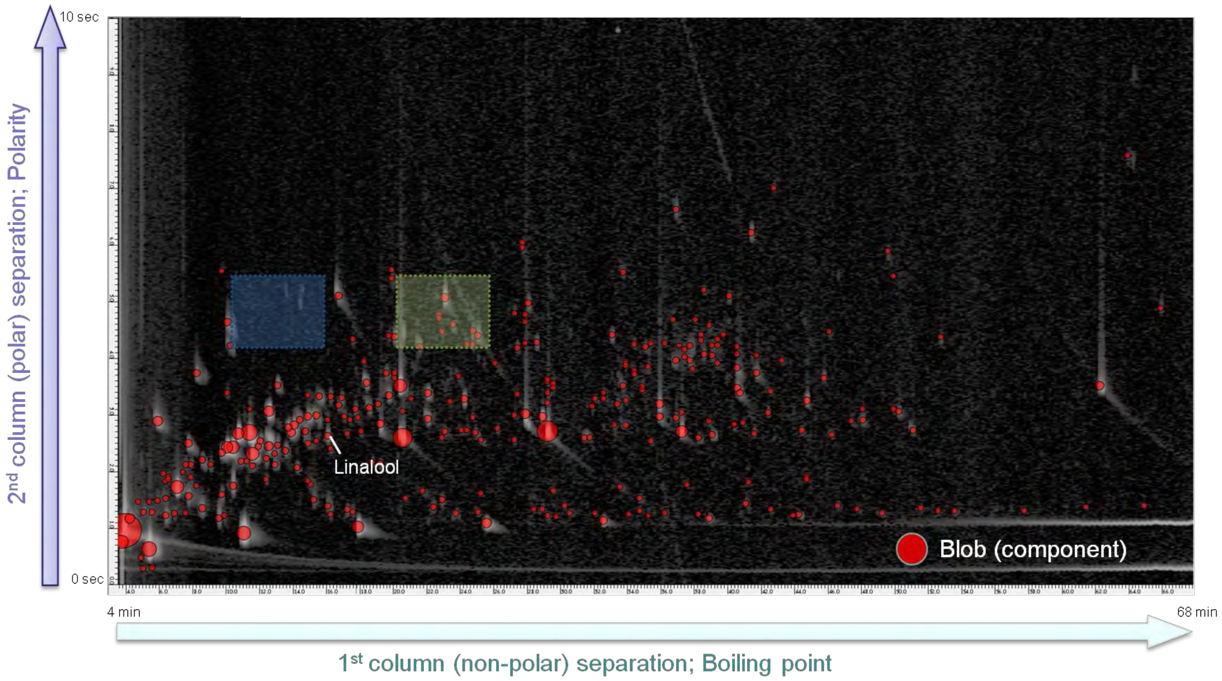
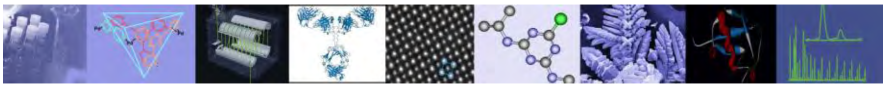


*Fig. 4. GCxGC/EI TIC chromatogram of a gold tequila.*



the EI mass spectrum for each component. The "Blob" size reflects the sum of the ion peak intensities for each chemical component.

As expected, the anejo tequila showed a more complex 2D TIC (i.e. more chemical components) than in the gold tequila 2D TIC image, which was the result of the longer anejo aging process. As an example of this, Area 1 (Blue region) and Area 2 (Green region) are highlighted in Figures 3 and 4.

Next, a NIST library search for all of the detected blobs was carried out for each sample. The NIST library search results are shown in Table 2. The anejo tequila had 409 chemicals detected in the 2D TIC with 236 of them (57.7%) identified with match factors of over 700, which is typically sufficient for reliable chemical identification. As for the gold tequila, 291 chemicals were detected with 141 of them (48.5%) identified with match factors of over 700.

In most cases, it is sufficient to use the NIST search results for identifying the compounds in the GCxGC TIC image. This step is easy to do as all blobs over the whole TIC image or for specific regions can be selected at once, and then a NIST library search can be carried out to find the best spectral matches. Afterwards, the GC Image software can then be used to automatically label each blob with the best match from the database search. Figure 5 shows the chemical identifications for a number of the blobs in the narrow Areas 1 and 2 TIC regions based on the NIST library search result.

| | **Component number** | |
|---|---|---|
| **NIST Library Match Factor** | **Anejo tequila** | **Gold tequila** |
| Over 900 | **31** | **23** |
| 900-800 | **101** | **57** |
| 800-700 | **104** | **61** |
| 700-600 | 85 | 60 |
| 600-500 | 63 | 66 |
| 500-400 | 18 | 21 |
| 400-300 | 7 | 3 |
| SUM | 409 | 291 |

*Table 2. NIST search library result.*

Figure 6 shows a measured EI mass spectrum that was very similar to the NIST data for linalool, which showed a match factor of 922. Linalool is a naturally occurring monoterpene alcohol that is found in many plants. This compound is widely used as a flavoring agent for many kinds of foods. The molecular ion for linalool was not observed in the EI mass spectrum. However, the fragment ion resulting from the dehydration of the molecular ion ($[M\text{-}H_2O]^+$) was observed and showed a mass accuracy of 1.57 mDa compared to the calculated value for $C_{10}H_{16}$ while using an external one-point drift compensation for the mass calibration. Figure 7 shows a measured EI mass spectrum that was very similar to the NIST data for vanillan, which showed a match factor of 905.

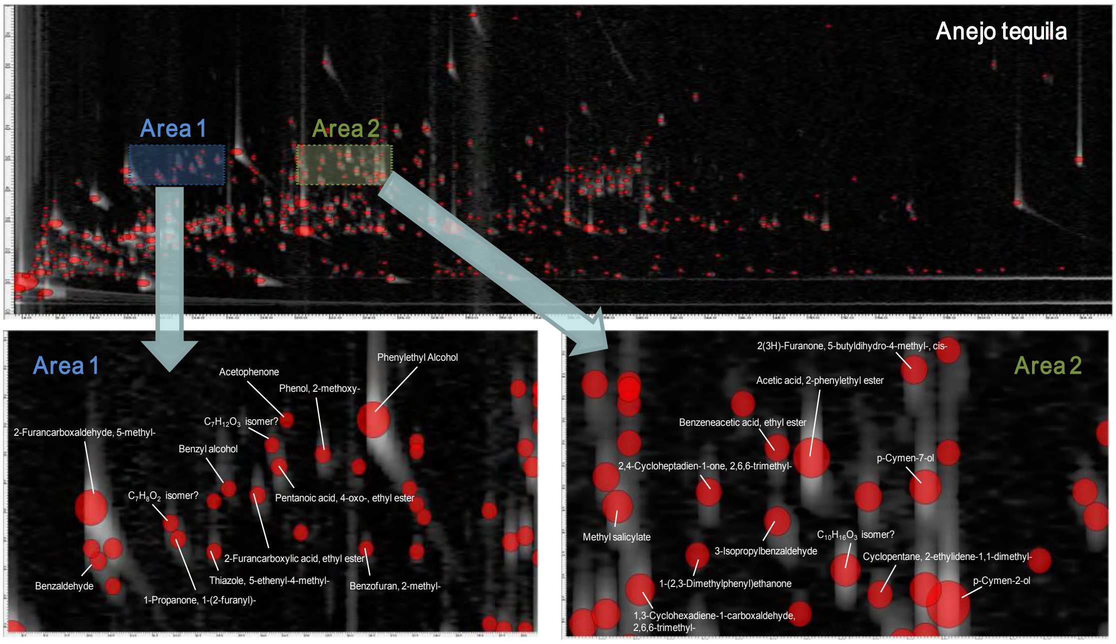
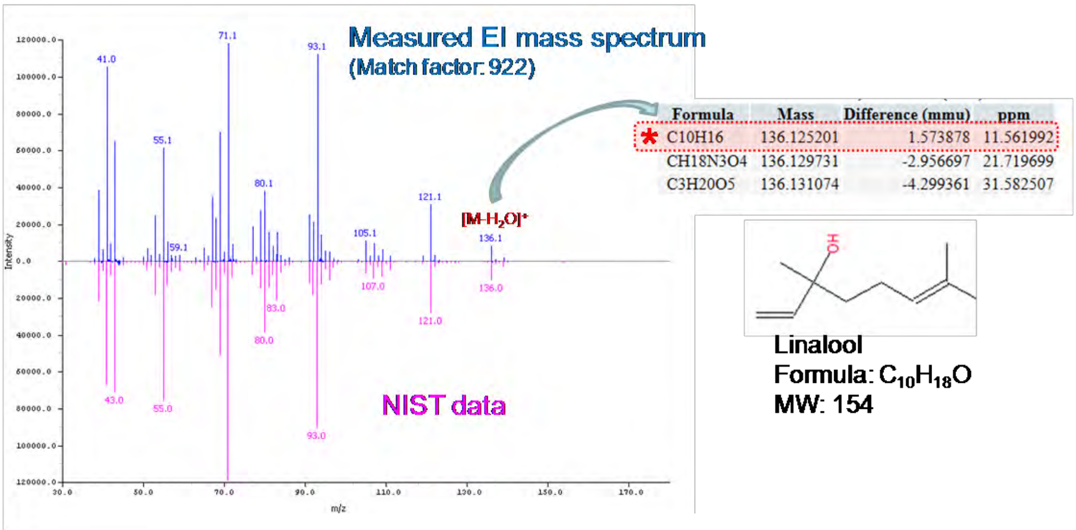


*Fig. 5. Example of chemical identifications result.*

Additionally, the molecular ion showed a mass accuracy of 0.88 mDa for the elemental composition of $C_8H_8O_3$. Vanillin is a phenolic aldehyde that was only detected in the anejo tequila (Figure 3). These results clearly show that even for 50Hz GCxGC measurement data, we can obtain normal EI mass spectral patterns that are directly comparable to NIST database mass spectra and high mass accuracy information to help further confirm the identity of unknown compounds through elemental composition calculations.

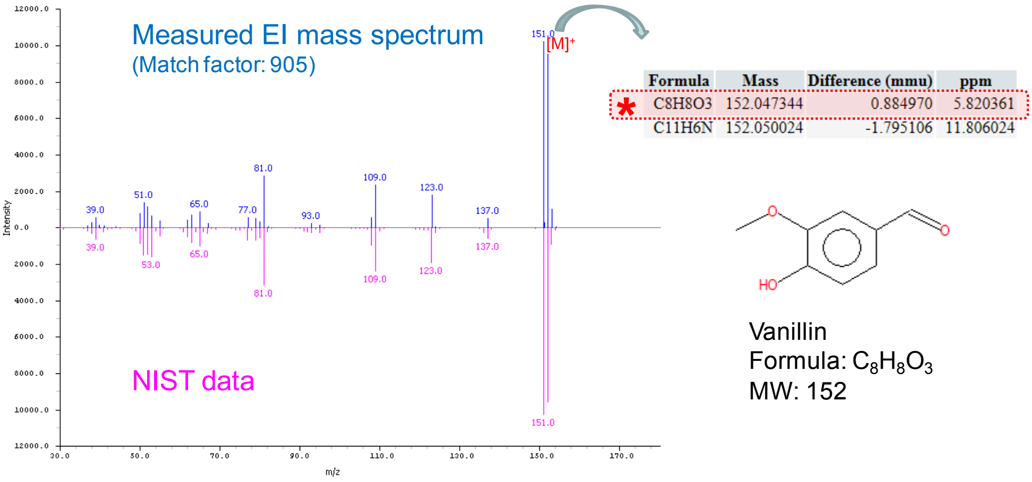
## Conclusion

The AccuTOF GCv 4G allows 50Hz GCxGC measurements with high sensitivity, high mass resolution and high mass accuracy, all simultaneously. Additionally, we can do NIST library searches using GCxGC data in exactly the same way as for regular 1D GC/MS. The AccuTOF GCv 4G coupled with the 2D GC technique is an extremely useful tool for the qualitative analysis of complicated samples.



| Formula | Mass | Difference (mmu) | ppm |
|---|---|---|---|
| * C10H16 | 136.125201 | 1.573878 | 11.561992 |
| CH18N3O4 | 136.129731 | -2.956697 | 21.719699 |
| C3H20O5 | 136.131074 | -4.299361 | 31.582507 |

*Fig. 6. Measured EI mass spectrum and NIST data of Linalool.*



| Formula | Mass | Difference (mmu) | ppm |
|---|---|---|---|
| * C8H8O3 | 152.047344 | 0.884970 | 5.820361 |
| C11H6N | 152.050024 | -1.795106 | 11.806024 |

*Fig. 7. EI mass spectrum and NIST data of Vanillin.*

*Specifications subject to change without prior notice.

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