

AccuTOF™ GC series

Petroleum & Petrochemicals Applications Notebook

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MultiAnalyzer – Unknown Compounds Analysis System

New Gas Chromatograph Time-of-Flight Mass Spectrometer

JMS-T2000GC “AccuTOF™ GC-Alpha”

Masaaki Ubukata MS Business Unit, JEOL Ltd.

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

Introduction

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

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

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

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

Overview of the Instrument

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

Basic High-Performance System for Non-Targeted Analysis

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

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

Fig. 1 History of JEOL GC-HR-TOFMS



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



Fig. 3 Schematics of ion optical system



High Sensitivity

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

High Mass-Resolving Power

The AccuTOF™ GC-Alpha has a much higher mass-resolving power than the previous generations of the instrument. To demonstrate this new resolution capability, **Fig. 5a** shows the EI mass spectrum for PFTBA in which the m/z 614 peak was enlarged to clearly display the FWHM resolution of $>30,000$, which is the new resolution specification. To further highlight how this improved resolving power can enhance sample analysis, **Fig. 5b** shows the baseline separation of CO^+ (m/z 27.9949) and N_2^+ (m/z 28.0061) which was not possible with the previous generation instruments. These results clearly demonstrate that the high mass-resolution of the AccuTOF™ GC-Alpha can easily separate closely related ions (same nominal mass) and thus can be a powerful tool for a wide range of analyses and applications involving analytes with the same nominal mass but different elemental compositions.

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

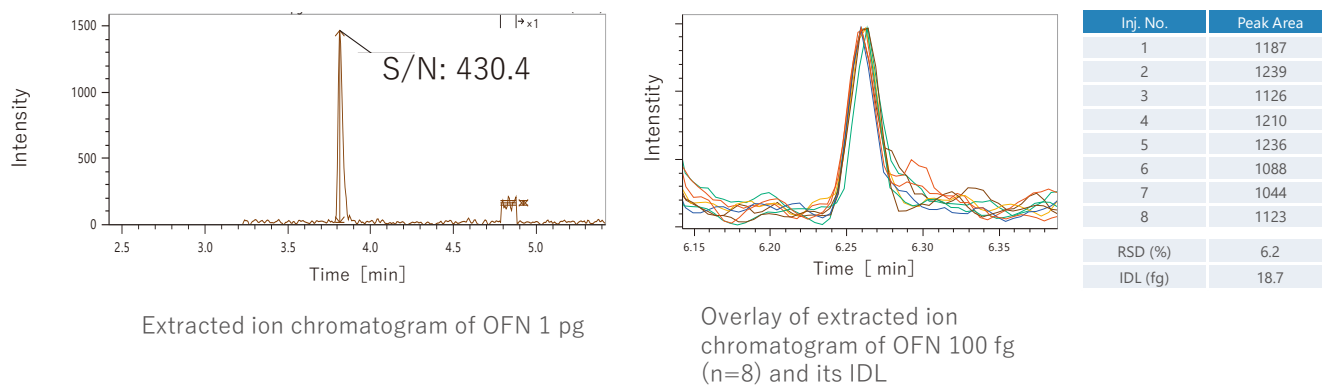
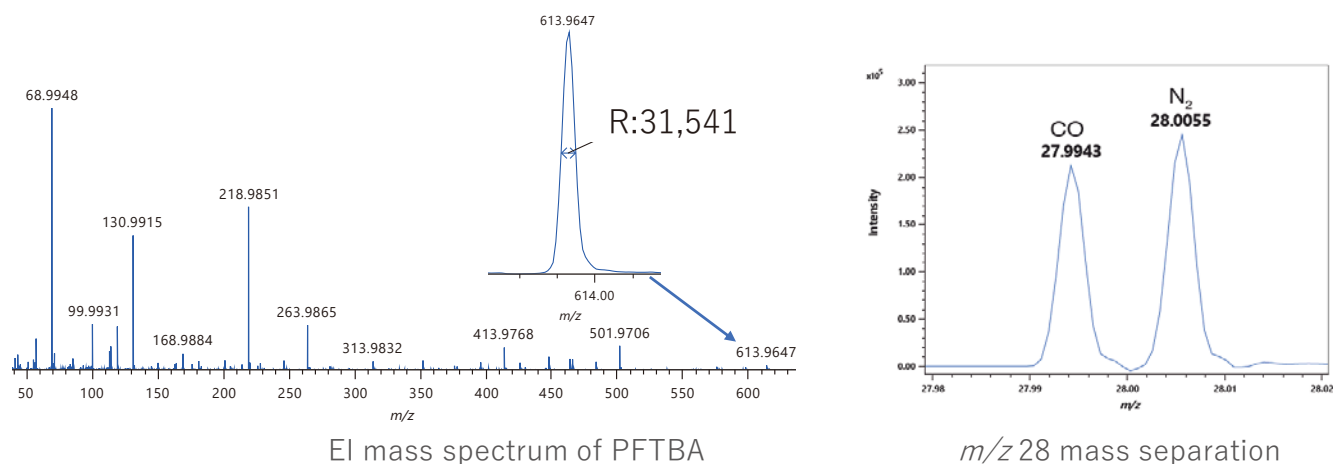


Fig. 5 EI mass spectrum of PFTBA and m/z 28 mass separation



High Mass-Accuracy

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

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

Powerful Capabilities for GC-MS Qualitative Analysis

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

Wide Mass Range

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

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

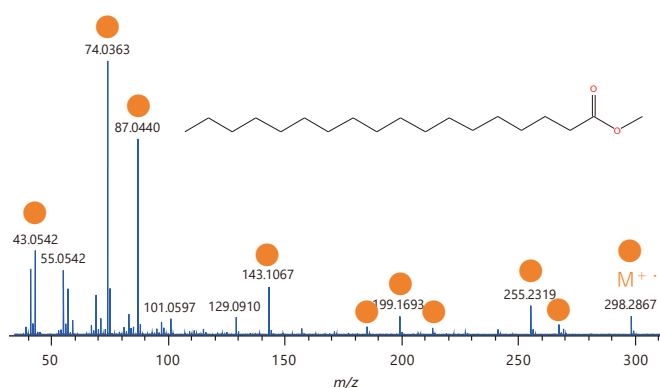
High-Speed Data Acquisition

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

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

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

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



EI mass spectrum of methyl stearate

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

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

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

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

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

qualitative analysis of unknown compounds.

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

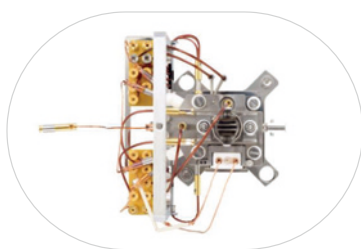
Automatic Qualitative Analysis Software “msFineAnalysis”

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

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

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

Fig. 7 Two combination ion sources



EI/FI/FD combination ion source

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



EI/PI combination ion source

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

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

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

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

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

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

Conclusions

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

Fig. 8 msFineAnalysis: Integrated analysis workflow

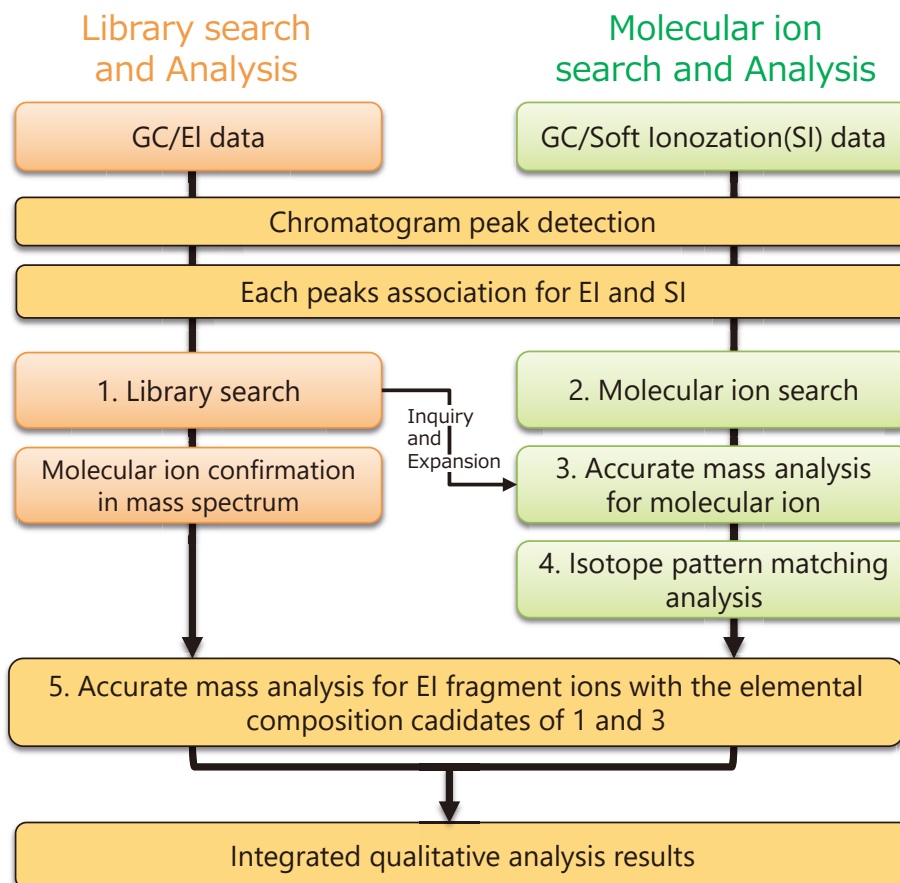


Fig. 9 msFineAnalysis Ver.3: 2-samples comparison GUI

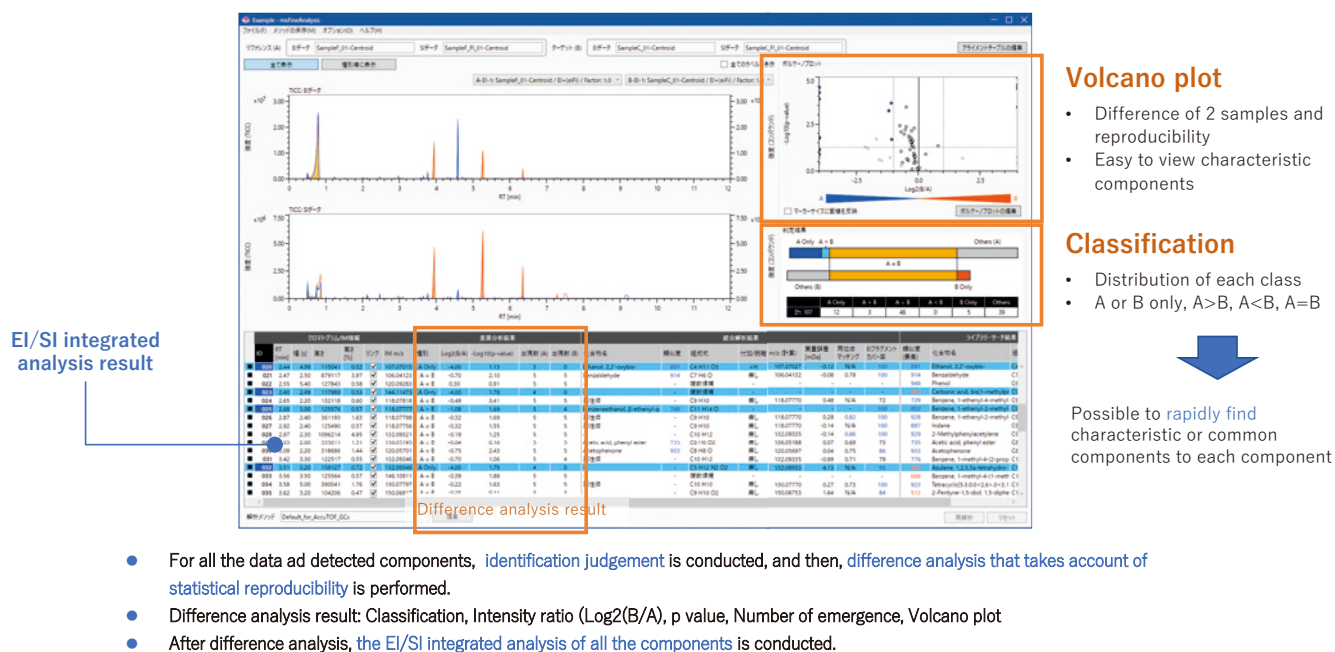
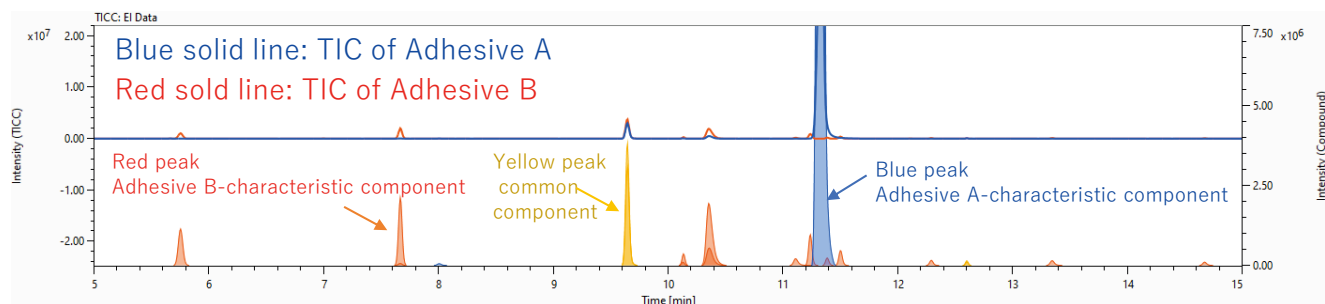


Fig. 10 Evolved-gas difference analysis of material components using HS-GC-TOFMS



Difference analysis + Integrated analysis result

クロマトグラム/IM情報						差異分析結果						統合解析結果									
ID	RT [min]	幅 [s]	高さ	高さ [%]	リンク	IM m/z	種別	Log2(B/A)	-Log10(p-value)	出現数 (A)	出現数 (B)	化合物名	類似度	組成式	付加/脱離	m/z (計算)	質量誤差 [mDa]	同位体 マッチング	EIフラグメント カバー率		
001	5.75	8.00	1139828	2.54	✓	222.05689	B Only	4.00	4.68	0	5	Cyclotrisiloxane, hexamethyl-	957	C6 H18 O3 Si3	無し	222.05583	1.06	N/A	100		
002	7.66	6.00	2120025	4.73	✓	281.05042	A < B	4.00	4.42	5	5	Cyclotetrasiloxane, octamethyl-	902	C7 H21 O4 Si4	-CH3	281.05114	-0.72	0.89	100		
003	8.00	6.80	597118	0.13	✓	130.13524	A Only	-4.00	5.00	5	0	n-Butyl ether	867	C8 H18 O	無し	130.13522	0.03	N/A	100		
004	9.64	7.60	3612139	8.50	✓	92.06221	A = B	0.12	1.28	5	5	Toluene	960	C7 H8	無し	92.06205	0.15	0.97	100		
005	10.12	4.80	361148	0.81	✓	355.06898	A < B	1.76	5.00	5	5	Cyclopentasiloxane, decamethyl-	933	C9 H27 O5 Si5	-CH3	355.06993	-0.95	0.66	100		
006	10.36	12.80	1936628	4.32	✓	74.07312	A < B	1.70	4.83	5	5	1-Propanol, 2-methyl-	819	C4 H10 O	無し	74.07262	0.51	0.69	100		
007	11.11	11.60	208814	0.47	✓	90.06757	B Only	4.00	5.00	0	5	2-Propanol, 1-methoxy-	824	C4 H10 O2	無し	90.06753	0.03	0.39	100		
008	11.24	6.80	960683	2.14	✓	106.07748	B Only	4.00	5.00	0	5	Ethylbenzene	963	C8 H10	無し	106.07770	-0.22	0.79	100		
009	11.33	12.40	44842834	100.00	✓	74.07291	A Only	-4.00	5.00	5	0	1-Butanol	803	C4 H10 O	無し	74.07262	0.29	N/A	100		
010	11.38	5.60	233859	0.52	✓	106.07764	B Only	4.00	5.00	0	5	p-Xylene	952	C8 H10	無し	106.07770	-0.07	N/A	100		
011	11.50	6.80	461857	1.03	✓	106.07784	B Only	4.00	5.00	0	5	Benzene, 1,3-dimethyl-	967	C8 H10	無し	106.07770	0.13	0.95	100		
012	12.29	6.80	159354	0.36	✓	106.07822	B Only	4.00	5.00	0	5	p-Xylene	954	C8 H10	無し	106.07770	0.51	0.93	100		
013	12.60	4.80	153832	0.34	✓	429.08815	A = B	0.34	3.19	5	5	Cyclohexasiloxane, dodecamethyl-	932	C11 H33 O6 Si6	-CH3	429.08872	-0.57	0.65	100		
014	13.34	8.40	148724	0.33	✓	119.10627	B Only	4.00	5.00	0	5	Ethanol, 2-(1,1-dimethylethoxy)-	872	C6 H15 O2	+H	119.10666	-0.39	N/A	100		
015	14.67	7.20	103236	0.23	✓	73.05243	B Only	4.00	5.00	0	5	Formamide, N,N-dimethyl-	863	C3 H7 N O	無し	73.05222	0.21	0.69	100		

Blue line: Adhesive A-characteristic component

Red line: Adhesive B-characteristic component

White line: Common component

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

Product used : Mass Spectrometer (MS)

Introduction

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

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

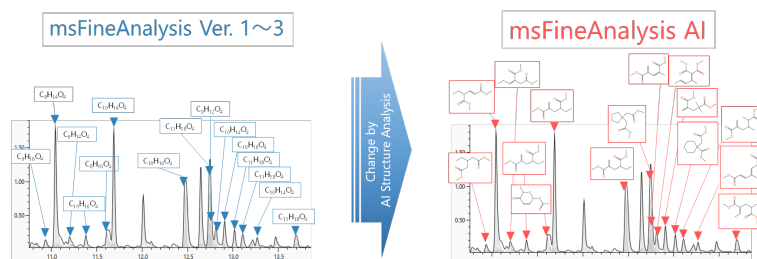


Figure 1 Image of analysis result in msFineAnalysis AI

About AI Structure Analysis Function

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

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

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

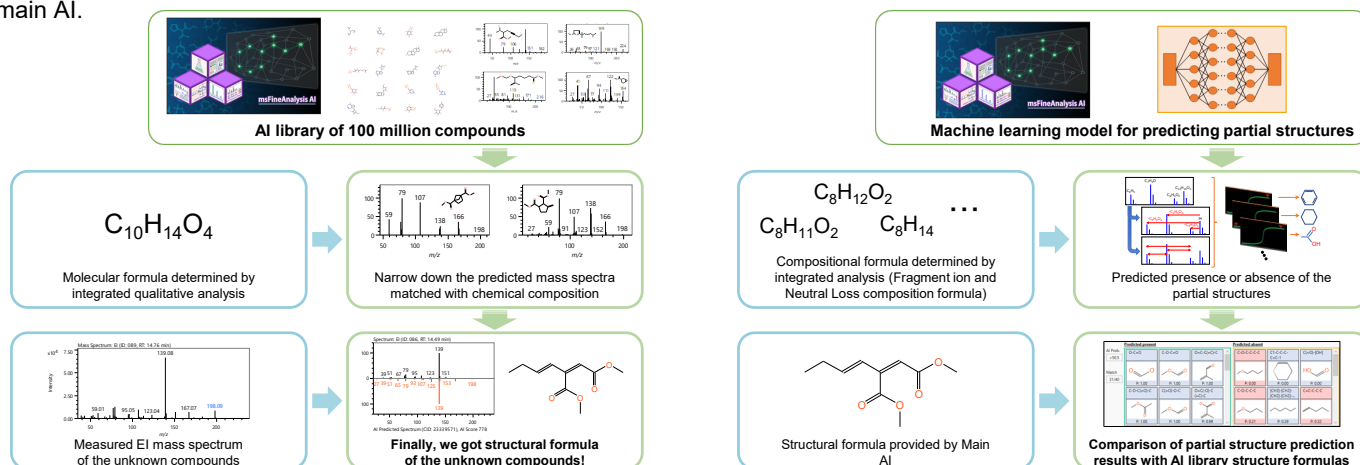


Figure 2 Main AI workflow

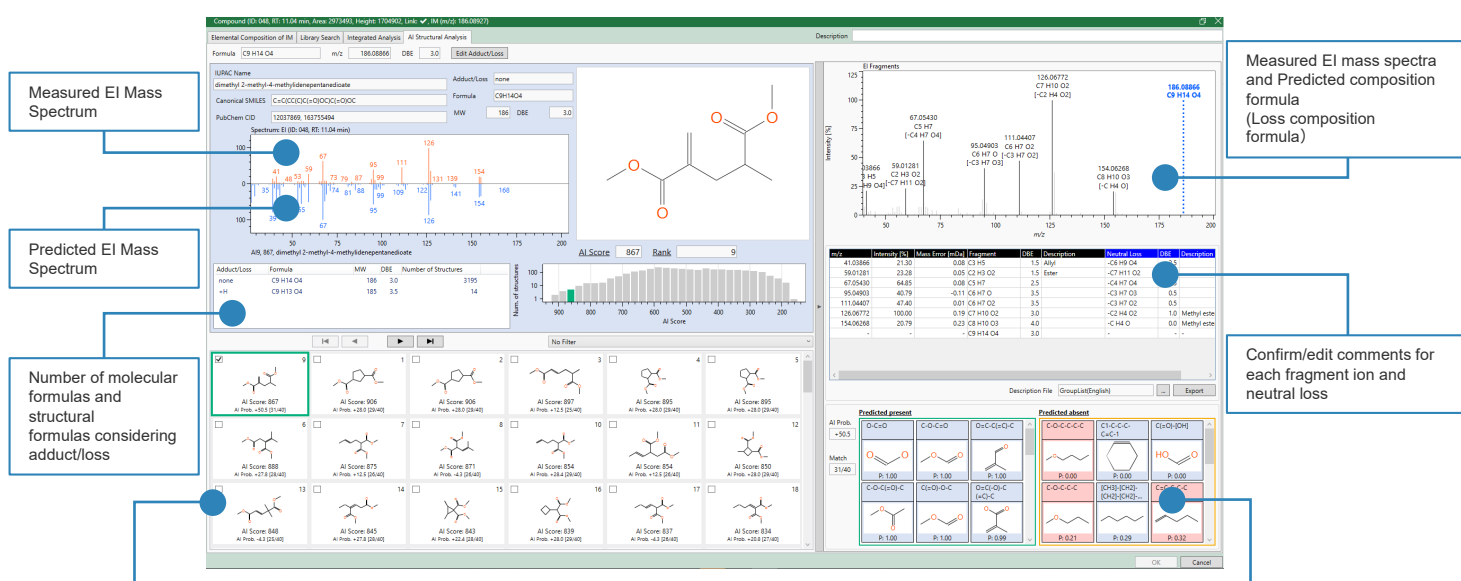
Figure 3 Support AI workflow

GUI of AI Structure Analysis Result

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

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

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



Structural Formula Prediction by Main AI

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

Partial Structure Prediction by Support AI

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

Figure 4 GUI of msFineAnalysis AI

Conclusion

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

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



JMS-T2000GC AccuTOF™ GC-Alpha

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

Related products: Mass spectrometer (MS)

Introduction

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

Measurement

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

Table 1. Measurement conditions

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

Results ① EI method

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

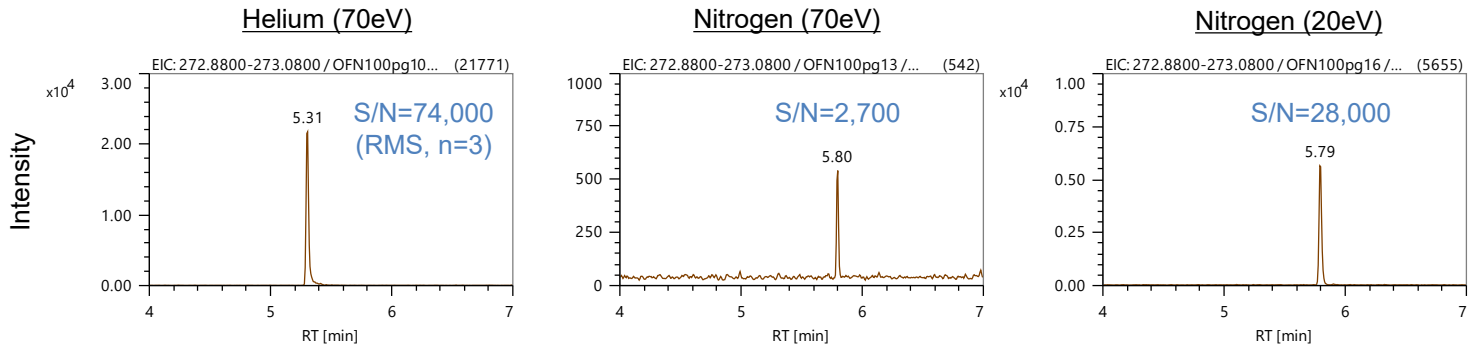


Figure 1. EICs of OFN (EI method)

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

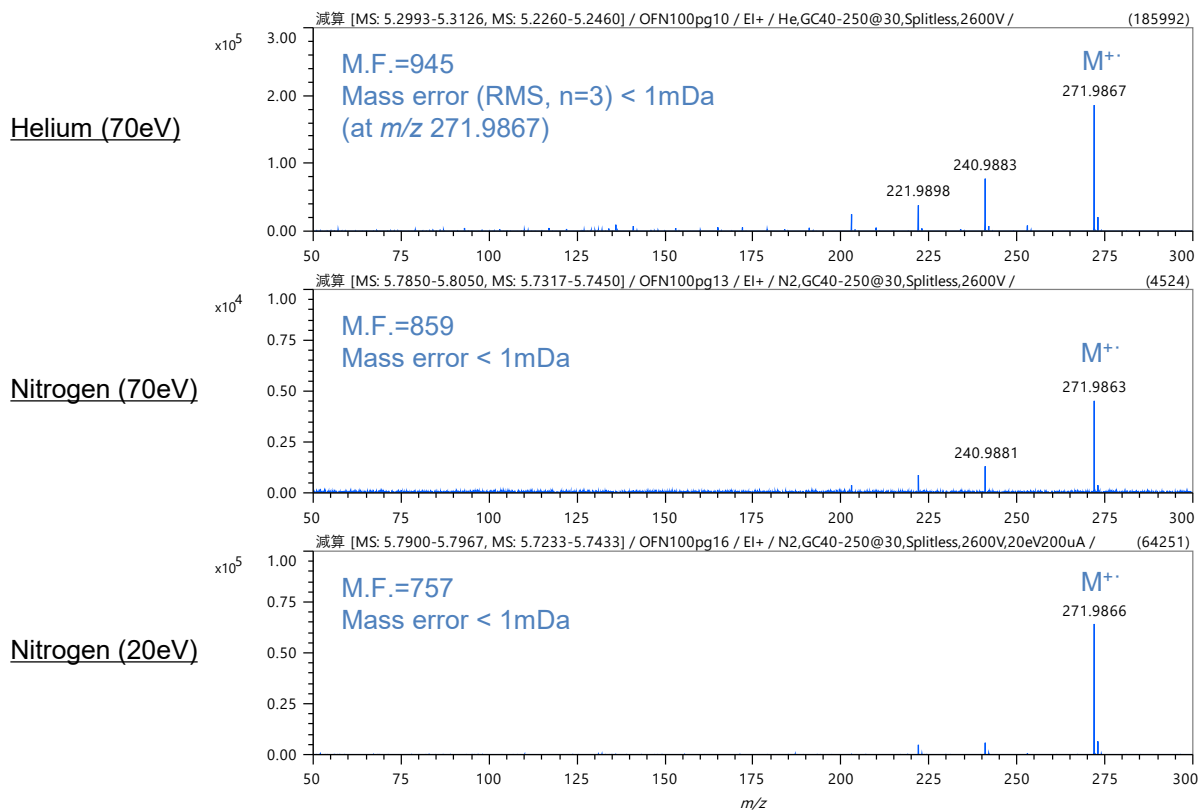


Figure 2. Mass spectra of OFN (EI method)

Results ② PI method

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

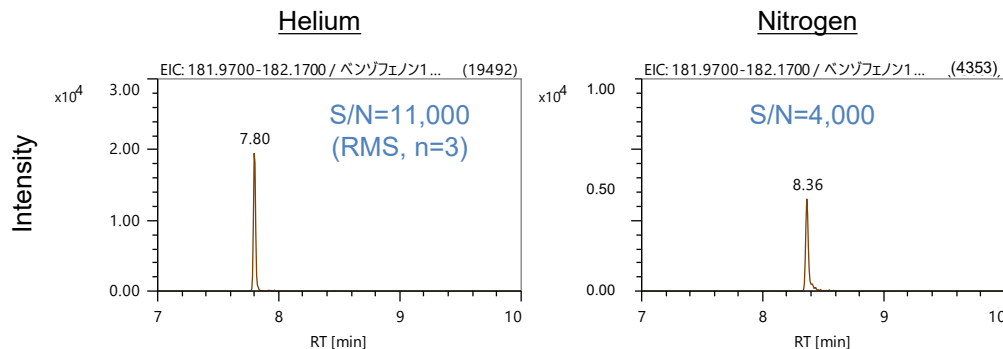


Figure 3. EICs of benzophenone (PI method)

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

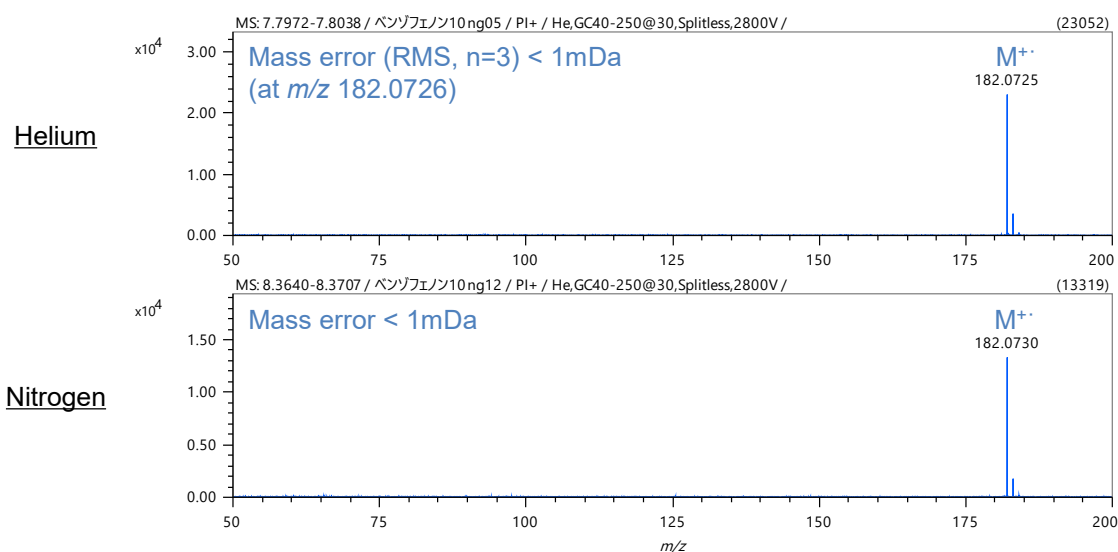


Figure 4. Mass spectra of benzophenone (PI method)

Conclusion

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



JMS-T2000GC AccuTOF™ GC-Alpha

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

Related products: Mass spectrometer (MS)

Introduction

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

Measurement

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

Table 1. Measurement conditions

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

Results ① EI method

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

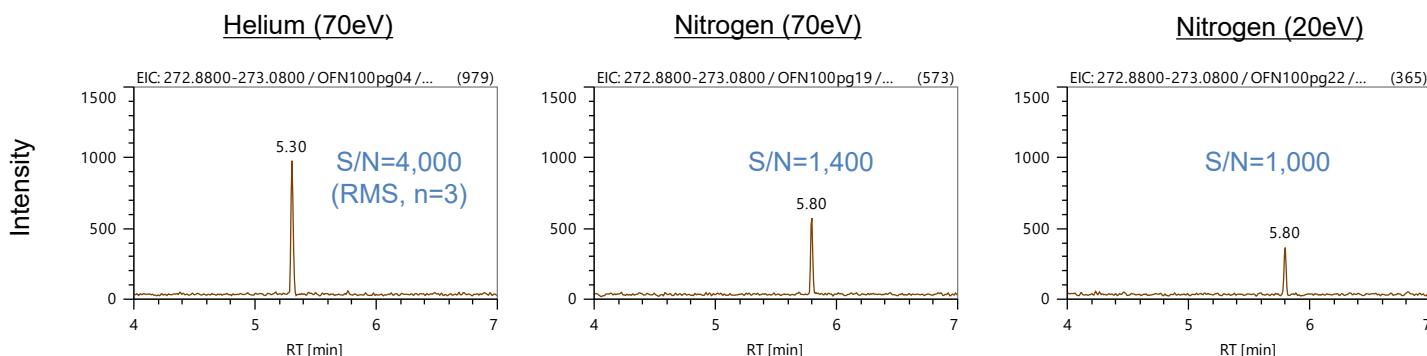


Figure 1. EICs of OFN (EI method)

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

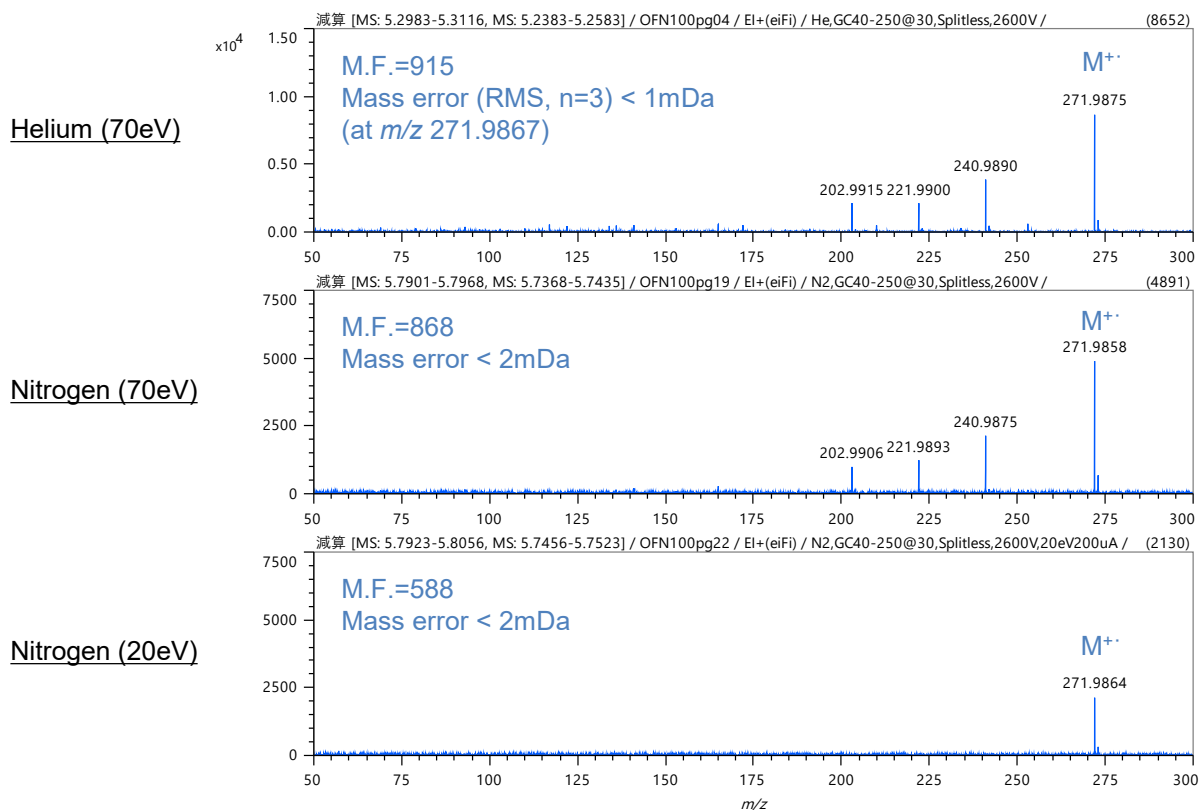


Figure 2. Mass spectra of OFN (EI method)

Results ② FI method

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

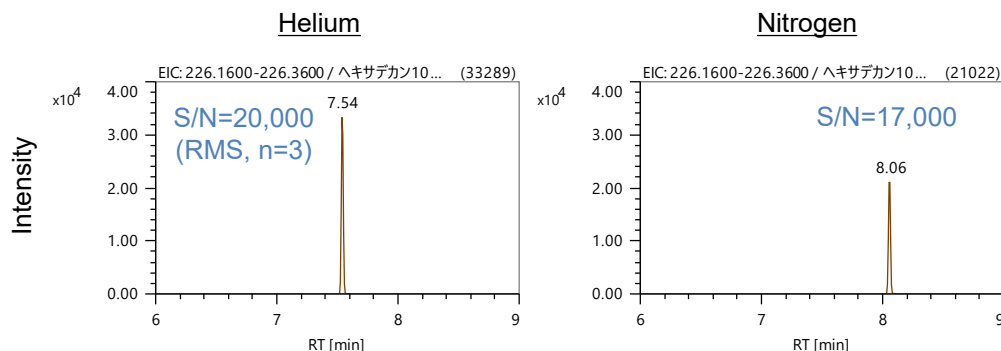


Figure 3. EICs of hexadecane (FI method)

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

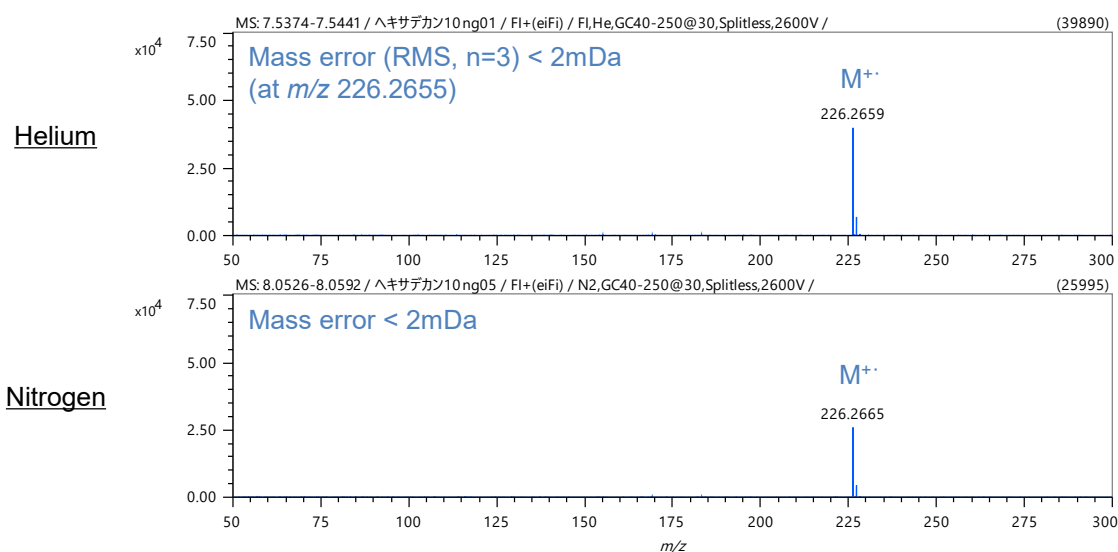


Figure 4. Mass spectra of hexadecane (FI method)

Conclusion

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

JMS-T2000GC AccuTOF™ GC-Alpha

Sensitivity in nitrogen carrier gas ③ - CI ion source

Related products: Mass spectrometer (MS)

Introduction

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

Measurement

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

Table 1. Measurement conditions

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

Results ① CI+ method

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

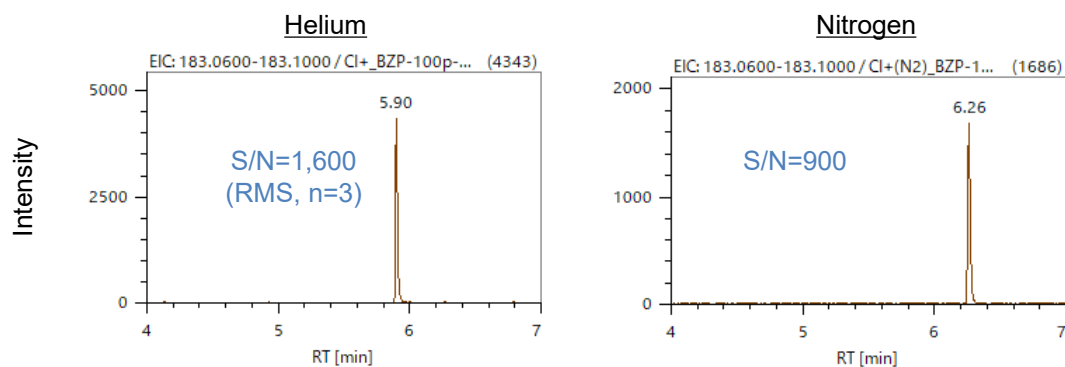


Figure 1. EICs of benzophenone (CI+ method)

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

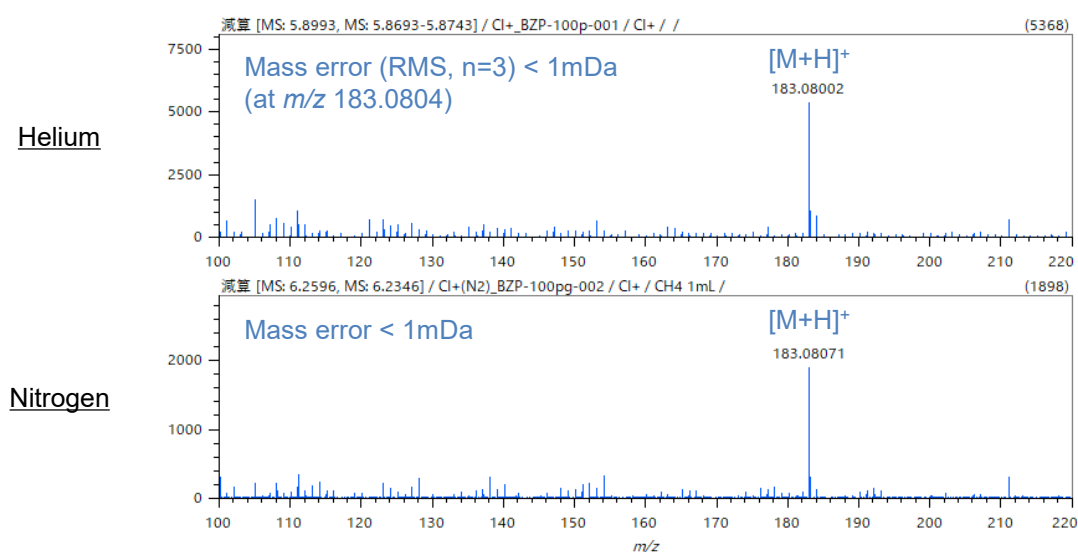


Figure 2. Mass spectra of benzophenone (CI+ method)

Results ②CI- method

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

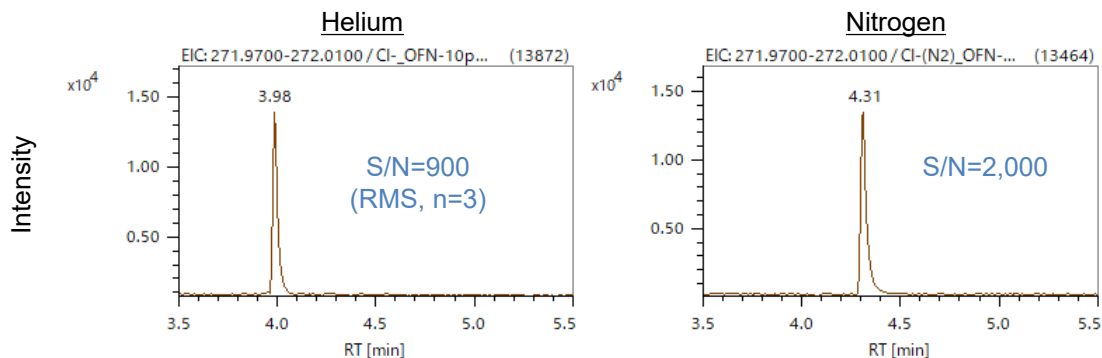


Figure 3. EICs of OFN (CI- method)

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

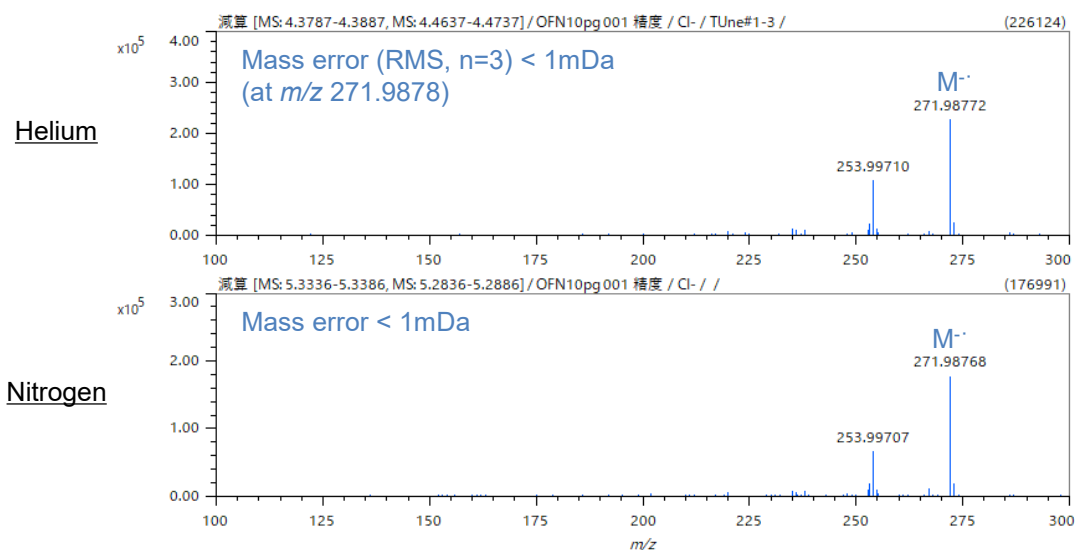


Figure 4. Mass spectra of OFN (CI- method)

Conclusion

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

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

Related Product: Mass Spectrometer(MS)

Introduction

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



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

Experimental

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

Table 1. Measurement and analysis conditions

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

Result

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

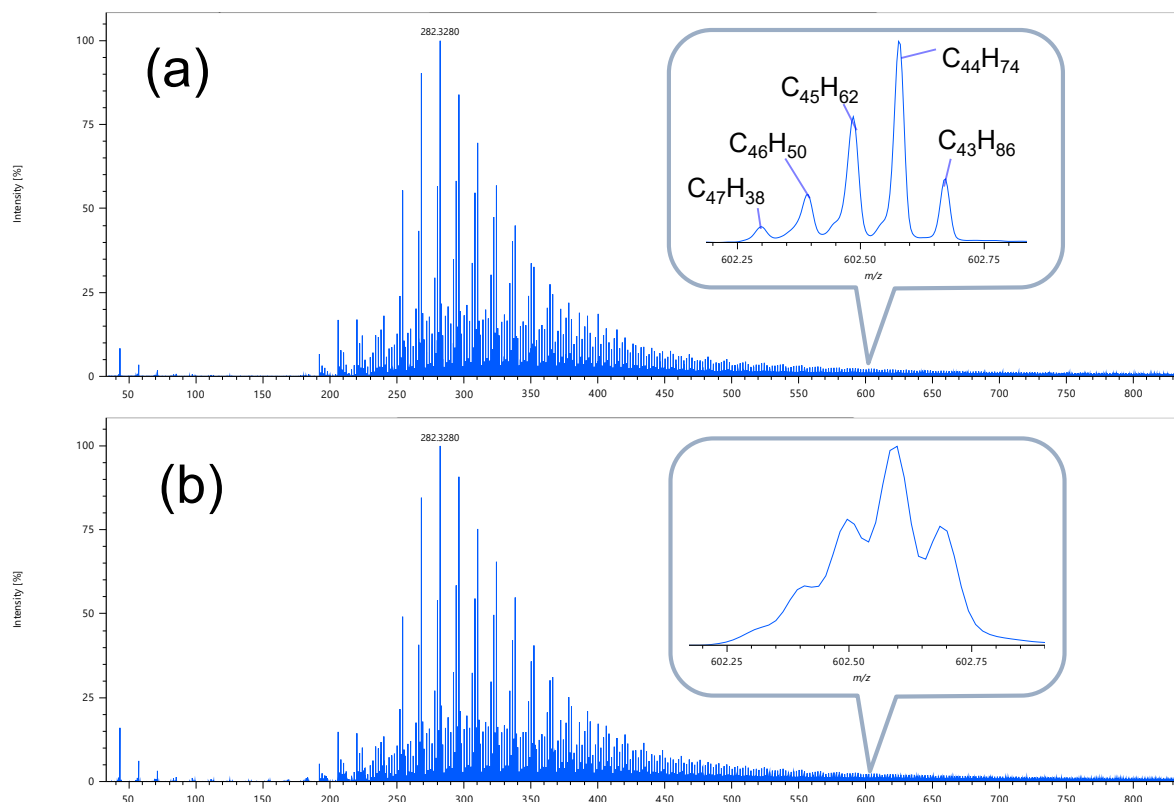


Fig. 2 FD mass spectra for crude oil: (a) JMS-T2000GC data, (b) Previous model data

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

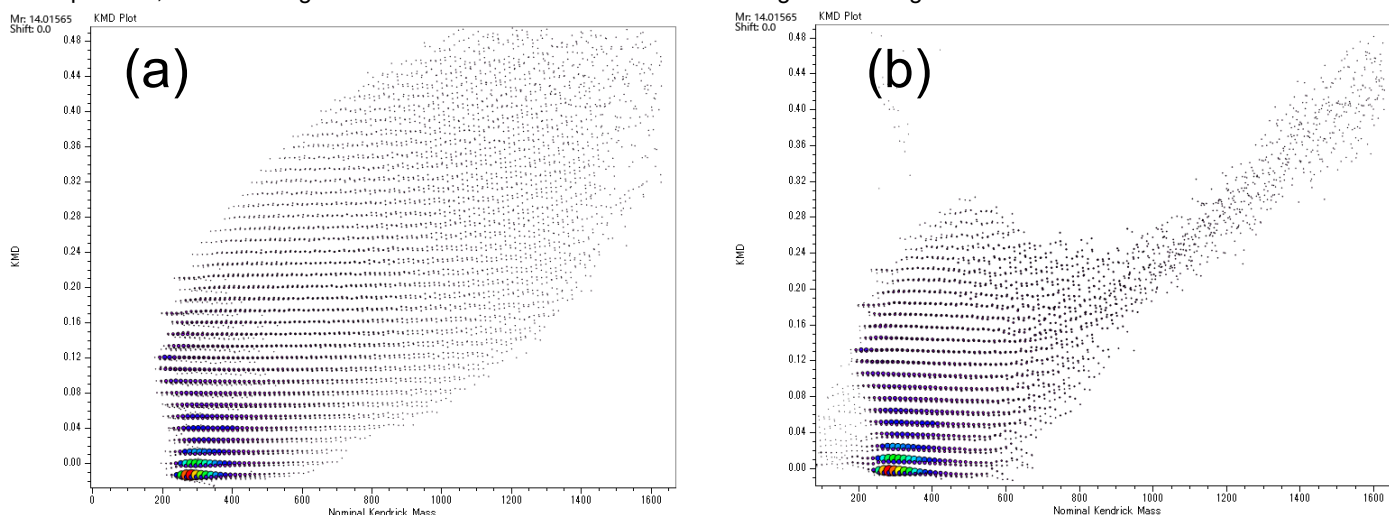


Fig. 3 KMD Plots of FD mass spectrum: (a) JMS-T2000GC data, (b) Previous model data

Conclusions

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

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

Related Product: Mass Spectrometer(MS)

Introduction

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

Experimental

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

Table 1. Measurement and analysis conditions

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



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

msFineAnalysis Software

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

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

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

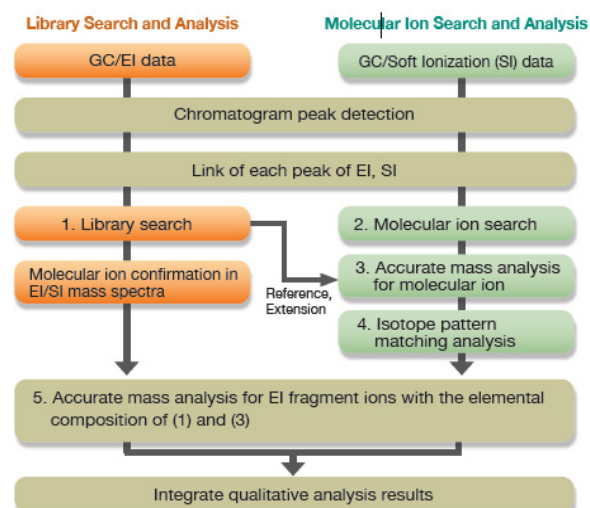


Fig. 2 msFineAnalysis workflow

Result

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

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

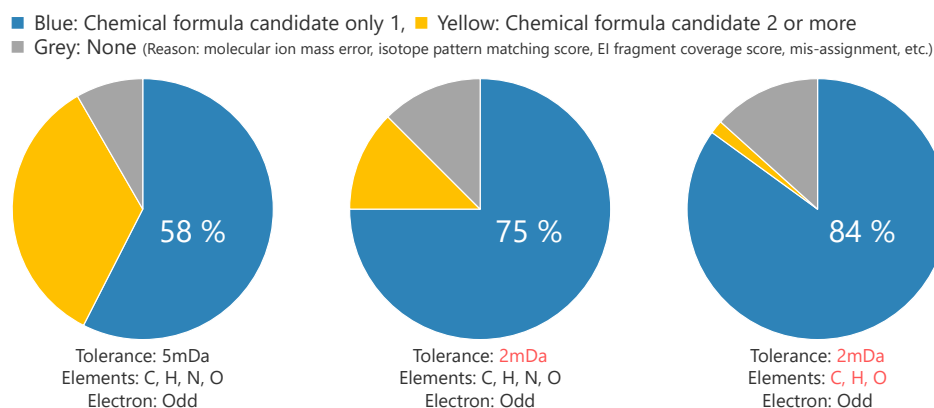


Fig. 3 Comparison of automatic analysis results for 120 components

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

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

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

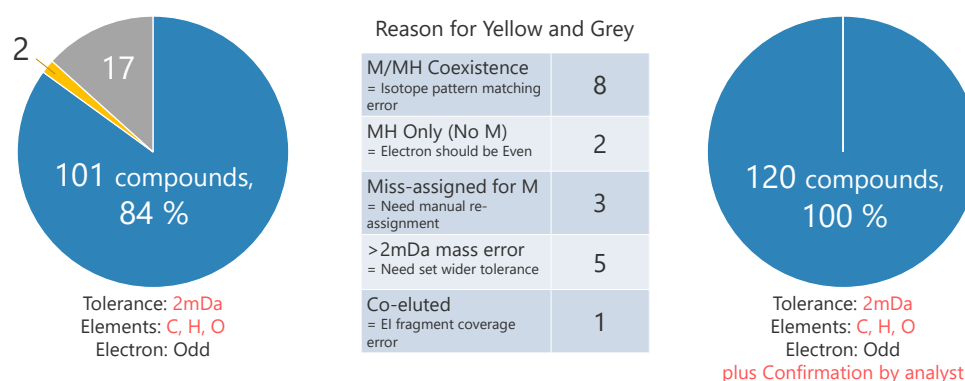


Fig. 4 Confirmation by analyst for 19 components

Conclusions

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

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

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

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

Introduction

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

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

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

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

Analysis Flow

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

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

Analysis Examples: Pyrolysis data analysis of vinyl acetate resin

(1) Analytical Condition

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

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

(2) Analysis Results

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

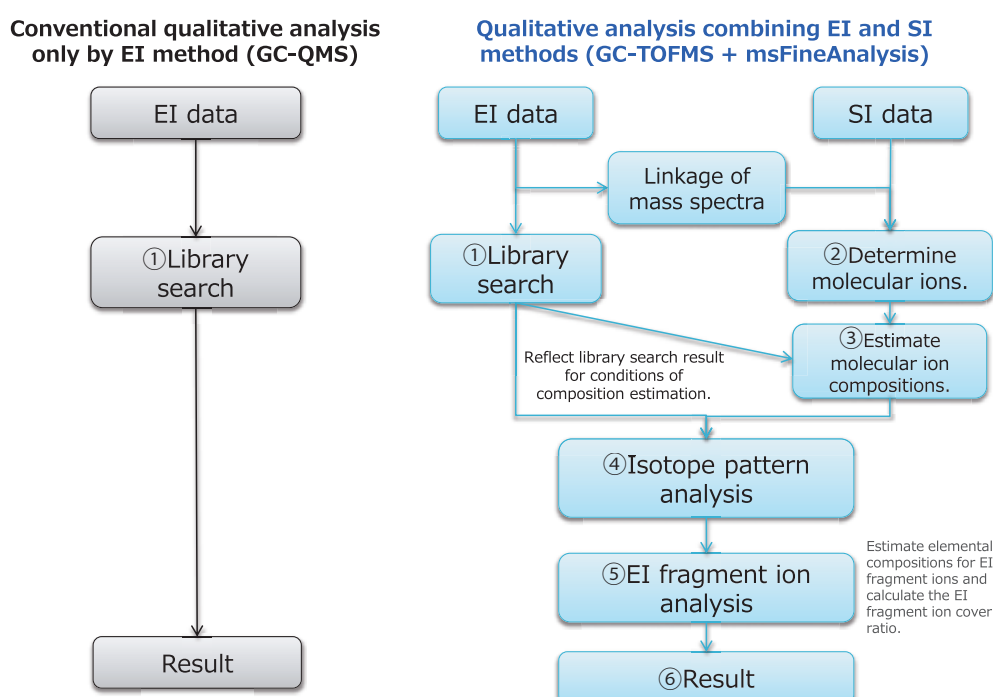
Green: EI search result had high similarity score and matched the identified SI molecular ion. High probability that the analyte has been identified correctly.

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

White: No significant molecular composition formula was obtained.

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

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



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

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

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

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

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

Table 1 Measurement Condition

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

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

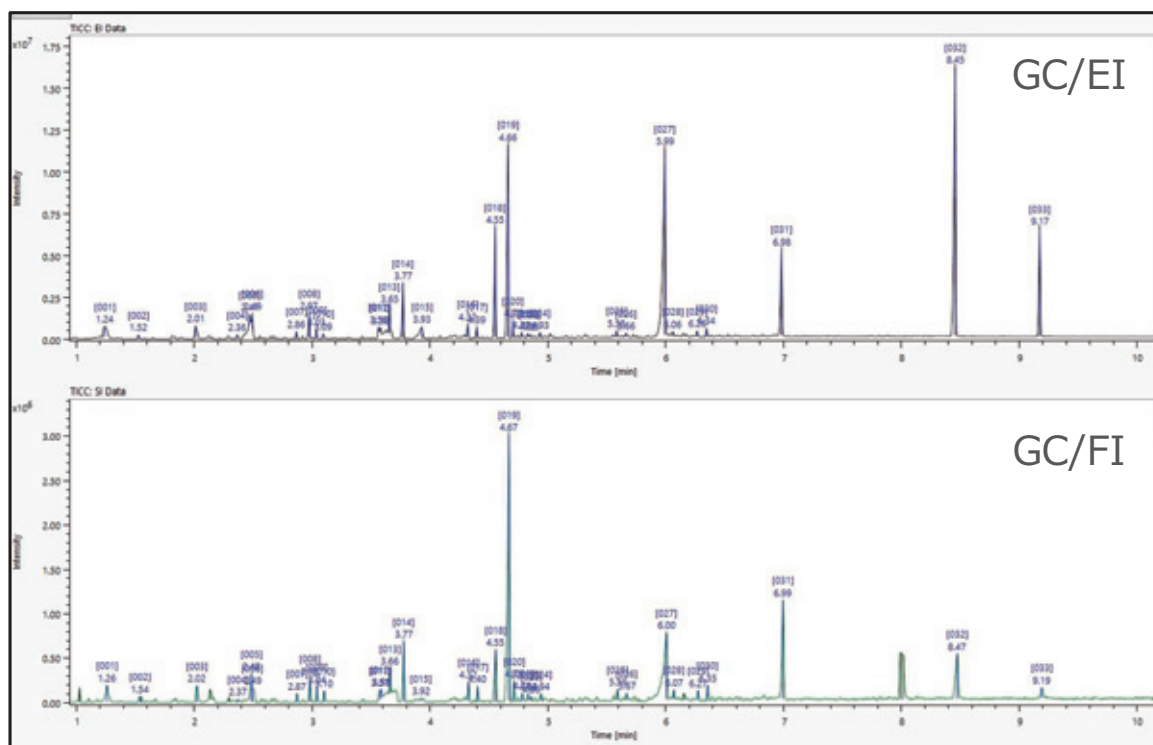


Fig. 3 Data analysis results of vinyl acetate sample by msFineAnalysis software

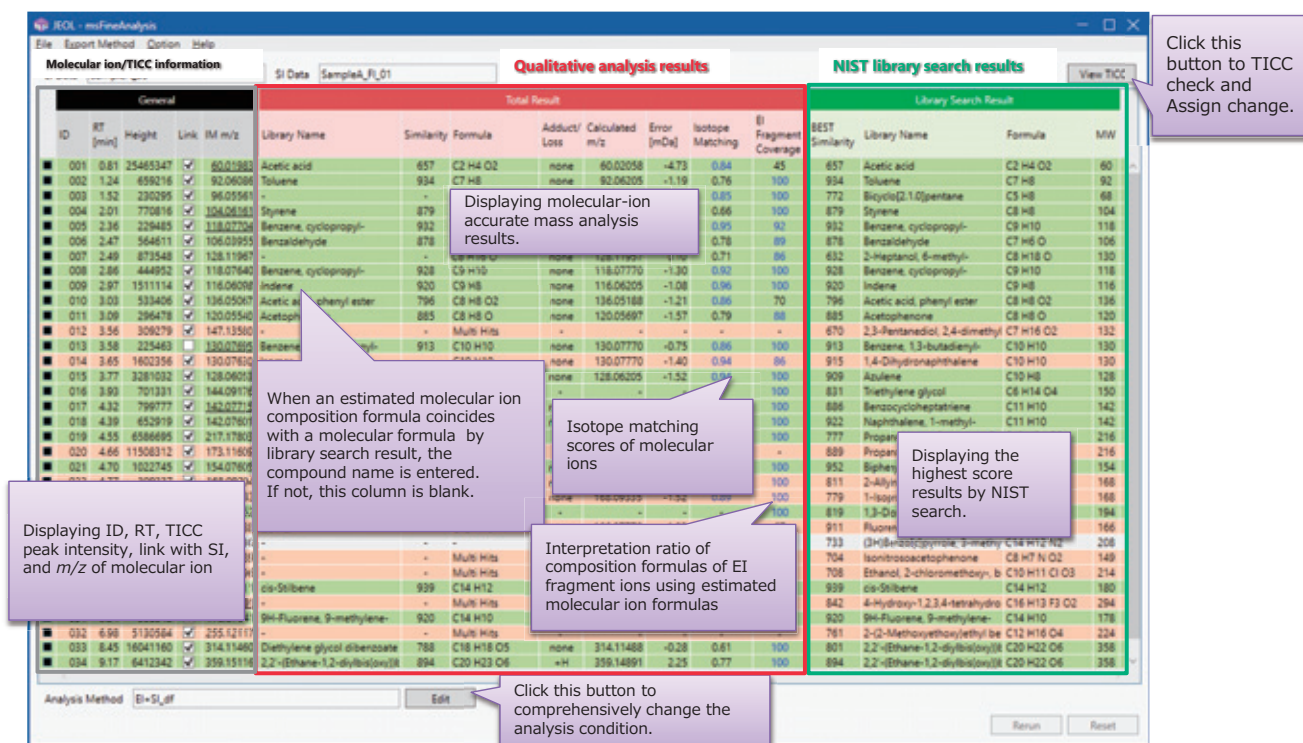
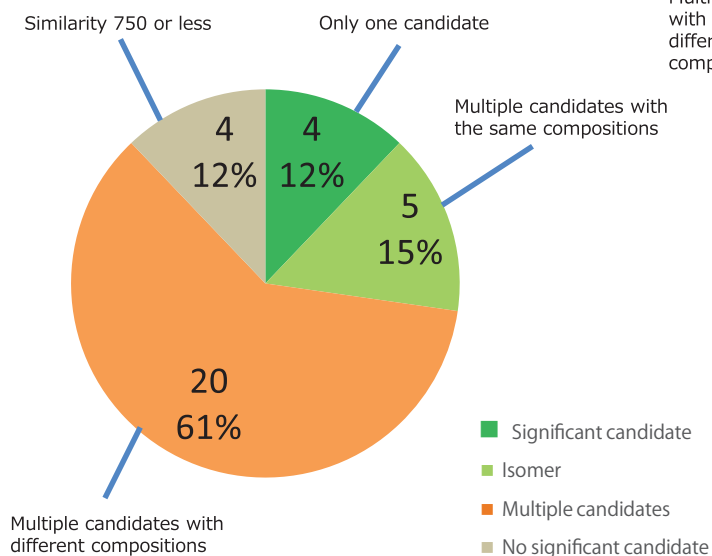
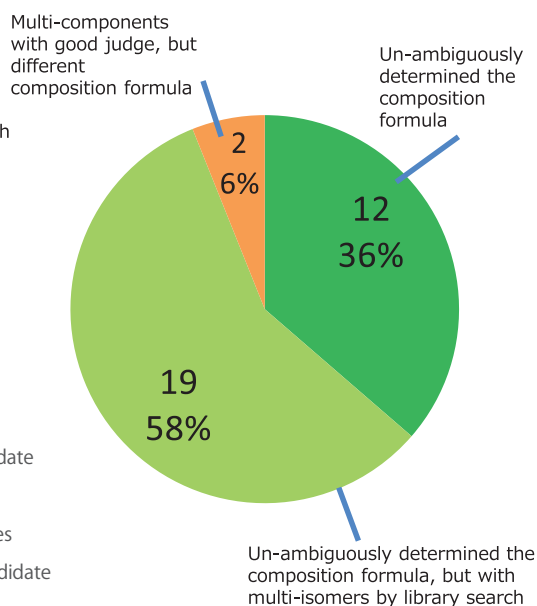


Fig. 4 Comparison of number of peaks that were identified between conventional data analysis flow and new work flow with msFineAnalysis software

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



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



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

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

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

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

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

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

Summary

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

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

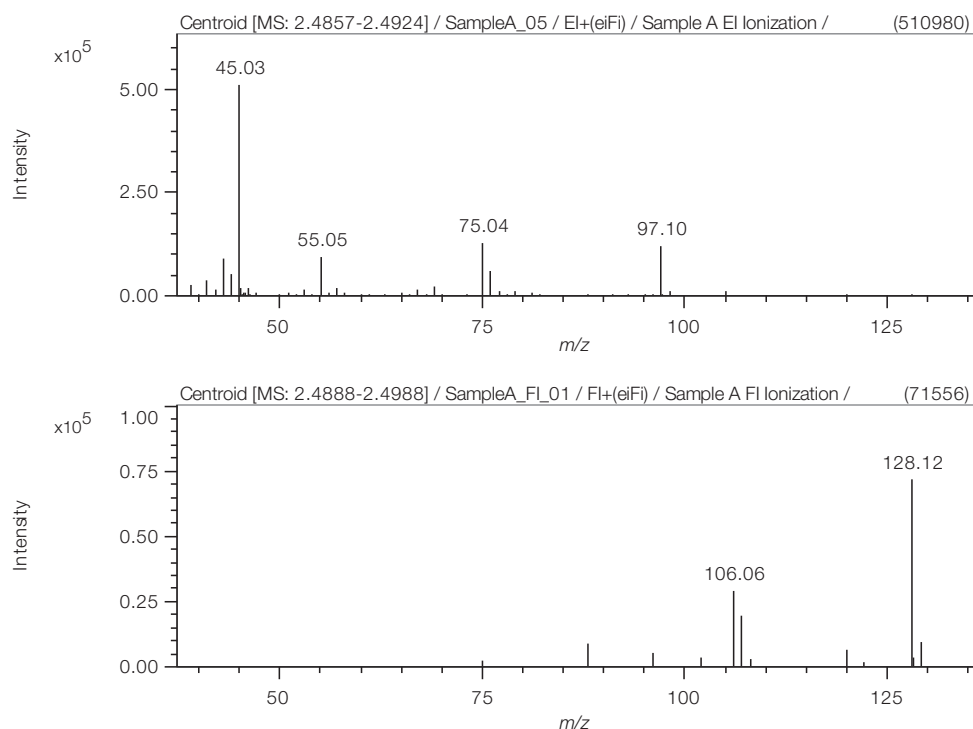


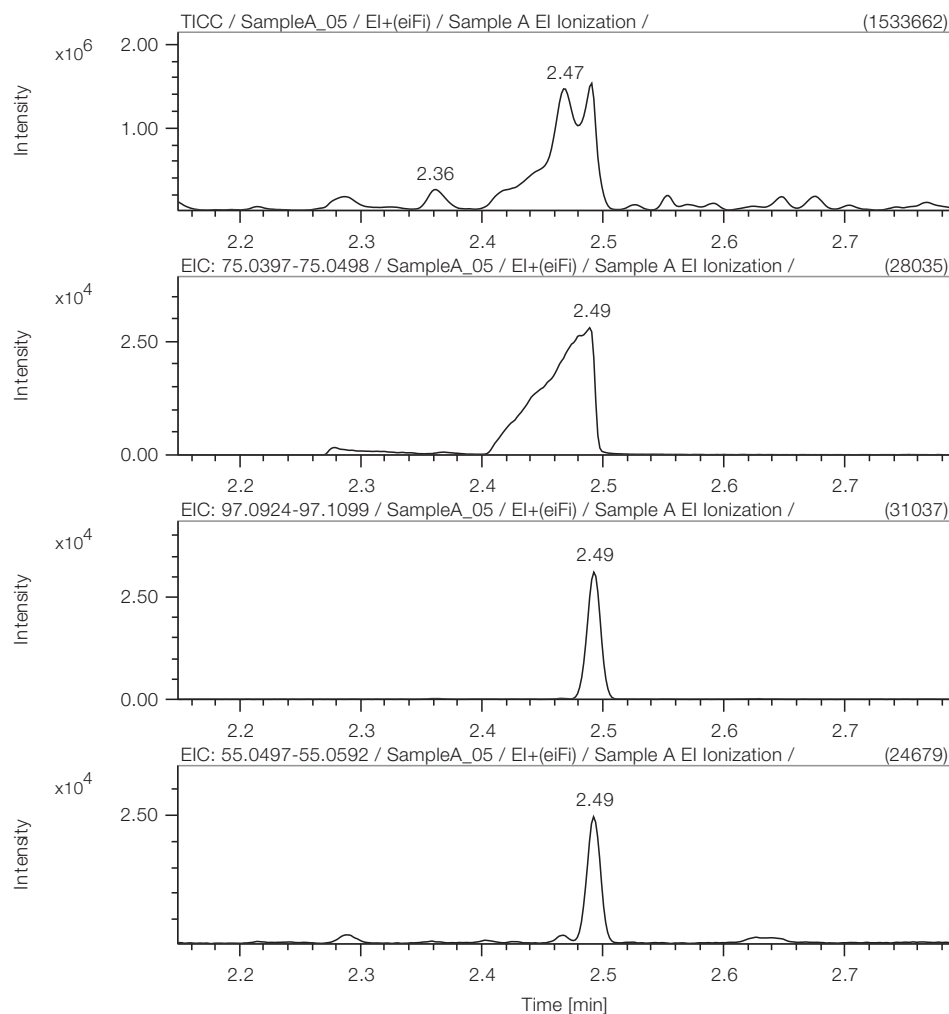
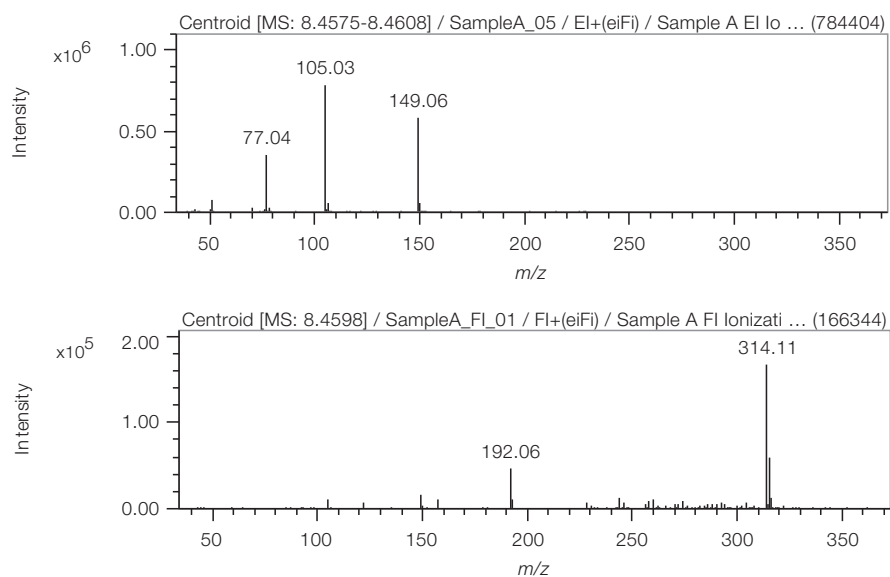
Fig. 6 TICC and EICC at around retention time 2.49 min**Fig. 7 Mass spectra at around retention time 8.45 min measured by EI and FI**

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

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

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

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

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

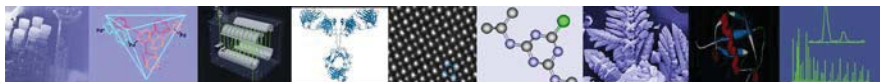
<i>m/z</i> of peak	Formula	Error/mDa
51.02244	C ₄ H ₃	-0.48
77.03809	C ₆ H ₅	-0.49
105.03439	H ₇ H ₅ O	0.9
105.08898	C ₅ H ₁₃ O ₂	-2.02
149.05995	C ₉ H ₉ O ₂	0.25

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

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

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AccuTOF-GCx Series

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

Introduction

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

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

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

Experiment

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

Table 1. Measurement Conditions

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

Results

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

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

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

Conclusion

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

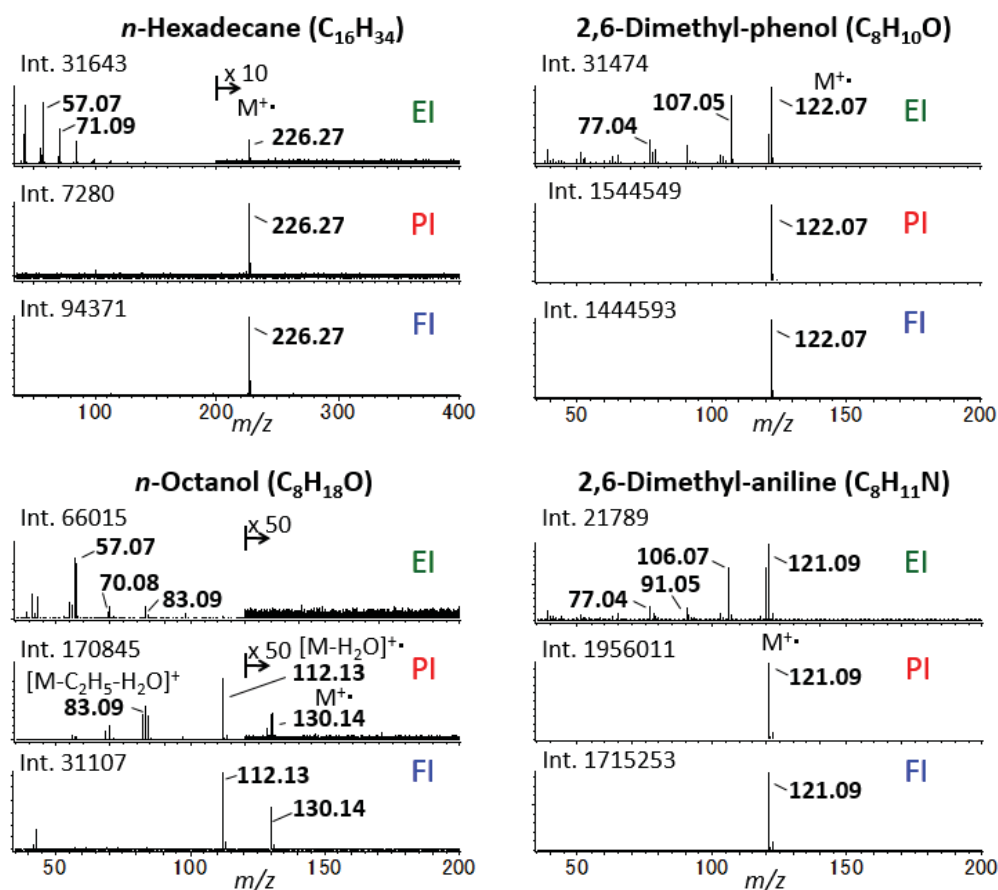


Fig. 1. Compared mass spectra by EI (top), PI (middle) and FI (bottom)

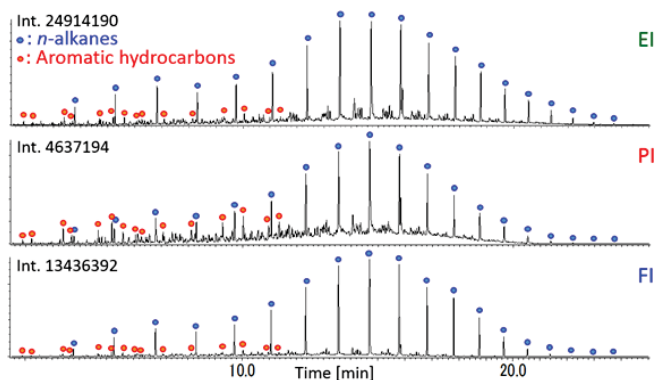
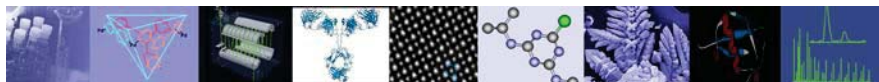


Table 2. Comparison of the molecular-ion detection by FI and PI

F.I. : Fragment ion

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

Fig.2. TICC chromatograms of diesel fuel

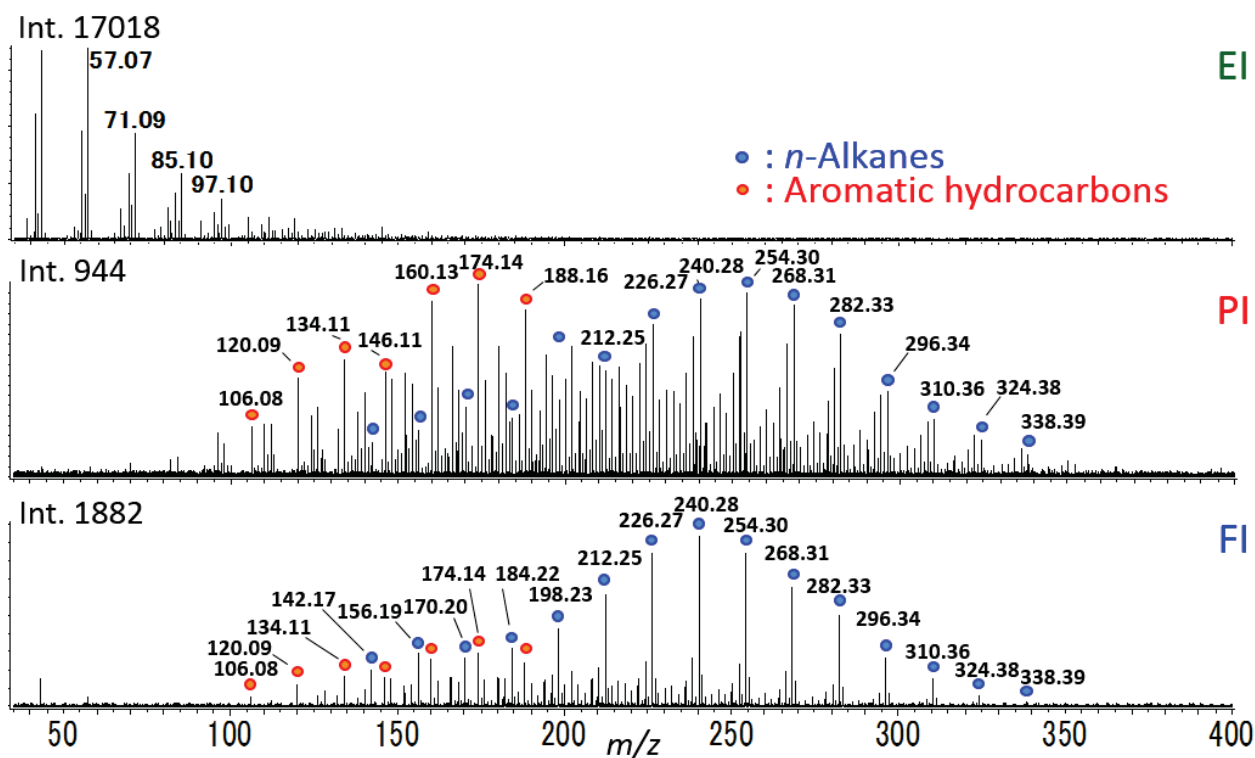
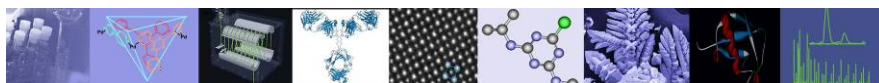


Fig.3. Average mass spectra of diesel fuel



AccuTOF-GCv Series

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

Introduction

The comprehensive 2-dimensional GC (GC x GC) technique provides higher-separation capabilities for complex mixtures than the typical 1-dimensional GC measurements. However, the GC x GC technique requires high speed data acquisition, e. g. > 20 Hz, for the GC detectors due to the shorter 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 condition are shown in Table 1.

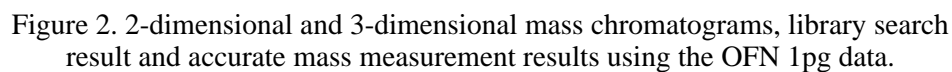
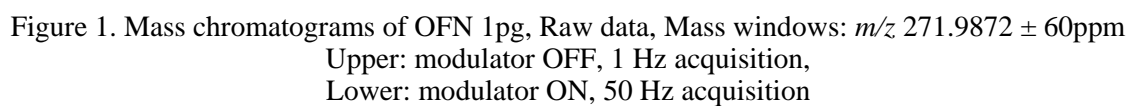
Results

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

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

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

Table 1. Measurement Condition.



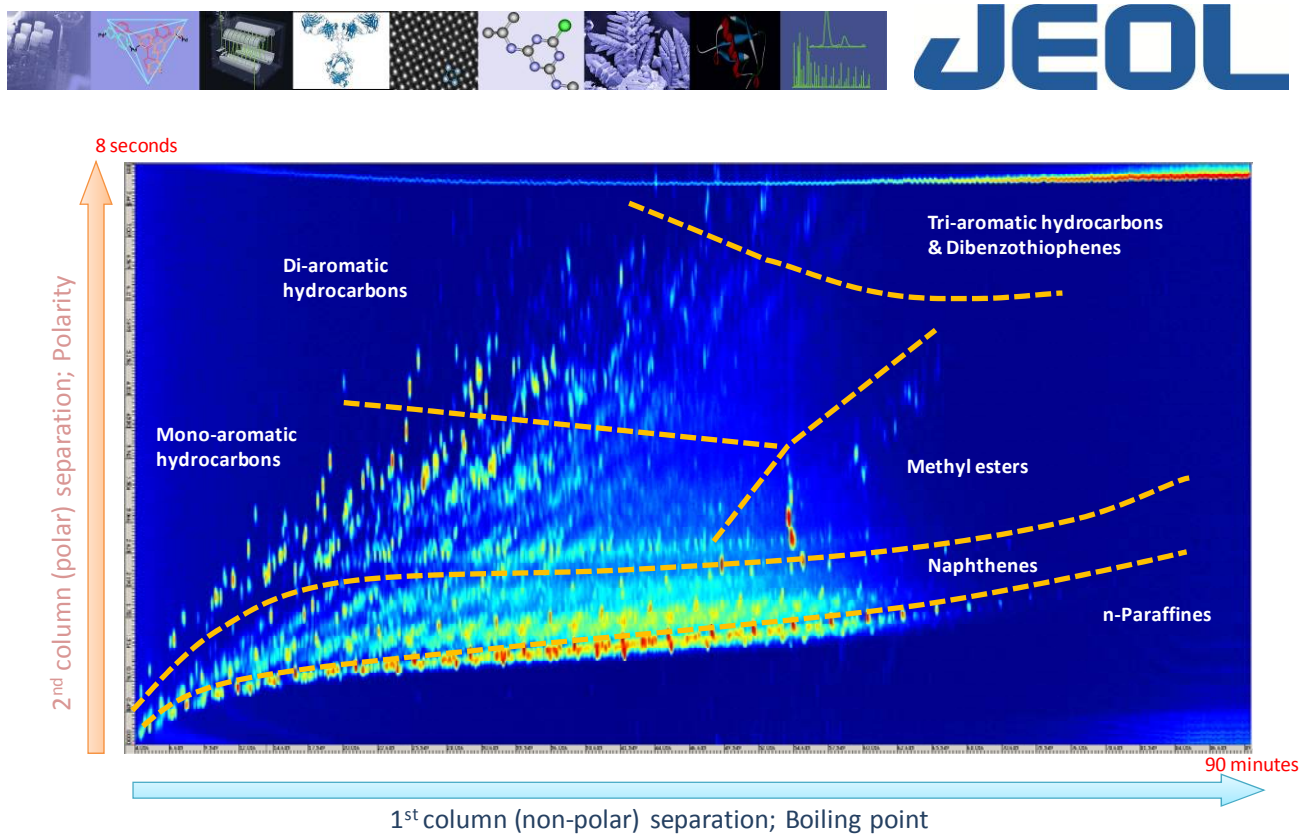


Figure 3. 2-dimensional TIC chromatogram for diesel fuel (50 Hz data acquisition).

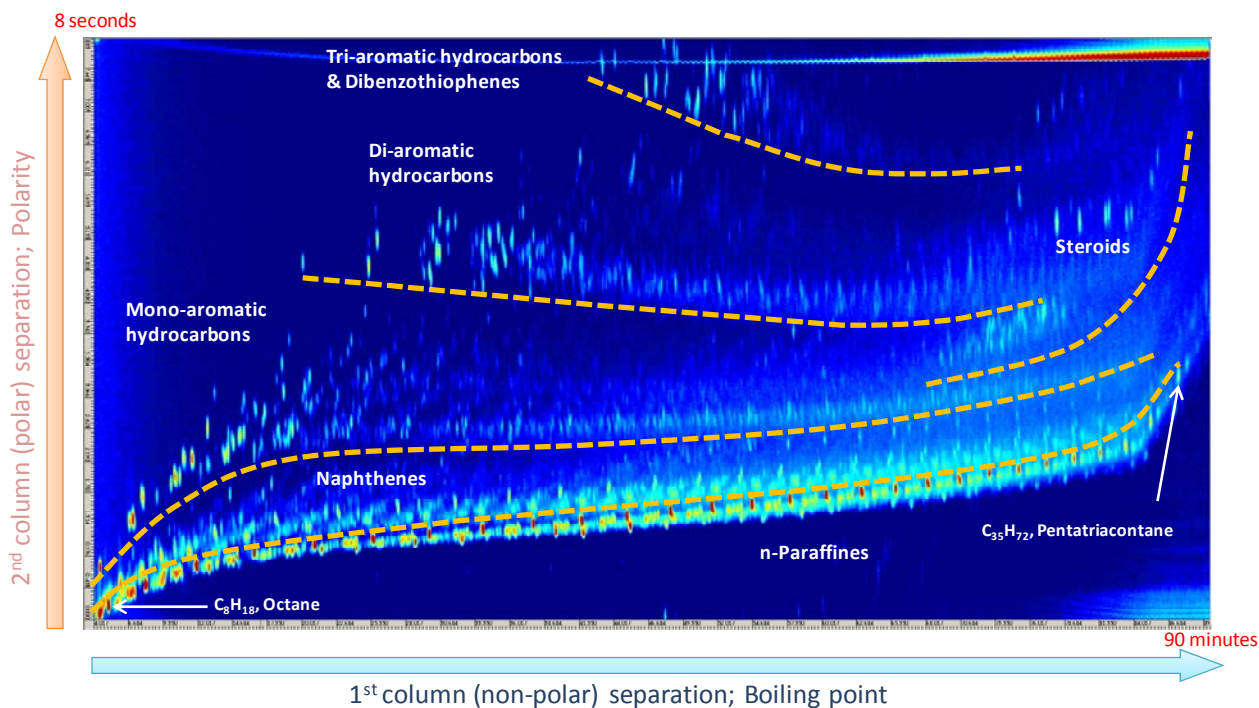


Figure 4. 2-dimensional TIC chromatogram for crude oil (50 Hz data acquisition).

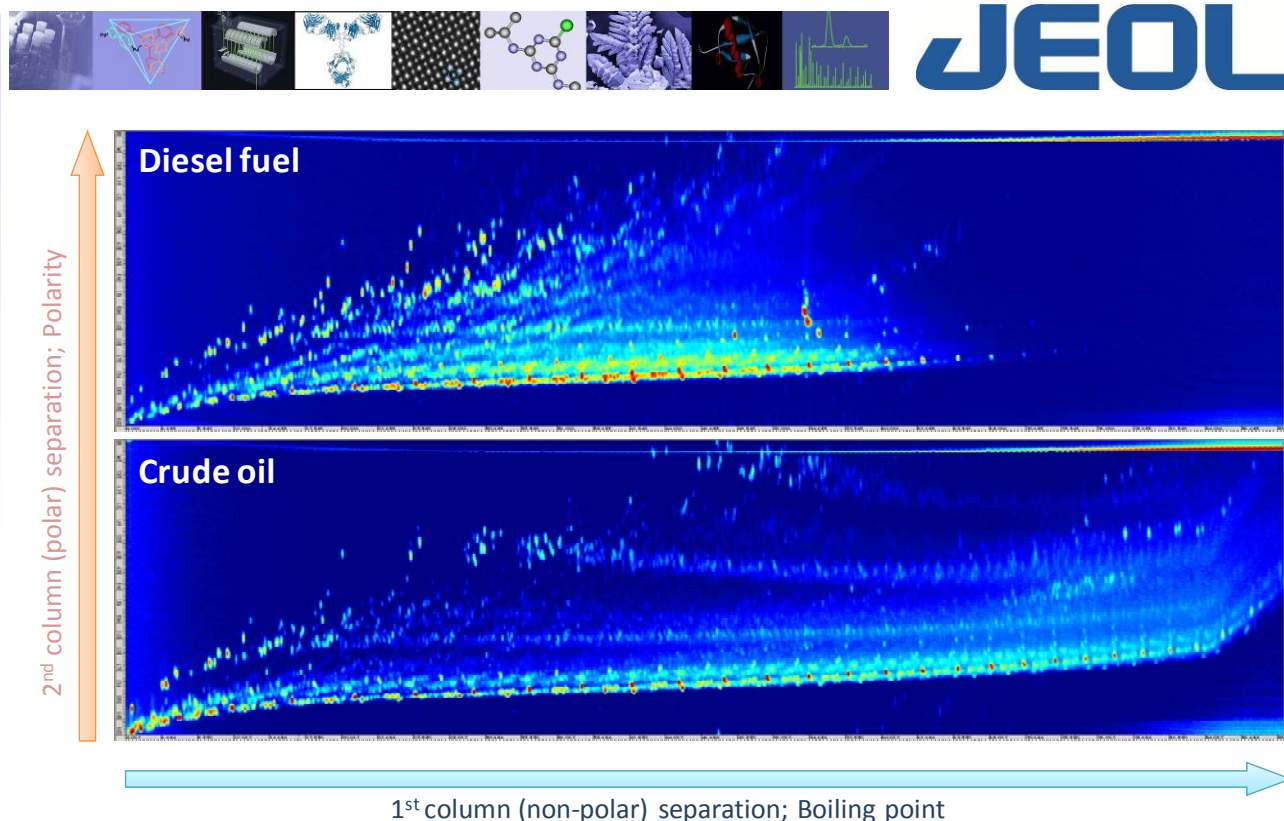


Figure 5. Comparing the 2-dimensional TIC chromatograms for diesel fuel and crude oil.

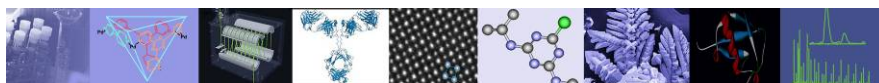
The data showed good spectral matching to the NIST data for OFN (also shown in Figure 2). Additionally, the mass accuracy obtained for the measurement was less than 1 mDa for the molecular ion ($C_{10}F_8^+$, m/z 271.9872) using an external one-point calibration for a GC column background ion (m/z 207.0329). 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.



AccuTOF-GCv Series

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

Introduction

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

Experimental

Sample information and measurement condition are shown in Table 1.

Results

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

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

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

Table 1. Measurement condition.

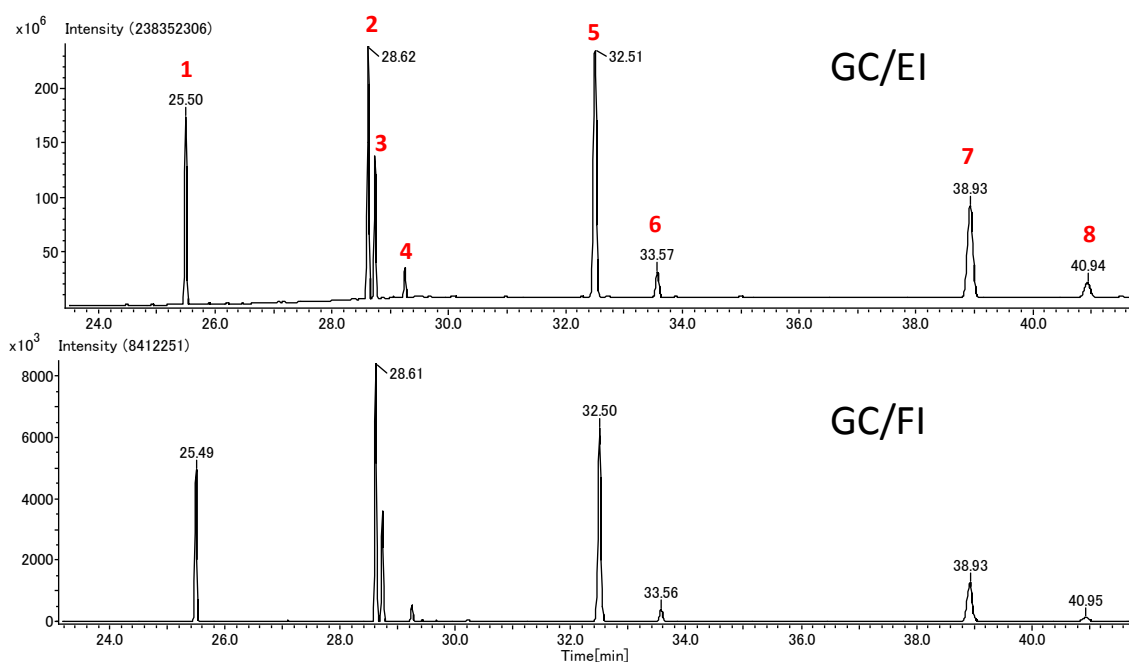
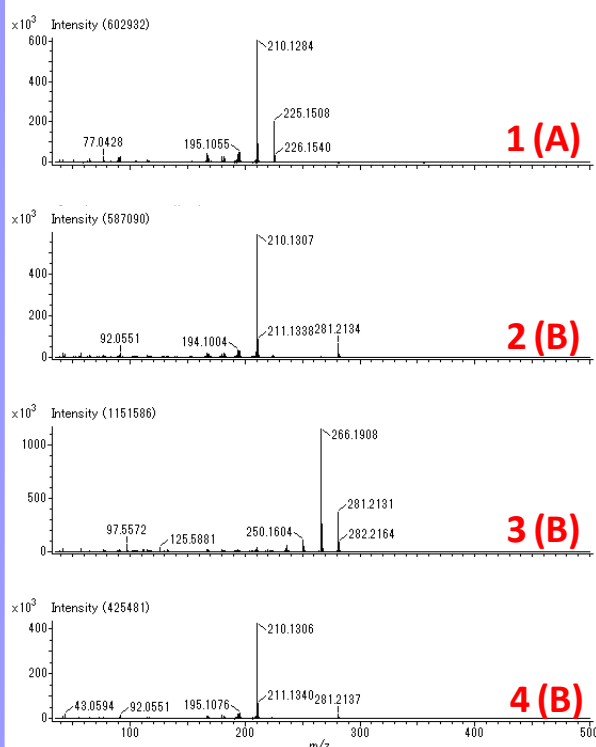


Figure 1. The TICs for GC/EI and GC/FI

EI mass spectra



FI mass spectra

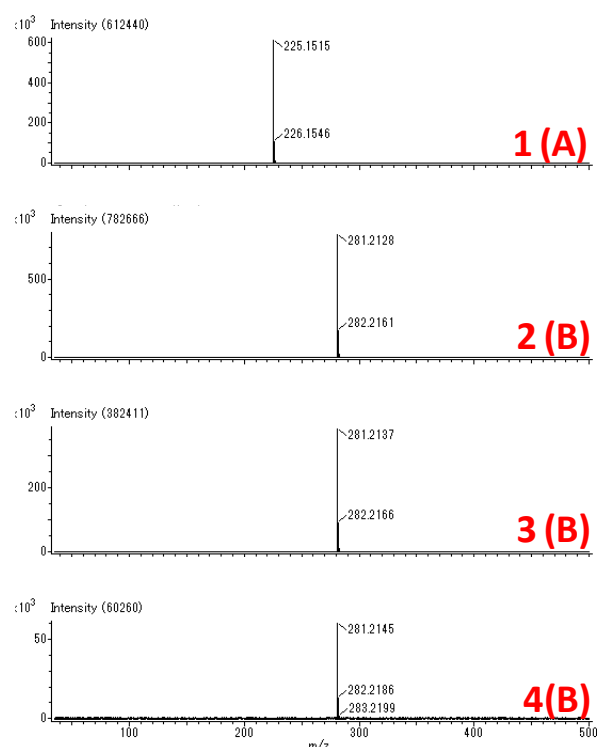


Figure 2. Mass spectra of component1-4, left: EI mass spectra, right: FI mass spectra (A,B: Isomer group)

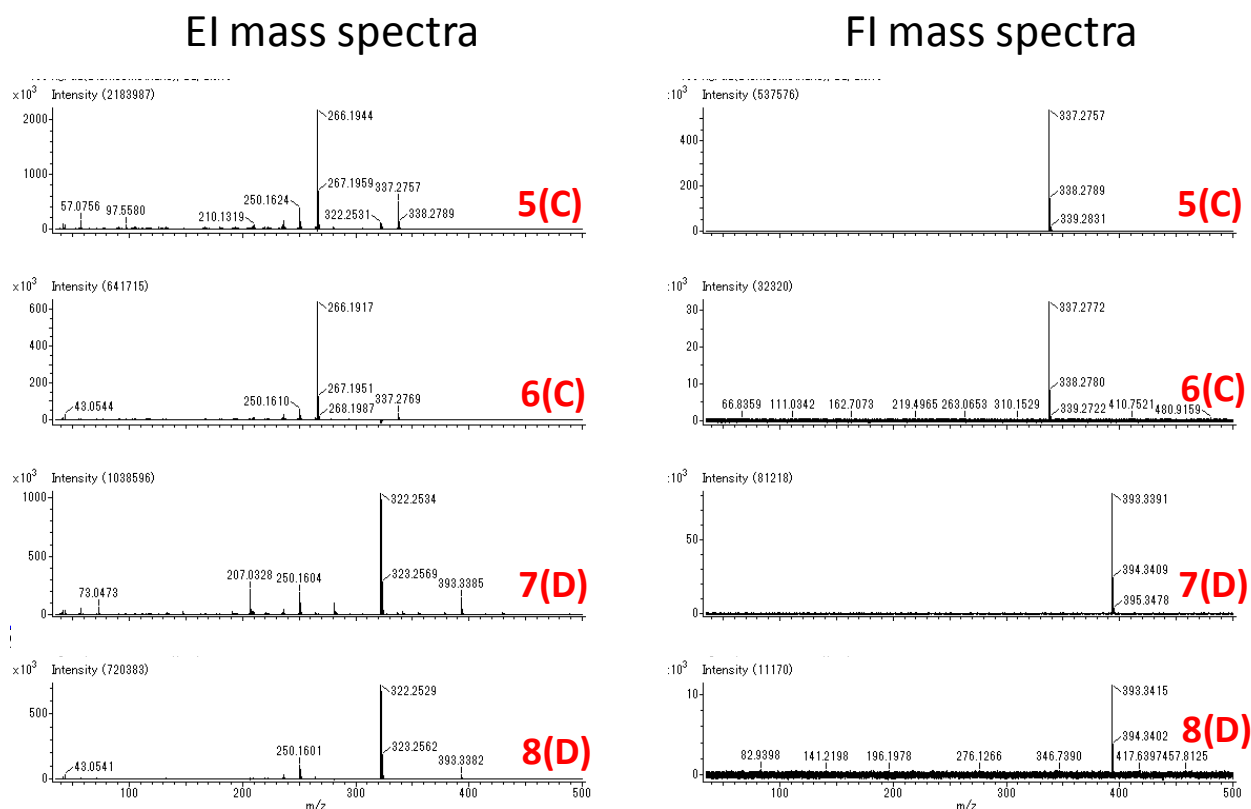


Figure 3. Mass spectra of component5-8, left: EI mass spectra, right: FI mass spectra (C,D: Isomer group)

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	393.3396	393.3396	-0.4	$C_{28}H_{43}N$

Table 2. Accurate mass measurement results

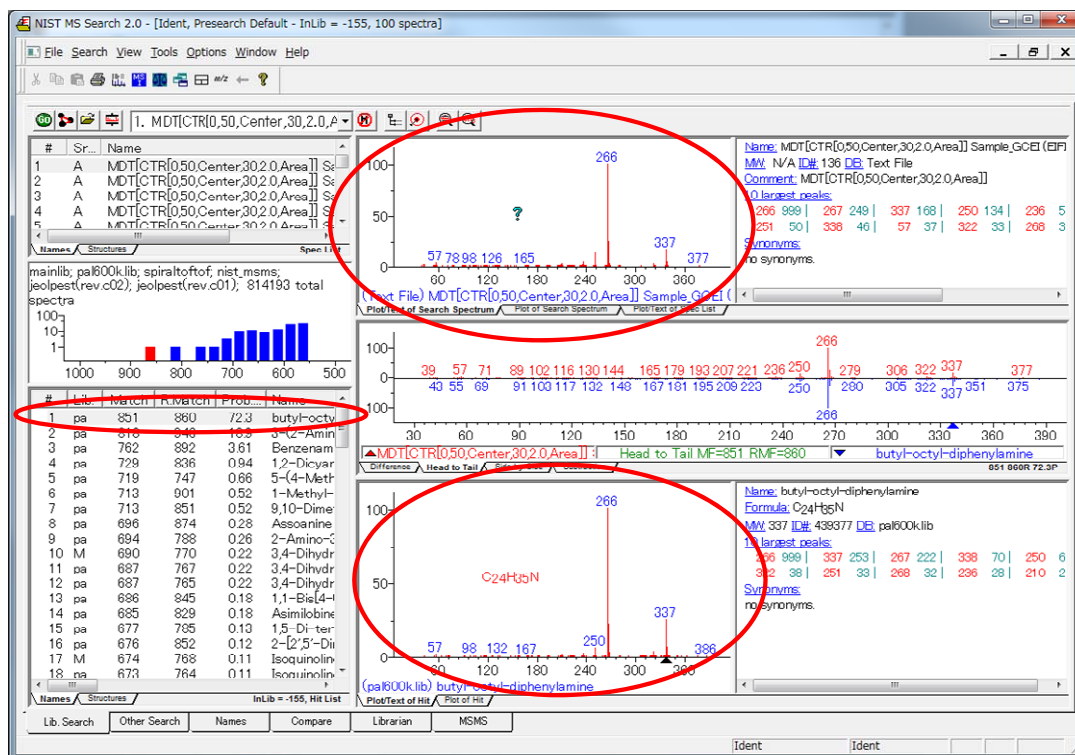
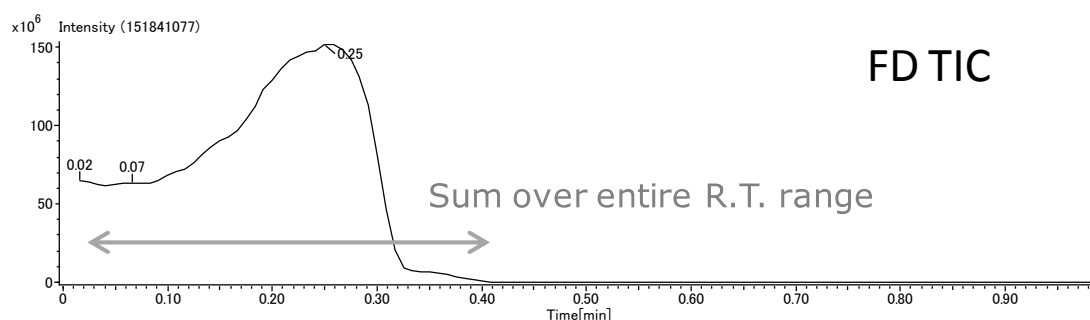
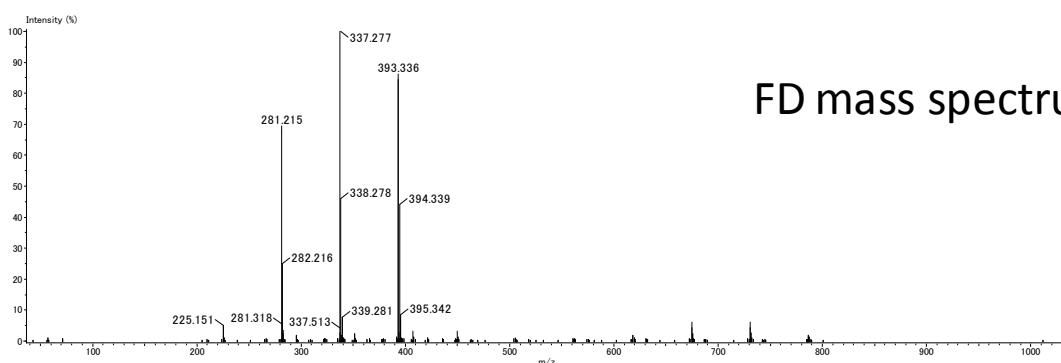


Figure 4. NIST search for component 5.

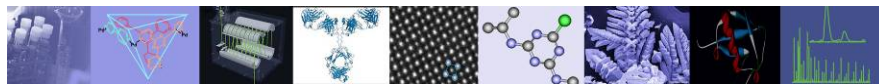


FD TIC



FD mass spectrum

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.

Biomarker Analysis in Petroleum Samples Using GC×GC-HRTOFMS with an Ion Source Combining Electron Ionization (EI) and Photo Ionization (PI)

Masaaki Ubukata and Yoshihisa Ueda MS Business Unit, JEOL Ltd.

Two kinds of petroleum samples were analyzed by “JMS-T200GC AccuTOF™ GCx-plus”, the latest model of JEOL GC-TOFMS (gas chromatograph time-of-flight mass spectrometer) that has high mass resolution and high-speed mass spectra acquisition capabilities combined with the photoionization source and the GC×GC system. Several kinds of biomarkers such as 18-Norabiotane, Cholestane, Hopane, Adamantane, Iceane and Diamantane could be separated and selectively detected by GC×GC and photoionization.

Introduction

As a result of recent advancement in gas chromatography (hereinafter referred to as “GC”) technologies, especially for capillary column technologies, a variety of capillary columns have been developed with different separation capabilities. Furthermore, comprehensive two-dimensional GC (hereinafter referred to as “GC×GC”) has been developed using these capillary column capabilities to separate chemical substances that have very complex compositions [1, 2]. GC×GC systems consist of two types of capillary columns with different separation modes connected in series. Additionally, there is a cryo-trap system (thermal modulator) placed between the first and second columns to modulate the sample injection into the second column. This two-column system allows GC×GC to use two different separation modes in a single analysis. The components are separated in the first column, cryo-trapped for 5-10 seconds, and then rapidly released by the thermal modulator into the second column which has a narrow inner diameter and short length. This process means that the eluted components from the first column are trapped and released at intervals of 5 to 10 seconds and then are continuously and rapidly separated in the second column. As a result, the two-dimensional chromatogram contains two retention time axes, one for the primary column and one for the secondary column.

In general, quadrupole mass spectrometers (hereinafter referred to as “QMS”) are widely used for GC-MS measurements. However, these systems are generally not suitable as a GC×GC detector. As described previously, the second column of the GC×GC system has a unique geometry (narrow diameter and short length) that separates

the components very rapidly. This feature results in chromatographically narrow peak widths that require high data-acquisition speeds in order to acquire enough data points across each analyte peak. If a QMS is used, then there are limited data points measured for the second-dimension peaks in the chromatogram, thus resulting in poor quality 2D chromatographic data. Therefore, it is not optimal to use a QMS system as the detector for GC×GC.

To overcome this problem, JEOL developed a gas chromatograph time-of-flight mass spectrometer (hereinafter referred to as GC-TOFMS) with both high mass resolution ($R=10,000$) and high-speed mass spectral data acquisition (up to 50 Hz) that is optimal for combining with GC×GC. This combination GC×GC-TOFMS system was first introduced in 2004 and is widely used for the analysis of various complex samples [3-7]. In this report, we use our 4th generation GC-TOFMS model “JMS-T200GC AccuTOF™ GCx” with an optional photoionization source and GC×GC system to analyze biomarkers in petroleum samples.

GC×GC-PI-TOFMS System

GC×GC system

A Zoex Corporation ZX2 GC×GC thermal modulator system was used with our GC-TOFMS system. The schematic diagrams of GC×GC thermal modulator was shown in **Fig. 1**. This modulator unit was placed between the two capillary columns in order to cryo-trap the components eluting from the first column using the “cold jet gas” and in order to release them using the “hot jet gas”. Since the “hot jet gas” is sprayed for very short period (300-400 msec) with regular interval (5-10 seconds), released

components are introduced into the second column each interval regularly, as a result the two-dimensional chromatographic separation is achieved as shown in **Fig. 2**.

Photoionization Source (PI)

The most commonly used ionization method for GC-MS is Electron Ionization (EI). EI is a hard ionization technique that uses high energy electrons to ionize the analytes, resulting in many fragment ions. These mass spectra can be very useful for chemical structural analysis of target compounds and can be compared to MS search libraries such as the NIST database to help confirm the identity of target compounds. However, the EI spectra can often have low intensity molecular ions, which can make it difficult to estimate the elemental composition from the measured exact mass. As a result, this technique is not always an ideal ionization method for these purposes. Alternatively, soft ionization techniques that use low energy methods to ionize the sample analytes can be used to generate higher intensity molecular ions. In the GC-MS analysis field, Chemical Ionization (CI) is the most common soft ionization method available. JEOL offers not only CI but also Field Ionization (FI) and Photoionization (PI) as optional soft ionization methods for the JMS-T200GC.

The PI photon source is a deuterium lamp with radiation wavelengths from 115 to 400 nm. The energy for the smallest wavelength (115 nm) is 10.8 eV which is a good match for the primary ionization energy for typical organic compounds (~10 eV). As a result, this source is suitable for the soft ionization of these types of analytes.

The PI source schematic is shown in **Fig. 3**. The JEOL PI source is incorporated into the standard EI source, which allows for the unique capability of switching between EI and PI without breaking vacuum. All that is necessary for EI measurements is to turn on the EI filament, and then for PI measurements, simply turn off the EI filament and turn on the deuterium lamp.

High resolution TOFMS system

A photo of the external view of JEOL AccuTOF™ GCx along with the schematics for the ion source, ion transfer system and ion optical system are shown in **Fig. 4**. The compounds eluting from the GC column are first ionized in the ion source and then transferred into the TOF analyzer using a low kinetic energy of approximately 30 eV. Afterwards, the ions are measured by using a single-stage reflectron TOF analyzer that orthogonally accelerates the ions away from the ion-transfer direction. This type of TOFMS is called an

Fig. 2 Conceptual view of 2D chromatogram obtained with GC×GC

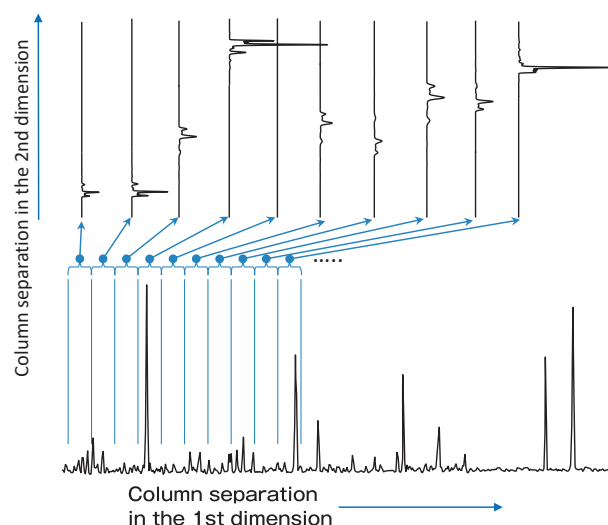


Fig. 3 Schematic of PI (photo ionization) source

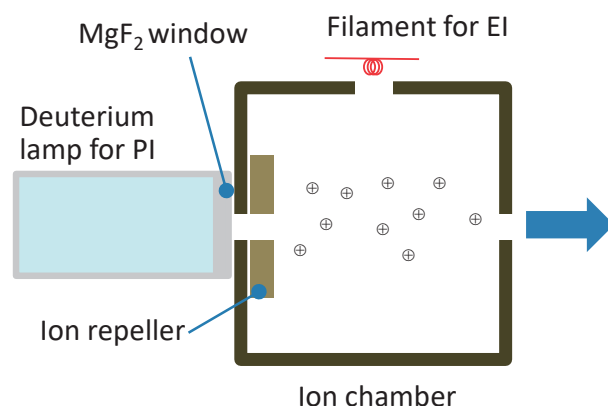


Fig. 4 Photo and schematics of JMS-T200GC

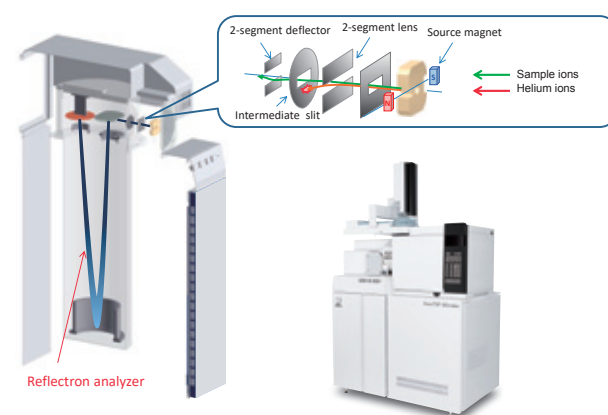
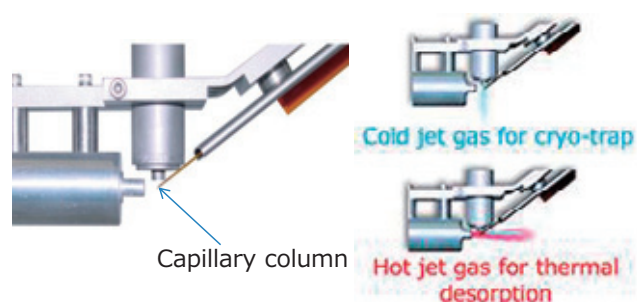


Fig. 1 Schematic of GC×GC modulator



“Orthogonal-Acceleration Time-of-Flight Mass Spectrometer” (oa-TOFMS).

It is worth noting that there are some challenges for using TOF instruments as GC-MS detectors. In particular, helium gas is used as the GC carrier gas which means that the volume of this gas is relatively large compared to the target compounds present in the sample injections. For EI, helium is also ionized and transferred together with the sample ions into the analyzer, thus resulting in a large number of helium ions in the ion beam. These ions can produce large space charging effects (charging, etc.) within the analyzer that can degrade the resolution of the instrument. Additionally, for TOFMS analyzers, these helium ions will reach the detector, resulting in the rapid deterioration of the microchannel plate (MCP). To overcome this problem, the JEOL GC-TOFMS system is innovatively designed so that the ion transfer system removes 99.9% or more of the helium ions produced in the ion source by adjusting the lens balance voltages.

Biomarker Analysis of Petroleum Samples Using GC×GC-PI-TOFMS

Biomarkers contained within crude oils and their source rocks are often investigated to index petroleum samples and to determine petroleum sample origins. Biomarkers are organic compounds that originated from the living organisms that were present in the source material of the oil. These biomarker molecules, which are indicators of the origin organic substances, sedimentary environments, maturity, etc.,

can be used to determine the origins of an unknown crude oil. However, petroleum samples are comprised from an aggregate of hundreds or even thousands of hydrocarbons. Further complicating the situation, biomarkers are hydrocarbons with specific structures found within these complex petroleum samples. As a result, comprehensively detecting biomarkers within petroleum samples is very difficult to accomplish.

In this report, we will use the high separation capabilities of GC×GC in combination with the combo EI/PI source and high mass resolution TOFMS to comprehensively detect the biomarkers within petroleum samples.

Measurement conditions

The measurement conditions are listed in **Table 1**. A ZX2 thermal modulation system (Zoex Corporation) was used for the GC×GC measurements. A nonpolar BPX5 column (SGE Corporation, 30 m length, 0.25 mm I. D., 0.25 μm liquid phase thickness) was used for the first column. A more polar BPX50 column (SGE Corporation, 3 m length, 0.1 mm I. D., 0.1 μm liquid phase thickness) was used for the second column. Two test samples (Petroleum Fractions A and B) were prepared for these tests, and the biomarker amounts were estimated and compared for each fraction.

Measurement results

The PI mass spectra for Cholestane and Adamantane, both of which are typical biomarkers, are shown in **Fig. 5**. The molecular ions $M^{+•}$ were detected as the base peak for each of these compounds, thus confirming that PI is effective for

Table 1 Measurement conditions

Instrument	JEOL AccuTOF™ GC series
	Zoex ZX2 thermal modulator
1 st Column	BPX5, 30 m × 0.25 mm, 0.25 μm
2 nd Column	BPX50, 3 m × 0.1 mm, 0.1 μm
Modulator period	6 sec
Inlet pressure	350 kPa (Out flow : 1.75 mL/min)
Inlet mode	Cool on column, Oven track mode, 1 μL Injection
Oven Temp.	50 °C (2 min) → 10 °C/min → 250 °C
Ion Source	EI/PI Combination Ion Source
Ionization mode	PI+ (D ₂ lamp, 115 to 400 nm)
<i>m/z</i> range	<i>m/z</i> 35 to 700
Spectrum recording speed	25 spectra / sec

Fig. 5 PI mass spectra of Cholestane and Adamantane

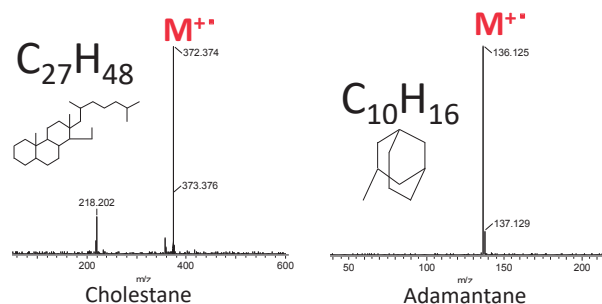


Fig. 6 2D TIC of Petroleum fraction A, measured by GC×GC/PI

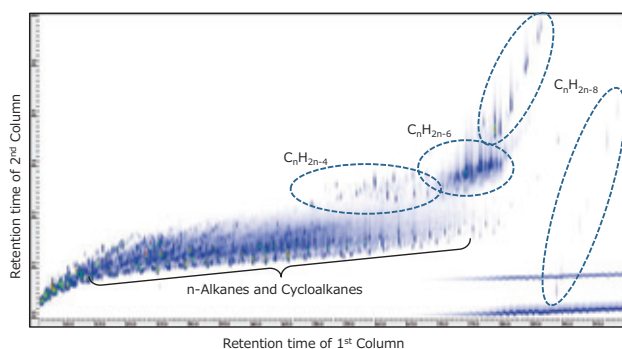
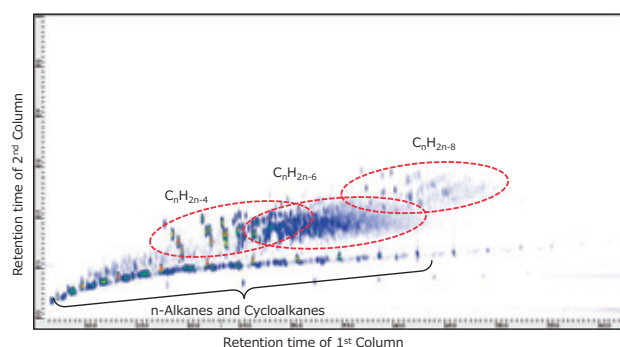


Fig. 7 2D TIC of Petroleum fraction B, measured by GC×GC/PI



detecting these biomarker molecular ions.

The 2D TICCs (total ion current chromatograms) for the GC×GC/PI measurements are shown in **Fig. 6** and **Fig. 7** for each crude oil sample. Both samples contained n-Alkanes (C_nH_{2n+2}) and Cycloalkanes (C_nH_{2n+1}) along with numerous chemical compounds detected at later secondary column retention times. These compounds were identified as C_nH_{2n-4} , C_nH_{2n-6} and C_nH_{2n-8} which have higher degrees of unsaturation than n-Alkanes and Cycloalkanes. Additionally, these two petroleum fraction samples were measured by GC×GC/EI under the same conditions. Based on the library search results

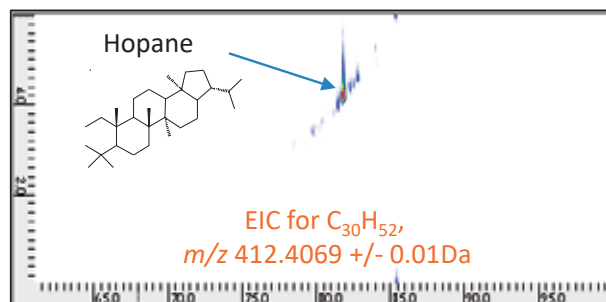
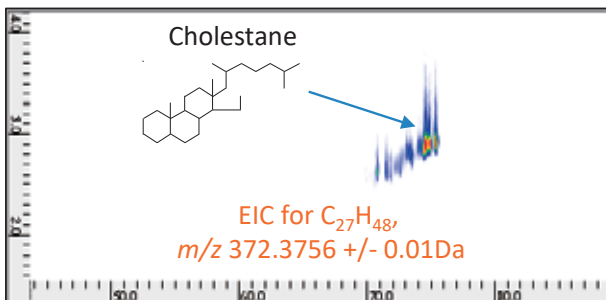
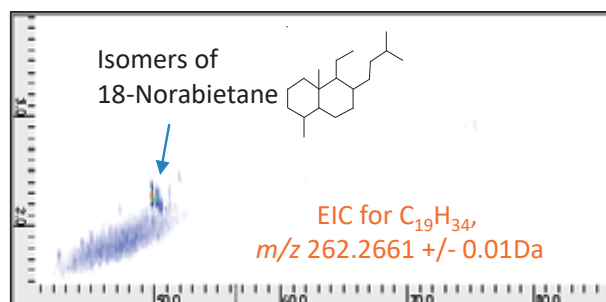
for the EI mass spectra corresponding to C_nH_{2n-4} , C_nH_{2n-6} and C_nH_{2n-8} , Petroleum Fraction A mainly contained the Cholestane polycyclic saturated hydrocarbons while Petroleum Fraction B mainly contained the Adamantane saturated-bridged cyclic hydrocarbons.

Next, high selectivity 2D EICs (Extracted Ion Chromatograms) were constructed for the molecular ions of six chemical compounds that are generally known as biomarkers (**Table 2**). As shown in **Fig. 8** and **Fig. 9**, 18-Norabietane, Cholestane and Hopane were specifically identified in Petroleum Fraction A, and Adamantane, Iceane and Diamantane were identified in

Table 2 Typical biomarkers and “ m/z ” of their molecular ions

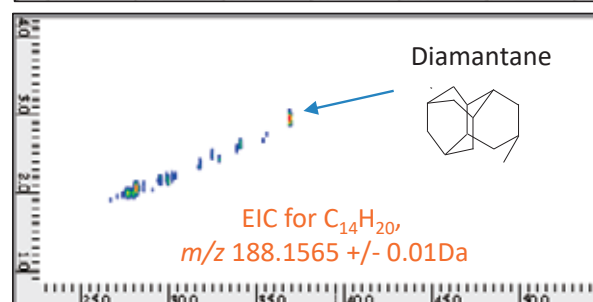
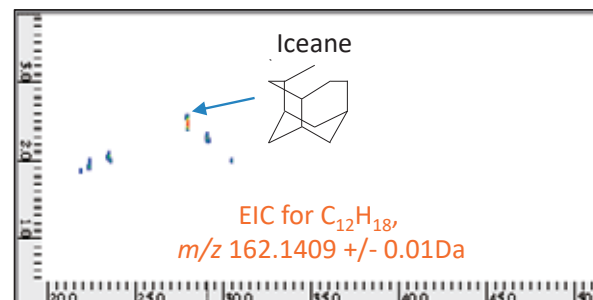
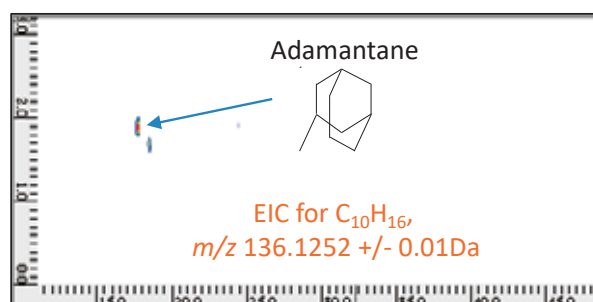
Compounds	Rational Formula	m/z
18-Norabietane	$C_{19}H_{34}$	262.2661
Cholestane	$C_{27}H_{48}$	372.3756
Hopane	$C_{30}H_{52}$	412.4069
Adamantane	$C_{10}H_{16}$	136.1252
Iceane	$C_{12}H_{18}$	162.1409
Diamantane	$C_{14}H_{20}$	188.1565

Fig. 8 2D EIC of Petroleum fraction A, measured by GC×GC/PI



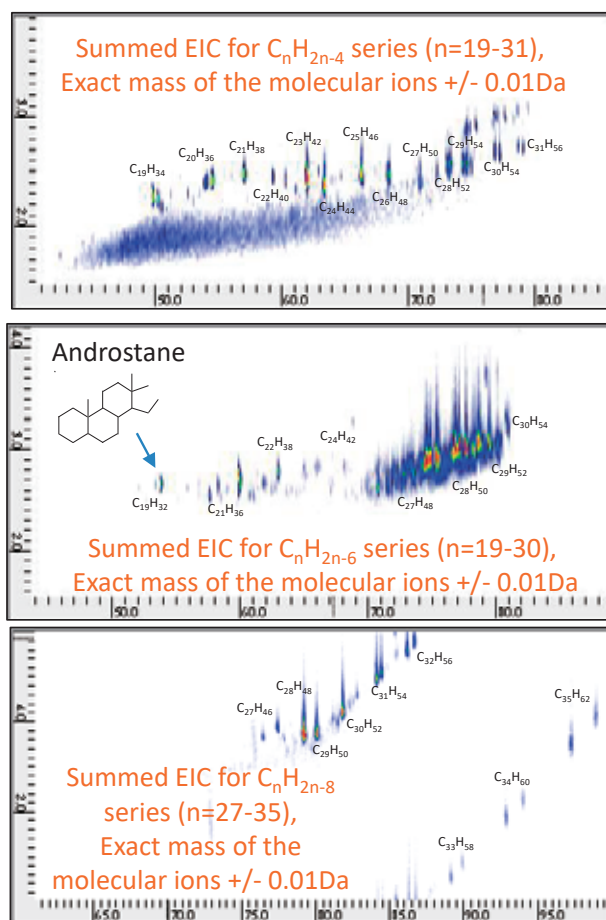
(m/z 262.2661, 372.3756, 412.4069)

Fig. 9 2D EIC of Petroleum fraction B, measured by GC×GC/PI



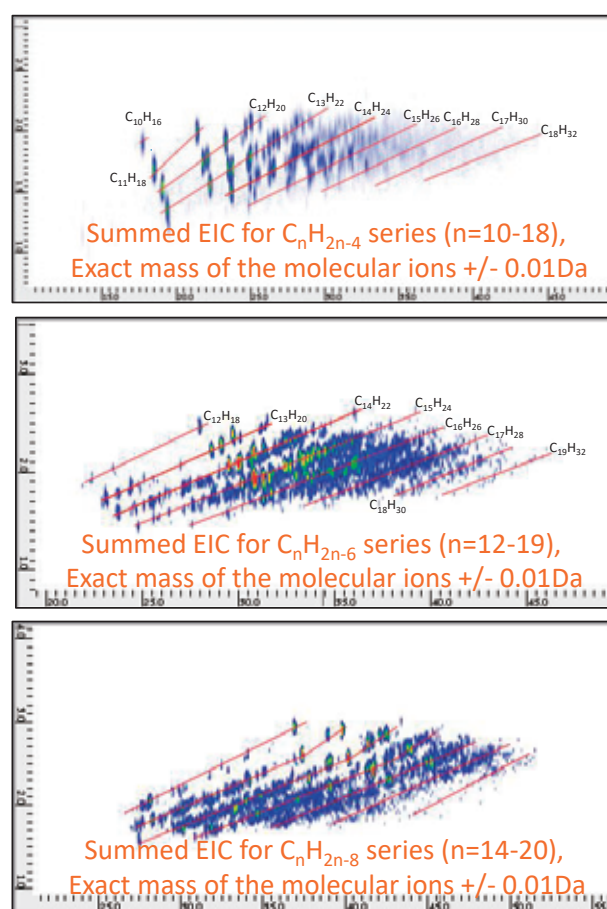
(m/z 136.1252, 162.1409, 188.1565)

Fig. 10 Total 2D EIC of Petroleum fraction A, measured by GC×GC/PI



(C_nH_{2n-4} : $n=19 \sim 31$, C_nH_{2n-6} : $n=19 \sim 31$, C_nH_{2n-8} : $n=27 \sim 35$)

Fig. 11 Total 2D EIC of Petroleum fraction B, measured by GC×GC/PI



(C_nH_{2n-4} : $n=10 \sim 18$, C_nH_{2n-6} : $n=12 \sim 19$, C_nH_{2n-8} : $n=14 \sim 20$)

Petroleum Fraction B. Next, the related compounds for these biomarkers were systematically evaluated by creating summed 2D EICs for the C_nH_{2n-4} , C_nH_{2n-6} and C_nH_{2n-8} series. The 2D EICs for these series are shown in **Fig. 10** and **Fig. 11**.

These results clearly showed that the biomarkers and their related compounds are present within each petroleum fraction. Since the PI method selectively produces molecular ions for these analytes, a systematic evaluation for the biomarker amounts was achieved by combining the high separation capabilities of GC×GC with the soft ionization of PI and high resolution TOFMS. Additionally, the 2D EICs for the PI measurements made it much easier to interpret the data and correctly assign the biomarker identities in the crude oil samples.

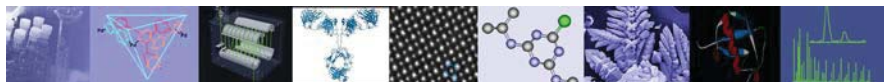
Summary

GC×GC is an advanced GC technology that offers dramatically higher chromatographic separation capabilities than that of conventional 1D GC. To maximize the quality of data obtained with this high-separation capability, it is effective to use a TOFMS that offers both high speed data acquisition and high mass resolution in combination with hard ionization and soft ionization methods. The JEOL GC×GC-TOFMS system equipped with the combination EI/PI source accomplishes all of this in a single package.

As reported in this application note, our latest GC×GC-TOFMS in combination with the optional EI/PI source is a very powerful tool for the analysis of complex mixtures like biomarkers in petroleum samples.

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AccuTOF-GCx Series

GCxGC TOFMS Analysis of Base Oils with CI, PI, FI

Introduction

Structural elucidation of hydrocarbon classes in petroleum products are always in high demand. Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GCxGC-TOFMS) with electron ionization (EI) is a powerful method for characterizing complex mixtures such as base oils. However, EI data can often lack a strong molecular ion signal. Therefore, it is necessary to measure samples with soft-ionization methods such as positive chemical ionization (PCI), field ionization (FI), or photo-ionization (PI) for the detection of molecular ions. Each technique is a little different so it is important to understand the characteristics of each soft ionization method.

In this application note, we compare the mass spectra of a base oil analyzed by GCxGC-TOFMS with EI, PCI, FI, and PI.

Experiment

The details for sample dilution in hexane as well as the instrumental conditions are listed in Table 1.

Results

Identification of each peak was carried out by a library search of the EI mass spectra and elemental composition estimation for the molecular ions (M^{+}) from the soft ionization results (Fig. 1, Fig.2 and Table 2). A *n*-paraffin (Peak A) and a branched-paraffin (Peak B) were identified in the base oil and showed a different peak pattern for each mass spectrum, especially in the FI results. The EI results consisted mainly of fragment ions with the paraffins showing very low intensity molecular ions. The PCI results showed many fragment ions along with the molecular ion, most commonly as $[M-H]^+$, thus making it less easy to identify the molecular ion from these results than for the FI and PI results. Steroids (peak C) and aromatics (peak D) showed mostly molecular ion for the FI and PI results, respectively.

Table 1. Sample and measurement conditions

Sample	Base oil dilution with Hexane (1:25(PCI, FI, PI), 1:100(EI))		
Instruments	AccuTOF GCv 4G (JEOL Ltd.) ZX-2 (GCxGC module : ZOEX Corporation)		
GCxGC conditions			
Inlet	Cool on column		
Inlet mode	Track Oven		
1 st column	ZB-1HT Inferno (15 m x 0.25 mm, film thickness 0.1 μm)		
Modulator loop	Guard column IP Deact (0.8 m x 0.18 mm)		
2 nd column	ZB-35HT Inferno (1 m x 0.1 mm, film thickness 0.05 μm)		
Transfer line	Guard column IP Deact (0.3 m x 0.1 mm)		
Oven temp. program	50°C (1min) => 3°C/min => 370°C (23min)		
Carrier gas flow	1.2 mL/min (He, Constant flow)		
Modulation period	5 sec		
Injection Volume	0.5 μL		
MS conditions			
Ion source	EI/PI, EI/CI, EI/FI/FD		
Ionization method	EI(+): 70 eV, 300 μA	CI(+): 200 eV, 300 μA,	CH ₄ (95%) + NH ₃ (5%), 1.0mL/min
	PI(+): D ₂ lamp	FI(+): -10 kV, Carbon emitter	
Interface temp.	300°C		
Ion source temp.	EI: 200 °C	CI: 200 °C	FI: OFF
	PI: 200 °C		
Spectrum recording interval	25 Hz (0.04 sec/spectrum)		
m/z range	EI, PI, FI: 40 ~ 900	CI: 100 ~ 900	

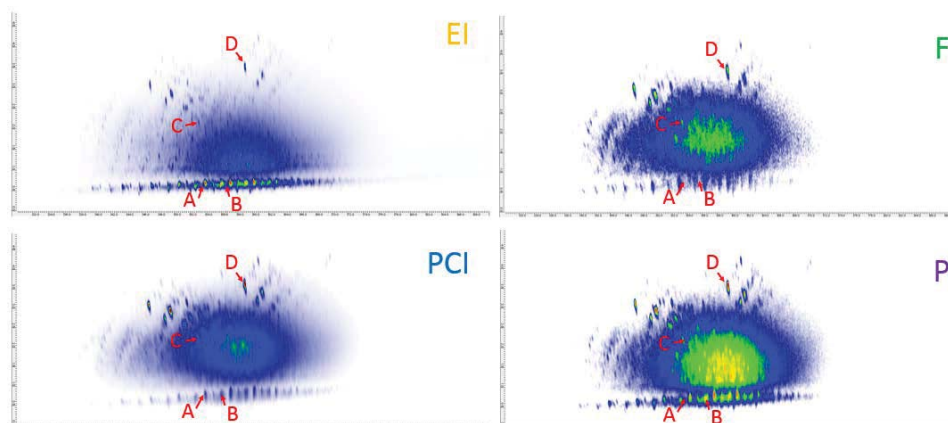


Fig. 1. Base oil 2D map for each ionization method.

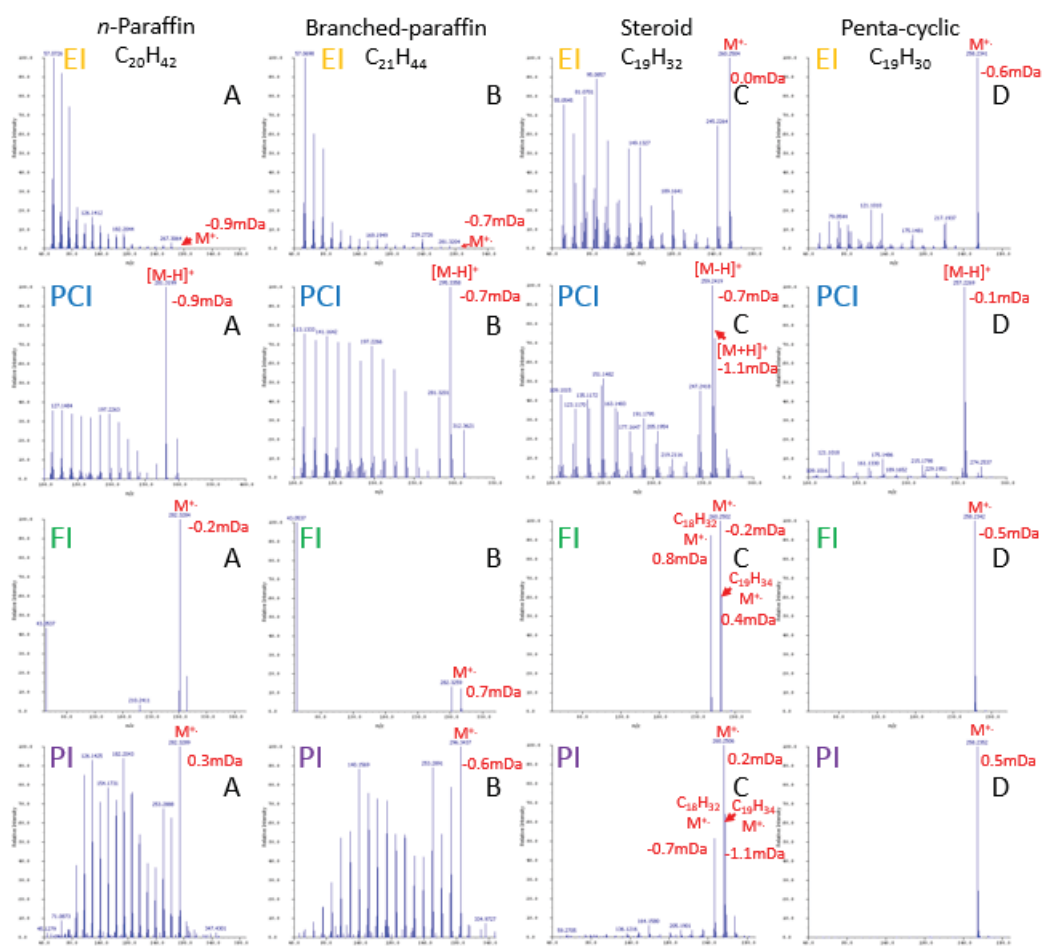
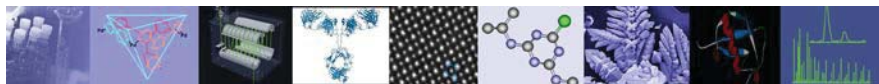


Fig. 2. Mass spectra for EI, PCI, FI, and PI.



Overall, the FI results showed the lowest number of fragment ions for all compounds, thus making it possible to perform type analyses. The PI results showed both molecular ion and fragment ion information, for simplified structural analyses.

Conclusion

The NIST library search of the EI mass spectra is a powerful verification tool for structural elucidation of compounds. However, the EI molecular ion peak intensities can be low for compounds like n-paraffins and branched paraffins. In fact, these molecular ions are often not detected when the compound concentration is too low. As a result, the identification of these compounds using the NIST library search becomes less reliable with the absence of the molecular ions in the EI spectrum.

On the other hand, using soft ionization with accurate mass measurements allows for the elemental composition estimations of the molecular ions. FI is the softest ionization method for showing the intact compounds. PI mass spectra showed strong molecular ions along with fragment ions. As the results here showed, PI and FI are clearly the easiest techniques for identifying the molecular ions, when compared to PCI.

Therefore, using a combination of EI for library searchable spectra and a soft ionization for molecular ion elemental composition estimations allows the analyst to more reliably identify the compounds of interest. The JEOL AccuTOF GC series offers an optionally available EI/FI combination ion source as well as an optionally available EI/PI combination ion source to allow soft and hard ionization to occur without breaking vacuum.

Table 2. Detected peaks by each ionization technique

	EI	PCI	FI	PI
<i>n</i> -paraffin	Fragments (mainly) M ⁺ (Very weak)	[M-H] ⁺ (mainly) + Fragments	M ⁺	M ⁺ (mainly) + Fragments
Branched-paraffin	Fragments (mainly) M ⁺ (Very weak)	[M-H] ⁺ (mainly) [M+H] ⁺ + Fragments	Fragments (mainly) M ⁺	M ⁺ (mainly) + Fragments
Steroids	M ⁺ (mainly) + Fragments	[M-H] ⁺ (mainly) + Fragments	M ⁺ (mainly) + Fragments	M ⁺ (mainly) + Fragments
Aromatics	M ⁺ (mainly) + Fragments	[M-H] ⁺ (mainly) + Fragments (weak)	M ⁺	M ⁺

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).

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 μ m
2nd column	Rxi-17SilMS, 2 m x 0.15 mm, 0.15 μ m
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 (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™ Version 2.5.0a2

Table 1. Measurement condition.

Results

The Kendrick mass scale that defines the mass of CH₂ 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:

$$\text{Kendrick Mass} = \text{IUPAC mass} \times (14.00000/14.01565)$$



Figure 1. JMS-T100GCv "AccuTOF GCv 4G" GC x GC/HR-TOFMS system

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:

$$\text{Kendrick Mass Defect (KMD)} = \text{Kendrick Mass} - \text{nominal Kendrick Mass}$$

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 CH₂ 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.

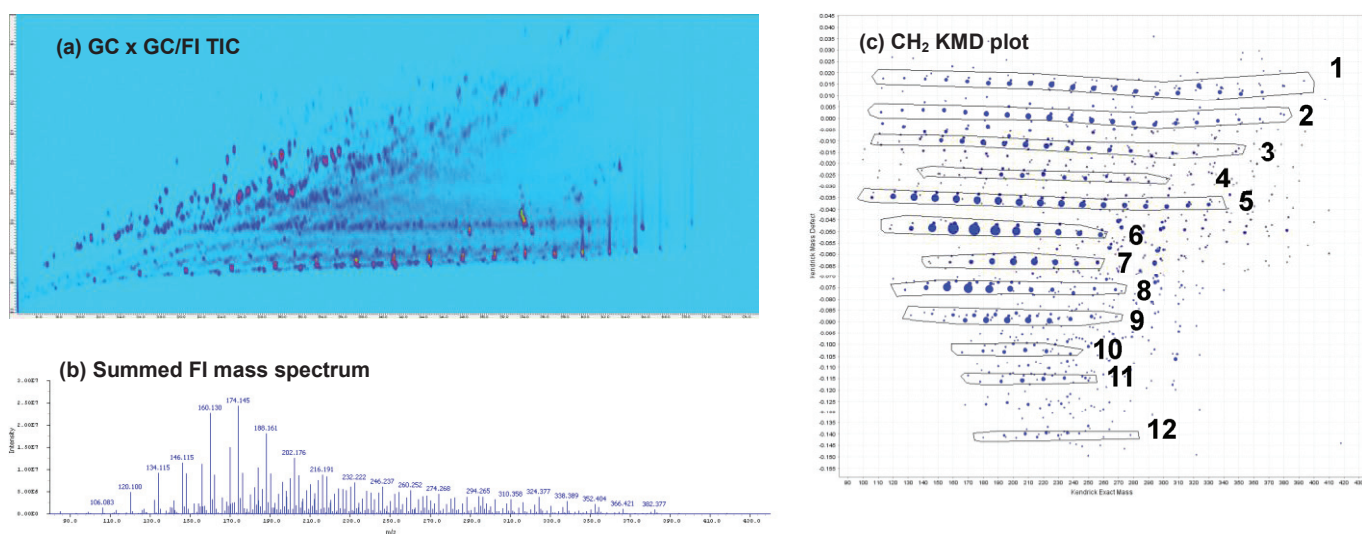
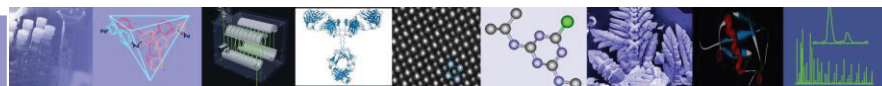


Figure 2. (a) 2-dimensional TIC chromatogram of the diesel sample, (b) the summed FI mass spectrum for the entire retention time region, (c) CH_2 Kendrick Mass Defect plot for the summed FI mass spectrum

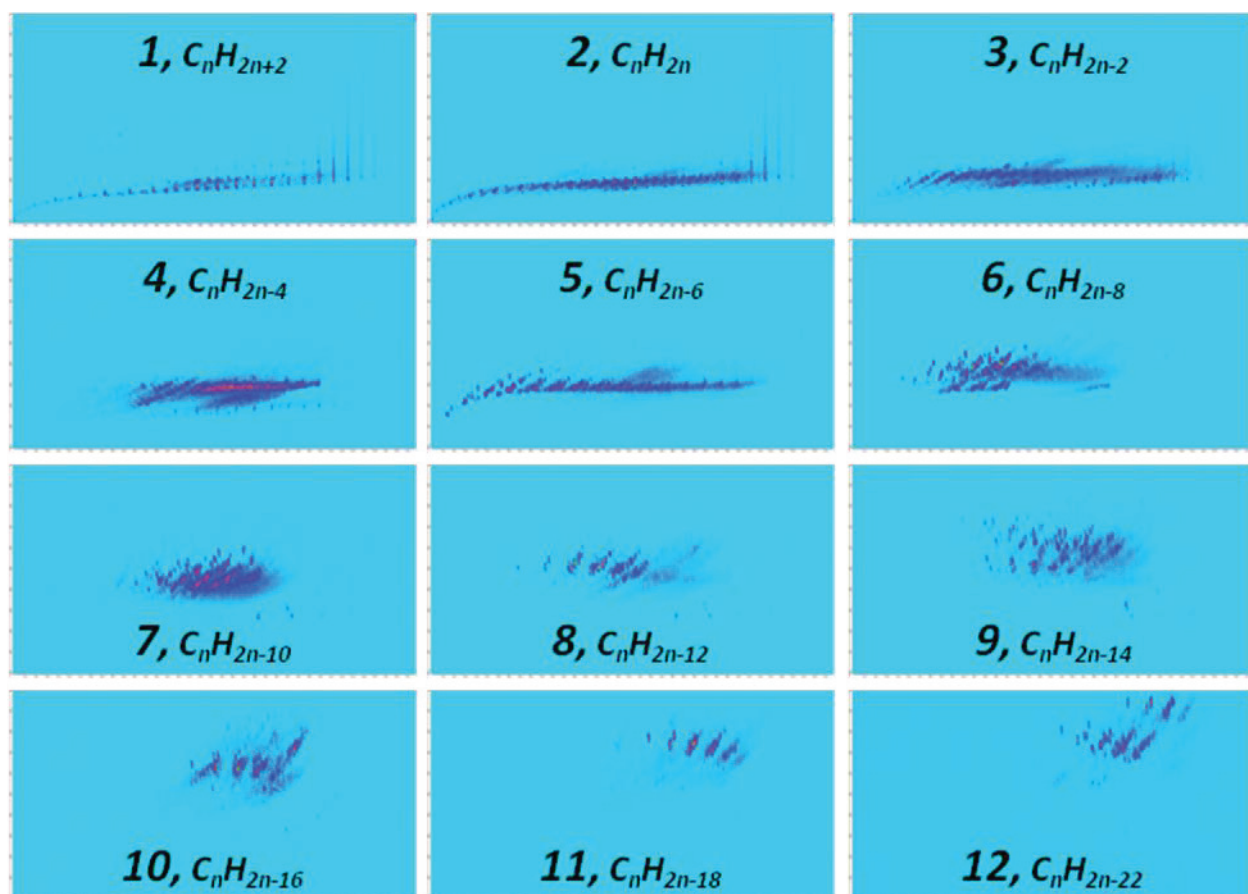
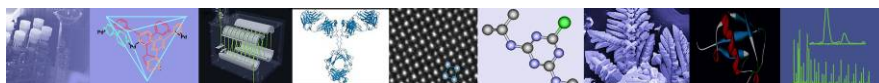


Figure 3. 2-dimensional SIC chromatograms using Kendrick m/z (in Figure 2) $\pm 0.015u$



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-5SiMS, 30 m x 0.25 mm, 0.25 μ m	
2nd column	Rxi-17SiMS, 2 m x 0.15 mm, 0.15 μ m	
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) \rightarrow 3 C/min \rightarrow 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 ($C_5H_{15}O_3Si_3^+$)	m/z 226.2661 ($C_{16}H_{34}^+$)

Table 1. Measurement Conditions

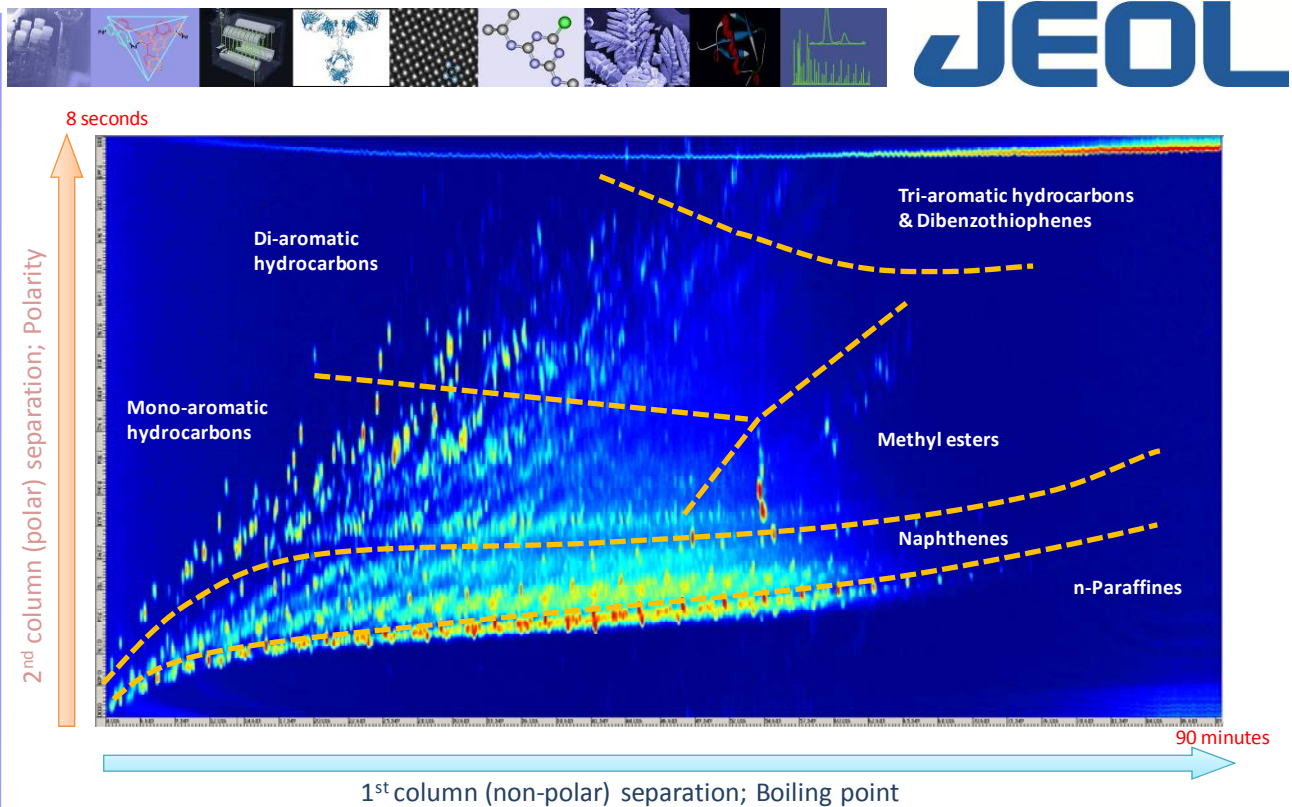


Figure 1. GCxGC/EI TIC for diesel fuel

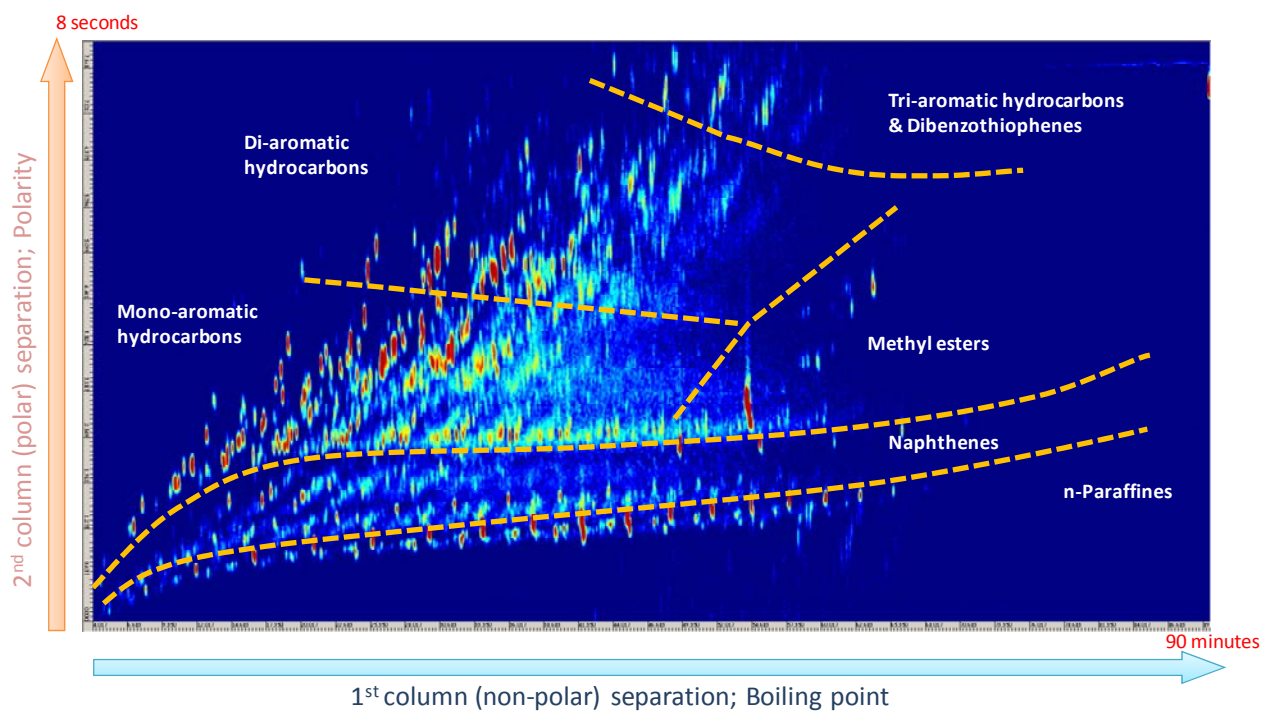
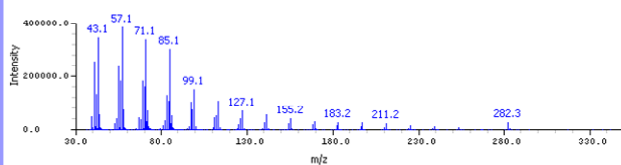


Figure 2. GCxGC/FI TIC for diesel fuel

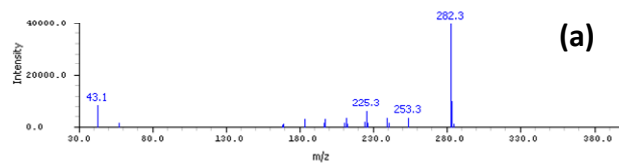


Electron Ionization

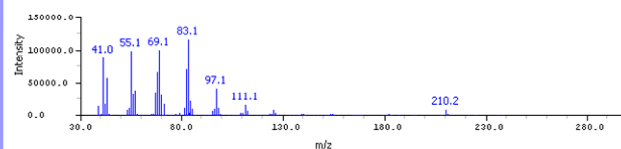
Field Ionization



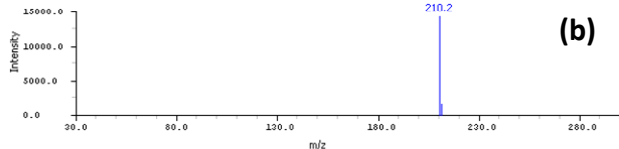
Formula	Mass	Difference (mmu)
C ₂₀ H ₄₂ +	282.328103	0.599596



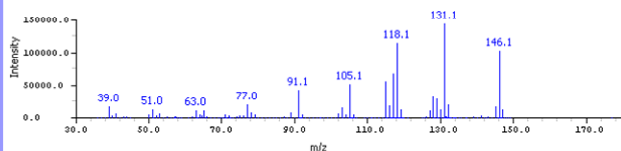
Formula	Mass	Difference (mmu)
C ₂₀ H ₄₂ +	282.328103	1.674657



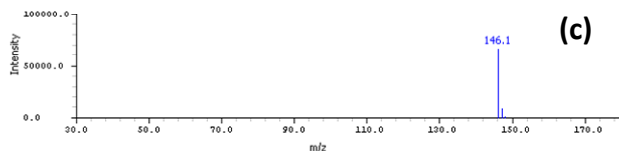
Formula	Mass	Difference (mmu)
C ₁₅ H ₃₀ +	210.234202	-1.675281



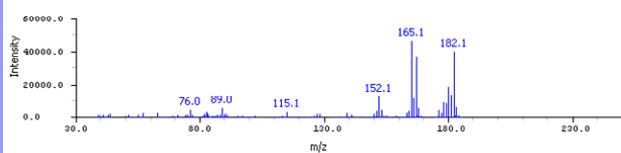
Formula	Mass	Difference (mmu)
C ₁₅ H ₃₀ +	210.234202	0.436990



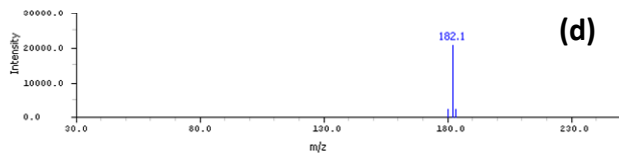
Formula	Mass	Difference (mmu)
C ₁₁ H ₁₄ +	146.109002	-0.538154



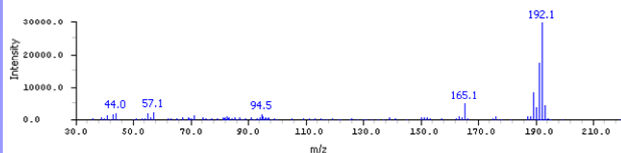
Formula	Mass	Difference (mmu)
C ₁₁ H ₁₄ +	146.109002	-1.267696



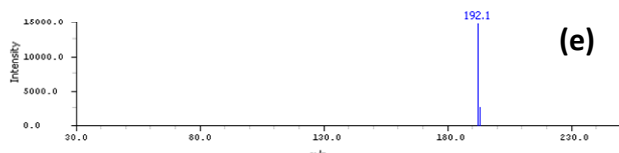
Formula	Mass	Difference (mmu)
C ₁₄ H ₁₄ +	182.109002	-1.570539



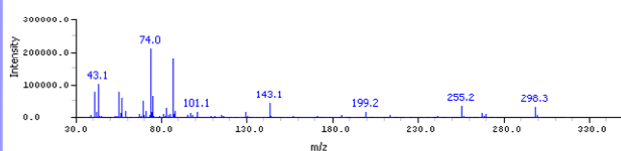
Formula	Mass	Difference (mmu)
C ₁₄ H ₁₄ +	182.109002	0.111317



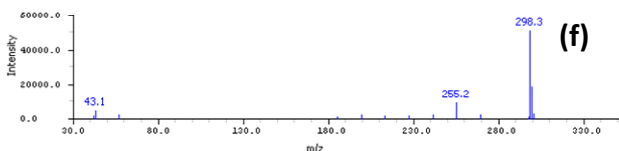
Formula	Mass	Difference (mmu)
C ₁₅ H ₁₂ +	192.093352	-0.541810



Formula	Mass	Difference (mmu)
C ₁₅ H ₁₂ +	192.093352	0.288982

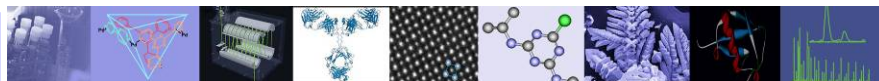


Formula	Mass	Difference (mmu)
C ₁₉ H ₃₈ O ₂ +	298.286632	-1.465507



Formula	Mass	Difference (mmu)
C ₁₉ H ₃₈ O ₂ +	298.286632	1.709336

Figure 3. EI and FI mass spectra for (a) n-parafin (C₂₀H₄₂), (b) naphthenes (C₁₅H₃₀), (c) monoaromatic hydrocarbon (C₁₁H₁₄), (d) diaromatic hydrocarbon (C₁₄H₁₄), (e) triaromatic hydrocarbon (C₁₅H₁₂), (f) ethyl esters (C₁₉H₃₈O₂).



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.

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.

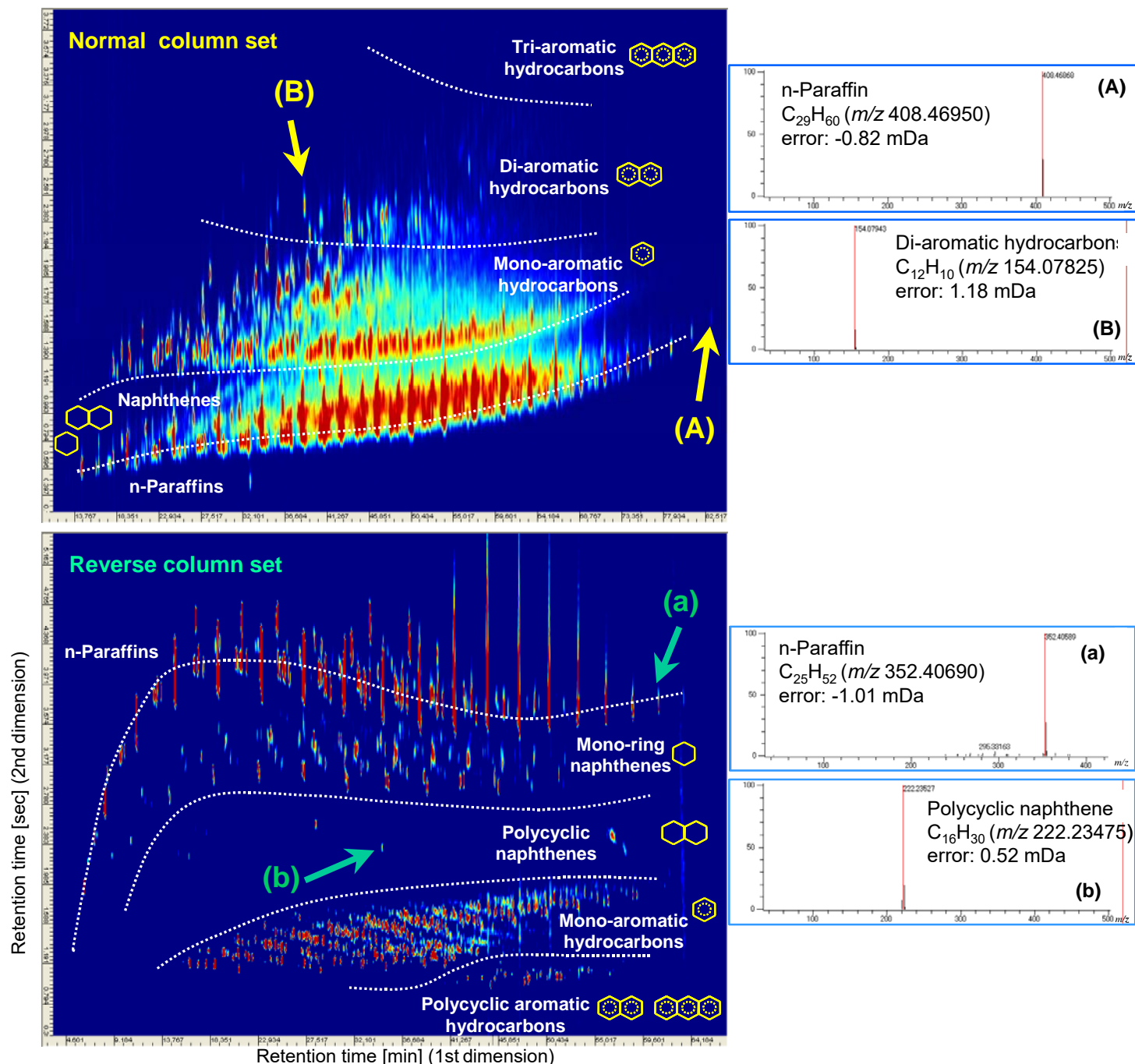


Fig.1 2-dimentional TIC chromatograms and FI mass spectra

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.

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.

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 (C₁₃H₂₈), 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.

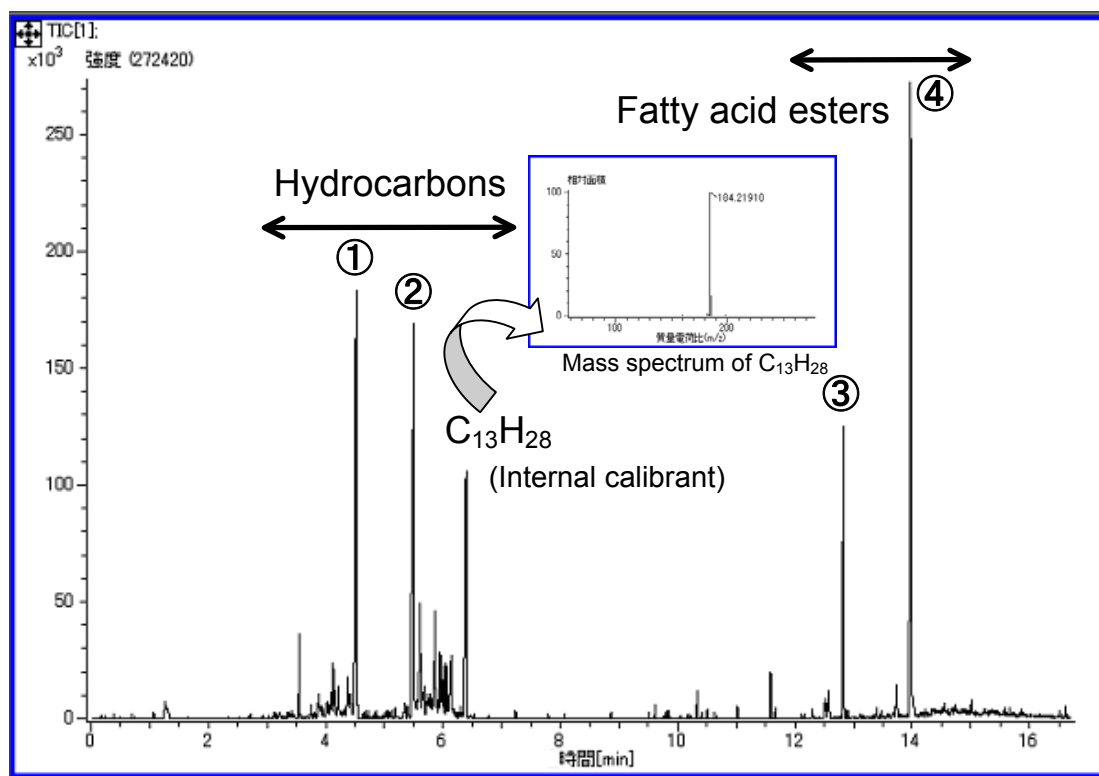


Fig.1 TICC of lube oil

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.

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 ZOEX KT2004
Column:	1 st : HP-1ms (30m × 0.25mm I.D., 0.25μm) 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 1st column on differences in boiling point and the Y axis corresponds with the separation by the 2nd 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.

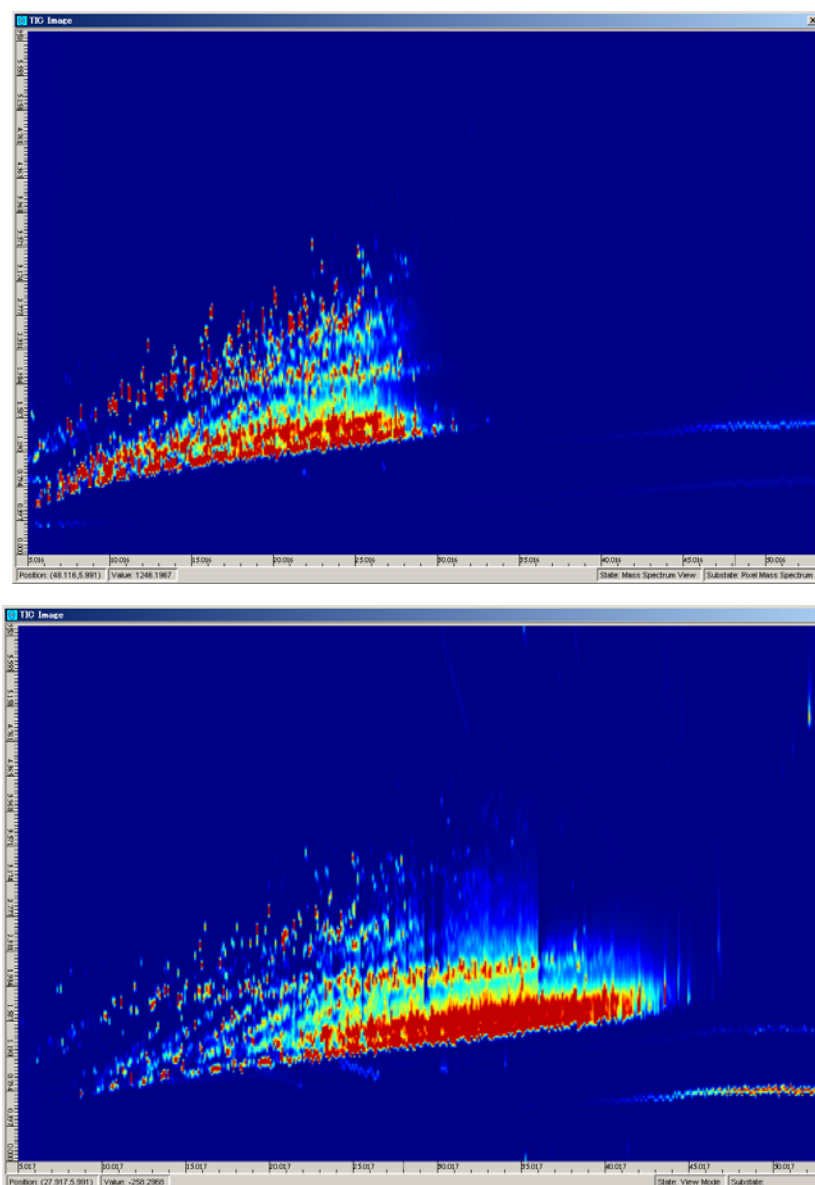


Fig.1 TICC by GC x GC (Top: kerosene, Bottom: diesel oil)

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.

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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 conditionsFor GC×GC

System:	Agilent 6890GC ZOEX KT2004
Column:	1 st : HP-1ms (30m × 0.25mm I.D., 0.25μm) 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 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.

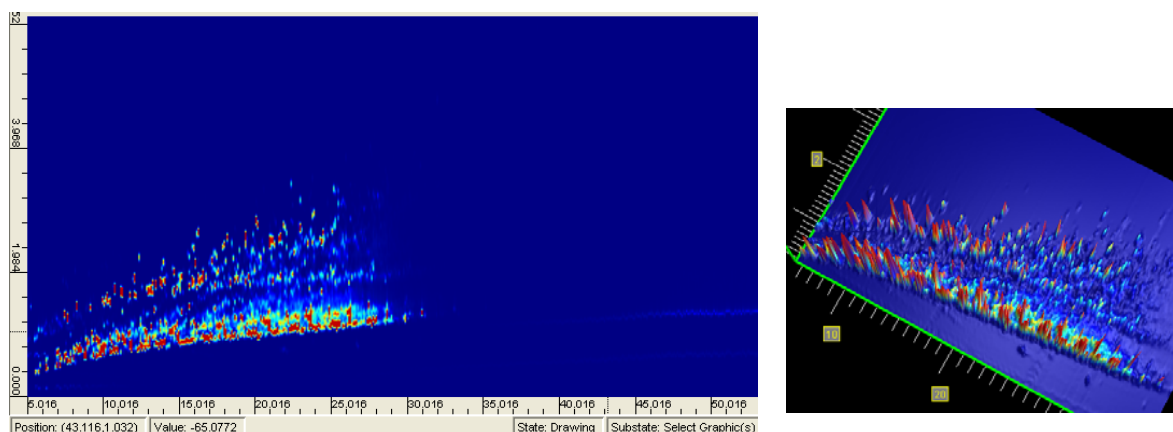


Fig.1 TICC of kerosene by GC x GC (Left: 2D image, Right: 3D image)

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).

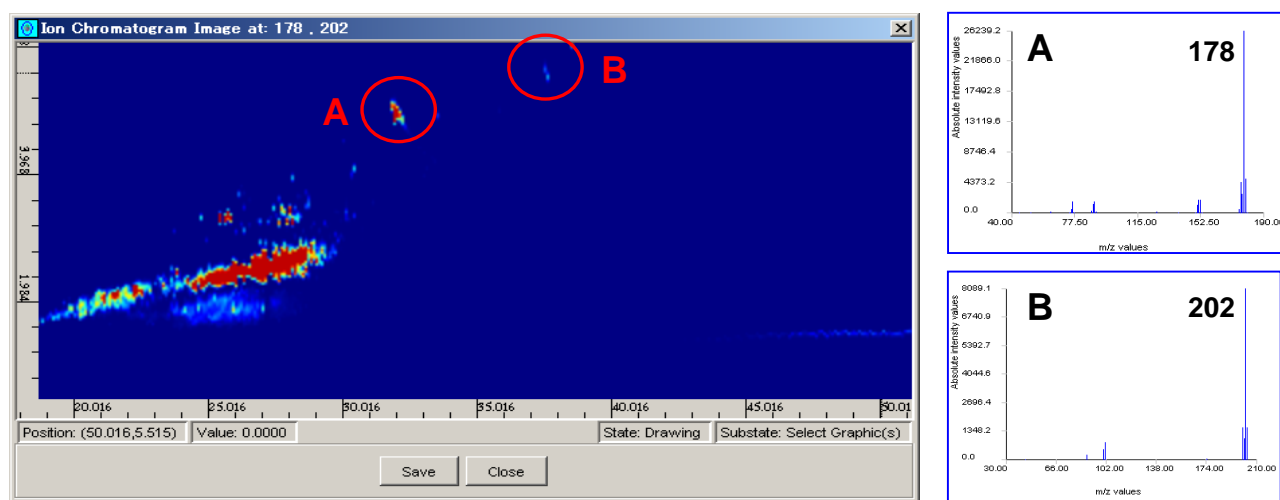


Fig.2 : GC x GC mass chromatogram of m/z 178 and 202 for polycyclic aromatic hydrocarbons and mass spectra of tri- and tetra-cyclic aromatic hydrocarbons.

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.

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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 ZOEX KT2004
Column:	1 st : HP-1ms (30m × 0.25mm I.D., 0.25μm) 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>

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

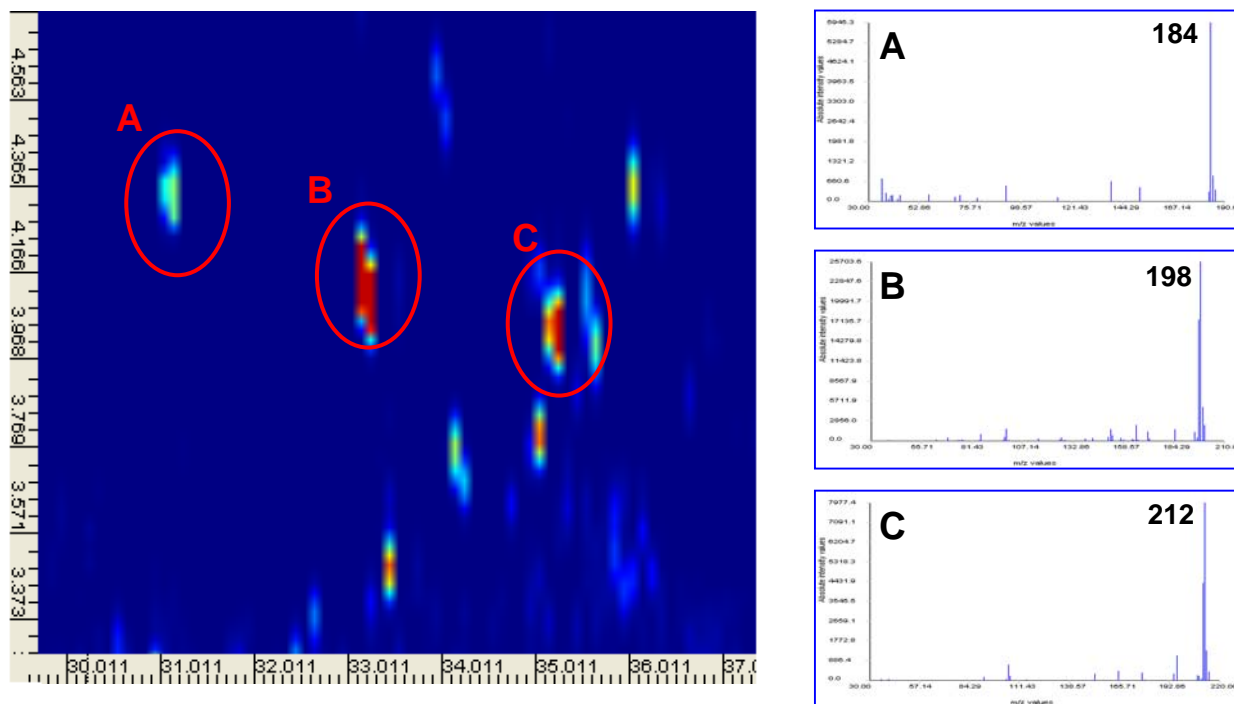


Fig.1 GC x GC mass chromatogram of m/z 184, 198 and 212 (Left) and mass spectra for compound A, B and C (Right)

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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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 shortened 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.

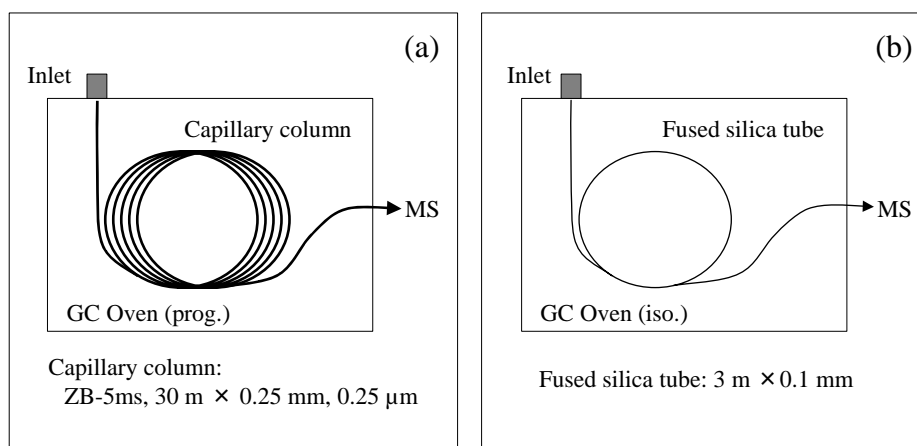


Fig.1 Schematic diagrams of sample introduction system by using GC,
(a) capillary GC/FI. (b) blank tube inlet/FI.

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.
- Larger amount of sample can be injected than in the GC/MS method; no GC column overloading.

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 ($n\text{-C}_{18}\text{H}_{38}$ (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).

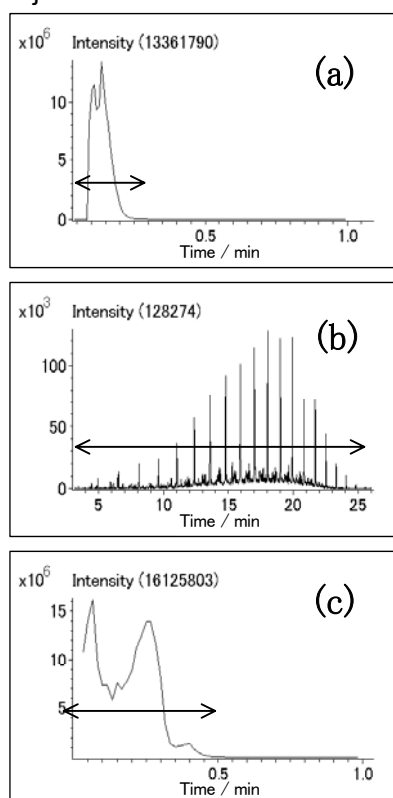


Fig.2 TICs of diesel oil
(a) blank tube inlet/FI,
(b) capillary GC/FI, (c) FD

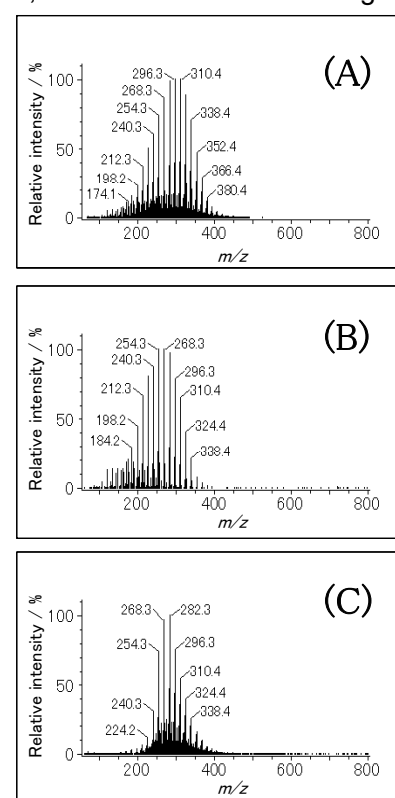


Fig.3 Mass spectra of diesel oil
(A) blank tube inlet/FI,
(B) capillary GC/FI, (C) FD

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. / °C	280	280	—
Column	—	ZB-5ms, 30 m × 0.25 mm, 0.25 µm	—
Fused silica tube	3 m × 0.1mm	—	—
Oven temp. / °C [hold time / min]	280 [1]	40[1]-300[1]	—
Oven temp. ramp rate/ °C 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. / °C	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.

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.

References

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

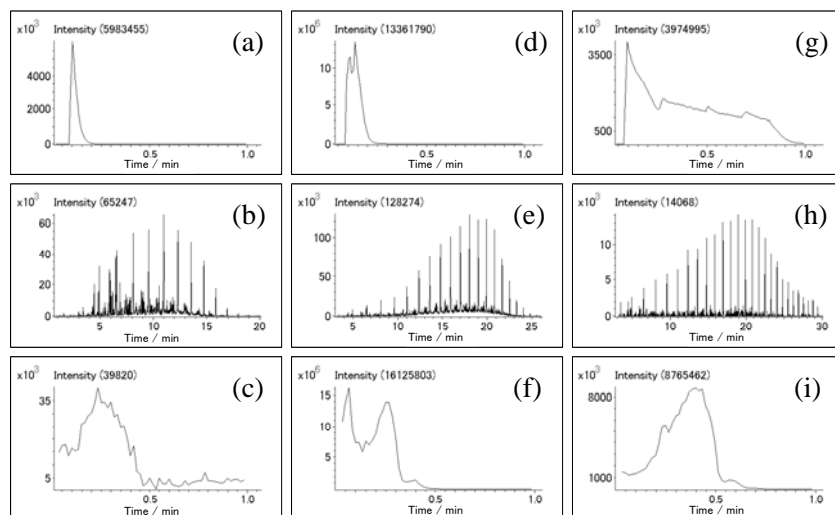


Fig. 1 Comparison of TICs of kerosene, diesel oil and crude oil by using differ methods; (a) kerosene by blank tube inlet/FI. (b) kerosene by capillary GC/FI. (c) kerosene by FD. (d) diesel oil by blank tube inlet/FI. (e) diesel oil by capillary GC/FI. (f) diesel oil by FD. (g) crude oil by blank tube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

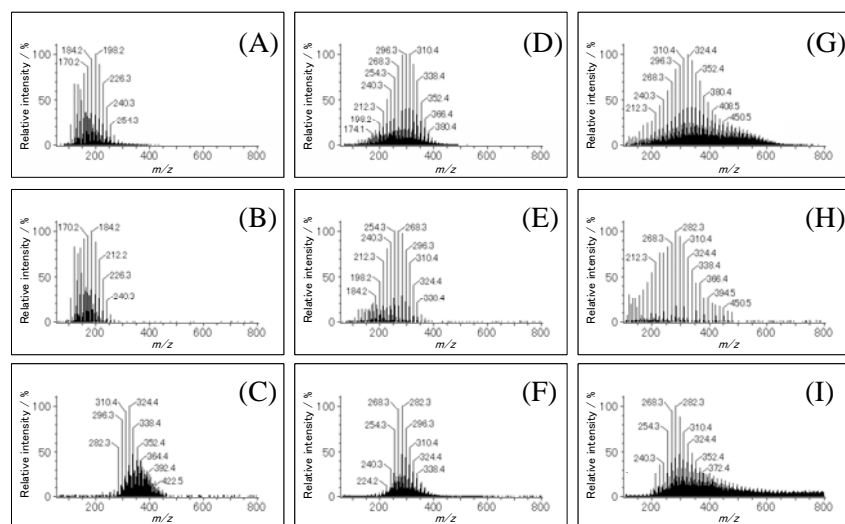


Fig. 2 Comparison of averaged mass spectra of kerosene, diesel oil and crude oil by using differ methods; (A) kerosene by blank tube inlet/FI. (B) kerosene by capillary GC/FI. (C) kerosene by FD. (D) diesel oil by blank tube inlet/FI. (E) diesel oil by capillary GC/FI. (F) diesel oil by FD. (G) crude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

Table 2 Summary of type analysis results.

	Blank tube inlet/FI	Capillary GC/FI	FD
Kerosene			
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

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.

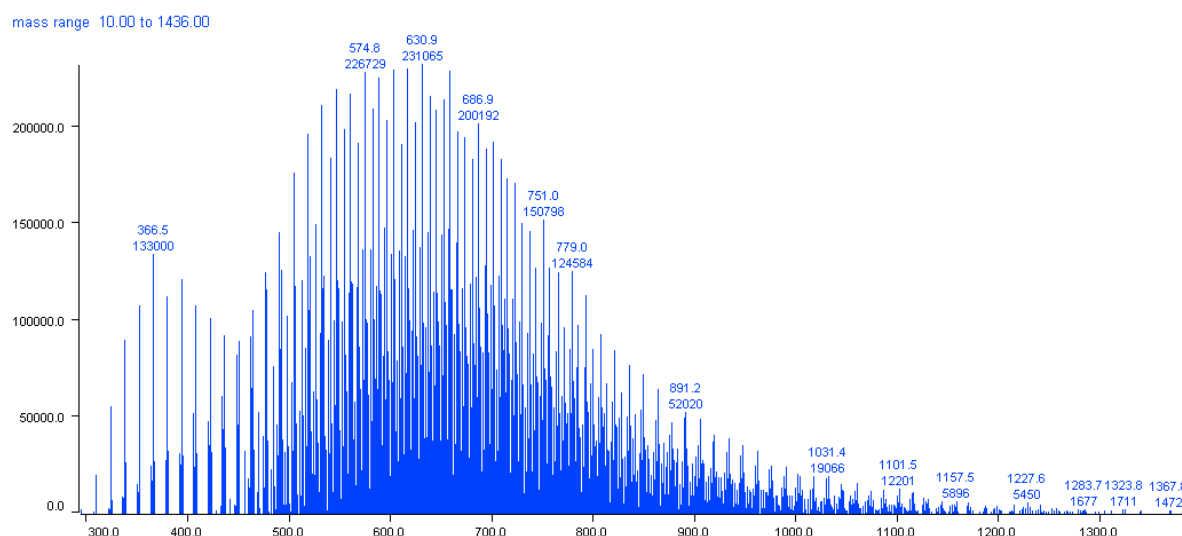


Figure 1. FD mass spectrum of micro crystalline wax

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 _n H _{2n+2}	571.1	617.3	665.3	1.1	33.6	36.9	40.3	17.3	11.1
S2	C _n H _{2n}	529.7	655.0	680.8	1.0	37.9	39.7	41.6	24.2	15.5
S3	C _n H _{2n-2}	670.5	692.3	715.6	1.0	41.0	42.5	44.2	13.1	8.4
S4	C _n H _{2n-4}	715.6	739.0	764.7	1.0	44.3	46.0	47.8	8.4	5.4
S5	C _n H _{2n-6}	688.3	717.9	751.1	1.0	42.5	44.7	47.0	22.5	14.5
S6	C _n H _{2n-8}	710.0	739.6	772.8	1.0	44.2	46.3	48.7	14.5	9.3

Mn: Average molecular weight

DPn: Mn/R

Mw: Weight-average molecular weight

DPw: Mw/R

Mz: Z-average molecular weight

DPz: Mz/R

PD: Polydispersity

(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.

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

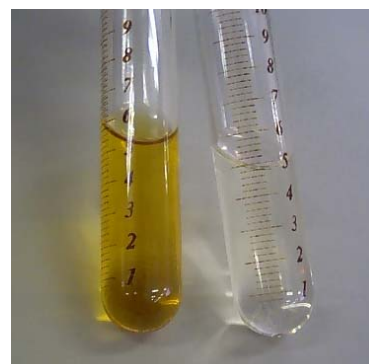


Fig. 1 RP oil (left: used, right: new)

Results and discussion

The acquired FD mass spectra are shown below.

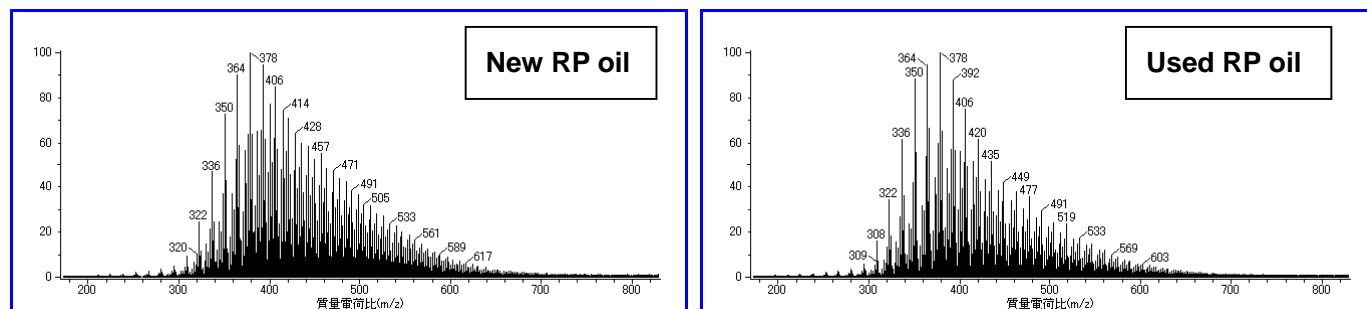


Fig. 2 Acquired FD mass spectra

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	DP _n	DP _w	DP _z	Percent Series
Total/Average	453.82	483.97	531.27	1.07	25.57	27.73	31.10	100.00
C _n H _{2n+2}	447.44	479.98	533.06	1.07	24.78	27.10	30.89	15.47
C _n H _{2n}	435.82	462.47	504.05	1.06	24.10	26.00	28.96	23.19
C _n H _{2n-2}	451.28	482.02	530.39	1.07	25.34	27.54	30.99	16.70
C _n H _{2n-4}	464.22	498.14	551.19	1.07	26.41	28.83	32.61	12.69
C _n H _{2n-6}	459.36	486.90	529.76	1.06	26.21	28.17	31.23	18.90
C _n H _{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	DP _n	DP _w	DP _z	Percent Series
Total/Average	446.82	483.77	546.99	1.08	25.05	27.68	32.20	100.00
C _n H _{2n+2}	434.74	473.54	544.08	1.09	23.88	26.64	31.68	16.76
C _n H _{2n}	425.93	455.81	507.39	1.07	23.39	25.52	29.20	26.43
C _n H _{2n-2}	444.90	481.25	543.39	1.08	24.89	27.48	31.91	17.57
C _n H _{2n-4}	461.91	506.41	581.41	1.10	26.24	29.42	34.77	12.03
C _n H _{2n-6}	458.94	494.97	555.72	1.08	26.18	28.75	33.08	16.65
C _n H _{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

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.

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

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

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
 30 m x 0.25 mm I.D., 0.25 μ m
 Oven: 50°C → 15°C/min → 280°C (5 min)
 Injection port: 280 °C, Split (1:200)
 Injection volume: 1.0 μ l
 Carrier 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.)

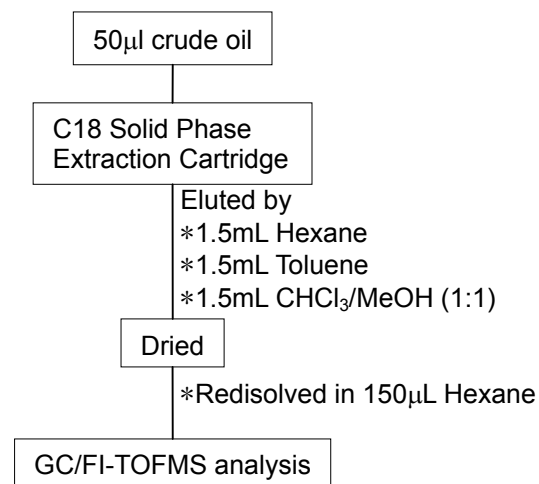
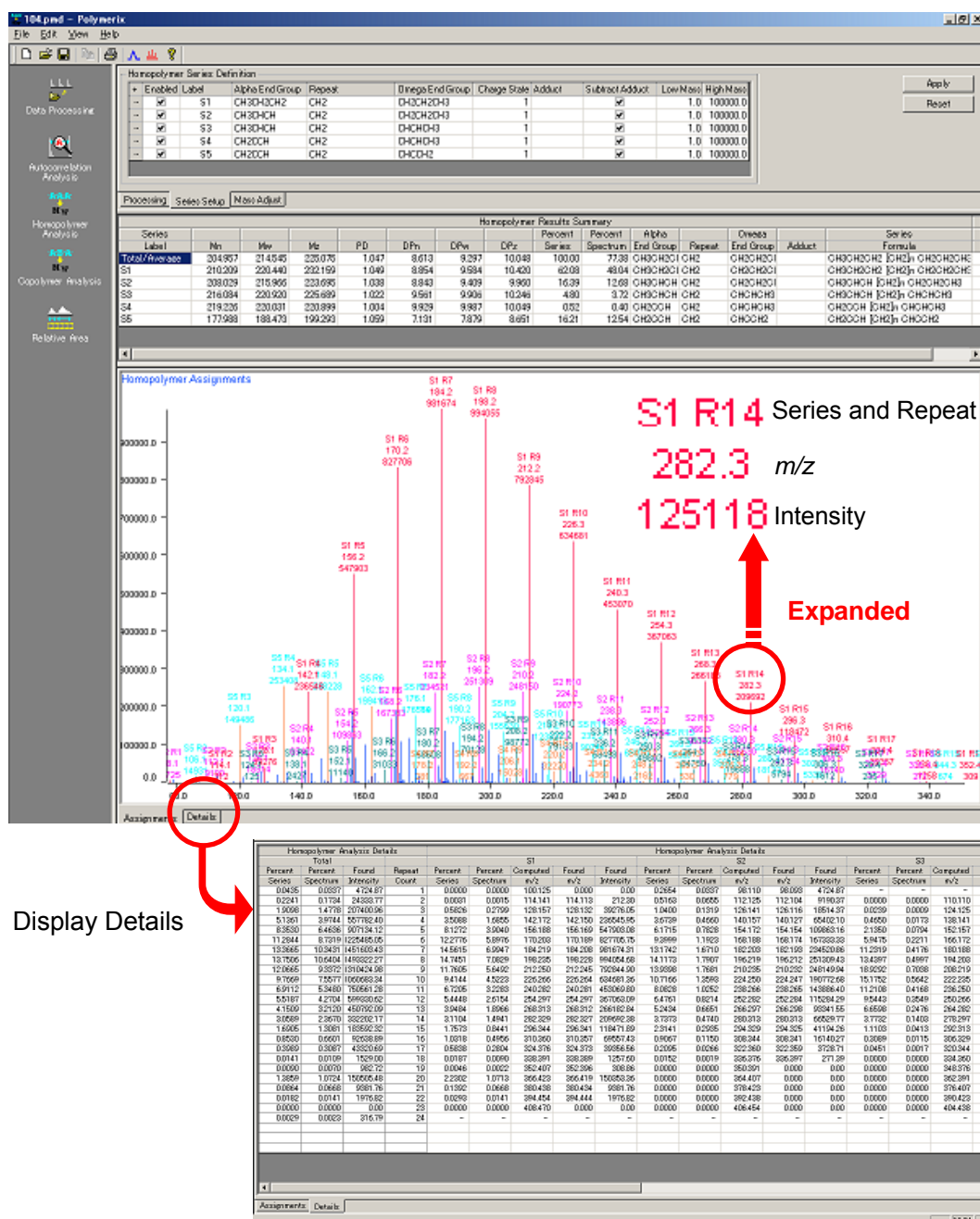


Fig. 1 Sample preparation flow

Results and Discussion

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



- 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.

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 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)

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 Column: DB-5ms
 30 m x 0.25 mm I.D., 0.25 μ m
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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.)

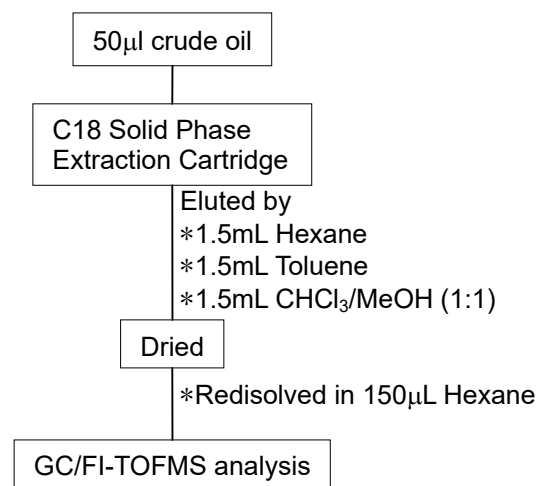


Fig. 1 Sample preparation flow

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.

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

Related products: Mass spectrometer (MS)

Introduction

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

Experiment

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

Table 1. Measurement conditions

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

Result

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

TIC chromatograms

Mass spectra

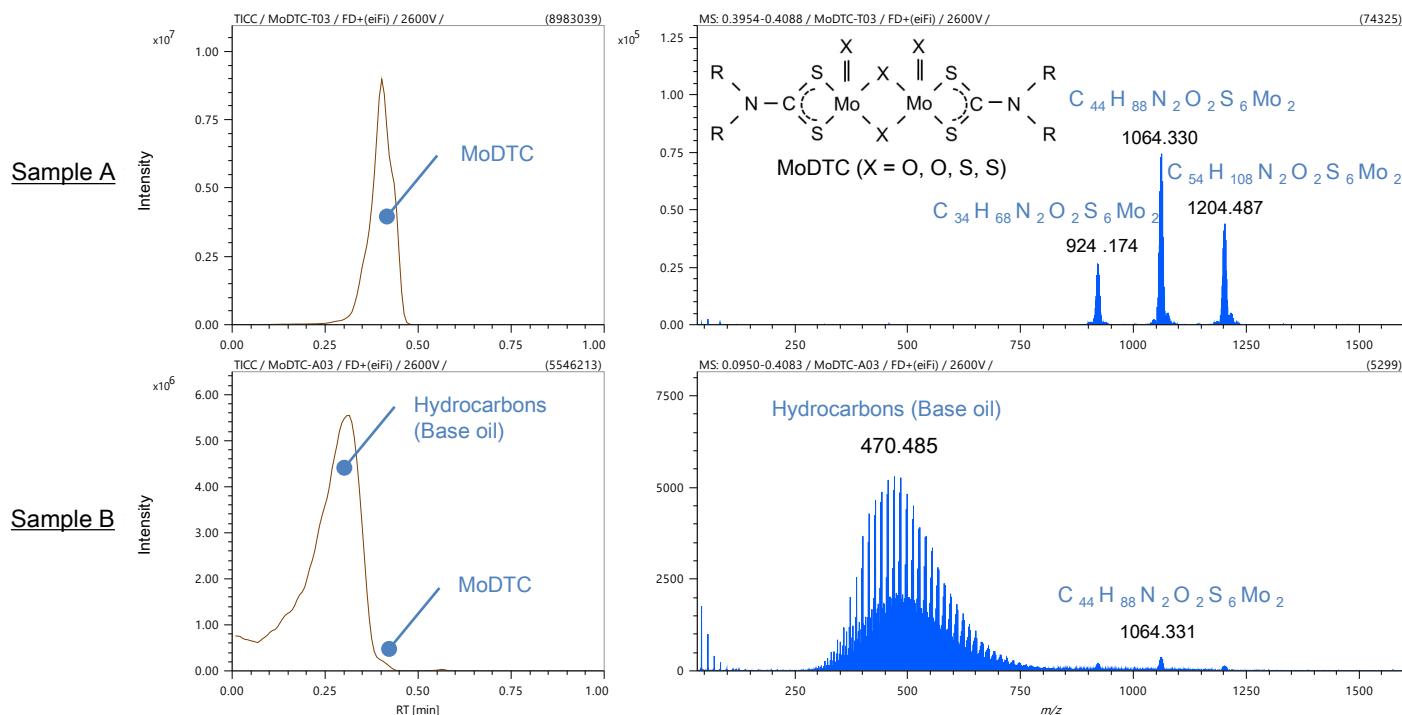


Figure 1. TIC chromatograms and mass spectra by FD method

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

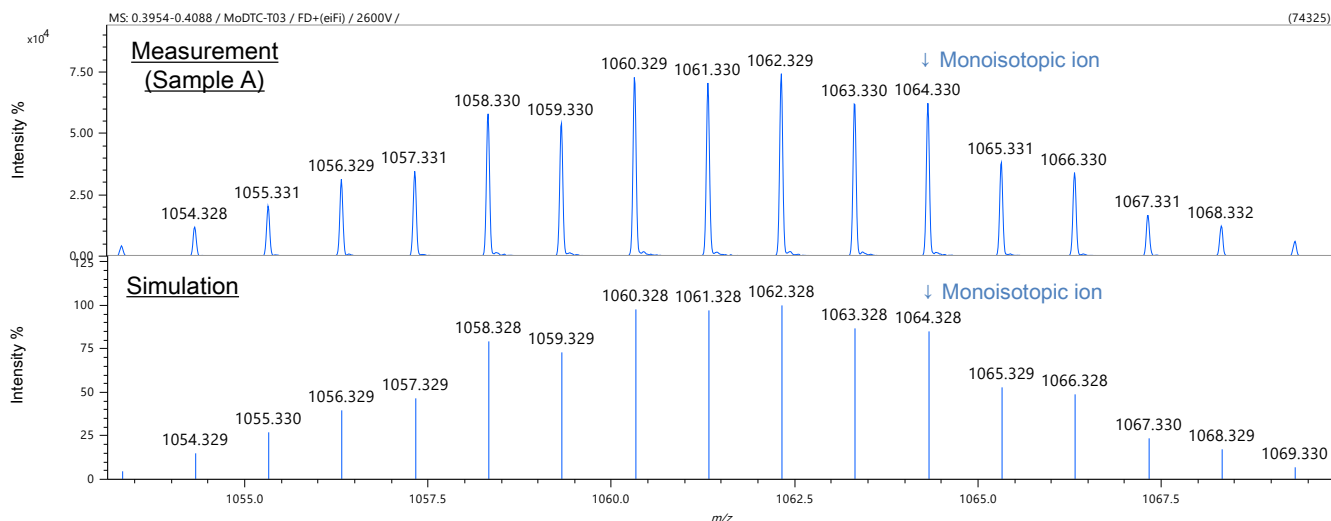


Figure 2. Mass spectra of MoDTC ($C_{44}H_{88}N_2O_2S_6Mo_2$)

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

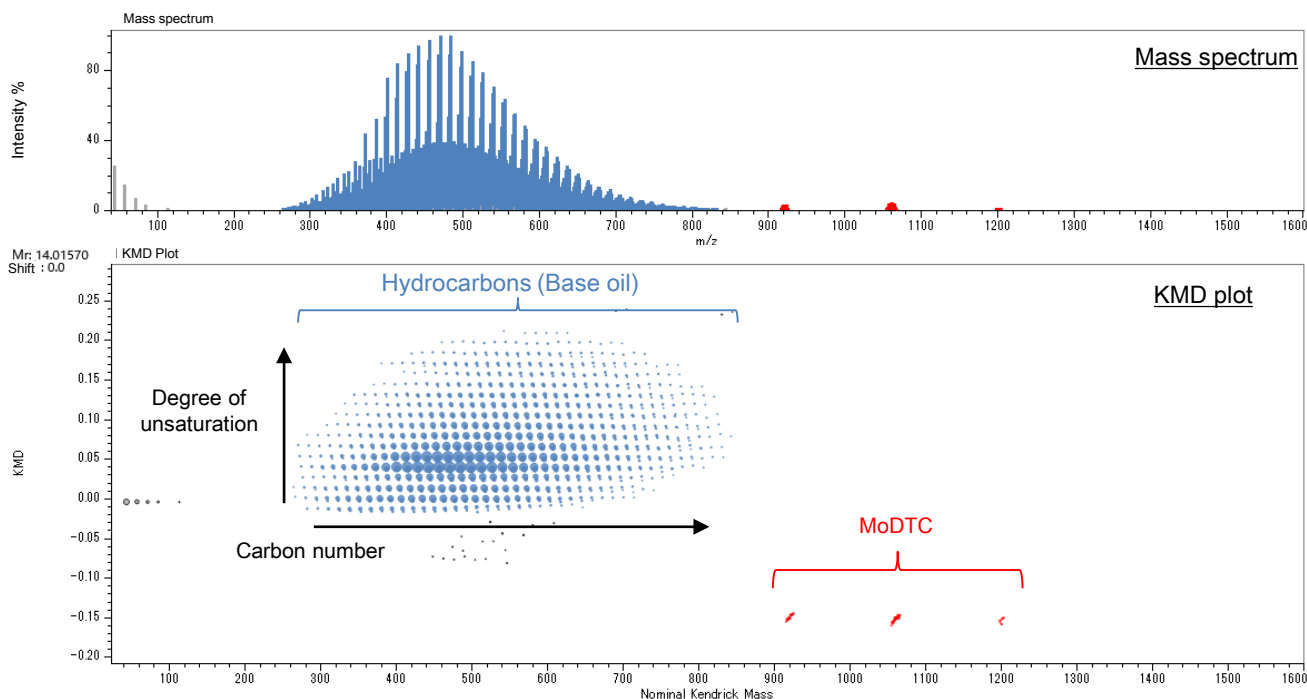


Figure 3. Mass Spectrum and KMD plot of Sample B

Summary

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

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