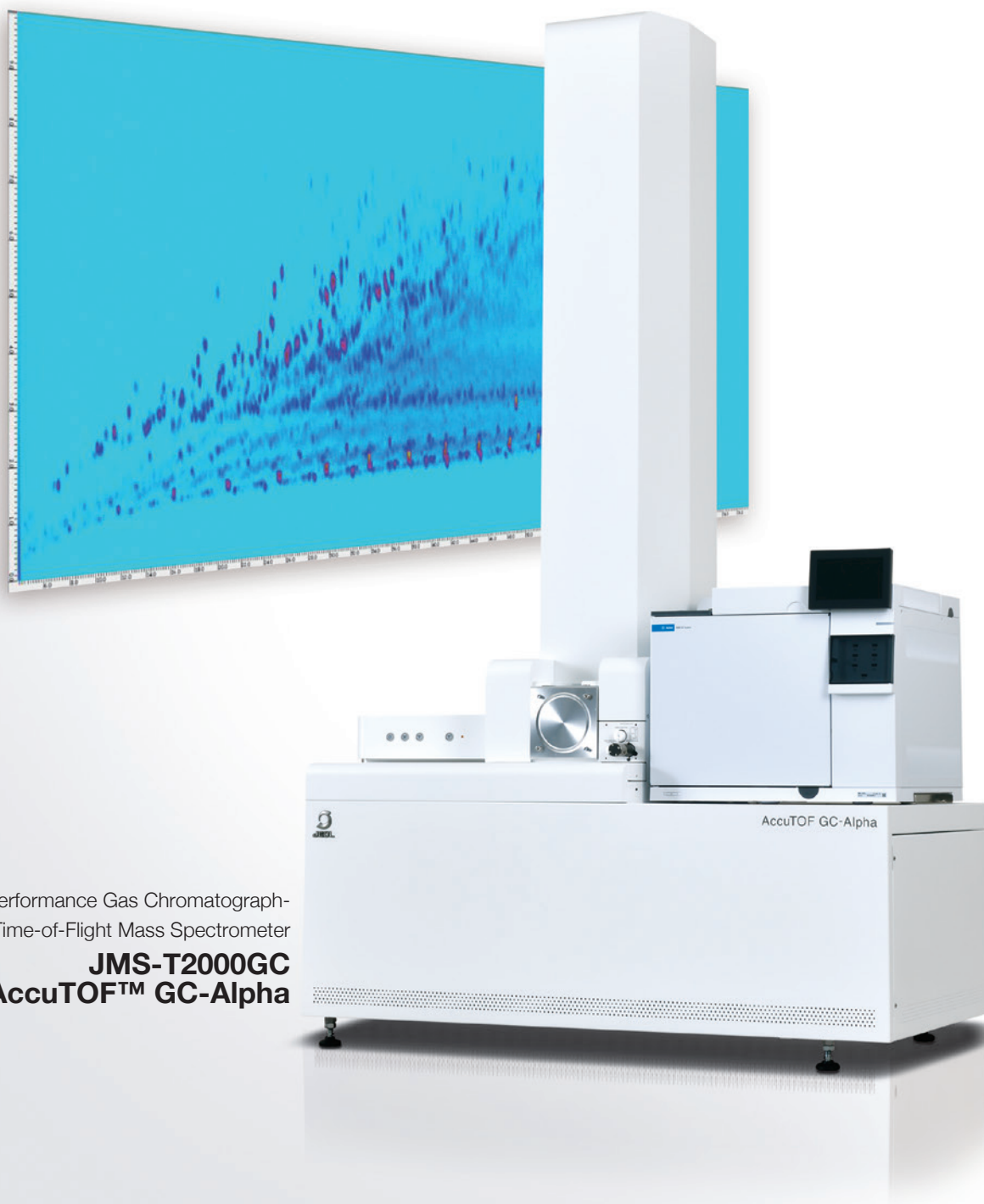Solutions for Innovation

Comprehensive 2D GC coupled with JEOL GC-HRTOFMS:
GCxGC Applications

High Performance Gas Chromatograph-
Time-of-Flight Mass Spectrometer
JMS-T2000GC
AccuTOF™ GC-Alpha

JEOL Ltd.

Diesel Fuel Analysis by GCxGC/EI
Hydrocarbon Classification

Comprehensive two-dimensional gas chromatography (GCxGC) consists of two different types of columns that are connected via a thermal modulator within the same GC oven. The GCxGC system requires a fast-acquisition detection system to measure the very narrow width peaks observed in the 2D GC chromatograms. The JEOL GC-TOFMS system called the AccuTOF™ GC-Alpha has a high-speed data acquisition capability with a spectral acquisition rate of up to 50 Hz (0.02sec/spectrum).

Therefore, the AccuTOF™ GC-Alpha system can be successfully used as a GCxGC detector.
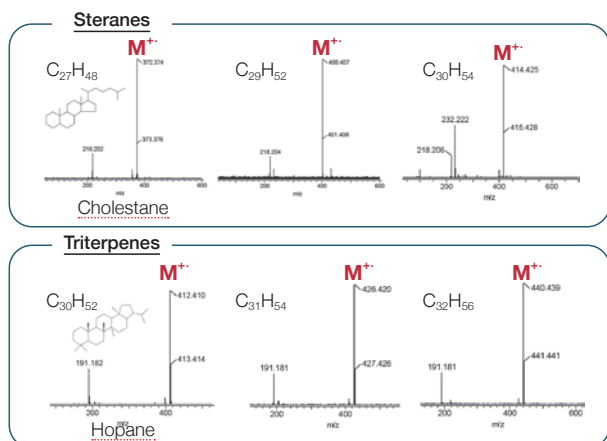
The TIC chromatograms for crude oil and 2 diesel fuels are shown on the left. Each sample shows a number of different compounds and different hydrocarbon distributions. As this data shows, GCxGC is a powerful separation technique for analyzing complex samples like oils and fuels.
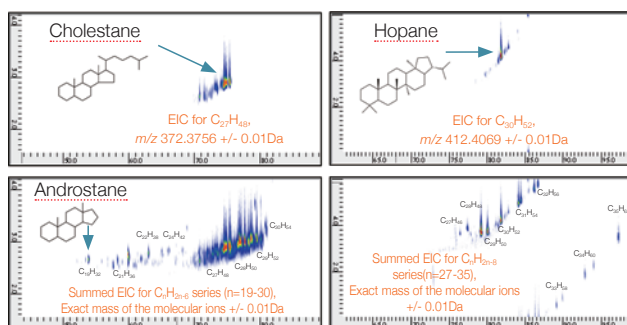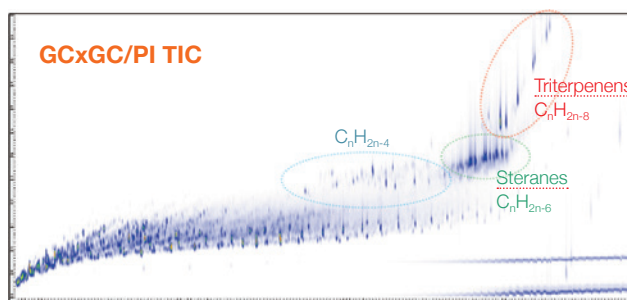

Crude oil

Diesel fuel

Bio diesel (Canola)
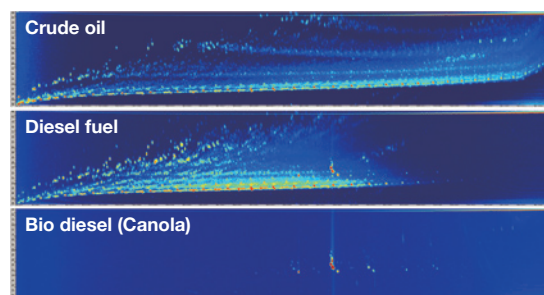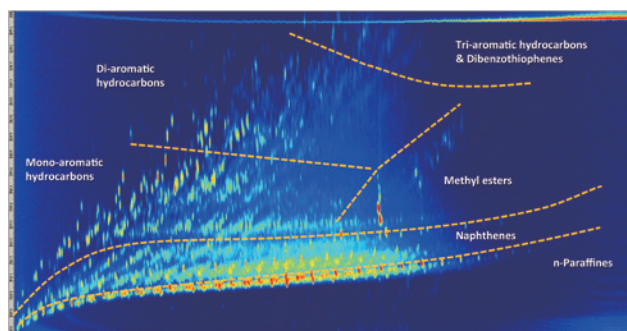
Biomarker Analysis by GCxGC/PI
Target Analysis using 2D EICC

Both GCxGC/PI and GCxGC/EI measurements for crude oil samples were done using the EI/PI combination ion source.

Each GCxGC measurement showed a number of biomarkers that included Steranes and Triterpenes. The PI mass spectra for these biomarkers showed strong molecular ion signals which were used to make high-selectivity (narrow m/z window) 2D extracted ion chromatograms (EIC) for quick identification of these compounds. Afterwards, these results were further confirmed by using NIST library database searches of the GCxGC/EI data.

GCxGC/PI TIC

C_nH_{2n-4}

Triterpenens C_nH_{2n-8}

Steranes C_nH_{2n-6}

Steranes

$C_{27}H_{48}$ M$^{+\cdot}$ 372.374

$C_{29}H_{52}$ M$^{+\cdot}$ 400.407

$C_{30}H_{54}$ M$^{+\cdot}$ 414.425

Cholestane

Triterpenes

$C_{30}H_{52}$ M$^{+\cdot}$ 412.410

$C_{31}H_{54}$ M$^{+\cdot}$ 426.420

$C_{32}H_{56}$ M$^{+\cdot}$ 440.439

Hopane

PI mass spectra

Cholestane

EIC for $C_{27}H_{48}$, m/z 372.3756 +/- 0.01Da

Hopane

EIC for $C_{30}H_{52}$, m/z 412.4069 +/- 0.01Da

Androstane

Summed EIC for C_nH_{2n-6} series (n=19-30), Exact mass of the molecular ions +/- 0.01Da

Summed EIC for C_nH_{2n-8} series(n=27-35), Exact mass of the molecular ions +/- 0.01Da

2D-PI chromatograms: Upper: TIC, Lower: EIC

# Type Analysis by GCxGC/FI
Hydrocarbon Type Analysis

Comprehensive GCxGC in combination with high-resolution mass spectrometry (HRMS) is a powerful tool for the analysis of complex mixtures. Field ionization (FI) is a soft ionization technique that is well suited for hydrocarbon analysis because it generates molecular ions for most compounds with minimal fragmentation. This data easily provides individual hydrocarbon information (formula, carbon number, intensity) by using the molecular ions that are generated by FI. As a result, it is not necessary to use complex EI fragmentation information for petroleum type analysis measurements. The key advantages of GCxGC/FIHRMS method for detailed type analysis of petroleum samples are:

1. FI is ideal for generating molecular ions for hydrocarbon compounds.
2. High selectivity (with narrow *m/z* windows) allows high-precision 2D extracted ion chromatograms.
3. GCxGC provides exceptional separation capacity with 2D structure-retention relationships.
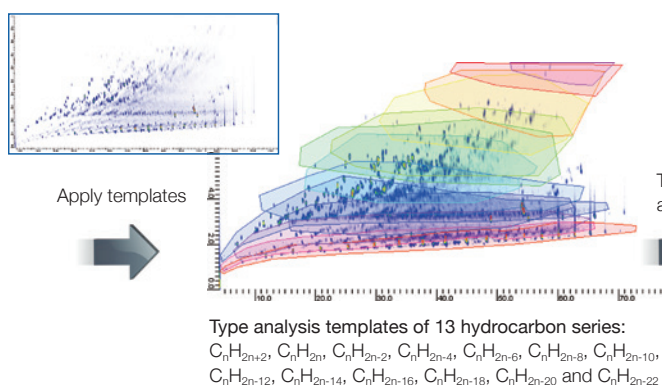
### FI is ideal for hydrocarbon compounds

FI can generate molecular ions with minimal fragmentation.
This makes it easy to identify the parent ion for each hydrocarbon.

n-$C_{16}H_{34}$

n-$C_{30}H_{62}$

FI mass spectra of n-Alkanes
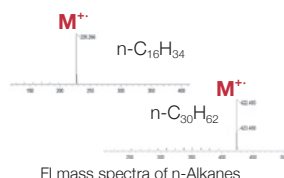
High selectivity extracted ion chromatograms (EIC)

High mass resolution can provide high selectivity (narrow *m/z* window) for the EIC.

The hydrocarbon peaks which have the same nominal mass but different exact mass can be separated completely.
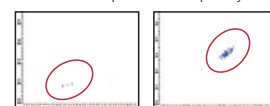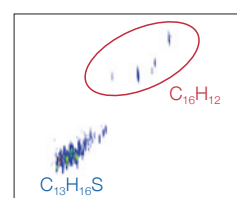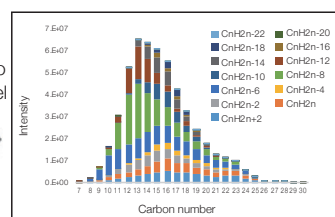

GCxGC/FI EIC of *m/z* 184.2192 ($C_{13}H_{28}$)

GCxGC/FI EIC of *m/z* 184.1253 ($C_{14}H_{16}$)

GCxGC provides exceptional separation

Although the AccuTOF™ GC-Alpha has excellent high mass resolution capabilities, some components are difficult to separate. For example, the separation between PAHs ($C_{16}H_{12}$) and Benzothiophenes ($C_{13}H_{16}S$) requires over 180,000 mass resolution. Despite the fact that the AccuTOF™ GC-Alpha does not have this high of a mass resolution, these groups can be clearly separated in time on the 2D EIC. As a result, we can ensure that only the actual components of interest are included in each polygon.

$C_{16}H_{12}$

$C_{13}H_{16}S$

GCxGC/FI EIC of *m/z* 204.0939

Apply templates

Type analysis

Export to MS Excel

Type analysis templates of 13 hydrocarbon series:
C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}, C_nH_{2n-12}, C_nH_{2n-14}, C_nH_{2n-16}, C_nH_{2n-18}, C_nH_{2n-20} and C_nH_{2n-22}

Key Technology -Soft Ionization-

A wide variety of soft ionization techniques from JEOL!

Soft ionization provides higher intensity molecular ion information than Electron Ionization (EI), the typical hard ionization method.

The JEOL GC-TOFMS system offers a wide variety of ionization methods. You can choose the most suitable soft ionization technique for your applications!

- Chemical Ionization (CI): Available with both positive and negative ion modes
- Field Ionization (FI): Softest ionization method
- Photoionization (PI): Soft ionization and sensitive for aromatic compounds
- Low energy EI (LE-EI): Available by adjusting the electron energy to lower voltages using the standard EI source.

[FI/FD]

Field Ionization (FI) and Field Desorption (FD) are well suited for hydrocarbons analysis because they generate molecular ions for almost all compounds, including saturated hydrocarbons, with minimal fragmentation. The ionization process for these techniques is carried out in the high-potential electric field (~10^8 V/cm) between the FI/FD emitter (Anode) and the counter electrode (Cathode). A molecular ion is formed within the high-potential electric field when an electron from the analyte molecule tunnels rapidly towards the emitter. The resulting mass spectra are dominated by molecular ions, whether from the GC output (FI) or from the emitter surface (FD).

CI
Ionization by ion-molecule reaction (protonation etc.) Methane, Isobutane, and ammonia are used as reaction gases.

FI
Ionization by electron tunneling effect in a highelectric field (10^7–10^8 V/cm).
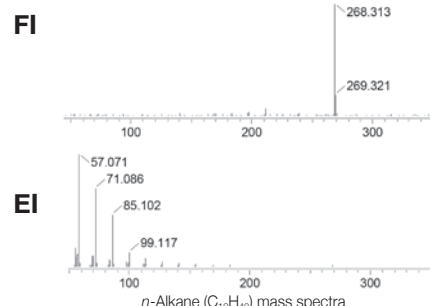
PI
Ionization by photon/molecule interaction that results in the emission of an electron from the molecule.

LE-EI
Ionization by electron impact same as traditional 70 eV EI. We can set electron ionization energy from 0 to 200 eV.


FI

$M^{+\cdot}$
268.313

269.321

EI

57.071
71.086
85.102
99.117

*n*-Alkane ($C_{19}H_{40}$) mass spectra

Synthetic Polymer Analysis by Pyrolysis GCxGC/EI and FI
Unknown Compounds Analysis in Nylon 66

The pyrolysis of Nylon 66 showed an unknown compound that did not show a reasonable match in the NIST database for the EI mass spectrum. The FI mass spectrum showed a molecular ion that was not present in the EI mass spectrum. Using the molecular ion accurate mass, an elemental composition was calculated. Afterwards, a chemical structure was suggested using the fragment ion information in the EI mass spectrum.
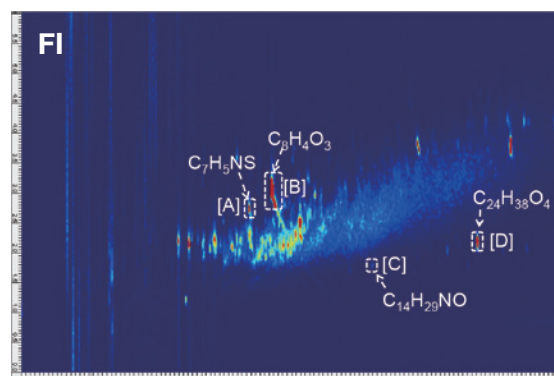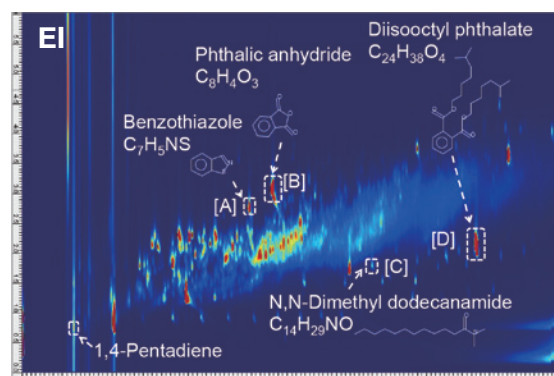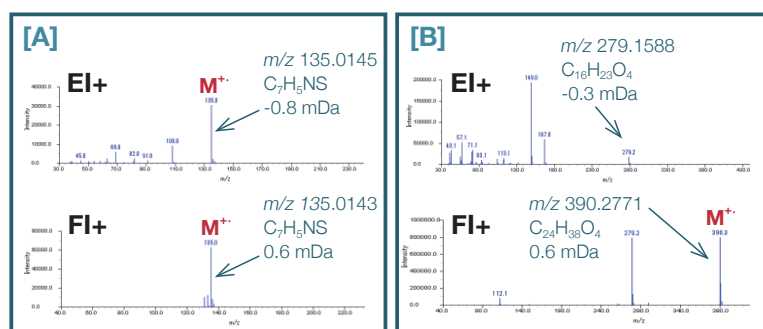

EI+

No molecule ion

2D TIC

2D-EI TIC chromatogram

FI+

m/z 210.1729
$C_{12}H_{22}N_2O$
Error: -0.4 mDa
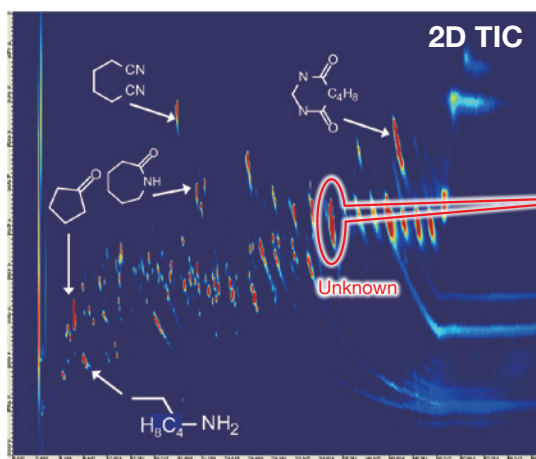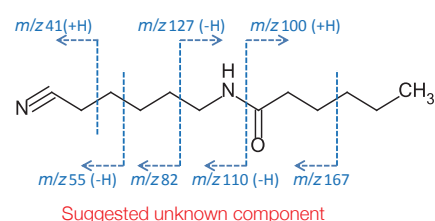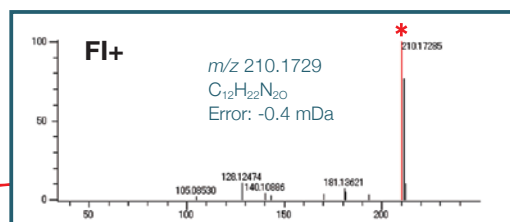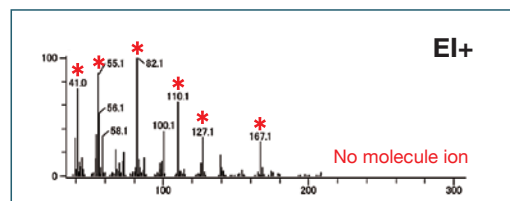
Suggested unknown component

Additives Analysis by Pyrolysis GCxGC/EI and FI
Targeted Additives Analysis in Nitrile Butadiene Rubber

[A]

EI+ M$^{+\cdot}$ m/z 135.0145 C_7H_5NS -0.8 mDa

FI+ M$^{+\cdot}$ m/z 135.0143 C_7H_5NS 0.6 mDa

[B]

EI+ m/z 279.1588 $C_{16}H_{23}O_4$ -0.3 mDa

FI+ M$^{+\cdot}$ m/z 390.2771 $C_{24}H_{38}O_4$ 0.6 mDa

EI

Diisooctyl phthalate $C_{24}H_{38}O_4$
Phthalic anhydride $C_8H_4O_3$
Benzothiazole C_7H_5NS
[A] [B] [D] [C]
N,N-Dimethyl dodecanamide $C_{14}H_{29}NO$
1,4-Pentadiene

FI

$C_8H_4O_3$
C_7H_5NS
[A] [B]
$C_{24}H_{38}O_4$
[D]
[C]
$C_{14}H_{29}NO$

2D-EI and FI TIC chromatograms

The characteristics of polymeric materials vary depending on the additives. Consequently, a variety of additives can be added into the raw polymer resin in order to achieve the required characteristics for the product. In this study, we identified the additives for a commercially available molded polymer, nitrile butadiene rubber using GCxGC/EI and GCxGC/FI.

The results showed that:
- Additives such as benzothiazole in the polymer material were easily separated chromatographically by using the GCxGC technique.
- The EI mass spectra produced good matches with the NIST library search which were further supported by the FI accurate mass elemental composition calculations for the molecular ions. These data, used together, were effective for qualitative identification of the additives.

Natural Polymer Analysis by Pyrolysis GCxGC/EI and PI
Powerful Separation of the Main Components in a Japanese Lacquer Film

A Japanese lacquer film called "Urushi" is a natural polymer that has been used as a paint and adhesive for living-wares and craft-wares for approximately 8,000 years. In this work, we measured "Urushi" samples using this unique Pyrolysis/GCxGC/TOFMS system in combination with our new combination EI/PI ion source.

"Urushi" picking (left) and traditional crafts coated with "Urushi" (right).
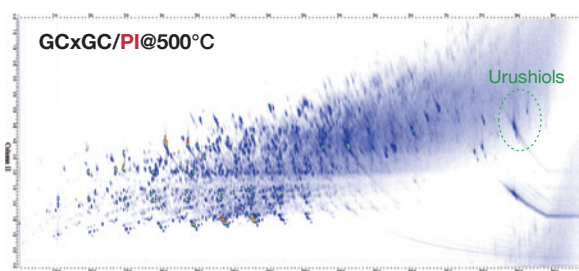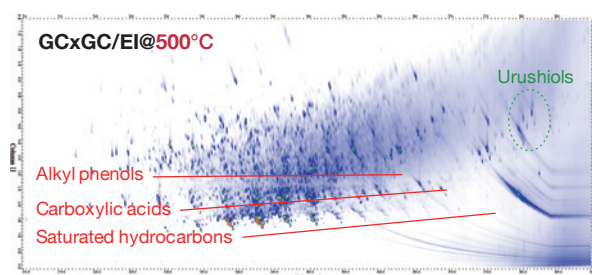
2D-TICCs of EI data and PI data

The sample was analyzed by both Py-GCxGC/EI and Py-GCxGC/PI using a pyrolysis temperature of 500°C.

Afterwards, the EI data was used to construct a 2-dimensional extracted ion chromatogram (2D-EIC) for m/z 123.0441 ($C_7H_7O_2$), a common fragment ion for alkyl catechols ($R-C_6H_3(OH)_2$). This 2D-EIC made it easy to identify two series of compounds, one for the alkyl catechols and one for the alkyl oricinols.

Subsequently, the PI mass spectra were checked for the main components, i.e., 3-Pentadecyl catechol and 3-Pentadecenyl catechol. PI is a soft ionization method that produced strong molecular ions for many of the compounds in the sample. The accurate masses of these ions were used to determine the elemental compositions for these compounds.
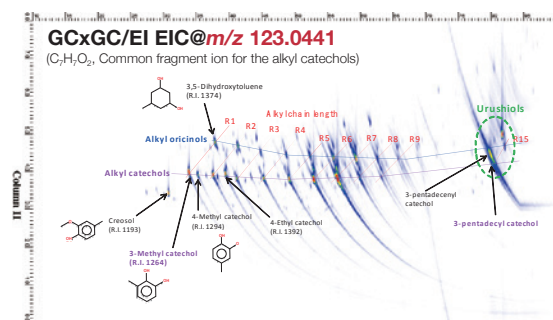
2D-EIC using m/z 123.0441 ($C_7H_7O_2$)±0.01 with EI data
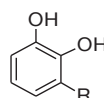
Urushiols(3-Alkyl catechols)
R=$C_{15}H_{31}$, 3-Pentadecyl catechol
R=$C_{15}H_{29}$, 3-Pentadecenyl catechol
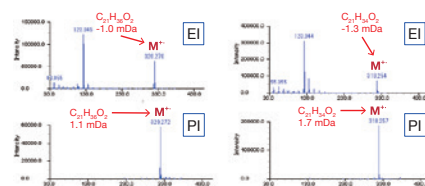
Mass spectra for 3-Pentadecyl catechol (left)
and 3-Pentadecenyl catechol (right)

Key Technology -Combination Ion Sources-

Two Optional Combination Ion Sources
– EI/FI/FD and EI/PI –

The EI/FI/FD combination ion source is a unique option that is only offered on the JEOL AccuTOF™ GC-Alpha system. EI and FI/FD modes can be switched by simply exchanging the EI repeller probe and the FI/FD emitter probe, without breaking vacuum. As a result, both GCxGC/EI and GCxGC/FI measurements can be done (along with FD) using a single ion source.

Additionally, JEOL offers an EI/Photoionization (PI) combination ion source for the AccuTOF™ GC-Alpha. While FI is still the softest ionization technique available, PI can also be used to generate molecular ions for hydrocarbons. In particular, aromatic hydrocarbons, which strongly absorb UV light, are preferentially ionized with PI, making the technique useful for detecting aromatic hydrocarbons in complex mixtures. In this case, each method is available by turning on the filament for EI or the UV lamp for PI. As a result, both GCxGC/EI and GCxGC/PI measurements can be done using a single ion source.

# Soluble Organic Fraction Analysis by GCxGC/EI
Analysis of PAHs in Exhaust Gas

Particulate material collected from exhaust gas was extracted into an organic solvent. The GCxGC/EI data shows that the PAHs were well separated from the saturated hydrocarbons,

which have the same 1st column retention time. The PAHs were then identified using a NIST database search with the EI mass spectra.
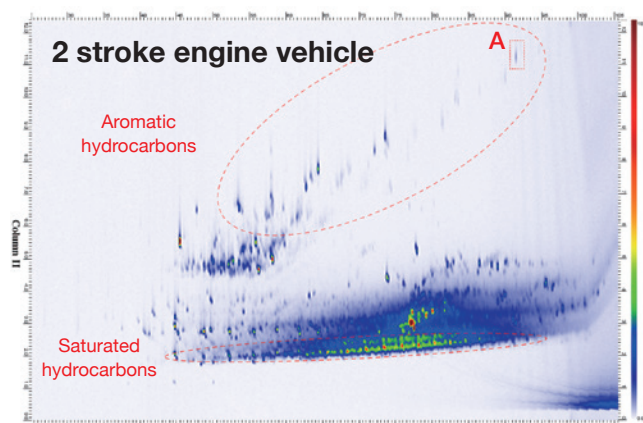
2D-EI TIC chromatogram
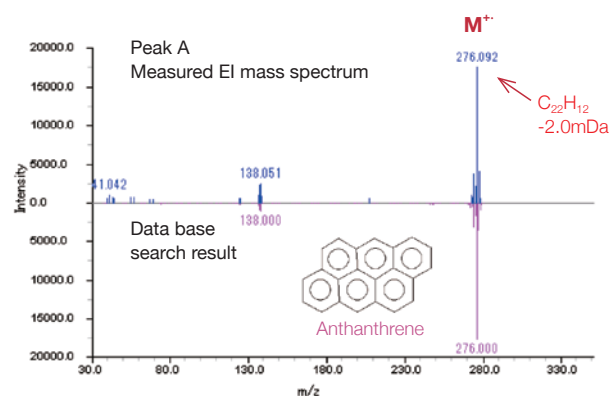
EI mass spectrum

Electronics Waste Analysis by GCxGC/EI and Negative CI
Halogenated Compounds Analysis

Dust samples collected from an electronics recycling facility were extracted into organic solvent and then analyzed by using GCxGC/EI and GCxGC/CI. The chlorinated and brominated compounds were identified by using acombination of Kendrick mass defects (KMD) and 2D mass chromatograms. The NIST library search results and accurate mass measurement results from the data acquired in EI mode were used to identify each compound in each series.

This combination of library search and elemental composition determination is a very powerful tool for detailed qualitative analysis.

Electron capture (often called "negative ion CI or NICI") measurements with GCxGC were investigated using KMD

analysis. Generally, each compound showed a strong molecular ion that agreed with the EI data. However, several compounds showed abundant Cl⁻ and Br⁻ peaks instead of molecular ions. The NICI method is effective for the analysis of low-concentration samples and quantitative analysis.

Reference:

[1] Karl J. Jobst, et al. *The use of mass defect plots for the identification of (novel) halogenated contaminants in the environment,* Anal Bioanal Chem (2013) 405:3289–3297

[2] Masaaki Ubukata, et al. *Non-targeted analysis of electronics waste by comprehensive two-dimensional gas chromatography with high-resolution mass spectrometry:*

Using accurate mass information and mass defect analysis to explore the data, Journal of Chromatography A,(2015) 1395, 152-159.
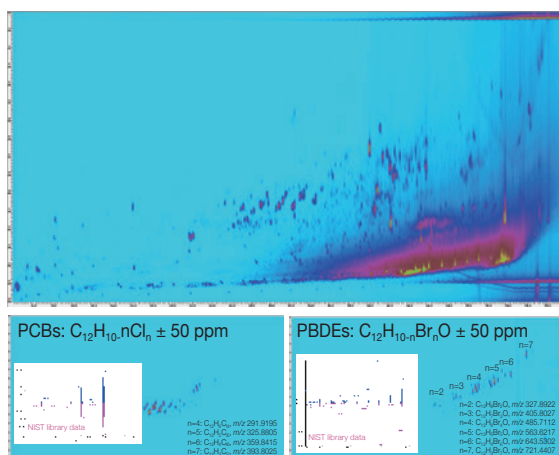
2D-EI chromatograms: Upper: TIC, Lower: EIC
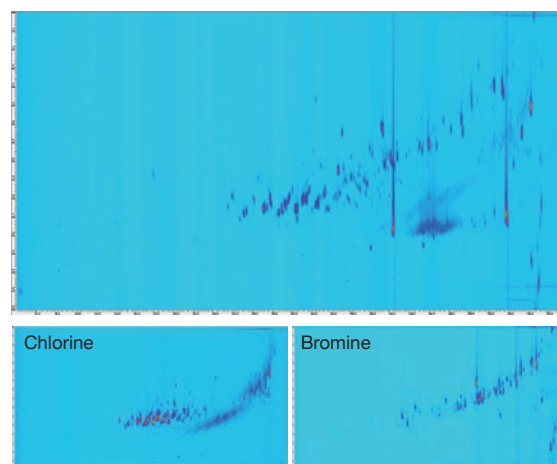
2D-Negative CI chromatograms: Upper: TIC, Lower: EIC

Aroma Oil (Fragrance) Analysis by GCxGC/EI and FI
## Molecular ion detection for Alcohol compounds

Aroma oils are a complex mixture of chemical compounds that include alcohols, terpenes, esters, etc.

Typically, alcohol compounds easily decompose during EI measurement, thus making it difficult to measure their molecular ions. As a result, the NIST database search for each EI mass spectrum will not necessarily show a good match for these compounds.

Therefore, it is important to use a soft ionization technique to confirm the molecular ions.

In this work an aroma oil was analyzed by both GCxGC/EI and GCxGC/FI. An EI and FI mass spectrum are shown for a representative diol and triol compound.

The EI mass spectra for these compounds do not show their molecular ions. However, the FI mass spectrum for each alcohol shows a high intensity molecular ion peak.

2D TIC chromatograms
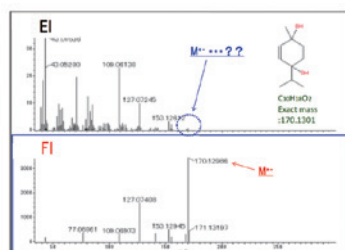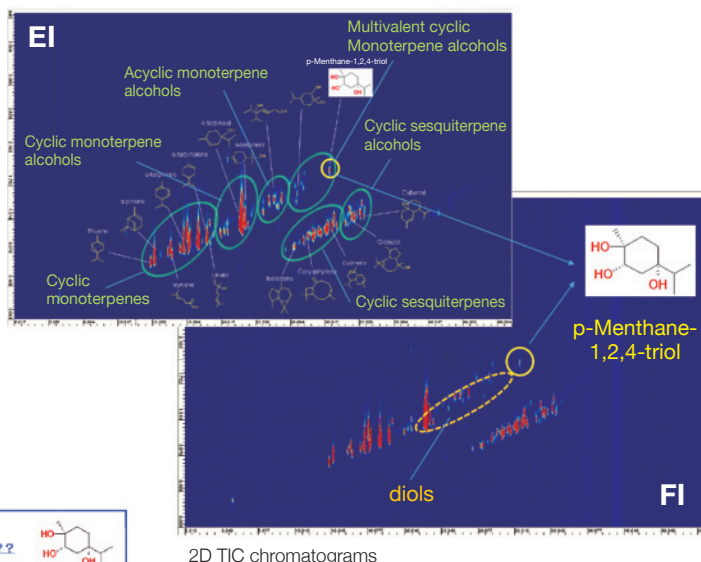
EI and FI mass spectra of a diol compound
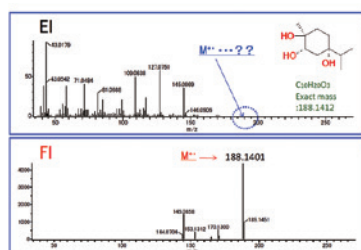
EI and FI mass spectra of a triol compound

Sebum Analysis by GCxGC/EI
Pharmaceutical application

Skin is an active metabolic tissue that synthesizes a variety of lipid compounds.

Sebum, an oily material secreted by the skin, is known to provide moisturizing effects, sun light protection, and antibacterial protection for the skin surface. The sebum consists of a complex mixture of free fatty acids, squalene, cholesterol, wax esters, diacylglycerols, and triacylglycerols. These species and their concentrations vary depending on skin conditions.

The 2D GC conditions resulted in high chromatographic separation of the lipid compounds from low boiling point fatty acids up to high boiling triglycerides in a single measurement. Additionally, these lipid compounds were comprehensively identified using a combination of accurate mass measurements and NIST library searches by HRTOFMS. As an example, peak [A] was matched to oleic acid using a NIST library search. Furthermore, this mass spectrum showed a molecular ion that coincided with the calculated accurate mass of oleic acid (error of 1.4 mDa). Peak [B] was matched to triolein using an NIST library search, and the characteristic high m/z ion was matched to the calculated accurate mass of $C_{35}H_{67}O_4$ which is a characteristic fragment ion of triolein (error of 1.1 mDa).
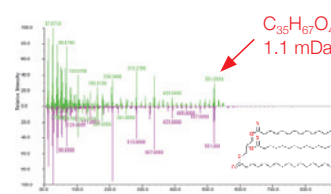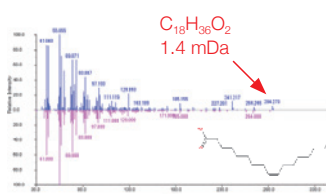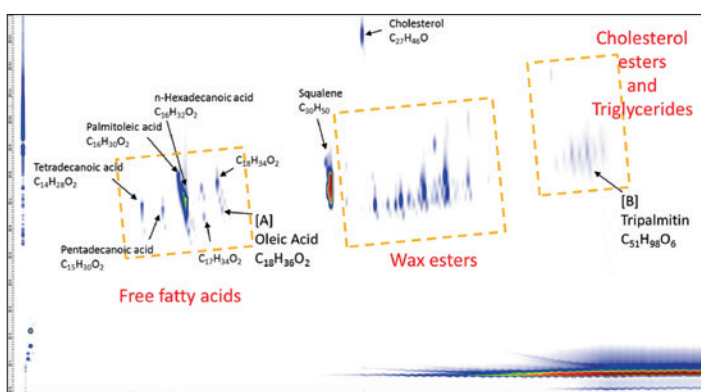
Zoex's GCxGC system is provided and supported thorough Zoex's sales and support network and may not be available in your territory. Contact your local JEOL representative for detail.