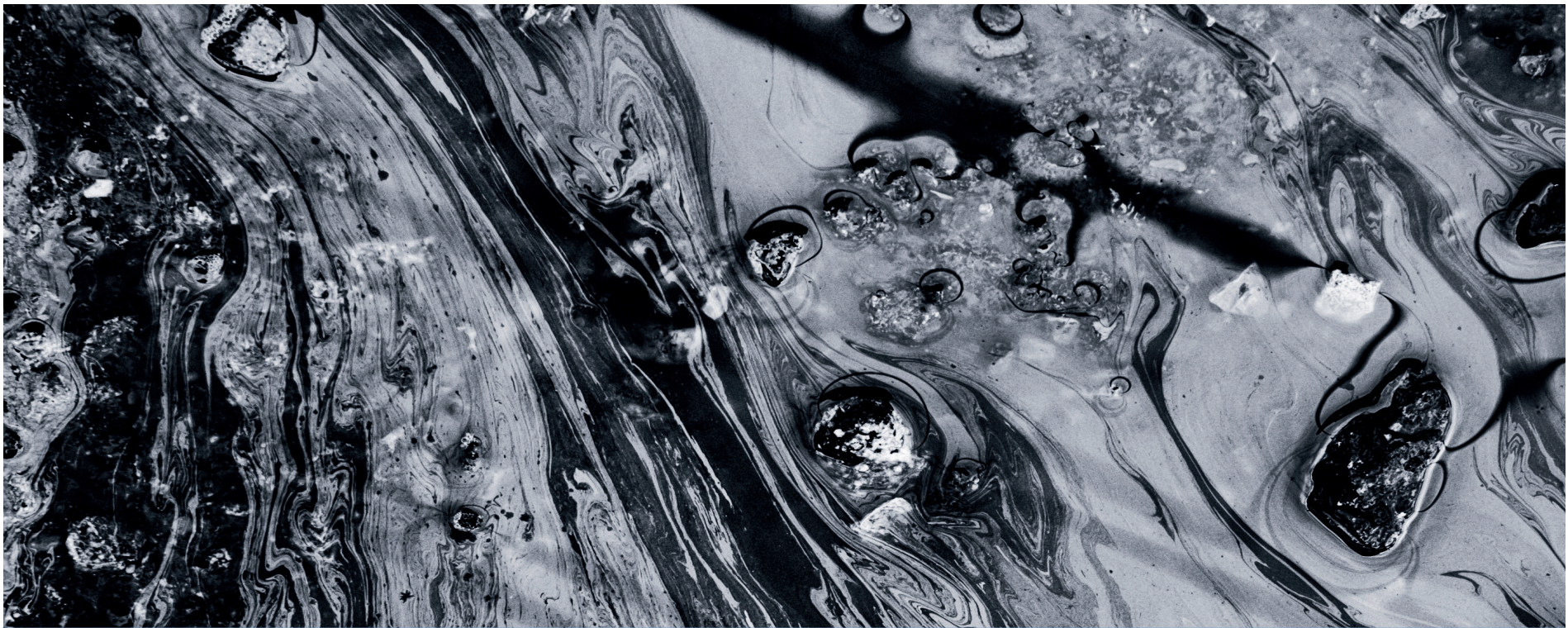




CHOOSING AN IONIZATION APPROACH FOR COMPLEX HYDROCARBON ANALYSIS

A CRUDE OIL CASE STUDY

Crude oil is not one compound. It is a highly complex mixture containing hydrocarbons and heteroatom-containing compounds spanning a wide range of boiling points and molecular weights.

This raises an important analytical question:

Which measurement method should be used?

The answer depends on what the scientist needs to learn. A GC separation may be needed to identify individual volatile components. Soft ionization may be needed to observe molecular ions. Direct MS measurement may be more suitable for quickly evaluating the molecular-weight distribution of heavier components. JEOL's GC-Alpha offers several approaches through its EI/FI/FD combination ion source. The ionization method can be changed without breaking the vacuum, allowing the same sample to be examined from different analytical perspectives. In this study, four measurement methods were used to characterize a reference crude oil material:

1. GC-EI
2. GC-FI
3. Blank tube-FI
4. FD

Figure 1 illustrates how the sample is introduced and measured for each method. Table 1 summarizes the strengths of the four approaches.

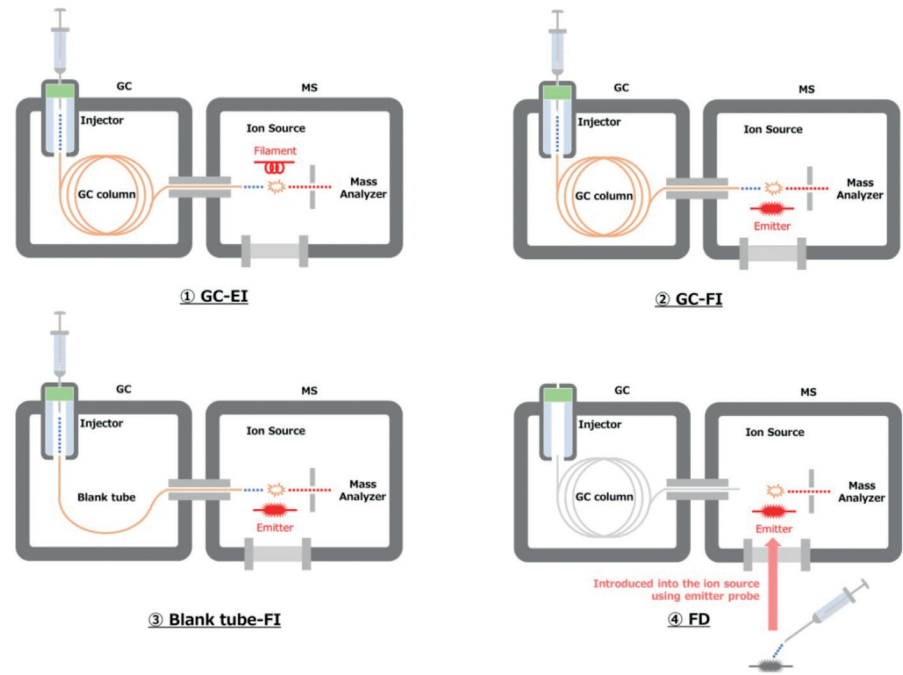


Figure 1. Measurement method for crude oil in the GC-Alpha.

Table 1. Characteristics of each measurement method.

Method	Separation	Low-boiling (b.p.< 200 Da)	High-boiling (b.p. up to 550 Da)	Very high-boiling (b.p.> 550 Da)	Meas. Time
GC-EI/GC-FI	GC + MS	Excellent	Fair	Not suitable	Long (30 min. ~)
Blank tube FI	MS only	Excellent	Good	Fair	Very quick (~1 min.)
FD	MS only	Not suitable	Excellent	Good	Very quick (~1 min.)

Why Use More Than One Ionization Method?

Electron ionization, or EI, is the most widely used ionization method for GC-MS. EI is considered a hard ionization technique because it produces extensive fragmentation. The resulting fragment ions produce characteristic mass spectra that are useful for library searching and structural interpretation. However, extensive fragmentation can also weaken the molecular ion or make it difficult to observe. Without a molecular ion, determining the molecular weight of an unknown compound may be more difficult. Field ionization, or FI, is a soft ionization technique that produces significantly less fragmentation and better preserves the molecular ion. This means that EI and FI provide different but complementary information:

- EI provides detailed fragmentation data.
- FI helps identify the molecular ion and molecular weight.

When GC-EI and GC-FI data are combined, the fragments from EI can be interpreted alongside the molecular-ion information from FI. This provides more evidence for identifying an unknown compound than either measurement alone.

GC-EI and GC-FI: Separating and Identifying Individual Components

In GC-EI and GC-FI, the sample is introduced through the GC inlet, separated on a GC column, and then enters the mass spectrometer. GC separation is important when the sample contains many individual components that need to be examined separately. The difference occurs at the ion source:

- GC-EI measures the separated compounds using hard ionization.
- GC-FI measures them via soft ionization.

As shown in Figure 2, a large number of peaks were detected in both chromatograms, including linear alkanes ranging from C5 to C32. The two datasets were then combined using msFineAnalysis AI, JEOL's qualitative software for the GC-Alpha.

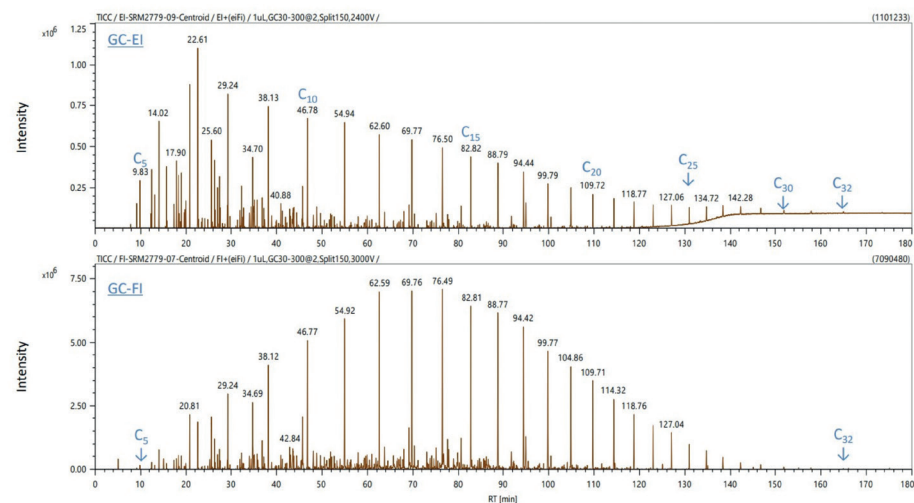


Figure 2. TIC chromatograms of GC-EI and GC-FI.

Figure 3 shows the integrated analysis of the retention-time region from heptadecane, C₁₇H₃₆, to eicosane, C₂₀H₄₂.

Most of the major compounds in this region were hydrocarbons composed solely of carbon and hydrogen. However, the integrated analysis also detected minor sulfur-containing components, identified as alkylated dibenzothiophenes.

This was especially valuable because the compound was not registered in the NIST library.

By combining GC-EI and GC-FI accurate-mass data, msFineAnalysis AI was able to propose a structural formula through AI structure analysis.

This example shows why complementary ionization can be important for unknown compound identification. EI provides fragment information, FI provides molecular-ion information, and the software integrates the information together.

Blank Tube-FI: A Fast View of Molecular-Weight Distribution

Sometimes the main objective is not to separate every compound.

Instead, the scientist may want to quickly assess the overall molecular-weight distribution of the sample. This can be accomplished by blank tube-FI.

For blank tube-FI, the sample is introduced through the GC inlet and passes through a blank tube rather than a separation column. The sample is then measured by FI.

Because there is no chromatographic separation, the measurement can be completed very quickly.

As shown in Figure 4, blank tube-FI provided molecular-weight information in less than one minute.

It detected a broad range of components, spanning relatively low- to high-mass compounds.

Blank tube-FI therefore provides a useful overview of the sample when rapid evaluation of the molecular-weight distribution is more important than resolving individual compounds.

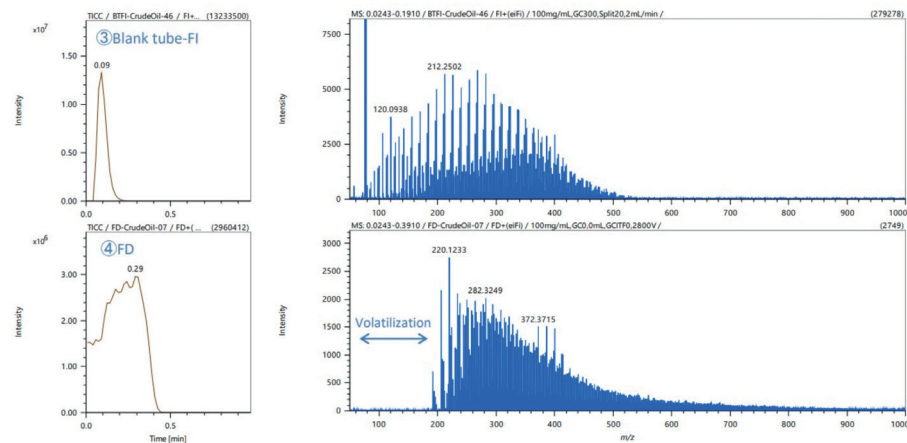


Figure 4. TIC chromatograms and mass spectra of Blank tube-FI and FD.

FD: Direct Measurement of Higher-Mass Components

Field desorption, or FD, is also a soft ionization technique, but sample introduction differs.

For FD, the sample is applied directly to an emitter. The emitter probe is then inserted into the ion source for measurement.

No GC column is used.

This direct approach makes FD particularly useful for high-boiling, high-mass compounds that may not be well suited to GC analysis.

Figure 4 shows that FD detected higher-mass components in the crude oil sample and provided the molecular-weight distribution in under one minute.

However, the figure also highlights an important practical consideration. Lower-mass components can be lost through volatilization when the emitter probe is introduced into the ion source.

This does not mean that one method is better than the other. It means the method should be selected based on the sample and the analytical objective:

- Blank tube-FI provides a broader view of components, spanning from lower- to higher-mass components.
- FD provides better access to higher-mass components.

TIC chromatograms(GC-EI/GC-FI)



Qualitative information for each peaks

Structure and spectrum obtained by AI analysis

Figure 3. Result of integrated analysis using msFineAnalysis AI.

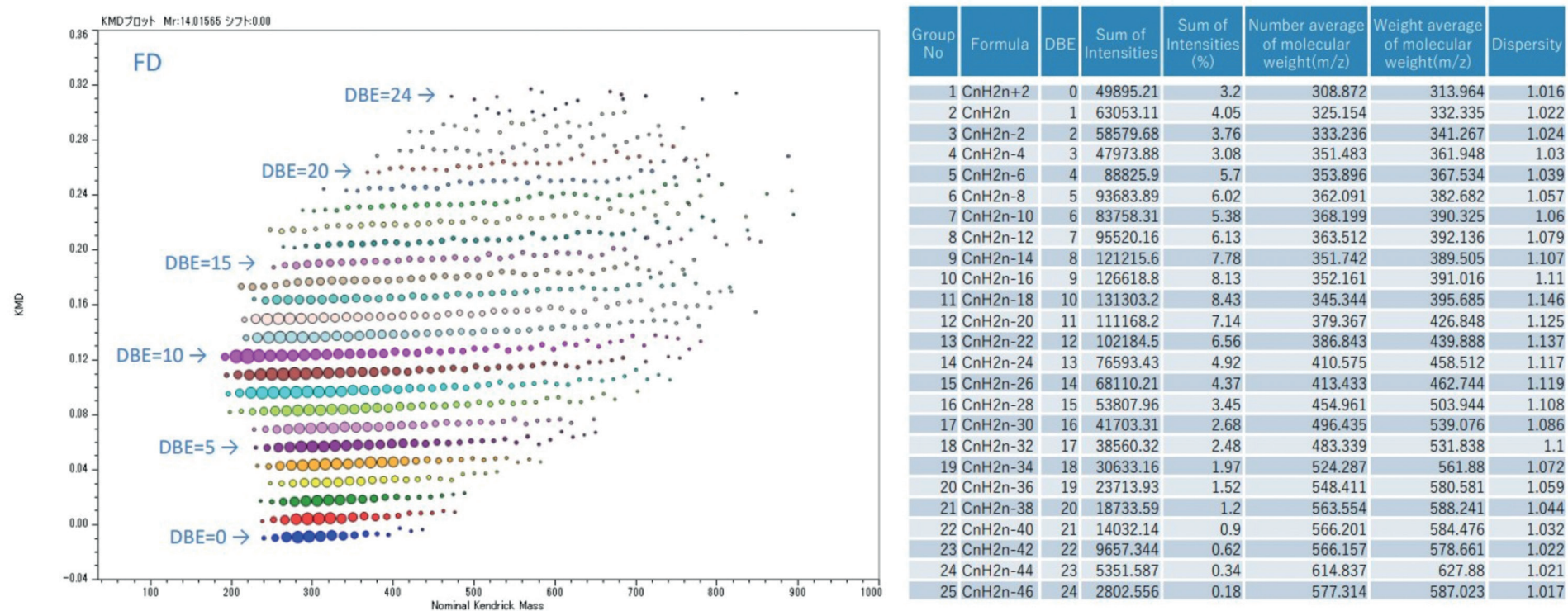


Figure 5. KMD plot and group data of FD.

• GC-EI and GC-FI provide chromatographic separation and information about individual compounds.

Looking Beyond Individual Peaks

Complex hydrocarbon samples often contain groups of related compounds rather than isolated components alone.

For FD data, it is often useful to organize these compounds using Kendrick mass defect, or KMD, analysis with JEOL's msRepeatFinder software.

The KMD plot and group data shown in Figure 5 enable the evaluation of key characteristics of the main hydrocarbon groups, including their degrees of unsaturation and polymerization.

A similar analysis can also be performed using blank tube-FI data.

This type of group analysis offers another way to understand the overall composition of a complex petroleum sample without identifying each detected ion individually.

Selecting the Method Based on the Analytical Question

This crude oil example demonstrates that complex samples often require more than one analytical approach.

When the goal is to separate and identify individual volatile components, GC-EI and GC-FI provide complementary information on fragmentation and molecular ions.

When a quick overview of the molecular-weight distribution is needed, blank tube-FI can examine a broad range of components without chromatographic separation.

When the focus is on higher-boiling, higher-mass components, FD provides direct measurement via soft ionization.

The software also depends on the type of information under examination:

- **msFineAnalysis** AI integrates GC-EI and GC-FI data for comprehensive analysis and AI-assisted structural analysis of unknown compounds.
- **msRepeatFinder** evaluates molecular weight patterns and related compound groups using KMD analysis.

The key lesson is not that one ionization method should replace another.

Each method answers a different question.

By selecting the appropriate combination of GC separation, hard ionization, soft ionization, and direct MS measurement, scientists can obtain a more complete view of complex hydrocarbon samples than would be possible using a single method alone.

Resources: This article was developed from an application study originally published by JEOL Ltd. The experimental data and figures are reproduced from the original JEOL MSTips No.452 publication.

- GC-Alpha, msFineAnalysis AI, and msRepeatFinder product webpages
- AccuTOF GC Series Petroleum & Petrochemicals Applications Notebook | Feb 2026 Edition | <https://www.jeol.com/solutions/applications/details/1947.php>



JEOL JMS-T2000GC GC-Alpha 2.0 is a high-resolution time-of-flight mass spectrometer coupled to a gas chromatograph.



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