



Analysis of Biomarkers in Crude Oil Using the Agilent 7200 GC/Q-TOF

Application Note

Petrochemical and Environmental

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Abstract

The analysis of biomarkers such as (alkyl-) dibenzothiophenes, hopanes, and steranes in crude oil is used in many petrochemical applications, including the characterization of oil sources and the identification of sources of oil spillage. The analysis is normally done by GC-MS after complex sample preparation and fractionation.

Using a high resolution time-of-flight mass spectrometer, a diluted sample can be analysed without fractionation and the biomarkers of interest can be measured by exploiting the high selectivity of ion extraction at accurate mass.

The excellent sensitivity of the system allows the selective detection of dibenzothiophene, alkylated dibenzothiophenes and hopanes. Using the Agilent GC/Q-TOF system in MS/MS mode, low levels of steranes could be selectively detected.



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Introduction

Biological markers or biomarkers include a large group of hydrocarbons, including alkanes, polycyclic aliphatics, and polycyclic aromatic hydrocarbons, that are persistent in the environment. These biomarkers can be used in many petrochemical applications including the characterization of oil sources, as indicators of oil maturity or oil weathering. The biomarkers can also be used to identify sources of environmental pollution by oil spillage [1,2].

Typical biomarkers are heterocyclic polycyclic aromatic hydrocarbons, such as alkyl-dibenzothiophenes, pentacyclic triterpanes such as hopanes, and sterol-derived polycyclic alkanes such as steranes (for example cholestane). Usually, the analysis of these biomarkers is performed by GC-MS. Prior to the analysis, sample fractionation by liquid-liquid extraction, column chromatography, and/or solid phase extraction is used to isolate alkane and aromatic fractions. Finally, the extracts are separated by GC, and detection is performed by MS operated in selected ion monitoring (SIM). Since a large number of markers are monitored, often multiple runs, each monitoring a group of markers might be necessary.

In this application note, the Agilent 7200 Q-TOF instrument was used to analyze dibenzothiophenes (DBTs), hopanes, and steranes in a crude oil by direct injection of a diluted solution of the oil. The time-of-flight instrument combines high sensitivity and resolution with accurate mass determination. This offers unique selectivity for the detection of trace analytes in a complex matrix. The GC/Q-TOF approach is also not limited to a group of preselected analytes (as in SIM or MRM operation using single quadrupole or triple quadrupole systems), but the different classes of biomarkers can be detected, identified and quantified by using extracted ion chromatograms at accurate masses of selective ions. In addition, the possibilities of MS/MS operation also enables additional selectivity at trace level if the selectivity in full scan mode is not sufficient.

Experimental

Chemicals and Sample

A reference solution NIST SRM 2260a (LGC, Molsheim, France) containing dibenzothiophene was used to check instrument performance. The test sample was diluted 10 times in hexane. The final concentration of dibenzothiophene was 0.38 ng/ μ L.

A crude oil was obtained from Total, France. From the crude oil, 100 mg was weighed and extracted in 10 mL hexane using sonication. The solution was centrifuged and an aliquot of the clear supernatant was diluted 10 times in hexane (final oil concentration: 1 mg/mL)

GC and MS conditions

An Agilent 7890A GC System, equipped with a SSL, combined with a 7200 Q-TOF system was used.

The analytical conditions are summarized in Table 1.

Table 1. GC/Q-TOF Conditions

Injection	Inlet type	Split/splitless
	Mode	Splitless
	Temperature	300 °C
	Volume	1 μ L
Column	DB-5MS, 30 m x 0.25 mm, 0.25 μ m	
Carrier	1.5 mL/min, helium, constant flow	
GC oven	50 °C (1 min) - 10 °C/min - 320 °C (8 min)	
Detection	Ionization mode	EI
	MS mode	scan 40–500 Da
	Acquisition rate	5 Hz
	MS/MS mode	scan 40–500 Da
		CE : 10 eV
	Source temp	280 °C
	Quad temp	150 °C

Results and Discussion

First a reference sample, containing 0.38 ng/ μ L dibenzothiophene was analyzed. The chromatogram (elution window 5–23.5 minutes) is shown in Figure 1. DBT elutes at 16.3 minutes. The mass spectrum is shown in Figure 1B. The most abundant ion, corresponding to the molecular ion, is detected at m/z 184.0338. The mass error was less than 2 ppm as compared to the exact mass of molecular ion ($C_{12}H_8S$, $M^{*+} = 184.0341$).

Next, the crude oil sample was analyzed using the same method. The total ion chromatogram is shown in Figure 2a. The profile is characterized by the typical homologue series of n-alkanes. The elution time of dibenzothiophene is indicated by an arrow. Using an extracted ion chromatogram at m/z 184 \pm 0.5 amu, as is typically done in single quadrupole MS systems, dibenzothiophene can be detected, as shown in Figure 2b. However, several other compounds are also detected, especially in a time window between 14–18 minutes. These compounds (probably C4-naphthalenes, $C_{14}H_{16}$, MW = 184) can potentially interfere with the selected biomarker.

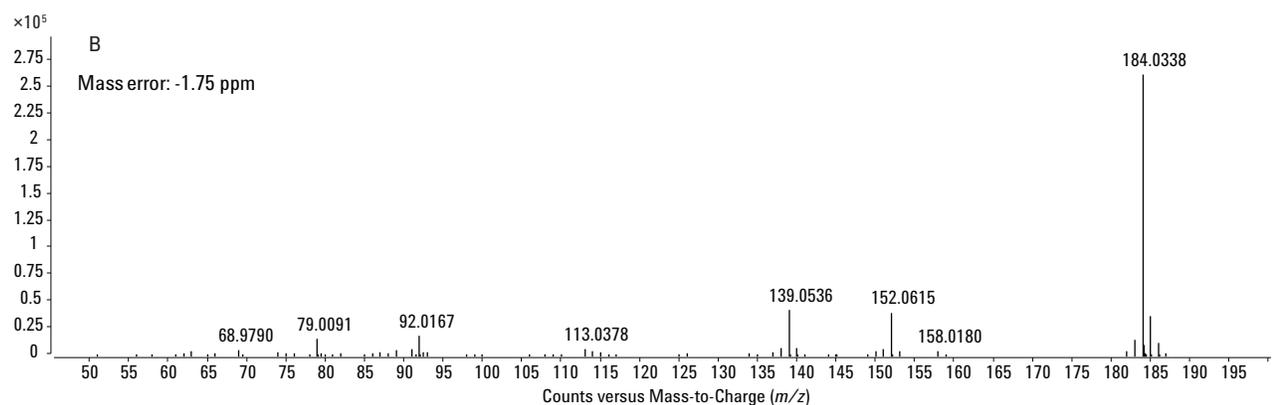
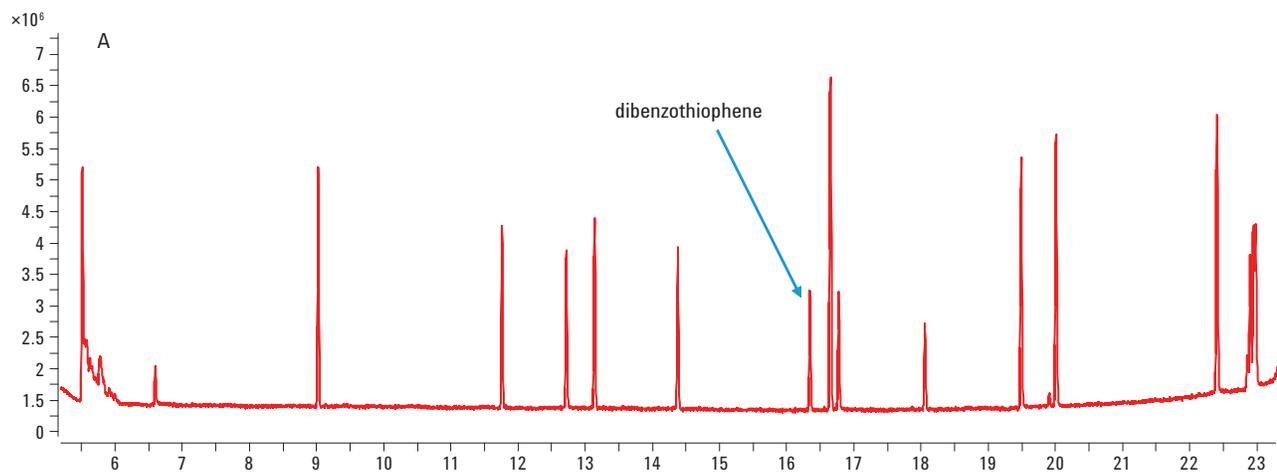


Figure 1. GC/Q-TOF analysis of aromatic hydrocarbon standard mixture. The spectrum obtained for 0.38 ng dibenzothiophene($C_{12}H_8S$, $M^+ = 184.0341$) is shown in B.

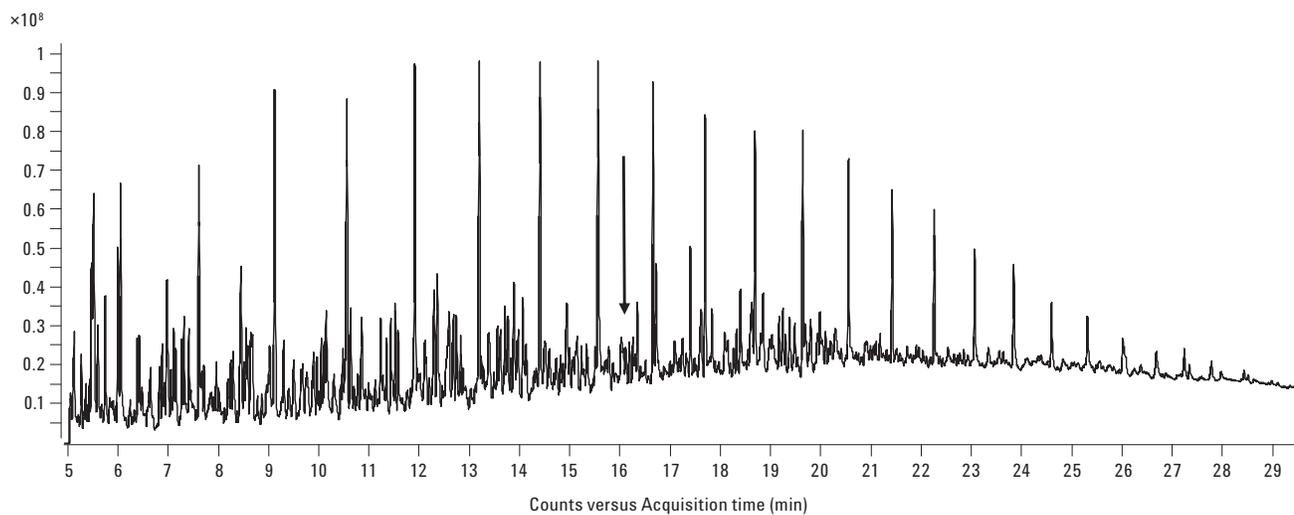


Figure 2a. Total ion chromatogram of crude oil, elution time of DBT is indicated by arrow.

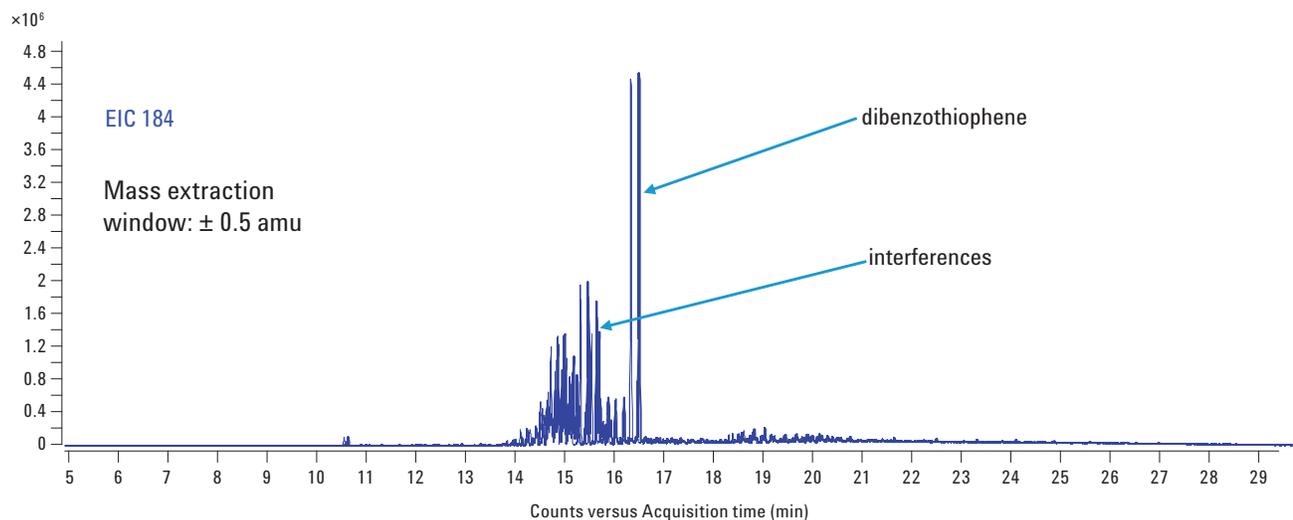


Figure 2b. Extracted ion chromatogram at 184 ± 0.5 amu.

Using an extracted ion chromatogram at exact mass (184.0341 ± 5 ppm), a much higher selectivity is obtained allowing to eliminate all the interferences as shown in Figure 2c. The mass spectrum acquired at 16.32 minutes is shown in Figure 2d. The mass accuracy obtained for DBT in the complex matrix is not significantly affected (m/z 184.0339) with a mass error below 2 ppm.

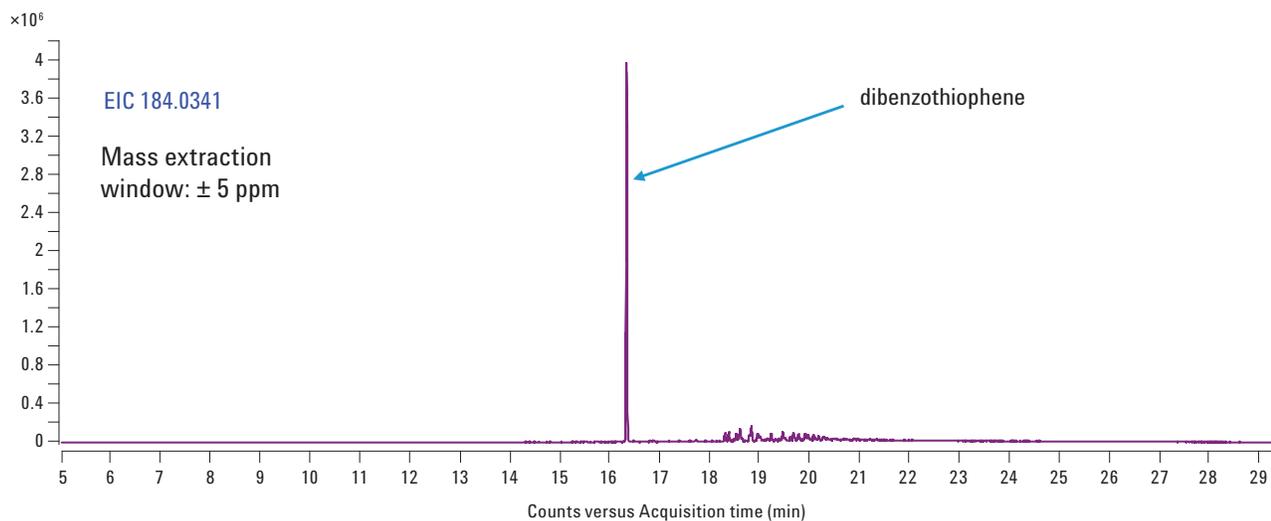


Figure 2c. Extracted ion chromatogram at 184.0341 ± 5 ppm.

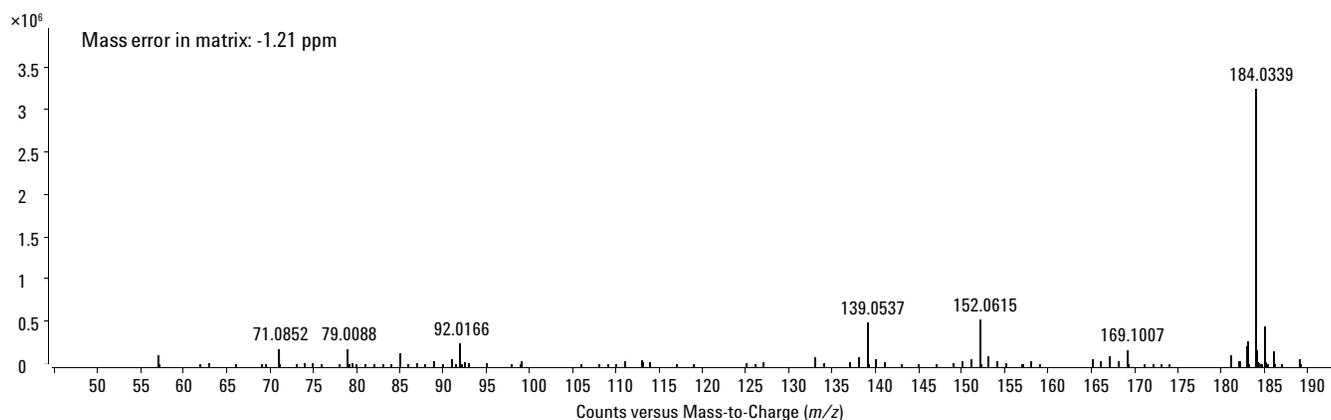


Figure 2d. Mass spectrum of dibenzothiophene in crude oil matrix.

In the same way, it was possible to extract ion chromatograms at m/z 198.0498 for methyl-dibenzothiophenes (C₁-DBT, 4 isomers, only three chromatographically resolved) and at m/z 212.0645 for C₂-dibenzothiophenes. These DBT biomarkers are easily detected as shown in Figure 3.

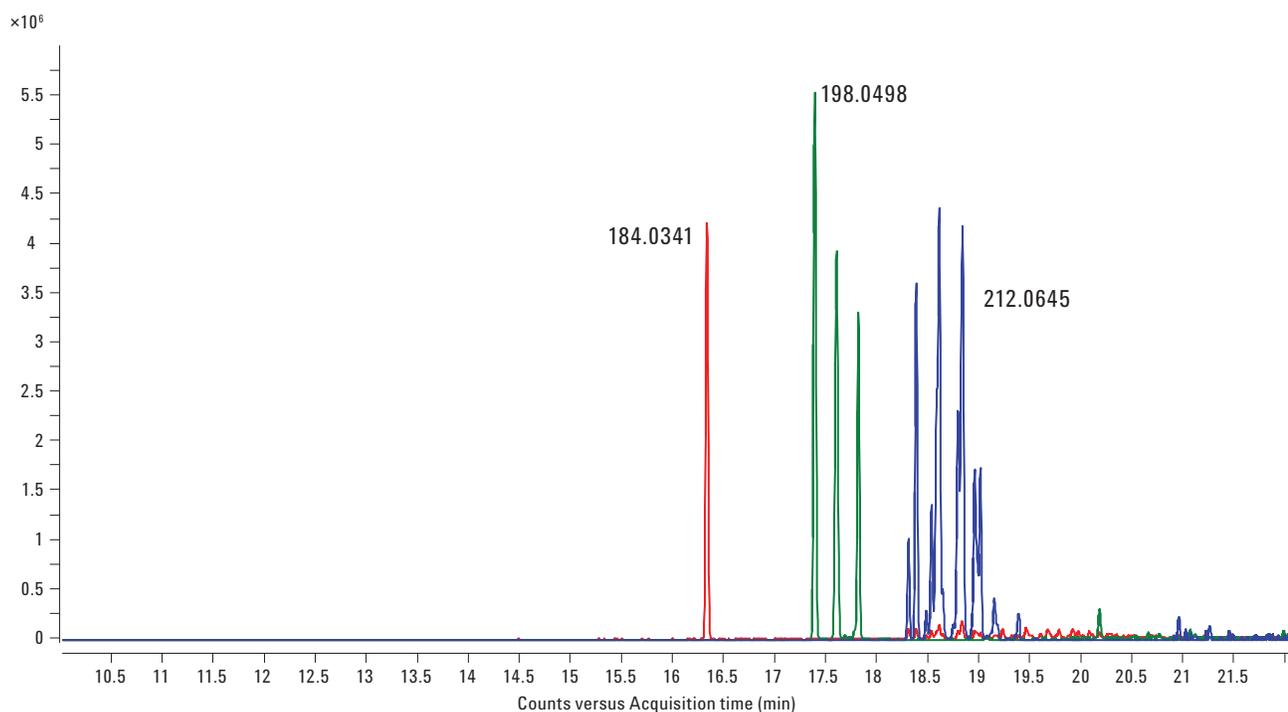


Figure 3. Extracted ion chromatograms at accurate mass (± 5 ppm) for the detection of DBT (ion 184.0341), methyl-dibenzothiophenes (ion 198.0498) and C₂-dibenzothiophenes (ion 212.0645).

Besides the S-containing PAHs, hopanes and steranes are also important biomarkers. In the same way, extracted ion chromatograms at accurate mass can be used to selectively detect these analytes in the complex crude oil matrix. In Figure 4, the extracted ion chromatograms at 191 ± 0.5 amu (top) and at 191.1794 ± 10 ppm (bottom) are compared. Much higher selectivity and, consequently, higher signal-to-noise are clearly obtained by using accurate mass detection. Several hopanes could be detected in the elution range between 26 and 30 minutes. Main peaks (27–28 minutes) probably correspond to nor-hopanes ($C_{29}H_{50}$, MW=398).

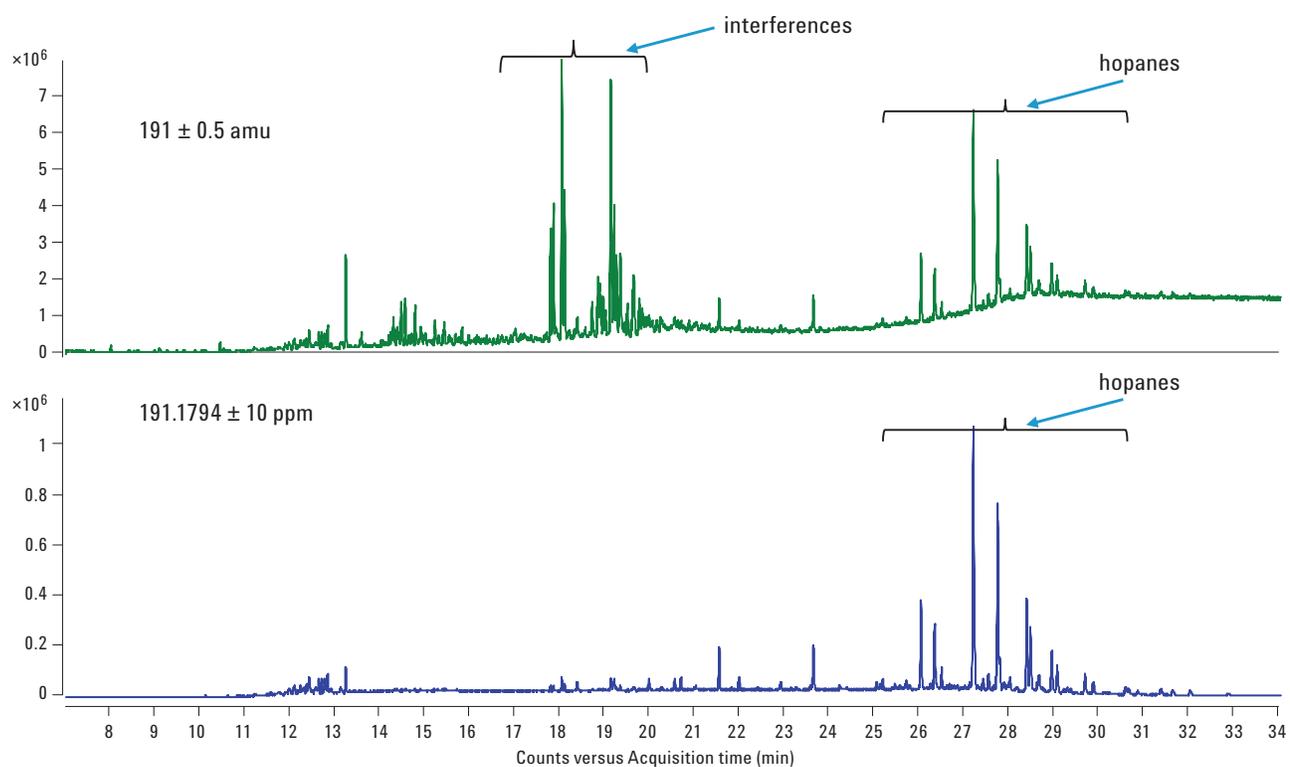


Figure 4. Extracted ion chromatograms at 191 ± 0.5 amu (top) and at accurate mass (191.1794 ± 10 ppm) for the detection of hopanes.

Finally, specific ions for steranes were extracted. As these analytes are present at lower concentration in this sample and interfered with by matrix ions even when using accurate mass EICs, as illustrated in Figure 5. Since the GC/Q-TOF also allows the operation in MS/MS mode, the analysis was repeated using ion 400 (M^{++} for $C_{29}H_{52}$ = ethylcholestane) as a precursor ion. The EIC of product ion at 217.1951 now shows improved selectivity of detection for the ethylcholestane steranes, as shown in Figure 6.

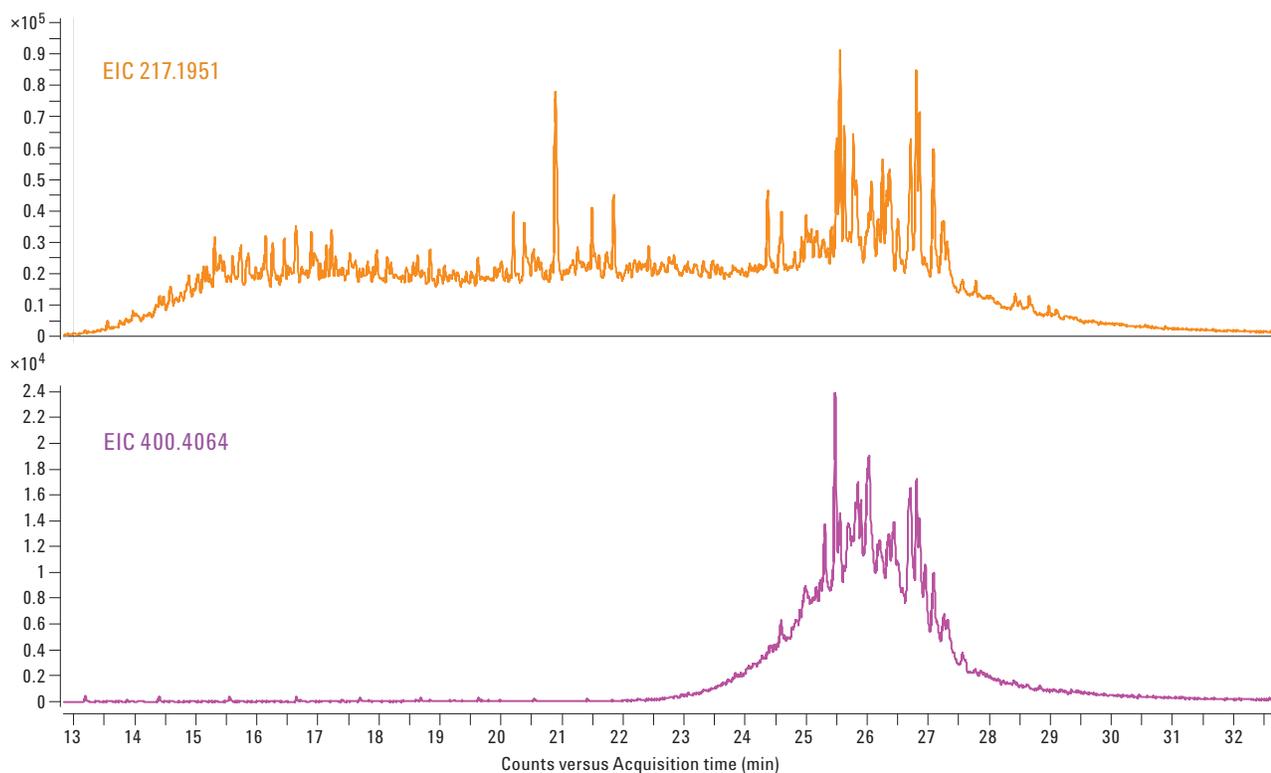


Figure 5. Extracted ion chromatograms at accurate masses ($217.1951 \pm 10\text{ppm}$ and $400.4064 \pm 10\text{ppm}$) for the detection of steranes.

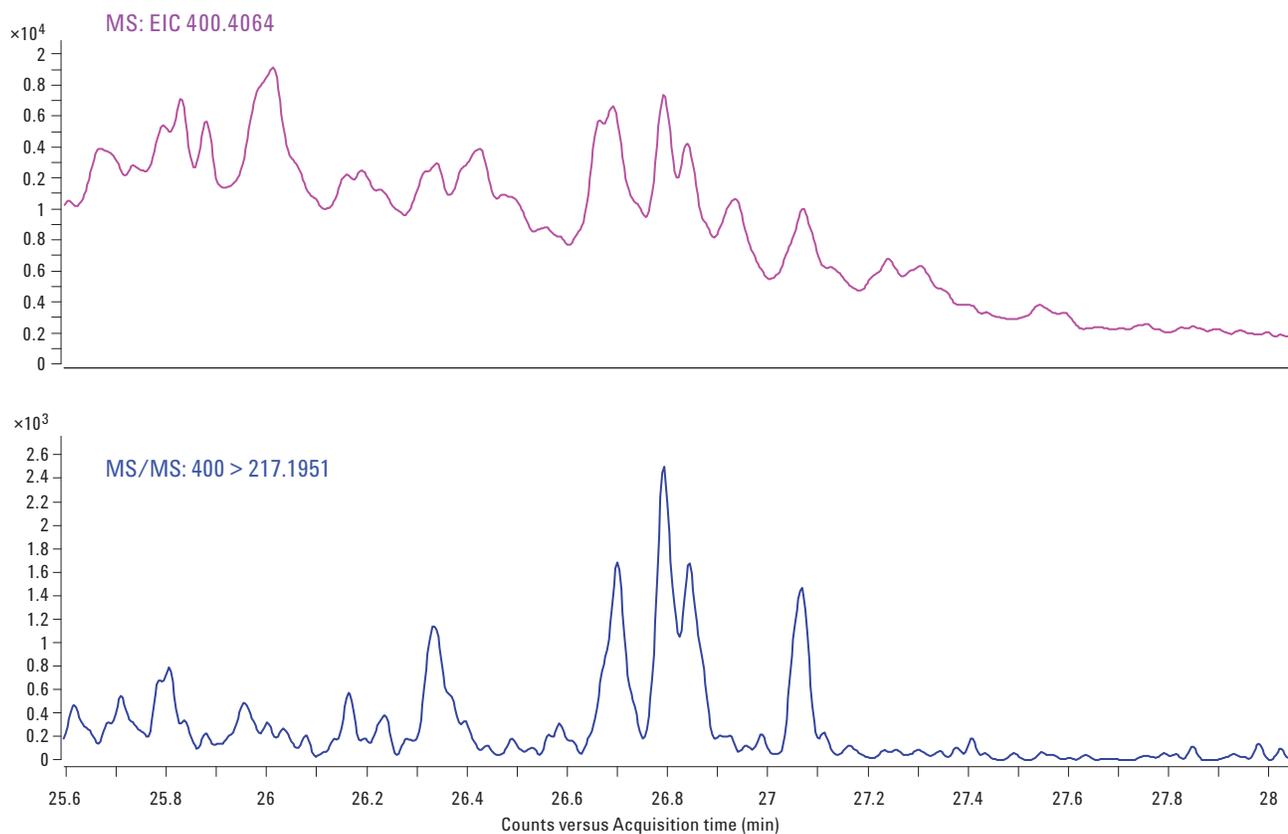


Figure 6. Comparison of extracted ion chromatogram at accurate mass (400.4064 ± 10 ppm) obtained in Full Scan mode (top) with the Extracted Product Ion ($400 > 217.1951 \pm 10$ ppm) obtained in MS/MS mode (bottom) for the detection of steranes.

Conclusions

The Agilent 7200 Q-TOF instrument allows the analysis of a wide range of biomarkers in crude oil without the need for pre-fractionation. The diluted crude oil is directly analyzed and biomarkers such as dibenzothiophenes and hopanes could be selectively monitored by using extracted ion chromatograms at exact masses and using a narrow extraction window.

The 7200 Q-TOF system operated in MS/MS mode also allowed the selective detection of traces of steranes.

In summary, the Agilent 7200 GC/Q-TOF system can be efficiently utilized in targeted and untargeted biomarker analysis in petroleum characterization.

References

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