



GC-APCI IMS of Diesel

Application Note

Energy and Chemicals

Authors

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Abstract

This Application Note describes the use of ion mobility and high-resolution GC/MS for profiling sulfur compounds in a very complex sample such as diesel fuel. The analysis of sulfur compounds in diesel can be challenging because of this matrix complexity. Gas chromatography/high-resolution mass spectrometry is a useful tool when identifying peaks, but, in the case of petroleum, such attempts are usually frustrated by isobaric coeluting hydrocarbons.

Ion mobility, coupled to high-resolution GC/MS, provides an extra dimension of separation based on size, charge, and shape. This study demonstrates the advantage of coupling GC-APCI to ion mobility high-resolution mass spectrometry for the study of aromatic sulfur compounds in diesel.



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Introduction

The economic value of diesel depends on its chemical composition. Molecules containing heteroatoms such as sulfur lower the value of fuel, as they burn in air and produce smog. The amount of sulfur in diesel is being decreased because of environmental regulations.

The distribution of sulfur-containing compounds in various feedstocks is important, as the refining process can be modified to meet regulations. Refineries use a process called hydrodesulfurization to remove sulfur from sulfur-containing compounds. For hydrodesulfurization, sulfur bound in aromatic structures such as benzothiophenes and dibenzothiophenes and their alkyl-substituted analogs is the most difficult to remove catalytically. Therefore, it is important to study these species.

The profiling of sulfur compounds in diesel can be challenging because of its very complex matrix. There are thousands of different compounds in diesel, ranging from alkanes, alkenes, aromatics, and heteroatomic sulfur, nitrogen, and oxygen compounds. The probability of completely resolving a single class of compound from all others in the sample is low.

Gas chromatography/high-resolution mass spectrometry is a useful tool when identifying peaks but, in the case of diesel, such attempts are usually frustrated by isobaric coeluting hydrocarbons. Ion mobility, coupled to GC/MS, provides an extra dimension of separation based on size, charge, and shape. After chromatographic separation, the ions formed in the source are separated again in the gas phase in the mobility cell. Larger ions traverse the drift tube at a slower rate than smaller ions resulting in gas-phase ion separation.

This Application Note demonstrates the use of ion mobility for separating aromatic sulfur-containing compounds from the matrix. Two samples of diesel are compared, before and after hydrodesulfurization.

Experimental

Sample preparation

Samples of processed and unprocessed diesel were diluted 1:10 with isooctane, and analyzed without any additional sample preparation.

Instrumentation

- Agilent 7890B GC with the GC-APCI interface
- Agilent 6560 Ion Mobility Q-TOF GC/MS

Software

- Agilent MassHunter Data Acquisition Software for Agilent Ion Mobility Q-TOF Mass Spectrometer, Version B.07.00
- Agilent MassHunter Qualitative Software, Version B.07.00

GC-APCI

Figure 1 shows a schematic of the GC-APCI IMS Q-TOF. The setup and operation of the GC-APCI is described in detail elsewhere¹. The source parameters for GC-APCI are listed in Table 1.

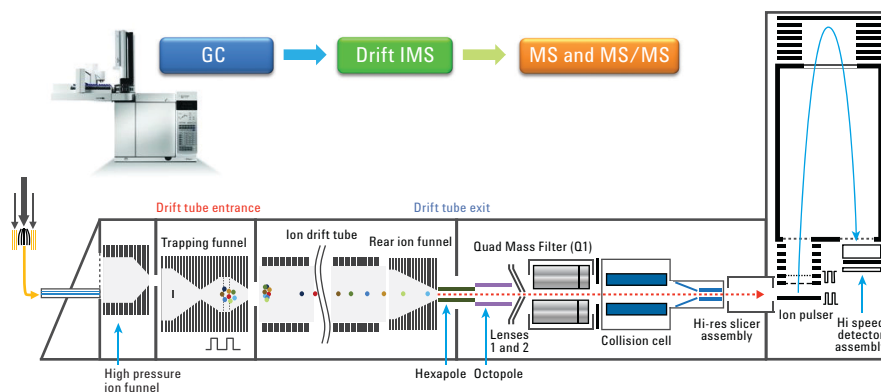


Figure 1. Schematic of the Agilent GC-APCI IMS Q-TOF system.

Table 1. GC and MS conditions.

Parameter	Value
Column	Agilent J&W DB-5ms, 30 m × 0.25, 0.25 μm
Injection port	Split/splitless
Injection volume	1 μL
Mode	Constant flow, 1.3 mL/min, 15 psi at 50 °C
Split ratio	1:10
Flow rate	1.3 mL/min
Oven program	50 °C (2 minutes) to 250 °C at 10 °C/min (10 minutes), then 300 °C at 15 °C/min (10 minutes)

Table 2. Agilent 6560 Ion Mobility Q-TOF LC/MS source parameters for positive ion mode method.

Parameter	Value
Ion mode	Positive
Drying gas temperature	250
Drying gas flow	11 L
Capillary voltage	1,000 V
Skimmer	65 V
Corona	1 μA
Fragmentor	150 V
Resolution at 121 <i>m/z</i>	

IMS Q-TOF

The Agilent 6560 IMS Q-TOF is a Q-TOF LC/MS system that can be run in either ion mobility mode or Q-TOF only mode. It consists of a trapping funnel, drift tube, and rear funnel between the front funnel and ion optics leading to the quadrupole mass filter. This design builds on the well-established Q-TOF system in the back end, and proven high-sensitivity ion-funnel technology. The fast duty cycle of ion mobility (milliseconds) is well matched with the fast acquisition of TOF (microseconds). The fast acquisition of the TOF is well-suited to sampling the very narrow peaks generated by the GC.

IMS is a gas-phase ion separation technique that is carried out in a drift tube filled with an inert drift gas (nitrogen), and energized with a low DC electric field. Larger ions traverse the drift tube at a slower rate than smaller ions,

resulting in gas-phase ion separation. The ability to separate ions at the millisecond time scale is particularly advantageous when chromatographic separation of complex mixtures is not possible. This powerful combination of separation, resolution, and structural information is key for solving the most challenging applications.

Results and Discussion

By coupling the GC to the 6560 IMS Q-TOF, we created an analytical system with much greater separation power for these types of complex compound analyses. The additional dimension of orthogonal separation greatly adds to the peak capacity/separation power of the overall system. As we demonstrate, ion mobility is effectively used to pull apart overlapped and smaller peaks in a complex mixture.

One of the most important attributes of ion mobility separation is its specificity. In particular, ion mobility effectively cleans up background chemical noise due to column bleed. The mobility heat map shows hundreds of components in the sample with overlapping compounds at nearly every m/z value. The highlighted polygon region in the heat map shows the fingerprint due to column bleed. The ion mobility of polysiloxanes is very different from the hydrocarbon matrix, and separate easily from sample-related compounds. Figure 2 shows the screen capture of these compounds.

The bottom graphic shows the mobility filtered mass spectrum that removes many of the overlapping chemical background ions. This eliminates the need to do any background subtraction.

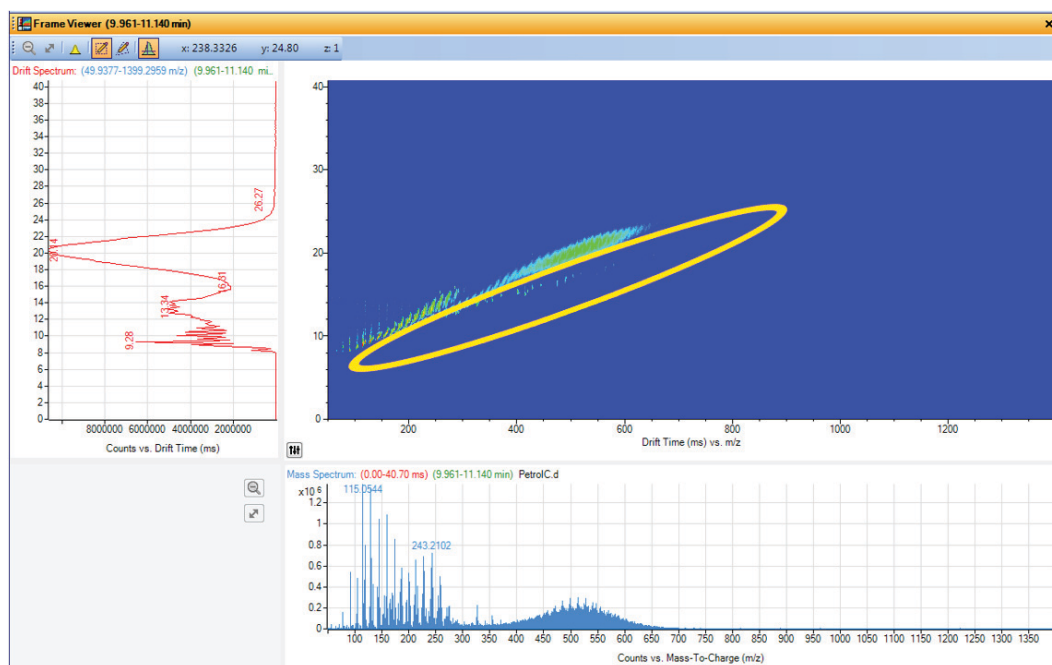


Figure 2. Compounds separated according to carbon number in the drift time domain. The circled area is column bleed, which has shorter drift times than the hydrocarbons, and separates out

Comparison of pre- and post-treatment diesel samples

Figure 3 shows a comparison of the two diesel samples pre- and post-treatment. A visual inspection of the graph shows differences in the distribution of molecular weights in the two samples. Sample C, which is the sample after hydrodesulfurization, shows a molecular weight distribution towards the lower molecular weights expected from this treatment.

The advantage of using high-resolution mass spectrometry is apparent in Figure 4, which shows a plot of an extracted ion chromatogram with a mass defect window set to mass defects below 0.1 amu. Figure 4A is the untreated sample, which shows an abundance of high-intensity peaks with the mass defects below 0.1 amu that are indicative of sulfur compounds.

The treated sample (Figure 4B) lacks these peaks. Figure 4C shows the mass spectrum of a region in the chromatogram of the untreated sample around 11.56 minutes retention time. The peak at 213 m/z , with its isotopic fit (superimposed in red), is indicative of dibenzothiophene species.

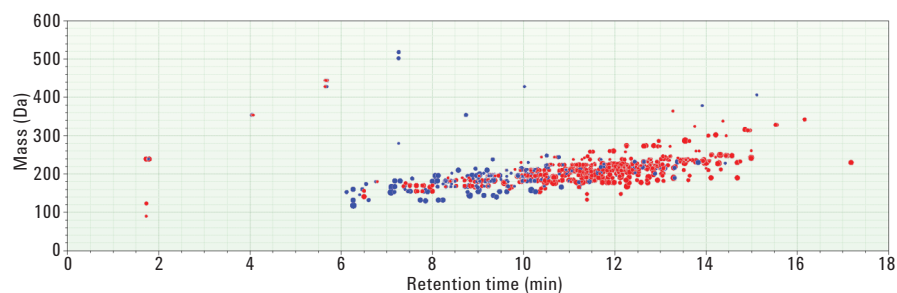


Figure 3. Comparison of diesel samples before and after hydrodesulfurization. The features in blue are from the diesel sample after treatment.

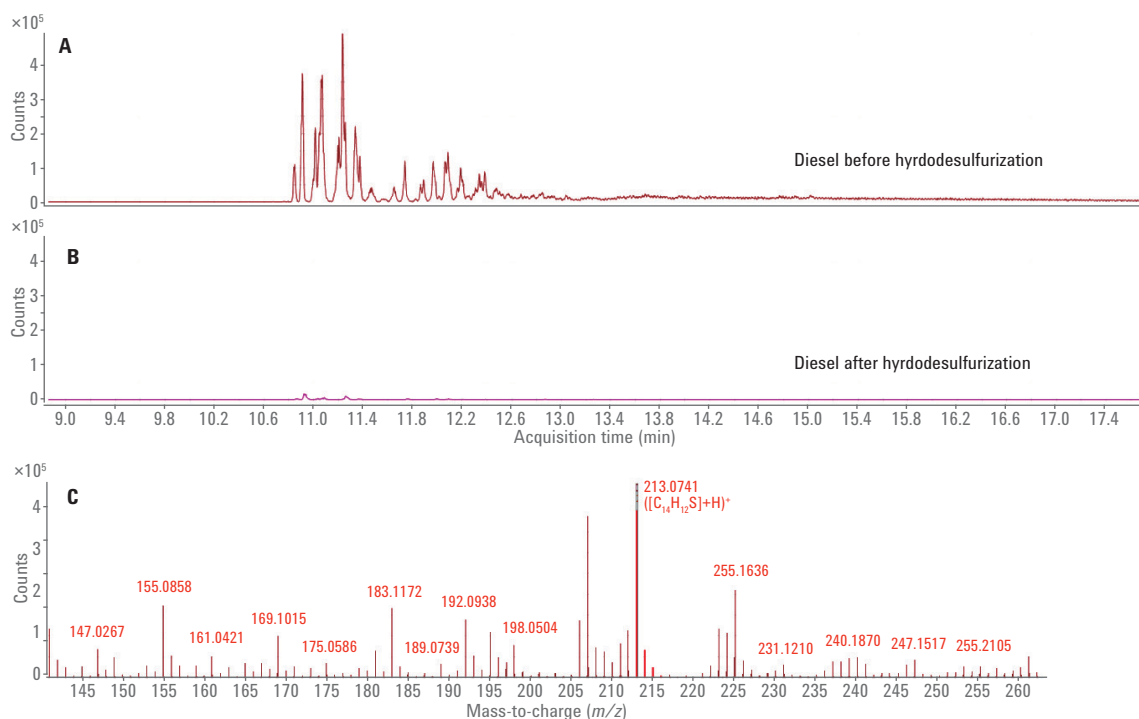


Figure 4. Extracting the dibenzothiophenes (mass defect below 0.1 amu)

Analysis of dibenzothiophenes

Figure 5 shows possible structures for dibenzothiophenes.

The use of Kendrick mass defect to identify series of related compounds is well established for complex samples^{3,4}. The Kendrick mass scale, which 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.

If we consider a homologous series of molecules of the same class and DBE, but varying degree of alkylation, members of the series will vary in composition by multiples of -CH₂, corresponding to multiples in a mass of 14.01565 Da. A particularly useful way to identify such a series is to convert the IUPAC mass to Kendrick mass. The Kendrick mass is calculated using Equation 1.

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

Equation 1

Successive members of an alkylation series will differ by 14.00000 in Kendrick mass and, therefore, each will have the same Kendrick mass defect (KMD). The Kendrick mass defect is the difference between nominal Kendrick mass and exact Kendrick mass (Equation 2).

$$\text{Kendrick mass defect (KMD)} = \text{Kendrick mass} - \text{nominal Kendrick mass}$$

Equation 2

Using this scheme, members of a given alkylation series are easily identified, and the assignments can be extended to higher masses by extrapolation.

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, and so on, increase.

We used *mMass*, a program available on the Internet that automatically calculates and plots Kendrick mass defect from raw mass spectral data (Figure 6).

Using the Kendrick mass defect plot allowed us to identify related dibenzothiophenes. The drift spectra of a series of related dibenzothiophenes are shown in Figure 7.

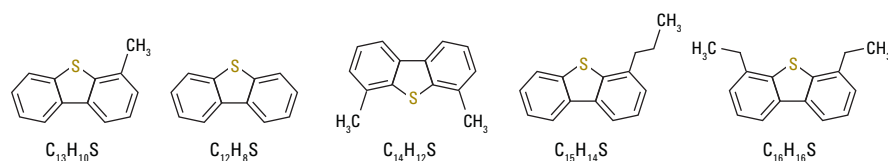


Figure 5. Possible structures of dibenzothiophenes. Note: several structural isomers are possible for each of these formulae.

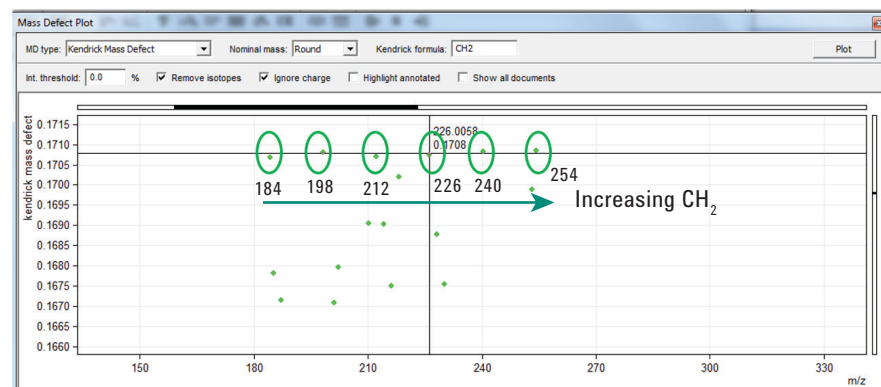


Figure 6. Kendrick mass defect plot showing series of related dibenzothiophenes with the same Kendrick mass defect.

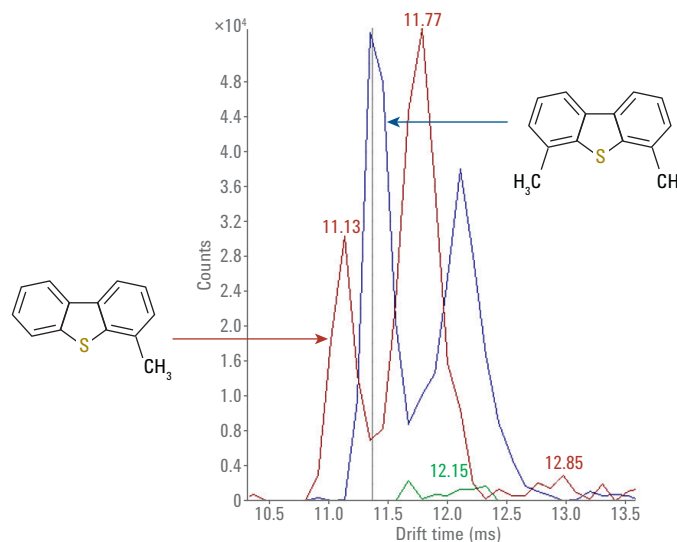


Figure 7. Drift spectra of a series of related dibenzothiophenes.

Each dibenzothiophene peak has interferences from other hydrocarbon species. This interference is revealed in the Kendrick mass defect plot, which shows unrelated compounds with the same nominal mass but different KMD on the vertical axis (Figure 8).

These unrelated interfering compounds can be separated with ion mobility (Figure 9).

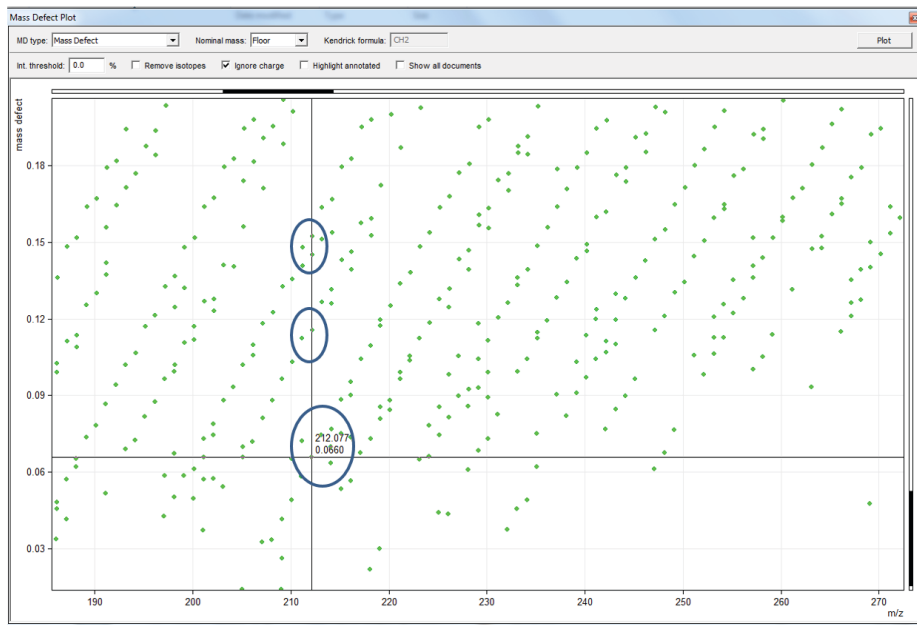


Figure 8. Kendrick mass defect plot showing background and dibenzothiophene with their respective different mass defects.

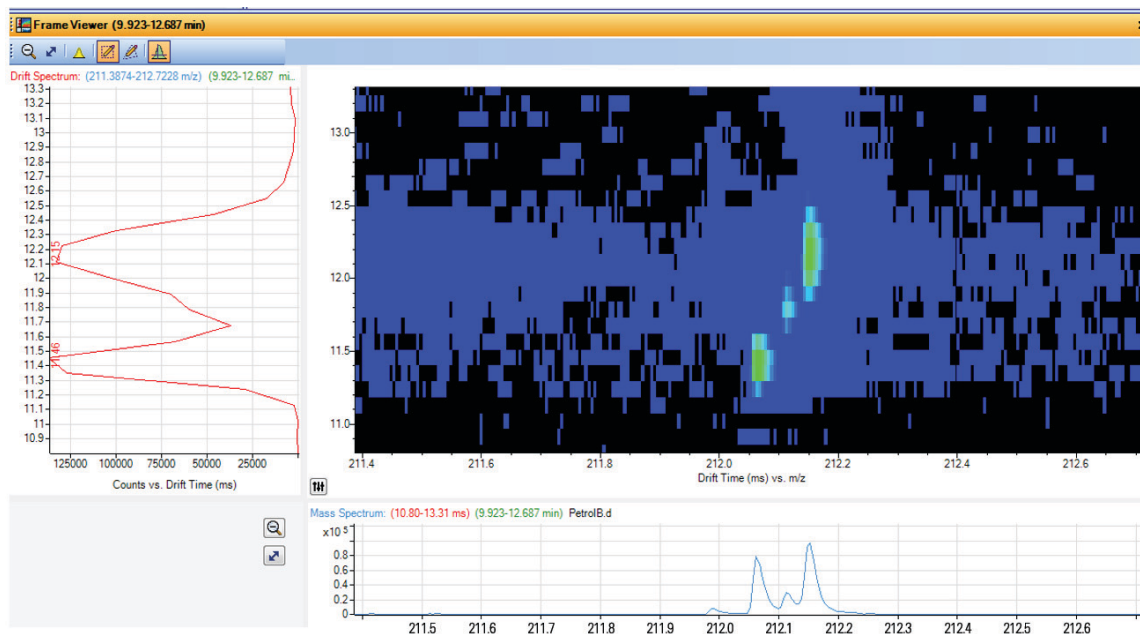


Figure 9. Ion mobility spectrum of dibenzothiophenes and other interfering hydrocarbons.

Analysis of hydrocarbons

Generally, diesel samples contain many series of hydrocarbon molecules that overlap in the same mass range, which can bring great challenges for data interpretation using conventional MS systems. By adding the ion mobility dimension of separation and using the data extraction feature in the Agilent IM browser, we easily obtain information on the ion series of interest for further study.

The Kendrick plot can also be used to observe complex patterns in the mass spectra of hydrocarbon species (Figure 10). The horizontal line in Figure 11 shows hydrocarbon species differing by a CH_2 unit but with the same DBE value. The next series of compounds on a horizontal line differ by 0.013, or 2H. These patterns are easily separated in the mobility domain, as shown in Figure 12.

Analysis of ASTM standards

In this study, we analyzed the ASTM standard compound mixture. In a very narrow GC peak at ~4.4 minutes, we found over 10 compounds, including many isomers in the mass range of 100 to 125 Da. The early eluters in the GC chromatogram have more interference and coelution of compounds in the low molecular weight range. Ion mobility provides higher peak capacity and much more detailed information about the individual species.

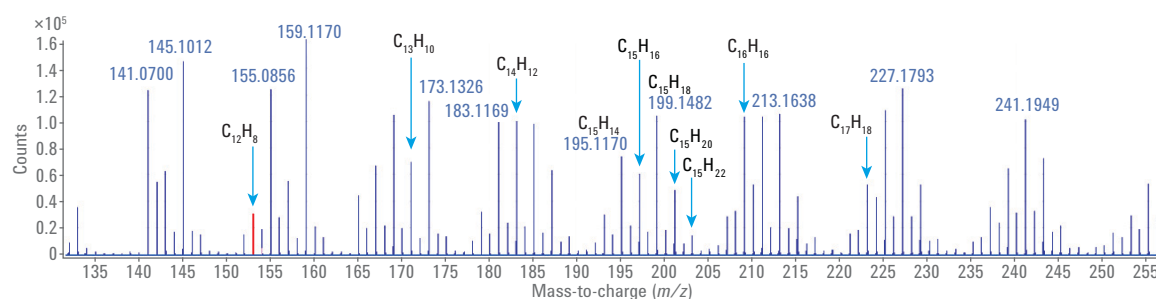


Figure 10. Hydrocarbon series differing by a CH_2 unit. The finer pattern within the series differs by 2H.

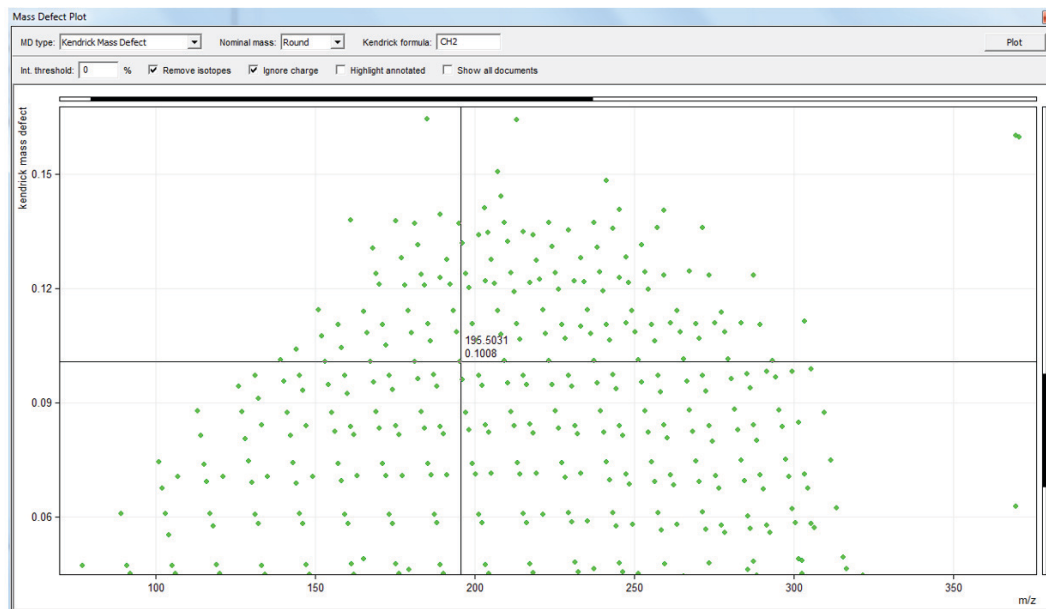


Figure 11. Kendrick mass defect plot for a series of related compounds with KMD of 0.1008.

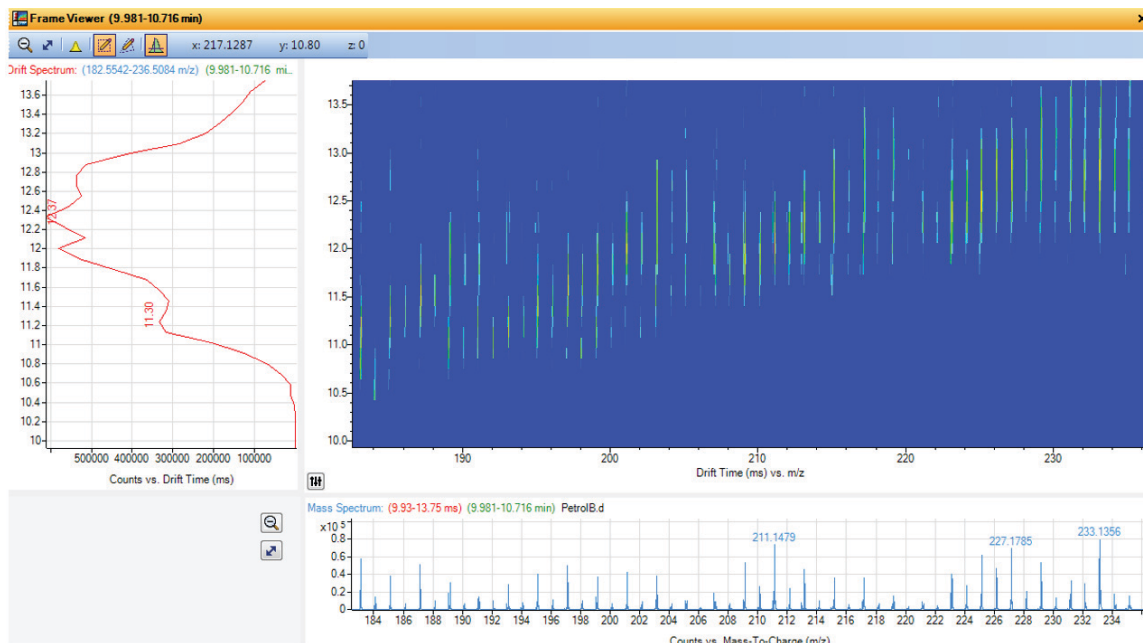


Figure 12. Ion mobility separation map for molecular weights from m/z 178 to 232.

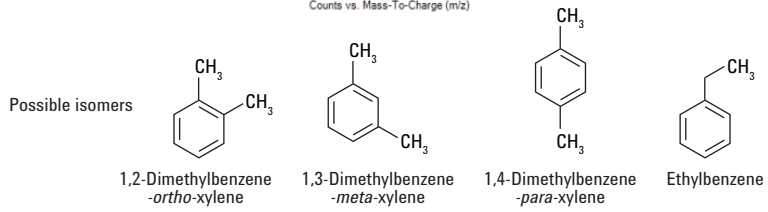
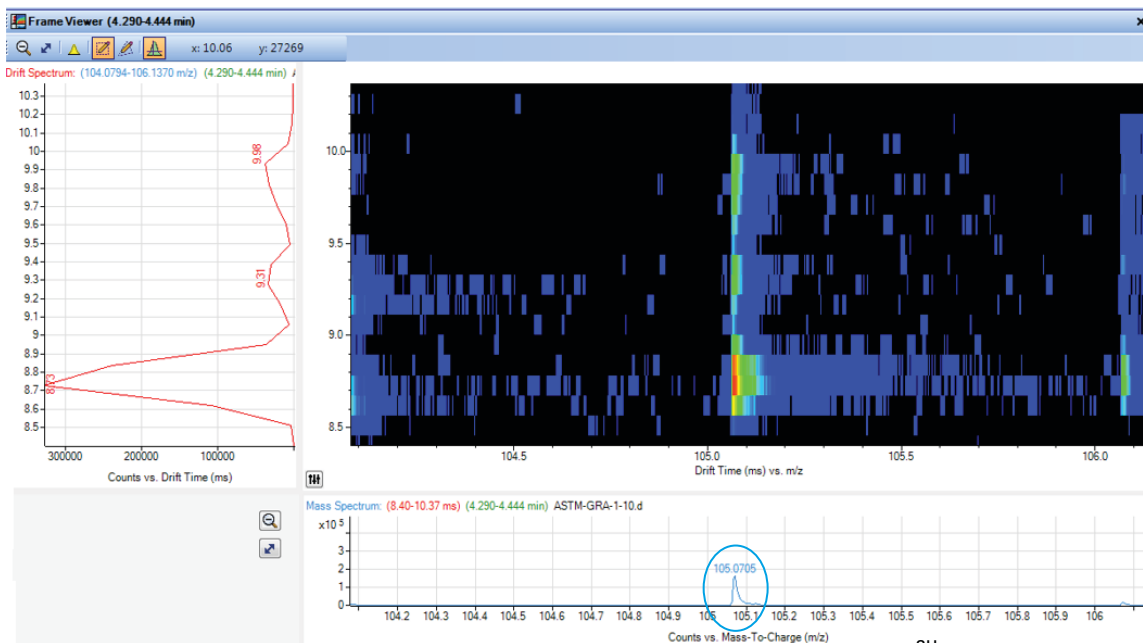


Figure 13. Possible structural isomers for C_8H_{10} .

Conclusions

Two samples of diesel fuel, before and after hydrodesulfurization, were compared. Aromatic sulfur-containing compounds were differentiated from hydrocarbons using high-resolution mass spectrometry by filtering the data on mass defect. Ion mobility offers an extra dimension in separating isobaric compounds based on drift time in this very complex mixture.

Ion series corresponding to alkylated and nonalkylated dibenzothiophenes were clearly separated, and the individual compounds were identified.

Kendrick mass defect plots were used to recognize families of homologous compounds. These plots allowed us to extract the ion series of interest for the analysis. Differential analysis of the two samples quickly revealed differences in the degree of sulfur removal between the two samples.

Various structural isomers of aromatic compounds coeluting early in the GC chromatogram were also identified.

References

1. Goodley, P.; Mohsin, S. B. The GC-APCI Interface for the Agilent Q-TOF LC/MS System Improves Sensitivity, Mass Accuracy, and Speed for a Wide Range of GC Applications. *Agilent Technologies, Inc. Technical Overview*, publication number 5991-2210EN, **2013**.
2. Jody C. M.; *et al.* Conformational Ordering of Biomolecules in the Gas Phase: Nitrogen Collision Cross Sections Measured on a Prototype High Resolution Drift Tube Ion Mobility-Mass Spectrometer. *Anal. Chem.* **2014**, *86* (4), pp 2107-2116.
3. Kendrick, E. A mass scale based on $\text{CH}_2 = 14.0000$ for high-resolution mass spectrometry of organic compounds. *Anal. Chem.* **1963**, *35*, pp 2146-2154.
4. Hughey, C. A.; *et al.* Kendrick mass defect spectroscopy: A compact visual analysis for ultrahigh-resolution broadband mass spectra. *Anal. Chem.* **2001**, *73*, pp 4676-4681.

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