ASMS 2015

MP 653

Analysis of Dibenzothiophenes in Diesel by GC-APCI Ion Mobility High-Resolution MS

Sheher Bano Mohsin[1]; David Wong[2]; F. Robert Ley[2]; [1]Agilent Technologies, Inc., Schaumburg, IL; [2]Agilent Technologies Inc., Santa Clara, CA

Introduction

This poster 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 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 to produce smog. The amount of sulfur in diesel is being driven to lower levels 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 the very complex matrix. There are thousands of different compounds in diesel, ranging from alkanes to alkenes to aromatics to 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 gas phase in the mobility cell. Ion mobility, coupled to high-resolution GC/MS, provides an extra dimension of separation based on size, charge, and shape. Larger ions traverse the drift tube at a slower rate than smaller ions resulting in gas-phase ion separation.

In this poster, we demonstrate 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
• G7890B GC with the G3212A GC-APCI interface
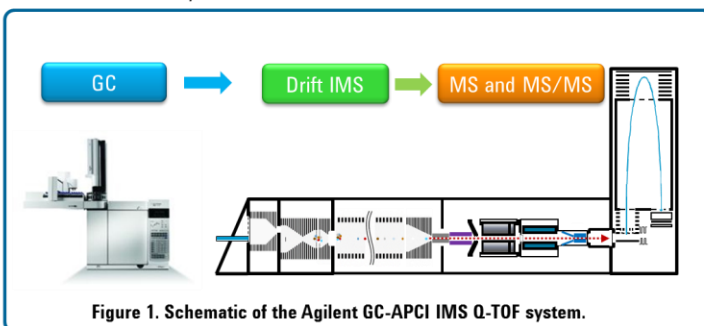• G6560A Ion Mobility Q-TOF LC/MS

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

GC and MS conditions:
Column: Agilent J&W DB-5ms, 30 m x 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 min) to 250 °C at 10 °C/min (10 min), then 300 °C at 15 °C/min (10 min).
Agilent 6560 MS source parameters for positive ion mode method:
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
GC-APCI:
A schematic of the GC-APCI IMS Q-TOF is shown in Figure 1. The setup and operation of the GC-APCI is described in detail elsewhere[1]. The source parameters for GC-APCI are listed above.
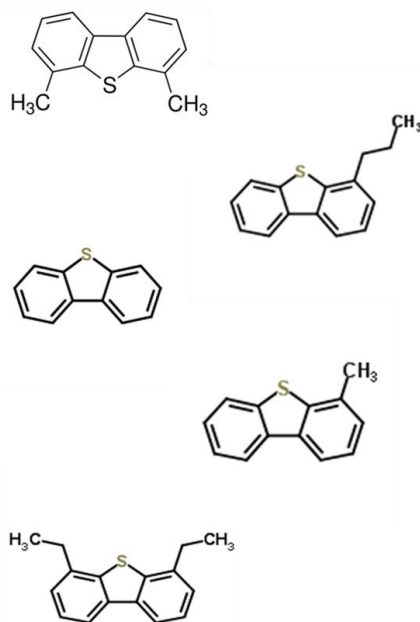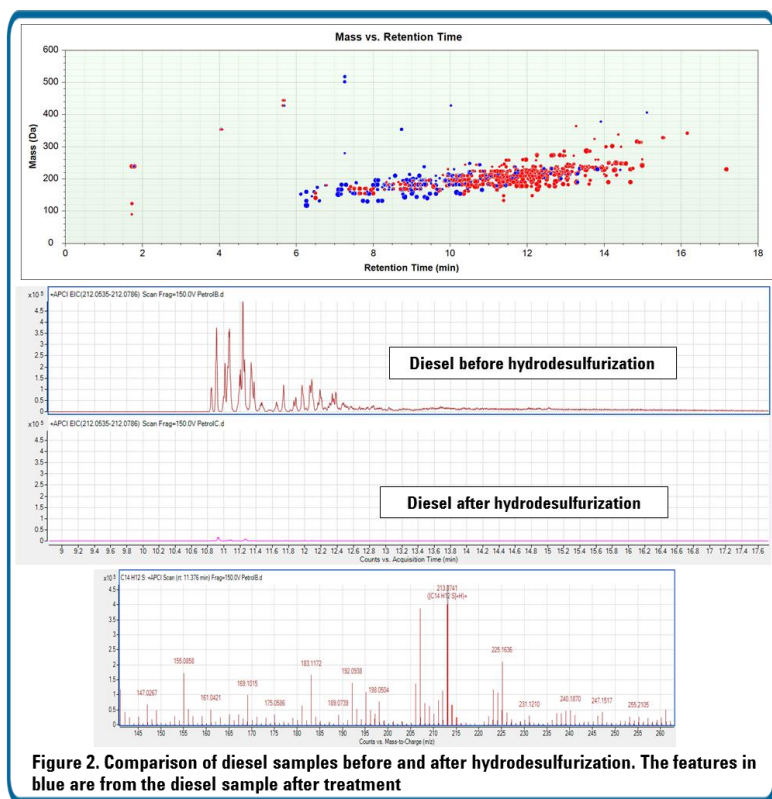**IMS Q-TOF:**
The Agilent 6560 IMS Q-TOF is a Q-TOF LC/MS system that can be run in either ion mobility mode or Q-TOF only mode. It consists of a trapping funnel, drift tube, and rear funnel between the front funnel and ion optics leading to the quadrupole mass filter. This design builds on the well-established 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. 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.

Agilent Technologies

Results and Discussion

Figure 2. 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 the bottom panel of Figure 2. A plot of an extracted ion chromatogram with a mass defect window set to mass defects below 0.1 amu. The top chromatogram 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 (bottom chromatogram) lacks these peaks. The mass spectrum of a region in the chromatogram of the untreated sample around 11.56 minutes' retention time is shown in Figure 4. The peak at 213 m/z, with its isotopic fit (superimposed in red), is indicative of dibenzothiophene species.

Figure 2. Comparison of diesel samples before and after hydrodesulfurization. The features in blue are from the diesel sample after treatment

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

By coupling the GC to the IM Q-TOF, we created an analytical system with much greater separation power for these types of complex compound analysis. 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 3 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.
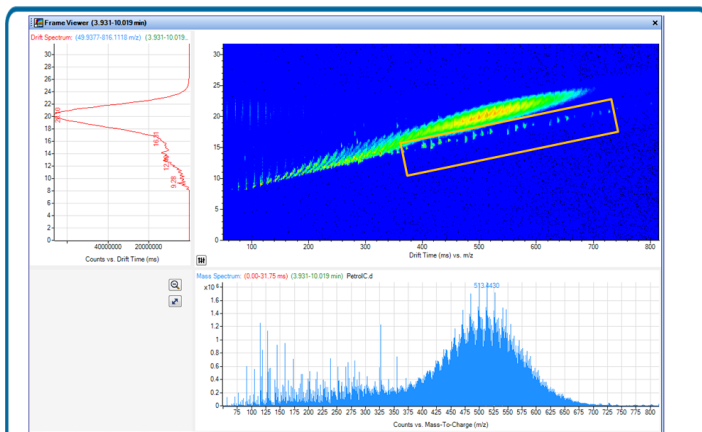
Results and Discussion

Figure 3. Compounds separated according to carbon number in the drift-time domain. The orange rectangle shows the area of column bleed, which has shorter drift times than the hydrocarbons and separates out.
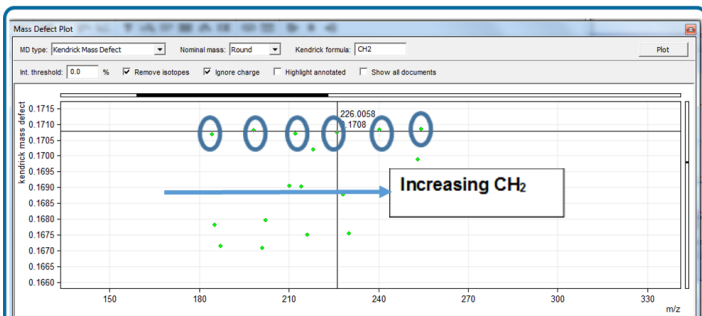

Figure 4. Kendrick mass defect plot showing series of related dibenzothiophenes with the same Kendrick mass defect.
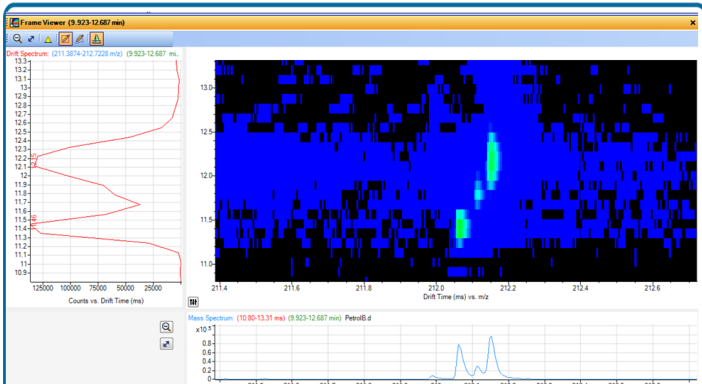

Figure 5. Ion mobility spectrum of dibenzothiophenes and other interfering hydrocarbons

The use of Kendrick mass defect to identify series of related compounds is well established for complex samples [2] 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. Using this scheme, members of a given alkylation series are easily identified and the assignments can be extended to higher masses by extrapolation.

We used mMass, a program available on the Internet that automatically calculates and plots Kendrick mass defect from raw mass spectral data. Using the Kendrick mass defect plot allowed us to identify related dibenzothiophenes (Figure 4). Each dibenzothiophene peak has interferences from other hydrocarbon species. These interferences can be revealed in the Kendrick mass defect plot, which shows unrelated compounds with the same nominal mass but different KMD on the vertical axis. These unrelated interfering compounds can be separated with ion mobility (Figure 5).

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. Technical overview, Agilent Technologies, Inc. Publication number 5991-2210EN, 2013.
2. Kendrick, E. (1963) A mass scale based on CH2 = 14.0000 for high-resolution mass spectrometry of organic compounds. Anal. Chem. 1963, 35, 2146–2154.

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 just 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 the differences in the degree of sulfur removal between the two samples.

Agilent Technologies