Application Note # FTMS-41

Analysis of Gas Oil by GC/APCI FTMS

Introduction

Fuel oil is a fraction obtained from petroleum distillation, either as a distillate or a residue. It is made up of long hydrocarbon chains, and contains alkanes, cycloalkanes and aromatics. Different types of fuel oil are classified according to their boiling point, composition and purpose (e.g. gas oil) and vary in their alkyl chain length by 50 carbon atoms. Mass spectrometry is one of the major analytical tools to identify hydrocarbons and characterize impurities. These impurities contain hetero atoms such as nitrogen or sulfur. Due to environmental regulations of impurities (especially sulfur containing compounds) in gas and fuel oil, the detection and identification of these compounds is becoming more and more important.
The ultra-high resolving power, mass accuracy and high dynamic range of Fourier Transform Mass Spectrometry (FTMS) improved the identification and detection of low-abundance impurities in these kind of samples. Techniques such as gas chromatography (GC) or liquid chromatography (LC) can be used to separate isomers which cannot be distinguished only by mass using direct infusion measurements. In this study, GC was coupled to an FTMS instrument using a GC/APCI source to separate and detect isomers and quantify impurities in gas oil.

Experimentals

Mass spectra were acquired using a solariX 12 T FT-ICR mass spectrometer (Bruker) equipped with a GC/APCI source (Bruker) in positive ion mode (Figure 1) and coupled to a GC system. To separate compounds of this extremely complex mixture, 1 µL of a 1:100 dilution of gas oil in dichloromethane was injected splittless. A temperature gradient between 5 and 10 °C/min was used with a HP-5 ms, 30 m, 0.25 mm ID, 0.25 µm film thickness column. Spectra were acquired at 1 Hz using 2 MW data points with a mass range m/z 73-1000, resulting in a resolving power of about 300,000 at m/z 200 with mass accuracies in the ppb range. Extracted ion chromatograms (EICs) with 1 mDa mass tolerance were calculated to identify isomers of a homologous series of alkylated benzothiophenes and dibenzothiophenes.

Results

APCI in combination with GC is an effective method for analysing substituted hydrocarbons, polycyclic aromatic hydrocarbons (PAH), and nitrogen and sulfur containing compounds. We focused in this study on sulfur containing compounds, especially thiophenes. A large number of isomers from a homologous series of alkylated benzothiophenes and dibenzothiophenes were detected

GC/APCI FTMS

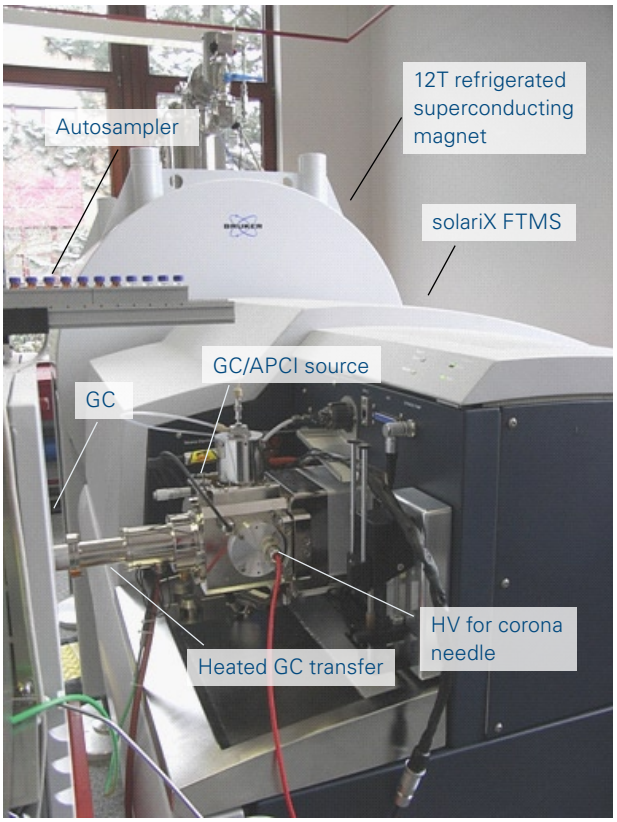

Figure 1: GC with autosampler coupled to a 12T solarix FTMS system using a GC/APCI source.

Highly complex sample

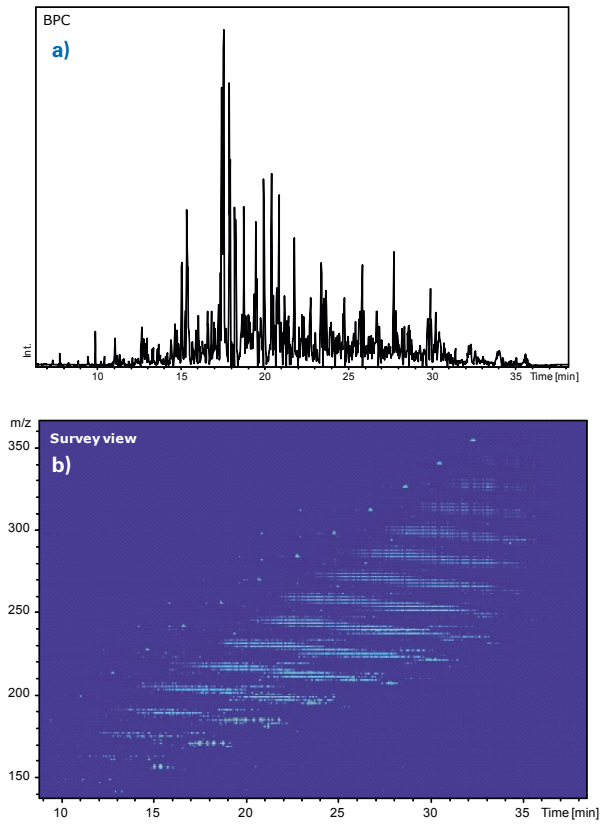

Figure 2: a) Base peak chromatogram and b) survey view of gas oil measured by GC/APCI showing the high complexity of this sample.

in gas oil using GC/APCI-FTMS. The complexity of the sample is indicated in Figure 2, which shows the base peak chromatogram (BPC) (Figure 2a) and the survey view (a plot of RT vs. m/z using a color coding for the intensity) (Figure 2b). The complexity of the compounds of higher mass is due to the rise in the number of possible chemical isomers due to the increase of the length and number of alkyl residues (Figure 3a and 3b).

The carbon number distributions of the homologous series of benzothiophenes and dibenzothiophenes were also compared with direct infusion APCI measurements (Figure 3c and 3d) of the same sample. We observed that GC/APCI and infusion APCI measurements result in different carbon distribution pattern due to (a) GC/APCI detecting compounds with lower boiling points than those detecting by APCI direct infusion and (b) ion suppression effects in direct infusion measurements caused by the high complexity of the sample (various isomers, isobars and compound classes). Co-eluting species with a mass difference of only 3.4 mDa were separated by the high resolving power of the FTMS technique (Figure 4). Thanks to the ability of GC to separate isomers, the intensities obtained from members of a homologous series can be used for a quantification approach of sulfur compounds in gas oil.

Summary

GC/APCI is a sensitive technique for detecting small volatile compounds with very accurate mass measurement. We have shown that sulfur containing compounds such as benzothiophenes and dibenzothiophenes can be detected and quantified in gas oil samples. Chemical isomers of these compound classes can be separated by gas chromatography and detected using ultra-high resolving power and the mass accuracy of FTMS. Ultra high resolving power is needed in very complex samples to separate isobars with a mass difference of only 3.4 mDa, which corresponds to the exact mass difference between C_3 and SH_4.

Carbon number distributions

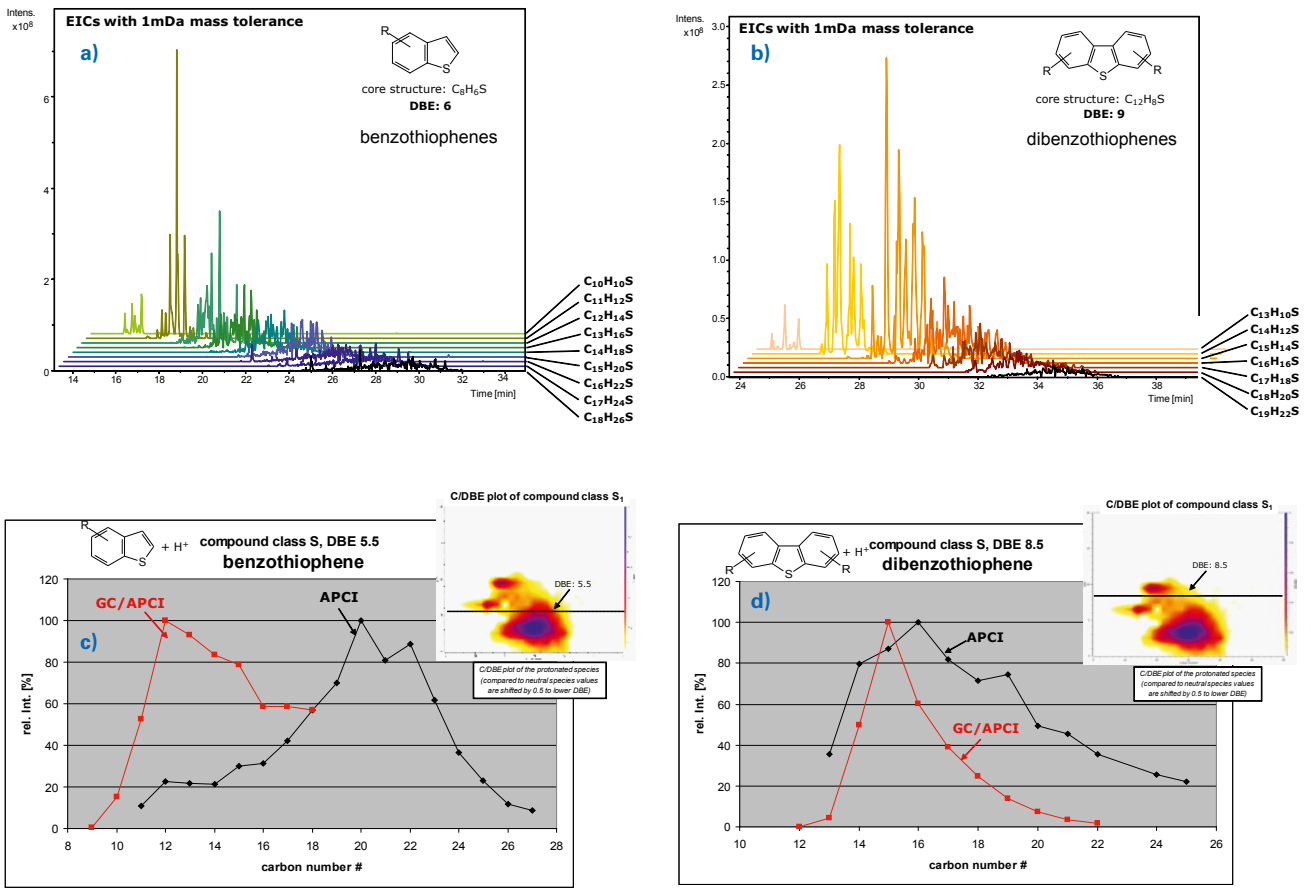

Figure 3: EICs of the homologous series of a) benzothiophenes and b) dibenzothiophenes. Comparison of GC/APCI and direct infusion APCI results of the carbon number distribution of the homologous series of c) benzothiophenes and d) dibenzothiophenes C/DBE plot of the compound class S_1 of the direct infusion APCI results.

High separation power

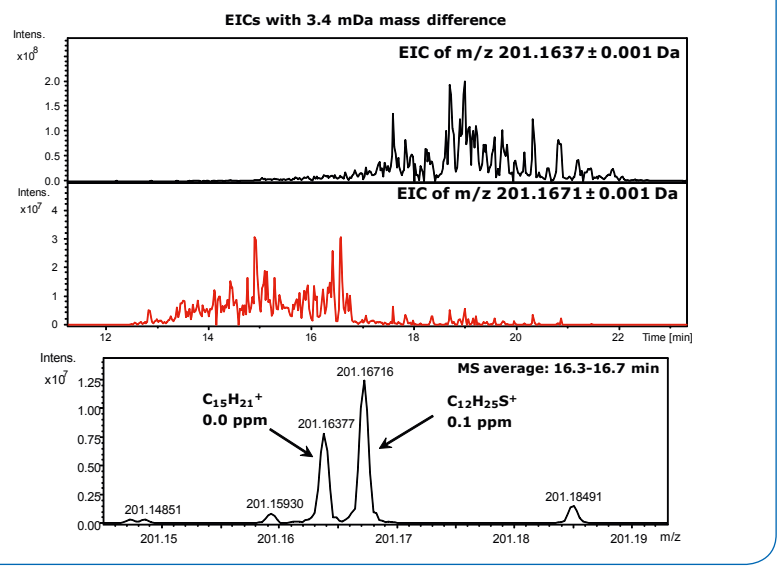

Figure 4: Example of EICs with a mass difference of only 3.4 mDa. Averaging mass spectra between retention time 16.3 min and 16.7 min results in the mass spectrum containing both compounds ($C_{15}H_{21}^+$ and $C_{12}H_{25}S^+$).

Authors

Matthias Witt, Thomas Arthen-Engeland, Bruker Daltonik GmbH.

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Instrumentation & Software
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DataAnalysis 4.0
GC/APCI source

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Bruker Daltonik GmbH

Bremen · Germany
Phone +49 (0)421-2205-0
Fax +49 (0)421-2205-103
sales@bdal.de

Bruker Daltonics Inc.

Billerica, MA · USA
Phone +1 (978) 663-3660
Fax +1 (978) 667-5993
ms-sales@bdal.com

www.bruker.com/ftms