Characterization of petroleum samples via thermal analysis coupled to APCI MRMS

Abstract

Thermal analysis, by means of a thermo balance (TG), was coupled to an atmospheric pressure chemical ionization source especially designed for gas phase analysis (Bruker GC-APCI II). Ultra-high resolution mass spectrometric analyses were done by an apex II Qe FT-ICR-MS (Magnetic Resonance Mass Spectrometer, MRMS).

Besides a fatty acid standard mixture (FAME) different petroleum samples were analyzed, such as a diesel fuel, a heavy fuel oil (HFO) and a crude oil. The petroleum samples revealed a high complex evolved gas mixture. Coupling of thermal analysis enables the analysis of heavy petroleum fractions, which are difficult to measure by gas chromatography. After thermo desorption at a certain tempera-

ture of roughly 300 - 350 °C, pyrolysis start to occur and the sample decompose. Decomposition products can be used for structural elucidation. Furthermore, a simulated distillation pattern can be recorded. Ultra-high resolution mass spectrometric detection enables the calculation of temperature profiles of individual molecular species as well as of chemical classes or double bond equivalent (DBE) groups.

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Key advantages of the thermal analysis are the minimal sample amount needed (less than 2 mg), no sample preparation steps as well as the opportunity to analyze high viscous and solid samples directly. Compared to the direct inlet probe (DIP, from Bruker available for the direct infusion APCI source) higher temperatures can be accessed up to 1000 °C (600 °C with aluminum crucible).

Introduction

The detailed chemical characterization of petroleum fractions is still an analytical challenge. Besides spray based sample delivery and ionization techniques, such as direct infusion ESI, APPI and APCI, evolved gas analysis (EGA) is a complementary approach. In thermal analysis a specific physical property, such as heat flux or mass, is measured, while a defined temperature program is applied. The sample heating will lead to vaporization and decomposition processes. The released evolved gas mixture can

be analyzed, e.g. by mass spectrometry, which offers an analytical tool to identify the molecular composition. With thermal analysis, employing a thermo balance, high temperatures are accessible, e.g. the pyrolysis regime above 300-350 °C. At lower temperatures in the desorption phase the vaporizable compounds of the mixture are evaporated and can be analyzed as intact molecules. In the pyrolysis phase complex molecular structures decompose and fragment characteristically providing access to structural information. The ultra-high resolving power, mass accuracy and high dynamic range of Fourier Transform Mass Spectrometry (MRMS) allow a sensitive detection and the assignment of elemental composition of individual species in a complex mixture. In this respect atmospheric pressure chemical ionization (APCI), which is highly sensitive towards polar species, allows the detection of certain compound classes, which cannot be ionized by ESI, such as polycyclic aromatic hydrocarbons (PAH) and their

sulphur and nitrogen containing derivatives. In this study, we show the capabilities of thermal analysis coupled to MRMS equipped with a gas phase APCI source for the analysis of petroleum samples.

Method and Material

A thermo balance (TG 209, Netzsch Gerätebau GmbH, Selb, Germany) was coupled to the GC-APCI II source (Bruker) via a heated transfer line (Figure 1) as described elsewhere (1). Mass spectra were acquired using an Apex Qe 7 T MRMS (Bruker) in positive ion mode. A temperature program from 20 to 600 °C with a 10 K/min gradient was used (~ 1 h). The samples were directly placed in an aluminum crucible and the mass loss curve was recorded from the TG. The oil samples were diluted in dichloromethane for easier handling. Roughly, 1 mg petroleomic sample material was used. Spectra were acquired from m/z 100-1000 with 2 MW data points and five spectra averaging resulting in an
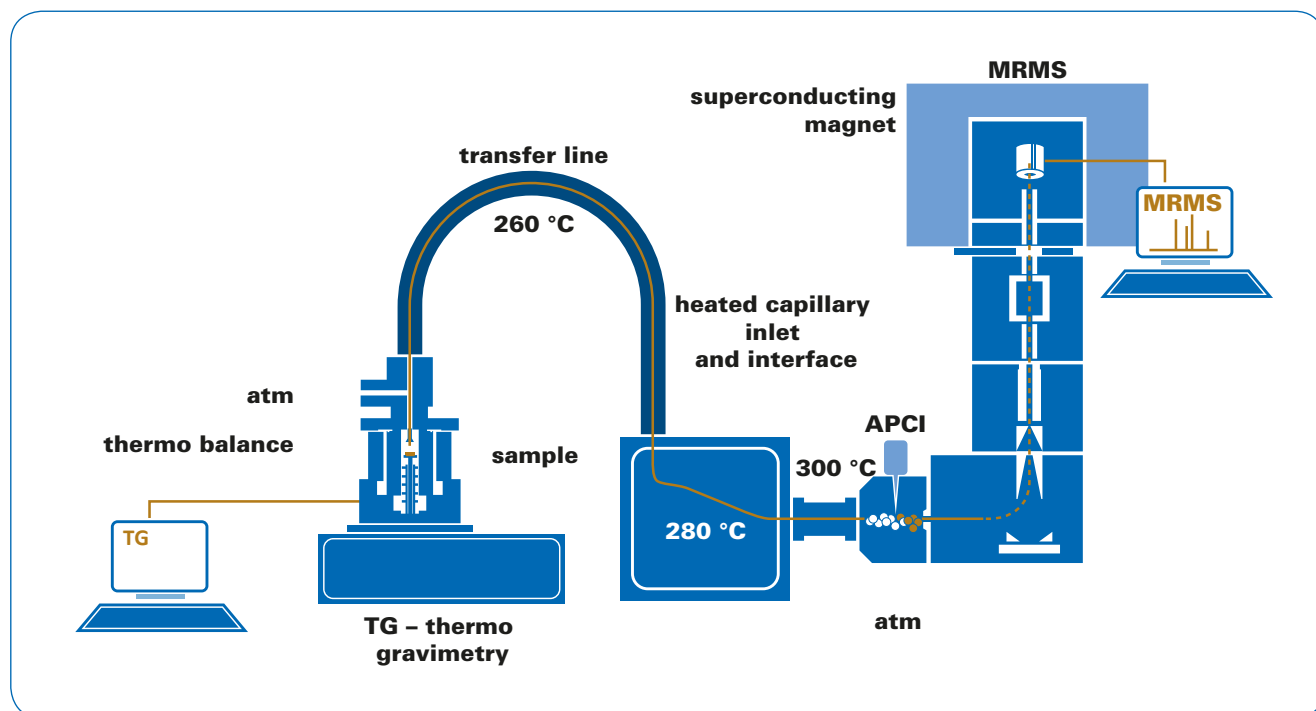

Fig. 1: Schematic representation of a TG coupled to a 7 T apex II ultra MRMS system using a GC-APCI II source.

acquisition frequency of approximately 0.4 Hz and a resolving power of about 260,000 at m/z 200. A fatty acid methyl ester standard mixture (FAME Mix, Sigma-Aldrich), a diesel fuel (DIN EN 590), a heavy fuel oil (HFO) and a crude oil (Greek crude) were investigated. Data were pre-processed (peak picking and m/z calibration) and exported using Data Analysis software (DA 4.0, Bruker) and processed utilizing self-written Matlab (MATLAB R2016a) scripts. Elemental compositions were assigned within a 2 ppm error range and the following restrictions: $C_{6-100}H_{6-200}N_{0-2}O_{0-10}S_{0-2}$. A comparable data processing approach was utilized in literature for GC-APCI data (2,3).

Results and Discussion

Evolved gas analysis, by means of thermal analysis coupled to mass spectrometry, is a powerful tool for insights into complex samples. The general application of TG-MRMS utilizing a GC-APCI II source for ionization in the framework of petroleum analysis is shown. The unbeaten resolving power and mass accuracy enables a characterization at the molecular level. Figure 2, the survey view (a plot of temperature versus m/z using a color coding for the intensity) represent the complexity of the investigated oil samples.

Several hundred features (elemental compositions with an individual temperature evolution profile) were detected for the diesel fuel and thousands for the HFO and crude oil, respectively. The evolved mixture spans a mass range from the lower acquired m/z boundary at 100 (for the diesel fuel) and up to 750 m/z for the crude oil and the HFO. The high resolution mass spectrometer allows an assignment of elemental compositions to the evolved mixture. The
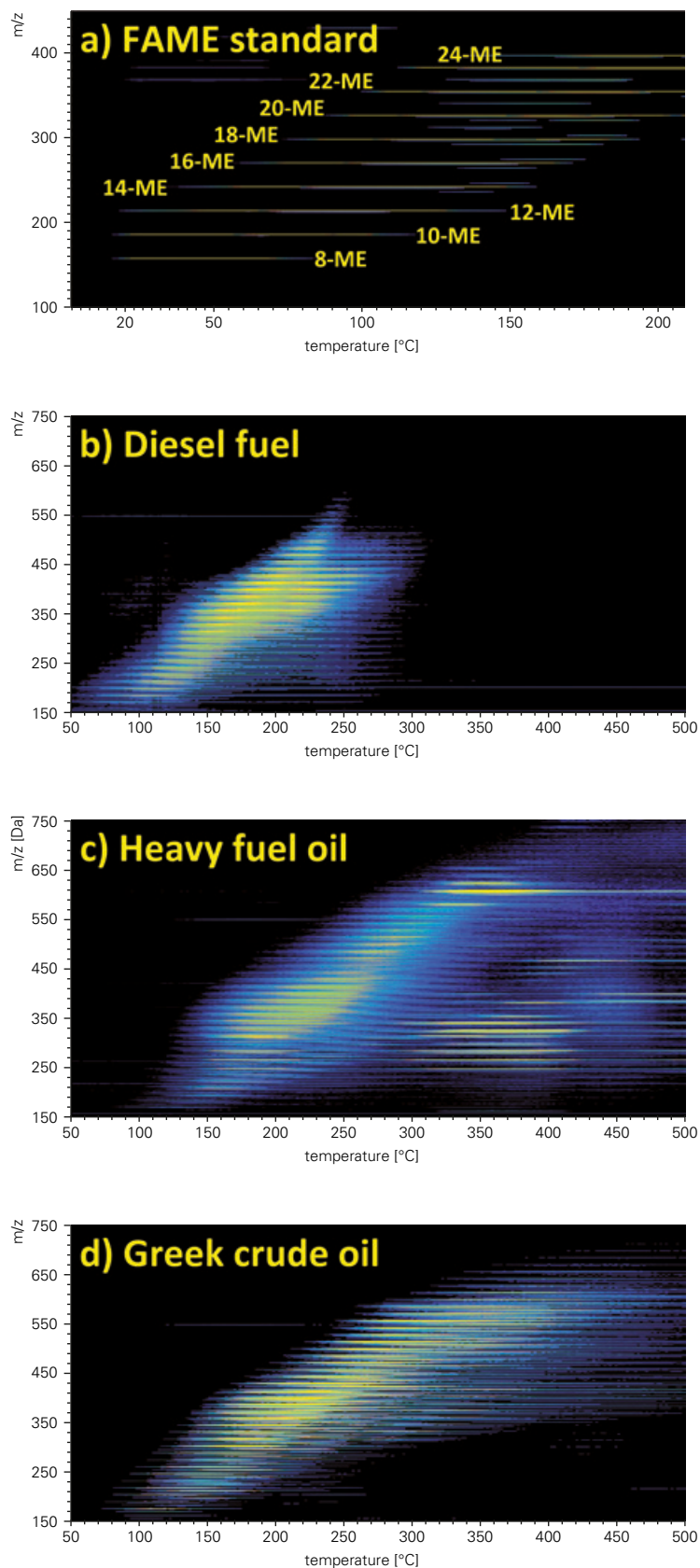

Fig. 2: Survey view of a) FAME standard, b) diesel fuel, c) heavy fuel oil and d) Greek crude oil measured by TG-APCI FT-MS. The high complexity and mass range of the petroleum samples is shown.
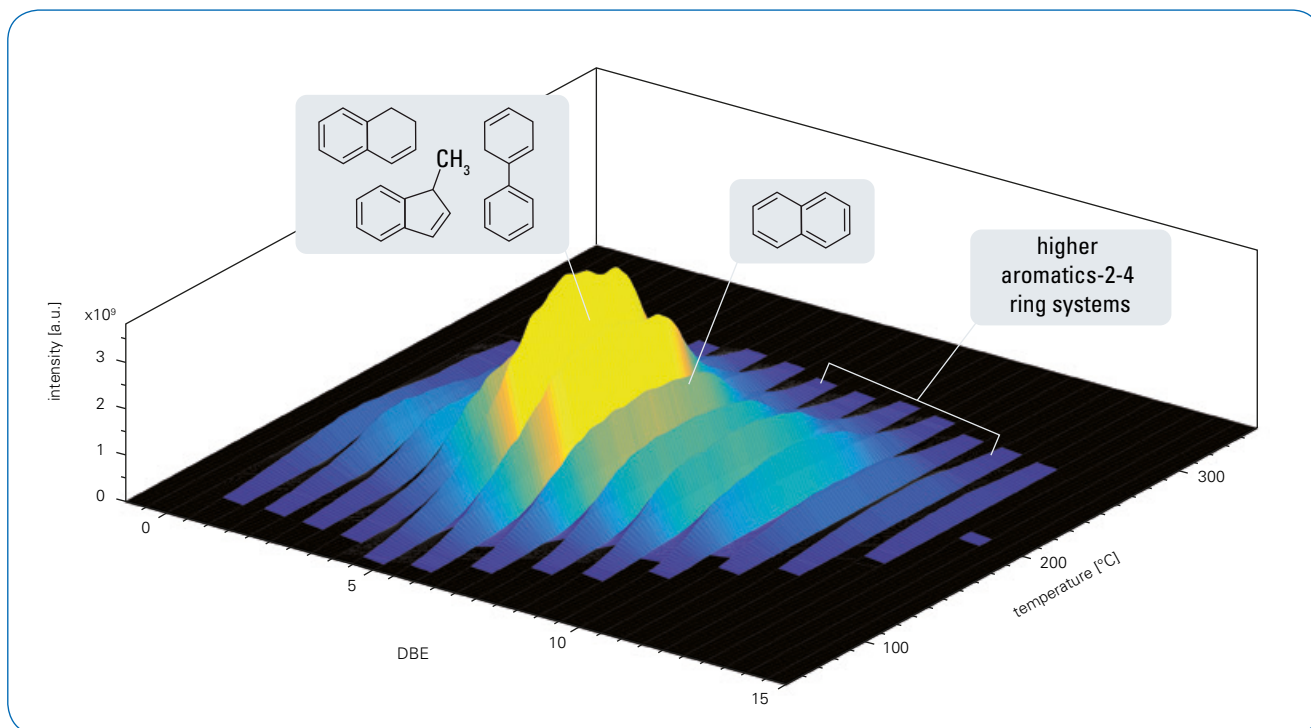
Fig. 3: Three dimensional visualization of the double bond distribution evolved over temperature for a diesel TG-MRMS measurement. Intensity is color coded and a selection of potential structures is given.
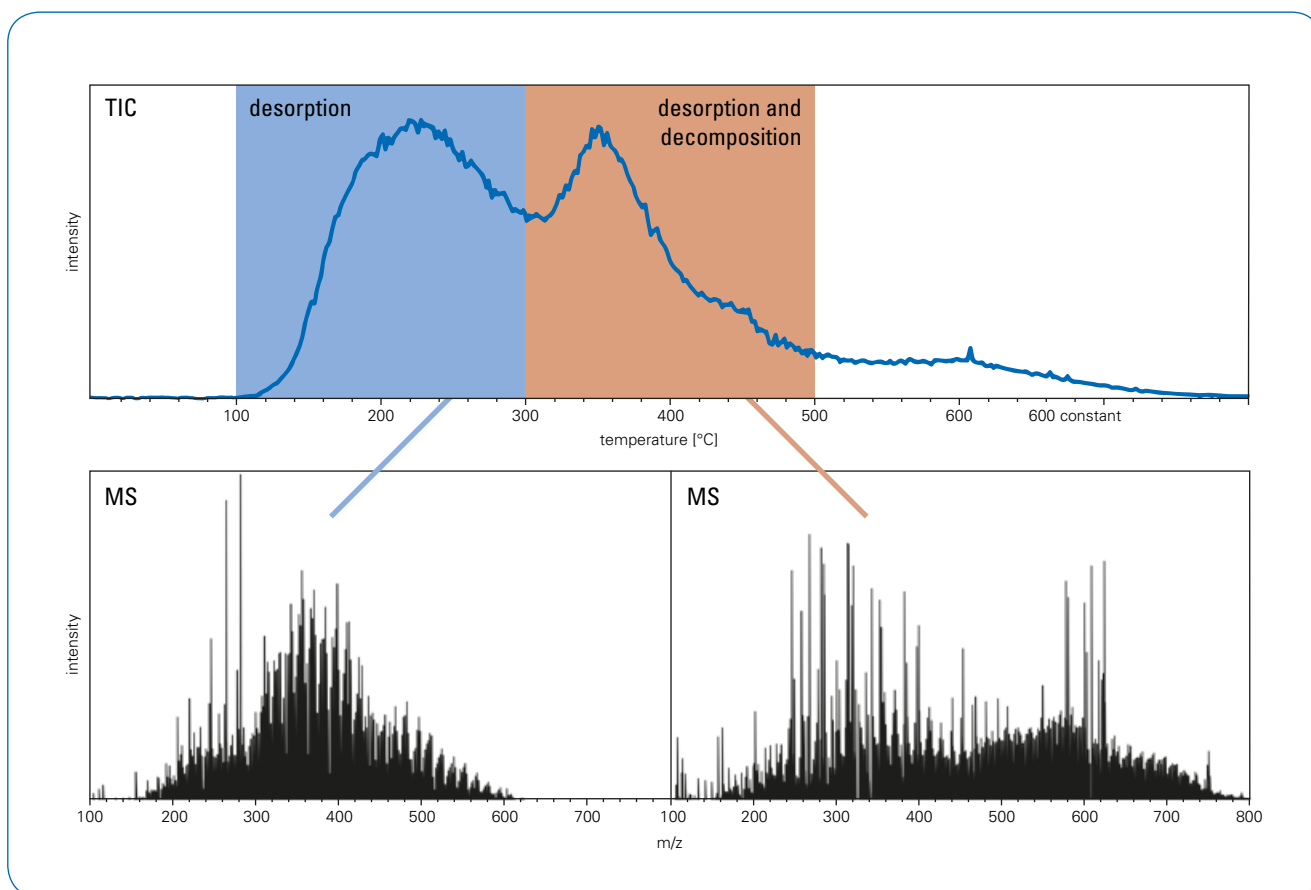

Fig. 4: Total ion count chromatogram with marked area of the desorption and desorption/pyrolysis phase for the heavy fuel oil TG-MRMS measurement. Averaged mass spectra of the marked areas are given below.

diesel fuel reveals a high abundance of CH-, CHO_1- and CHO_2-class species, whereas the heavy fuel oil exhibit mainly CH and CHS-class species. The double bond equivalent (DBE) can be used for molecular interpretation of the results. In figure 3 a temperature resolved visualization of the DBE pattern evolved from the diesel fuel sample is shown.

As common thermal behavior of high boiling fuels with some non volatile residues thermal analysis revealed a desorption and pyrolysis phase (Figure 4). The pyrolysis phase is characterized by a shift in molecular pattern towards smaller m/z, which is caused by decomposition products from larger molecular structures. In Figure 4 the shift in pattern can be seen in the averaged mass spectra for the 300 - 500 °C temperature range. A high proportion of CHO_x-class compounds is detected during pyrolysis.

The decomposition pattern is overlaid with the desorption of heavier species, extending the upper m/z. Due to the complex mixture, both phases are not completely separated.

Conclusion

Thermal analysis coupled to ultra-high resolution mass spectrometry enables the detailed temperature resolved chemical characterization of the evolved gas mixtures on the molecular level. It can be used as complementary technique to direct infusion experiments or GC-APCI. Additional information is gained due to higher temperatures feasible with the thermo balance, e.g. pyrolysis fragments can give structural information about larger molecular entities. APCI is a sensitive technique for detecting the polar and medium-polar species released during the heating process. We have shown that TG-APCI MRMS can be applied for various petroleum samples from different distillation ranges. Ultra-high resolution was needed to differentiate between the chemical species in the complex evolved mixture.

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