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Application of pyrolysis–mass spectrometry and pyrolysis–gas chromatography–mass spectrometry with electron-ionization or resonance-enhanced-multi-photon ionization for characterization of crude oils

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HIGHLIGHTS

- Gas chromatography setup with two MS detectors applying different ionization methods.
- In parallel structural information and sensitive detection of aromatic species.
- Characterization of setup and application for crude oil samples.
- Detection of polycyclic aromatic hydrocarbons next to sulfur containing aromatics.

GRAPHICAL ABSTRACT
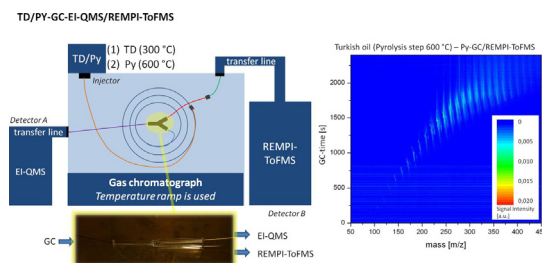
ABSTRACT

A novel analytical system for gas-chromatographic investigation of complex samples has been developed, that combines the advantages of several analytical principles to enhance the analytical information. Decomposition of high molecular weight structures is achieved by pyrolysis and a high separation capacity due to the chromatographic step provides both an universal as well as a selective and sensitive substance detection. The latter is achieved by simultaneously applying electron ionization quadrupole mass spectrometry (EI-QMS) for structural elucidation and [1 + 1]-resonance-enhanced-multi-photon ionization (REMPI) combined with time-of-flight mass spectrometry (ToFMS). The system has been evaluated and tested with polycyclic aromatic hydrocarbon (PAH) standards. It was applied to crude oil samples for the first time. In such highly complex samples several thousands of compounds are present and the identification especially of low concentrated chemical species such as PAH or their polycyclic aromatic sulfur containing heterocyclic (PASH) derivatives is often difficult. Detection of unalkylated and alkylated PAH together with PASH is considerably enhanced by REMPI–ToFMS, at times revealing aromatic structures which are not observable by EI-QMS due to their low abundance. On the other hand, the databased structure proposals of the EI-QMS analysis are needed to confirm structural

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information and isomers distinction. The technique allows a complex structure analysis as well as selective assessment of aromatic substances in one measurement. Information about the content of sulfur containing compounds plays a significant role for the increase of efficiency in the processing of petroleum.

1. Introduction

With the increasing consumption of crude oil and decreasing reserves fractions with higher boiling points will have to been used in the future. They are more complex and composed different than traditional commercial crude oils [1–3]. Aromatic compounds, especially polycyclic aromatic hydrocarbons (PAH) play an important role in fossil fuels and their byproducts. They are considered to be environmental pollutants causing risks to the human health [4,5]. PAH and their alkylated homologues can be persistent and nearly resistant to biodegradation, this holds especially for higher molecular compounds [6,7]. As referred by Mullins et al. [8] in heavy oil feedstock the content of high molecular species as well as the aromaticity increases. The fractions of compounds containing sulfur, often in the form of PAH analogues (polycyclic aromatic sulfur containing heterocycles, PASH) are increasing as well. All this causes problems with the refinery process, desulfurization and storage, which is the reason that these procedures are getting more and more complicated. PASH and PAH are similar in properties and they often have the same nominal mass [9]. The most dominant representatives of PASH in crude oils are thiophene, benzothiophene (BT), dibenzothiophene (DBT) and benzonaphtothiophene (BNT) [10]. In the last years, there has been much research dedicated to the separation and detection of PAH and PASH using GC based techniques [4,9,12,13], but especially for the high molecular fraction new analytical techniques or methods are still needed.

Crude oil is a supercomplex sample [1] of different chemical species. Therefore, the identification and quantification of individual compounds is difficult. As a consequence, there is the need to develop efficient methods to characterize heavy crude oil fractions and to get structural information. Often the low concentrations of many constituents are challenging in this context [14]. The structural diversity is extremely increasing when moving to higher boiling point components. This could be targeted with the help of SARA separation, whereby crude oil is divided into saturated, aromatic, resin and asphaltene fractions [15]. The molecular nature of the latter is still relatively unclear [16]. The main components will be represented by aromatic nuclei, that carry alkyl and alicyclic systems with heteroelements, whereby the aromaticity and the proportion of heteroelements increases over this lower-boiling fraction [17].

It requires a high degree of resolution power and selectivity to analyze crude oil. A variety of analytical systems and methods are available. An overview of chromatographic and mass spectrometric methods is given by Herod et al. [12]. A coupling of high-performance systems is desirable to get as much information as possible with one measurement cycle. It is possible to use selective methods such as high-resolution mass spectrometry (HRMS) in combination with photo ionization (PI) and no chromatographic separation as an intermediate step. Special types of PI have a high selectivity and can be coupled directly to an oven (thermal analysis) or a pyrolysis system [18–21]. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICRMS), which is characterized by achieving a very high mass resolution, can also be applied without prior chromatographic separation, mostly combined with electron ionization (EI) or electrospray ionization (ESI)

[2,3,22,23]. On the other hand, a chromatographic separation is required, if MS with low selectivity and resolution is used. Especially, when multidimensional GC (GC $\times$ GC) is applied the analytical resolution power increases extremely [21,24–27]. Time-of-flight mass spectrometry (ToFMS) has been employed as detection method for GC $\times$ GC based investigations of crude oil or oil-like samples [25,27].

EI ionization in combination with chromatography is nevertheless very powerful and is still used frequently. It is a hard ionization technique, because the kinetic energy of the electrons is typically above the ionization energy of organic molecules, resulting in fragmentation. Albeit the molecular information then often is lost, the fragmentation pattern is characteristic for each chemical compound and available in mass spectrometric libraries for comparative purposes. The lack of the molecular ion signal can be prevented or reduced by soft ionization techniques such as chemical ionization, field ionization and photo ionization (PI). One such PI technique is the resonance-enhanced-multi-photon ionization (REMPI) technique. Especially for the one-dimensional GC coupled with multi-photon ionization mass spectrometry, there are promising developments in terms of selectivity and sensitivity [28–31]. Its selectivity depends on the used photon wavelength and additionally on the UV absorption bands as well as on the ionization energy threshold, since the molecules absorb two photons via an intermediate state [32–35]. REMPI in combination with ToFMS is a useful method for trace analysis and shows a very high selectivity and sensitivity for polycyclic aromatic hydrocarbons [19,29,36–39].

Eschner et al. [27] developed a quasi-simultaneous acquisition of hard EI- and soft single photon ionization mass spectrometry (SPI-MS) for GC/MS analysis by rapid switching between both ionization methods. The system has been successfully applied to diesel fuel, which consists largely of volatile components. It is obvious to transfer this approach to a coupled system utilizing REMPI-MS instead of SPI-MS. Therefore, in this work an analytical system has been developed, that is able to break high molecular weight structures efficiently. With its high separating capacity it provides a universal, but also selective and sensitive substance spectrum. For the sample injection or break down a pyrolyzer is used. This allows both the analysis of solid (e.g., soil samples), as well as viscous (e.g., heavy oil) natural samples and artificial materials. Pyrolysis at certain temperatures is well known in the pyrolysis community [40,41]. Additionally several temperature levels, can be selected, so that a fractionation of heavy oil is imitated. By applying simultaneous detection of the GC separated pyrolysis products with two mass spectrometry units a universal fingerprint of the sample (by EI) as well as an aromatic fingerprint (by REMPI) results. This system was applied to complex crude oil samples for the first time.

2. Material and methods

The experimental implementation (Fig. 1) can be divided into the following sections. Firstly, the pyrolyzer is directly connected to the REMPI–ToFMS. A thermogram is obtained to get a first overview of the sample. In the second step, the system is expanded by a GC with an EI-QMS (quadrupole mass spectrometer) as a second detection system.