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Investigation of different crude oils applying thermal analysis/mass spectrometry with soft photoionisation

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Abstract A variety of crude oil samples have been investigated by the combined methods of thermal analysis and mass spectrometry by means of a newly developed prototype of a thermogravimetry—single photon ionisation time-of-flight mass spectrometer coupling (TG-SPI-TOF-MS). Single photon ionisation (SPI) was conducted utilising a novel electron beam pumped argon excimer lamp (EBEL) as photon source, and a TOFMS with orthogonal acceleration has been applied for the detection of the mass to charge signals. The advantage of the soft SPI technique over EI for the analysis of such complex samples could be clearly demonstrated, as the aliphatic hydrocarbons present in crude oil may be detected via their respective molecular ion signals, not showing the intense fragmentation typical for EI spectra of this substance class. The application of SPI revealed furthermore two distinct decomposition regions, dominated by evaporation and pyrolysis processes, respectively. Moreover, different crude oils could be distinguished by TA/SPI mass spectra due to their unique molecular signatures.

Keywords Crude oil · EBEL · Evolved gas analysis · Single photon ionisation · Soft ionisation · Thermal analysis · Time-of-flight mass spectrometry

Introduction

Crude oils are often characterized according to their physical properties such as density, viscosity, colour, and odour. Furthermore, they may be distinguished by determining their chemical composition on a molecular level, which is challenging due to the enormous number of components present in the oils. An analytical technique often used for the chemical characterization of crude oils is gas chromatography/mass spectrometry (GC-MS). The chromatographic boiling point separation and identification of e.g. hydrocarbons indicate certain properties of the crude oil such as age or origin [1–3]. Other techniques utilised in this respect are laser desorption ionisation mass spectrometry (LDI-MS) [4] and high performance liquid chromatography (HPLC) [5].

Thermal analysis (TA) is a well established analytical method for investigation of temperature dependent properties and thermal decomposition. Using TA, extensive research [6] has been performed on fossil fuels, particularly on combustion kinetics of crude oils [7, 8]. Coupling TA to further analytical techniques such as gas chromatography [9–11], Fourier transform infrared spectroscopy (FT-IR) [12] and mass spectrometry (MS) [13–16] enables the analysis of the composition of the evolved gases. Especially time-of-flight mass spectrometry (TOF-MS) as a fast, on-line capable technique is well suited in this vein, since the resulting mass spectra can easily be correlated to TA related information such as mass loss or DSC signal.

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In order to analyse the composition of crude oils via their thermal decomposition by TA-MS, an ionisation technique for MS is required which is suitable for the expected large number of organic substances present in the evolved gases from the TA instrument, i.e. conserves the molecular information.

However, the most common ionisation technique in mass spectrometry, electron ionisation (EI), does not meet these requirements particularly well. EI is usually performed with electrons of 70 eV, introducing a large excess energy to organic molecules, which ionisation potentials (IP) are in the range of 7–12 eV. Hence, especially aliphatic hydrocarbons, which form the main part of the crude oil, are heavily fragmented during ionisation, thus making the interpretation of the mass spectra on a molecular level virtually impossible. The application of soft ionisation techniques such as chemical ionisation or photo ionisation could offer a possibility to overcome this drawback.

Single photon ionisation (SPI) utilising Vacuum-UV photons is a semi-selective ionisation method as only compounds are accessible that have an IP lower than the photon energy. VUV photons can be generated by frequency tripling of 355-nm third harmonic Nd:YAG pulses to $\lambda = 118$ nm using a rare gas cell. Electron beam pumped excimer lamps (EBEL) [17–19], which act as continuous or pulsed VUV photon sources provide a cost effective alternative for the generation of VUV photons. Either way, the photon energies are in the same region as the ionisation potentials of organic species, thus preventing the introduction of excess energy during ionisation. First thermal desorption studies, pyrolysis studies [20, 21] as well as TG studies using laser based soft ionisation mass spectrometry as detector [22] revealed that highly valuable information on the molecular signature of the thermal decomposition processes can be achieved. In this respect, a newly developed prototype of a TG-single photon ionisation orthogonal accelerated time-of-flight mass spectrometer coupling (TG-SPI-oaTOFMS) is applied in this study to analyse the decomposition products of several crude oils. A similar approach applying a quadrupole mass spectrometer has recently been applied successfully [23] for the investigation of thermal degradation of various polymers such as polyethylene and ABS.

Experimental

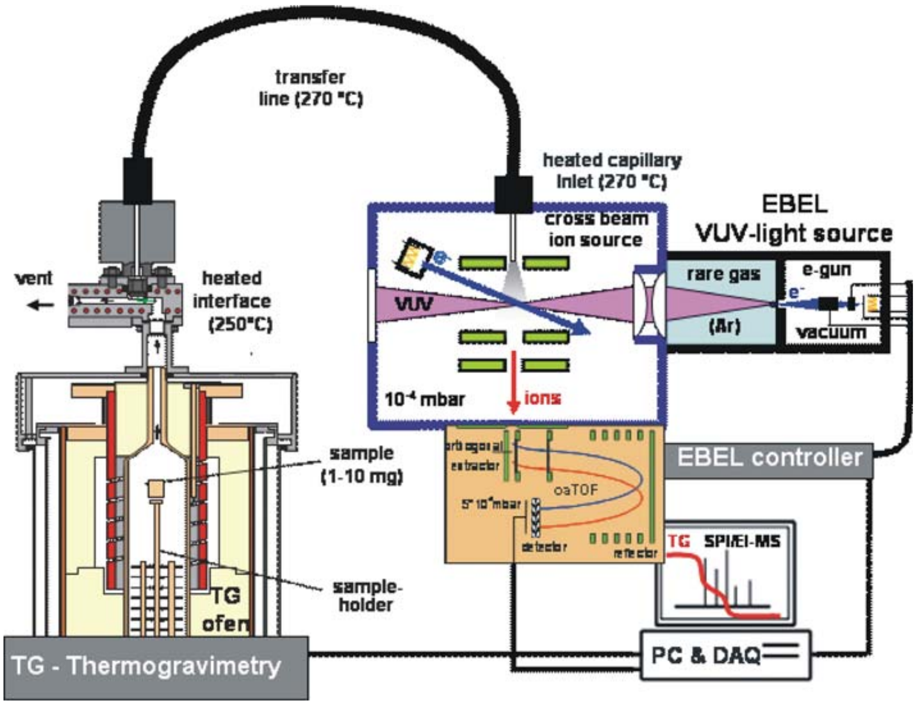
The working principles of the EBEL were described previously in the literature [18, 19] as well as the fundamentals on the coupling of the thermo gravimetric analyser to SPI mass spectrometric devices [23]. The complete setup of the experiment is shown in Fig. 1. An STA 409 PG Luxx thermobalance (Netzsch Gerätebau GmbH, Selb, Germany) has been used for the thermal decomposition studies. Crude oil samples have been heated from 40 up to 800 °C with a heating rate of 10 °C min^{-1} in an aluminum oxide crucible in N_2 atmosphere. The heating rate is controlled and measured respective to the temperature at the crucible surface. The nitrogen flow through the sample chamber was set to 60 mL min^{-1}. The gas flow has been measured and adjusted via the appropriate connected gas flow controllers, temperature accuracy has been ascertained semi-annually with calibration using melting points of different metal calibration samples. Weighted crude oil samples were in the range of 15–25 mg for all measurements. No sample preparation has been performed prior to the measurements. Evolved gases were guided into the ion source of the mass spectrometer using a deactivated 250 °C heated fused silica capillary with an inner diameter of 150 µm and length of 2.1 m. A home-made EBEL was flange-mounted on the ion source. The EBEL consists of an evacuated electron gun that emits electrons with a kinetic energy of 12 keV through a 300 nm thick SiN_x film into a volume filled with argon at a pressure of approximately 2.5×10^5 Pa. The electrons partly excite the argon atoms, which form excited dimers (excimers), which decay into two atoms emitting photons of characteristic energy (in the case of Argon: emission maximum: 126 nm, 9.8 eV). The excimer formation occurs in a small volume in the close proximity of the electron entrance foil. The emitted continuous light is first collimated and then focussed on the effusive gas inlet with two MgF_2 lenses. A schematic drawing of the EBEL is shown in Fig. 2.

The generated ions were drawn into the mass spectrometer and accelerated orthogonally to their original direction of movement into the free drift tube of the reflectron (Tofwerk AG, Thun, Switzerland). The spectra gained from the TOFMS are buffered on an Acqiris AP240 averager card (Agilent Technologies, Plan-les-Ouates, Switzerland, 1–2 GS s^{-1}). Each second, 62500 spectra are sent to the card and averaged. The available mass range with this acquisition rate is $m/z = 0 \ldots 410$. The mass resolution with the used parameters is $R = 1000$ according to the FWHM method.

The sensitivity of the system was determined using nitrogen containing 10 ppm benzene, toluene, and *p*-xylene, respectively. The limit of detection (LOD) for a signal to noise ratio S/N = 2 has been calculated to 22 ppb for toluene.

Five crude oil samples have been investigated with the described setup, which derived from different geographical zones: Greek, North Sea, Turkish and Californian oil as well as a sample named as “R820”, the origin of which is unknown. The Turkish crude oil is significantly more viscous than the other oils, which among themselves differ in colour. The physical properties in detail are unknown due

Fig. 1 Schematic representation of the TG-EBEL-SPI-TOFMS system



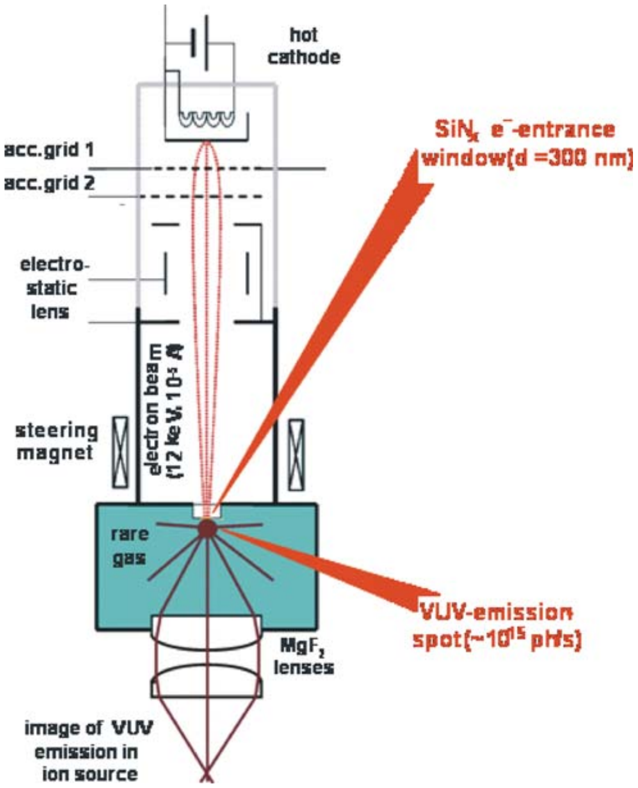


Fig. 2 Schematic of the electron beam pumped excimer lamp (EBEL)

to the lack of appropriate measurement devices at the site. Repetition and continuation of the herein presented promising assays with more accurately identified crude oil samples should be considered. Measurements have been repeated up to six times per sample. TA assays have proven to be invariant up to repeating of the measurements while the weighted sample was in the aforementioned mass bracket. Mass spectrometric results of the same sample done with the same excimer lamp do also not vary significantly.

Results and discussion

In this preliminary study, the effect of applying soft single photo ionisation for the characterisation of the complex crude oil samples should be evaluated. Furthermore, the potential of the fast mass spectrometric detection for distinguishing different crude oils should be demonstrated in terms of a comprehensive overview of the thermal process in a single graph. A more detailed analysis of the obtained data comprising, e.g. mass spectrometric profiles at selected temperatures and a thorough statistical analysis will be presented in a forthcoming publication. Hence, the results of the TG/SPI-MS investigations of the various samples are presented here in the following way: The data is depicted in a two-dimensional contour plot. The *y*-axis shows the temperature, while along the *x*-axis the *m*/*z* value is plotted. In this way the mass spectrometric signal recorded at the corresponding oven temperature can be seen at one glance for the whole thermal degradation process. The respective intensity of the mass signal is depicted as false colour display. In addition to the two-dimensional plots, averaged profiles covering a broader range of temperatures are shown, allowing the assignment of homologous series of substance groups to the measured mass signals. However, it has to be noted that in principle at every single temperature such a mass spectrum can be derived, the here presented averaged spectra serve as an exemplary case to demonstrate the advantages of the soft ionisation.

Figure 3 shows the accordant two-dimensional TA data of Turkish crude oil. As described above, the figures depict the whole thermal analysis of the oil sample at one glance. The graph on the left has been recorded with electron ionisation, the one to the right with single photon ionisation. The difference between the ionisation techniques becomes obvious from the figures. With electron ionisation, very intense signals are observed, which can be assigned to the typical alkyl fragments known to be formed in mass spectrometry from alkanes and alkenes with EI (m/z = 43, 57, 71, 85, 99 and m/z = 41, 55, 56, 69, 83, 97). Especially for the smaller fragments, no significant changes can be seen throughout the whole process up to a temperature of approximately 500 °C. The signals start to appear at very low temperatures, indicating that small volatile alkanes are evaporated already at the beginning of the measurement. However, since all alkanes tend to form these same fragment ions, a distinction on a molecular level between single species as a function of temperature is not possible. As a consequence, information from this figure is limited to the determination of sum values of alkanes at a given temperature.

The respective graph recorded with TA/SPI-oaTOFMS provides an entirely different view on the thermal analysis of the Turkish crude oil. The intense alkyl fragment peaks are not detected, in contrast well-defined mass signals are observed, even at higher values of m/z. Moreover, it can be determined that the mass loss of the crude oil is separated into two distinct steps, which is only hinted at in the EI spectrum, when the interim decrease and increase of intensity for fragment peaks such as m/z = 85 and 97 between 300 and 400 °C is consulted. The first step is a quasi-continuous evaporation process which ends at a temperature of about 300–350 °C. The second step starting at a temperature of 400 °C is the release of products of a pyrolytic decomposition of non-volatile compounds. Above 500 °C, no more evolving species could be detected. The evaporation phase features the appearance of substances according to their

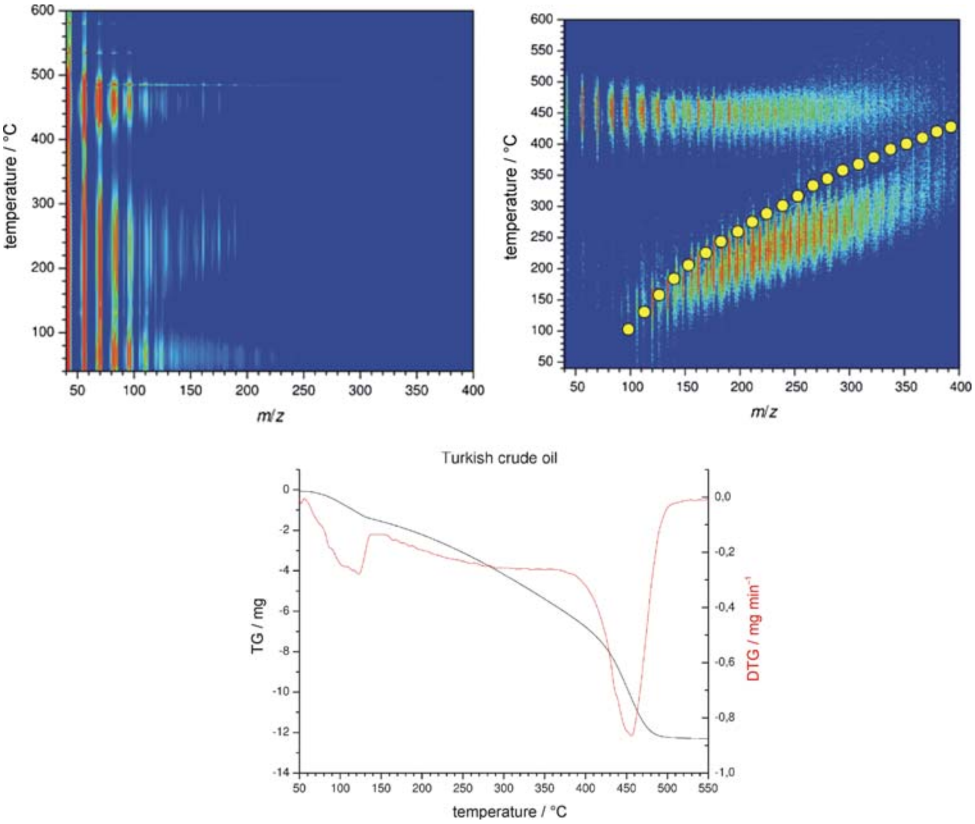


Fig. 3 Two-dimensional graphs of TG-SPI-oaTOFMS measurement of Turkish crude oil. (*left*) Ionisation by means of EI. (*right*) Ionisation by means of SPI. Yellow dots (colour online) represent the boiling points of *n*-alkanes. (*bottom*) TG and DTG signals correlate well with ion signals (color figure online)

volatility. It resembles a boiling point separation of the elevated compounds. With increasing temperature, components with higher molecular masses can be detected, leading to a shift in the molecular pattern to higher *m*/*z*. This is emphasised by the yellow dots in the graph, which represent the boiling points of the *n*-alkanes from heptane to octacosane. These are following the same trend as the mass signals, and every dot corresponds with an *m*/*z* signal, suggesting that the *n*-alkanes may be monitored according to their molecular mass. Alkanes smaller than heptane cannot be detected, because their ionisation potentials are above 9.8 eV, thus there are no signals observable in the lower mass range. During the pyrolysis phase between 400 and 500 °C, fragments of high molecular compounds over the complete observable *m*/*z* region are released, stemming from species of low volatility, which do not undergo evaporation, but are decomposed at elevated temperatures, forming a large number of smaller compounds.

Figure 4 shows summed up mass spectra for both ionisation methods. The spectra in the upper row summarise the mass signals recorded in the temperature range from 40 to 400 °C, depicting the evaporation region up to the onset of pyrolysis. Spectra in the lower row are added up in the temperature range from 400 to 600 °C, covering the whole pyrolytic decomposition. This behaviour is in accordance with previous studies of the pyrolytic decomposition using TG/DSC [24]. Again with EI, solely the alkyl fragment peaks are visible, allowing no further insight in the hydrocarbon species from which they are derived. The SPI-oaTOFMS sum spectrum of the evaporation region, however, shows a large number of distinct molecular ion peaks, which can be assigned to various

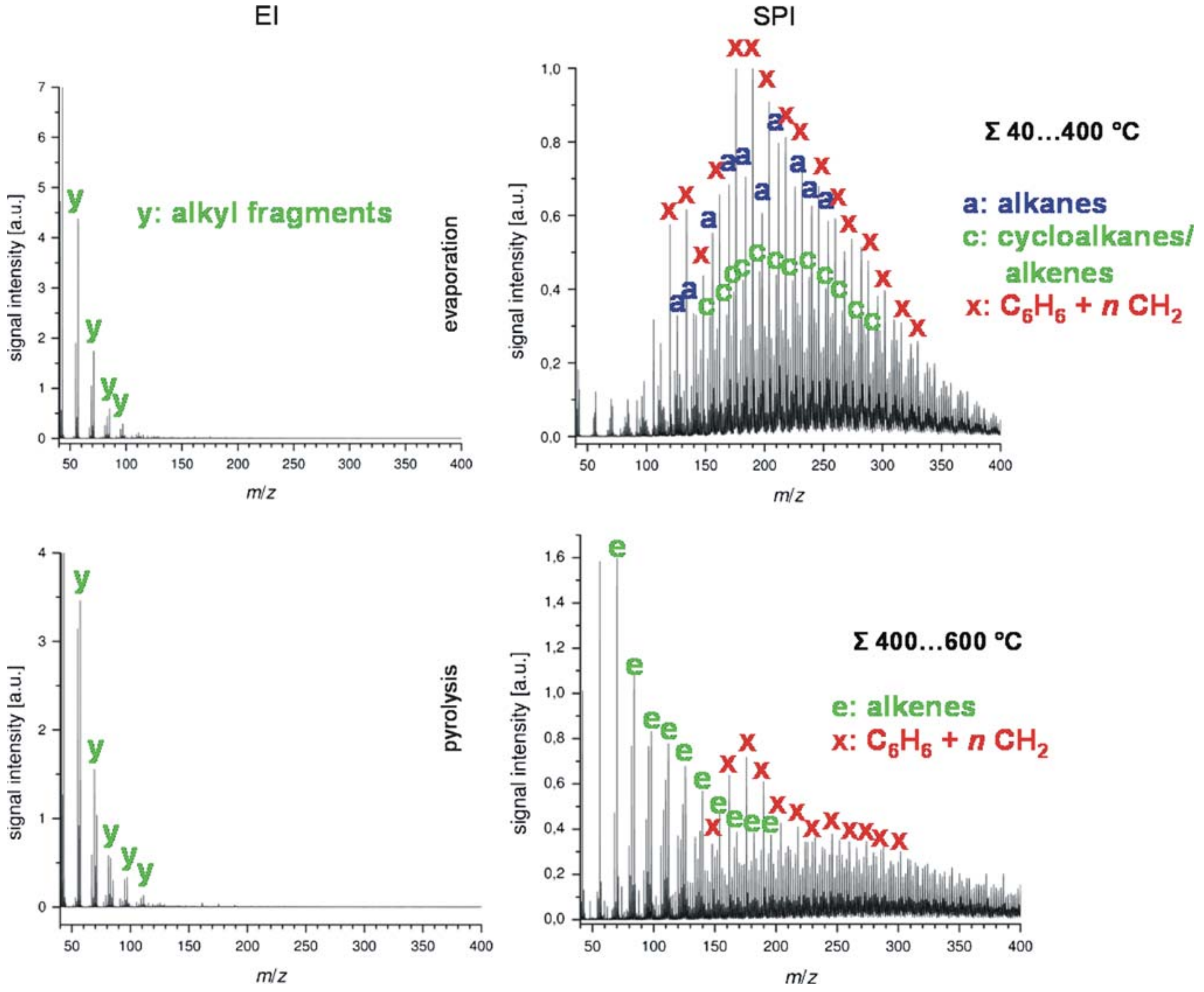


Fig. 4 Summed up mass spectra from the thermal analysis of Turkish crude oil. In the *upper row*, the evaporation region is depicted, whereas the *lower row* shows the pyrolysis region. The *left column* displays EI-MS spectra, the *right* one SPI-MS spectra

homologous series of alkanes, cycloalkanes, and alkylated benzenes, which account for the most important substance classes present in crude oil. If the presupposition holds that all alkanes exhibit comparable cross sections for SPI ionisation [25], the relative contribution of each alkane, i.e. all isomers of a given *m*/*z* value, may be estimated.

The respective spectrum from the pyrolytic region shows two predominant homologous series, viz. alkenes and alkylated benzenes. This could be expected, since thermal decomposition of alkanes would lead to the formation of smaller unsaturated units. On the other hand, aromatic species are stable enough to survive the higher temperatures without complete decomposition.

Figure 5 depicts two dimensional temperature versus *m*/*z* graphs for the other four crude oils that have been investigated. Despite all oils show in principle the same trends as described before for the Turkish oil—an evaporation region up to a temperature of 300–350 °C followed from a pyrolysis region producing smaller molecules—all samples could be distinguished of each other, since they exhibit different signal patterns. In contrast to Turkish oil, which showed almost no signals at low temperatures, evaporation of chemical species is happening from the beginning of the measurement for the other crude oils. This indicates that these oils contain a larger amount of volatile substances, which is substantiated by their lower viscosity compared to

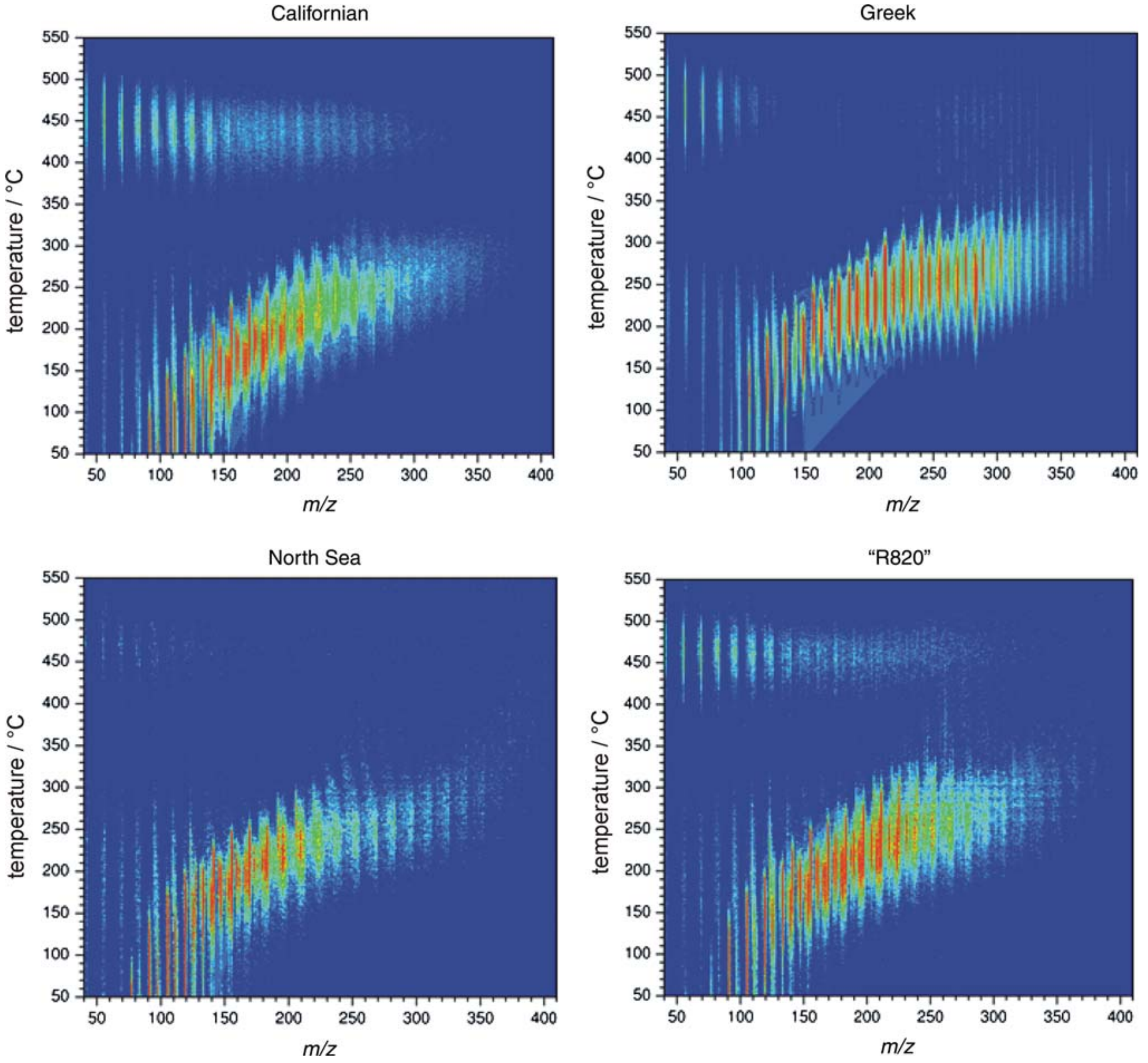


Fig. 5 Two-dimensional graphs of TG-SPI-oaTOFMS measurements of different crude oil samples. From the *upper left clockwise*: Californian crude oil, Greek crude oil, "R820" crude oil, and North Sea crude oil are depicted

Turkish oil. The intensity pattern of the substances elevated during evaporation differs for each oil sample. Especially for Greek oil, in the mass range above $m/z = 200$ more intense mass signals can be observed and species with higher molecular masses can be detected more clearly. This allows the deduction that Greek oil is has a larger content of heavier hydrocarbons than the other oils. In a similar way, the pattern of the mass signals depicted in the pyrolytic region enables to distinct between the various oils, too. Whereas Californian oil and the "R820" sample show many signals similar to Turkish oil, albeit with much lower intensities, Greek oil exhibits only a few molecules (alkenes and benzene) in the lower mass range ($m/z < 100$), and for North Sea oil there are almost no species formed during the pyrolysis. As a consequence, North Sea oil seems to contain relatively few high molecular non-volatile species which would decompose at higher temperatures.

For a more detailed examination of the differences between the investigated crude oils, the survey of the two dimensional graphs is not sufficient. For this, a thorough statistical analysis is necessary. Such an appraisal will be carried out based on the existing data and will be the topic of a future publication.

Conclusions

The potential of hyphenating thermogravimetry and soft photo ionisation mass spectrometry using VUV excimer lamps (EBEL-SPI-MS) for material analysis in the field of fossile fuels was demonstrated. The SPI mass spectra from thermal analysis of crude oil display the advantage of soft photo ionisation for the characterisation of the evolving gases. Since fragmentation does not occur, each hydrocarbon may be identified according to its molecular peak. The utilisation of EI leads to intense fragmentation of the molecules to the respective same fragment ions making identification of distinct compounds impossible. Different crude oils could be told apart based on their distinct molecular patterns of the elevated products.

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