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Evolved gas analysis (EGA) in TG and DSC with single photon ionisation mass spectrometry (SPI-MS): molecular organic signatures from pyrolysis of soft and hard wood, coal, crude oil and ABS polymer

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Abstract A combined *thermogravimetry/differential scanning calorimetry* device (TG/DSC) was coupled to *single photon ionisation mass spectrometry* (SPI-MS) for *evolved gas analysis* (EGA). *Single photon ionisation* (SPI) was performed with a new type of VUV light source, the so called *electron beam pumped rare gas excimer lamp* (EBEL). SPI does not fragment molecules upon the ionisation process. Thus the molecular mass signature of the evolving gases from thermal composition of carbonaceous material can be directly on-line recorded. In this work the thermo-analytical data and the SPI-MS information on the released organics is presented and discussed for various samples. Namely biomass (soft and hard wood), fossil fuel (crude oil and coal) as well as a complex polymer (ABS) are investigated. The general potential of hyphenating thermal analysis and soft photo ionisation mass spectrometry (EBEL-SPI-MS) for fundamental and applied research and material analysis is discussed.

Keywords TG/MS · Photo-ionisation · Wood · Fossil fuels

Introduction

In thermogravimetry (TG) the course of the mass loss of a sample due to pyrolytic decomposition and vaporisation processes during a thermal protocol is recorded with a thermobalance. For industrial applications the information obtained from the TG curve (sample mass versus temperature curve) or the differential thermal analysis curve (DTG: First derivative of sample mass versus temperature curve) are used for e.g. quality control. More advanced applications, e.g. in fundamental research, often require an analysis of thermal properties (i.e. the heat flux to/from the sample by differential scanning calorimetriy (DSC)) [1–4] or chemical analysis of the evolved gases (evolved gas analysis, EGA). EGA can be performed by using sensors for simple chemical gases such as carbon dioxide or water at high or medium concentrations. The detailed analysis of evolved organic vapours can be done either by coupling of TG to a sequentially working analytical device such as gas chromatography (with or without mass spectrometric detector, TG-GC(-MS)) [5–7] or by coupling of TG to an on-line real-time analytical technology such as Fourier-transform infrared spectrometry (FTIR) [8] or mass spectrometry (MS) [9–12]. Common TA-MS couplings are based on quadrupole mass spectrometers with electron impact ionisation (EI). The coupling between the TG oven and MS is realized either via a transfer capillary [13], jet-separator [14] or a skimmed supersonic expansion [15]. Although MS is a very powerful analytical technique for elemental and molecular analysis, the currently commercially available TA-MS systems with EI ionisation can not

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provide a realistic representation of complex organic vapours evolved. The reason for this is the large degree of fragmentation of the organics molecules upon the standard electron impact ionisation with electrons of 70 eV kinetic energy. First thermal desorption and pyrolysis studies [16, 17] as well as TG studies using laser or deuterium lamp based soft ionisation mass spectrometry as detector [18, 19] revealed that highly valuable information on the molecular signature of the thermal decomposition processes can be achieved. In this paper, a newly developed prototype of a coupling of a thermal analyser with a single photon ionisation orthogonal acceleration time-of-flight mass spectrometer (TG/DSC-SPI-oaTOFMS) is applied. The thermal analyser simultaneously records the TG and the DSC curve. An *e*lectron *b*eam pumped rare gas *e*xcimer VUV-*l*amp (EBEL) technique is used for the soft photo ionisation process [20–22] in the mass spectrometer. In this paper, the thermal behaviour/decomposition of different carbonaceous materials is compared. In addition to a common complex polymer, also wood, coal and mineral oil were investigated.

Experimental

The working principles of the EBEL VUV-light source [23] and the application of EBEL as light source was described previously in the literature [22, 24, 25], as well as the fundamentals on the coupling of a thermogravimetry analyser to EBEL SPI quadrupol mass spectrometry [26]. In this work, an orthogonal acceleration time-of-flight mass spectrometer (oaTOFMA, type: C-TOF, Tofwerk AG, Thun, Switzerland) was equipped with a homebuilt EBEL-VUV light source for soft single photon ionisation. In the patented EBEL-VUV light source, a 0.7 × 0.7 mm^2 ceramic silicon nitride (SiN$_x$) foil of only about 300 nm thickness separates rare gas volume (i.e. the luminescence medium, pressure $>$1 bar) from a vacuum chamber which is containing an electron gun (EG). A 13-keV electron beam is generated by the EG and directed onto the foil. Electrons penetrate through the SiN$_x$ foil into the rare gas volume with low energy loss and excite the rare gas atoms. In successive processes, excited meta-stable diatomic rare gas molecules (excimers) are formed and subsequently are disintegrating again within typically a few microseconds. Upon the disintegration of the rare gas excimers, VUV-radiation is emitted. The excimer formation occurs solely in a small volume in the vicinity of the SiN$_x$ electron entrance foil. The homebuilt EBEL can be filled with different rare gases or gas mixtures, in this experiments Ar was used (emission maximum: 126 nm ~ 9.8 eV centre photon energy). The EBEL SPI-oaTOFMS exhibit detection limits for benzene in the 35 ppb range for a measurement time of 1 s [27]. For the here presented experiments, the homebuilt gas inlet of the mass analyser was coupled via a heated transfer line to the TG

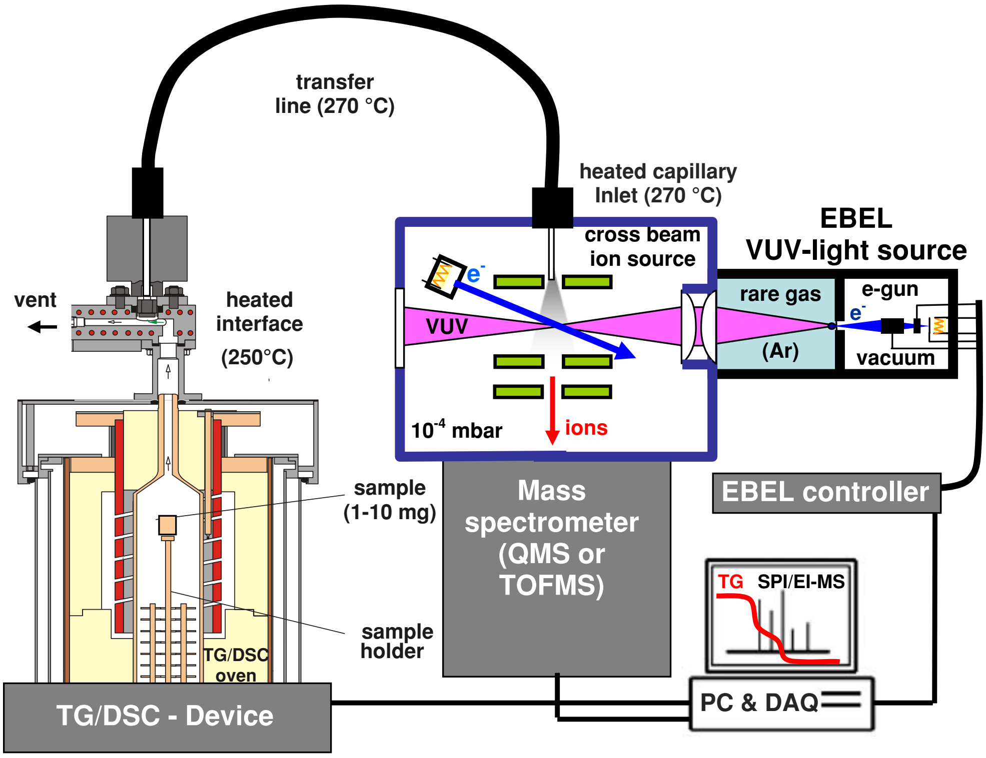

Fig. 1 Schematic representation of the TG/DSC-EBEL-SPI-oaTOFMS system

system (Typ STA 409, Netzsch Gerätebau, Selb, Germany). A special heated adapter was developed for the TG-system to avoid memory effects of the released higher boiling organic compounds [26]. Note that the oaTOFMS could be operated in both, electron impact ionisation or photo ionisation (SPI) mode. A sketch of the setup of the device is shown in Fig. 1.

The investigated samples are soft wood (spruce), hard wood (beech), black coal, crude oil (geochemically mature sort from Turkey) and ABS polymer, the co-polymer of acrylonitrile, butadiene and styrene). About 10 mg of the investigated samples were placed in an aluminium oxide pan of the thermal analysis system, respectively. The reference pan for recording the DSC data was kept empty, thus the recorded DSC curves have qualitative character only. This, however, is sufficient for the here intended initial general discussion. The heating rate in all cases was 10 K min^{-1}, the atmosphere was pure nitrogen with a flow rate of 60 ml min^{-1}.

Results and discussion

The main objective of the here presented coupling of thermal analysis and soft ionisation mass spectrometry is the on-line detection of the signatures of the evolved organic compounds. As it can be easily seen in the Figs. 2, 3, 4, 5 and 6, which are summarizing the TG, DSC and SPI-MS results for the investigated samples, respectively, it is possible to get specific mass spectrometric signatures for the different samples by EBEL-SPI photo ionisation mass spectrometry. For all samples, a typical SPI mass spectrum is given, recorded at a temperature where rapid mass loss and thus a high formation rate of gaseous decomposition products occur. Prominent masses are assigned by their mass number, in some cases also likely molecular structures are depicted. Furthermore, a contour plot of the mass spectral data versus the oven temperature is given for each sample. This representation depicts the release-characteristics of organic molecules as function of the temperature on the glance. The molecular mass signals obtained by the on-line SPI-oaTOFMS measurement in many cases can be readily assigned to molecular structures, at least if some chemical pre-knowledge on the sample composition and typical pyrolytic products is available. In Table 1, the tentative assignment of the more pronounced mass spectral peaks is given for the investigated samples. The evolved gases from the wood samples contain typical pyrolysis products of lignin and cellulose (Figs. 2, 3) [28] while

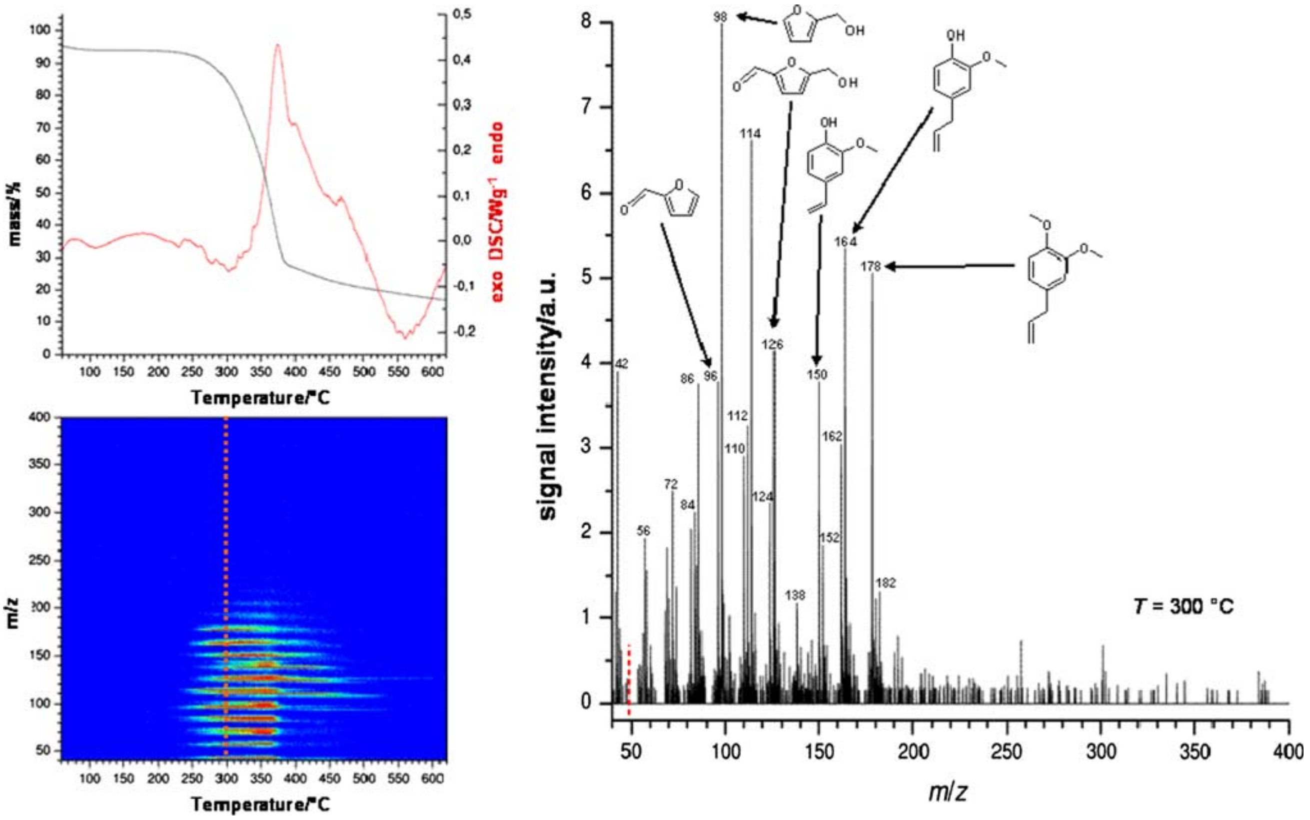

Fig. 2 TA/SPI-oaTOFMS investigation of soft wood (spruce/fir mixture). The left column shows the TG- and DSC curve (*above*) and a two-dimensional contour plot of the measurement (*below*). The right column depicts one selected single mass spectrum recorded at a temperature where heavy mass loss occurred. For m/z assignments see Table 1

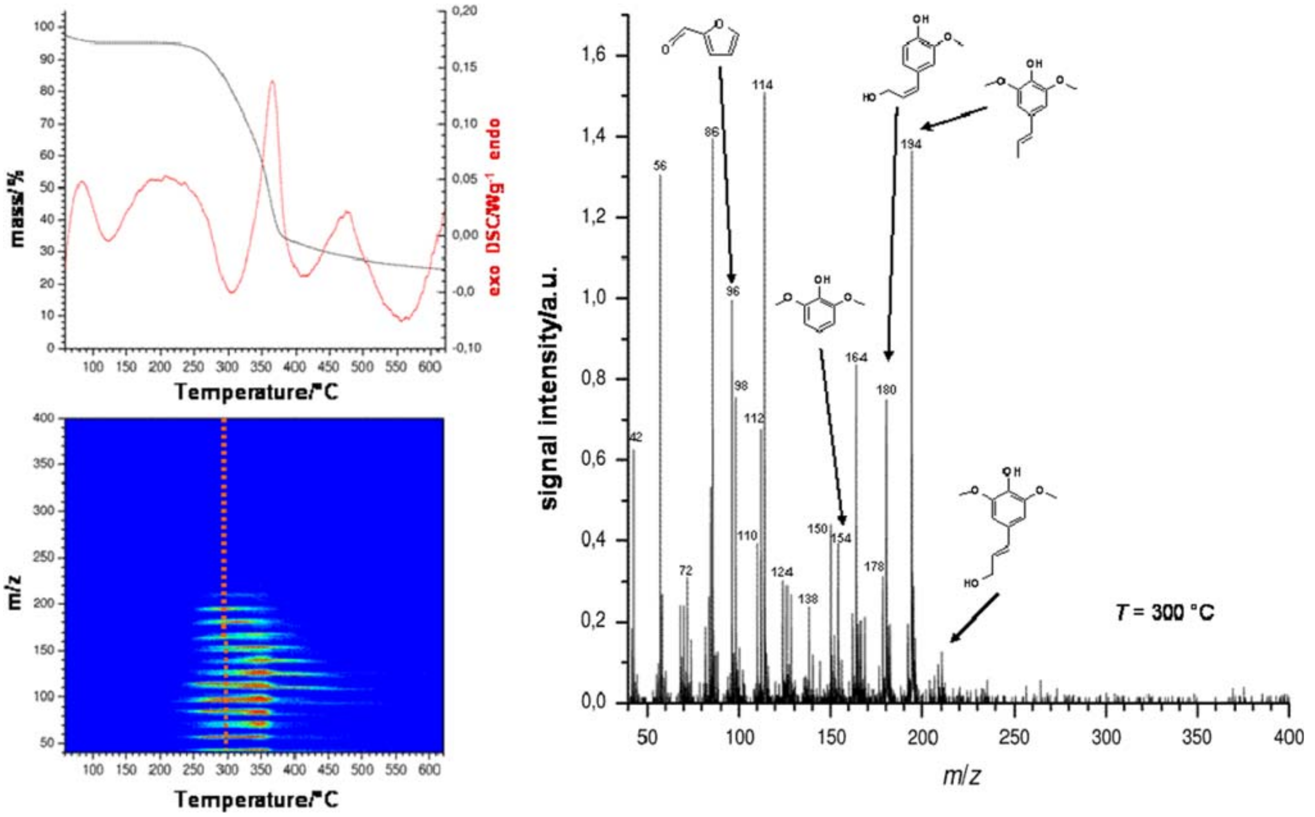

Fig. 3 TA/SPI-oaTOFMS investigation of hard wood (*beech*). The left column shows the TG- and DSC curve (*above*) and a two-dimensional contour plot of the measurement (*below*). The right column depicts one selected single mass spectrum recorded at a temperature where heavy mass loss occurred

during coal pyrolysis predominately alkenes as well as alkylated benzenes and phenols are released. The mass spectra from crude oil EGA-analysis are dominated by the homologous series of alkanes, cycloalkanes (or more likely alkylated cyclopentanes and cyclohexanes) and alkylated benzenes for the evaporative part of the temperature program (40–400 °C), while alkenes become very prominent for the pyrolytic part of the temperature program (400–600 °C, pyrolysis of asphaltenes). A remarkably different appearance has the EGA TG-SPI-mass spectrum of the ABS polymer pyrolysis. Here, typical monomers (styrene) and break-down products of the polymer chain are detectable, resulting in a rather "empty" mass spectrum. In the following, the results for the investigated samples are individually discussed.

Wood samples

In Figs. 2 and 3 the results on a fir/spruce mixture (soft wood) and beech (hard wood) are summarized, respectively. In the left part of Fig. 2 the TG/DSC curves and the soft ionisation mass spectrometric signature as a function of the oven temperature (2D contour plot) are depicted. The right part of the figure depicts a typical SPI mass spectrum at 300 °C. The TG curve initially indicates some water loss (drying till around 100 °C). The main mass loss step (~92–28 mass %) occurs due to pyrolytic gasification of the wood in the temperature region 250–380 °C, leaving char and ashes as residue. The gasification temperature region is accompanied with strong signals of organic compounds in the SPI mass spectrum, mainly in the region below 200 m/z. The DSC curve depicts a shallow exotherm at about 300 °C followed by increasing endothermic behaviour peaking in a rather strong endotherm at 380 °C. Subsequently, the DSC decline again resulting in an exotherm at 560 °C. The latter exotherms at 300 and 560 °C likely can be assigned to cellulose and lignin decomposition, respectively [29]. During increase of the endothermic behaviour (i.e. thermal flux to the sample), the emission of gaseous organic compounds also increases as shown by the SPI mass spectrometric data. The TG curve shows that at the peaking of the endotherm (380 °C) the mass loss rate instantaneously is reduced. This is going along with a

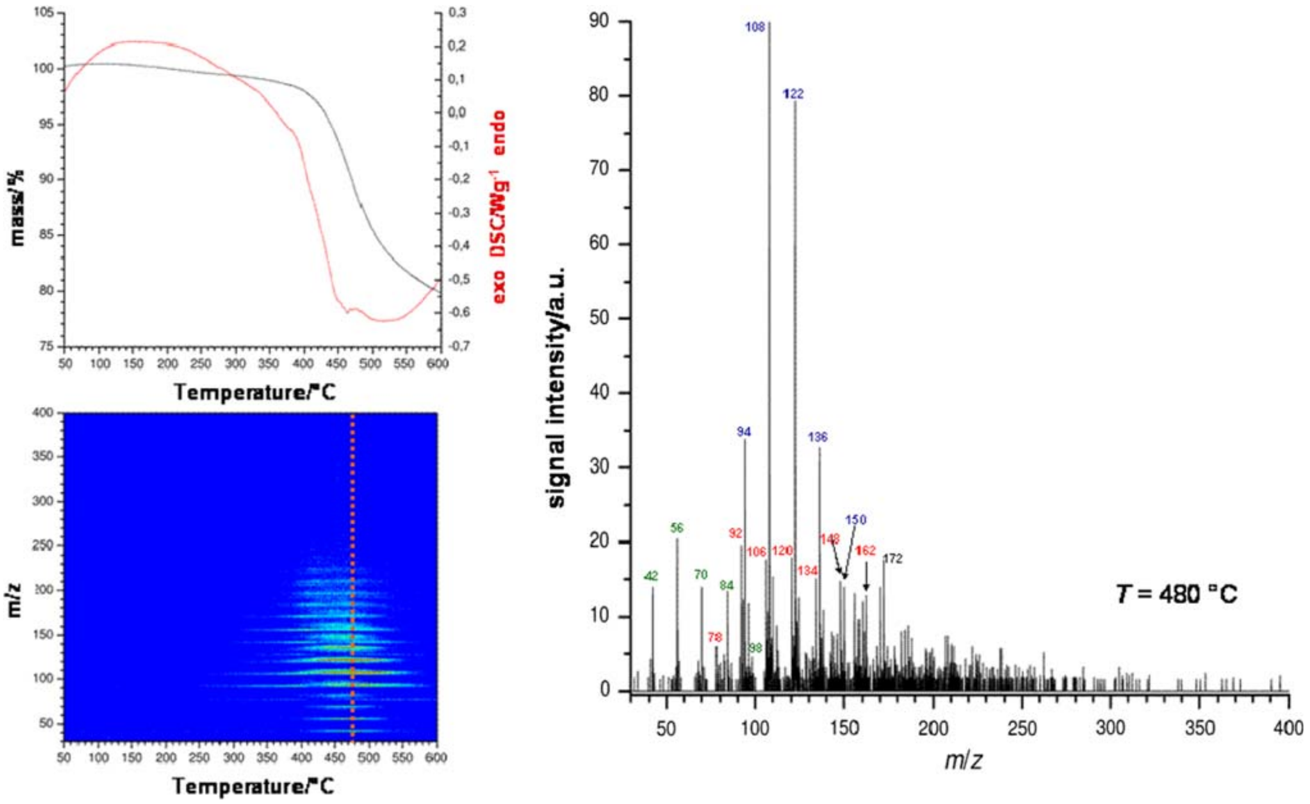

Fig. 4 TA/SPI-oaTOFMS investigation of black coal. The left column shows the TG- and DSC curve (*above*) and a two-dimensional contour plot of the measurement (*below*). The right column depicts one selected single mass spectrum recorded at a temperature where heavy mass loss occurred

coincident sudden reduction of the released organic compounds above 370 °C as being visible from the SPI-MS data. The mass spectrum at 300 °C (Fig. 2, right) depicts predominately typical masses of phenolic species and furan based compounds which are known to be originated from the pyrolytic decomposition of lignin and cellulose. Typical phenolic compounds are the cresols (108 m/z), guajacol (124 m/z), 4-vinylguajacol (150 m/z), dimethoxystyrene (164 m/z) and dimethoxypropenylbenzenes (178 m/z) while the furan based species are furfural (96 m/z), furfurylalcohol (98 m/z) and hydroxymethylfurfural (126 m/z). Furthermore aliphatic aldehydes and ketones are detectable (58, 72 and 86 m/z). At higher temperatures (>500 °C) even a slightly exothermic behaviour is observable. This can be explained by oxidation processes due to the pyrolytically released oxygen containing compounds/species. In the case of hard wood, similar TG and SPI-MS results are obtained (Fig. 3). However, the mass spectrum additionally shows the typical bio markers for hard wood, syringol (154 m/z), coniferyl alcohol (180 m/z) and propenylsyringol (194 m/z). The profile of the DSC curve, however, is less pronounced. Similar as in the case of soft wood, exotherms at 300 and 560 °C as well as an additional exotherm at about 400 °C are detectable [29], while at 370 °C the relative strong endotherm is observed.

Black coal

In Fig. 4, the results on black coal are given. Up to a temperature of 600 °C the TG curve depicts about 20% mass loss due to the release of volatiles. Significant gasification, however, starts not before 450 °C, thus at much higher temperatures as in the case of the wood samples (Figs. 2, 3). The released organic vapours mainly are composed of the homologous series of the alkylated benzenes and phenol derivatives (starting at 78 and 94 m/z) as well as alkenes (starting at 42 m/z). The SPI-MS peak assignment is given in Table 1. Note that small organic compounds that might play a role in the coal gasification such as ethene or methane as well as inorganic compounds such as CO or H_2 are not accessible by SPI-MS. For a further development stage of the TG/DSC-SPI-MS technique, which is currently under construction, a rapidly alternating SPI and EI ionisation, i.e. quasi simultaneous SPI-MS and EI-MS, is foreseen in order to enhance the

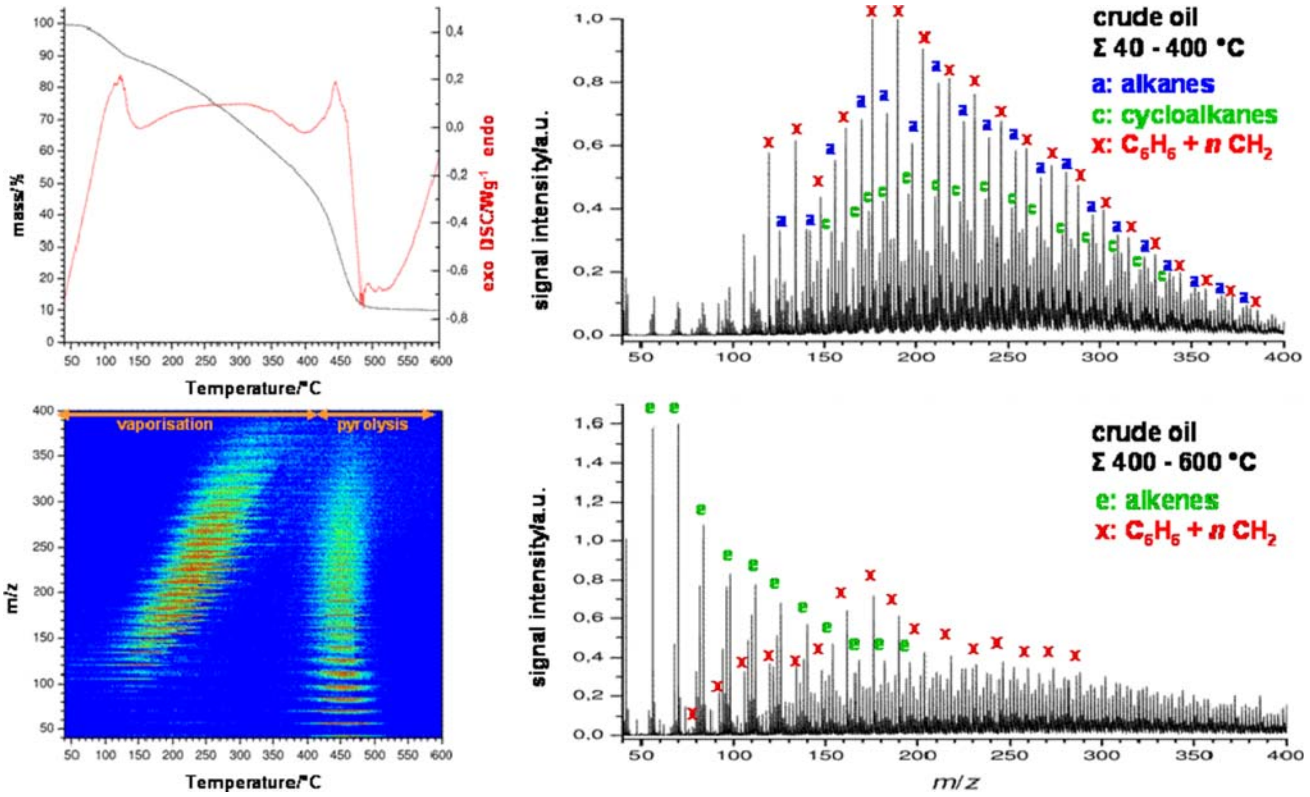

Fig. 5 TA/SPI-oaTOFMS investigation of crude oil. The left column shows the TG- and DSC curve (*above*) and a two-dimensional contour plot of the measurement (*below*). The right column depicts summed up mass spectra recorded in the evaporation (*above*) and pyrolysis regions (*below*)

comprehensiveness of the on-line mass spectral coverage in EGA. The DSC curve starts with a typical endotherm around 150 °C, which is due to water evaporation (drying) [30, 31]. In the following, an exotherm with peaks at 460 and 520 °C is observed. The DSC curves of coals, however, depend very much on the type of coal, as well as on the temperature program and the particle size of the milled sample [30, 31].

Crude oil

The thermal and chemical behaviour for the crude oil shows large differences to the before discussed solid carbonaceous materials wood and coal. About 60 mass % of the investigated, geochemical rather mature crude oil are due to directly vaporizable volatile and semi-volatile organic compounds. Furthermore higher molecular mass polymeric fractions, including the so called asphaltenes are present. The latter fractions are pyrolytically disintegrated at higher temperatures. The TG curve in Fig. 5 shows three regions with different mass loss rates. Up to 130 °C, water vaporizes as well as hydrocarbons with higher volatility. This region is also visible in the DSC curve through an endotherm at about 120 °C. In the region between 130 and ~400 °C a rather constant mass loss rate is observed. The two-dimensional temperature versus molecular mass plot (Fig. 5 left/bottom) and the sum SPI-mass spectrum for the temperature 40–400 °C (Fig. 5 right/top) show that here the semi-volatile organic compounds are vaporized. In the mass spectrum alkanes (linear and branched), cycloalkanes and substituted benzenes occur in long homologous series and are assigned by the letters a, c and x, respectively. Note that the cross-sections are diverse for different substance classes [32]. For examples alkanes are by a factor of 5–10 less sensitively SPI ionized if compared to aromatic compounds. Thus alkanes appear underestimated in the mass spectrum if compared with alkenes and aromatics. This effect must be considered for quantitative studies, which will be subject to a future publication. For the lower mass range (up to ~200 m/z) the peak assignation is given in Table 1. The DSC-curve depicts no significant thermal flux in this region. From about 400 °C an increased mass loss rate is observable. Simultaneously, the chemical signature of the evolved gases changes drastically as it can be seen in the SPI-mass spectral data (see mass spectrum bottom/right

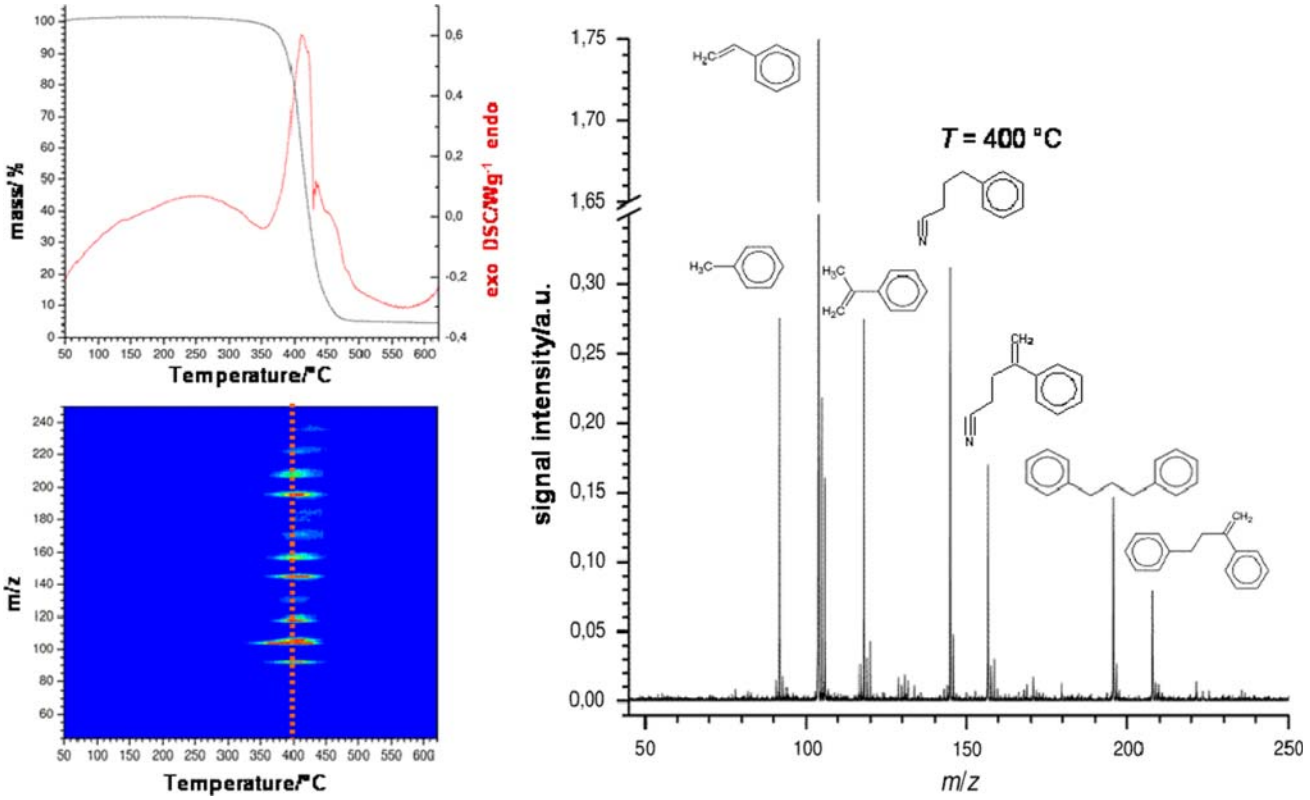

Fig. 6 TA/SPI-oaTOFMS investigation of ABS. The left column shows the TG- and DSC curve (*above*) and a two-dimensional contour plot of the measurement (*below*). The right column depicts one selected single mass spectra recorded at a temperature where heavy mass loss occurred

in Fig. 5). The SPI mass spectrum is dominated by alkenes which are typical pyrolysis products. Here the higher molecular mass fractions (asphaltenes) that are not directly vaporizable are pyrolysed. The DSC curve in this region shows a second endotherm starting at about 410 °C and peaking at ~450 °C followed by an exotherm which is peaking at 490 °C.

ABS polymer

The ABS polymer (Acrylonitrile, Butadiene, Styrene) is a copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene resulting in long chains of polybutadiene grafted with side-chains of poly(styrene-acrylonitrile). Due to the bipolar nitrile groups neighbouring polymer chains attract each other, making ABS stronger than pure polystyrene. The TG curve of ABS in Fig. 6 shows one-step decomposition between 400 and 450 °C with a maximal mass loss rate at about 420 °C which is correlated with a endotherm in the DSC curve. This mass-loss is accompanied by a strong emission of organic compounds. The by far most dominant species in the evolved gas phase SPI mass spectrum is styrene (104 m/z) surrounded by the C1 and C3-benzene products from the polymer chain degradation (toluene and propenylbenzene). At 157 m/z the condensation product of acrylonitrile and styrene is visible and at 208 m/z the styrene dimer can be seen in the SPI mass spectrum. For a tentative assignment of the other peaks in the mass spectrum see Table 1.

Conclusion

The potential of soft photo ionisation mass spectrometry (EBEL-SPI-MS) for evolved gas analysis in thermal analysis (e.g. TG and DSC) was demonstrated. SPI-MS allows recording the molecular organic signature of the evolved organic vapours from carbonaceous samples. A commercial, integrated TG/DSC-SPI-quadrupol mass spectrometer system based on the here presented instrument is currently under development in cooperation with Netzsch-Gerätebau GmbH, Selb, Germany in order to make the technology available for a broader research community. The commercial system will be operable with both, soft single photon ionisation as well as conventional electron impact ionisation (EI).

Table 1 Tentative assignment of m/z signals for all measurements

Mass (m/z)	Sample					
	Soft wood (Fig. 2)	Hard wood (Fig. 3)	Black coal (Fig. 4)	Crude oil Vaporization regime (40–400 °C) (Fig. 5)	Crude oil Pyrolysis regime (400–60 0 °C) (Fig. 5)	ABS (Fig. 6)
42	Propene	Propene	Propene	–	Propene	–
56	Butene	Butene	Butene	–	Butene	–
58	Acetone	Acetone	–	–	–	–
70	–	–	Pentene	Cyclopentan	Pentene	–
72	C4-Ketone/Aldehyde	C4-Ketone/Aldehyde	–	Pentan		–
78	–	–	Benzene	Benzene	Benzene	–
84	Hexene	–	Hexene	Cyclohexan	Hexene	–
86	C5-Ketone/Aldehyde	C5-Ketone/Aldehyde	–	–	–	
92	–	–	Toluene	Toluene	Toluene	Toluene
94	–	–	Phenol	–	–	–
96	Furfural	Furfural	–			–
98	Furfurylalcohol	Furfurylalcohol	Heptene	Cycloheptane	Heptene	–
100	–	–		Heptane		–
104	–	–				Styrene
106	–	–	C2-Benzenes (Xylenes, Ethylbenzene)	C2-Benzenes (Xylenes, Ethylbenzene)	C2-Benzenes (Xylenes, Ethylbenzene)	Ethylbenzene
108	–	–	C1-Phenols (Cresols)			–
110	Dihydroxybenzene	Dihydroxybenzene				–
112				Cyclooctane	Octene	–
114				Octane	Octane	–
118	–	–				Propenylbenzene
120	–	–		C3-Benzenes	C3-Benzenes	–
122			C2-Phenols			
124	Guajacol	Guajacol				–
126	Hydrxoymethyl-furfural	Hydrxoymethyl-furfural		Cyclononane	Nonene	–
128	–	–		Nonane	Nonane	–
134	–	–	C4-Benzenes	C4-Benzenes	C4-Benzenes	–
136			C3-Phenols			
138	Methylguiacol	Methylguiacol				–
140	–	–		Cyclodecane	Decene	–
142	–	–		Decane	Decane	–
145	–	–				Cyanopropanyl-benzene
148	–	–	C5-Benzenes	C5-Benzenes	C5-Benzenes	–
150	4-Vinylguajacol	4-Vinylguajacol	C4-Phenols			–

Table 1 continued

Mass (m/z)	Sample					
	Soft wood (Fig. 2)	Hard wood (Fig. 3)	Black coal (Fig. 4)	Crude oil Vaporization regime (40–400 °C) (Fig. 5)	Crude oil Pyrolysis regime (400–60 0 °C) (Fig. 5)	ABS (Fig. 6)
152	Ethylguajacol	–				
154	–	Syringol		Cyclodecane	Undecene	–
156	–	–		Undecane	Undecane	–
157	–	–				Styrene-acetonitrile
162	Dimethoxystyrene	Dimethoxystyrene	C6-Benzenes	C6-Benzenes	C6-Benzenes	–
164	?	–	C5-Phenols			–
168	–	–		Cyclododecane	Dodecene	–
170	–	–		Dodecane	Dodecane	–
172	–	–		–	–	
176	–	–		C7-Benzenes	C7-Benzenes	–
178	?	–				
180	–	Coniferylalcohol				
182	?	–		Cyclotridecane	Tridecene	–
184	?	–		Tridecane	Tridecane	–
190	–	–		C8-Benzenes	C8-Benzenes	–
194	–	Propenylsyringol				–
196	–	–		Cyclotetradecane	Tetradecene	Phenylpropanyl-benzene
198				Tetradecane		–
204				C9-Benzenes	C9-Benzenes	–
208	–					Styrene-dimer
210		Synapyl alcohol		Cyclopentadecane	Pentadecene	–
212				Pentadecane		–

Note: ‘?’ stands for ‘not identified’

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