

Detection of organic products of polymer pyrolysis by thermogravimetry-supersonic jet-skimmer time-of-flight mass spectrometry (TG-Skimmer-SPI-TOFMS) using an electron beam pumped rare gas excimer VUV-light source (EBEL) for soft photo ionisation

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Abstract A commercial thermogravimetry—supersonic jet-skimmer quadrupole mass spectrometer system (TG-Skimmer-QMS, Netzsch GmbH, Germany) was successfully converted for soft single photon ionisation time-of-flight mass spectrometric (SPI-TOFMS) detection of organic compounds. VUV light for SPI was generated by an electron beam pumped argon excimer light source (EBEL; $E_{\text{photon}} = 9.8$ eV). Furthermore, the versatility of the system was conserved, as high temperature TG and DSC measurements as well as electron ionisation mass spectrometry for the detection of inorganic compounds are still possible. The new system was tested with two polymers and a hydrocarbon mixture (diesel). It was demonstrated that aliphatic and aromatic organic compounds can be detected without fragmentation. Thus the system allows the recording of a readily interpretable organic signature of, e.g. thermal polymer decomposition. The thermal degradation of polystyrene shows a rich signature of the monomer, some oligomers and minor products of irregular

cleavings of carbon chains. Polycarbonate exhibits a thermal decomposition fingerprint which is dominated by products of bisphenol A. The bisphenol A monomer, however, is also detectable.

Keywords Thermogravimetry · Mass spectrometry · Polymer · Skimmer · Soft ionisation

Introduction

Evolved gas analysis (EGA) has been developed to be a widely used tool in thermal analysis. Ahead of spectroscopic techniques (TA-FTIR) and gas chromatographic approaches (TA-GC) the coupling of mass spectrometry to thermal analysis has become the most widely used EGA method [1]. Several hyphenated TA-MS instruments are commercially available. In most cases sampling and transfer of the species evolved in the thermal process is performed via a heated capillary. This simple and reliable approach, however, does not allow the transfer of low volatile species such as, e.g. metal vapours into the mass spectrometer. A wall contact free sampling is possible by a supersonic jet-skimmer inlet technology. Figure 1 shows principle sketches of the heated capillary and the skimmer interfaces between the thermal process, which usually is operated at ambient pressure (1×10^{-5} Pa or 1 bar) and the vacuum of the mass analyser ion source ($\sim 10^{-8}$ bar). In the skimmer approach, gas from the furnace, containing vaporised sample material and pyrolysis products, is expanded into an expansion chamber in which a pressure of about 10^{-4} bar is maintained by intense pumping. A so called supersonic expansion is formed in which the gas

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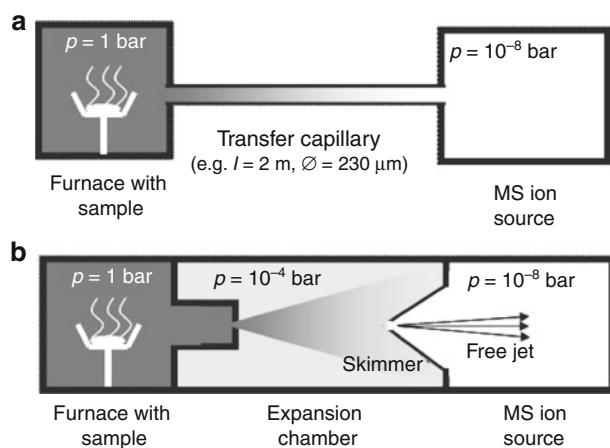


Fig. 1 Coupling of a TA Instrument with a mass spectrometer via **a** transfer capillary interface (standard coupling technology), **b** a free supersonic jet-skimmer interface

molecules or atoms are moving with only few or without collisions. Furthermore the internal energy of expanded molecules is reduced, resulting in a cooling of the different degrees of freedom (lateral translation, rotations and vibrations). After some mm or cm of free flow, the supersonic jet, however, gets disturbed due to collision of the gas particles from the expansion with the residual gas particles in the expansion chamber (mach disc). The skimmer, which in the used version of the technology represents a conically distended ceramic aluminium oxide aperture with a small opening at the tip, is looming into the undisturbed part of the jet expansion and extracts the very central part of the jet into the vacuum chamber of the MS ion source. The supersonic jet-skimmer technology has been used in conjunction with mass spectrometry in thermal analysis [2–5]. Furthermore the cooling effect of supersonic expansions is used in order to reduce mass spectral fragmentation [6, 7] or to enhance the optical selectivity in laser resonance ionisation of molecules [8–11]. Currently in commercial TG-MS Instruments quadrupole mass spectrometers (QMS) are used. QMS systems are rugged and relatively cheap “workhorse” mass analysers. However, a drawback of the QMS-technology is the necessity to repetitively scan the mass range. This results in a reduced time resolution and sensitivity if compared to fast modern time-of-flight mass analysers.

In this work for the first time a supersonic jet-skimmer technology was used for direct sampling of evolved gases from thermogravimetry (TG) in conjunction with a time-of-flight mass spectrometric detection (TOFMS) and a photo ionisation with VUV light (single photon ionisation, SPI). Furthermore an innovative VUV light source, the so called EBEL (electron beam pumped rare gas excimer light source) is used for soft ionisation of organic molecules. The TOF mass spectrometer can also be operated with

conventional electron ionisation (EI) to ionise inorganic compounds such as metal clusters, rare gases or small molecules (e.g. carbon dioxide or hydrogen) which are not easily ionised by photo ionisation. Note that it is possible to operate SPI and EI in a rapidly alternating mode, for quasi-simultaneous recording of mass spectra recorded with the respective ionisation technology [12]. Mass spectrometry (MS) with soft (i.e. fragmentation-less) ionisation is a particularly useful tool for EGA of organic compounds in thermal analysis (TA). Mass spectrometers with different soft ionisation approaches such as chemical ionisation (CI) or photo ionisation (single photon ionisation, SPI and resonance enhanced multi photon ionisation, REMPI) have been coupled to TA devices [13–21]. Previous EGA experiments with heated capillary coupling and soft photo ionisation mass spectrometry have shown that a memory effect free analysis of the pyrolysis of complex samples such as polymers, coal, wood or crude oil is possible, even for large molecules above 250 m/z . This can be explained by the reduced pressure extended into the capillary. Low volatile inorganic compounds such as vaporised salts or metals, however, cannot be transferred in a capillary but need to be transferred by the wall contact-less skimmer approach.

Experimental

In previous work the coupling of oa-TOF mass spectrometer (C-TOF, Tofwerk AG, Thun, Switzerland) equipped with a homebuilt EBEL light source to a modified commercial thermal analysis system (STA 409 PG Luxx, Netzsch GmbH, Selb, Germany) via a capillary transfer line was described [18]. In this work the same TOF mass spectrometer was used to replace the standard quadrupole mass spectrometer of a commercial TA-Jet-Skimmer-QMS system STA-409 CD (Netzsch GmbH, Selb, Germany) equipped with a QMG 421, quadrupole mass analyser (Balzers AG, Liechtenstein). For this purpose a new vacuum recipient was designed and built, which allows to replace the QMG 421 quadrupole mass analyser by the C-TOF time-of-flight mass analyser. Furthermore the distance between the tip of the skimmer and the centre of the ion source was reduced by 15 mm. The furnace of the skimmer system can be operated in a temperature range between ambient and about 2000 °C depending on the used oven type (here: 1500 °C). Both, the plate with the expansion orifice as well as the skimmer are made of heat resistant aluminium oxide ceramics. The primary ion source of the oa-TOFMS system is based on a modified version of a commercial available “fly-through ion” source for the QMG quadrupole mass analyser (Balzers AG, Liechtenstein). The critical distances between the sample

crucible and the expansion orifice, the expansion orifice and the skimmer tip as well as the skimmer tip and the ionisation region are 11, 3.9, and 98 mm, respectively. The expansion orifice and the skimmer tip exhibit opening diameters in the range of 80–120 μm [3]. The expansion volumes were pumped by a feed-back regulated two-stage rough pump (1.5–4.5 m^3/min), the ion source and the TOF drift tube are pumped by 260 L/s turbo molecular pumps. The resulting pressures in the furnace, expansion chamber, ion source and the TOF analyser were 1 bar, some mbar, 10^{-5} mbar, 10^{-6} mbar, respectively. The initial experiments reported here were performed in nitrogen atmosphere. A flow of typical 150 mL/min of N_2 was applied to the furnace. A home built EBEL light source filled with one bar of pure argon (126 nm/9.8 eV centre wavelength/photon energy) was attached via an optical interface unit equipped with two aluminium parabolic mirrors ($f_1 = 76.20$ mm (30"9), $f_2 = 152.60$ (60"9)). The mirror surfaces were coated with MgF_2 in order to increase the reflectivity in the VUV spectral range. The EBEL light source was operated at an electron energy of 12 keV and a current of 5 μA . The light emitting spot in the argon gas cell in the vicinity of the SiN_x membrane exhibited a diameter of approximately 1.5 mm and was imaged by the optical interface unit in a ratio of 1:2 into the centre of ion source for SPI ionisation. Measurements of organic samples were done under conditions and settings as given in Table 1. The experimental setup is shown schematically in Fig 2.

Results and discussion

In the following, the first TG-Skimmer-SPI-*oa*-TOFMS results of samples of complex organic composition are presented in order to demonstrate the capabilities of organic profiling/finger printing by the TG-Skimmer-SPI-TOFMS approach. Diesel fuel as well as the polymers polystyrene (PS) and polycarbonate (PC) were investigated. The respective TG curves of the investigated samples are depicted in Fig. 3. While diesel fuel (Fig. 3a) shows a pure distillation/vaporisation behaviour (i.e. a rather gradual mass loss with increasing temperature), the

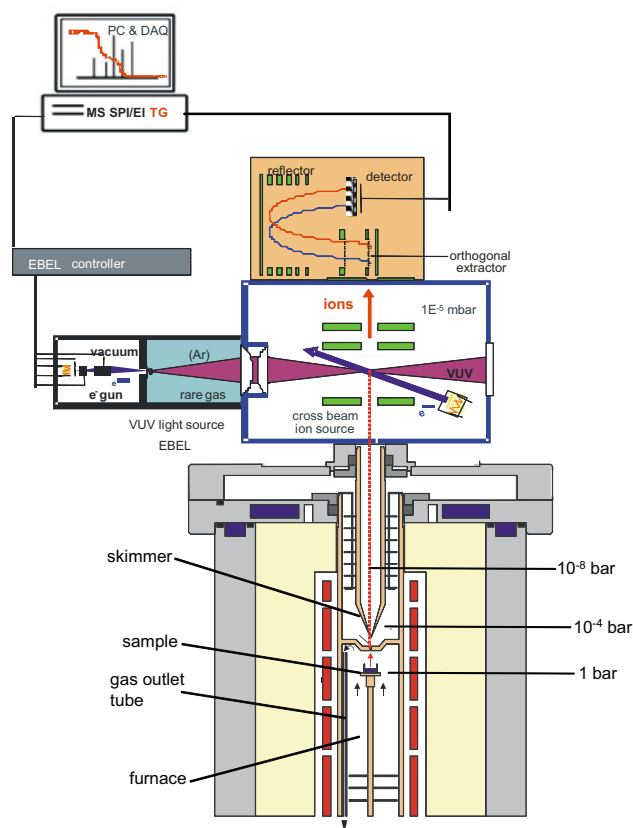


Fig. 2 Schematic representation of the modified TG Jet-Skimmer system (Netzsch GmbH, Selb, Germany) coupled to a *oa*-time-of-flight mass analyser (C-TOF, TOFWERK AG, Thun, Switzerland) using a homebuilt electron beam pumped rare gas excimer VUV light source (EBEL) for soft single photon ionisation (SPI)

polymer samples show decomposition/depolymerisation in a single step upon a specific decomposition temperature (PS at ~ 412 $^{\circ}\text{C}$, Fig. 3b and PC at ~ 515 $^{\circ}\text{C}$, Fig. 3c). Note that the PC decomposition leaves a residue of about 30 mass percent of carbonaceous refractory material which only volatilises when oxygen is added at high temperatures. In Fig. 4, the three-dimensional plot (temperature \times molecular mass \times ion signal intensity) of the diesel fuel measurement as well as the corresponding mass spectrum at 190 $^{\circ}\text{C}$ is shown. Similarly as in previous published results on mineral oil analysed by a TG-capillary

Table 1 Performed TG Jet-Skimmer-SPI/EI-*oa*-TOFMS measurements

Measurement	TG/heating rate/ K min^{-1}	Sample amount/ mg	Gas flow/ $\text{mL N}_2 \text{ min}^{-1}$	<i>oa</i> -TOF parameters	EBEL VUV light source parameters
Diesel fuel	10	57.5	150	Internal average 62,500 extraction/s	Argon excimer (9.8 eV), electron beam energy: 12 kV, electron current through foil: 5 μA
Polystyrene (PS)	10	17.9	150	Internal average 62,500 extraction/s	Argon excimer (9.8 eV), electron beam energy: 12 kV, electron current through foil: 5 μA
Polycarbonate (PC)	10	27	150	Internal average 62500 extraction/s	Argon excimer (9.8 eV), electron beam energy: 12 kV, electron current through foil: 5 μA

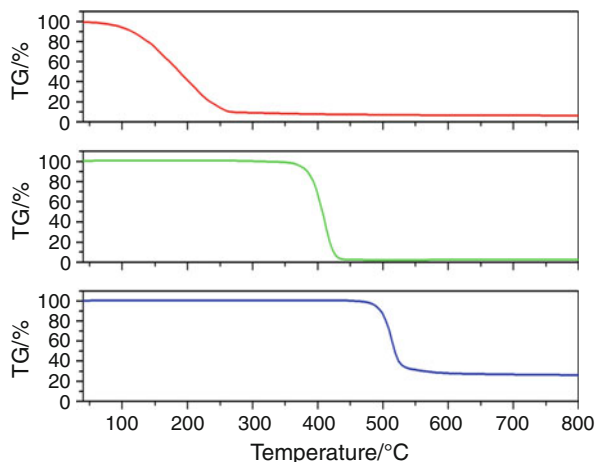


Fig. 3 Thermogravimetric curves of the investigated samples: **a** Diesel fuel; **b** polystyrene (PS); **c** polycarbonate (PC)

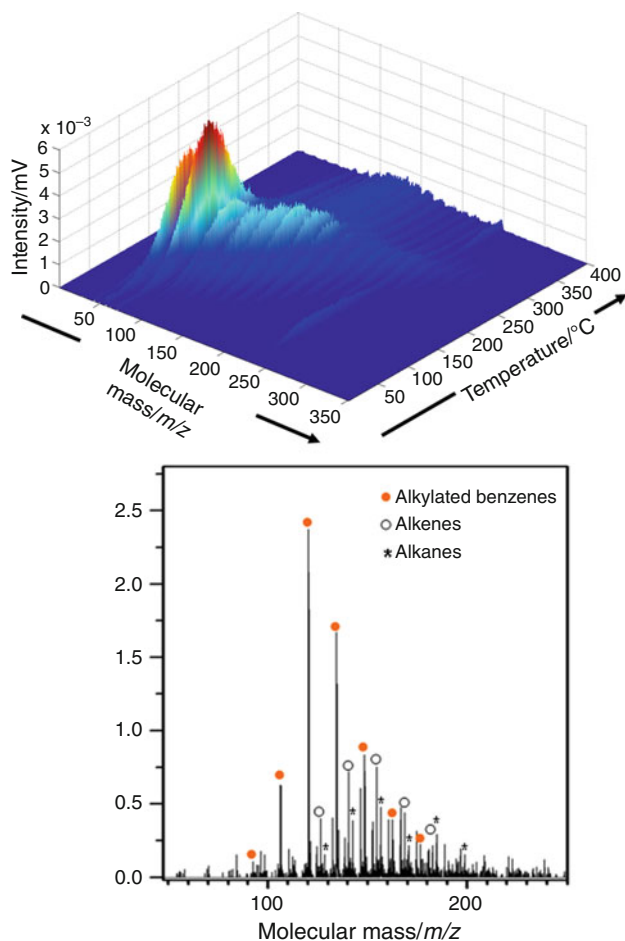


Fig. 4 TG-skimmer-SPI-TOF mass spectrometric results for diesel fuel: **a** Three-dimensional representation of the TG-skimmer-SPI-TOF mass spectrometric profile of diesel fuel as a function of the sample temperature. **b** TG-skimmer-SPI-TOF mass spectrum of diesel fluke recorded at the sample temperature 190 °C

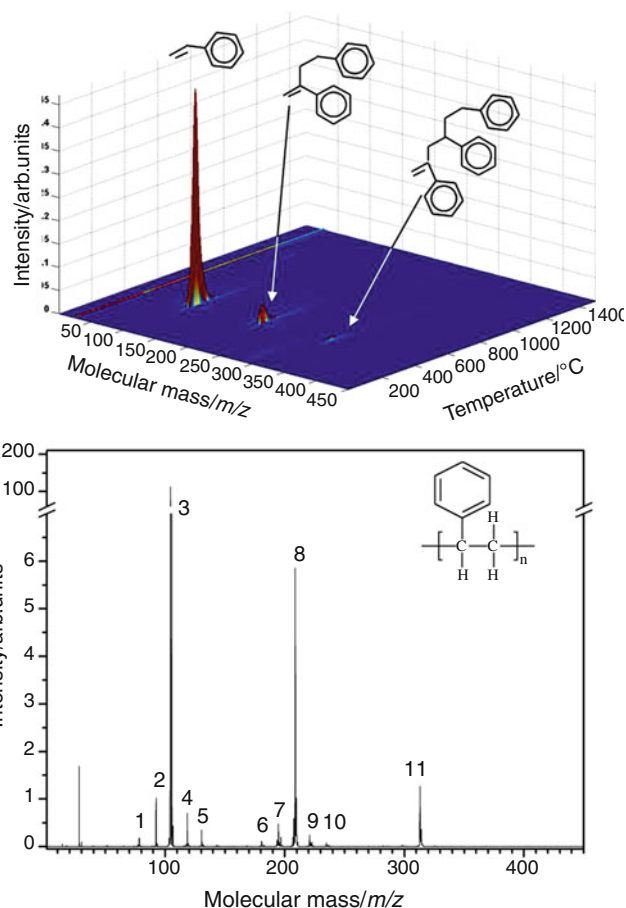


Fig. 5 TG-skimmer-SPI-TOF mass spectrometric results for polystyrene (PS): **a** Three-dimensional representation of the TG-skimmer-SPI-TOF mass spectrometric profile of PS as a function of the sample temperature. **b** TG-skimmer-SPI-TOF mass spectrum of PS recorded at the sample temperature 412 °C

coupling—SPI-QMS, typical distillation behaviour is observed in Fig. 4a. Upon an increase of the temperature, the molecular weight distribution is shifting towards heavier compounds of lower volatility. In the mass spectrum recorded at 190 °C (Fig. 4b) the homologous series of typical diesel fuel compounds are indicated, namely the alkanes (*), alkenes/cycloalkanes (○) and the alkylated benzenes (●). In the lower mass range below 78 m/z (benzene) the mass spectrum is virtually absent of peaks with exception to 28 m/z (nitrogen) which is due to residual electron impact ionisation by photoelectrons. This demonstrates the softness of SPI. Note that the supersonic jet expansion possibly further supports the reduction of residual thermal fragmentation due to its cooling effect. In the three-dimensional plot also some carry over-effect is observed for mass 282 m/z . These sometimes occurring weak memory or carry-over effects are likely due to a re-evaporation from material deposited during previous experiments within or at the gas outlet tube in the furnace.

Table 2 Tentative assignment of peaks observed in the SPI mass spectrum of Polystyrene (PS) depicted in Fig. 5b)

Peak #	Mass/ <i>m/z</i>	Relative Intensity	Compound (tentative assignment)	Ionisation energy/eV
1	78	0.2	Benzene	9.4
2	92	1.0	Toluene	8.8
3	104	112.5	Styrene	8.46
4	118	0.7	Phenylpropene	8.5 (1-phenyl-1-propene)
5	130	0.4	1,3-Butadienylbenzene	8.39
6	180	0.1	Stilbene (diphenylethene)	7.66 (<i>trans</i>) 7.80 (<i>cis</i>)
7	194	0.5	Diphenylpropene	–
8	208	5.8	Diphenylbutene (styrene dimer)	–
9	222	0.08	Diphenylpentene	–
10	236	0.03	Diphenylhexene	–
11	312	1.2	Triphenylhexene (styrene trimer)	–

Figure 5 depicts the result on the thermogravimetric analysis of polystyrene (PS). The three-dimensional plot shows that in addition to the dominating peak at 104 *m/z*, which is representing the monomer styrene also the styrene dimer (208 *m/z*) and styrene trimer (312 *m/z*) are formed. The styrene dimer was also observed in the previous experiments with capillary coupling. The mass spectrum recorded at around 412 °C shows 11 peaks, which are tentatively assigned in Table 2. In addition the ionisation energies are given, if available [22].

Due to the resonance stabilisation of the styrene monomer the alkane backbone of the PS polymer readily is breaking after every second chain-carbon, forming predominately styrene (C₂-phenyl unit). However, the occurrence of toluene (C₁-phenyl unit), phenylpropene (C₃-phenyl unit) and phenylbutadiene (C₄-phenyl unit) shows that other chain-breaking positions are possible, although less probable. A similar behaviour is observed for the styrene dimer (208 *m/z*) which is the most abundant pyrolysis product in the 200 *m/z* mass region (C₄-diphenyl unit). This peak is flanked by much

Table 3 Tentative assignment of peaks observed in the SPI mass spectrum of Polycarbonate (PC) depicted in Fig. 5b)

Peak #	<i>m/z</i>	Relative intensity (<i>m/z</i> 108 = 100; bold for >5)	Compound	Ionisation energy/eV
1	92	2.1	Toluene	8.8
2	94	31	Phenol	8.49
3	106	2.6	Ethylbenzene	8.77
4	108	100	Cresole methoxybenzene	8.35 (<i>p</i> -cresole) 8.25
5	120	9.7	Propylbenzene, vinylphenol	8.71 (propylbenzene)
6	122	34	Ethylphenol	7.8 (4-ethylphenol)
7	134	5.4	Propylphenol	–
8	136	6.5	Propylphenol	–
9	182	1.1	Diphenylethane	9.1 (1,2-diphenylethane)
10	184	1.1	<i>p</i> -Phenol, phenyl-methane	–
11	198	4.3	<i>p</i> -Phenol, phenyl-ethane	–
12	210	0.7	<i>p</i> -Phenol, phenyl-propene	–
13	212	4.4	<i>p</i> -Phenol, phenyl-propane	–
14	214	1.6	Di(<i>p</i> -phenol)-ethane	–
15	226	1.4	Di(<i>p</i> -phenol)-propene	–
16	228	6.5	Di(<i>p</i> -phenol)-propane (=bisphenol A)	–
17	242	1.4	<i>p</i> -Phenol, - <i>p</i> -penylmethoxy-propane	–
18	256	1.1	Di(<i>p</i> -penylmethoxy)-propane	–

weaker peaks at 180 m/z (stilbene, C₂-diphenyl unit), 194 m/z (diphenylpropene, C₃-diphenyl unit), 222 m/z (diphenylpentene, C₅-diphenyl unit) and 236 m/z (diphenylhexene, C₆-diphenyl unit). The highest mass peak in the skimmer SPI-TOFMS EGA mass spectrum is the styrene trimer peak at 312 m/z (triphenylhexene, C₆-diphenyl unit). Note that with the commercial thermogravimetry—supersonic jet-skimmer quadrupole mass spectrometer system using “hard” electron ionisation, the mass spectra are dominated by the electron ionisation fragments [23].

Polycarbonate (PC) is the polymer of bisphenol A and phosgene. In contrast to polystyrene, where the pyrolysis mainly leads to a depolymerisation with the non-decomposed monomeric styrene molecule as main product, polycarbonate (PC) is forming mainly smaller pyrolysis products originated by decomposition of the phenolic monomer component. The carboxylic group introduced by phosgene is rapidly transformed to CO₂ upon the breakdown of the polymer. Thus the bisphenol A component of the polymer and its pyrolysis products are dominating the TG-SPI mass spectrum at around 515 °C. The bisphenol A monomer itself can be detected at 228 m/z , but exhibits a rather weak intensity. The most intense peak at 108 m/z is due to methylated phenol, i.e. the cresol-isomers and methoxybenzene, followed by ethylphenol and phenol. In Table 3 a tentative assignment of the peaks observed in the TG jet-skimmer SPI-TOF mass spectrum of polycarbonate is given.

The presented results show that the commercial TG jet-skimmer system could be very well adapted for organic profiling using a photo ionisation time-of-flight mass spectrometer instead of the standard quadrupole mass analyser. The jet-skimmer interface is designed and usually used for analysis of inorganic pyrolysis products, partially at very high temperatures. The implementation of an additional photo ionisation source, however, increases the versatility of the jet-skimmer system considerably, which is an important issue for an expensive high-end instrumental analytical technology. A critical point of analysis of organic pyrolysis products, however, is the sensitivity. As it can be seen in mass spectra in Figs. 4, 5, 6 organic samples often decompose into a complex substance mixture. Furthermore, in many cases a larger fraction of the organic material breaks down pyrolytically into small inorganic or organic compounds such as CO₂, H₂, CH₄ which contribute little to the usable organic fingerprint information. Due to this broad distribution, the relative intensity of individual compounds may become rather low and slip below the detection limit. The detection strength of a capillary coupling, where the analyte gas from the TG-furnace is directly swept in the ion source, is of course much higher than in a jet-skimmer approach where the gas is expanding freely from the expansion orifice towards the

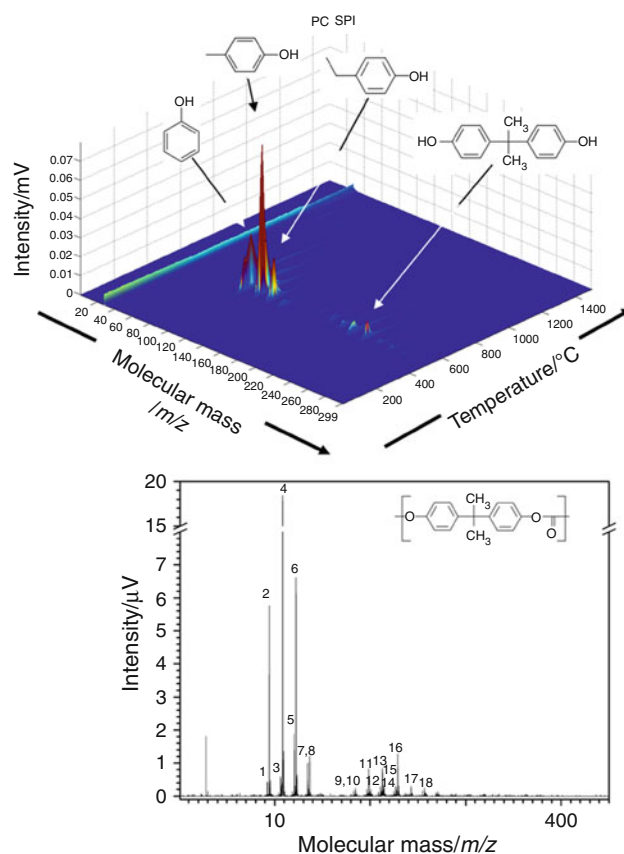


Fig. 6 TG-skimmer-SPI-TOF mass spectrometric results for polycarbonate (PC): **a** Three-dimensional representation of the SPI mass spectrometric profile of PC as a function of the sample temperature. **b** TG-skimmer-SPI-TOF mass spectrum of PC recorded at the sample temperature 515 °C

ionisation source. On its way towards the ion source, the gas density ρ reduces with the square of the distance d from the expansion point ($\rho \sim d^{-2}$). As mentioned above the distance between the expansion orifice and the ion source is still rather large (98 mm). Thus one important reason for the use of the rather expensive oa-time-of-flight mass spectrometry technology is its inherently large duty cycle, leading to superior detection sensitivities if compared to quadrupole MS systems. The results shown in this work (Figs. 4, 5, 6) demonstrate that the achieved detection strength is sufficient to perform organic fingerprinting/profiling of carbonaceous samples. Future work, however, will be conducted in order to increase the detection sensitivity. In principle there are two straightforward possibilities to increase the sensitivity of the skimmer inlet without changing the ionisation or MS detection technology. On the one hand obviously d could be minimised; on the other hand the orifice diameter can be enlarged in order to generate a higher sampling flow. The first possibility encounters geometrical challenges (i.e. considering that the orifice is at the end of the furnace with a maximum temperature of

2000 °C) while the latter one is restricted due to the available pumping speed of the used vacuum system (and herewith a question of price). In conclusion, within this work for the first time a successful direct jet expansion skimmer coupling of a thermal analysis device and a photo ionisation time-of-flight mass analyser was realised. In the future, the versatile system will be developed, which allows in addition to the SPI-TOFMS analysis of organic signatures also high temperature TG and DSC measurements as well as evolved gas analysis using electron ionisation mass spectrometry. The high potential of the approach motivates further application studies as well as an improvement of the concept in order to increase sensitivity and reduce memory effects in the furnace.

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