

Hyphenation of a thermobalance to soft single photon ionisation mass spectrometry for evolved gas analysis in thermogravimetry (TG-EGA)

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Abstract The potential of hyphenating thermogravimetry (TG) and soft photo ionisation mass spectrometry (EBEL-SPI-MS) for fundamental and applied research and material analysis has been demonstrated by a newly developed TG-SPI quadrupole MS coupling (TG-SPI-QMS). Thermal decomposition of three common plastics, polyethylene (PE), polystyrene (PS) and polyvinylchloride (PVC) has been studied. While the decomposition of PE and PS in inert atmosphere takes place in a one step process (main mass loss at about 490 and 420 °C, respectively), PVC decomposes in a two step mechanism. The organic signature of the PE decomposition shows homologous series of alkenes and polyenes, while PS is forming mainly styrene mono- and oligomers. In the PVC decomposition, firstly hydrogen chloride (HCl) is eliminated in a hydro-dechlorination reaction (1st mass loss step: 285–305 °C), this is accompanied by the emission of the carbon skeletons of small aromatics (predominately benzene and naphthalene). In the second step (2nd mass loss step: 490–510 °C), the

residual cross-linked polyolefin moieties decompose under release of heavily alkylated aromatics, including larger PAH. Chlorinated aromatics are formed only in trace levels.

Keywords Mass spectrometry · Photon ionisation · Thermogravimetry

Introduction

In thermogravimetry (TG) the course of the mass loss of a sample due to pyrolysis and vaporisation processes during a thermal protocol is recorded with a thermo-balance. For many research and industrial applications the information obtained from the TG curve (sample mass vs. temperature curve) or the derivative TG curve (DTG, first derivative of sample mass vs. temperature curve) are used for e.g. quality control or applied material research. For more advanced applications, however, often a chemical analysis of the evolved gases is required. This 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)) [1] or by coupling of an on-line real-time analytical technology. Examples for the latter case are Fourier-transform infrared spectrometry (FTIR) for analysis of the evolved organic compound classes and mass spectrometry (MS) [2]. The mass spectrometry method commonly used in conjunction with TG is quadrupole mass spectrometry with electron impact ionisation (EI). The coupling between the TG oven and the mass spectrometer is realised either via a transfer capillary or a skimmed supersonic expansion. Although MS is a very powerful analytical technique for elemental and molecular analysis, the currently available TA-MS systems with EI

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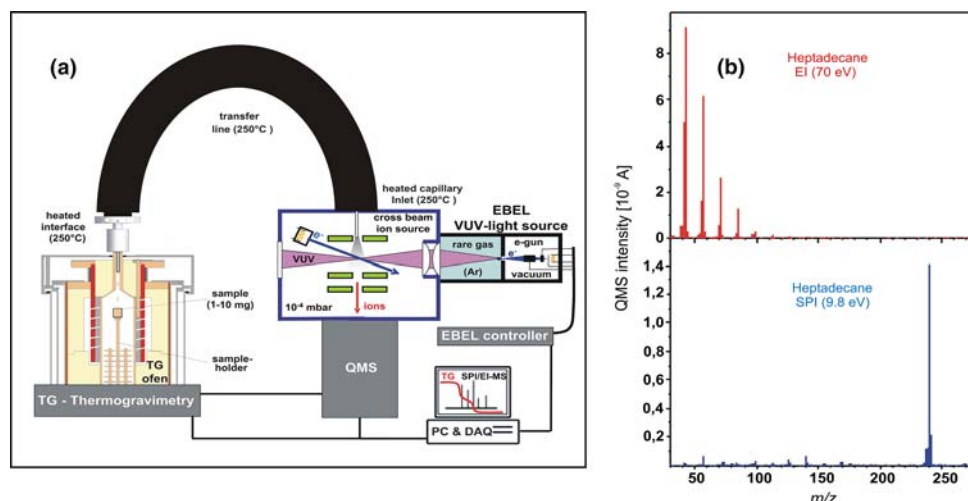
ionisation in most cases can not provide a realistic fingerprint of the composition of the organic trace species in the evolved gases. This is mainly due to the fact that electron impact ionisation with 70 eV electron energy inherently causes a large extent of fragmentation of the organic molecules upon ionisation. First thermal desorption studies, pyrolysis studies [3, 4] as well as TG studies using laser or deuterium lamp based soft ionisation mass spectrometry as detector [5, 6] revealed that highly valuable information on the molecular signature of the thermal decomposition processes can be achieved. In this contribution, a newly developed prototype of a TG-single photon ionisation quadrupole mass spectrometer coupling (TG-SPI-QMS) is applied. A novel electron beam pumped rare gas excimer VUV-lamp (EBEL) technique is used for the soft photo ionisation process [7–9]. The fundamentals of the TG-QMS coupling [10] and the EBEL based photo-ionisation [9, 11, 12] have recently been described in detail and therefore are only briefly given in the following. In this paper exemplarily data on the decomposition of the polymers polystyrene (PS), polyethylene (PE) and polyvinylchloride (PVC) are presented and discussed.

Experimental

The working principles of the EBEL [13] and the EBEL-QMS system were described previously in the literature [8, 9] as well as the fundamentals on the coupling of the thermogravimetric analyzer and the SPI mass spectrometer [10]. Briefly, a homebuilt EBEL-VUV light source was used for single photon ionisation in a simple QMS system (QMS 200, 6-mm rod system, Balzers-Pfeiffer, Switzerland). One important innovation of the novel EBEL-VUV light source is a $0.7 \times 0.7 \text{ mm}^2$ ceramic silicon nitride (SiNx) foil of only about 300 nm thickness that separates

the rare gas volume ($p > 1 \text{ bar}$) from a vacuum chamber containing an electron gun (EG). The EG generates a 13 keV electron beam which is shot into the rare gas through the SiNx foil with low-energy loss. The energetic electrons excite and ionise the rare gas atoms. In successive processes, excited diatomic rare gas molecules (excimers) are formed. These excimers do not have a stable molecular ground state and decay typically within a few microseconds. Upon the decay of the rare gas excimers, VUV-radiation is emitted. As a result of the high gas pressure, the excimer formation occurs in a small volume in the close proximity of the electron entrance foil. The rare gas volume was filled with Argon (emission maximum: 126 nm, 9.8 eV centre photon energy) for the here presented results. The EBEL SPI-QMS exhibit detection limits in the 50 ppb range for a scan rate of 1 m/z s^{-1} . Note that future TA-EBEL-SPI-MS systems will be equipped with more intense EBEL sources as well as with more powerful mass analyzers (high-end quadrupole systems with e.g. 8 mm rod system, time-of-flight mass spectrometers or ion traps) and thus will exhibit further decreased detection limits. For the here presented experiments on PS, PVC and PE, the gas inlet of the QMS was coupled via a heated transfer line to the TG system (Type STA 409, Netzsch Gerätebau, Selb, Germany). A special heated adapter and deactivates transfer line ($250 \text{ }^\circ\text{C}$) were developed for the TG-system to avoid memory effects of the released higher boiling organic compounds. Note that the QMS 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. 1a. Different polymer samples were investigated, namely polyethylene (PE), polystyrene (PS) and polyvinylchloride (PVC). The experiments were performed under nitrogen atmosphere and at a fast heating rate ($40 \text{ }^\circ\text{C/min}$ for PE, PVC and $10 \text{ }^\circ\text{C/min}$ for PS).

Fig. 1 **a** Schematic representation of the TG-EBEL-SPI-QMS prototype. **b** TG-quadrupole mass spectra of heptadecane recorded with the developed TG-QMS instruments using the conventional electron impact ionisation (EI, 70 eV; hard ionisation, *top*) single photon ionisation (Ar-EBEL, 9.8 eV; soft ionisation, *bottom*)

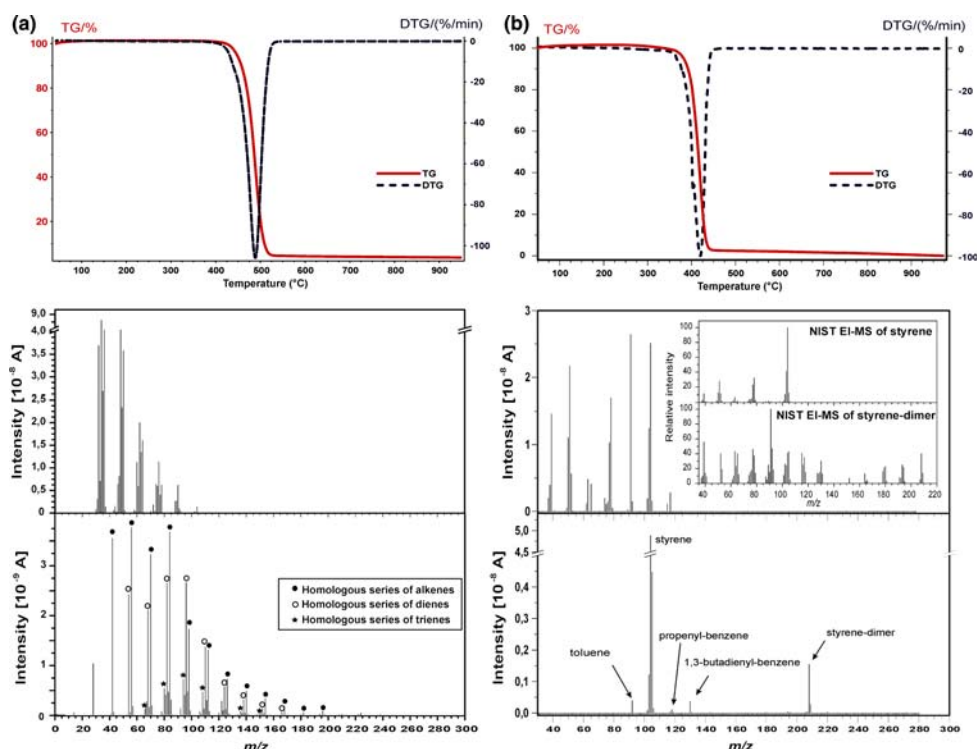


Results and discussion

It is crucial for an on-line detection of organic signatures that a very soft ionisation could be achieved. In Fig. 1b mass spectra of heptadecane obtained with the above mentioned TG-QMS coupling are presented. The mass spectrometer was operated in SPI (Fig. 1b, top) and EI (Fig. 1b, bottom) modes. The heptadecane sample was placed in the sample pan, the oven temperature was set to 40 °C and the transfer line temperature was set to 250 °C. Figure 1b clearly demonstrates that heptadecane, a rather fragile long-chain alkane, could be detected as molecular peak solely by SPI-MS while the EI-MS is dominated by fragment peaks. In the following experiments the novel TG-EBEL-SPI-QMS device was applied to analyse the thermal decomposition of common plastics, namely of polyethylene (PE), polystyrene (PS) and polyvinylchloride (PVC). It is known from literature that the main products of PE pyrolysis are unsaturated hydrocarbons (alkenes, polyenes) while the amount of aromatic products is low [14]. Figure 2a shows the TG/DTG curves of PE (upper panel) as well as two mass spectra obtained from the evolved gases at 480–510 °C using either conventional EI ionisation (middle panel) or the EBEL-SPI photo ionisation (lower panel). Note that the used lamp for SPI (Ar-excimer, 9.8 eV) does not address the smaller alkanes. The EI mass spectrum is dominated by fragments. From the EI mass spectrum thus it can only be stated that the content of aromatics is rather low in comparison to the aliphatic

pyrolysis products. In contrast, the soft EBEL-SPI mass spectrum reveals clearly the homologous series of alkenes, dienes as well as trienes up to C_{14} . With a further improved heated inlet and the more sensitive 8 mm rod quadrupole mass analyzer, it should be possible to detect organic PE pyrolysis products of even higher molecular mass. In Fig. 2b the thermogravimetric curves (TG, DTG) of polystyrene (PS) are shown. The maximal decomposition rate is reached at 420 °C. The corresponding TG-EI and TG-SPI mass spectra are depicted in Fig. 2b, middle and lower panel, respectively. The conventional EI mass spectrum is dominated by fragment peaks of odd mass number, with 39, 51, 77, 91 m/z (tropylium ion) and 103 m/z being the most prominent ones. The most prominent even mass number peaks in the EI mass spectrum are 78 (benzene) and 104 m/z (styrene monomer). From this TG-EI-MS mass spectrum one may conclude that the main decomposition products of PS at the maximal decomposition rate (420 °C) are styrene (from 104/103 m/z peaks), toluene (from 91 m/z) and benzene (from 78/77 m/z peaks). This however is disproved by the corresponding soft ionisation mass spectrum (Fig. 2b, bottom). The TG-SPI mass spectrum shows that the by far dominant organic PS decomposition products are the styrene monomer (104 m/z) and the respective dimer of styrene (208 m/z) which, however, are the “natural” polystyrene de-polymerisation products. Furthermore a rather tiny signals at 92 m/z (toluene), 118 m/z (propenyl-benzene) and 130 m/z (1,3-butadienyl-benzene) are detectable in the chemical signature of

Fig. 2 a Thermogravimetry-single photo ionisation quadrupole mass spectrometry (TG-SPI-QMS with EBEL) results of polyethylene (PE): (top) TG and DTG curves (middle) Electron impact mass spectrum (EI, 70 eV; bottom) SPI mass spectrum recorded during the maximal decomposition rate. b Thermogravimetry-single photo ionisation quadrupole mass spectrometry (TG-SPI-QMS with EBEL) results of polystyrene (PS): (top) TG and DTG curves of PS (middle) Electron impact mass spectrum (EI, 70 eV) at a temperature of 420 °C. In the inset NIST standard EI reference mass spectra of styrene and the styrene dimer are shown (bottom) SPI mass spectrum recorded during the maximal decomposition rate at a temperature of 420 °C



thermal PS decomposition. These C_1 -, C_3 - and C_4 -benzene species originate from irregularly breaking of the polymer backbone as trace products. In consequence the majority of the peaks visible in the EI mass spectrum (Fig. 2b middle panel) are proven to be fragments, originated by the high-energetic electron impact ionisation. Note, that the structure of the observed TG-EI mass spectrum can be roughly explained by the superposition of the NIST reference EI mass spectra of the main PS decomposition products, styrene and styrene dimer (NIST EI-MS shown in the inset of Fig. 2b, middle panel). The styrene monomer forms EI-MS fragments at 78 m/z (benzene) and at lower masses while the EI mass spectrum of the styrene dimer generates intensive signals at 91 m/z . Due to the high temperature of the gaseous decomposition products in the TG-MS analysis the degree of fragmentation, however, is increased. Subsequently the higher mass fragments are decreased or even absent in the TG-EI-mass spectrum.

As the TG-SPI-QMS technology in principle allows a real-time on-line analysis, the chain length distribution of the evolved organic species can be monitored as function of the temperature. This, however, may be of restricted interest in the analysis of simple polymers such as PE or PS but motivates studies on the mechanisms of thermal degradation of more complex polymers or polymer blends. The thermal decomposition of polyvinylchloride (PVC) e.g. is much more complicated than the one of PE [14]. Briefly, PVC decomposes in a two-step mechanism. The first step is due to a hydrodechlorination process (HDC), where HCl is eliminated (in the TG-EI-QMS experiment strong HCl signals are visible) leaving a polyolefinic structure as residue [14, 15]. From the polyolefin moieties efficiently benzene is formed. Different mechanisms have been proposed for the HDC and benzene formation. For example, a radical chain mechanism for the HDC, involving Diels-Alder-type reactions for formation of the benzene moieties was proposed by Bockhorn et al. [10]. The residual polyolefin structure is believed to undergo cross-linking reactions at the elevated temperatures. In the further course of the decomposition process the cross-linked polyolefin structures brake apart and release a very complex mixture of alkylated monocyclic as well as condensed polycyclic aromatic compounds. The final residue then represents a char-like, refractory material. In Fig. 3, the TG and DTG curves of PVC (upper panel), as well as TG-EBEL-SPI-QMS mass spectra of the first (middle panel) and second (lower panel) mass loss step are shown. The TG and DTG curves clearly show the well known two-step decomposition behaviour (steps at ~ 300 °C and at ~ 500 °C) of PVC. The soft ionisation mass spectrum recorded at the maximal mass loss rate of the first step (285–305 °C) depicts predominantly benzene and naphthalene as organic decomposition products in accordance with the literature

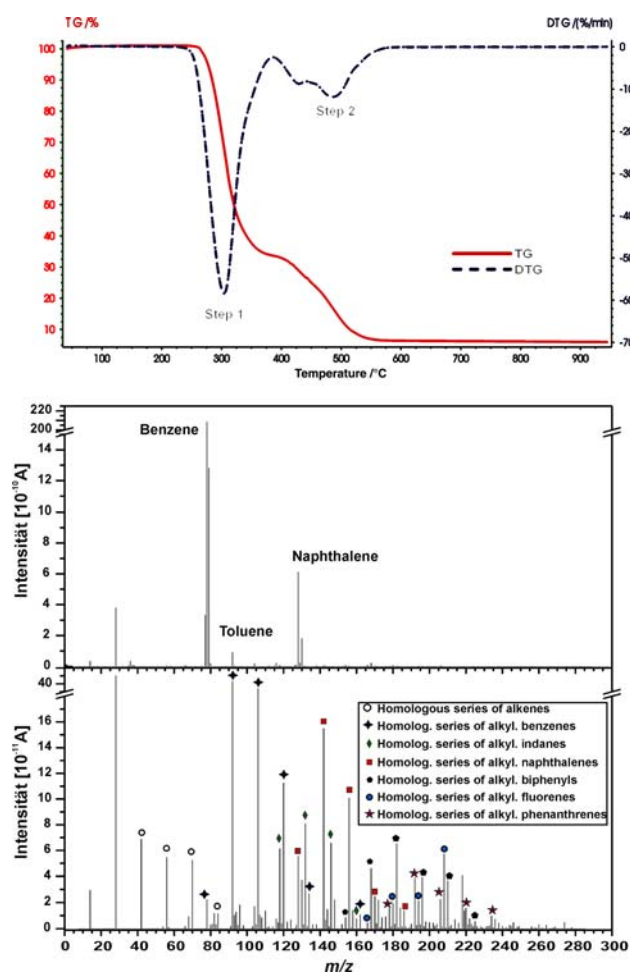


Fig. 3 Thermogravimetry-single photo ionisation quadrupole mass spectrometry (TG-SPI-QMS with EBEL) results of polyvinylchloride (PVC) (*Top*) TG and DTG curves (*Middle*) SPI mass spectrum of the first decomposition step (*Bottom*) SPI mass spectrum of the second decomposition step

(here also HCl is released but not covered by the soft ionisation at 9.8 eV). This picture changes if the second mass loss maximum at 490–510 °C is considered. During the decomposition of the cross-linked polyolefin structure a complex pattern of aromatic carbon skeletons evolves with various alkyl substitutions. In particular homologous series based on benzene, indane, naphthalene, biphenyl, fluorene and phenanthrene are detectable. In most cases, the C_1 -substituted congener is the most abundant one (mono-methyl-derivatives). According to the theory, the structure of the cross-linked polyolefin determines the profile of the substitutions. As the evolution of the substitution profile is now dynamically detectable by SPI-MS, a re-evaluation of the course of the thermolysis of PVC might be of interest. Note, that neither chlorinated benzenes (PCBz) nor chlorinated aliphatics have been detected under the current experimental TG-SPI-QMS conditions. This is in contrast to the results of preceding flash-pyrolysis experiments with

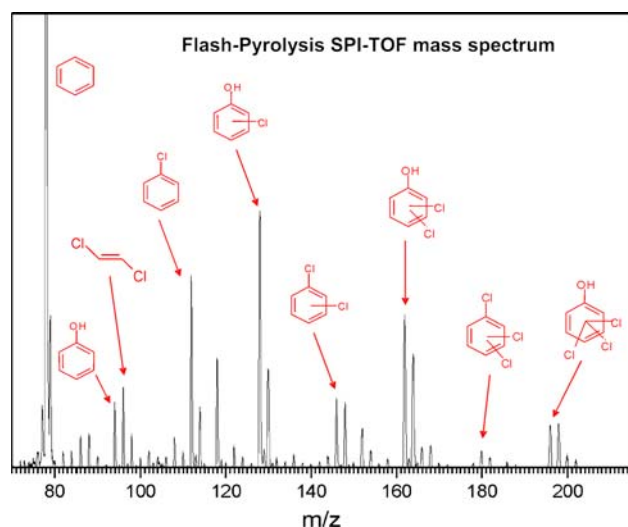


Fig. 4 Single photo ionisation time-of-flight mass spectrum (118 nm) of pyrolysis gases from a flash-pyrolysis experiment on PVC (700 °C nitrogen), after reference [4]. Here chlorinated aromatics are rather prominent

laser based EBEL-SPI-TOFMS detection [4]. As shown in Fig. 4, strong PCBz signals as well as signals of chlorinated phenols (PCPh, in experiments under oxygen containing atmosphere) and chlorinated aliphatics (e.g. dichloroethylene) are detected [4], which suggest also the potential formation of toxic chlorinated trace components such as polychlorinated dibenzo-p-dioxins and furans (PCDD/F) and polychlorinated biphenyls (PCB). The reason for the formation of chlorinated aromatics in case of rapid heating of the PVC sample to temperatures above 600 °C (flash-pyrolysis), however, is that the above described hydrodechlorination process—which takes place at lower temperatures during a slowly heating of the sample and removes the majority of the chlorine as HCl—is overridden. The flash-pyrolytic breakdown of the PVC backbone at high temperatures thus takes place in the presence of high amount of chlorine, resulting in the formation of chlorinated aromatic and aliphatic species. In summary it was shown SPI-MS allows the recording of organic signatures of the evolved gases from decomposing polymers in a thermobalance.

Conclusions

The potential of hyphenating thermogravimetry and soft photo ionisation mass spectrometry (EBEL-SPI-MS) for fundamental and applied research and material analysis in the field of polymer science was demonstrated. SPI-MS is capable of recording the molecular organic signature of the evolved organic gases from the pyrolysis of polymers such

as PE, PS or PVC. This includes e.g. dimers or oligomeric products which up to now have not been detectable by the conventional TG mass spectrometric methods using electron impact ionisation (EI). Other successful applications of the TG-EBEL-SPI-MS technique include food material, biomass, mineral oil and coal. A commercial, integrated TG-SPI-QMS 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.

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