Application of time-of-flight mass spectrometry with laser-based photoionization methods for analytical pyrolysis of PVC

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Introduction

Polyvinylchloride (PVC) is a widely used plastic material. It is present in municipal solid waste (MSW) in a range of 0.5-1 % by weight[1]. Furthermore, it can be found on waste steel, which will be recycled by melting in an electric arc furnace. Either way, the combustion and pyrolysis of PVC lead to the formation of various pollutants such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and polychlorinated dibenzo-p-dioxins and –furans (PCDD/F) bearing serious health issues. To meet the emission thresholds put up for these substances, e.g. in waste incinerators, costly secondary measures are necessary.

Chlorinated benzenes and phenols generated from PVC pyrolysis are known to be precursors of PCDD/F formation[2,3]. Therefore, selective and sensitive monitoring of these substances during PVC pyrolysis processes on an on-line, real-time basis could be very useful for the understanding of PCDD/F formation pathways. In this study, we investigated the pyrolysis gas from PVC samples derived from steel recycling by means of simultaneous single photon ionization/resonance-enhanced multiphoton ionization time-of-flight mass spectrometry (SPI/REMPI-TOFMS)[4,5]. The application of these soft photo-ionization techniques in mass spectrometry enables a fast and comprehensive analysis of this complex matrix without generating fragment ions, which would interfere with molecule ions making interpretation of the obtained mass spectra very difficult.

Materials and Methods

The schematic diagram (Figure 1) of the pyrolysis-SPI/REMPI-TOFMS system shows the experimental setup. A rotary furnace (Carbolite GmbH, Germany) with an inserted quartz glass tube (I.D. 10 mm) was used for the pyrolysis experiments. The samples were placed into a quartz "boat" and placed inside the tube. PVC coating material typically found on recyclable waste steels were collected from Chinese steel plants. PVC materials are normally derived from car decorations and colored steel plates, the latter representing a new and popular building material in China, on which a layer of PVC material is coated. Therefore, these contaminants are transferred to the electric arc furnace along with the recyclable waste steels. The PVC content is approximately hundreds of grams per ton of steel. The sample size for each individual measurement was 15 mg.

Furnace temperature was set to 400, 500, 600, 800, 900, and 1000 ºC, respectively. A flow rate of 1 l/min of either synthetic air (80 % nitrogen, 20 % oxygen) or nitrogen was provided for investigation of the PVC samples.

A quartz fiber filter was placed at the outlet of the furnace to separate particles from the gas stream. A deactivated fused silica capillary (350 µm i.d.) running in a heated transfer line was placed orthogonally to the main gas flow, extracting a small portion. At the other ending the capillary is running inside a heated, hollow inlet needle made of stainless steel. Behind the orifice of the fused-silica capillary, which is situated inside the ion source, an effusive molecular beam is formed. All the connection parts outside of the furnace and the transfer line were constantly heated to 250 ºC to prevent condensation and memory effects.

The setup of the SPI/REMPI-TOFMS device for analyzing the pyrolysis gases conveyed from the furnace via the transfer line is described elsewhere[5,6], therefore, only a brief description is given here. Fundamental Nd:YAG laser pulses (1064 nm, repetition rate 10 Hz) are used for non-linear generation of UV and VUV laser pulses for REMPI and SPI ionization, respectively. The initial laser beam is frequency tripled, and the resulting 355 nm beam is split into two parts. The first one is used to pump an β-BBO crystal (of a thermally stabilized OPO-laser) to generate UV-laser pulses for the REMPI ionization. It generates OPO-laser pulses of tunable wavelengths in the range from 205 to 2500 nm. Results presented in this work were carried out by adjusting the crystal to provide 266 nm laser pulses, because this wavelength has been proven to be well suited for REMPI ionization of aromatic compounds in a sequential two-photon absorption process via an electronic transition state[7]. Experiments using other wavelengths are not shown here. The other part of the 355 nm beam is guided into a gas cell filled with xenon, where it is frequency tripled due to a non-linear polarization effect in the isotropic gas medium. Subsequently, the formed VUV beam with a wavelength of 118 nm passes the ionization chamber and is used for the single photon ionization of the organic molecules in the gas sample. Since only 0.001 % of the 355 nm beam is converted into 118 nm, the remaining 355 nm beam has to be separated from the generated VUV beam. This is achieved by utilization of the different refraction indices with respect to a MgF_2 lens and subsequent dumping of the deflected 355 nm beam. Two computer controlled beam blockers are used to select between the REMPI and SPI beams, allowing alternating application of REMPI and SPI with the corresponding frequency of 5 Hz. Both beams are focused curtly underneath the inlet needle of the sampling line by means of appropriate optical elements. The generated molecular ions are extracted into the flight tube of the reflectron time-of-flight mass spectrometer (Kaesdorf Instruments, Germany). The TOF mass spectra are recorded via a transient recorder PC card (Aquiris, Switzerland, 250 MHz, 1 GS/s, 128 k). The recorded

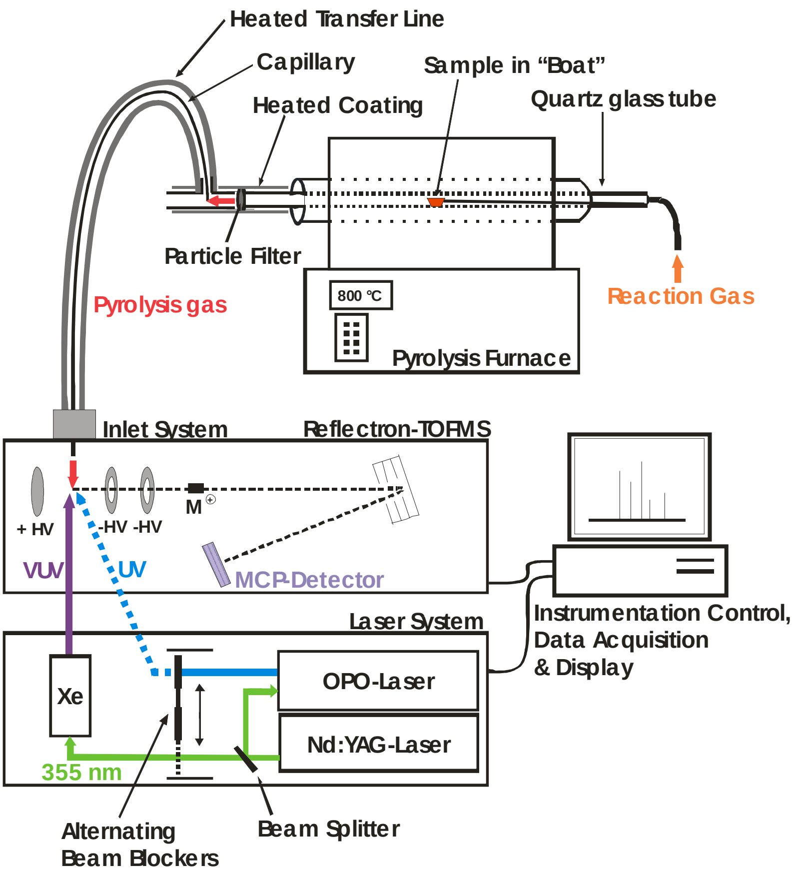

Figure 1: Schematic diagram of the pyrolysis-SPI/REMPI-TOFMS system

mass range reached from 0 m/z to 300 m/z. Data processing is done by a LabView (National Instruments, USA) based home-written software. Quantification of the analyzed compounds is principally possible by applying commercial calibration gases or homebuilt gas standards. However, in this study only a qualitative evaluation was performed. The decomposition of the samples usually took different time spans according to the varying conditions. On average, 80 s after the beginning of the experiment no pyrolysis products could be observed anymore. Regarding PVC pyrolysis five single laser shot mass spectra were averaged for the REMPI and SPI spectra, respectively, resulting in corresponding full range mass spectra every second. For the purposes of the present study, sum- spectra of the whole time range of the pyrolysis process are considered for discussion.

Results and Discussion

Figure 2 shows the respective SPI and REMPI@266nm mass spectra of PVC pyrolysis at 500 °C in air atmosphere. The figure clearly exhibits the different patterns that are visible when the two ionization techniques are applied simultaneously. With SPI, mainly aliphatic hydrocarbons as well as benzene and its methylated derivatives can be detected. The latter ones and the homologue row of the alkenes starting with propene are indicated in the figure. With increasing molecular weight the concentration level of the chemical species apparently decreases, so that in fact naphthalene (128 m/z) and methylnaphthalene (142 m/z) are still visible in the SPI mass spectrum, but the polycyclic aromatic hydrocarbons (PAH) are situated near the detection limit. However, REMPI@266 nm is highly sensitive for detection of PAH[8,9], thus from the REMPI mass spectrum it becomes obvious that a great number of PAH are present in the pyrolysis gas. Homologue rows of methylated naphthalenes, phenanthrenes and chrysenes can be observed. Although benzene is one of the major products of PVC pyrolysis[10,11] and it actually exhibits the largest peak in the SPI mass spectrum, the benzene signal in the REMPI mass spectrum is very small. This is founded in the well known fact that with the chosen wavelength of 266 nm for REMPI ionization the ionization efficiency for the benzene molecule is relatively low[12]. Nevertheless the application of this wavelength allows good detection limits for PAH. As a consequence, the comprehensive character of the combined utilization of SPI and REMPI@266nm in mass spectrometry is revealed in Figure 2 making it possible to get information of aliphatic as well as aromatic hydrocarbons almost instantaneously within a few laser shots devoid getting fragmentation reactions.

Since the formation of HCl is one of the first processes taking place during PVC pyrolysis[10], there should always be enough chlorine present to form chlorinated organic compounds such as chlorinated benzenes and phenols. These compounds should in turn be accessible with SPI@118 nm ionization, because their respective ionization potentials are below 10.5 eV. Due to their apparently very low concentration levels in the pyrolysis gas, the signals are expected to be relatively weak. Therefore, Figure 3 shows the same SPI mass spectra as in Figure 2 with a larger zoom factor to reveal the small peaks at higher molecular masses. From the spectrum it is indeed possible to identify several chlorinated compounds such as dichloroethylene (96 m/z), mono- (112 m/z), di- (146 m/z), and trichlorobenzene (180 m/z) on the basis of their respective chlorine isotopic patterns. Since monochlorophenol has the same molecular mass as naphthalene (128 m/z), it is difficult to determine its respective proportion from the peaks at 128 and 130 m/z.

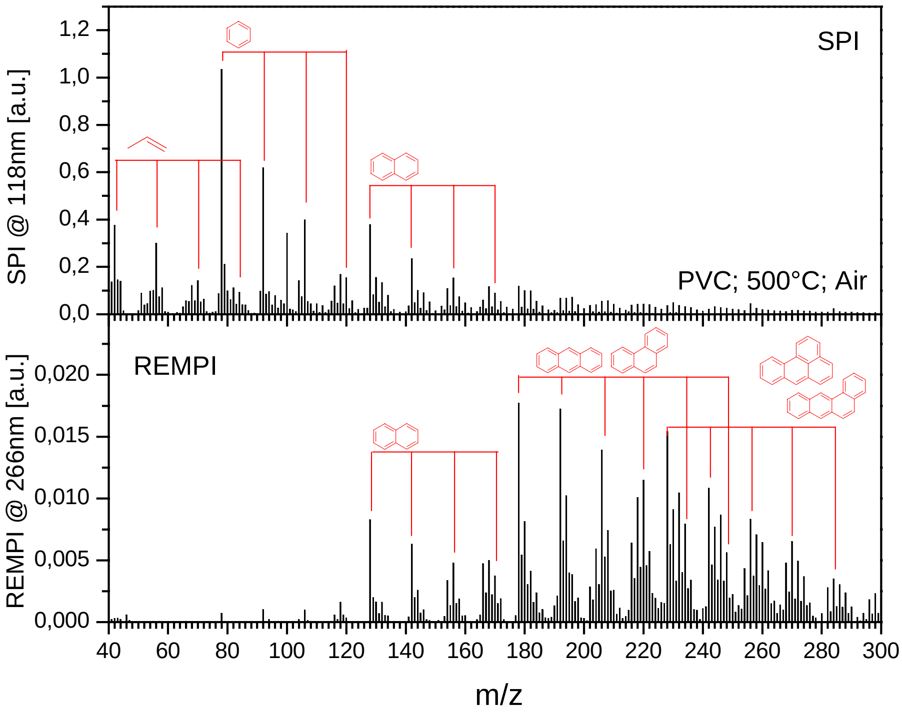

Figure 2: *SPI and REMPI@266nm mass spectra of PVC pyrolysis at 500 °C in air atmosphere*

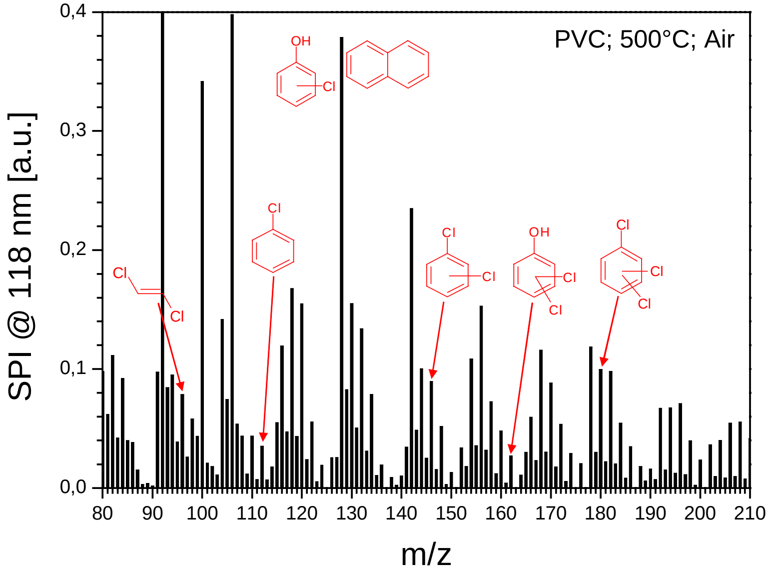

Figure 3: PVC mass spectra in air at 500°C showing chlorinated aromatic compounds

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