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J. Anal. Appl. Pyrolysis 74 (2005) 454–464
JOURNAL of ANALYTICAL and APPLIED PYROLYSIS
www.elsevier.com/locate/jaap

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

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Received 12 July 2004; accepted 22 November 2004
Available online 31 March 2005

Abstract

PVC and tobacco samples were pyrolyzed in a rotary furnace at different temperatures and reaction gas compositions. Released gaseous products were analyzed using single photon ionization (SPI)/resonance enhanced multiphoton ionization (REMPI)–time-of-flight mass spectrometry (TOFMS). These soft and selective ionization techniques allow fast and comprehensive on-line monitoring of a large variety of aliphatic and aromatic substances without fragmentation of the molecular ions. The thermal decomposition of PVC led to the appearance of chlorinated aromatic compounds at trace levels, which could be detected with SPI–TOFMS. Polycyclic aromatic hydrocarbons (PAH) were simultaneously accessible by REMPI–TOFMS. Different tobacco types can be distinguished by photoionization mass spectrometry of their gaseous pyrolysis products. In addition, pyrolysis products can be classified in three groups depending on their behaviour at different pyrolysis temperatures, which might help to unravel formation mechanisms and chemical pathways of hazardous substances.

Keywords: Single photon ionization; Tobacco; PVC; Pyrolysis

1. Introduction

Pyrolysis is a well-established and reliable method for the analytical investigation of polymers and other matrices such as rubber, paint, and coatings (see e.g. [1–3]). In this regard, pyrolytic techniques provide one of the classic approaches for degradation of large molecules and subsequent analysis of the pyrolysis products. As an analytical tool, it even predates gas chromatography and mass spectrometry [3]. However, most analytical pyrolysis applications today are carried out using the latter methods for thorough analysis of the pyrolysis products, thus leading to routinely employment of commercially available pyrolysis-GC, pyrolysis-MS, and pyrolysis-GC/MS instruments [3]. In recent years, several other analytical techniques have been utilized for the investigation of pyrolysis products, e.g. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) [4], infrared spectroscopy (IR) [5], and comprehensive two-dimensional gas chromatography (GC $\times$ GC) [6].

An ideal gas monitor for characterization of pyrolysis processes should be able to detect relevant minor and trace species on a real-time basis. Furthermore, there is often a need for studying dynamic fluctuations occurring during the evolvement of gaseous products from pyrolysis processes. However, conventional mass spectrometers for on-line analysis of complex gas mixtures often do not meet these prerequisites and their utilization is restricted to specific problems. Moreover, usually in mass spectrometry electron impact (EI) ionization is utilized as the ionization technique,

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0165-2370/$ – see front matter
doi:10.1016/j.jaap.2004.11.021

which leads to intense fragmentation pattern in the resulting mass spectra. Hence, when analyzing complex mixtures such as product gases from pyrolysis or combustion processes, respectively, containing a large number of chemical species, interpretation of mass spectra obtained by means of EI is often very difficult or even impossible.

Therefore, utilization of soft, fragmentationless ionization methods such as photoionization or chemical ionization should be considered for the investigation of complex gas mixtures. In particular, resonance enhanced multiphoton ionization (REMPI) [7–12] and single photon ionization (SPI) [13–16] is applied with respect to soft ionization of organic molecules. The REMPI technique uses at least two photons for photoionization, which takes place via an optical resonance absorption step. Due to this resonant absorption, the selectivity of UV gas-phase laser spectroscopy is included in the ionization process. Only those molecules, which exhibit a suited electronic transition with a respective excitation wavelength, may be ionized by two-photon ionization, if in addition, the energy of the two photons is equal or higher than the ionization potential (IP) of the molecule. Particularly, the REMPI-technique is well suited for the on-line analysis of aromatic compounds [17–20].

Single photon ionization technique using vacuum ultraviolet (VUV) photons for ionization can be used to detect additional compounds, e.g. aliphatic hydrocarbons or carbonylic compounds [15,21,22]. Like REMPI, SPI is a soft ionization technique, i.e. in general, no fragmentation of molecules occurs. However, the selectivity of the SPI process is lower compared to REMPI, because all compounds with an IP lower than the photon energy may be ionized. A typical wavelength for VUV–SPI is 118 nm, which can be generated by frequency tripling of intensive 355 nm Nd:YAG laser pulses in a rare gas cell. A wavelength of 118 nm is equivalent to a photon energy of 10.49 eV. As with REMPI, most background gases like nitrogen (IP = 15.58 eV), oxygen (IP = 12.06 eV), carbon dioxide (IP = 13.77 eV), and water (IP = 12.62 eV) cannot be ionized, and thus are not detected in a mass spectrometer.

Combining both ionization techniques with time-of-flight mass spectrometry (TOFMS) results in a fast, on-line capable measurement system for trace compounds in complex gaseous matrices [15,23,24]. The successful application of REMPI–TOFMS and SPI–TOFMS techniques has been demonstrated on various occasions, e.g. for on-line analysis of flue gas of industrial incineration plants [12,25–28], and monitoring of automotive exhaust gas [15,29]. Another example was the time resolved analysis of coffee-roasting off-gas [30,31].

The success of the above mentioned applications motivated the investigation of other pyrolytic processes. Recently, REMPI–TOFMS measurements were carried out to analyze volatile components in cigarette smoke [32,33]. Furthermore, SPI/REMPI–TOFMS was applied for analysis of pyrolysis gas derived from thermal treatment of typical steel contaminants occurring in the steel recycling process from waste and scrap metals [34]. These contaminants such as cooling oil, lubricant, and paint will undergo pyrolytic processes when the waste steel is treated in an electric arc furnace.

In this study, we focus on the investigation of pyrolysis of PVC, a typical contaminant of waste steel. Furthermore, in order to broaden the approach of studying pyrolytic processes related to smoking with real-time mass spectrometry using soft ionization techniques, pyrolysis of several tobacco samples has been carried out.

2. Experimental

The schematic diagram (Fig. 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 coloured 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.

Tobacco samples, each containing 50 mg tobacco, have been taken from three different tobacco types: Burley,

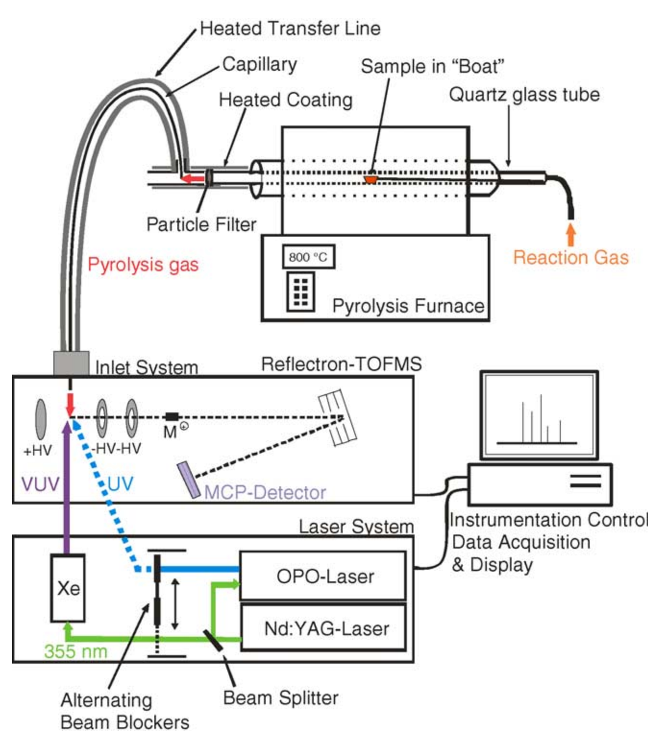

Fig. 1. Schematic diagram of the pyrolysis-SPI/REMPI–TOFMS system.