



Direct inlet probe ion mobility spectrometry

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ABSTRACT

Direct inlet probe (DIP) was used as an introduction and a pre-separation step for atmospheric pressure photoionization time-of-flight ion mobility spectrometry (APPI-TOF-IMS) for the first time. IMS is an analytical technique used to separate and identify ionized molecules in the gas phase and under atmospheric pressure based on their mobility. The utilization of DIP prior to IMS gives the possibility to introduce the analytes into the gas phase and provides an additional separation based on their vapor pressure. The proof-of-principle study was done on example of eight polycyclic aromatic hydrocarbons (PAHs) with the ring number from 2 to 5, namely naphthalene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, benzo[a]pyrene, and benzo[k]fluoranthene. All these compounds are included in EPA priority pollutant list. Moreover, benzo[a]pyrene and benzo[k]fluoranthene are marked by EPA as probably carcinogen compounds and also included into SCF and EU lists. To increase the sensitivity of DIP-APPI-IMS the analysis was performed using a dopant assisted ionization method (benzene, 74 mg L⁻¹ in N₂). It was found that the heating rate of the interface plays a crucial role for the whole analytical procedure. To prove the ability of this method to analyze PAHs in the mixture, the mixtures containing up to five PAHs were analyzed. The LODs for the analyzed compounds obtained with DIP-APPI-IMS were found to be in the tens- or hundreds-of-microgram-per-liter range. The obtained results are promising enough to ensure the potential of DIP as an introduction and a pre-separation step for ion mobility based methods.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are nonpolar environmental pollutants that can be present in both particulate and gaseous phases. Some PAHs have been demonstrated to be carcinogenic in humans and experimental animals, and they are classified as carcinogenic materials by many organizations, including the United States Agency for Toxic Substances and Disease Registry (ATSDR), the International Agency for Research on Cancer (IARC), the Department of Health and Human Services (DHHS), the National Occupation Safety and Health Administration (OSHA), the United States Environmental Protection Agency (EPA), the European Union Scientific Committee on Food (SCF), and European Union (EU) [1–3,5].

Carcinogenic PAHs are found in all surface soils. The concentration of carcinogenic PAHs in forest and rural soils ranges from 5 to 100 µg kg⁻¹ [4]. However, values of about 1000 µg kg⁻¹ can be found occasionally. In metropolitan areas the concentrations of PAHs are higher as compared to those of forest and agriculture areas. The concentrations of PAHs in urban soils are usually within the range of 600–3000 µg kg⁻¹. However, levels of 8000–336000 µg kg⁻¹ have

been reported for road dust [4]. PAHs in the atmosphere are mainly collected for the analysis by two sampling models: active sampling and passive sampling. Active sampling utilizes deposition or adsorption of target PAH compounds on filters or sorbent materials. After sampling, PAHs are extracted using organic solvents such as mixtures of *n*-hexane and dichloromethane. For qualitative and quantitative analysis of extracted PAHs, gas chromatography, combined with mass spectrometry (GC-MS) or high performance liquid chromatography (HPLC), are often used [5]. This techniques are laboratory-based and therefore require time-consuming sampling and transport procedures. Therefore, the possibility to build the analytical system as a small and transportable device gives analytical systems an additional attractiveness. The driving force for the development of miniaturized systems are the reduced cost, short analysis time, and the possibility to integrate all steps (e.g. sample preparation, separation, and detection of the analytes) in a single and portable device.

Time-of-flight ion mobility spectrometry (TOF-IMS) is the simplest and, in the same time, the most used ion mobility technique [6]. It works at atmospheric pressure and allows a direct mobility measurement. Using this technique, the complete mobility spectra can be

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analyzed within the time range of several tens to several hundreds of milliseconds. It was demonstrated that the resolution of 180 and 250 can be achieved with the drift tube length of 10 and 15 cm, respectively [7,8]. This technique has found many applications, e.g. detection of drugs and chemical warfare agents, quality control, determinations of contaminants in food and in environmental samples [9,10]. Over the past decades, ion mobility spectrometry has grown into an inexpensive and powerful analytical technique for the detection of gas phase samples at ambient pressure [11]. Moreover, it was demonstrated that addition of the appropriate amount of volatile organic compounds (dopant) to the sample gas can significantly enhance the sensitivity of IMS [12].

However, many of environmental pollutant have a low vapor pressure, and as a result, cannot be effectively detected by the head-space analysis. Therefore, the development of analytical methods for the detection of nonpolar compounds of limited volatility is essential.

Direct Inlet Probe (DIP) was originally developed for introduction of samples into the mass spectrometer. This technique allows fast and simple introduction of liquid and solid samples without any or with minimal sample preparation [13,14]. It is fully automatic and programmable. It provides the temperature-programmed heating of the sample (heating rates of $0.1\text{--}3\text{ }^{\circ}\text{C s}^{-1}$ up to $400\text{ }^{\circ}\text{C}$) resulting in time-shifted evaporation of analytes based on the difference in vapor pressures. For non-complex samples it can be considered as an alternative to the gas/liquid chromatography. In combination with mass spectrometry, this technique was used successfully for analysis of plasticizers and bisphenol A [13,15]. However, no applications of direct inlet probe and as an introduction and a pre-separation stage for ion mobility spectrometry can be found in literature.

In this work, the utilization of direct inlet probe as an introduction and pre-separation step for stand-alone ion mobility spectrometry has been introduced for the first time. Eight PAHs with the ring number from 2 to 5, namely naphthalene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, benzo[a]pyrene, and benzo[k]fluoranthene were selected as a model compounds for this study. All these compounds are included in EPA priority pollutant list. Two of selected compounds, namely benzo[a]pyrene and benzo[k]fluoranthene are marked by EPA as probably carcinogen compounds and also included into SCF and EU lists [1–3].

2. Experimental section

2.1. Experimental setup

The developed in this work direct inlet probe - ion mobility spectrometer (DIP-IMS) consists of a commercially available (for different MS systems) temperature-programmed push rod (DIP) coupled to a homemade ion mobility spectrometer (IMS). The ion mobility spectrometer was equipped with atmospheric pressure photo ionization source (krypton $10.0/10.6\text{ eV}$). The principle scheme and the picture of the experimental setup used in this study are shown in Fig. 1 (Top) and Fig. S-1, respectively. In all experiments, the drift gas and sample gas was pure nitrogen (99.999%, Air Liquide, Germany). To introduce a dopant (benzene) in the sample gas, the sample gas flow, controlled by mass flow controller (MFC, GFC17, $0\text{--}50\text{ mL min}^{-1}$, N_2), was passing through a temperature controlled vapor generator (VG; modified GC injector) equipped with a permeation tube oven. The concentration of dopant (benzene) in the carrier gas was calculated using the weight loss of the long-term stable permeation tube (PTFE, ID = 4.5 mm, OD = 6.2 mm, length = 40 mm, sealed and crimped at both ends) over a time. In the experiments presented in this work the concentration of benzene was of $74\text{ }\mu\text{g L}^{-1}$ (in N_2).

2.2. Direct Inlet Probe (DIP)

The DIP, DIP-IMS interface, and IMS electronics were constructed

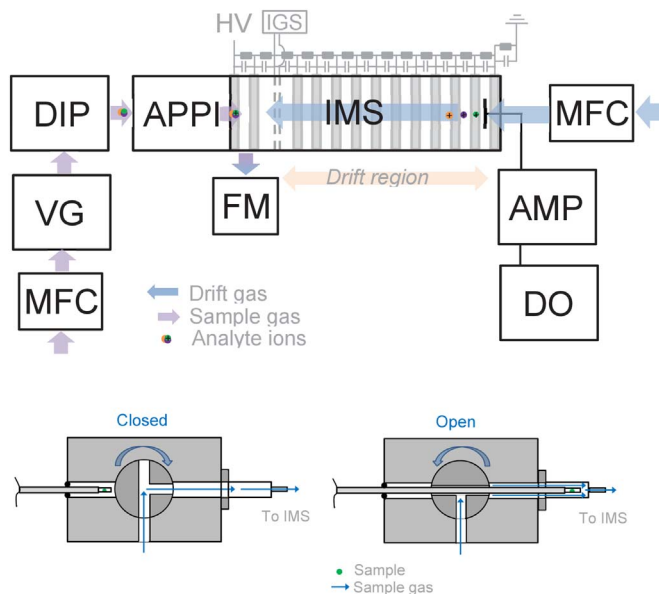


Fig. 1. Top: The principle scheme of the experimental setup. Bottom: Sample gas valve in “open” and “closed” positions.

by SIM GmbH (Oberhausen, Germany). The sample can be loaded into the sample vessel (volume of $10\text{ }\mu\text{L}$) when the DIP is in load-position (see Supporting information, Fig. S-2). In time between the measurements, the software controlled valve is in closed-position to prevent the entering of sample into the IMS. To introduce the push rod into the interface the valve is switched to the open-position (see Fig. 1, bottom). In this position the sample gas flow is directed around the push rod and the sample vessel. The temperature of the push rod tip is controlled by temperature program set in the software (Direct Inlet Probe, SIM GmbH, Oberhausen, Germany, max. 3 ramps, heating rate $0.1\text{--}2.0\text{ }^{\circ}\text{C s}^{-1}$, $T_{\text{max}} = 400\text{ }^{\circ}\text{C}$). This enables the temperature controlled evaporation and separation of analytes according to their vapor pressures. Detailed description of working principle of DIP can be found elsewhere [13]. The overview of the parameters and settings can be found in supporting information (see Fig. S-3, right).

Valve block of DIP is connected with the IMS inlet over the stainless steel interface (ID = 7 mm, OD = 8 mm, length = 33 mm). During the analysis of the sample the tip of the push rod is positioned in the interface close to the inlet of stainless steel capillary (ID = 0.8 mm, OD = 1.6 mm, length = 25 mm). This capillary connects the interface with the entrance of the IMS ionization region (see Fig. 1, bottom). In this work two different heaters was constructed to enable the heating of the interface. The first heater was the silicone mate with the maximal power of 25 W (Minco Products, USA) which was rolled around the interface. The second heater was constructed from the resistance wire (0.8 m, 1 NICRO 0.5; Nickel-Chrom 80/20, $D = 0.5\text{ mm}$, $7\text{ }\Omega/\text{m}$) and the ceramic adhesive glue (Resbond 940, Cotronics Corp, USA) directly on the outer surface of the interface ($P_{\text{max}} = 30\text{ W}$). The outer surface of ceramic heater was isolated by about 10 mm thick glass wool.

To avoid the matrix effects, after each measurement the DIP-IMS interface was heated at 11 V (2.75 A, $\sim 500\text{ }^{\circ}\text{C}$) for 5 min.

2.3. Ion Mobility Spectrometer (IMS)

The drift tube consists of ten cylindrical electrodes and ion gate positioned in a stack. The drift electrodes were constructed according to Gormally and Philipps [16] with an inner diameter of 25 mm, an outer diameter of 40 mm, outer thickness 5 mm, and inner thickness 1 mm. Neighbouring electrodes were insulated with spacers made out of machinable glass ceramic (Macor, O.D. 40 mm, I.D. 25 mm, and 4 mm thick). The distance between the last electrode and the detector was

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