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Compact, ultra-fast polarity switching ion mobility spectrometer with gas chromatographic pre-separation

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Introduction

Ion mobility spectrometers (IMS) are highly sensitive measurement devices that allow detection of trace gases in air in the low ppt$_v$ range in less than one second. A gaseous sample is characterized by ionization and subsequent drift of the formed ions in an electric field at atmospheric pressure. In this way, different ion species can be separated based on their specific ion mobility in a neutral gas. [1,2]

In real applications, gas mixtures often consist of a large number of different substances, which can lead to chemical interferences during the ionization process. Thus, identification of individual substances in a gas mixture with IMS can be difficult. However, chemical interferences can be minimized by pre-separation, e.g. by gas chromatography (GC). Such pre-separation significantly reduces chemical interferences and thus target compound discrimination during ionization and adds another dimension of separation – the retention time. [1]

Ion mobility spectrometry is an established analytical technique. Especially the combination with pre-separation by GC can be found in different applications, for example in food industry [3] and breath analysis [4].

The aim of this work is to combine a small, ultra-fast polarity switching IMS with gas chromatographic pre-separation in a compact setup including a GC convection oven to analyze complex gas mixtures within two minutes.

Experimental

Ultra-fast polarity switching ion mobility spectrometer

A drift tube IMS has three main components – an ionization region, a drift region and a detector. There are different physical and chemical options to ionize a gaseous sample as described in [2] and [5]. Here, X-rays are used for ionization. Subsequently, the ions are injected into the drift tube by an electrical pulse. Driven by an electric field E, the ions drift through the drift tube towards the detector. During their drift, the ions collide with molecules of the neutral gas and lose kinetic energy. The combination of acceleration by the electrical field and deceleration by collisions leads to a specific average drift velocity v of each ion species. [2,5,6]

The ion mobility K can be described as a function of the charge number of the ion species z, the particle density of the neutral gas N, the Boltzman constant k_B, the absolute temperature T, the ion mass m, the mass of neutral gas molecules M and the collision cross-section between the ions and the neutral gas molecules Ω as described in [2] and [7]:

$$K = \frac{v}{E} = \frac{3}{16}\frac{z}{N}\sqrt{\frac{2\pi}{k_b T}\left[\frac{1}{m}+\frac{1}{M}\right]}\,\frac{1}{\Omega}$$

Due to their specific ion mobility, the ions reach the detector, often a Faraday plate, separated in time. When the ions reach the detector, an ion current can be measured. Plotted over time, the ion current generates the ion mobility spectrum. [2]

Usually, drift tube IMS analyze ions of one polarity, where the polarity is determined by the orientation of the electric field. Since ionization of gas mixtures usually generates positively and negatively charged target ions, [8] describes an ultra-fast polarity switching IMS. It allows switching polarity of all required voltages, including the drift voltage of 2700 V, and thus the direction of the electric fields in just 25 ms.

If the drift voltage U_{drift} from the injection grid to the detector is positive, positively charged ions can be detected. Accordingly, if this voltage is negative, negatively charged ions reach the detector which leads to a negative ion current in the ion mobility spectrum. Requiring just 25 ms for polarity switching, two gas chromatograms in both ion polarities can be recorded during one single GC run, which cuts the total measuring time in half. Fig. 1 illustrates polarity switching with an exemplary ion mobility spectrum of negatively charged ions (Fig. 1 – blue dots) and positively charged ions (Fig. 1 – red dots), where dot size represents the effect of collision cross section.

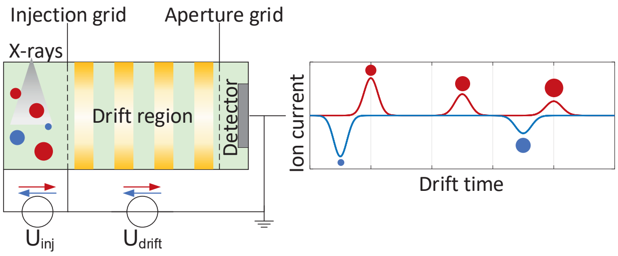

Fig. 1: Schematic of an ultra-fast polarity switching IMS with an exemplary dual ion mobility spectrum. Positively charged ions (red) lead to a positive ion current and negatively charged ions (blue) lead to a negative ion current.

Fig. 2 shows a photo of the IMS with its X-ray source on top. The IMS is based on printed circuit boards. This makes it a cost-effective system compared to classical IMS mainly made of ceramics or polyether ether ketone (PEEK) and metal drift rings. Outer dimensions of the miniaturized IMS drift tube are 25 mm x 25 mm in cross-section and a total length of 65 mm. With a drift voltage of 2700 V over the 50 mm long drift region (electrical field E = 54 V/mm), the resolving power is R_P = 60.

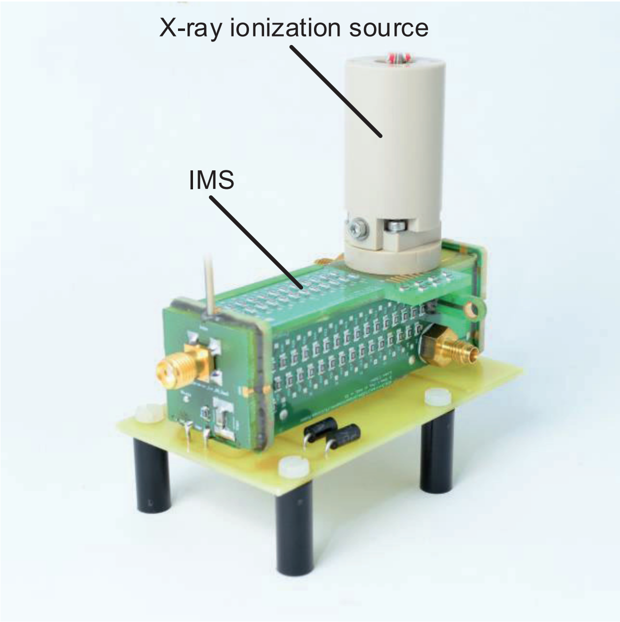

Fig. 2: Ultra-fast polarity switching IMS with X-ray ionization source.

GC convection oven

In case of gas mixtures consisting of a large number of substances, an analysis by IMS is difficult. Reasons are chemical interferences during the ionization process and spectral overlap of peaks. To minimize these effects pre-separation, e.g. by GC, is useful.

In GC, the gaseous sample flows through a capillary coated with a liquid stationary phase driven by a carrier gas (mobile phase). The individual sample components interact to different extents with the stationary phase, so that the individual substances of the sample leave the GC separated by retention time and thus reach the IMS one after the other. [1,9]

In this work, a small GC convection oven is built. Inside two parallel columns (MXT-5) with inner diameter of 500 µm and a length of 300 cm are placed. For high efficiency of pre-separation, it is essential that all columns have exactly the same length. Otherwise differences in retention times of the same compound due to different column lengths can lead to peak broadening and thus limited GC resolving power.

In this oven, exchange of the GC columns is simple. Thus, GC parameters e.g. column type, length, inner diameter and number of columns can be adapted easily. Using special ferrules made of Polytetrafluorethylene (PTFE), it is possible to mount up to seven parallel GC columns in the oven, as shown in Fig. 3 and Fig. 4.

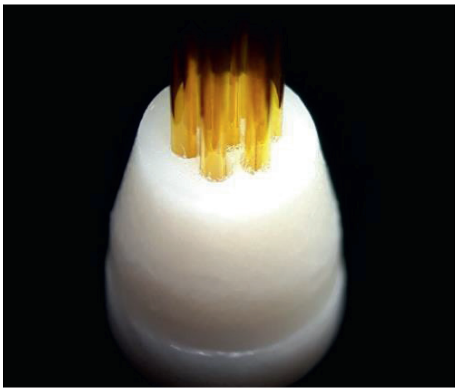

Fig. 3: 1/16” PTFE-ferrule for bundling seven GC columns (Rtx-Volatiles, 250 µm ID) [1].

The convection oven has an inner housing (10 cm x 10 cm x 3 cm) and an outer housing (12 cm x 12 cm x 5 cm) as depicted in Fig. 4. In the middle of the oven a small fan is placed to circulate the air inside the oven. A second bigger fan on the top cover cools down the oven after a GC run (see Fig. 5). Between the bottom and top layers two heaters made of high temperature resistant printed circuit boards (PCB) are placed. Electrically connected in parallel the heaters resistance is 1.65 Ω. Applying a voltage of 24 V, an electric heating power of up to 350 W is available.

Fig. 4: GC convection oven with seven parallel columns.

The oven is controlled by a temperature controller (PXU10030, red lion controls). By programming the controller, a temperature ramp can be driven. This enables fast GC runs. Increasing the temperature during a GC run causes the less volatile components to lower retention times. Thereupon, the range of retention times is smaller and the hole sample passes the GC faster, what minimizes the analysis time.

The maximum temperature ramp is 20 K/min. Thus, a GC run with a linear ramp from 40 °C to 70 °C lasts only 90 s.

GC-IMS

Fig. 5 shows the measuring setup with the electric, temperature controllers, IMS, GC oven and a six-port valve.

Fig. 5: Photo of a compact, ultra-fast polarity switching IMS with GC pre-separation and X-rays ionization source.

Fig. 6 depicts the gas flows inside the GC-IMS. Carrier gas and drift gas (Fig. 6 – blue lines) are synthetic air (Westfalen, 20.5 Vol.-% Oxygen, 79.5 Vol.-% Nitrogen, $\leq$ 5.0 ppm$_v$ humidity). GC carrier gas continuously flushes the six-port valve and GC columns, while a sample (Fig. 6 – green line) streams continuously through the sample loop. If a GC measurement starts, six-port valve switches and the sample volume of 250 µl is injected into the GC by carrier gas (Fig. 6 – orange line).

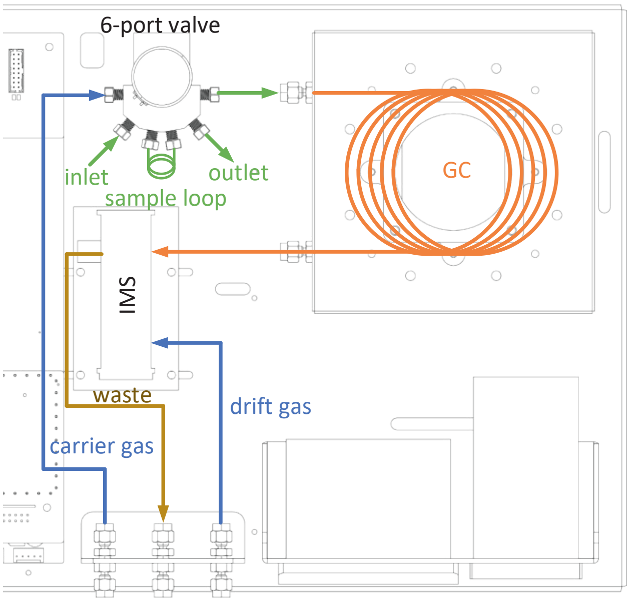

Fig. 6: Schematic of the gas flows inside the GC-IMS.

The GC separates the components of the sample based on their retention times. The pre-separated components reach the IMS separated in time and are ionized by X-rays. Afterwards, the components are separated again in an electric field based on their ion mobility and can be measured as ion current at the detector. Plotting this current in a so-called heat map allows an analysis of the sample based on retention time, drift time and amplitude of the ion current, which represents the concentration of the different ion species. The operating parameters of the GC-IMS are listed in Tab.1.

Tab. 1: Operating parameters of the GC-IMS.

	Parameter	**Value**
IMS	Drift length	50 mm
	Drift voltage	2700 V
	Injection voltage	350 V
	Resolving power	60
	Temperature	25 °C
X-rays	Filament current	650 µA
	Acceleration voltage	-3700 V
Flows	Drift gas flow	150 ml$_s$/min*
	Sample gas flow	10 ml$_s$/min
	GC carrier gas flow	15 ml$_s$/min
	Sample loop volume	250 µl
GC oven	Max. temperature	90 °C
	Max. temperature ramp	20 K/min
	Length GC columns	300 cm
	ID GC columns	500 µm
	Film thickness	5 µm

*ml$_s$/min (milliliter standard per minute, mass flow at reference conditions 20 °C and 1013 mbar)

Results and Discussion

To test the system, a mixture of 200 ppb$_\mathrm{v}$ Ethanol, 200 ppb$_\mathrm{v}$ 1-Propanol, 200 ppb$_\mathrm{v}$ 1-Butanol and 3 ppb$_\mathrm{v}$ Potassium cyanide is investigated. Potassium cyanide reacts with humidity to Hydrogen cyanide before injection into the GC. The sample is mixed in a bag made of Polyethylene terephthalate (PET). Thus, it can be contaminated with carbon dioxide and humidity from the environment. Starting at 40 °C the temperature in the GC oven rises with 20 K/min up to 70 °C. Thus, the alcohols and Hydrogen cyanide are separated well according to their retention times and enter the IMS one after the other. Ionization by X-rays forms positively charged ions of the alcohols and negatively charged ions of Hydrogen cyanide.

The system provides three parameters – retention time, drift time and amplitude of the ion current. Plotted as a heat map, see Fig. 7, the drift time is on the ordinate, the retention time on the abscissa and the amplitude in color range from -400 pA (Fig. 7 – blue) to +400 pA (Fig. 7 – red).

In positive IMS polarity, humidity elutes first, followed by Ethanol, 1-Propanol and 1-Butanol. In the IMS, the humidity reacts with Nitrogen to form Ammonia, that can be seen in the following heat map [10]. In negative IMS polarity, Carbon dioxide can be observed first, followed by Hydrogen cyanide.

While the GC already separates the test mixture, the IMS gives additional information, such as drift time and formation of dimers and trimers that underpin substance identification. The formation of alcohol monomers, dimers and trimers can be seen in the heat map below. Furthermore, co-eluting compounds seen in the same IMS polarity can be separated by IMS drift time but quantitative analysis is difficult due to chemical interferences during the ionization process.

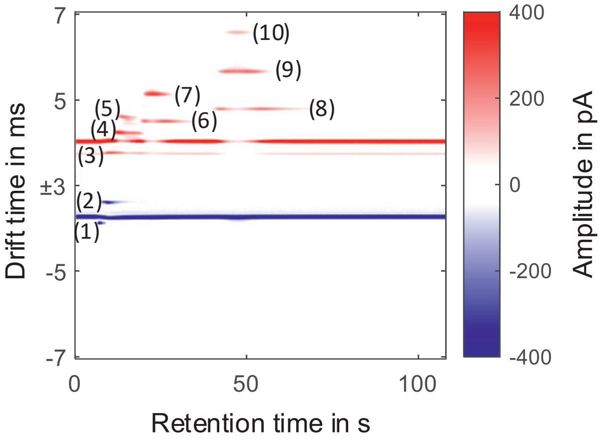

Fig. 7: GC-IMS heat map of positively and negatively charged ions of a sample mixture of (1) Carbon dioxide, (2) Hydrogen cyanide, (3) Ammonia, (4) Ethanol monomer, (5) Ethanol dimer, (6) 1-Propanol monomer, (7) 1-Propanol dimer, (8) 1-Butanol monomer, (9) 1-Butanol dimer, (10) 1-Butanol trimer.

Conclusion

This work presents a small GC convection oven with two parallel columns (MXT-5, 500 µm ID, 300 cm in length) for efficient and fast pre-separation of a sample consisting of Ethanol, 1-Propanol, 1-Butanol and Potassium cyanide. The mixture is pre-separated by the GC with a temperature ramp of 20 K/min from 40 °C up to 70 °C within 90 s. Coupling of GC with an ultra-fast polarity switching IMS with resolving power of $R_P = 60$ allows an additional dimension of separation of both positively and negatively charged ions by drift time and thus an analysis of the eluate in both polarities. Plotting of the orthogonal information of GC and IMS in a so-called heat map shows clear separation of the test mixture containing 200 ppb$_\mathrm{v}$ Ethanol, 200 ppb$_\mathrm{v}$ 1-Propanol, 200 ppb$_\mathrm{v}$ 1-Butanol and 3 ppb$_\mathrm{v}$ Potassium cyanide (converting to Hydrogen cyanide with humidity).

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