

Bundled column GC-IMS – a miniaturized system for fast and sensitive on-site analytics

André Ahrens, Stefan Zimmermann

*Leibniz University Hannover, Institute of Electrical Engineering and Measurement Technology,
Appelstr. 9A, 30167 Hannover, Germany
Contact: ahrens@geml.uni-hannover.de*

Introduction

Ion mobility spectrometers (IMS) are powerful analytical tools for monitoring, detecting and identifying compounds at trace levels. Drift tube IMS separate and analyze ions within milliseconds based on their motion through a neutral gas along a homogeneous electric field.

Nowadays, IMS are established in various kinds of analytical applications, e.g. in the field of safety and security [1,2], food industries [3] and the medical sector [4,5]. For some of these applications, mobile or hand-held devices are required. Thus, miniaturized and lightweight systems are needed and different approaches have been reported [6–8]. The key challenge of miniaturization is to keep the analytical power of the instrument. Major performance factors are the limits of detection (LoDs) and the resolving power R_p . As shown in Eq. 1, the latter is defined as the quotient of the drift time t_d of a peak in the ion mobility spectrum and the related full width at half maximum w_{FWHM} .

$$R_p = \frac{t_d}{w_{FWHM}} \quad (1)$$

Furthermore, the LoD is typically given based on the 3σ definition, i.e. a concentration generating a signal amplitude equal to three times the standard deviation σ of the noise at zero concentration. Today's IMS are capable of detecting compounds in the pptv range and even less. In addition, the ion mobility K itself depends on the ion-neutral pair collision cross section and the ion mass [9]. It is typically given as reduced ion mobility K_0 as shown in Eq. 2

$$K_0 = \frac{L^2}{t_d \cdot U_d} \cdot \frac{T_0}{T} \cdot \frac{p}{p_0} \quad (2)$$

Here, L is drift length, U_d is drift voltage, $T_0 = 273.15$ K, $p_0 = 1013.25$ mbar, T is operating temperature and p is operating pressure.

Despite of the high sensitivity and fast response times of drift tube IMS, competing ionization is a drawback when analyzing complex mixtures. Thus, pre-separation, e.g. by chromatographic techniques, is required and has been investigated in the past [10,11]. In a gas chromatograph (GC) a carrier gas containing the compounds being analyzed (mobile

phase) flows through a metal or glass tubing (column). The inner walls of the tubing are coated with a liquid (stationary phase, unpacked column). Different compounds of the sample interact differently with the stationary phase and thus, they elute at different times (retention times). Inner diameters (ID) of commercially available standard columns are in the range of 0.15 mm up to 0.53 mm, whereas the film thickness varies between 0.1 μm up to 10 μm . Without discussing the detailed theory of gas chromatography, a relevant effect needs to be mentioned here: Bundling small inner diameter GC columns leads to short retention times for fast on-site detection with portable and hand-held devices, while keeping sufficient separation power and providing proper flow rates for IMS [12].

In this work, focusing on the instrumentation, we show a miniaturized GC built of bundled standard columns without use of any adhesive. The GC is operated with a six-port-valve and a sample loop of 250 μl for direct sample injection. A miniaturized drift tube IMS is coupled to this GC and thus, provides orthogonal analytical information about the analyzed samples and exceptional high detector sensitivities reaching pptv detection limits.

Experimental

Drift tube ion mobility spectrometer

The basic design of a drift tube IMS consisting of an ionization region, a drift region and a shielded Faraday plate as ion detector. This typical setup, depicted in Fig. 1, is known for years and has been reported elsewhere [9].

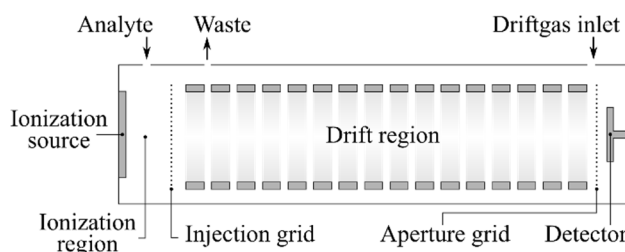


Fig. 1: Basic design of a drift tube IMS.

For ionization, a 130 MBq tritium source is used in this work. However, other non-radioactive sources can be easily used [13]. Once the ions are injected in the drift region by a field switching shutter [14], they

are moving along the drift tube, driven by an electrical field. Here, based on their ion mobility, ion species are separated in the counter-flow drift gas. At the end of the drift region, a Faraday plate, shielded by an aperture grid, is placed to detect the ion current. Plotting this current over time generates the ion mobility spectrum.

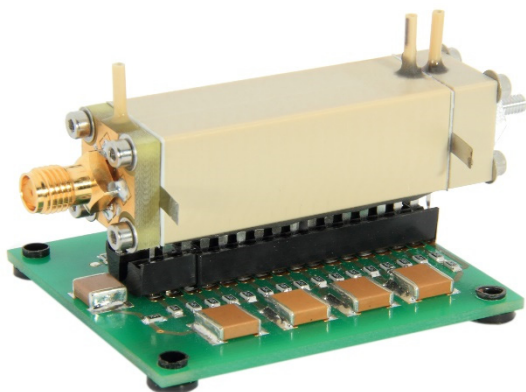


Fig. 2: Photo of the miniaturized drift tube IMS.

The drift tube IMS used in this work has been described recently [13]. Key parameters of the device, shown in Fig. 2, are the small outer dimensions of just 15 mm x 15 mm in cross section and a total length of 56 mm (outer dimensions). Furthermore, the lightweight drift tube design has a total mass of 40 g and is easy-to integrate into PCB designs for driver electronics, due to the use of a commercially available DIP sockets (7.62 mm row-to-row spacing, 34 pins with 2.54 mm pitch).

Bundled column gas chromatograph

The GC used in this work is built of seven parallel standard GC columns (Restek, Rtx-Volatiles) with 250 μm ID and 1 m in length.

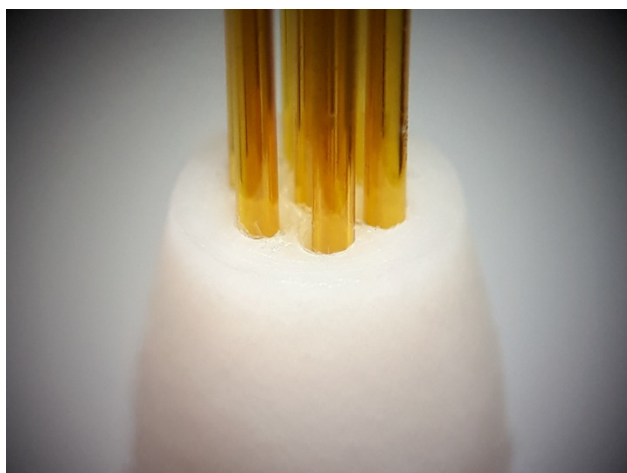


Fig. 3: 1/16" PTFE ferrule with seven GC columns in 0.5 mm bores.

Since the alignment of the single columns to each other is crucial for the analytical performance in parallel operation, commercially available 1/16" no-hole PTFE Ferrules (BGB Analytik Vertriebs GmbH, Rheinfelden, Germany, No. T1600) are modified with seven 0.5 mm bores, see Fig. 3, to seal each GC column without any adhesive.

This allows an exact alignment of each column during installation into the GC heater. The heater is in-house manufactured based on a stacked aluminum plate design. In the center of the rectangular cross section, the bundled GC columns are placed in a larger channel. Equidistant to this center channel, four smaller channels are milled to take the insulated heating wire (NiCr 80/20, 0.7 mm diameter). Connections of the bundled column are formed by standard 1/16" unions, as shown in the upper part of Fig. 4. The outer dimensions are just 80 mm x 105 mm x 11 mm (width x length x height).

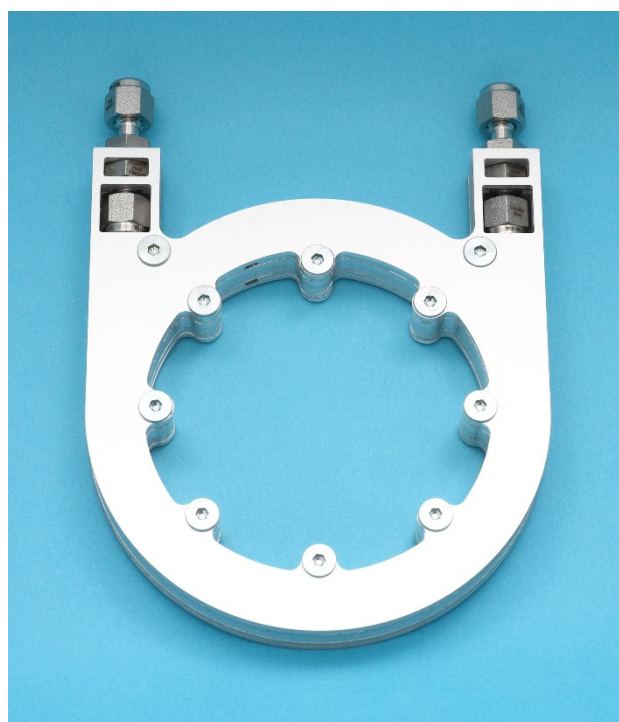


Fig. 4: Photo of the in-house manufactured miniaturized GC.

GC-IMS setup

Fig. 5 depicts the measurement setup. Purified, dry (< 1 ppmv H₂O) air is used as carrier and drift gas.

The sample gas is continuously flowing from the sample inlet (Fig. 5 - orange, continuous line) through the 250 μl sample loop. When a GC run is started, the gas within the sample loop is injected via a six-port-valve into the GC by a carrier gas flow (Fig. 5 - red, dotted line) of 10 ml/min (at 20°C and 1013.25 hPa). The temporal pre-separated eluate directly enters the ionization region of the IMS and gets ionized and sep-

arated based on its ion mobility, while the IMS is continuously flushed with a drift gas flow (Fig. 5 - blue, dashed line) of 120 ml_s/min. The operating parameters are listed in Tab. 1.

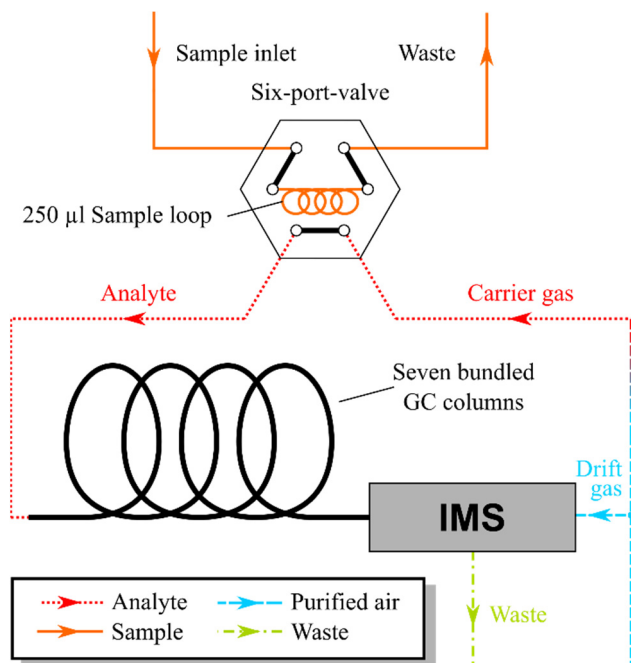


Fig. 5: Schematic of the measurement setup.

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

Parameter	Value
Drift length	40 mm
Drift voltage	2.7 kV
Injection voltage	500 V
Repetition rate	40 Hz
Drift gas flow	120 ml _s /min
Analyte gas flow	10 ml _s /min
GC carrier gas flow	10 ml _s /min
Sample loop volume	250 µl
Sample loop temperature	40°C
IMS temperature	25°C
GC temperature (isothermal)	40°C
Six-port-valve temperature	40°C

Results and Discussion

Ion mobility spectra of purified, dry air for the positive and negative ion mode are given in Fig. 6. Both, the resolving power of the positive reactant ion peak at $t_d = 2.96$ ms (RIP⁺, $K_0 = 2.01$ cm²/(Vs)) and the negative reactant ion peak at $t_d = 2.74$ ms (RIP⁻, $K_0 = 2.15$ cm²/(Vs) and $K_0 = 2.08$ cm²/(Vs)) is $R_P = 63$. The detection limits of the miniaturized IMS are in the range of ppt_v for averaging times less than a second and have been reported recently [13].

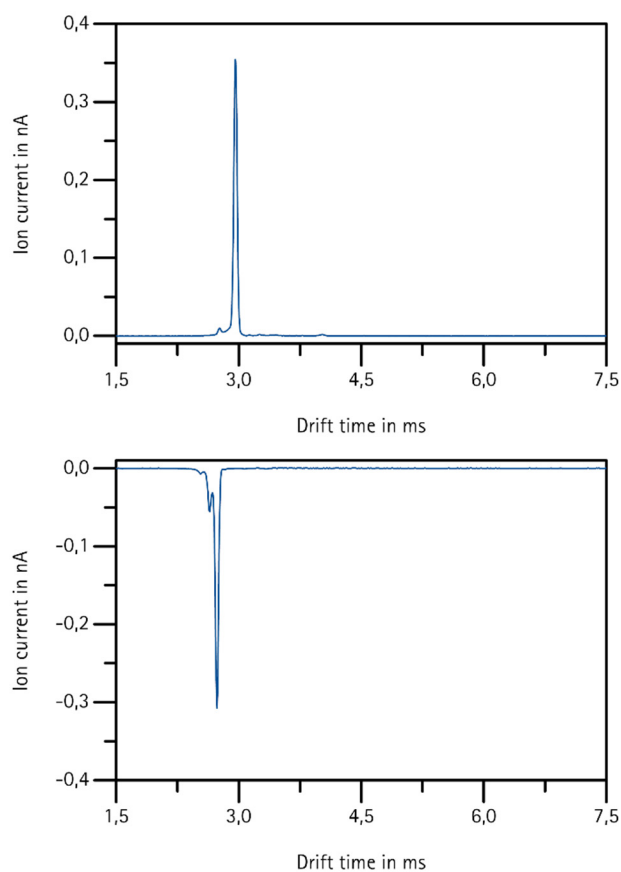


Fig. 6: Ion mobility spectra of positive (top) and negative (bottom) reactant ion peaks in purified, dry air with a resolving power of $R_P = 63$, each.

As a first benchmark of the miniaturized GC-IMS coupling, a mixture of seven alcohols (Ethanol, 2-Propanol, 1-Propanol, tert-Butanol, 1-Butanol, 3-Methyl-1-Butanol, and 1-Pentanol) has been investigated.

Due to the orthogonal information provided by the system, the results are plotted in a heat map shown in Fig. 7, where the ion drift time is given on the y-axis and the GC's retention time on the x-axis.

Ethanol (1), 2-Propanol (2), and tert-Butanol (4), are eluting almost at the same retention times between 6 s to 7 s, due the moderate separation power of the GC, designed for fast on-site applications. However, the IMS clearly separates these ions and thus, a clear differentiation is possible. Furthermore, 3-Methyl-1-Butanol (6) and 1-Pentanol (7) cannot be separated by the IMS, due to quite similar ion mobilities, but they are eluting from the GC well separated at different retention times.

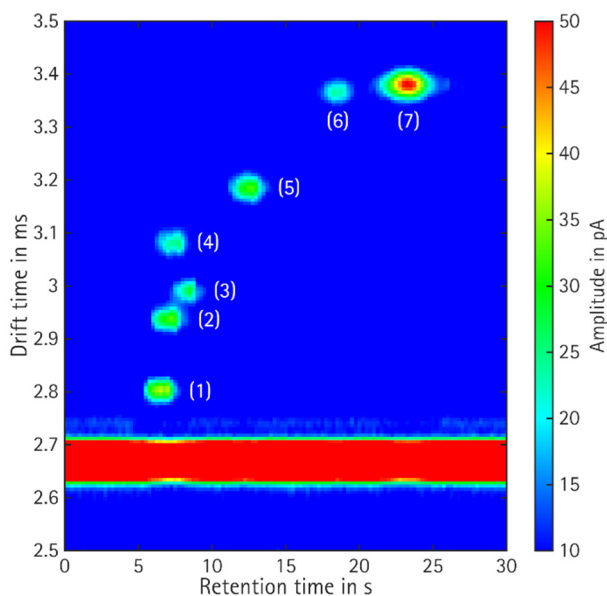


Fig. 7: GC-IMS heat map of an alcohol mixture of (1) Ethanol, (2) 2-Propanol, (3) 1-Propanol, (4) tert-Butanol, (5) 1-Butanol, (6) 3-Methyl-1-Butanol and (7) 1-Pentanol.

Conclusion

In this work, we present a miniaturized GC built of seven parallel standard columns with 250 μm ID and 1 m in length. The isothermal operated GC (40°C) has been coupled to a miniaturized high performance drift tube IMS with detection limits in the pptv-range within averaging times of less than one second and high resolving power of $R_P = 63$. The system has been benchmark with a mixture of Ethanol, 2-Propanol, 1-Propanol, tert-Butanol, 1-Butanol, 3-Methyl-1-Butanol and 1-Pentanol, which can be clearly separated, due to the orthogonal information by the temporal separation of the GC and the ion mobility based information from the drift tube IMS.

References

- [1] K. B. Pfeifer, R. C. Sanchez, Miniaturized Ion Mobility Spectrometer System for Explosives and Contraband Detection, *International Journal for Ion Mobility Spectrometry* 5, 63–66 (2002).
- [2] G. A. Eiceman, J. A. Stone, Peer Reviewed: Ion Mobility Spectrometers in National Defense, *Analytical Chemistry* 76, 390A–397A (2004); doi: 10.1021/ac041665c.
- [3] Z. Karpas, Applications of ion mobility spectrometry (IMS) in the field of foodomics, *Food Research International* 54, 1146–1151 (2013); doi: 10.1016/j.foodres.2012.11.029.
- [4] T. Perl, E. Carstens, A. Hirn, M. Quintel, W. Vautz, J. Nolte, M. Jünger, Determination of serum propofol concentrations by breath analysis using ion mobility spectrometry, *British journal of anaesthesia* 103, 822–827 (2009); doi: 10.1093/bja/aep312.

- [5] M. Allers, J. Langejuergen, A. Gaida, O. Holz, S. Schuchardt, J. M. Hohlfeld, S. Zimmermann, Measurement of exhaled volatile organic compounds from patients with chronic obstructive pulmonary disease (COPD) using closed gas loop GC-IMS and GC-APCI-MS, *Journal of Breath Research* 10, 26004 (2016); doi: 10.1088/1752-7155/10/2/026004.
- [6] J. S. Babis, R. P. Sperline, A. K. Knight, D. A. Jones, C. A. Gresham, M. B. Denton, Performance evaluation of a miniature ion mobility spectrometer drift cell for application in hand-held explosives detection ion mobility spectrometers, *Analytical and bioanalytical chemistry* 395, 411–419 (2009); doi: 10.1007/s00216-009-2818-5.
- [7] K. B. Pfeifer, S. B. Rohde, K. A. Peterson, A. N. Rumpf, Development of Rolled Miniature Drift Tubes Using Low Temperature Co-Fired Ceramics (LTCC), *International Journal for Ion Mobility Spectrometry* 7, 52–58 (2004).
- [8] J. Xu, W. B. Whitten, J. M. Ramsey, Space Charge Effects on Resolution in a Miniature Ion Mobility Spectrometer, *Analytical Chemistry* 72, 5787–5791 (2000); doi: 10.1021/ac0005464.
- [9] G. A. Eiceman, Z. Karpas, H. H. Hill, *Ion mobility spectrometry*. CRC Press, Boca Raton; 2013.
- [10] A. P. Snyder, C. S. Harden, A. H. Brittain, M. G. Kim, N. S. Arnold, H. L. C. Meuzelaar, Portable hand-held gas chromatography/ion mobility spectrometry device, *Analytical Chemistry* 65, 299–306 (1993); doi: 10.1021/ac00051a019.
- [11] J. Langejuergen, C. Wagner, S. Beutel, T. Hopmeier, T. Scheper, S. Zimmermann, Non-invasive monitoring of bacterial growth and auto-induced protein production in a bioreactor with a closed-loop GC-IMS, *International Journal for Ion Mobility Spectrometry* 18, 9–15 (2015); doi: 10.1007/s12127-014-0163-7.
- [12] G. A. Eiceman, Y. Feng, Limits of separation of a multi-capillary column with mixtures of volatile organic compounds for a flame ionization detector and a differential mobility detector, *Journal of Chromatography A* 1216, 985–993 (2009); doi: 10.1016/j.chroma.2008.11.091.
- [13] A. Ahrens, M. Hitzemann, S. Zimmermann, Miniaturized high-performance drift tube ion mobility spectrometer, *International Journal for Ion Mobility Spectrometry* 22, 77–83 (2019); doi: 10.1007/s12127-019-00248-w.
- [14] A. T. Kirk, S. Zimmermann, Bradbury-Nielsen vs. Field switching shutters for high resolution drift tube ion mobility spectrometers, *International Journal for Ion Mobility Spectrometry* 17, 131–137 (2014); doi: 10.1007/s12127-014-0153-9.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 653409.