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A compact high resolution electrospray ionization ion mobility spectrometer

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ABSTRACT

Electrospray is a commonly used ionization method for the analysis of liquids. An electrospray is a dispersed nebular of charged droplets produced under the influence of a strong electrical field. Subsequently, ions are produced in a complex process initiated by evaporation of neutral solvent molecules from these droplets. We coupled an electrospray ionization source to our previously described high resolution ion mobility spectrometer with 75 mm drift tube length and a drift voltage of 5 kV. When using a tritium source for chemical gas phase ionization, a resolving power of $R = 100$ was reported for this setup. We replaced the tritium source and the field switching shutter by an electrospray needle, a desolvation region with variable length and a three-grid shutter for injecting ions into the drift region. Preliminary measurements with tetraalkylammonium halides show that the current configuration with the electrospray ionization source maintains the resolving power of $R = 100$. In this work, we present the characterization of our setup. One major advantage of our setup is that the desolvation region can be heated separately from the drift region so that the temperature in the drift region stays at room temperature even up to desolvation region temperatures of 100 °C. We perform parametric studies for the investigation of the influence of temperature on solvent evaporation with different ratios of water and methanol in the solvent for different analyte substances. Furthermore, the setup is operated in negative mode and spectra of bentazon with different solvents are presented.

1. Introduction

Ion mobility spectrometry (IMS) is a well-established technique for fast trace gas detection, offering limits of detection in the low ppt$_v$-range for measuring times of less than a second. The sensing principle of IMS is based on a separation of ions by their ion-specific mobility in a drift gas under the influence of an electric field [1]. Due to its analytical performance and comparably compact realization, it is attractive for a wide range of applications. IMS are commonly used for security applications such as the detection of chemical warfare agents [2,3], hazardous substances [4] or drugs of abuse [5]. However, today there exists a variety of other applications, e.g. in food industry [6] or medical applications [7,8]. For the analysis of liquids, a commonly used ionization method is electrospray ionization (ESI). In a fundamental work, Dole et al. first investigated electrospray ionization [9]. They showed that it is possible to produce ions in the gas phase from a dilute solution by electrospraying this solution. From the electrospray, little droplets are generated and subsequently solvent evaporation from these droplets and repeated droplet fissions [10] result in charged analyte molecules. Based on these works, numerous setups with ESI-IMS were published and ESI-IMS is still a topic in recent research [11–15]. Application of ESI-IMS is found in aqueous nitrate and nitrite analysis, drug detection or detecting inorganic ions in water [16–19]. In the present work, we show a setup with a resolving power of $R = 100$ using an only 75 mm long drift tube. As the desolvation region is thermally isolated from the drift tube, a parametric study for finding an optimal desolvation region temperature is performed. Furthermore, optimal solvent composition with focus on measuring aqueous samples is investigated.

2. Experimental

Fig. 1 depicts a schematic of the setup consisting of an emitter, a desolvation region, a drift region and a Faraday detector. New Objective Metal Taper Tip emitters with an inner diameter of 50 µm are used. Furthermore, we use a programmable syringe pump *KDS LEGATO 100, KD scientific*, USA with a 100 µl syringe (#1710) by *Hamilton*, Switzerland. For all our experiments, the flow rate is set in the realm of 0.5–1.5 µl/min. The ESI voltage is applied between emitter and the first ring of the desolvation region.

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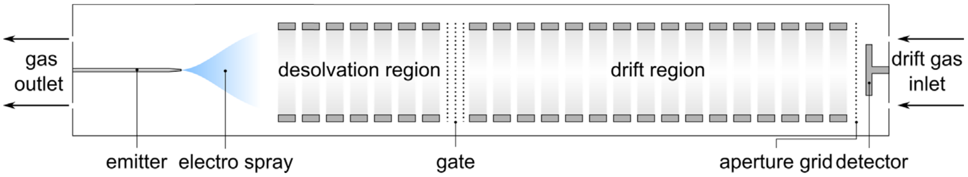

Fig. 1. Schematic of the ESI-IMS.

Generally, liquid samples are diluted with a solvent in order to support a stable electrospray and enhance the ionization process. One major task in electrospray ionization is the optimal evaporation of neutral solvent molecules. The length of the desolvation region in our setup is variable and can be extended up to a length of 75 mm. However, to ensure a complete desolvation, all experiments in this paper are performed with maximum desolvation region length. Furthermore, the desolvation region is equipped with four temperature controlled resistive heaters, *MP9100, Caddock, USA* and one temperature sensor, *DS18B20, maxim integrated,* USA, all mounted on an aluminum coat. In Section 3.2, the influence of the desolvation region temperature on the analytical performance is discussed in detail.

A three grid shutter first described in [20] separates the desolvation region from the drift region. The schematic of the three grid shutter is depicted in Fig. 2. The distance between the grids is 450 µm and is realized via PTFE spacers. When the switch is open, the voltage divider between the three grids sets the electrical field equal to the electrical field in drift region and desolvation region respectively. When the closing voltage $U_c = 75$ V is applied, the direction of the electrical field between grid 1 and grid 2 is reversed. Thus, the ions are stopped from transmitting from the desolvation region to the drift region, while the electrical field in drift and desolvation region remains unchanged. The typical time ions are injected into the drift region is $t_{inj} = 175$ µs. The used drift tube design is described in [21]. Here, we use a tube with a drift length of 75 mm. The drift voltage of 4.9 kV is applied via a resistive voltage divider over stainless steel ring electrodes separated by PEEK isolation rings. Therefore, a homogeneous field inside the drift tube is realized. A faraday detector with aperture grid terminates the drift region. The drift tube and desolvation region are purged with the same gas flow of dry clean air at a flow rate of 250 ml/min. Table 1 summarizes the relevant operating parameters. Concluding this section, Fig. 3 depicts a photograph of the realized high resolution ESI-IMS to show the compact realization of the setup.

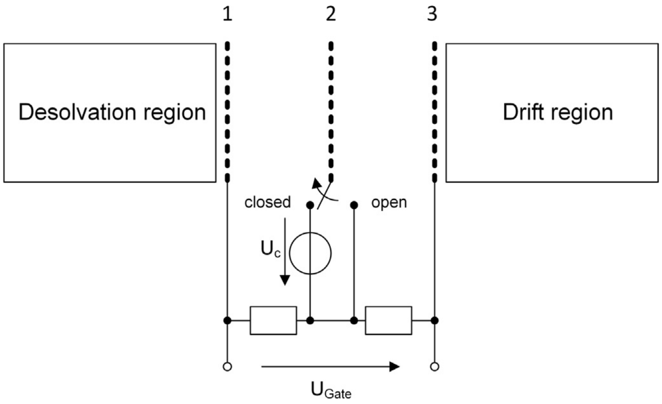

Fig. 2. Three grid shutter between desolvation and drift region.

Table 1
Operating parameter.

Length drift region (l_D)	75 mm	Dew point	−85 °C
Length desolation region	75 mm	Drift region temperature (T)	23 °C
Drift voltage (U_D)	4.9 kV	Desolvation region temperature	23–60 °C
Desolvation voltage (75 mm length)	5 kV	Ambient and inner IMS pressure(P)	1013 mbar
Emitter-to-ring voltage	2–2.8 kV	Liquid flow	0.5–1.5 µl/min
Drift gas flow	250 ml/min	Emitter diameter	50 µm
Desolvation gas flow	250 ml/min		

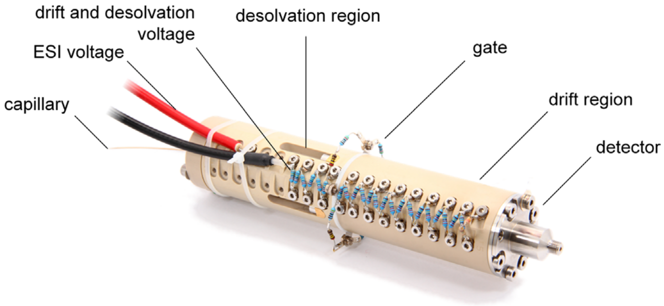

Fig. 3. Photo of the compact realization of the ESI-IMS.

2.1. Chemicals

In this work the following chemicals are investigated: tetraethylammoniumiodide, ACS reagent, tetraproylammoniumiodide, ACS reagent, tetrabutylammoniumiodide, ACS reagent, tetrahexylammoniumbromide, ACS reagent, tetraoctylammoniumbromide, ACS reagent, Triton X-100, [4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol, t-Octylphenoxypolyethoxyethanol], Polyethylene glycol tert-octylphenyl ether, metalaxyl [N-(2,6-Dimethylphenyl)-N-(methoxyacetyl)-DL-alanine methyl ester], laboratory grade, carbamazepine [5*H*-Dibenz[*b,f*]azepine-5-carboxamide] and bentazon, analytical standard. All compounds where purchased from Sigma-Aldrich Chemie GmbH, Germany, except carbamazepine, which was generously provided by the group of Ursula Telgheder, University Duisburg-Essen. As solvents, methanol, HPLC grade, and acetonitrile, HPLC grade from CS-Chromatographie Service GmbH, Germany and ethanol, reag. ISO, reag. Ph. Eur. Sigma-Aldrich Chemie GmbH, Germany, are used. A solution containing 2 ppm of each tetraalkylammonium halide in ethanol and solutions of 50 µl/l Triton X-100, 100 µg/l metalaxyl, 500 µg/l carbamazepine 500 µg/l bentazon in pure methanol and mixtures of methanol and high purity water with different mixing ratios are prepared. Furthermore, for the analysis in negative mode, a solution of 500 µg/l bentazon in pure acetonitrile and in mixtures of acetonitrile and high purity water are prepared.

3. Results and discussion

In this section, the setup is characterized in both positive and negative mode. Initially, the general performance of the setup is tested via measurements of tetraalkylammonium halides to determine the maximum resolving power that can be achieved. Subsequently, metalaxyl and carbamazepine are measured and the