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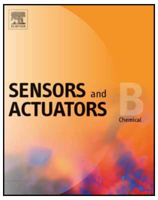

The effect of humidity on gas sensing with ion mobility spectrometry

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ABSTRACT

Vaporized water molecules are unavoidable present in the ambient atmosphere and can considerably affect the analytical signals obtained with sensor techniques during real-time field measurements. Also the introduction of humidity into stand-alone ion mobility spectrometers cannot completely be avoided and the water vapor is transported via the carrier gas into spectrometer. For this case, we systematically investigated the way in which ion mobility measurements in positive mode are influenced. The drift times obtained with humid carrier gas are the same as those detected under dry conditions. They are constant over a range of water concentrations up to 2000 ppm. The nature of ions formed during the atmospheric chemical ionization processes is therefore independent on the humidity. However, the relative abundance of product ions can strongly be affected depending on the properties of substances investigated. While the signal intensity obtained for amines is comparatively unaffected by humidity, a significant decrease is observable for toluenes, chlorinated compounds and ketones.

1. Introduction

A key advantage of ion mobility spectrometry (IMS) has been the ability to perform high speed on-site measurements using handheld or transportable instruments. IMS analyzers exhibit a fast response within few seconds and excellent detection limits for numerous chemical substances. In contrast to other field screening techniques, ion mobility measurements provide characteristic spectra for the investigated samples and do not merely provide a sum signal [1]. While IMS was solely used as military chemical-agent detector [2] or drug test [3] in the past, it is nowadays a well-established sensor technique for civilian and non-security applications [4] and it is routinely applied in environmental analysis [5], clinical diagnostic [6], pharmacy [7] and biomedical science [8].

Ion mobility measurements are based on drift velocities of ion swarms derived from sample molecules. In the first step, these ions are formed from neutral sample molecules at ambient pressure. The most commonly used method for ionization in conventional ion mobility analysis is via chemical reactions between sample and reactant ions that are created by the emission of electrons from radioactive Nickel (^{63}Ni) or Tritium (^{3}H) into a supporting atmosphere. The ions are injected at a given time interval of a few microseconds via an electronic shutter into the drift region with typical lengths ranging between 5 and 15 cm. The ion packet moves as a swarm toward a detector down a voltage gradient and through a gas flow (normally either air or nitrogen) with a direction opposite to that of ion motion. The ion swarm has characteristic drift velocities which provide the basis for ion separation. The drift velocities may be associated with the ions through mass, charge and collision cross-section, which includes structural parameters (physical size and shape) and the charge location or distribution describing the ion-neutral interaction forces [4].

A general limitation in the on-site application of field-deployable sensor techniques is the varying measuring conditions at different sampling sites (e.g. humidity and environmental temperature) which can considerably vary in comparison to the analysis in the lab [9,10]. Especially the influence of ambient humidity on the signal response of sensors cannot be eliminated completely. This holds true for nearly all types of sensors (e.g. optical sensors, surface acoustic wave sensors) where the signal intensity is less or more affected by humidity [11–14]. This limitation also occurs during measurements with ion mobility spectrometers.

The first pioneering paper about these effects in IMS was published as far back as 1928 where the influence of water vapor on mobility of gaseous ions was described for the first time [15]. However, only a few systematic investigations have been undertaken with modern ion mobility spectrometers to date. Although the influence of humidity is a well-known problem in experimental

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work with IMS, it is not well documented. This limited number surprises because the importance of moisture on ion mobility measurements was identified as one of the most significant influencing parameters [16].

Using ^{63}Ni ionization, the effect of moisture was solely investigated for negative ions. The composition of reactant ions and negative chlorinated product ions was investigated by coupling a membrane inlet ion mobility spectrometer with ^{63}Ni ionization and mass spectrometry [17]. In this study, water was added to the adsorbent traps in order to simulate the aging of filter media and to increase the moisture of drift gas. No changes were observed for the composition of product ions with increasing humidity, while reduced sensitivity was found and the peaks appeared at higher drift times. However, the effect of humidity depends on the way in which the water vapor is introduced into the ion mobility spectrometer [18]. The transportation of humidity via the carrier gas into the ion mobility spectrometer causes changes in ionization pathways and additional negative reactant ions are formed. Furthermore, a lower relative abundance of negative product ions from halogenated compounds was generally observed. The peak position within the ion mobility spectrum is comparatively unaffected for the same ions. In contrast, considerable differences in drift times detected were found with increasing humidity of drift gas, while the influence on calibration was not as significant for chlorinated and brominated substances as observed for humid carrier gases [18].

The dependence of moisture on positive ion mobility spectra was only studied for triethylamine with IMS using a ^{63}Ni ionization source [19]. While detection sensitivity in this case is to a certain extent dependent on humidity, considerable differences were observable for peak position and shape.

Additionally, Vautz et al. investigated terpenes with photoionization and observed decreased signal intensities of positively charged ions with increasing carrier gas humidity [20,21].

As can be seen, there is a lack of in-depth knowledge regarding the qualitative and quantitative influence of humidity on the positive ion mobility spectra while the influence of other operational parameters (temperature [22–24] and pressure [25–27]) on ion formation and drift behavior in IMS have been investigated for several classes of substances more in detail.

While the main application of IMS in negative mode is primarily restricted to halogenated compounds, possible influences of humidity on ionization pathways are probably much more complex due to the variety of physicochemical properties of detectable substances in positive mode. Therefore, we investigated four classes of chemical compounds (toluenes, chlorobenzenes, anilines, ketones) in dependence on the humidity of carrier gas. In contrast to the drift gas, where the moisture can accurately be adjusted using filters, the humidity of sample gas stream (carrier gas) into the ion mobility spectrometer can be little influenced. Only membrane inlets can prevent the entry of moisture. However, its application goes along with elevated detection limits due the restricted permeability through the inlet membranes [28].

2. Experimental

2.1. Chemicals

We use four classes of chemical compounds for our studies including anilines, toluenes, chlorobenzenes and ketones. The structures of substances investigated are summarized in Fig. 1. Chemicals were obtained in 99% or better purity from Sigma–Aldrich (Taufkirchen, Germany), and Merck (Darmstadt, Germany).

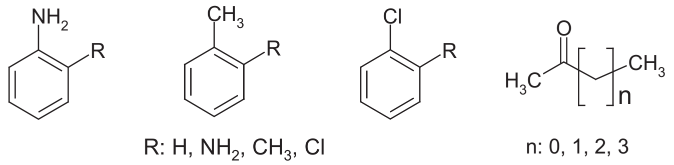

Fig. 1. Structures of investigated compounds.

2.2. Sample introduction system

The challenge in the design of our introduction system resulted from the requirement for adjusting a broad range of concentrations and different levels of humidity within a series of measurement. This approach requires a careful optimization of the experimental design, in order to ensure adjustable flow rates and to avoid potential over-pressurization. The liquid compounds must be transferred into the gas phase and the samples were therefore introduced via permeation tubes. The sample introduction system is shown in Fig. 2.

Approximately 300 μL of the neat sample was filled in a 1 mL glass vial which was closed with a standard screw cap with hole. The hole was covered with up to three polyethylene membrane layers with a thickness of 0.45 mm in dependence on the permeation rate. This vial was placed in a temperature-controlled glass column with an integrated frit as holder for the permeation vessel. Nitrogen (5.0 grade quality with moisture content of up to 5 ppm) was passed through the glass column with a flow rate of 500 mL min^{-1}. This flow rate was kept constant for approximately 8 h as the substances passed through the permeation vessel. Using a needle valve and controlling flow with a mass flow meter (Analyt, Müllheim, Germany), the sample gas stream was split and a portion of flow was guided into a mixing chamber. Here, the sample gas stream can be additionally diluted by two mass flow controllers (Analyt, Müllheim, Germany) with a range of 0–500 mL min^{-1}. An aliquot of this diluted sample gas stream is transported into a second mixing chamber via a rotary vane pump (model G12/01EB, GD Thomas, Puchheim, Germany). The second mixing chamber permits the additional dilution of the sample gas with nitrogen and its subsequent humidification. The gas stream for humidification is generated by mixing gas flows with 0% and 100% relative humidity. Both gas flows can be adjusted with needle valves. The resulting gas flow into the mixing chamber is also controlled by a mass flow meter. The carrier gas stream that flows into the IMS was then taken from this mixing chamber via a rotary vane pump (95 mL min^{-1}). The humidity of this final gas flow was monitored with an AMX1 humidity sensor (Panametrics, Hofheim, Germany).

As stated above, the whole system works with nitrogen. All mass flow meters and mass flow controllers were calibrated with a bubble meter before use. The concentration of the compounds in the sample gas stream was calculated using the weight loss of the permeation tube over a certain time considering the total gas throughput. Before weighting, the samples were pre-permeated for equilibration of the permeation rate for a few hours. Each series of measurements was performed at least three times.

2.3. Ion mobility measurements

An experimental setup based on a commercially available ion mobility spectrometer (STEP Sensortechnik und Elektronik Pockau GmbH, Pockau, Germany) was used. The device is equipped with a tritium ionization source (50 MBq). A metallic grid separates the ion source from the drift region. It is located approximately 2 mm away from the ion source and has the same potential as the first drift ring. The ions formed are gated to the drift tube via an 80 μs impulse (approximately 400 V higher, in comparison to the metallic grid)