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The effect of humidity on sensitivity of amine detection in ion mobility spectrometry

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ABSTRACT

Vaporized water molecules are unavoidably present in every ion mobility spectrometry (IMS) measurement. In general, this humidity is seen in positive mode IMS-spectra as protonated water clusters producing reactant ions. Clusters containing water molecules are also abundant among ions generated by an analyte. In this paper the influence of humidity on IMS-spectra was systematically investigated and determined by measuring different concentrations of a selected amine at various levels of humidity. The selected amine, trimethylamine (TMA), was chosen as the model analyte due to its atmospheric importance. During the measurements, surplus water vapor was introduced into the drift section inside the IMS instrument; the concentrations of both amine and water were adjusted by controlling the gas flows. The simultaneous presence of water vapor and analyte at various predefined concentrations revealed the sensitivity of the IMS-technique to water and the effect of moisture on the ion mobility distribution. The results indicated that the existence, positions and shapes of the peaks are strongly dependent on the amount of moisture. However, the sensitivity of detection is weakly dependent on humidity if this detection is based on monomer ion peak or the sum of peaks generated by the analyte, In addition, the main principles of the adjustment of sample and water concentrations are presented here.

1. Introduction

1.1. IMS as an analytical method

Ion mobility spectrometry (IMS) can be useful for a wide variety of analytical purposes. In general, IMS instruments are used to detect trace amounts of various organic compounds in the air. In the field of security screening, IMS has recently become one of the most popular methods for the detection of hazardous compounds such as explosives, chemical warfare agents and illicit drugs [1–4]. Other possible uses include, for example, detection of ammonia in water [5], detection of both veterinary [6] and human pharmaceuticals [7] as well human metabolites [8], meat spoilage monitoring [9], bacterial analysis [10], detection of halocompounds [11] and space exploration [12]. IMS is also a potential technique for use in atmospheric research [13].

The IMS detection method has several advantages. Firstly, the equipment needed is relatively simple and it can work at ambient pressure, i.e. vacuum systems with heavy vacuum pumps are not needed. Secondly, the instrument can be small in size (handheld models are common), easy to use and also solid and rugged for field use. These structural features, together with its analytical properties such as relatively low detection limits, selectivity of response, rapid sample analysis and the possibility for doing both qualitative and quantitative analyses, make IMS an attractive and practical solution for many analytical problems. One main reason for the rapidly increasing interest in the IMS-technique is the novel need for higher levels of security. More specifically, IMS is suitable for fast and reliable detection of trace amounts of suspicious chemicals.

Amine compounds have been found at trace levels in the atmosphere [14]. This is understandable since amines are known to be produced by many kinds of biological activities due to the breakdown of amino acids. Di- and trimethylamine have especially been postulated to be involved in atmospheric nucleation, i.e. the natural process whereby new particles are generated [15,16]. Early IMS (at that time called plasma chromatography) measurements of ammonium reactant ions and some amines were made in the late 70s [17]. An extensive investigation of different proton-bound dimers detected by IMS has been published. It was found that the main factors affecting the dimer formation were the types of molecules being analyzed and the temperature of operation [18]. The kinetics

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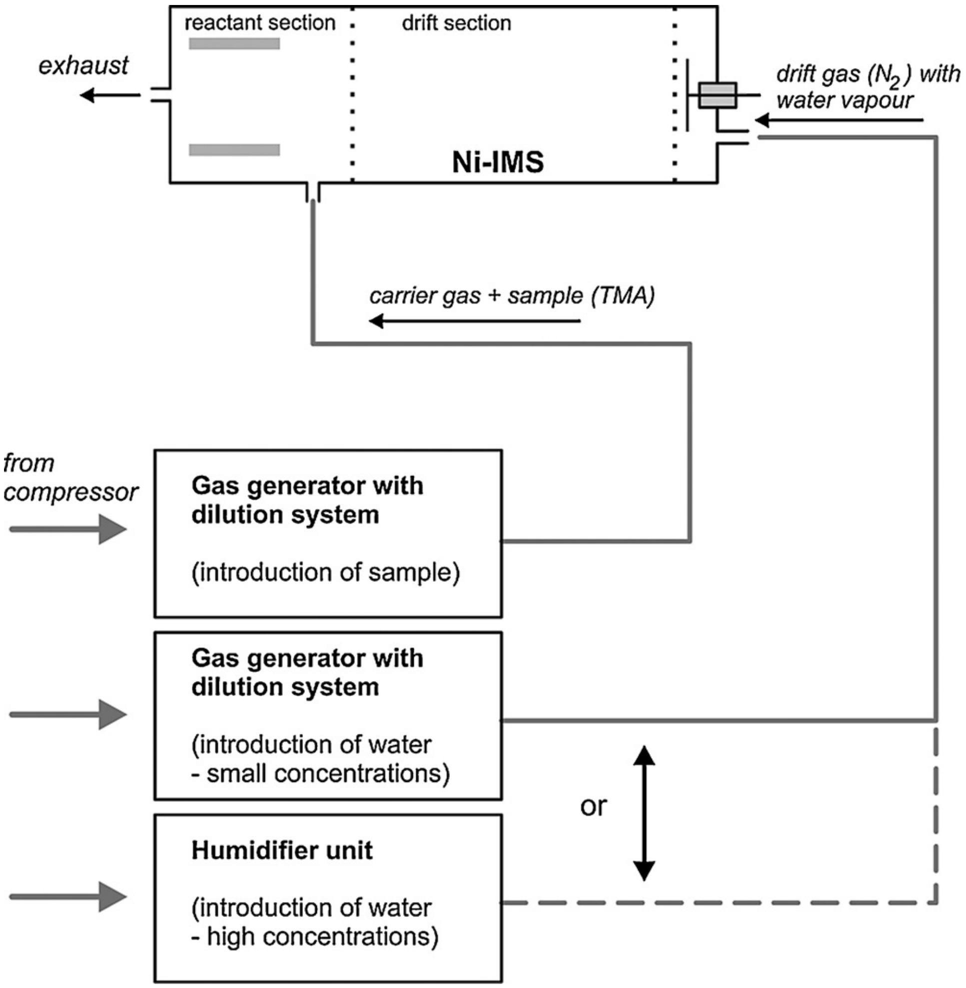

Fig. 1. Scheme of the measurement system.

and thermodynamics of ion solvation in IMS have also been evaluated [19], and a mass spectrometric study of the kinetics of the clustering reaction forming $H^+(H_2O)_n$ has been conducted [20]. The reduced mobilities of numerous amines and related compounds have been reported at three different temperatures [21]. An article describing the effects of various ion–molecule reactions in the drift region on peaks observed in IMS spectra has been recently published: it was demonstrated that these reactions have a major effect on the spectra [22].

1.2. Ion formation

The process of sample ionization in positive mode IMS consists of two stages: creation of reactant ions and chemical ionization of the sample. The latter is the result of the interaction between the reactant ions and the sample molecules. In air or in nitrogen containing a small amount (a few ppm) of water, the main kind of reactant ions are hydronium ions $H^+(H_2O)_n$. These ionic species contain a variable number of water molecules. Collisions of hydronium ions with neutral molecules can cause detachment or attachment of water molecules, thereby changing the number n. At a given temperature and a defined humidity level, certain values of n resulting from the reaction equilibrium are most probable [19,23].

When the analyte M and the reactant ions are simultaneously present in the reaction region of IMS, the following reactions are assumed to occur: the formation of protonated molecules (1) and proton-bound dimers (2) [24].

$$\mathrm{M} + \mathrm{H}^+(\mathrm{H_2O})_n \rightarrow \mathrm{MH}^+(\mathrm{H_2O})_{n-x} + x\mathrm{H_2O} \quad (1)$$

$$\mathrm{M} + \mathrm{MH}^+(\mathrm{H_2O})_m \rightarrow \mathrm{M_2H}^+(\mathrm{H_2O})_{m-y} + y\mathrm{H_2O} \quad (2)$$

In ambient conditions all aforementioned ionic species can form clusters with water molecules, but they can also form clusters with nitrogen molecules. The average degree of solvation depends on temperature and the properties of the ions that form the clusters' core. Usually, proton-bound dimers create clusters in which the number of water molecules is less than in clusters produced by the reactant and monomer ions. It was also found that solvation of ions created by oxygen bases, e.g. ketones, is higher than for nitrogen bases, e.g. amines [18]. Reactions (1) and (2) are reversible. This means that proton-bound dimers can dissociate to neutral and protonated molecules. Detachment of the proton from a monomer ion is also possible. In the reaction region of an IMS detector both forward and backward reactions can occur. However, this situation is assumed to change when the ionic swarm is introduced to the drift region. There are no analyte molecules in that space and for this reason only reverse reactions may occur. In the drift region proton-bound dimers will dissociate in pseudo-first-order reactions with different time constants [18].

The analytical consequences of moisture level include both changes in relative sensitivities, and formation of novel ions that are not commonly observed [25]. It seems obvious that with increased humidity both selectivity and sensitivity decrease, with the limit of detection simultaneously increasing. In the case of terpenes, for-

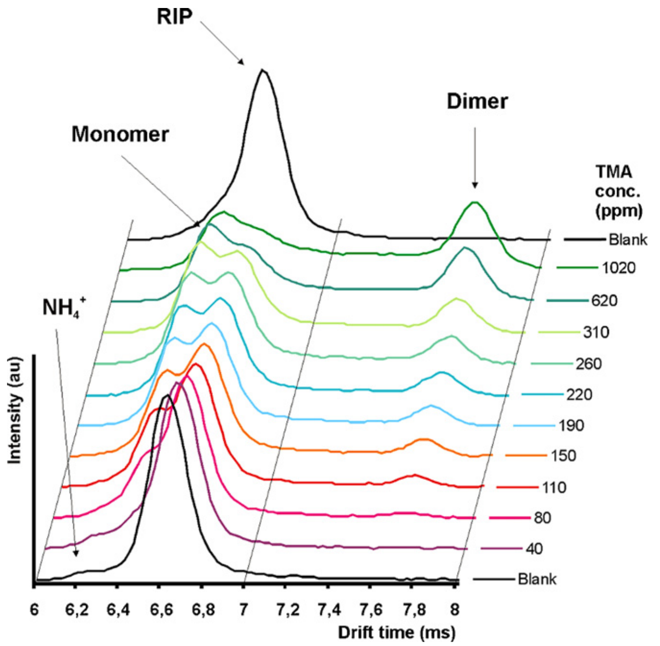

Fig. 2. Spectra of TMA at different concentrations measured with dry drift gas.

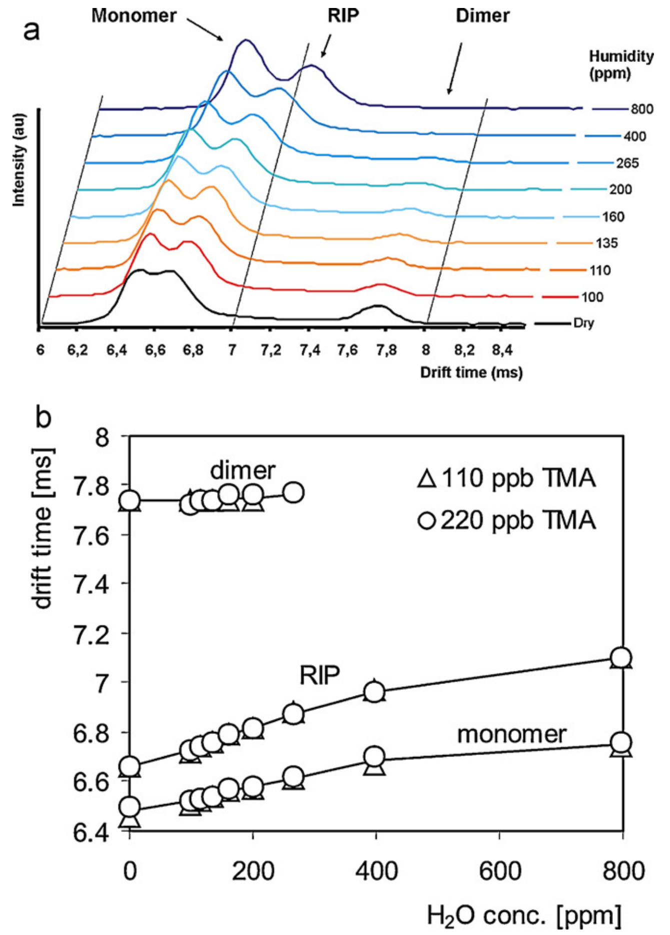

Fig. 3. (a) Spectra of TMA at a constant concentration (220 ppb) measured with low concentrations of water vapor. (b) The relationships between water concentration and drift times for ionic species.

mation of additional peaks occurs, but on the other hand, there is a notable decrease in the total number of ions. As a result, the influence of humidity makes the identification of unknown analytes more difficult [26]. The effect of unwanted ion–molecule reactions on peaks in IMS spectra has also been studied. It has been found that water present in the drift region causes peak broadening and shifting, thus interfering with the identification of analytes [22]. Some closely related preliminary research has been done concerning the reactant ion peak shifting caused by moisture [27] and stimulated formation of hydronium water clusters in gas phase [28]. The effect of moisture on field dependence of the mobility coefficients of gas phase organophosphorus compounds with another IMS technique, field asymmetric ion mobility spectrometry (FAIMS), has been determined. It was found that this field dependence was constant at very low moisture concentrations, with the onset of an effect at 50 ppm water. With higher water concentrations this effect increased [29].

It seems obvious that for successful IMS analyses, the presence of and possible interference by water has to be taken into account. This applies especially to field measurements, where the moisture levels may vary drastically. The magnitude of this influence can be investigated by adjusting the sample and/or water concentrations. In this study the influence of humidity on sensitivity of detection was determined using trimethylamine as the analyte. Our intention is to show the methodologies used for the investigations and for analysis of results. During the measurements, surplus water was introduced to the drift region of the IMS instrument. The amounts of both analyte and water were adjusted by controlling the gas flows; by this means it was possible to do the measurements at well-defined concentrations.

2. Experimental

2.1. Samples and sample introduction

Aqueous solutions of analytical grade 40% trimethylamine and distilled water were purchased from a commercial supplier (Merck) and were used as received without further purification. Purified air was used both as the carrier gas and as the drift gas: water and other possible contaminants were removed by passing the air through a molecular sieve trap filled with 13× molecular sieves (⌀ 1/8″, Alfa Aesar). The air was directed into two inlet systems for introducing the analyte and water to IMS; the amount of gas flow was monitored with flow meters.

The amine sample was placed inside a custom-made teflon tube sampling vessel, which is sealed at both ends with Swagelok caps (Manchester Valves and Fittings, Warrington, UK). The introduction of the amine molecules occurred via permeation through the teflon. The low concentrations of moisture were generated by water vaporization from an open chromatography vial. Both of these sampling vessels were regularly weighed. Evaporation of TMA and water were determined by gravimetric methods to determine the amount of volatiles, which were converted to concentrations. The concentration of evaporated water present in the instrument was on the ppm level, while the concentrations of TMA were on the ppb level.

Thereafter, the sampling vessels were placed in separate stainless steel cylindrical sample containers. These containers were connected to the instrument with teflon tubing having Swagelok connections. The analyte molecules were introduced from the sample container to the reaction region of IMS by the carrier gas after dilution using a pneumatic system with gas flow controllers. The water was introduced from another container having drift gas flow-through; i.e. the water vapor was swept into the drift region of the IMS instrument by a stream of drift gas. In the measurements with higher humidity (moisture concentrations ≥10% RH) the drift gas was routed through a special humidifier unit; the level of moisture was monitored by a Vaisala Humitter 50Y humidity sensor.

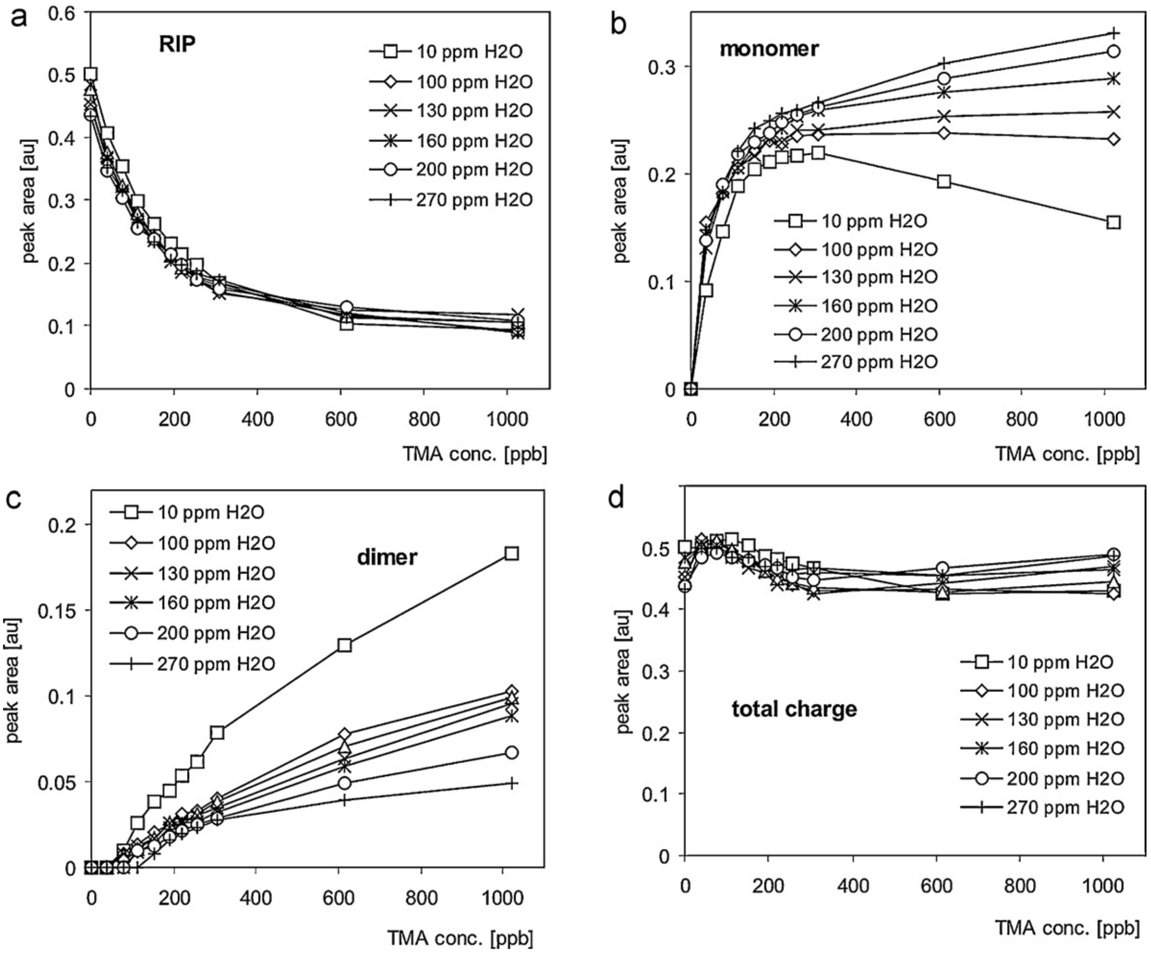

Fig. 4. Peak areas of TMA ionic species as a function of sample concentration measured at different humidity levels.

The sampling region has a two-stage dilution system with four adjustable mass flow-bus controller units (Bronkhorst High-Tech B.V., Netherlands) for providing the requisite sample concentrations. Desired concentrations were achieved by adjusting these flow buses, after which the sample was introduced to the reaction region of the IMS instrument. The amount of water was adjusted with a separate one-stage dilution system. The exact construction will be presented elsewhere; a schematic diagram is given in Fig. 1.

2.2. IMS spectrometer

A Ni-IMS-portable ion mobility spectrometer, manufactured by G.A.S. (Gesellschaft für analytische Sensorsysteme mbH, Dortmund, Germany), was used for the experiments reported here. The instrument is equipped with a ^{63}Ni radioactive source, 6 cm drift tube and has a conventional linear design with unidirectional gas flow. The Windows-based program GASpector v.3.99.035 DSP was used for measurements and data handling. Other typical operating conditions were as follows: electric field approximately 200 V cm^{-1} and the temperature of the drift tube was 70 °C. All measurements were made at carrier and drift gas flows equal to 200 mL/min. Signal acquisition parameters were as follows: 1024 points per spectrum, signal sampling rate 50 kHz, 128 averages per scan, and scan repetition rate 250 ms.

2.3. Data processing for peak separation and peak area determination

Peak areas were used for quantitative analysis. In TMA spectra, reactant ion and monomer ion peaks are overlapping; for this reason peak separation before peak area calculation is needed. The procedure for separation consisted in finding the best fit of mathematical functions describing peaks to measured drift time spectra. The theoretical shape of a single peak was described by the formula:

$$y = A_0 \exp[-A_1(t-t_0)^2]\{1+\mathrm{erf}[A_2(t-t_0)]\} \qquad (3)$$

where t is the time and A_0, A_1, A_2 and t_0 are the parameters.

Drift time spectra were described as the sum of 3 or 4 peaks given by formula (3). Parameters of every peak were found using an optimization procedure: the optimization criterion was minimization of the difference between the experimental spectrum and the spectrum calculated as the sum of the theoretical peaks. The calculations were carried out with *Matlab* and *PeakFit* software. The final result of the calculation was the set of peak areas and positions of their maxima.

3. Results and discussion

3.1. TMA without water

Firstly, TMA at different concentrations was measured in dry conditions without additional humidity to characterize ion formation processes and to locate corresponding peak positions in the spectrum. The spectra originating from these measurements are collected and depicted in Fig. 2.

For dry sample, four peaks are clearly observable: ammonium ion NH_4^+ with a drift time (t_d) of about 6.25 ms, TMA monomer TMAH$^+$ ($t_d \approx 6.47$ ms), hydronium reactant ion peak (RIP) ($t_d \approx 6.63$ ms) and proton-bound dimer containing two molecules of TMA, TMA_2H^+ ($t_d \approx 7.68$ ms) at higher sample concentrations. Reduced mobilities calculated for these peaks on the basis of drift times and the operating parameters for IMS are: 2.33 $cm^2 V s^{-1}$ for NH_4^+, 2.25 $cm^2 V s^{-1}$ for $TMAH^+$, 2.20 $cm^2 V s^{-1}$ for RIP and 1.90 $cm^2 V s^{-1}$ for TMA_2H^+. It is notable that no shifting is seen: these peaks stay in their positions no matter what the concentration of TMA is. The RIP peak remains the most intense until the concentration of TMA reaches ∼250 ppb. After that, a brief domination by monomer peak is seen, then with even higher concentrations of TMA, the RIP fades and dimeric species dominate the spectra.

Other facts are clearly seen from the spectra in Fig. 2. For example, the monomeric and RIP peaks are notably overlapping but the tops of the peaks are detached. With high concentrations of TMA, the signal, i.e. the ion current between the dimer and monomer/RIP peaks, rises due to dissociation of dimeric species while they are traveling through the drift tube. In addition, due to the sensitivity of detection, even minor changes in TMA concentrations at ppb-levels have a significant effect on the spectra. The relative intensities of the peaks change notably as a function of sample concentration. With very low sample concentrations dimer is not detected.

3.2. The effect of moisture present in low concentrations

In the measurements described above, the level of humidity was determined by the method of drying used. In these measurements additional water was added to give concentrations between 10 and 800 ppm. This relatively minor amount of excess moisture causes significant changes in the resulting spectra. The spectra having a TMA concentration of 220 ppm were chosen as representatives and are depicted in Fig. 3a.

The first notable change with humidity is the gradual diminution of the dimer peak when the moisture concentration increases. The explanation of this phenomenon should include two possible mechanisms. First, it could be the result of low reactivity of highly solvated monomeric ions which do not form dimers with other TMA molecules. The second alternative is the process of dimer dissociation taking place in the drift region; this dissociation is more effective when the number of collisions with water molecules increases. Such collisions could dissociate dimer ion more effectively than collisions with nitrogen or oxygen molecules. The position of the dimer peak is still stable; no significant shifting is observed. The stability of the dimer position means that their degree of solvation is constant and independent of water concentration. It is probable that they are not solvated. At the same time the peaks representing monomeric TMA and reactant ions complexes shift rightwards. When the concentration of water vapor changes from 10 to 800 ppm, the increase in drift time is relatively significant, approximately 0.3 ms for the monomer and 0.4 ms for the reactant ions. For higher water concentrations both peaks remain well separated. Fig. 3b represents observed drift times as a function of water concentration with two different sample concentrations. As seen from the figure, the relationships between water concentration (C_{H_2O}) and drift time (t_d) are obvious. It should be noticed that these dependencies are stronger for lower humidity. For the beginning intervals, the slopes of the t_d vs (C_{H_2O}) curves are 0.078 ms/100 ppm for reactant ions and 0.058 ms/100 ppm for monomer. The sample concentration does not drastically affect the drift times at a given moisture concentration.

Peak areas are directly equivalent to the abundance of a given analyte ion and are therefore the basis for quantitative analyses. They can also be used to evaluate the sensitivity of the IMS instrument. The detected TMA peak areas at a given humidity as a function of sample concentration are described in Fig. 4. At water concentrations >267 ppm, dimer formation is negligible, therefore those values are omitted from all the figures.

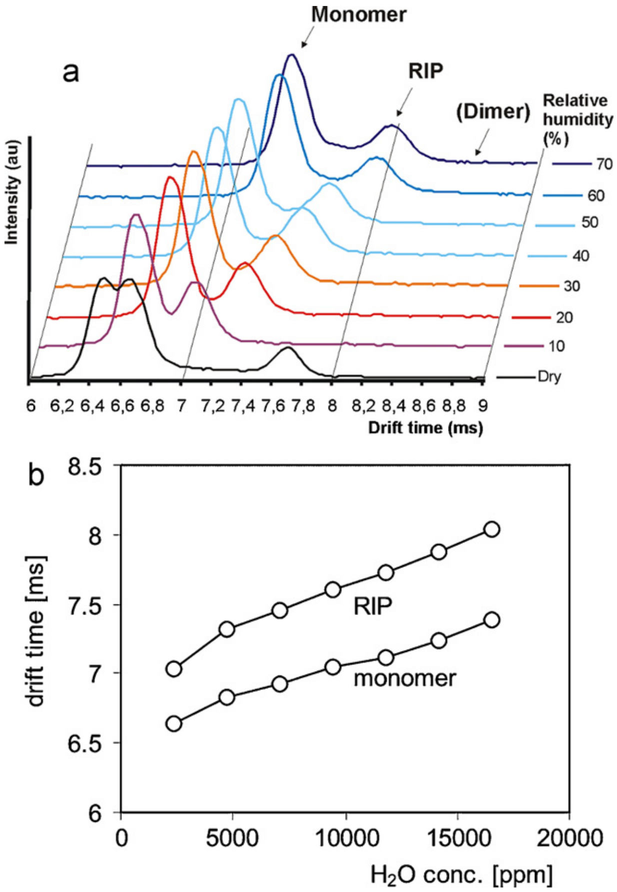

Fig. 5. (a) Spectra of TMA at a constant concentration (220 ppb) measured with high concentrations of water vapor. (b) The relationships between water concentration and drift times of the reactant ions and the monomer ions.

Some trends concerning the occurrence of different ionic species are clearly observable. When the TMA concentration increases the amount of ions producing RIP decrease because of sample ionization processes. For a given TMA concentration the amount of humidity has only a slight effect on the area of RIP, indicating that the abundances of ions producing the RIP remain fairly constant. This indicates that the degree of hydronium solvation has a weak influence on the monomer formation reaction.

For monomer and dimer species (Fig. 4b and c) the divergences caused by humidity are more distinct. Increased moisture favors the formation of monomeric species. The possible reasons for such behavior were discussed earlier. In general increasing humidity does not strongly influence the sensitivity of detection in non-selective mode. The sensitivity of detection based on observation of a single peak increased with humidity for monomer and decreased for dimer ions. Even though the relative abundances of monomeric and dimeric species fluctuate, the total abundances of ions are fairly equal, within approximately 20% of each other (Fig. 4d). It means that ionization processes and loses of ions (recombination) are weakly dependent on sample concentration and humidity.

3.3. The effect of moisture present in high concentrations

High moisture is a relative humidity between 10% and 70%; these values correspond to approximately 2300 ppm and 16,500 ppm, respectively. The measured spectra are depicted in Fig. 5a.

As seen, the peak representing dimer structures is only present in the “dry” spectrum measured without any additional humidity. The explicit shift of monomer and RIP peaks rightwards (towards longer drift times) is directly related to the amount of water. With 70% RH, the additional drift times are approximately 1 and 1.5 ms for the monomer and RIP peaks, respectively. The relationship between humidity and peak positions is presented in Fig. 5b. It is clear that the drift time for reactant ions increases with humidity faster than for monomer. However the slopes of t_d vs (C_{H_2O}) dependencies are much smaller than for low values of humidity and are equal to about 0.007 and 0.005 ms/100 ppm for RIP and monomer, respectively.

4. Conclusions

In this study various ion mobility spectra of trimethylamine were measured in variable but controlled environments: both the concentration of water and TMA were varied. The main focus was on the influence of water concentration on the detector signal and especially its quantitative characteristics, and on clarifying how humidity inside the IMS instrument affects parameters of detection. It was shown that the detection of TMA can be carried out at different levels of humidity. If this detection is based on monomer ion peak or the sum of peaks generated by the analyte, the sensitivity of detection is not strongly dependent on humidity. In contrast, the utilization of the peak generated by TMA dimer ions is possible only when the humidity is low.

These measurements also indicated that IMS is an extremely sensitive technique, responding to ppb-level concentration changes in the TMA sample. It has been shown that additional moisture has a noticeable effect on the appearance of IMS spectra: the existence, positions and shapes of the peaks are strongly dependent on the amount of moisture. Furthermore the abundances of different ionic species are influenced by both sample and moisture concentrations.

The presence of water in the drift region of the IMS detector changes the drift times of ionic species. We have observed a very strong influence of humidity on drift times of hydronium reactant ions and also on protonated molecules (monomers) of TMA. This means that these ions are solvated and the average degree of solvation increases with humidity. The change in drift time for a given increase in water concentration is stronger in the low humidity range. The drift time of TMA dimers does not change when humidity increases. A possible explanation is that the dimer ions are not hydrated.

From the analytical point of view, environmental moisture presents a challenge to the performance of the conventional TOF-IMS instrument. Therefore in conventional IMS measurements the control of moisture is of primary importance to achieve reliable and precise data and has to be taken into account when analyzing and explaining the results observed from samples containing water. It is highly probable that, when operating at relatively high humidities, conventional IMS cannot perform reliable qualitative analyses. Nevertheless, in many cases IMS remains a sensitive analytical tool for both qualitative and quantitative studies of a variety of compounds through their characteristic mobility spectra.

Acknowledgments

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