Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

Determining the water content of a drift gas using reduced ion mobility measurements

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ARTICLE INFO

ABSTRACT

Ion mobility spectrometry is widely used in national defense areas, and field-deployed IMS units are subject to various environmental conditions; one of the most important and least controlled being the humidity of the sample and drift gas. Varying drift gas water content can significantly alter the drift time and reduce the mobility constant (K_0 value) of the ion. While the effect of drift gas water content has been previously characterized, no means to quantitatively measure the water content of the drift gas under field conditions have been developed. In this work, using an IMS-TOFMS instrument capable of high precision (± 0.005 cm^2 V^{-1} s^{-1} or better) measurements of K_0 values, we investigated the protonated monomer and proton-bound dimer ions of dimethyl methylphosphonate as standards that are sensitive and insensitive, respectively, to the formation of water cluster ions. It was found that the ratio of mobilities of these two ions could measure the water content of the drift gas in field-deployed instruments. When water vapor was added in the presence of an ammonia dopant, K_0 was found to decrease as a function of water content to a lesser degree than under conditions without dopant. This study was conducted at atmospheric pressure and at temperatures from 30 °C to 150 °C. The experimental data were supported by complementary density functional theory calculations that examined the interactions of the DMMP monomer with successive number of waters. The reduced ion mobility cross-sections in N$_2$ were subsequently predicted using the trajectory method.
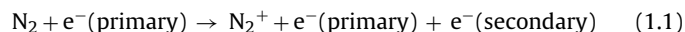
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1. Introduction

Ion mobility spectrometry (IMS) is an analytical technique used for the separation of gas phase ions in a weak electric field based on size-to-charge ratios and the reduced mass of the ion with respect to the surrounding drift gas [1]. IMS has many advantages as a field detector including instrumental simplicity, small size, and low weight. Instruments also exhibit real time monitoring capability, fast response, short analysis time, low power consumption, low operating cost, and high sensitivity. These attributes all lead to the technique's ability to be portable, user-friendly, and reproducible [2]. IMS is particularly sensitive to chemical warfare agents (CWA) [2–4], explosives [5,6], and drugs [7,8]. Thus, when combined with

the previously mentioned advantages, IMS is an ideal instrument for use in the field as a handheld unit within military and national defense areas. However, field-deployed IMS units are subject to various environmental conditions, one of the most important and least controlled being the humidity of the sample and drift gas.
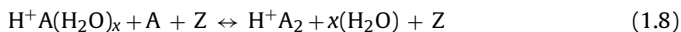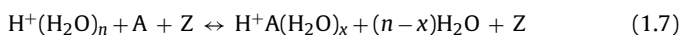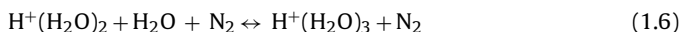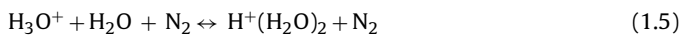
1.1. Effects of moisture content on reduced mobility

Water reactant ion chemistry is the primary ionization mechanism in IMS. The role that atmospheric water plays in reactant ion chemistry is shown in Eqs. (1.1)–(1.8) [1,9].

$$N_2 + e^-(\text{primary}) \rightarrow N_2^+ + e^-(\text{primary}) + e^-(\text{secondary}) \quad (1.1)$$

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \quad (1.2)$$

$$N_4^+ + H_2O \rightarrow 2N_2 + H_2O^+ \quad (1.3)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (1.4)$$

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$$H_3O^+ + H_2O + N_2 \leftrightarrow H^+(H_2O)_2 + N_2 \tag{1.5}$$

$$H^+(H_2O)_2 + H_2O + N_2 \leftrightarrow H^+(H_2O)_3 + N_2 \tag{1.6}$$

$$H^+(H_2O)_n + A + Z \leftrightarrow H^+A(H_2O)_x + (n-x)H_2O + Z \tag{1.7}$$

$$H^+A(H_2O)_x + A + Z \leftrightarrow H^+A_2 + x(H_2O) + Z \tag{1.8}$$

In the case of the positive ion mode in air, nitrogen in the air is initially ionized (typically by β^- emitting ^{63}Ni or electric discharge) to form a reactive N_2^+ ion (Eq. (1.1)) that rapidly undergoes charge transfer reactions with N_2 and traces of H_2O in the air to produce H_3O^+ ions (Eqs. (1.2)–(1.4)). The H_3O^+ ions undergo clustering reactions with H_2O molecules to form a mixture of $H^+(H_2O)_n$ ions, which serve as the reactant ions for the ion mobility spectrometer (Eqs. (1.5) and (1.6)). In the presence of a gas phase base A (often the analyte), a proton-bound monomer cluster may be formed, transferring the proton to A (Eq. (1.7)). When analyte A is sufficiently concentrated in the gas phase, a proton-bound dimer may also form (Eq. (1.8)) [1,9]. Eqs. (1.7) and (1.8) are generalized and show the requisite third-body collisions that may be required for stabilization of observable product ions. Because field-deployed instruments employ ambient air as the drift gas [5,10], the relative humidity or water content of the atmosphere may affect both the ion's chemistry and K_0. Water may cause a shift in the drift time peaks of certain target ions as a result of the analyte clustering with water neutrals, effectively increasing the collision cross-section of the ion [11]. The broadening or appearance of new peaks may also occur [12]. These effects make the identification of suspect mobility peaks in field-deployed instruments more difficult if the water content is not managed.

1.2. Management of water in field-deployed instruments

The effects that water has on mobility analyses can be alleviated in field-deployed instruments by changing the reactant ion chemistry and removing water from the internal atmosphere of the instrument. An ammonia dopant may be introduced into the sample gas as it will undergo a proton transfer from any hydronium reactant ions present [9,13]. In some cases ammonia is added to the drift gas of the IMS instrument as well as the sample gas in an attempt to reduce the clustering of ions with water and other neutrals, thereby decreasing the drift time shift resulting from changing water content levels in the drift gas during operation. The addition of ammonia to the drift gas has also been found to decrease the peak broadening and appearance of new ion mobility peaks from contaminants, due to its higher proton affinity (204 kcal/mol), as described previously [9,14].

In order to remove water from the IMS instrument, the sample or drift gas may also be cleaned. For air samples, a silicon membrane between the sample gas and the ionization region may be used [14], while a molecular sieve pack is used to scrub moisture from the ionization and drift regions of the spectrometer [15]. However, the use of membranes and sieve packs only reduces the amount of water in the drift gas, and the use of dopants (as well as membranes and sieve packs) only reduces the overall effect that water has on the mobility analysis. None of them are methods to quantify or monitor the water concentration within the drift gas, and there are currently no indicators to signal when these components need replacement once they are spent. As a result, unmonitored water content in the drift gas may lead to error and potential false alarms due to "creeping" mobility shift as these systems begin to fail and water content increases.

In order to take field measurements of the water concentration in the drift gas, we propose to use two standard ions; the K_0 of one compound will depend on the water concentration in the drift gas while the K_0 of the other compound will be insensitive to water in the drift gas. Recently, Fernàndez-Maestre et al. proposed the
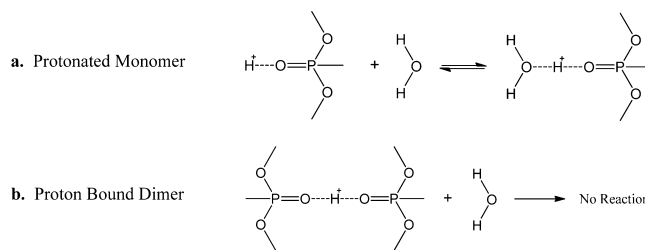
Scheme 1. Interaction of DMMP protonated monomer and proton-bound dimer ions with water.

simultaneous use of two mobility standards to detect drift gas contamination. The first standard was termed the "mobility standard" and was sensitive to drift gas contaminants as well as conditions within the mobility cell. The second standard was called the "instrument standard" and was only affected by the conditions within the mobility cell but not by contaminants in the drift gas [16].

Here, we hypothesize that the protonated monomer and proton-bound dimer ions known to form from dimethyl methylphosphonate (DMMP) [17] can be used as both the mobility standard and the instrument standard. The K_0 of the DMMP monomer is strongly dependent on water vapor concentration while the K_0 of the proton-bound dimer is much less dependent – this is the case over a wide range of drift gas temperatures [18]. The advantage of using DMMP is that a single chemical produces both standards. The protonated monomer ion of DMMP is small and does not have steric hindrance at the charge site, allowing it to cluster with water neutrals as shown in Scheme 1a. Alternatively, the proton-bound dimer ion is large and has steric hindrance at the charging site, inhibiting it from interacting with water neutrals as shown in Scheme 1b [16]. Thus, the K_0 of the protonated monomer decreases (the ion becomes larger) with increasing water content of the drift gas, while the K_0 of the proton-bound dimer ion is relatively unaffected by the drift gas water concentration [17,19].

The two objectives of this study were to: first evaluate whether DMMP can be used as a standard to measure water concentration in the drift gas of an ion mobility spectrometer by measuring the mobilities of the DMMP monomer and dimer ions as a function of drift gas water content, and second, measure these mobilities to a precision of ± 0.005 cm^2 V^{-1} s^{-1} or better. If water concentration can be effectively measured in the field, improved detection algorithms can be developed to correct for water content and ultimately reduce false alarm rates.

2. Experimental

2.1. Chemicals and solvents

The CWA simulant dimethyl methylphosphonate (DMMP) was obtained as a 97% pure standard from Sigma–Aldrich Chemical Co. (St. Louis, MO). Ammonia as a drift gas dopant was obtained in the form of Dynacal permeation tubes from Valco Instruments Inc. Co. (Houston, TX). Compressed air was used as the drift gas inside the ion mobility spectrometer. HPLC grade water from Fisher Scientific (Waltham, MA) was used to increase the water content of the drift gas.

2.2. Ion mobility time-of-flight mass spectrometer (IM-TOFMS)

The IM-TOFMS instrument with accompanying ^{63}Ni ionization source used here has previously been described in detail [4,17,20,21]. The stacked ring drift tube had electrodes with a 5.50 cm diameter and 0.75 cm width, which were stacked on 0.75 cm centers with 0.25 cm between the electrodes.