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Temperature effects in differential mobility spectrometry

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ABSTRACT

Drift gas temperature and pressure influence differential mobility spectrometer (DMS) performance, changing DMS peak positions, heights and widths. This study characterizes the effect of temperature on DMS peak positions. Positive ions of methyl salicylate, DMMP, and toluene, and negative ions of methyl salicylate and the reactant ion peaks were observed in purified nitrogen in the Sionex microDMx planar DMS. Measurements were made at ambient pressure (1 atm) at temperatures from 25 °C to 150 °C in a planar sensor with height 0.5 mm. Peak value of the separation voltage asymmetric waveform was scanned from 500 V to 1500 V. Compensation voltage (DMS peak position) showed a strong variation with temperature for all investigated ions. By generalizing the concept of effective ion temperature to include the effects of inelastic ion–molecular collisions, we have been able to condense peak position dependence on separation field and temperature to dependence on a redefined effective temperature including a smoothly varying inelasticity correction. It allows prediction and correction of the gas temperature effect on DMS peak positions.

Differential mobility spectrometry (DMS) [1–3] is recognized as a powerful tool for separation and characterization of gas-phase ions. In DMS, ions are distinguished by the difference between mobilities at high and low electric fields, exploiting the fact that ion mobility values depend on the applied field strength. Developed and refined over the past decade, DMS is also known as field-asymmetric waveform ion mobility spectrometry (FAIMS) [4] (FAIMS is often used to refer to a coaxial configuration). Several configurations of DMS analyzers have shown response to trace amounts of chemical species including explosives [5,6], chemical warfare agents and simulants [7], volatile organic compounds [8], and a variety of other organic and inorganic substances [9]. Hybrid DMS techniques such as GC–DMS [10], DMS–IMS [11], DMS–MS [12] and ESI–DMS–MS [13,14] can provide detection and identification traces of chemicals for many applications, including biomarkers and biological materials [15].

Stability and repeatability of DMS spectra are important issues in the use of DMS in analytical applications. Drift gas pressure and temperature are known to influence the field dependence of ion mobility, changing peak positions in DMS spectra. This study characterizes the effects of temperature on differential ion mobility and differential mobility spectrum peak position for several typical ion species. The findings provide deeper understanding of the role of the drift gas temperature in interactions between molecular ions and neutrals and the temperature effect on DMS separation. These results allow the development of algorithms to account for the influence of the drift gas conditions that will improve DMS performance under varying environmental conditions.

Pressure and temperature effects on DMS parameters are especially relevant to applications such at the use of planar DMS as an ion prefilter for mass spectrometric analysis. Including a compact planar DMS ion filter in the interface area of the API-MS instrument reduces spectral complexity and suppresses chemical noise, resulting in lower detection levels and better quantitation accuracy [16].

We previously found [17] that pressure variation of DMS peak positions may be eliminated by a rescaling of the coordinates, expressing both compensation and separation fields in Townsend units (electric field divided by density). At fixed temperature, Townsend-rescaled DMS spectra are independent of the drift gas pressure (see Fig. 1a). In contrast, DMS spectra recorded at fixed pressure but varying temperature do not simplify in a similar way. Even in terms of Townsend DMS spectra are distinguished for different bulk temperatures (see Fig. 1b).

The present study focuses on the temperature effect in differential mobility spectrometry. The general aim is to improve DMS spectral stability and repeatability under varying ambient conditions. We present experimental investigations of the temperature dependence of the DMS peak positions and an empirical physical model to represent the obtained experimental data. Our model can be used for temperature correction of DMS spectra.

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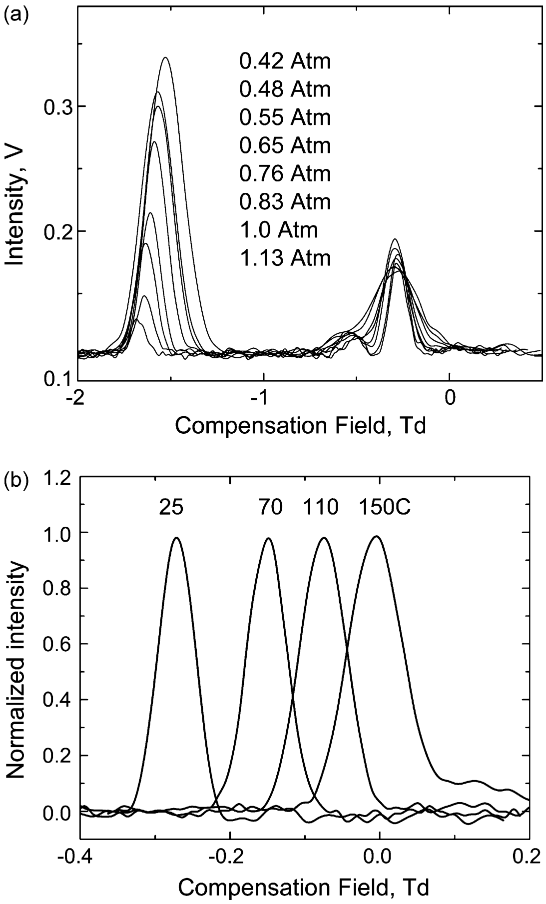

Fig. 1. Positive DMS spectra of methyl salicylate ions at the same 100 Td separation field, but with different drift gas pressures (a) and temperatures (b). Pressure does not affect the DMS spectrum scaled in Td units. Variation of peak position with temperature remains even after Townsend scaling.

We begin with a general review of ion mobility and differential mobility spectrometry. Section 3 describes the experimental setup, data collection and analysis. Then, an empirical model and generalized effective temperature capable of simplifying our observations is presented.

1. Ion mobility

The current understanding of ion mobility has been described in detail in [18,19] but we provide here a brief overview of the basic phenomena involved in our studies.

An electric field of strength *E* causes ions to move through a gas media of density *N*. Simple physical considerations, confirmed by calculations and experiments, show that the ion drift velocity is proportional to the parameter *E*/*N* through the coefficient of mobility, *K*. This result is exact as long as only binary ion–molecule collisions are important and many-body collisions are negligible. It was experimentally verified in our previous work [17]. If the electric field strength, *E*, changes proportional to density (or, equivalently, pressure for ideal gases), *E*/*N* remains unchanged and the coefficient of ion mobility processes is unchanged. This scaling rule had been proven to work well in DMS at fixed gas temperature.

To account for the gas temperature effect in DMS let us consider high field ion mobility in detail. Approximately constant ion mobility, defined as the ratio of velocity to field strength, is determined by the ion-neutral interaction at higher pressures. The high frequency of ion-neutral collisions (∼30 GHz) causes ion velocity in a field to reach a limiting value rapidly. When the collision duration is much shorter than the time between collisions, the binary ion-neutral scattering momentum transfer, scaled by the collision rate, determines the ion mobility. Thus, the ion mobility depends on the ion-neutral interaction potential as well as the distribution of collision energies. If the energy gained by the ion from the electric field is small in comparison with the thermal energy, the mobility coefficient *K* is independent of *E*/*N*. In that low field case, the mean interaction energy does not differ significantly from the mean energy of thermal collisions.

At higher electric fields, ions acquire substantial energy from the field and the frequency and strength of the ion-neutral interaction changes. As a result, the mobility coefficient *K* at fixed bulk gas temperature becomes dependent on the electric field as shown in Eq. (1):

$$K\left(\frac{E}{N}\right) = K(0)\left\{1+\alpha\left(\frac{E}{N}\right)\right\}, \tag{1}$$

where $K(0)$ is the mobility coefficient under low field conditions; $\alpha(E/N) \ll 1$ is nondimensional function characterizing the field mobility dependence (called the alpha function below); E/N is the electric field in Townsend (Td) units ($1\,\mathrm{Td} = 10^{-17}\,\mathrm{V\,cm^2}$). Under standard conditions (1 atm, 0 °C), $N_0 = 2.687 \times 10^{19}\,\mathrm{cm^{-3}}$, so 1 Td corresponds to 268.7 V/cm.

Temperature affects the ion mobility in two distinct ways. Temperature changes gas density, *N*, and hence the value of *E*/*N* and the field contribution to ion kinetic energy. In addition, gas temperature changes the ion and neutral kinetic energy distributions and hence changes the distribution of ion-neutral collision energies and the ion mobility.

A fundamental analysis of the temperature dependence of ion mobility would require knowledge of the ion-neutral interaction potential. But an empirical generalization is still possible if we make use of the fact that temperature and field affect ion transport in the same way, by increasing ion-neutral interaction energy. The most important result of the two-temperature theory is a scaling rule which condenses the two variables *T* and *E*/*N* into the single variable, effective temperature, T_{eff} [20]

$$\tfrac{3}{2}kT_{\mathrm{eff}} = \tfrac{3}{2}kT + \tfrac{1}{2}MV_{\mathrm{d}}^2, \tag{2}$$

where *T* is the drift gas temperature in K, *M* is the drift gas molecular weight, V_{d} is the ion drift velocity, and *k* is Boltzmann's gas constant. For nitrogen drift gas, this becomes

$$T_{\mathrm{eff}} \approx T + 8.09 \times 10^{-3} K_0^2 \left(\frac{E}{N}\right)^2, \tag{3}$$

where K_0 is the reduced coefficient of ion mobility in $\mathrm{cm^2/V\,s}$, and *E*/*N* is electric field in Td. The reduced mobility is $K_0 = KN/N_0$, where *K* and *N* are observed values of the ion mobility and drift gas density; N_0 is the standard gas density. Reduced mobility has a reduced variation with pressure and temperature and is utilized for species identification in conventional ion mobility spectrometry [21].

When ions and neutrals are both atomic, so that only elastic collisions take place, the scaling rule works well. Temperature and field mobility dependences of the atomic ion in noble gases coincide in the effective temperature scale. The situation is more complicated for polyatomic ions and/or neutrals. In molecular systems we must account for inelastic collisions involving rotational and vibrational degrees of freedom. In high field conditions, inelastic collisions transfer energy between the different degrees of freedom and so influence the effective temperature. Lacking information on inelastic cross-sections, we can still combine *T* and *E*/*N* into a generalized $T_{\mathrm{eff}}(T,E/N)$, with the expectation that a smooth inelasticity correction will allow the field and temperature dependences of the