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Gas-phase ion dynamics in a periodic-focusing DC ion guide

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ABSTRACT

In this work, we provide a comprehensive understanding of the radial ion focusing mechanism in the periodic-focusing DC ion guide (PDC IG). The PDC IG was developed in our laboratory to improve the sensitivity and throughput of ion mobility spectrometry (IMS) with respect to conventional uniform field IMS. Radial ion focusing, which is responsible for the sensitivity improvement, is attributed to the presence of effective potentials created by the fringing electric fields of thick ring electrodes and collisional cooling of the ions with the neutral buffer gas. The ion focusing mechanism is affirmed by investigating the variations in the effective ion temperature (T_{eff}) which are dependent upon axial position in the device. The concepts derived herein outline guidelines for the design of high performance PDC IG ion mobility instruments and other ion optical devices such as periodic-focusing DC ion funnels.

1. Introduction

Ion mobility spectrometry (IMS) is a gas-phase electrophoretic separation of ions carried out in the presence of a neutral gas, under the influence of an electric field. In the past few decades, several research groups have coupled IMS to mass spectrometry (MS) to obtain a separation dimension based on the ion-neutral collision cross-section (σ), which complements the mass-to-charge (m/z) separation of MS [1–4]. Ion mobility-mass spectrometry (IM-MS) affords several attractive analytical attributes including rapid separations of complex mixtures, isobars, and isomers, reduction of chemical noise, and determination of ion size—all of which are difficult or impossible to achieve by MS alone. Moreover, IM-MS has the capability of differentiating ions belonging to chemical classes along distinctive mobility-mass trendlines [5–7]. Although a relatively old technique, the aforementioned characteristics have allowed IMS and IM-MS to emerge as a powerful analytical tool with a broad range of applications including the study of atmospheric ions [8], aerosol particles [9], and ion cluster geometries [10–13], detection of airborne chemical agents [14,15], separation of electronic isomeric forms of small molecules [16,17], assignment of ground and excited states in transition metals [18], and characterization of hydrocarbons in crude oils [19,20]. Additionally, the separation speed and information-rich data have allowed for biological applications aimed at investigating molecular structure [21,22] and/or carrying out high-throughput separations of complex mixtures in the fields of proteomics [7,23], glycomics [24,25], and metabolomics [26].

Owing to the versatility of IM-MS, the study of novel instrument design platforms and applications continues to be one of the most rapidly growing areas in the field. Moreover, several research groups have focused on achieving high resolution ($R > 50$) IMS separations as this factor chiefly limits overall IM-MS peak capacity and the information content that can be experimentally derived [2,27,28]. The resolution of the ion mobility measurement is defined as the ratio between the average drift time, t_D, and the full width of the mobility peak at half-maximum height, Δt_{FWHM}. Theoretically, resolution is limited by several factors, although for a sufficiently small packet of ions, the dominant contribution is longitudinal diffusional broadening in the drift tube. A practical definition of resolution in terms of experimental parameters is given by [29],

$$R = \frac{t_D}{\Delta t_{FWHM}} = \left(\frac{LEq}{16\ln 2K_BT}\right)^{1/2} \quad (1)$$

where T is the temperature, q is the ion charge, K_B is Boltzmann's constant, L is the length of the drift tube, E is the electric field, and the product LE translates into the overall voltage drop, V, across the drift tube. Hence, Jarrold and coworkers reported among the highest measured mobility resolution to date, 172, for singly charged fullerene radical cations using 10,000 V applied across a 63 cm drift tube maintained at a pressure of 500 Torr [28] while Clemmer and coworkers recently achieved a mobility resolution of 345 for the

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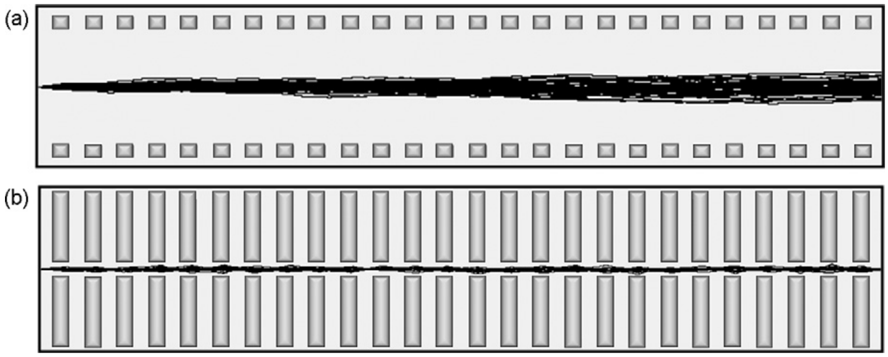

Fig. 1. Longitudinal cross-sections of uniform field (a) and periodic-focusing field (b) IMS drift tubes showing ion trajectories in black. Ion transmission is increased in the PDC IG *via* the periodic-focusing mechanism which confines ions near the central drift axis and maximizes ion transport through the exit of the drift tube.

(+2) charge state of Substance P using a pulsed cyclic drift tube design [30].

Sensitivity, however, is the most sacrificed analytical figure of merit in high resolution IM-MS, owing to the loss of radially-diffuse ions at conductance limiting apertures required for efficient integration of the relatively high pressure drift tube and the vacuum region of the mass analyzer. Typically, ion transmission is increased by coupling RF ion funnel interfaces at the front and/or back of uniform field drift tubes to increase ion introduction and collection efficiency prior to MS [31]. Conversely, the electrostatic periodic-focusing DC ion guide (PDC IG) incorporates two major modifications to the uniform field IMS ring electrode geometry to achieve radial confinement of ions during the IMS separation: (1) a decrease in the inner diameter and (2) an increase in the thickness of the lens element with respect to the electrode spacing, while a linear axial voltage drop is maintained across the electrode stack [32,33]. The novel geometry takes advantage of the fringing electric fields created near the edges of thick electrodes that generate the periodic-focusing phenomenon. As a result, the PDC IG can operate in the low pressure regime between 1 and 10 Torr to produce rapid IMS separations on the μs–ms timescale and allow for utilization of kHz electronic pulsing and/or various multiplexing strategies for ion injection into the drift tube [34,35]; under these conditions, the signal-to-noise is greatly enhanced and the duty cycle of the IM-MS instrument can approach unity.

Fig. 1 contains simulated ion trajectories in the PDC IG and uniform field IMS drift tubes. The ion trajectories illustrate that the PDC IG yields increased ion transmission compared to uniform field IMS and our most recent investigations show up to a 40-fold increase in ion transmission with only a 10% decrease in resolution [36]. The PDC IG has been used for rapid IMS separations of fullerene and model peptides with mobility resolution up to 80 for a 1.25 m length drift tube [36]. Although excellent analytical figures of merit have been demonstrated, ion dynamics in the PDC IG have not been described in detail. In the present work, we explain the role of electrode geometry, compare radial ion confinement to the focusing mechanism in a stacked-ring DC ion guide (termed "DC IG" for simplicity), and briefly discuss the subsequent effects of radial focusing on the analytical separation as compared to uniform field IMS.

1.1. Uniform field IMS

Ion mobility separation in conventional uniform field IMS (also termed drift time IMS) occurs as ions traverse a drift tube containing an inert buffer gas under the influence of a low uniform electric field. The force exerted on the ion by the electric field is opposed by the forces created by ion-neutral collisions resulting in an average velocity for the ion, termed the drift velocity, V_D. The mobility constant, K, is the proportionality constant between the drift velocity and the electric field and is related to the collision cross-section by the following relationship [37],

$$K = \frac{V_D}{E} = \left(\frac{3q}{16N}\right)\cdot\left(\frac{1}{m}+\frac{1}{M}\right)^{1/2}\cdot\left(\frac{2\pi}{K_B T_{eff}}\right)^{1/2}\cdot\left(\frac{1}{\sigma}\right) \qquad (2)$$

The terms N, m, M and T_{eff} represent particle number density of the buffer gas, the mass of the ion, the mass of the buffer gas, and the effective ion temperature, respectively. Eq. (2) is derived under the assumption that interaction potentials between ions and gas particles (*i.e.*, ion-induced dipole) are negligible—a condition that may be experimentally approached using helium as the buffer gas. Additionally, Eq. (2) applies when the kinetic energy the ions gain in the electric field ($(1/2)mV_D{}^2$) is not significantly above the thermal energy (K_BT), defining a "low field limit" which can be attained for atomic ions and IMS separations near atmospheric pressure.

Although it is generally assumed that IMS is carried out under the "low field limit", ions present in a drift tube can have a different temperature than the buffer gas (T_{eff}) owing to the electric field acting upon them [38]. Ion heating becomes significant for IMS measurements of macromolecules at reduced pressures (0.1–1 Torr). Under these conditions, $T_{eff} > T$ because the field contribution to the ion kinetic energy is nonzero. That is, the translational kinetic energy gained by a macromolecule from the electric field between subsequent collisions cannot be completely quenched by a single collision with the buffer gas; however, at sufficiently low field strength, K remains independent of E/N defining an "intermediate-field region" where Eq. (2) still applies [39,40]. In this region, variations in T_{eff} can be used to indicate fluctuations in the electric field strength and the frequency of ion-neutral collisions [41]. Here, we use T_{eff} calculations in combination with effective potentials to yield a comprehensive understanding of the ion dynamics in a PDC IG under static pressure conditions.

1.2. The concept of effective potentials

In contrast to uniform field IMS, the PDC IG contains radial focusing properties analogous to the effective potentials found in a DC IG reported by Guan and Marshall [42]. The effective potential concept, however, was originally derived to explain radial confinement of gas-phase ions moving relatively slow (or at rest) with respect to fast inhomogeneous RF (time-varying waveform) electric fields [43]. The radial effective potential, $V^*(r)$, of a multipole ion guide with an applied RF voltage is described by the relationship,

$$V^*(r) = \frac{q^2 E_0{}^2(r)}{4m\Omega^2} \qquad (3)$$

where $E_0(r)$ is the amplitude of the instantaneous electric field in the radial direction and Ω is the frequency of the applied RF voltage. While $V^*(r)$ is well established for a number of electrodynamic