

Fundamentals of Coulombic Ion-Ion Repulsion Effects in Ion Mobility Spectrometry

Aleksey V. Tolmachev, Brian H. Clowers, Mikhail E. Belov and Richard D. Smith
Pacific Northwest National Laboratory, Richland, WA



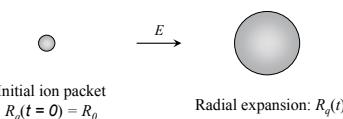
Pacific Northwest
NATIONAL LABORATORY

Overview

- Relationships are reported for IMS resolving power due to space charge repulsion
- A computer model has been developed and used to evaluate the Coulombic effects of ion interaction in IMS
- Theoretical and modeling results are compared with experimental data on IMS resolution for a range of ion populations

Introduction

Ion mobility spectrometry (IMS) coupled with mass spectrometers is a powerful analytical tool for separating complex samples and investigating molecular structure. Implementation of an ion trap for accumulation and pulsed ion injection to IMS has provided considerably increased ion currents, and thus, a basis for improved sensitivity and measurement throughput. However, large ion populations may manifest Coulombic effects that contribute to spatial dispersion of ions traveling in the IMS drift tube, which affects the IMS peak shape, and thus resolving power and effective drift times. In the study reported herein we present an analysis of ion/ion Coulombic repulsion effects in IMS.



Methods

Coulombic effects on the spatial dispersion of ions in IMS were evaluated analytically and modeled using a computer simulation approach based on equations of ion motion in the bath gas. The theoretical results were compared with experimental data. In the experimental portion of the study, the IMS apparatus utilized an ion funnel trap as an ion storage and packet delivery system prior to ion mobility separation. Ions were generated using an electrospray ion source, and variable ion accumulation time was employed to control the total charge of ion packets ejected into the IMS drift tube. A shielded Faraday plate was placed after the rear ion funnel to accurately record the total ion current exiting the IMS system and ascertain peak shape.

$$R_{comb} = [R_{SC}^{-2} + R_D^{-2}]^{1/2}$$

Results

We first consider a high ion density packet, such that Coulombic repulsion is the dominant factor leading to spatial dispersion of ion packets. The expansion of the ion cloud is driven by the electric field strength E_{SC} at its surface. According to Gauss' law, the field is defined by the surface area A and the total charge Q contained within this surface: $E_{SC} = Q / \epsilon_0 A$, where ϵ_0 is vacuum permittivity. The packet boundary projection on the IMS drift axis z , relative to the packet's center, extends as a function of time t :

$$\Delta = KE_{SC}t_c$$

Here K is ion mobility and $t_c = t - t_0$ is time corrected by an integration constant t_0 that accounts for initial packet width. Substituting the Coulombic field, we obtain for a planar ion packet configuration:

$$\Delta(t) = Kt_c Q_A / \epsilon_0$$

Here $Q_A = Q / A$ is ion packet charge per surface area. For a linear ion packet orthogonal to z , the projection Δ is equal to the outer radius r :

$$r(t) = \sqrt{\frac{KQ_L}{\pi\epsilon_0}t_c}$$

Here Q_L is ion packet charge per unit length of the linear ion packet. In a case of spherical symmetry

$$r(t) = \left(\frac{3QK}{4\pi\epsilon_0}t_c \right)^{1/3}$$

IMS resolving power can be estimated as $R = L / 2\Delta$, where the drift length L is related to the time t and IMS voltage V as $t = L^2/V$. Substituting t into above relationships for time-dependent ion packet width, we obtain estimations for IMS resolving power defined by Coulombic expansion. For the spherical symmetry case:

$$R_{SC} = \frac{1}{C_S} \left(\frac{\pi\epsilon_0 LV}{6Q} \right)^{1/3} \quad C_S^{-1} = \sqrt{2}$$

The factor C_S accounts for full width half max (fwhm), assuming uniform spatial distribution within the spherical boundary [1]. This relationship corresponds to a classical IMS resolving power due to diffusion, which also assumes spherical symmetry and neglects initial ion packet width:

$$R_D = \left(\frac{zeV}{16k_B T \ln 2} \right)^{1/2}$$

The initial spatial and/or temporal ion packet width can be accounted for using a square root of a sum of the squared increments contributing to the total ion packet width. Similarly, the Coulombic and diffusional resolving powers can be combined to obtain the total IMS resolving power:

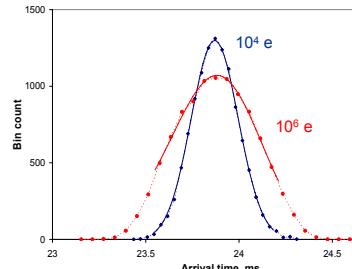


Fig. 1. Computer modeling of IMS resolution. Arrival time distributions obtained for ion packets having 10^4 and 10^6 elementary charges (e). Non-Gaussian distributions were obtained for ion charges $>10^4$ e.

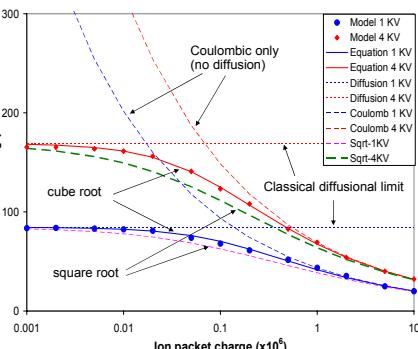


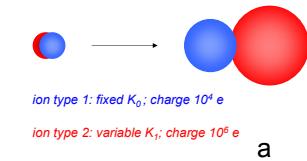
Fig. 2 IMS resolving power, calculated for $V = 1\text{kV}$ and 4kV ; $L = 1\text{ m}$, drift gas N_2 , 4 Torr , $T = 293\text{ K}$, doubly charged ions.

Coulombic repulsion produces a noticeable effect on resolution for ion charge $>\sim 10,000$ e. In the range where both diffusion and space charge produce comparable contribution, the resolving power can be closely approximated by the following cube root relationship:

$$R_{comb} = [R_{SC}^{-3} + R_D^{-3}]^{-1/3}$$

Computer modeling

The computer model simulated ion motion in IMS drift tube, taking into account diffusion and drift motion caused by electric fields. The macro-ion approach [2] was used to calculate the space charge effects caused by Coulombic ion-ion interactions. A random number generator used to model diffusional motion was configured to produce Gaussian distributions for zero space charge, in agreement with the diffusion theory. IMS resolution was calculated as FWHM of arrival time histograms (Fig.1).



ion type 1: fixed K_0 ; charge 10^4 e
ion type 2: variable K_1 ; charge 10^6 e

Ion mobility ratio $F_K = K_1 / K_0$

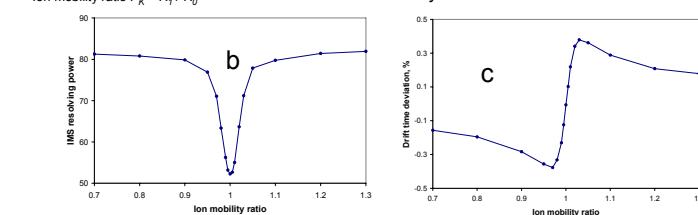
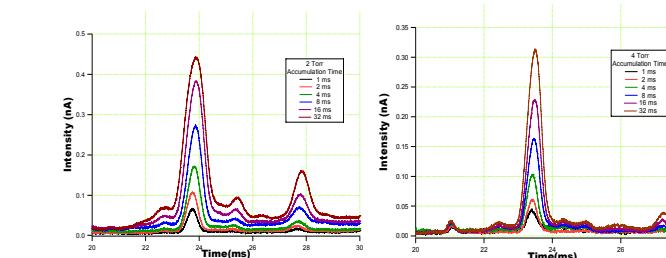


Fig. 3. (a) Bi-component system: 10^4 e and 10^6 e, mobility differs by factor F_K ; (b) resolving power and (c) observed drift time for the lower charge component (fixed mobility K_0)

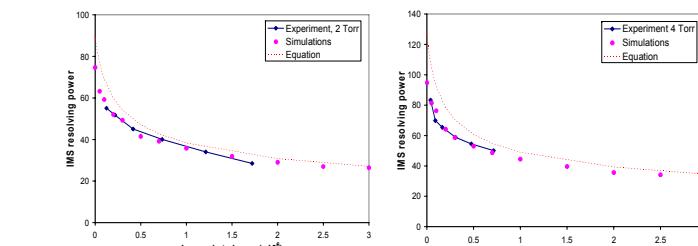
Resolution of the low charge component is affected most, when the two mobilities are close, $K_0 \sim K_1$. Systematic changes in observed drift times (i.e. observed ion mobility) occur when mobilities slightly differ ($\sim \pm 3\%$)

Experiment

Theoretical results were compared with experimental data obtained using an IMS apparatus utilizing an ion funnel trap (IFT) [3]. A shielded Faraday plate was used to collect ions at the IMS exit. Experimental traces obtained for a range of ion accumulation times are shown below.



IMS resolving power measured experimentally was compared to modeling results and the cube root relationship; a good agreement has been obtained.



Conclusions

- Relationships for IMS resolution due to Coulombic interaction have been obtained
- Computer simulations closely agree with expected results at the diffusional and Coulombic limits
- Combined diffusion and Coulombic relationship matching the modeling results has been formulated
- Coulombic effects emerge for ion populations $>\sim 10^4$ e
- For bi-component ion packets, Coulombic repulsion affects average drift velocity of ions, creating systematic deviations in ion mobility measurements
- Increasing the drift voltage helps to improve the resolution, with the Coulombic limit increasing slower than the diffusion limit, i.e., cube root vs. square root.
- Unlike the diffusion limit, the Coulombic limit explicitly depends on the drift region length, so that longer drift regions have an advantage
- Relationships and simulations were found to be in agreement with experimental measurements for a range of ion populations

Acknowledgements

This work was funded by the National Center for Research Resources (RR 018522), the National Institute of Allergy and Infectious Diseases (NIH/DHHS through interagency agreement Y1-AI-4894-01), the National Institute of General Medical Sciences (NIGMS, R01 GM063883), and the U.S. Department of Energy Office of Biological and Environmental Research (DOE/BER). Significant portions of the work were performed in the Environmental Molecular Science Laboratory, a DOE/BER national scientific user facility at Pacific Northwest National Laboratory (PNNL) Richland, Washington. PNNL is operated for the DOE by Battelle under contract DE-AC05-76RLO-1830.

References

- Tolmachev, A. V.; Clowers, B. H.; Belov, M. E.; Smith R. D. *Anal. Chem.*, Article ASAP, published online May 2009.
- Tolmachev, A. V.; Kim, T.; Udseth, H. R.; Smith, R. D.; Bailey, T. B.; Futrell, J. H. *Int. J. Mass. Spectrom.* 2000, 203, 31–47.
- Clowers, B. H.; Ibrahim, Y. M.; Prior, D. C.; Danielson, W. F.; Belov, M. E.; Smith, R. D. *Anal. Chem.* 2008, 80 (3), 612–623.

CONTACT: Aleksey Tolmachev, Ph.D.
Biological Sciences Division, K8-98
Pacific Northwest National Laboratory
P.O. Box 999, Richland, WA 99352
E-mail: tolmachev@pnl.gov