

Orthogonal Extraction Ion Mobility Spectrometry

Victor V. Laiko
MassTech, Inc., Columbia, MD



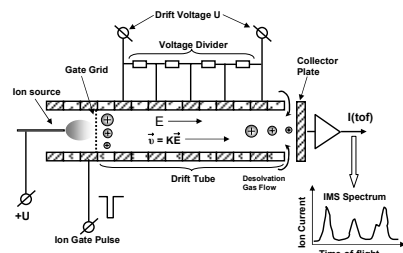
INTRODUCTION

Ion Mobility Spectrometry (IMS) separates gas-phase ions based on ion mobility. Coupled to mass spectrometers, IMS provides a unique tool for the study of molecular conformations, separation of isomers, analysis of complex mixtures and suppression of chemical background. IMS of two types are known: drift-tube IMS and differential mobility analyzer (DMA). The factors that limit the capabilities of both types of IMS include relatively low resolving power and duty cycle.

The development of a new type of mobility analyzer, *orthogonal extraction IMS* (ortho-IMS), which can provide both high resolution and detection sensitivity, is the subject of present study.

CURRENT IMS DESIGNS

Drift-tube IMS

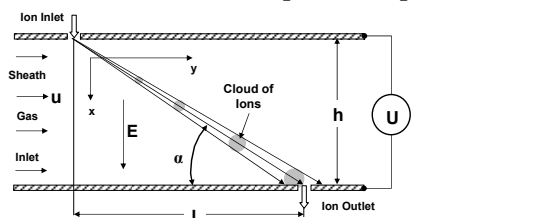


Diffusion-limited resolution: $R_D = \frac{1}{4\sqrt{\ln 2}} \sqrt{\frac{qU}{kT}} = 16.5 \sqrt{\frac{U}{T}}$

If $R_D=300$ and $T=300^\circ$: $U > 100kV$ (for singly charged ions)

If resolution 100 is targeted, the gate is closed 99% of the time

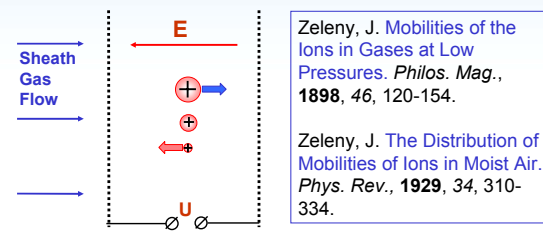
Differential Mobility Analyzer



Diffusion-limited resolution: $R_{DMA} = \sqrt{1 + h^2 / L^2} \sqrt{\frac{eU}{8kT}}$

Limited sensitivity: ions are passing through the two slits

Parallel flow analyzer

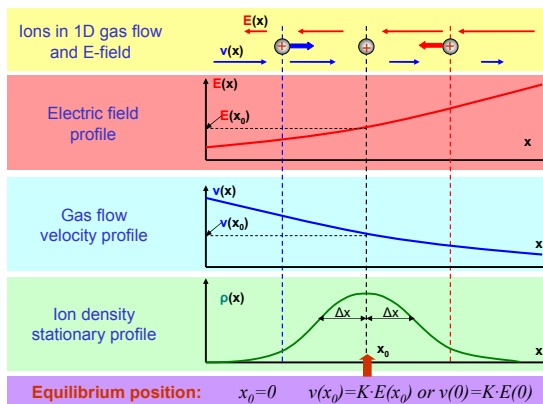


Zeleny, J. Mobilities of the Ions in Gases at Low Pressures. *Philos. Mag.*, 1898, 46, 120-154.

Zeleny, J. The Distribution of Mobilities of Ions in Moist Air. *Phys. Rev.*, 1929, 34, 310-334.

Advantage: unlimited resolution at the given voltage U
Disadvantage: ion density drops with crease of resolution

FOCUSING IMS PRINCIPLE



One-dimensional Theory

Analytical calculation of *ion density distribution* $\rho(x)$:

$$v(x) = v(0) + \frac{dv}{dx} \cdot x = v(0) - ax \quad E(x) = E(0) + \frac{dE}{dx} \cdot x = E(0) + \beta x = \frac{v(0)}{K} + \beta x$$

$$D \cdot \frac{d\rho(x)}{dx} = \rho \cdot [v(x) - K \cdot E(x)] = \rho \cdot [v(0) - ax - K \cdot (\frac{v(0)}{K} + \beta x)] = -\rho \cdot (a + K\beta)x$$

Nernst-Townsend-Einstein: $K = eD/kT$

$$\rho(x) = \rho_0 \cdot \exp\left[-\left(\frac{a + \beta \cdot e}{2D + 2kT}\right) \cdot x^2\right] = \rho_0 \cdot \exp\left[-\left(\frac{x}{\Delta x}\right)^2\right] \quad \Delta x = \frac{1}{\sqrt{\frac{a + \beta \cdot e}{2D + 2kT}}}$$

$E(x)$ – electric field profile	K – ion mobility	T – absolute temperature
$v(x)$ – flow velocity profile	D – diffusion coefficient	k – Boltzmann's constant
$\rho(x)$ – ion density profile	β – electric field gradient	e – ion charge
Δx – density profile width	a – flow acceleration	R_F – focusing IMS resolution

Analytical calculation of *focusing IMS* resolution:

Ions with mobilities K_x and K_y are focused at different positions x_0 and x_1 :

$$v(x_0) - K_x E(x_0) = 0 \quad v(x_1) - K_y E(x_1) = 0$$

The condition for the two Gaussian distributions to be resolved:

$$|x_0 - x_1| = 2\Delta x = \frac{2}{\sqrt{\frac{a + \beta \cdot e}{2D + 2kT}}}$$

The variations of all of the values are small compared to the values itself:

$$\Delta K = \frac{v\beta + Ea}{E^2} |x_1 - x_0| = K \cdot \left(\frac{\beta}{E} + \frac{a}{KE}\right) \cdot \frac{2}{\sqrt{\frac{a + \beta \cdot e}{2D + 2kT}}}$$

Diffusion-limited resolution:

$$R_F = \frac{K}{\Delta K} = \frac{KE \cdot \sqrt{\frac{a + \beta \cdot e}{2D + 2kT}}}{2(K\beta + a)}$$

(A) Uniform gas flow, electric field is increasing downstream:

$$\Delta x = \sqrt{\frac{2kT}{\beta \cdot e}} \quad R_F = E \cdot \sqrt{\frac{e}{8kT \cdot \beta}}$$

$E=200V/cm$; $\beta=dE/dx=1V/cm^2$; $k=1.38 \cdot 10^{-23}J/grad$; $T=300^\circ K$; $e=1.6 \cdot 10^{-19}K$ (for singly-charged ions).

$\Rightarrow \Delta x=2.3mm$
 $R_F=440$

(B) Uniform electric field, decelerating gas flow:

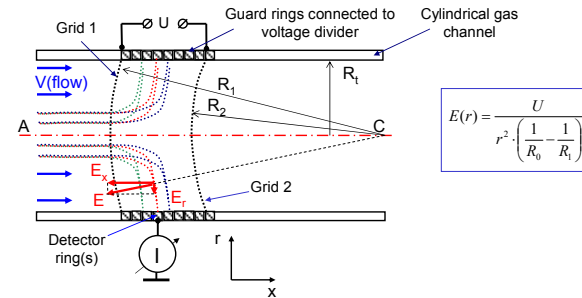
$$\Delta x = \sqrt{\frac{2D}{a}} \quad R_F = \frac{v}{\sqrt{8Da}} = E \cdot \sqrt{\frac{eK}{8akT}}$$

$v=200cm/s$; $a=1cm/s^2$; $K=0.5cm^2/Vs$

$\Rightarrow \Delta x=1.6mm$
 $R_F=620$

Design (A): standalone ortho-IMS

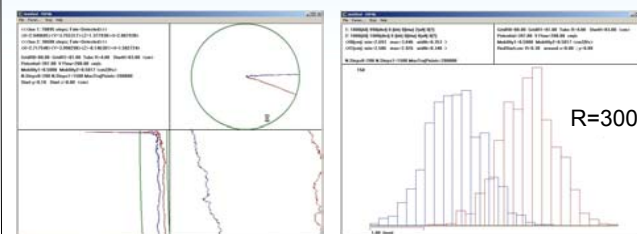
Uniform gas flow, electric field is increasing downstream:



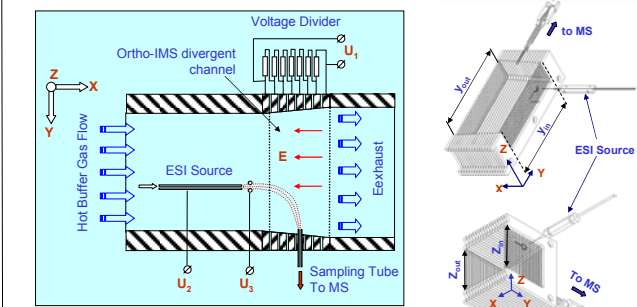
Ortho-IMS: numerical simulation

- Special software was developed in-house to simulate the three-dimensional ion motion inside ortho-IMS.
- A model with uniform plug gas flow profile were used for the calculations. Three-dimensional trajectory of each ion was calculated.
- Ion diffusion was simulated using the Monte-Carlo method.
- The displacement Δl of ion at fixed short time interval Δt was calculated as a sum of displacements Δl_1 (due to the influence of electrical field and gas flow) and Δl_2 (in randomly selected direction due to diffusion effect). The diffusion constant D is related to Δt and Δl_2 : $D=(\Delta l_2)^2/4\Delta t$.

Design (A): numerical simulation



Design (B): interface to MS instrument

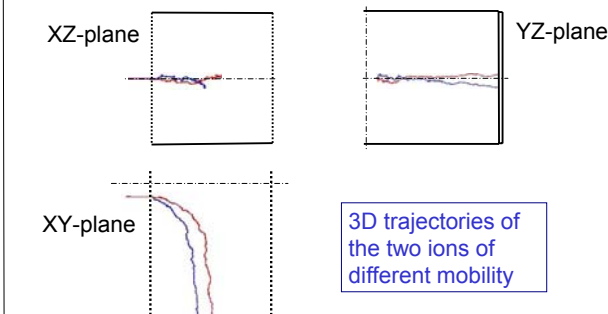


Ortho-IMS scheme with uniform electric field and decelerating gas flow provides both mobility separation and 3D ion focusing toward the sampling capillary

$$y_{in} < y_{out} \\ z_{in} > z_{out} \\ y_{in} \cdot z_{in} < y_{out} \cdot z_{out}$$

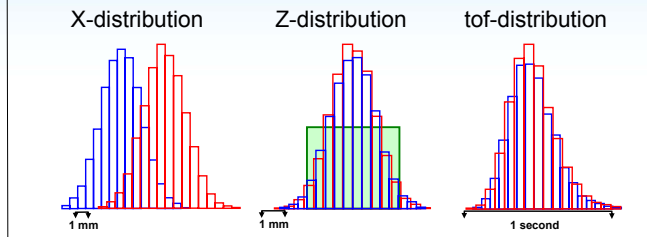
Design (B): numerical simulation

ortho-IMS parameters used in numerical simulation:
inlet grid: 8x4 cm; outlet grid: 8.2x3.95 cm;
channel length: 4cm; voltage: 1586 V; flow velocity: 2 m/s
ion mobilities: 0.5000 / 0.5008 cm²/Vs, difference: 0.15 %



3D trajectories of the two ions of different mobility

Design (B): numerical simulation



2 x 10,000 trajectories are calculated for the two kind of ions. Ion starts were chosen randomly inside the circle of Ø4 mm shifted by 2 mm off-axes. X-distribution of arrival coordinates shows the resolution of 625, Z-distribution proves that ions are well-focused. Time-of-flight distribution has min/max times of 1.41 s and 2.73 s.

CONCLUSIONS

- Focusing IMS** uses the ion focusing/separation under combined action of electrostatic field and gas flow; either gas flow velocity, electrical field, or both of them are not uniform.
- The analytical **one-dimensional theory** demonstrates a diffusion-limited resolution of several hundred at moderate values of voltages and flow rates.
- Two possible implementations of the focusing IMS principle called **orthogonal IMS** are discussed. The first design uses uniform gas flow and increasing downstream electric field. It is useful for standalone applications.
- Another ortho-IMS is designed as a **pre-separation** device for MS. Gas flow convergent in one direction and divergent in another direction focuses the ion beam providing the efficient sampling of the ions to MS in the direction orthogonal to the gas flow.
- 3D Monte-Carlo **numerical simulation** of ion motion predicts a diffusion-limited resolution of ortho-IMS devices of several hundred and efficient ion focusing toward the detector electrode or sampling capillary.

Acknowledgment

I have conducted the present research having being inspired by the development of ortho-TOF technique by Alexander Dodonov – my Teacher in the field of Mass Spectrometry and far beyond. It is my homework for him. Unfortunately, I have completed it too late. Prof. Dodonov passed away on August 31, 2005. This study is dedicated to his memory.