

Modeling Ion Motion in a Miniaturized Ion Mobility Spectrometer

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Abstract: Ion mobility spectrometry provides fast detection of very low concentrations of chemical substances. Simple instrumentation combined with high sensitivity and high selectivity are the advantages of this technique. One well established field of application is the detection of hazardous compounds in air, such as chemical warfare agents, explosives and pollutants.

A numerical model based on finite element analysis has been developed for rapid design and optimization of ion mobility spectrometers with respect to physical and economic constraints. All significant physical effects on the ion transport in an IMS are considered within the simulation, such as diffusion, coulomb repulsion, electric fields and gas flows. For developing, studying and optimizing a new concept of a miniaturized low-cost IMS COMSOL Multiphysics has been successfully used.

Keywords: Ion mobility spectrometry, Migration, Convection, Diffusion, Coulomb repulsion

1 Introduction

Ion mobility spectrometry (IMS) is based on the separation of ions by electric fields within gaseous media. At about atmospheric pressure, ions travel within an electric field \mathbf{E} with a substance specific drift velocity

$$v = K\mathbf{E}. \quad (1)$$

The macroscopic movement, the migration of ions, results from the acceleration of the ions due to the electric field followed by repeated collisions with neutral molecules. The ratio between the drift velocity and the electric field is the ion mobility K . A fundamental equation for this substance specific measure was discussed by Revercomb and

Mason assuming sphere models [3]:

$$K = \frac{3}{16} \frac{ze}{N} \frac{1}{\Omega_0} \sqrt{\frac{2\pi}{k_b T} \left(\frac{1}{m} + \frac{1}{M} \right)} \quad (2)$$

As is commonly known, the acceleration of an ion in an electrostatic field depends on its mass m and charge ze . On the other hand, undisturbed acceleration is restricted in terms of the mean free path. For this reason K is inversely proportional to the effective collision cross section of the ion Ω_0 , the square root of the temperature T and the pressure or number density N of the gas the ion is moving in. Furthermore, the efficiency of the collisions is influenced by both, the mass m of the ions and the mass M of the neutral molecules. k_b denotes Boltzmann constant.

The collision process is comparable to that resulting from Brownian motion. Therefore, it stands to reason that K is directly proportional to the diffusion coefficient:

$$D = K \frac{k_b T}{ze}. \quad (3)$$

This fundamental relation also states that the migration of ions is intrinsically tied to the diffusion process at a given temperature. At room temperature the thermal movement of an ion is typically some orders of magnitude faster than its drift velocity within moderate electric fields. Nevertheless, unlike the migration, the average spatial movement due to diffusion is proportional to the square root of the time. For this reason – over a given time interval – the net migration flux Φ^M can considerably exceed the net diffusion flux Φ^D at sufficient high electric field intensities.

This effect is utilized in ion mobility spectrometry to separate different ion species and to identify them according to their mobility. A common approach for high-resolution ion mobility spectrometry is

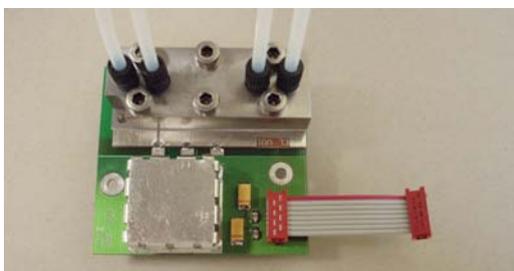


Figure 1: Photograph of a current prototype. The IMS cell (upper part) is mounted on a PCB containing a current amplifier for testing purposes. Without the fluidic connectors, radioactive source and mounting screws the IMS cell consists of five parts only. They are fabricated using conventional machining and are easy to assemble. Since the volume of the separation region is just about 25 mm^3 the outer dimensions of the system can further be reduced if required.

the time-of-flight method (TOF-IMS). Ions are injected repeatedly into a homogeneous electric field. The ion mobility is then calculated from the time the ions need to travel a certain distance. Over the past decades TOF-IMS have evolved to high sensitive and selective analytical devices [2]. Commercial IMS are used for the detection of hazardous compounds, such as chemical warfare agents (CWA), toxic industrial compounds (TIC) and explosives. Other applications are drug detection, breath analysis or process analytics.

1.1 Miniaturization approaches

Besides this, several attempts were made to design miniaturized IMS devices [2]. They are especially interesting for hand-held applications and sensor networks for personal air and public area monitoring. One miniaturization approach is to reduce the size of TOF-IMS. However, the time-of-flight approach requires complex instrumentation. Homogeneous electric fields, high voltages, narrow ion pulses and fast measurement of low ion currents are some of the crucial components in this design.

A miniaturized IMS is reported here which can be easily manufactured and is especially suited for low-end, low-cost applications [5, 6]. A Photograph of a current prototype is shown in Fig. 1.

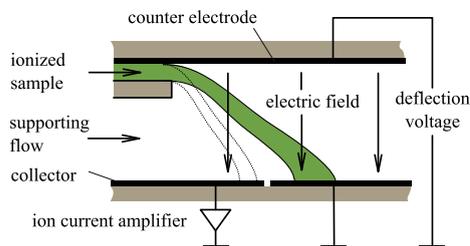


Figure 2: Principle of the miniaturized planar ion mobility spectrometer. At laminar conditions a thin layer of gas containing the ionized sample forms above a supporting flow of purified air. Ions are separated according to their polarity and mobility within a variable electric field. They are selectively discharged at the collector.

The concept is shown in Fig. 2. It is partially based on earlier designs reported by Tammet [4] and others. The sample gas is ionized by means of a $100 \text{ MBq } ^{63}\text{Ni}$ beta-ray source. Gaseous anions and cations are entering the separation region through a narrow gap. Ions of different mobilities are spatially separated by an electric field while traveling in a precisely regulated transverse gas flow. When a positive deflection voltage is applied, anions are discharged at the counter electrode while cations are deflected towards the bottom electrode configuration and vice versa. Ions with appropriate polarity and with ion mobilities smaller than a certain threshold are discharged at the collector resulting in electric ion currents of up to 10^{-10} ampere. The ion current is recorded as a function of the deflection voltage. It can be shown that the ion mobility distribution can be reconstructed from this signal by differentiating the recorded current with respect to the deflection voltage [5].

1.2 Fast system design by numerical modeling

Analytical solutions of phenomena that degrade the analytical power of ion mobility spectrometers can be obtained only for a very limited number of cases. However, especially for miniaturization and optimization an in-depth understanding of ion motion in gaseous media is required. A FEM-based model is presented in this paper that covers all important physical effects on ion motion within an IMS.

2 Numerical Model

In the type of IMS discussed here ion separation is achieved by the combination of two effects: migration (the transport of ions in the electric field relative to the neutral gas) and convection (the transport within the flow of the neutral gas). Consequently, in the first step the flow field \mathbf{u} , the electric potential Ψ and the electric field $\mathbf{E} = -\nabla\Psi$ are computed. In the second step the local ion concentration c_s is calculated for every ion species s , considering the three transport mechanisms migration, convection and diffusion. Fig. 3 shows the structure of the simulation.

2.1 Governing Equations

The calculation of the flow field \mathbf{u} is described by the steady state Navier-Stokes equations:

$$-\eta\nabla^2\mathbf{u} + \rho(\mathbf{u} \cdot \nabla)\mathbf{u} + \nabla p = 0 \quad (4)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (5)$$

with the dynamic viscosity η , the density ρ and the pressure p of the fluid. The flow of the neutral molecules results in a convective transport of the ions. The convective flux Φ^C is computed by the product of the ion concentration within a small volume element and its flow velocity:

$$\Phi^C = c\mathbf{u}. \quad (6)$$

The drift velocity of the ions is in the same order of magnitude as the average flow velocity, but their concentration within the neutral gas is typically very low. For this reason the influence of the ions on the motion of the fluid is neglected.

Electrostatic fields are commonly solved with FEM by expressing Gauss's law as a Poisson equation with respect to the electrostatic potential Ψ :

$$\nabla \cdot (\nabla\Psi) = -\rho_q/\varepsilon \quad (7)$$

Since changes of the deflection voltage are slow, coupling effects between electric and magnetic properties can be neglected. The space charge density is modeled as $\rho_q = F \sum_s z_s c_s$, thus considering the influence of every ion species s on the electric field. This describes the electrostatic ion-ion interaction - also known as Coulomb repulsion.

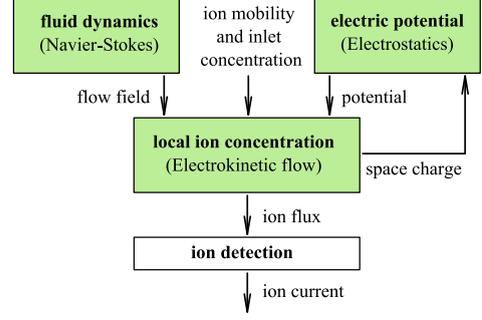


Figure 3: The numeric model is divided into three parts. Ion charge is also considered for the computation of the electric field and electric potential respectively.

F denotes the Faraday constant. Obviously the local ion concentrations c_s are not known without computing the electric field. As will be discussed later, this problem can be solved iteratively. Since most boundaries of the simulated domain correspond to metalized surfaces simple Dirichlet boundary conditions apply.

Assuming the charge number is $z = 1$ for single charged cations and $z = -1$ for single charged anions respectively, the migration ion flux is given by

$$\Phi^M = -z c K \nabla \Psi. \quad (8)$$

Gathering the three transport mechanisms from equations (6), (8) and from (3) using Fick's first law, a total ion flux $\Phi_s = \Phi_s^M + \Phi_s^C + \Phi_s^D$ can be formulated for each ion species s . Assuming that no ions are generated or disappear within the region of interest, the conservation of mass applies

$$\nabla \cdot (c_s \mathbf{u} - z_s K_s c_s \nabla \Psi - D_s \nabla c_s) = 0 \quad (9)$$

This assumption is feasible since ions of opposite polarity are separated directly after entering the separation region. Therefore, recombination reactions are negligible.

Finally, the electric ion current at the collector can be computed by integrating the total ion flux over the area A of the collector (normal vector \mathbf{n})

$$i_s = - \int_A \mathbf{n} F z_s \Phi_s dA \quad (10)$$

Since the ion current is recorded, this value can directly be compared to measured data.

2.2 Solving the model

Both, the Navier-Stokes equations and the electrostatics problem are predefined application modes in COMSOL Multiphysics. The ion transport equation (9) is available within the Chemical Engineering Module. Therefore, the complete model can be implemented using the graphical user interface without using coefficient form PDEs. However, for automated optimizations a Matlab front-end was developed to create models parametrically. Postprocessing routines were used to evaluate the performance of the simulated IMS and to compare the simulations with measured results.

Since the movement of ions is also influenced by the Coulomb repulsion, usually several iterations between the computation of the electric field (equation 7) and the local ion concentration (9) are required. In this case however, the multiphysics approach is used. Except for the Navier-Stokes equations all equations are collected into one equation system and are solved in parallel. It is important to note that anions and cations are entering the system at the same concentration for reasons of charge conservation during the ionization process. This results in charge neutrality at the inlet gap. Therefore, at least two ion species of different polarity have to be simulated at the same time to prevent from inaccurate ion repulsion. Convergence can be improved by computing an initial solution without Coulomb repulsion or by adding a damping factor to the space charge term in equation (7). However, this was not required in the current application.

The IMS and the fluidic connections are designed to achieve laminar, steady state flow within the separation region over a wide range of operating conditions. Separate fluid dynamics simulations were performed to ensure this. Consequently, the stationary solution of the flow field is used for further investigations. In general, however, this might be extended to the non-steady case if required. Furthermore, the distribution of the ion concentration is constant as long as the deflection field, the flow field and the inlet concentration remain constant. Consequently, the steady state solution of the local ion concentration, the total ion flux and the electric ion current are calculated. The simulation is repeated with various deflection voltages to compute the ion mobility spectrum.

3 Experimental results

In order to achieve fast computations the model has been optimized in various fashions. Great reduction of the computational effort could be achieved by a two dimensional model. This is feasible as a first approximation due to the planar configuration of the system. However, the inlet boundary conditions for the fluid dynamics simulation have to be adapted to match proper volume flows. With the simplified model direct solvers (UMFPAK) could be used and convergence was usually achieved in less than 12 iterations using the default stopping criterion. Fig. 4 shows a simulated ion concentration profile at a constant deflection voltage.

A prototype of the miniaturized IMS was used to verify the simulated results [1]. In Fig. 5 a typical spectrum of the miniaturized IMS under clean conditions is shown. Purified, dry air was used for both the supporting gas (1 l/min) and sample gas (300 ml/min) in this case. The parameters of the simulation, such as the physical dimensions, the flow rates, voltages and material properties are carefully chosen to match the conditions of the experiment. Since there is no accurate possibility to compute the ion mobility of a given substance [2], the peak position has to be matched with the measurement. As seen in Fig. 5, the width and the shape of the simulated peak almost perfectly matches to the measured peak. Measurements at different conditions could also be reproduced. This is a hint that all significant ion transport effects that contribute to peak broadening are correctly considered in the simulation.

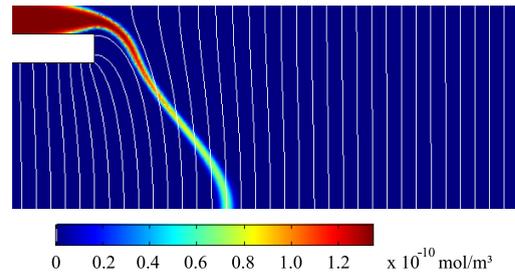


Figure 4: Illustration of electric field lines and simulated ion concentration of a single ion species at a constant deflection voltage of 120 V. Ions are forming a narrow ion beam and hit the bottom electrode configuration.

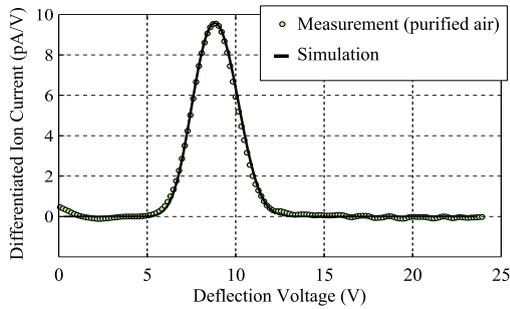


Figure 5: A single peak can be observed when measuring the positive spectrum of purified air. The simulation ($K = 2.47 \text{ cm}^2(\text{Vs})^{-1}$) matches the measurement very well.

The model was used to investigate the influence of several parameters on the performance of the IMS. The variation of two geometric parameters is shown in Fig. 6 as an example. One important measure for the analytical power of an IMS is the resolution – defined as the ratio of the position and the width of a single peak. As can be seen from Fig. 6, the resolution increases when the cross section of the separation region transverse to the flow is reduced at a constant aspect ratio. This is due to the reduced diffusion broadening of the ion beam at higher flow velocities and higher deflection voltages. Additionally, higher resolutions can be achieved with smaller sizes of the ion inlet gap due to improved initial ion focusing. However, the improvement of the resolution becomes smaller at very small dimensions. With this knowledge, the optimal parameters can be chosen considering the manufacturing effort and the power consumption due to the required volume flow and pressure drop.

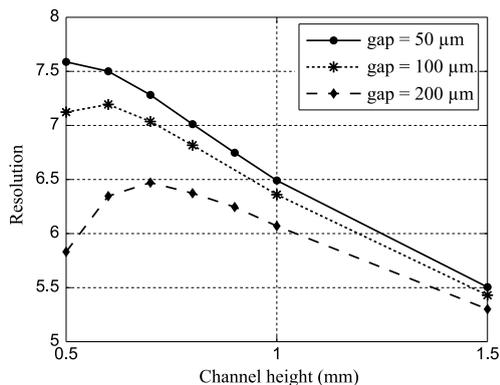


Figure 6: Simulated resolution of the IMS in dependence of the height of the separation region and the height of the inlet gap. The sample gas and the supporting gas flow are 200 ml/min and 2000 ml/min respectively.

4 Conclusion

A numerical model of the physical ion transport mechanisms in a miniaturized ion mobility spectrometer has been developed, considering electric fields, gas flow, diffusion and coulomb repulsion. The simulation is able to reproduce our measurements and could successfully be used for fast system optimization including the resolution, size and complexity of the ion mobility spectrometer.

The model was implemented and solved with COMSOL Multiphysics using predefined application modes. Matlab was used for advanced post processing and to create and evaluate various design variants for parametric studies.

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