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Numerical algorithm for the accurate evaluation of ion beams in transversal modulation ion mobility spectrometry: Understanding realistic geometries

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ABSTRACT

In this study, we analyzed the different physical mechanisms that affect the shape of a thin ion beam in time-dependent electric fields for the particular configuration of a transversal modulation ion mobility spectrometry (TMIMS) device. In this configuration, the ion beam is focused in a narrow region, which is simultaneously broadened by diffusion; the quality and shape of this focus determines the resolving power of the spectrometer. We analyzed different numerical approaches and developed a compounded algorithm in which the diffusion effect is superimposed onto purely convective trajectories. With a relatively low computational cost, this method solves the challenges associated with the disparate scales of the problem. The new algorithm was validated against the experimental results, and it estimates the maximum resolving power of the spectrometer with errors below 10%. It also enabled an optimization of the geometry of the electrodes and the wave shape.

1. Introduction

When an ion is subjected to an electric field in a gaseous environment, it is accelerated by the electrostatic force and dragged by subsequent collisions and interactions with neutral gas molecules [1]. At the macroscopic level, similar ions acquire a mean average velocity. The mobility of an ionic species is defined as the ratio between this mean velocity and the electric field strength. Ion mobility spectrometry (IMS) [2] is gaining interest as a stand-alone analysis technique or combined with mass spectrometry (MS) [3,4]. Different technological approaches can be used to separate ions according to their mobility; the most prevalent techniques include: Drift Tube IMS (DT-IMS) [5–10], Field Asymmetric waveform IMS (FAIMS) [11–13], also known as differential mobility spectrometry (DMS) [14–16], traveling wave IMS (TWIMS) [17–19], and differential mobility analysis (DMA) [20–23].

Transversal modulation IMS (TMIMS) [24,25] could be particularly advantageous in tandem with trap MS, because it provides a steady flow of mobility-selected ions. TMIMS utilizes an axial and steady electric field, which pushes the beam of ions forward at a velocity that is proportional to their mobility, and a perpendicular and oscillating electric filed, which deflects the ions laterally. These two fields combined only re-focus those ions for which the time of residence is equivalent to the period of the oscillating electric field. The TMIMS only collects the focused ions. And mobility spectra is produced by scanning the frequency of the oscillating field. Each type of ion produces a peak at its corresponding frequency. Fig. 1 illustrates the shape of the trajectories of the ions in a TMIMS, which is highly dependent on the shape and position of each electrode.

Aberration of the re-focused beam, as well as Brownian diffusion, which spreads the trajectories, can limit the resolving power of the instrument. One objective of this study was to develop specific numerical tools to evaluate, design, and optimize the performance of a TMIMS, which is given by two basic parameters: (i) the resolving power of the spectra (R), which is here defined by the full width at half maximum (FWHM) algorithm and (ii) the transmission of the selected ions.

The first attempt to estimate R is described in [24], and it considers uniform electric fields, for which the ion trajectories can be analytically solved. According to this model, the resolving power is given by the following equation (Eq. (1))

$$R = 0.187\frac{E_1}{E_0}\sqrt{\frac{eV_0}{k_BT}} \qquad (1)$$

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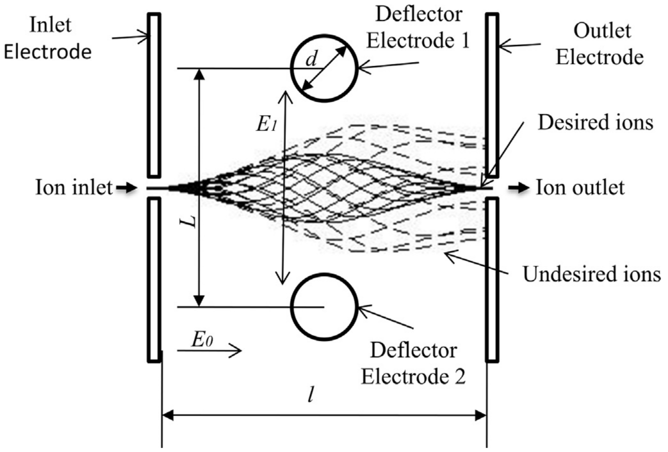

Fig. 1. Principle of the operation of the TMIMS: only ions of the elected mobility are refocused at the outlet.

where E_0, E_1 and V_0 are the axial electric field, the transversal electric field amplitude and the axial voltage, respectively, and k_B, T, and e are the diffusivity, the Boltzmann constant, the absolute temperature of the gas, and the charge of an ion, respectively. The theoretical model quantitatively corresponds with the experimental results. However, it overestimates R by a factor of 2, likely because it does not consider geometrical parameters. For instance, the predicted R is $R = 117$ for $E_1/E_0 = 1$, $V_0 = 10$ kV and $T = 300$ K but the experimental result is $R = 55$ [24].

To optimize the design of a TMIMS, a numerical tool that can predict these performances for a given geometry and operating conditions would prove useful. However, this simulation is not straightforward because the problem has very different scales, which must be accurately resolved: the typical distance between electrodes is in the range of a few centimeters, and the width of the focused ion beam is in the range of tens of microns (a difference of four orders of magnitude). A direct Eulerian approach would require extremely fine meshes to capture the scale disparity. Commercially available software packages (such as ITSIM [26,27], GEMIOS [28], microDMX [29], COMSOL Multiphysics [30,31] or, SIMION [32]) provide an Eulerian approach for the electric field and a Lagrangian approach for the ion trajectories. These codes evaluate the trajectories of the particles (independently) and include mechanistic kinetic collision models (i.e., hard sphere models), which provide mobility and diffusional scattering. Although these methods are suitable for low-pressure environments, they are impracticable for use at atmospheric pressure because the number of collisions and the computational cost are impracticable. Simplified diffusion models that are generally based on statistic models of collision mechanics or Monte Carlo methods [33–37] can reduce the computational effort for a given configuration. However, in this time-dependent study, in which we need to scan the frequency of operation of the TMIMS and other geometric parameters that are utilized to optimize the geometry, a large number of simulations is required and the speed of these approaches remain inadequate.

To the best of the author's knowledge, there are currently no computational packages capable of addressing the numerical simulation of the TMIMS. Consequently, the objectives of this study were: (i) to develop the new numerical tool, (ii) to analyze the factors that limit the resolving power of the TMIMS, and (iii) to find optimum geometries and wave shapes. In Section 2 we analyze the physical processes involved in the TMIMS, and we discuss the simplification hypothesis. In Section 3 we analyze the coherence of the numerical methods, and we compare the numerical results with experimental data. Section 4 describes the geometrical optimization results of this numerical simulation tool. And finally Section 5 summarizes the conclusions of the study.

2. Theoretical background, hypothesis and problem formulation

If a continuum is assumed, the broadest formulation of the problem includes solving the electrostatic potential, the gas flow velocities and the thermodynamic properties, as well as the concentrations and the dynamics of the charged particles. The problem is time-dependent and the electrostatic potential is dependent on the charge concentration distribution, which is also dependent on the electric field and flow velocities; they are also affected by the movement of ions, which also exchange momentum with the gas. Although the problem seems highly coupled, some hypotheses can be formulated to simplify it for the normal conditions of operation of the TMIMS. The configuration is two-dimensional (the TMIMS is defined as a planar device), and we consider that the electrostatic solutions are steady, since the typical period of oscillation is 1 ms, greater than the electromagnetic resonance of the TMIMS.

2.1. *Effect of the movement of charged particles on the movement of the gas*

Considering that the typical voltage of the TMIMS is 10 kV, that the current of ions is $I = 10$ pA [24], that the ionic speed is approximately $v_i = 20$ m/s, and that the ideal beam of ions is planar with a projected area of 5 cm^2, the power dissipated by the ionic flow is approximately 100 nW, which implies a net force of 5 nN and an averaged shear stress of approximately 10 μPa. This force produces a negligible effect on the gas, which is renewed in the lateral direction (perpendicular to the two main directions of the 2D problem) at a rate of 1 lpm (1.67×10^{-5} m^3/s). In view of this, we hypothesize that the movement of ions has no effect on the movement of the gas.

2.2. *Effect of the coulombic repulsion of the ion beam on the electric potential*

In first approximation, the total amount of charge in the ion beam is $Q = I \times l/v_i$, where l is the length of the ion beam. For $l = 5$ cm, $I = 10$ pA, and $v_i = 20$ m/s, Q is $Q = 2.5 \times 10^{-14}$ C, the electric fields induced by this charge at a distance l is approximately four orders of magnitude lower than the electric fields produced by the electrodes. Thus, we hypothesize that the effect of the beam space charge on the TMIMS performance is negligible, at least for the case in which the intensity is low enough. Obviously, at higher intensities, the effect of space charge will not be negligible. In a typical situation, very abundant ions will also distort the trajectories of the less abundant ions. The effect of these interactions, and the intensities that start to affect the performance of the TMIMS, are important aspects to determine the performance of the TMIMS, and should be addressed in a future study. However, for the optimization of the geometry (which is one of the main purposes of the current study), it is not required to evaluate these effects because the TMIMS will be normally operated below the threshold of maximum intensity, in a regime for which space charge effects are negligible (at least in first approximation).

2.3. *Effect of the gas velocity*

The TMIMS incorporates two gas inlets, which are designed to introduce the gas at low velocities and prevent turbulence. Because the gas enters laterally, its effect in the two coordinates of the planar problem can be neglected in the majority of the domain. At the inlet slit, a small gas stream exits from TMIMS and flows against