

THE LIMITS OF AIR ION MOBILITY RESOLUTION

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ABSTRACT: An innovation by *Loscertales* [1998] forced the revision of the theory of the diffusion-limited mobility resolution. Traditionally, the limit of resolution has been estimated according to the ratio of the thermal energy kT to the work of the electric field expressed as qV , where q is the ion charge and V is the voltage between electrodes. This is correct when the electric field is transverse to the air flow. Otherwise, the term qV should be replaced by the term qEL , where L is the Lagrangian length of the passage of an ion through the air in the mobility separation zone. The work qEL exceeds qV in the longitudinal or inclined field analyzers which promise further improvement of the mobility resolution when compared with traditional transverse field instruments. The inclined field method can be accomplished as proposed by *Loscertales* [1998] or by using inclined grids as suggested in the present paper.

INTRODUCTION

Understanding of the limits of mobility resolution is important because of increasing interest in the nanometer particle and airborne cluster research during the present decade. The resolution of existing mobility spectrometers does not fully satisfy the requirements of analytic instruments, and any improvement promises new applications of ion mobility spectrometry.

Three factors limit the resolution: (1) finite width of electrodes and slits of a differential analyzer, (2) background noise of the measured electric current, (3) air ion diffusion, or Brownian motion, in a mobility analyzer. Primitive estimates of the limits of resolution due to electrode width are simple and well known, but far from faithful. The reason for this is that these estimates neglect the possibility of mathematical inversion. Possibility of computational enhancing of the resolution is limited by the noise of the measured electric current. Thus the first two factors should be discussed together. The problem is mathematically complicated and no satisfactory solution is known up to now.

The third factor is physically the most fundamental and is discussed in many papers. A review of publications has been given by *Flagan* [1998]. However, the problem seems not to be exhausted. Recently *Loscertales* [1998] suggested a new idea to make an aspiration condenser in which the electric field is inclined relative to the air flow, and he showed that the commonly accepted resolution limit can be surpassed in a new instrument. The proposal by *Loscertales* makes it necessary to revise some concepts and correct misunderstandings in the common theory of diffusion-limited mobility resolution.

STANDARD INTERPRETATION OF DIFFUSION-LIMITED RESOLUTION

Brownian diffusion of air ions results in a Gaussian dispersion of coordinates of air ions in a uniform separating field inside an analyzer. Although the images of the mobility lines are not Gaussian, they can well be approximated by Gaussians. The mobility resolution is measured by the ratio of the Gaussian standard deviation σ_z to the center of the mobility line Z_0 : $\delta = \sigma_z / Z_0$.

In a simplest mobility analyzer the mobility is measured by the drift on an ion during a predetermined time or by the time (TOF method) of drifting a predetermined distance. *Zeleny*

[1929] showed that the Brownian motion or diffusion of ions limits the resolution of the simplest mobility analyzer to the value

$$\delta = \delta_0 = \sqrt{2 \frac{kT}{qV}} , \quad (1)$$

where q is the ion charge and V is the voltage between the beginning and the end of the drift path. Solutions of specified problems have been given by *Tammet* [1970], *Stolzenburg* [1988], *Rosell-Llompart* [1996] and others.

The resolution of a specific analyzer can be written as $\delta = f \times \delta_0$, where the factor f exceeds the value of 1 in any classic aspiration or TOF mobility analyzer. E.g., $f = \sqrt{1 + h^2 / l_0^2}$ in a plain aspiration condenser with a plug flow, where h is the distance between the electrodes and l_0 is the length of the condenser.

The value of δ_0 is determined by the ratio of the average thermal energy of an ion and the work of the electric field separating the ions. The resolution limit δ_0 has a fundamental physical nature: the ratio of the standard deviation of the ion flight distance to the average flight distance in the free molecule regime is expressed by the same Equation 1, and the solution for the free molecule regime can be immediately transformed to the solution of the macroscopic problem by using simple mechanical and probabilistic calculations [*Tammet*, 1970].

INNOVATION BY LOSCERTALES

Loscertales [1998] proposed a new method improving the diffusion-limited mobility resolution by means of the longitudinal electric field in an aspiration mobility analyzer. The plain Loscertales analyzer is explained in Figure 1. The plates are not equipotential and the electric field is not perpendicular to the air flow as assumed in traditional mobility analyzers. The deviation from a traditional analyzer is characterized by the ratio of longitudinal and transverse components of the electric field, $Lo = E_x / E_y$, called the Loscertales number below. When discussing the diffusive broadening of the mobility lines or the transfer function, the flow rate of ionized air is assumed negligible compared with the neutral sheath air flow rate. The electric field between the plates is inclined but uniform, and the

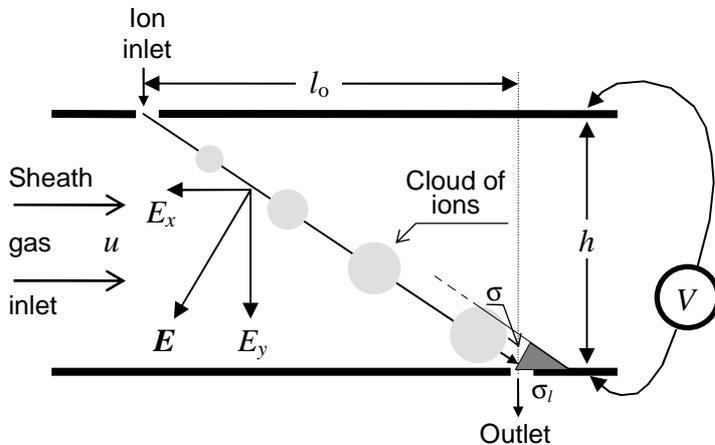


Figure 1. The plain Loscertales mobility analyzer.

The voltage V between any pair of facing points in Figure 1 is the same along the plates. Due to the Brownian diffusion, the cloud of simultaneously entering particles of mobility Z expands during the passage as illustrated in Figure 1. The center of the cloud is deposited at the distance

$$l = \left(\frac{uh}{ZV} - Lo \right) h . \quad (2)$$

The mobility Z_0 of ions emerging through the outlet corresponds to the length of the analyzer l_0 .

The mobility resolution $\delta = \sigma_Z/Z_0$ is to be estimated according to the Brownian standard deviation of the sedimentation length σ_l and taking note of the derivative

$$\frac{\sigma_l}{\sigma_Z} \approx \left| \frac{dl}{dZ} \right| = \frac{uh^2}{Z_0^2 V}. \quad (3)$$

In a traditional analyzer $|dl/dZ| = l/Z$ and $\delta = \sigma_l/l_0$. When the analyzer is too short, the denominator l_0 suppresses the resolution. In a Loscertales analyzer the derivative $|dl/dZ|$ remains finite even if the length of the analyzer approaches zero. Thus a further increase in resolution is possible. Calculations [Loscertales, 1998; Tammet, 1998] yield the result

$$f = \sqrt{1 + \frac{l_0^2}{h^2}} / \left(L_0 + \frac{l_0}{h} \right). \quad (4)$$

The value of the Loscertales number has no upper limit and the situation $f < 1$ is possible which seems to be paradoxical from the viewpoint of traditional interpretation explained above.

REVISION OF THE STANDARD INTERPRETATION

The standard interpretation is based on the assumption that the term qV equals the work done by electric field in separating the ions. The assumption is correct when the electric field is transverse to the air flow as expected in the classic aspiration method. The assumption fails in the Loscertales analyzer, where the work of the electric field $W > qV$. So the apparent paradox can be easily solved. It should be pointed out as a little known fact that the limit of resolution expressed as δ_0 was surpassed a century ago in an instrument by Zeleny [1898] who proposed the method of parallel velocities. In this instrument the voltage V is applied between two grids, and the ionized air flows through the grids parallel to the electric field. The average velocity of ions between the grids is $v = EZ - u$, where u is the air flow velocity, and the mobility is calculated as $Z = h/Et + u/E$, where h is the geometric, or Eulerian, drift of ions. The resolution limit of the method is

$$\delta = \sqrt{2 \frac{kT}{qE(h + ut)}}. \quad (5)$$

When compared with Equation 1, the expression of the work of the electric field, $W = qV$, is replaced by $W = qE(h + ut)$. The quantity $L = h + ut$ can be interpreted as the Lagrangian distance of ion drift in the separation region and the work of the separating field can be written as qEL . Thus the essence of revision of the standard interpretation of the diffusion-limited mobility resolution is that the drift distance in the resolution calculation should not be considered as a geometric distance but as the Lagrangian distance of passage of ions through the air.

Unfortunately, the parallel flow method has no known applications today because it does not allow injection and extraction of ions with air flows.

METHOD OF INCLINED GRIDS

The proposal of Loscertales to make an aspiration analyzer with non-equipotential electrodes has not materialized due to troublesome technical problems. A combination of the grid method of Zeleny and the non-equipotential electrode method of Loscertales promises easier technical realization of the instrument. The schematic design of the new instrument is explained in Figure 2. The orientation of the electric field in the analyzer is the same as in the Loscertales analyzer, and the diffusion-limited resolution is determined with the same equations. As distinct from the Zeleny grid instrument, the new analyzer has inlet and outlet slits for ions like the tra-

ditional DMA-s. The ions to be separated do not pass through the grids and there is no harmful effect of adsorption of ions on the grids. To

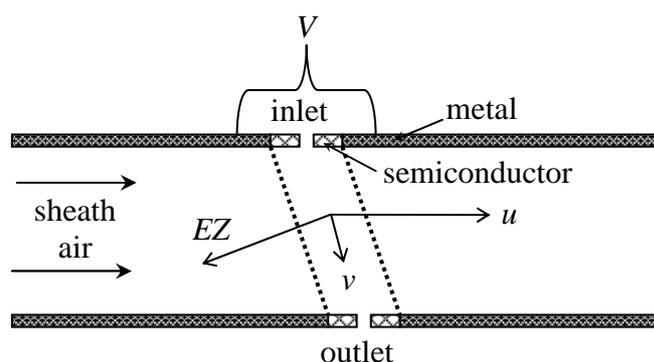


Figure 2. Mobility analyzer with inclined grids

the contrary, the adsorption is even useful as a means of additionally cleaning the sheath air. An essential advantage of the method is that the grids suppress the turbulence and maintain the plug flow profile. The required total voltage in the inclined grid instrument is less than in the Loscertales instrument, and the voltage dividers are short and simple. Sheath air can be easily cleaned from background ions by inclusion of additional grids into the air flow before the analyzer.

CONCLUSIONS

The limit of resolution estimated according to the ratio of the thermal energy kT to the work of the electric field expressed as qV is correct when the electric field is transverse to the air flow. Otherwise, the work of the electric field exceeds qV and can be expressed as qEL , where L is the Lagrangian drift of the ion through the air. Longitudinal or inclined field analyzers promise further improvement of the mobility resolution when compared with traditional transverse field instruments. Actually, the improved resolution is characteristic of the oldest flow-through-grids method by Zeleny [1898]. However, the Zeleny grid method does not allow injection and extraction of ions with air flows. This disadvantage is prevented in the inclined field method suggested by Loscertales [1998]. The instrument of Loscertales is difficult to manufacture, but the same theoretical advantages can be achieved in a simpler instrument with inclined grids as suggested above.

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