THE LIMITS OF AIR ION MOBILITY RESOLUTION

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INTRODUCTION

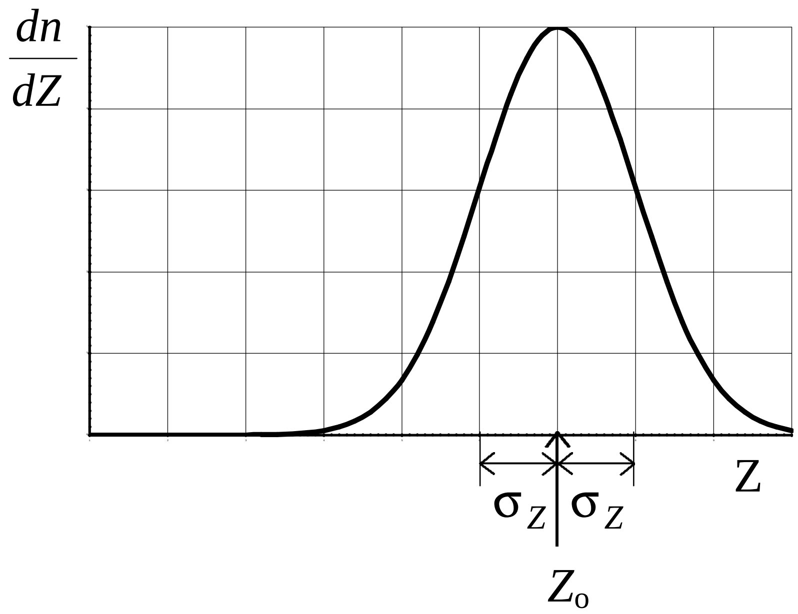
Understanding of the limits of mobility resolution is important because of increasing interest in the nanometer particle and airborne cluster research during the present decade. The resolution of existing mobility spectrometers does no fully satisfy the requirements of analytic instruments, and any improvement 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. 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.

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 exactly 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_o : $\delta = \sigma_Z / Z_o$.

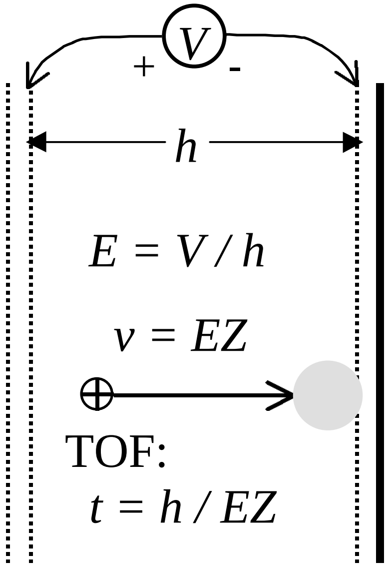


Resolution is measured by

$$\delta = \frac{\sigma_Z}{Z_o}$$

CALM AIR ANALYZER (TOF METHOD, DRIFT TUBE)

History: AC method was proposed by *Rutherford* 1898, contemporary configuration was proposed simultaneously by *Van De Graaff* 1928 and Tyndall 1928.



Mobility: $$Z_\circ = \frac{h}{Et}$$

Two possibilities: h fixed t measured; t fixed h measured } resolution nearly the same

$$\delta = \frac{\sigma_Z}{Z_\circ} \approx \frac{\sigma_h}{h} \quad \& \quad \sigma_h = \sqrt{2Dt} = \sqrt{2\frac{kTZ}{q}t} \quad \Rightarrow \quad \delta = \sqrt{2\frac{kTZt}{qh^2}} = \sqrt{2\frac{kT}{qV}}$$

Standard resolution δ_o : $$\delta_\circ = \sqrt{2\frac{kT}{qV}}$$

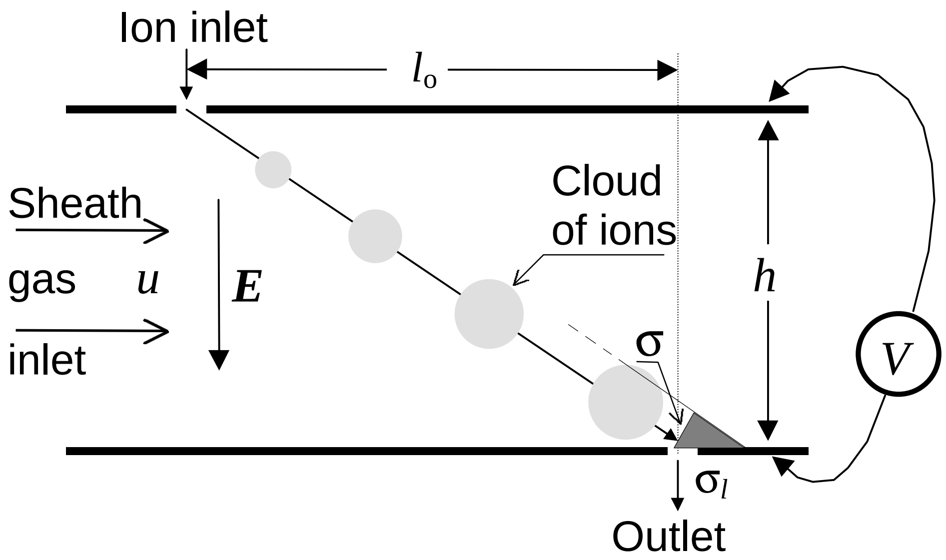
q is the ion charge and V is the voltage between the beginning and the end of the drift path.

Example (q = 1 e, T = 20°C, any value of Z)

V =	1 V	10 V	100 V	1000 V
δ_o =	22%	7%	2.2%	0.7%

The fact that the diffusion-limited resolution is determined by the energy ratio *kT/qV* has been shown by *Zeleny* [1929]. The direct molecular-kinetic interpretation of this result was explained by *Tammet* [1970] (see page 67 of the book).

PERPENDICULAR FLOW ANALYZER (ASPIRATION CONDENSER)



Plain condenser with a plug flow:

$$Z = \frac{uh^2}{Vl} = \frac{\text{const}}{l} \quad \& \quad \delta = \frac{\sigma_l}{l_\circ} \quad \& \quad \sigma_l = \sigma\sqrt{1+\frac{h^2}{l_\circ^2}}$$

$$\Longrightarrow \qquad \delta = \delta_\circ\sqrt{1+\frac{h^2}{l_\circ^2}}$$

Solutions of specified problems have been given by *Tammet* [1970], *Salm* [1970], *Stolzenburg* [1988], *Rosell-Llompart* [1996] and others.

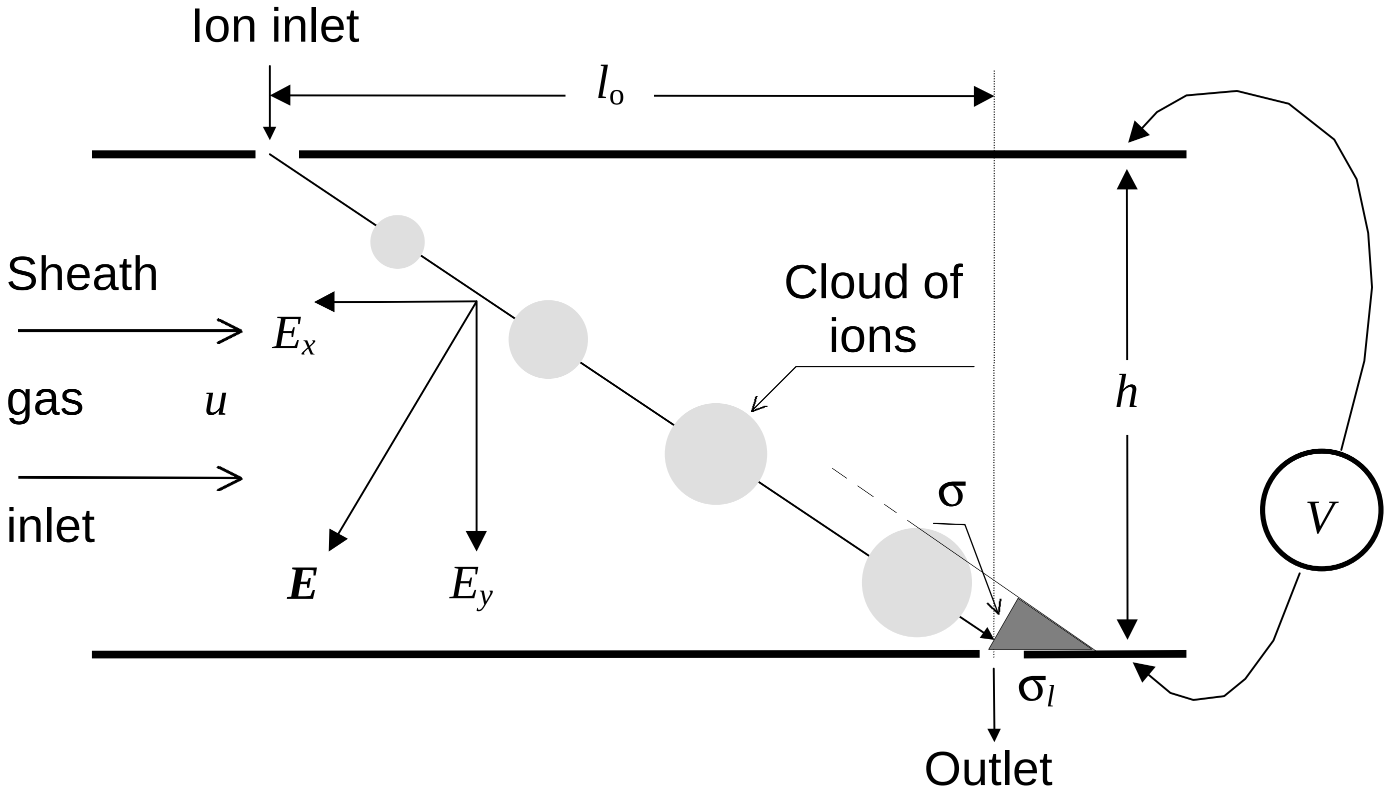
The resolution of a specific analyzer can be written as $\delta = f \times \delta_o$, where the factor f exceeds the value of 1 in any classic aspiration or TOF mobility analyzer. E.g., $f = \sqrt{1 + h^2 / l_\circ^2}$ in a plain aspiration condenser with a plug flow, where h is the distance between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

The problem of optimum length. $l_o \to \infty \Rightarrow f \to 1$. Why not increase the length?

If V = const & $l_o \to \infty$ then $\mathrm{Re} \to \infty$.

If Re = const, the optimum is at $l_o = h$ and the best value of f is $f = \sqrt{2}$ [*Rosell-Llompart et al*. 1996].

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 analyzer is explained in Figure. The plates of a Loscertales analyzer 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,

$$\mathrm{Lo} = \frac{E_x}{E_y} \ ,$$

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 voltage V between any pair of facing points in Figure above 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. The center of the cloud is deposited at the distance

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

The mobility Z_o of ions emerging through the outlet corresponds to the length of the analyzer l_o. The mobility resolution $\delta = \sigma_Z / Z_o$ is to be estimated according to the Brownian standard deviation of the sedimentation length σ_l and taking note of the derivative

$$\frac{\sigma_l}{\sigma_Z} \approx \left| \frac{\mathrm{d}\, l}{\mathrm{d}\, Z} \right| = \frac{uh^2}{Z_\circ^2 V} \ .$$

In a traditional analyzer

$$|\mathrm{d}l/\mathrm{d}Z| = l/Z \ \text{ and } \ \delta = \sigma_l / l_o.$$

When the analyzer is too short, the denominator l_o suppresses the resolution. In a Loscertales analyzer the derivative $|\mathrm{d}l/\mathrm{d}Z|$ 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

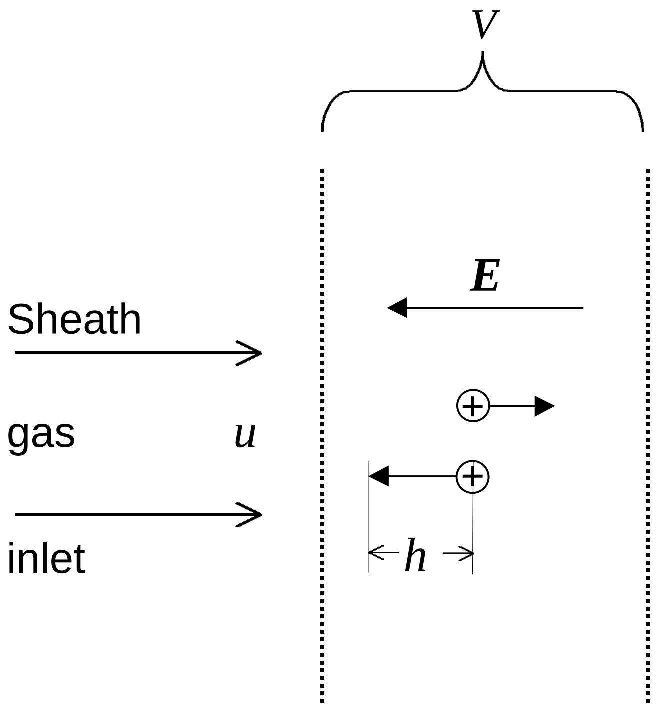
$$f = \sqrt{1 + \frac{l_\circ^2}{h^2}} \Bigg/ \left(\mathrm{Lo} + \frac{l_\circ}{h} \right).$$

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.

A remark. Loscertales expects that cylindrical design is preferred when compared with the plain design of an mobility analyzer, as a matter of course. It should be pointed out that this is not the generally accepted opinion, see e.g. *Hoegl* [1975]. Actually, the resolution of a cylindrical analyzer is lower than the resolution of a plain analyzer of the same length and the same distance between electrodes.

THE PARALLEL FLOW ANALYZER OF ZELENY

Actually, the resolution limit of δ_o was overpassed already in the oldest mobility analyzer of *Zeleny* [1898]. The parallel flow method of Zeleny has been forgotten as it has an essential shortcoming: it does not allow injection and extraction of ions by means of air flows as is required in most applications. The air is blown through two grids and the electric field forces the drift of ions against the air flow. The ions should be created inside the instrument between the grids. The ions of high mobility drift left in the Figure and those of low mobility drift right, being carried by air flow.



Calculation of the resolution:

Velocity $v = EZ - u$, drift along E during t: $h = EZt - ut$

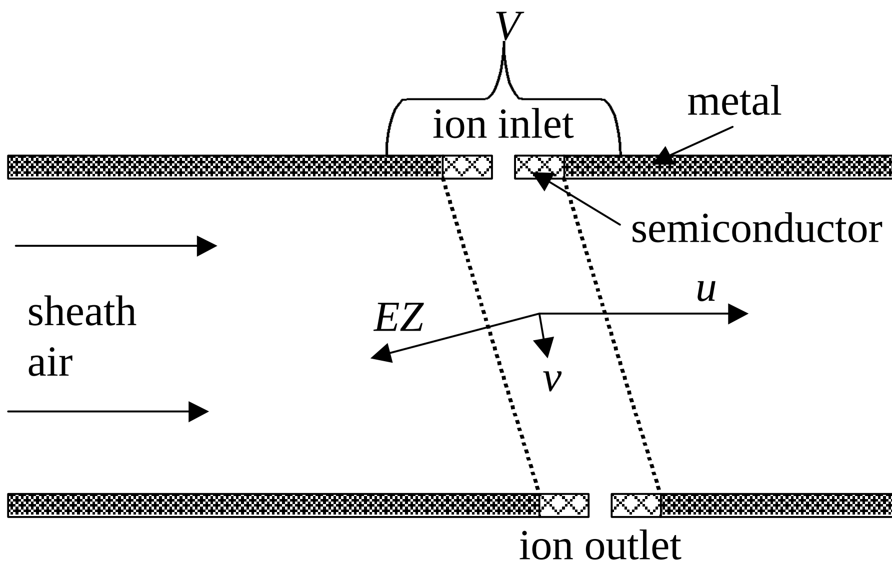
$$Z = \frac{h}{Et} + \frac{u}{E} \qquad \sigma_Z = \frac{\sigma_h}{Et} = \frac{1}{Et}\sqrt{2\frac{kTZ}{q}t}$$

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

$h + ut = h_{\mathrm{Lagrange}}$, $E(h + ut) = W =$ work of electrical force

$$\delta = \delta_\circ\sqrt{\frac{h}{h_{\mathrm{Lagrange}}}} = \sqrt{2\frac{kT}{W}} < \delta_o\,.$$

METHOD OF INCLINED GRIDS (A NEW PROPOSAL)



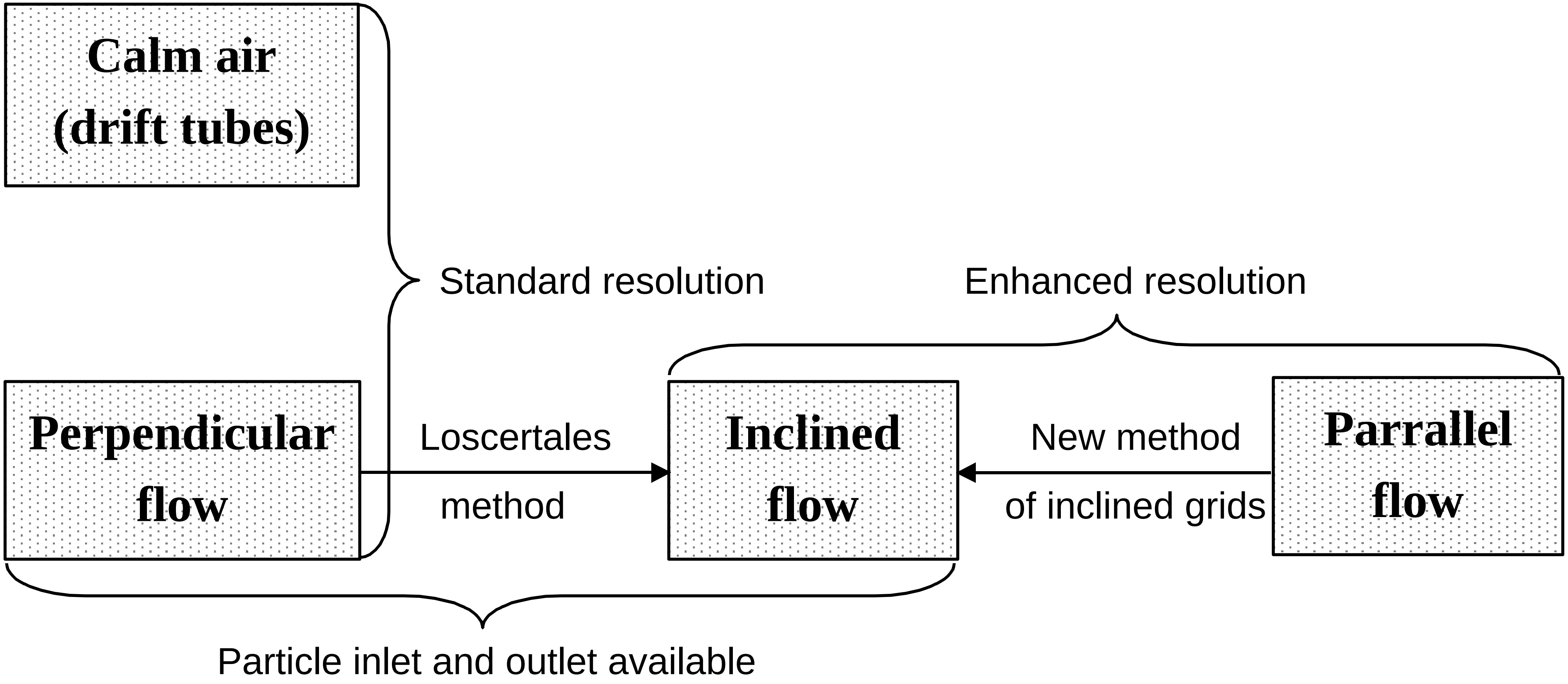
This is a modification of the Zeleny grid method. However, the configuration of fields is just the same as in a plain Loscertales analyzer.

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 left in Figure.

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 traditional DMAs. 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 the contrary, 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 the inclusion of additional grids into the air flow before the analyzer.

CLASSIFICATION OF THE METHODS



DISCUSSION AND CONCLUSIONS

An innovation by *Loscertales* [1998] forced a revision of the theory of the diffusion-limited mobility resolution. Traditionally, the limit of resolution $\delta = \sigma_Z / Z$ has been estimated according to the ratio of the thermal energy of the Brownian motion kT to the work of the electric field expressed as qV:

$$\delta = f \sqrt{2 \frac{kT}{qV}} \ .$$

Here q is the ion charge, V is the voltage between electrodes, and f is a nondimensional geometric factor that reaches the maximum value of 1 in drift tubes and the value of $\sqrt{2}$ in a plain aspiration analyzer of optimum length according to *Rosell-Llompart et al*. [1996].

The traditional theory of the diffusion-limited mobility resolution is correct for calm air analyzers (drift tubes) and for classic aspiration analyzers in which the electric field is expected to be transverse to the air flow. It fails in the case of Loscertales analyzer as well as the old parallel flow analyzer of Zeleny where the term qV does not express the actual work W of the electric field. If the air flow is not perpendicular to the electric field, then 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. Thus the formula of resolution should be written in a more universal form as

$$\delta = f \sqrt{2 \frac{kT}{W}} \ .$$

If the air flow is not perpendicular to the electric field, the work W depends on the Lagrangian length L of the passage of an ion through the air in the mobility separation zone. In a uniform field the work W can be expressed as $W = qEL$. The term qEL exceeds the term qV in longitudinal or inclined field analyzers, which promise further improvement of the mobility resolution when compared with traditional transverse field instruments. In an old and forgotten instrument of *Zeleny* [1898] the work of the electric field, $W = qE(h + ut)$, essentially exceeds the term $qV = qEh$. Unfortunately, the Zeleny grid method does not allow injection and extraction of ions by means of air flows which is required in most applications. The injection and extraction of ions is possible in the inclined field method proposed by *Loscertales* [1998] The instrument of Loscertales offers improved resolution when compared with classic instruments but it is difficult to manufacture.

The same theoretical advantages as in the Loscertales analyzer can be achieved in a simpler instrument with inclined grids suggested in the present paper. The latter instrument could be interpreted as a hybride of the Zeleny grid instrument and a classic DMA which inherits the favorable features from both predecessors.

Acknowledgements

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