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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Performance evaluation of a high-resolution parallel-plate differential mobility analyzer" *by* J. P. Santos et al.

J. P. Santos et al.

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Authors Reply to ACPD 8, S9441-S9445 (Anonymous Referee 1)

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C1. but none of the critical dimensions are stated. The length, height and width of the classification channel should all be stated.

It is noted that the dimensions of the working region of the DMA-X1 are given in page 17636 (lines 5-7):

The separation between the electrodes is 5 mm, the distance from the ion inlet slit to the ion outlet slit is also 5 mm and the width of the classification region is 10 mm.

C2. The basic characteristics of the so-called trumpet should also be provided, i.e., at

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a minimum the contraction ratio should be specified, and it should be stated whether the contraction was only in the height dimension or also in width. If both dimensions were varied, the contraction in each dimension should be specified.

The contraction ratio of the trumpet is specified in page 17636 (line 14). The text has been modified to account for the referee comment:

The contraction is only in the height dimension and the inlet to outlet area ratio of the trumpet is 8.

C3. While the authors totally neglect edge effects in their analysis (a reasonable first order approximation), the side walls of the channel do alter the flow so it is not strictly parallel as a simplistic 2-dimensional model would suggest.

C4. They need to describe how and the extent to which they ensured that the sample flow entering the classification region is uniform over the length of the sample entrance slot.

C5. The authors suggest that the width of the entrance and exit slots may be narrower than the channel. If that is the case, lateral diffusion may reduce the transmission efficiency just as diffusion in the migration direction reduces the resolution. The authors need to discuss how they deal with the lateral nonuniformities in their system.

C6. The authors achieve an impressive resolving power of about 40 at the highest voltages, but theory predicts a value of almost 90. The authors provide some suggestions for this result on p. 17646. Another possible explanation is edge effects, i.e., the flow is not the ideal two-dimensional flow that they model. The authors state that there has been no systematic study of the effect of slit width on resolution. That is not true. Eichler et al. (Aerosol Sci. Technol. 29: 1-49, 1998) and Chen et al. (J. Aerosol Sci. 30: 983-999, 1999) have both performed careful analyses and improved resolution of DMAs as a result.

A new section on nonidealities in the IONER X1 (2.4 Non-ideal behaviour) has been

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introduced (at the top of page 17644) in the new manuscript in reply to comments C3 to C6 of the referee:

Besides Brownian motion, other nonidealities may affect the DMA resolution. The theory on the ideal DMA assumes that the flow and the electric fields are fully uniform, unidirectional and perpendicular to each other along the entire length of the classification region. In this case, ion trajectories are properly described by the 2D model presented in section 2.1. However, the experience gained in cylindrical DMAs reveals that deviations from the ideal flow and electric fields in the classification zone can degrade severely the DMA performance. In particular, a lot of work has been dedicated to optimise the means (filters, meshes) to attain a laminar, unidirectional and uniform sheath flow as well as the design (inclination, width) of the ion inlet slit, which are major potential sources of loss of DMA resolution (Chen and Pui, 1997; Eichler et al., 1998; Chen et al., 1999). Nonidealities in planar DMAs have not been studied as extensively as for cylindrical DMAs. On that regard, a disadvantage of the DMAs of rectangular plates with respect to radial DMAs is the existence of lateral edges in the classification zone and in the ion inlet and outlet slits, which induce undesirable nonuniformities and 3D features in the flow and electric fields. Numerical and experimental studies have provided some insight into the edge effects in the IONER X1, although to date their impact on the performance of the instrument has not been fully assessed. On one side, the flow in the IONER X1 was simulated numerically by using a commercial CFD programme (FLUENT). The simulations show that, at the high Reynolds numbers of the flow in the classification zone (Re $>$ 2x10e4), the flow profile is quite flat expect in a thin region ($<$ 2 mm) over the surface of the channel side walls. In addition, the distribution of the ion sample flow over the length of the entrance slit was investigated experimentally. A pH indicator paper was fixed onto the electrode surface, immediately downstream of the inlet slit. A stream of nitrogen was passed through a bubbler containing a liquid sample of either clorhidric acid or ammonium and then introduced into the IONER X1 through the sample flow injector. In the classification zone the sample flow travels confined to a narrow region close to the electrode surface, so the vapour

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of clorhidric acid (HCl) or ammonia (NH3) diffuses to the surface of the indicator paper changing its colour accordingly. The spots on the paper provide a qualitative indication of the distribution of the sample flow over the slit. Experiments were performed at sheath flow rates in the range of 200 to 700 lmin-1, sample flow rates between 2 and 6 lmin-1 and slit widths of 50, 100 and 150 m. In all the cases the spots exhibited a rather uniform colour over the entire length of the ion inlet slit, except in the close vicinity of the edges. It is noticed that the width of the electrodes of the IONER X1 is 10 mm, while the length of the ion inlet and outlet slits carved on their surface is 6 mm. The lateral walls of the rectangular channel and the edges of the slits are then separated by a distance of 2 mm. This is a way to minimize the effect of the non-uniform three-dimensional flow and electric fields that develop near the corners between the side walls (Ertalyte insulating material, PTE) and the top and bottom walls (aluminium) of the flow channel on the trajectories of the ions. Finally, ion losses by diffusion (either lateral or in the direction of migration) to the walls play no role in the IONER X1. As the flow velocity is very high ($>$100 ms-1), the residence time of the ions in the classification region is less than 30 s, whereas the time it takes the ions to reach the walls is much longer, in the order of 1 s.

The following references have been added also:

Chen, D.R., and Pui, D.Y.H.: Numerical modeling of the performance of differential mobility analyzers for nanometer aerosol measurements, J. Aerosol Sci., 28, 985-1004, 1997. Eichler, T., de Juan, L., and Fernández de la Mora J.: Improvement of the resolution of TSI 3071 DMA via redesigned sheath air and aerosol inlets. Aerosol Sci. Technol., 29, 39-49, 1998.

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C7. The paper fails to cite a number of key references to similar instruments. The first parallel plate differential mobility classifier was produced by Erikson in 1918, and was applied to gas ion mobilty measurements, with those ions produced by a radioactive

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ionizer. More recently, Zhang and Wexler (International Journal of Mass Spectrometry 2006) described a modern, miniaturized version, albeit one with much lower resolution than the present instrument. Another parallel electrode analyzer that avoids the edge effects inherent in the present instrument is the radial differential mobility analyzer (Zhang et al., Aerosol Sci. Technol. 23: 357-372, 1995; and the SMEC, Fissan et al. Aerosol Sci. Technol. 24: 1013, 1996). The RDMA also avoids a number of the fabrication challenges of the CDMA that the authors describe in the introduction, although the previous instruments have not been designed to attain the resolving power of the present instrument. A paragraph has been added to the Introduction (following line 18 in page 17635) in the new manuscript to account for previous works on parallel-plate DMAs, as requested by the referee:

The first parallel-plate differential mobility classifier was produced by Erikson in 1918. This instrument was used to measure the mobility of gas ions produced by a radioactive source (Erikson, 1921) and the size of smoke and fog particles (Rohmann, 1923). More recently, Zhang and Wexler (2006) described a modern, miniaturized version of a multi-channel parallel-plate DMA suitable for analyzing gas phase compounds or volatile particle phase compounds. In these DMAs the electrodes were rectangular planar plates. Circular disks are used as electrodes in radial DMAs like the ones used for the sizing of ultrafine particles (RDMA, Zhang et al., 1995, Zhang and Flagan, 1996; SMEC, Fissan et al., 1996) or for classifying low mobility nanoparticles and ions (Nano-RDMA, Brunelli et al., 2009).

The following references have been added too:

Brunelli, N.A., Flagan, R.C., and Giapis, K.P.: Radial differential mobility analyzer for one nanometer particle classification, Aerosol Sci. Technol., 43, 53-39, 2009. Erikson, H.A.: The change of mobility of the positive ions in air with age, Phys. Rev. 18, 100-101, 1921. Fissan, H., Pocher, A., Neumann, S., Boulaud, D., and Pourprix, M.: Analytical and empirical transfer functions of a simplified spectrometre de mobilite electrique circulaire (SMEC) for nano particles - a theoretical study, J. Aerosol Sci., 29, 289-293,

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1998. Rohmann, H.: Methode für Messung der Grösse von Schwebeteilchen. Z. Phys. 17, 253-265, 1923. Zhang, S.-H., Akutsu, Y., Russell, L.M., Flagan, R.C., and Seinfeld, J.H.: Radial differential mobility analyzer, Aerosol Sci. Technol., 23, 357-372, 2005. Zhang, S.-H., and Flagan, R.C.: Resolution of the radial differential mobility analyzer for ultrafine particles, J. Aerosol Sci. 27, 1179-1200, 1996. Zhang, M., and Wexler, A.S.: Cross flow ion mobility spectrometry: Theory and initial prototype testing, Int. J. Mass Spectrom., 258, 13-20, 2006.

C8. In the introduction, the authors indicate that the DMA electrodes are held at constant potentials. The most common use of the DMA today is as a component of the scanning mobility particle sizer in which the voltages are continuously ramped. That might not be desirable for the present application in which the focus is on attaining very high resolving power, but might be worth mentioning to explain the reasons.

The term constant has been removed from the Introduction (page 17633, lines 7-8):

in which the ions migrate between two electrodes held at different potentials while been transported

C9. The introduction states that the resolving power of the early instruments was too low to measure mobilities of ions with similar mobilities. While this is true, the way it is stated makes it sound as though the instruments were inferior. In fact, no mobility analyzer can attain high resolution of ions or particles that are much smaller than those for which the instrument was designed, or with mobilities that are much higher than the design range. Moreover, the maximum attainable resolving power is determined by the flow rate ratio; the earlier instruments attained resolution near that for which they were designed, for the particles that they were designed to measure. Had the developers of the earlier instruments that are criticized attempted the high resolution that the present authors seek, counting statistics would have limited the value of the resulting measurements. The authors should state the limitations of the earlier measurements in an objective and unbiased way.

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The last statement in lines 17 and 18 of page 17635:

and, hence, the resolution of our proposed mobility analyzer is better that attainable with a conventional coaxial cylindrical DMA.

has been eliminated, and the text (from line 27 in page 17634 to line 18 in page 17635) has been rewritten, as follows:

All the above mentioned improvements were implemented in concentric cylindrical DMAs. With this geometry, electrode centering is critical to the performance of a DMA; even a very small misalignment of the electrodes can lead to a severe deterioration of the resolving power of the instrument. To avoid this difficulty, we have preferred to re-design the DMA using parallel-plate geometry, so that electrode centering is no longer an issue. An additional reason for choosing the parallel-plate geometry is related to the strong Brownian motion of nanoparticles and ions. In general, the Brownian motion makes the particles or ions to deviate from their otherwise deterministic trajectories given by the electric and gas flow velocity fields. As a consequence, the trajectories of particles of different mobilities get mixed up and the instrument resolution deteriorates. The extent of Brownian dispersion depends on the uniformity of the electric field and on the average direction of particle motion in the field (Alonso, 2002; Song and Dhaniyala, 2007). Thus, if particles move in the direction of increasing electric field strength, which is the usual case in cylindrical DMAs, the resolution worsens because the variance of the distribution of particle positions is larger than for a free particle, i.e. larger than 2Dt (D is the particle or ion diffusion coefficient, and t is its mean residence time between the inlet and outlet slits). If the electric field is uniform, as in the parallel-plate geometry, the variance is exactly 2Dt. Other issues like the mechanical machining and positioning of the electrodes are also important. They are both easier and more precise for DMAs of planar plates than for cylindrical DMAs, thereby reducing the cost of the instrument and enhancing its acceptance by potential users.

The arguments above are fully objective and justify by themselves the election of the

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parallel-plate geometry. It is noticed that the present paper is not intended to demonstrate the superior performance of planar DMAs over cylindrical DMAs. The IONER X1 is presented here just an alternative to cylindrical DMAs for classifying with high-resolution ions, which are referred to in the Introduction of the paper (lines 20-26 in page 17634). Some of these DMAs have shown better resolving power than the IONER X1 when classifying THA ions in experiments similar to the ones described in our paper (last paragraph of section 3). Nonetheless, some aspects must be kept in mind when comparing the experimental resolution values of the IONER X1 displayed in Fig. 5 either to the resolution values of cylindrical DMAs or to the theoretical values given by Eq. (29). Two paragraphs have been added to section 3 to explain these issues:

The reasons for the deviations between experimental and theoretical values of the relative FWHH observed in Fig.5 are presently not understood. They are attributed to nonideal behaviour of the flow and the electric fields in the classification zone of the IONER X1, potentially induced by the lateral walls, the edges of the ion slits, nonoptimal design of the ion sample injector and/or inlet slit, etc. Nonidealities in the IONER X1 have not been addressed in this work; they will be the subject of a future work. Relative FWHH values as low as 0.01 has been attained for THA ions with high-resolution cylindrical DMAs (Martínez-Lozano et al., 2005, 2006) in experiments similar to the ones previously described. Nonetheless, the IONER X1 and the cylindrical DMAs operated at different sheath and ion flow rates, thereby different flow rate ratios Qsh/Qa and classification voltages V, which renders difficult the comparison of the resolving power of cylindrical and planar DMAs. On this regard, the lowest value of the relative FWHH for monomer THA found with the IONER X1 is limited by the maximum voltage attainable (8 kV), above which electric sparks occurred in the experiments.

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C10. The authors should document the temperature rise in the recirculating sheath or otherwise comment on how they have prevented this bias.

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See the reply of the authors to comment C12.

C11. The performance evaluation needs to be rewritten to make clear what ions they are examining in each experiment. The resolution was inferred from measurements of electrosprayed THAB ions, but which THAB ions were studied, monomer, dimer, singly charged, etc.

The last paragraph of section 3 has been rewritten to clarify the issue raised by the referee:

Experiments were conducted to assess the resolution of IONER X1 too. A solution of tetraheptylammonium bromide (THABr) in ethanol (103 ppm w/v) was electrosprayed (Fenn et al., 1989), resulting in two ions of tetraheptylammonium (THA) of well-defined electrical mobilities (20 C, 1 atm): 0.96 cm2V-1s-1 (monomer) and 0.67 cm2V-1s-1 (dimer), both carrying a single positive charge (Gamero-Castaño and Fernández de la Mora, 2000). A stream of nitrogen was used to help nebulize the liquid and evaporate the neutral solvent in the droplets. The flow of nitrogen carrying the THA ions was then injected to the IONER X1. The ion flow rate Qa was maintained constant at 4 lmin-1, while the sheath flow rate Qsh was varied between 200 and 540 lmin-1; the corresponding classification voltage V ranged from 3.5 to 7.8 kV. The ion mobility peaks could be well fitted to Gaussians. The relative full width at half height (FWHH) of the mobility peaks corresponding to monomer THA (k = 0.96 cm2V-1s-1) is plotted as a function of the classification voltage in Fig.5; the theoretical values predicted by (30) are also shown for comparison. Several series of experiments were carried out in which the relative positions of the laminarizing screens were changed with respect to a standard configuration. The best resolution value of 0.025 was obtained at the maximum classification voltage (V = 7.8 kV), while the theory predicts a value of 0.011.

The correspondent references have been added:

Fenn, J.B., Mann, M., Meng, C.K., Wong, S.F., and Whitehouse C.M.: Electrospray ionization for mass spectrometry of large biomolecules, Science, 246, 64-71, 1989.

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Gamero-Castaño, M., and Fernández de la Mora, J.: Mechanisms of electrospray ionization of singly and multiply charged salt clusters, Anal. Chim. Acta, 406, 67-91, 2000.

C12. Unfortunately, unless the authors have ensured that their sheath recirculation system does not alter the temperature of the sheath gas and, thereby, its relative humidity, the measurements may be only a qualitative indication of what might be done with proper care. If the RH in the sheath is the same as that in the incoming sample, the authors should make comment on this important issue. If not, they should either remove this section or repeat the experiments with suitable controls. They should note that it is the water activity, or relative humidity, that will determine the extent of clustering, not the absolute humidity that they report.

The sheath gas temperature was kept constant (overall variations less than 0.5 C) in each set of experiments except one by using a simple cooler, due to the good heat transfer through the metallic walls of the sheath duct. In one of the experiments the rise of temperature of about 2 C involved a decrease in relative humidity of less than 9 percent. Modifications have been made in sections 2 and 4 of the paper to take account for these facts.

(line 22 in page 17637) As the DMA operates in closed loop the temperature of the sheath gas tends to increase with operating time. A fan was placed above the section between the pump and the flowmeter to cool the gas. This simple setup is enough to keep the gas temperature constant due to the good heat transfer through the metallic walls of the sheath loop

(after line 6 in page 17648) Sheath gas temperature changes are below 0.5 C in all experiments above except for the spectra of Fig. 6 where the temperature increased 1.8 C along the measurements which corresponds to a decrease of less than 9 per cent in relative humidity from the first spectrum to the last one.

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C13. p. 4, l. 1: trajectories ... mix up is poor wording

The text has been reworded:

the trajectories of particles of different mobilities get mixed up

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