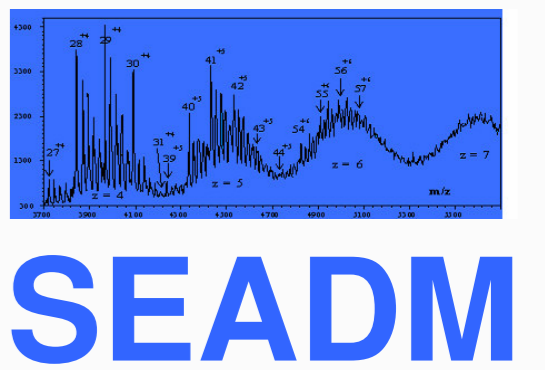


A high flow rate DMA with high transmission and resolution designed for new API instruments



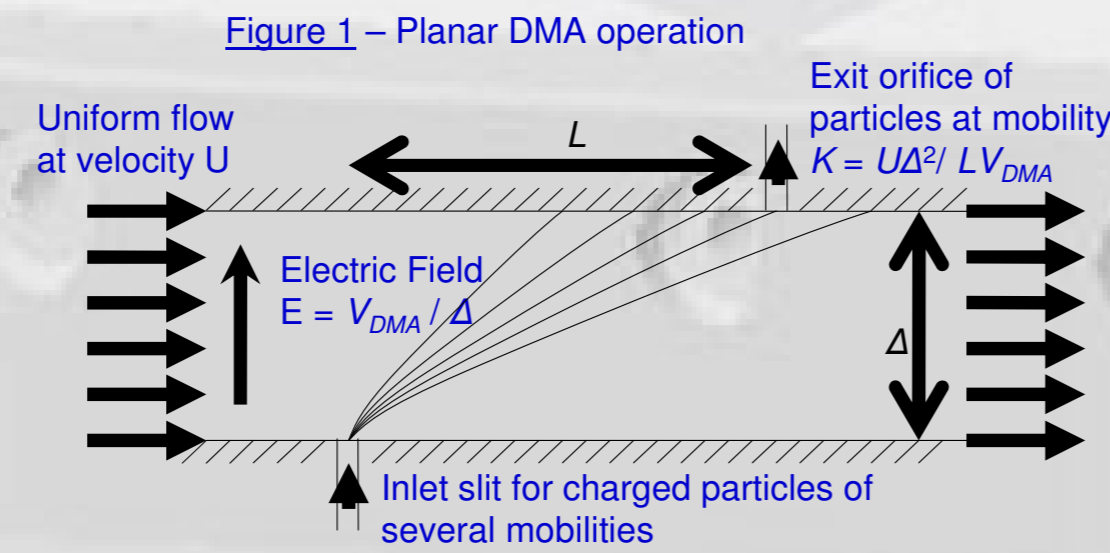
Juan Rus¹✉; David Moro^{1,2}; Juan A. Sillero¹; Jordi Freixa¹; Juan Fernández de la Mora²

¹SEADM, Boecillo, Spain ✉ juan.rus@seadm.com; ²Yale University, New Haven, CT

Overview

New generation planar DMAs ready to be coupled to different MS are tested for transmission and resolution. The main improvement with respect to previous SEADM DMAs is a higher flow rate sampled and delivered to the MS, achieved without significantly reducing resolution. DMA transmission is measured and the possible causes for inefficiency are discussed

Mobility separation in a planar DMA



- Separation of ions is based on electrical mobility (IMS)
- Mobility spectra are obtained by scanning over the voltage difference V_{DMA} between two parallel plates
- Planar design allows for delivery of mobility-selected ions with high transmission from the electro spray source to the DMA inlet, and from the DMA outlet to the MS
- Aerodynamic design is key to operate in high speed-high resolution conditions

Transmission measurements

- Relevant parameter for DMA-MS applications: signal transmitted to MS vs. maximum possible value, for a given ion concentration at the DMA inlet
- 100% transmission is understood as the ability to fill the DMA outlet flow to the MS with ions of a selected mobility at the same concentration as at the DMA inlet. Transmission is diminished by:
 - Dilution due to diffusion or space charge effects through the DMA
 - Outlet flow not being completely filled with ion streamlines
 - Electrophoretic losses at the outlet geometry

METHODS

Tandem DMA-DMA system for transmission measurement developed by P. McMurry (U. Minnesota), where the first DMA delivers a known ion density into the DMA tested:

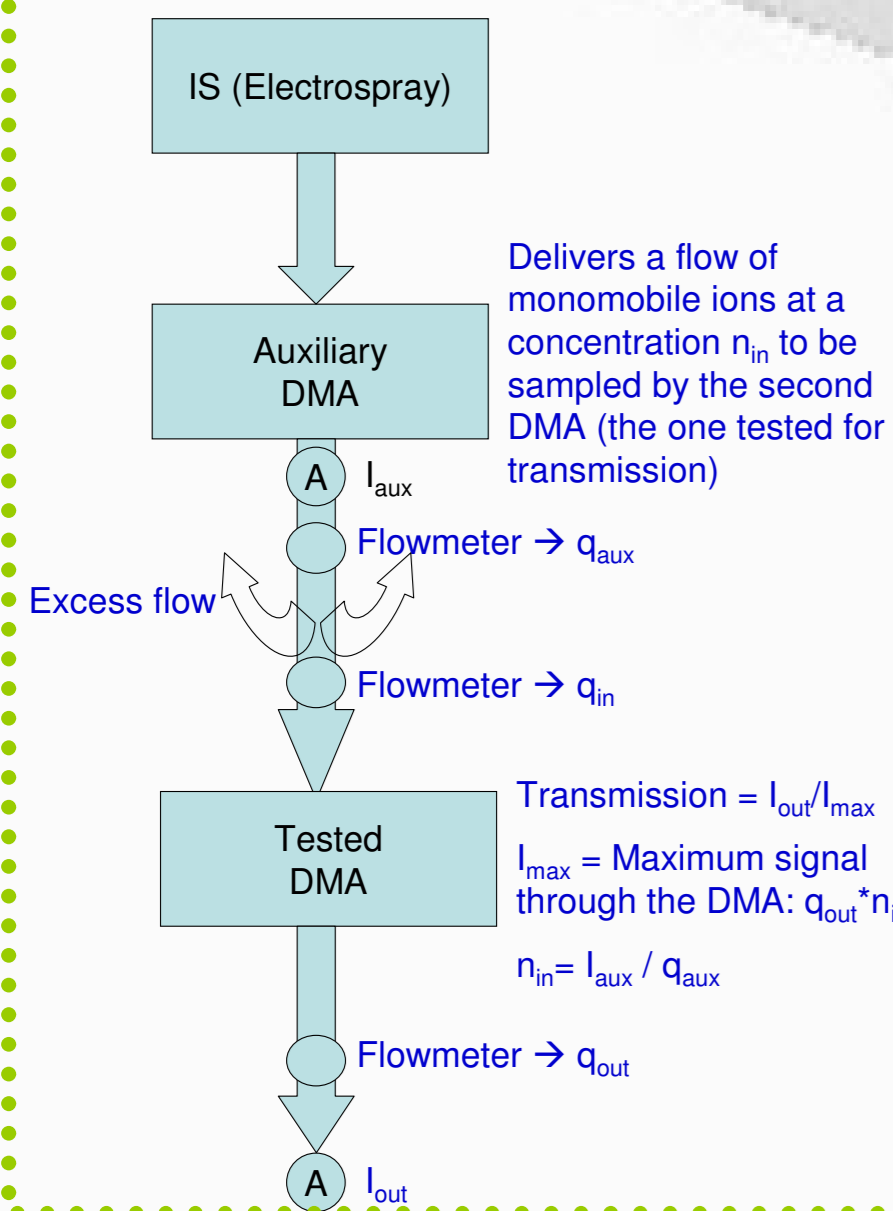
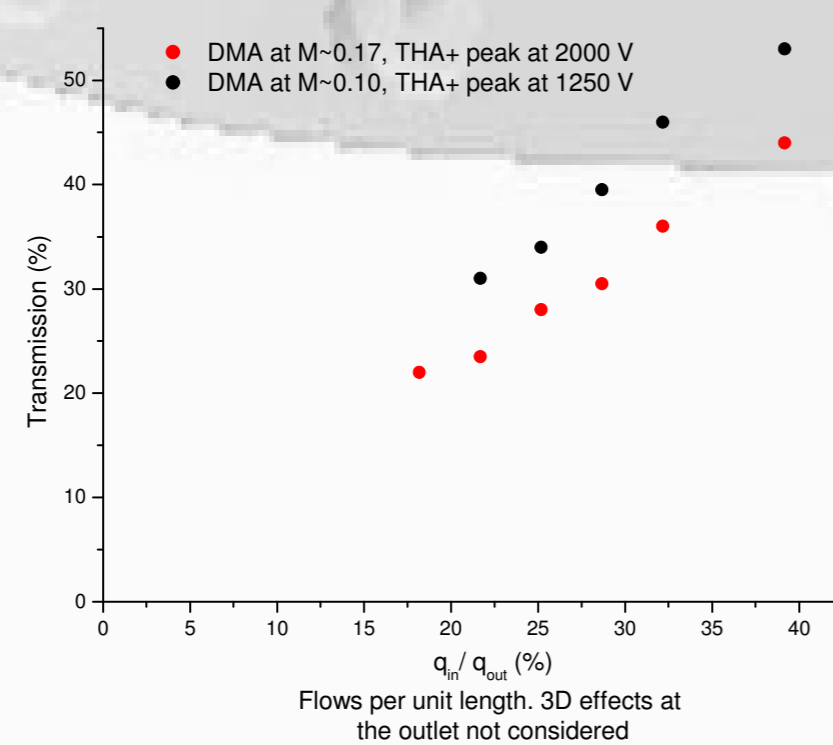


Figure 2 - Transmission tests for DMA model P4, which samples $q_{out} = 0.8$ lpm. Tested with THA+, at low DMA speeds (Mach ~ 0.15, DMA Resolution ~ 40)



- Linearity with inlet flow shows that virtually ALL the ions entering the DMA are passed to the MS
- Further characterization underway on improved electrostatic injection of ions and effect of counterflow drying gas

Introduction/Background

- SEADM's ion mobility separation system to be used in tandem IMS-MS analysis, based on a Differential Mobility Analyzer (DMA), was first presented in ASMS 07. It achieved flow Mach number $M=0.75$ and resolving power of 60-80 when sampling ~ 0.3 lpm into the MS. We noted that resolution and transmission are coupled in planar DMA designs, such that high resolution ensures high transmission. But DMA transmission was not previously measured.
- New developments in DMA-MS system have focused on delivering higher flow rates to the MS without significantly decreasing the DMA resolving power, and on achieving a good transmission of ions in this coupling.
- The DMA accepts ions from an ES source through an inlet orifice, separates them in space by combining an electric and a gas flow field between two parallel plates (Figure 1), and feeds mobility selected ions into the inlet of the MS with high transmission efficiency.
- While this analyzer was first designed for coupling with Sciex's QStar and API 3000 models (sampling 0.5 lpm), its planar design allows for high transmission coupling to other instruments. The DMA outlet has been enlarged with respect to previous prototypes to allow sampling of up to 2 lpm, approaching the target of 3 lpm required for high transmission coupling to more modern and sensitive API-MS instruments.
- Other DMA-MS developments are reported at ASMS-08 by Javaheri et al (poster 61 of this ion mobility session) and Fernández de la Mora at. (WOG am 09:50)

Conclusions

- High transmission measured (~100%) of ions ingested at DMA inlet for a DMA delivering 0.8 lpm sample flow into the MS. Signal limited to 50% of maximum possible due to limited ion injection at the inlet slit of the DMA
- High resolution (> 50) for mobility separation is maintained when delivering up to 2 lpm into the MS. Higher sampling rates through the DMA are possible still at high resolution with different DMA outlet-MS inlet designs
- Transmission needs to be further quantified for the positive effect of external electric fields to increase ion injection, and of drying counterflow gas

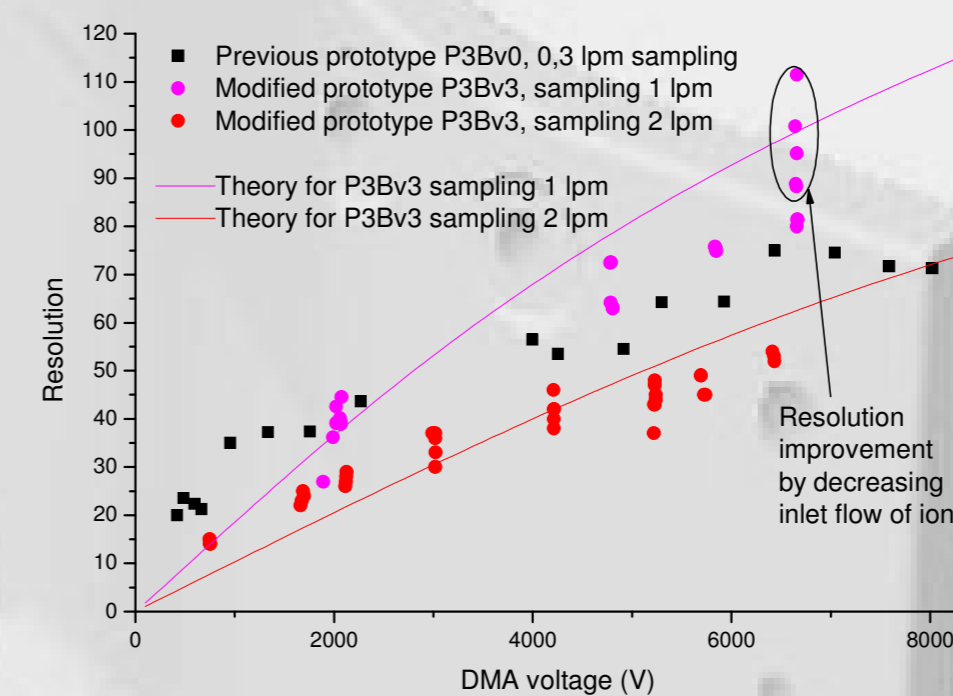
High sampled flow rates separation

METHODS

- New or modified DMAs with better outlet geometries (sampling up to 2 lpm) outperform prior DMA prototypes (sampling 0.3 lpm)
- One high flow rate DMA has been coupled to Shimadzu's LCMS2010EV single quad.

Except for the DMA-LCMS2010EV data (figure 4) the experiments have excluded mass analysis, relying on ion current measurement of the full free jet formed by the DMA outlet-MS inlet orifice. Tetra-alkyl ammonium ions are electrosprayed near the sampling orifice of the DMA and drawn by the field into the DMA inlet, against a stream of countercurrent air. Mobility spectra are obtained by fixing the sheath gas speed inside the DMA, and scanning over the voltage difference V_{DMA} between the two DMA plates. This yields current vs. V_{DMA} spectra exhibiting sharp peaks. The DMA performance is tested with the tetraheptylammonium bromide monomer, THA+, of $K_0 = 1.0$ cm²/Vs. In the experiments testing the effect of the sampled MS flow, this is regulated by a valve downstream of the outlet orifice. The flow rate is derived from pressure measurements on both sides of the orifice and a previous calibration.

Figure 3 - Sampling ability improvement on DMA prototype P3B Resolution for tetraheptylammonium ion (THA+) at different DMA speeds (different DMA voltages for THA+)



DMA prototype modified for coupling to Shimadzu's 1 lpm sampling single quad

Figure 4 - DMA-LCMS2010EV combination Mobility spectrum of two species separated 1 Da Resolution ~ 40 for both peaks

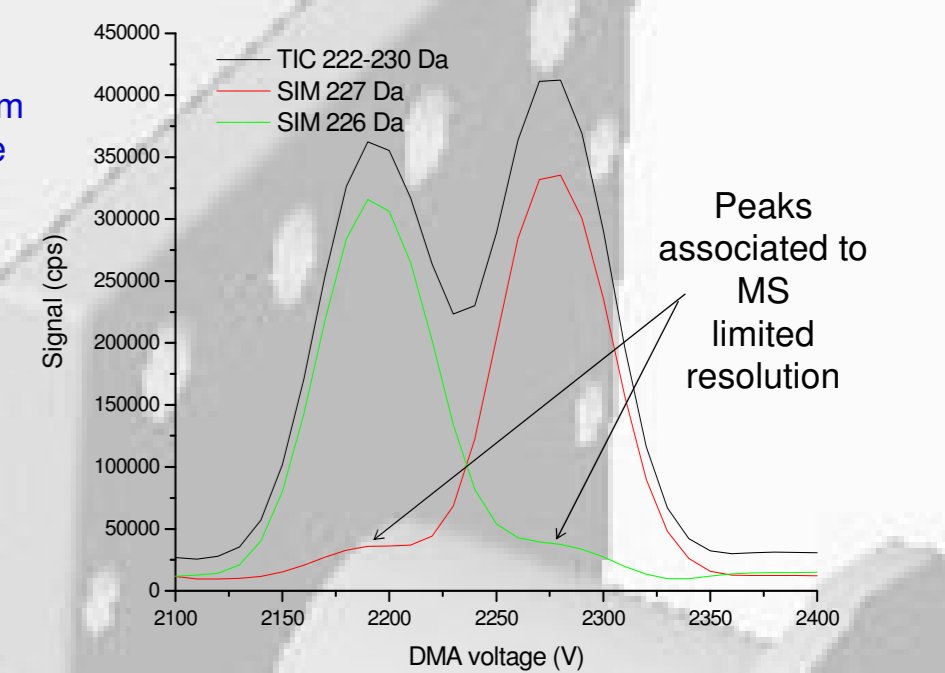


Figure 5 - DMA P3Bv3 (optimized for LCMS2010EV 1 lpm sampling), effect of sampled flow when DMA is run at relatively low speeds (M~0.2).

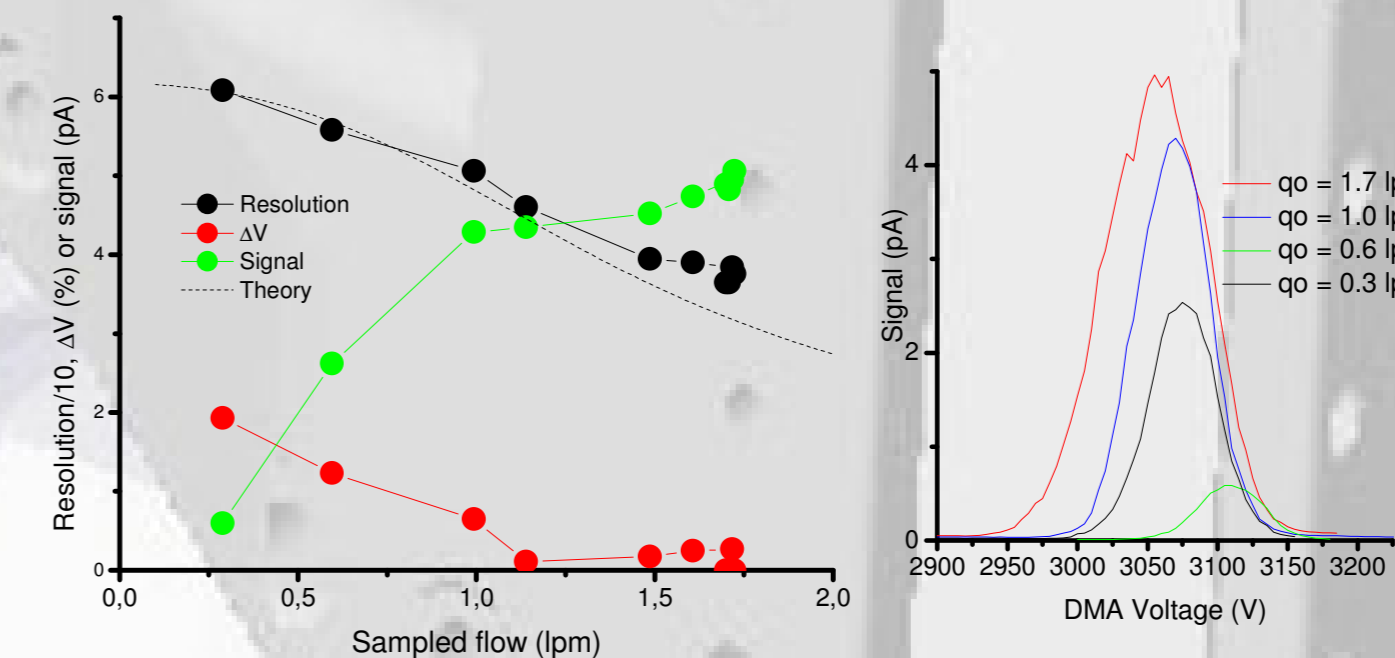


Figure 5a - Effect of sampled flow on total transmitted THA+ signal, peak resolution and THA+ classification voltage (ΔV , deviation from the 3055 V at which THA+ signal is maximum at maximum sampling rate).

Figure 5b - THA+ Peak shape shift with sampled flow

- The theoretical model seems well suited to predict the DMAs behavior at different sampled flows (Figure 5) and at different DMA speeds (Figure 3)
- Higher sampling rates up to 5 lpm are achievable at high resolution, with DMAs specifically designed for the purpose
- Signal plateau between 1-2 lpm sampling indicates nearly 100% collection of the ions entering the DMA by the outlet flow, therefore:
 - Dilution due to diffusion and space charge is negligible (at least at this slow-speed regime, where the sampled flow effect is dominant)
 - Measurement of electrophoretic losses at the outlet is still pending. But the small dependence of transmission on the fluid velocities in the outlet orifice (signal drops 15% when they drop 40%) suggests this to be a small effect.