**Supplementary information section**

**Instant Acquisition of High Resolution Mobility Spectra in a Differential Mobility Analyzer with 100 Independent Ion Collectors: Instrument calibration**

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**Diffusive broadening in slowly converging DMAs.**

We consider a simple model problem where the velocity field is only in the *x* direction, and depends only on the *x* coordinate. The description is realistic only in the vicinity of the plane of symmetry half way between the two side insulating walls. The particle concentration *N* obeys

 *U(x)∂N(x,y)/∂x+ZE∂N(x,y)/∂y=D∇2N* (S1)

with initial condition

 *y=0, N=(x)*, (S2)

where *D* is the particle diffusivity, taken to be relatively small compared to *U*. The electric field *E* is assumed to be uniform. We are interested in determining the axial dependence of the particle concentration *N(x)* at the collector electrode, where *y=*. Ignoring diffusion, the resulting first order partial differential equation may be solved by the method of characteristics, with the following characteristic equations:

 *dx/U(x)=dy/(ZE); dN=0.* (S3)

Using mass conservation for an incompressible fluid

 *Q=U(x)A(x),* (S4)

the characteristic trajectories may be integrated into

 *y - ZEv(x)/Q* = constant, with *v(x)=* (S5)

 *N = constant* (S6)

The solution is the original delta function evolving along the trajectory (20) going through the inlet slit, where *y=x*=0:

 *N~[y-ZEv(x)/Q].* (S7)

Because this *N* is constant along trajectories but decays infinitely fast normally to the trajectories, it is clear that diffusive effects will be important normally to the trajectories and irrelevant along them, suggesting the use of the following independent variables:

 *= y-ZEv(x)/Q* (S8)

 *y’=y.* (S9)

Noting that *Nx=-NZEA(x)/Q; Ny=Ny’+N; Nyy=Ny’y’+2Ny’ + N; Nxx=N[ZEA(x)/Q]2-NZEA/Q*, we may rewrite (S1) as

 *ZEny=DN[1+(ZEA/Q)2]* (S10)

where the prime in *y’* has been removed for terminological convenience, and among the diffusive terms we have neglected first order derivatives compared to second derivatives in **. The simplification is based on the fact that *∂/∂* corresponds to large changes orthogonally to the particle trajectory, whence *∂/∂ ∂2/∂2*. These are standard assumptions in the method of subcharacteristic solution of this class of problems (Cole, 1968). We now note that the term *A(x)* in the right hand side must be expressed in terms of the new independent variables *y* and **. However, **=0 in the vicinity of the particle trajectory, so, from (S8), *x* and *y* are simply related via *ZEv(x)Q=y,* and the coefficient *[1+(ZEA/Q)2]* can be treated as a function of only *y*. This *y* dependence may hence be absorbed into the new time-like independent variable *t* via

 *dt=dy[1+(ZEA/Q)2].* (S11)

It is more convenient to revert to *x* instead of *y* to integrate (S11), again taking **=0, leading to

 *dt=dx (x)[1+2]*, with *(x)= ZEA(x)/Q* (S12a)

The integration is straightforward for a constant area channel, as well as for a channel like ours with an area varying linearly with *x*. In that second case *d=ZEA’(x)/Q=-2dxtan/Q* resulting in

 *dt=-d [1+2] Q/(2tan)*.(S12b)

(S12b) integrates into

 *t(x)=* *(oo(x)(x) Q/(2tan)*, (S13)

where *o=(0).* The problem in terms of *t* becomes the standard diffusion equation *ZENt= DN*, with the following general solution to our initial value formulation:

 (S14)

The quantity of interest is the ion concentration at the collector electrode, where *y=*, and

 (S15)

All the functions involved have been explicitly obtained, so the ion concentration is completely known as a function of *x*. *x* is the same thing as the main position variable *L*.

We have compared the observed and predicted distributions for the hexamer ion at *V*=1.5 kV, *Q/Qo*=0.634 and found that the predicted peak shape is quite symmetric. The observed fairly asymmetric right tail is accordingly not the result of channel convergence, but of a flow non-ideality.

**References**

Cole. J. D. (1968) Perturbation Methods in Applied Mathematics. Blaisdell, New York.