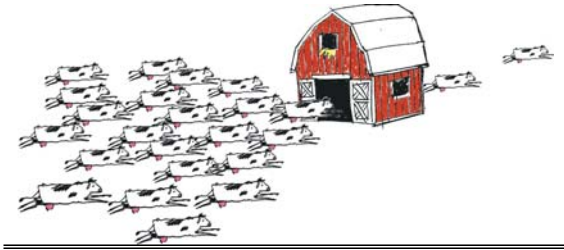

How Do We Eliminate Ion Losses at AP?

Keeping the Barn Doors Open

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Where do ion losses occur?

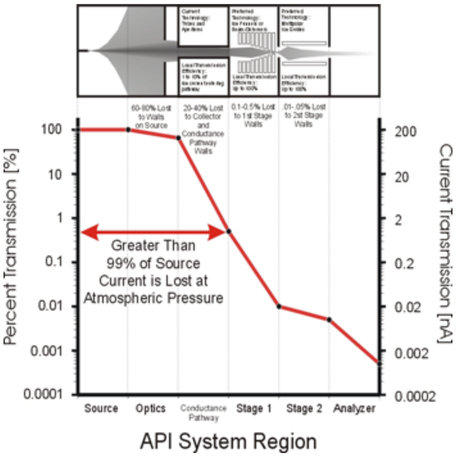

Figure 1- Transmission losses of source current and ions from atmospheric pressure ionization sources into vacuum analyzers and detectors.

☑ **Source Losses-** To truly address the significant ion losses that occur from sources at atmospheric pressure, we must evaluate where and how ions are lost. Figure 1 shows the relative loss of ions in each region of the analytical chain from AP to high vacuum. The inherent dispersive nature of sprays and field-dispersion from electro-hydrodynamic sources makes sampling ions through a typical conductance-opening diameter of several hundreds of microns problematic. Even highly directed sprays from precision made nebulizers will produce spray cross-sections of over a centimeter in diameter. Losses in the spray or source region are in the 60% to 99% range and depend largely on the position, shapes, flows and electric fields that occur in the source/optics regions.

Another 10% to 30% of ion current is lost in the conductance region, primarily due to "rim losses." Conductance losses will depend on the geometry, dimensions, and relative fields of the conductance pathway into vacuum.

In summary, well over 99% of ions from conventional AP sources are lost before they reach the vacuum. Precision molecular beam skimmers, ion funnels (1), and ion guides (2) operating at reduced pressure are valuable technologies, but "the cows have already left the barn" by the time the ions reach the vacuum. The only way to significantly enhance transmission efficiency and sensitivity from AP sources is to address and reduce source and conductance losses.

This particular article will concentrate on losses associated with the conductance region or pressure restriction into vacuum. Typically, single-axis tubes or pinhole apertures accomplish the pressure reduction process. These devices are also generally operated at lower electric fields than adjacent optics regions. This condition does not favor efficient transmission and exacerbates losses to the rim of their respective openings.

☑ **Rim Losses-** Figures 2 are simulations showing trajectories as ions move from a higher field focusing region into a relatively field-free tube. These simulations take into account both ion mobility in local fields and gas flow directed down the tube. These results illustrate that most conductance losses occur in the "rim" region of a conductance-limiting tube. These results also dispel the myth that ions are entrained in the viscous flow from gases, irrespective of electric field. Only ions originating from the axis region of the tube are capable of overcoming field dispersion. We denote the diameter of the sampled ions entering the tube as the effective aperture [a_{eff}]. Comparing Figs 2a and 2b we observe that the effective aperture decreases with increase of upstream field at the tube entrance. This observation has significant ramifications for focusing at atmospheric pressure. The higher the focusing fields at AP, the smaller the effective aperture. Focusing benefits are offset by decrease in effective aperture at higher fields.

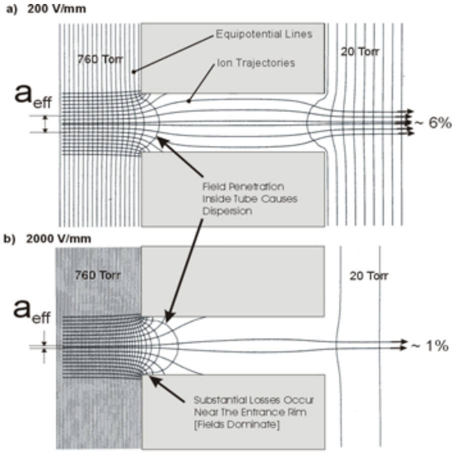

Figure 2- Mechanism of transmission losses of source current and ions from atmospheric pressure ionization sources by rim loss and dispersion into low-field conductance pathways.

How do we eliminate rim losses?

☑ **Laminated Tubes-** The solution to rim losses is to more fully control the electric field along the conductance pathway. One alternative is shown in Figure 3, known as laminated tubes (3). Laminating the conductance path with successive layers of conductor and dielectric (or insulator) will allow us to apply a voltage to each layer to generate a desirable electric field throughout the entire conductance pathway.

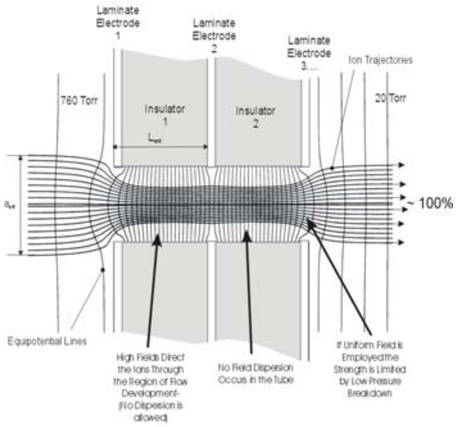

Figure 3- Laminated conductance tube that concentrates ions along the center axis of the conductance path. The effective aperture is much larger than the diameter of the tube. This configuration operates with a uniform field throughout the flow path.

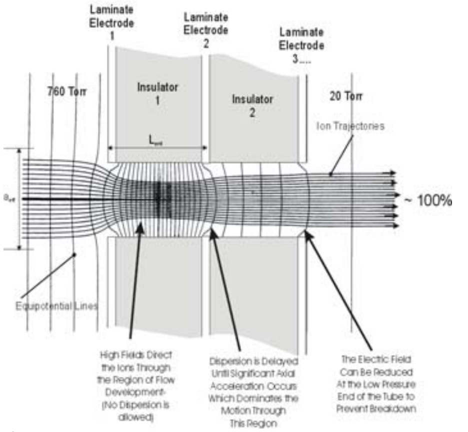

Figure 4. Laminated conductance tube that concentrates ions along the center axis of the conductance path. This configuration operates with a diminishing electric field as the ions proceed down the tube to reduce the field at the low-pressure end of the tube, and prevent discharge and back losses.

$5.00 US

The ion trajectories illustrated in Fig 3 show no rim losses and ions being concentrated along the axis of the conductance tube. Both field and flow vectors are oriented in the favorable direction away from the walls.

We have constructed a wide variety of laminated tubes (so far up to ten electrode layers) to evaluate transmission from high-field source and optics regions to low-field vacuum stages. We have been able to apply up to 3000 volts across a given laminate without discharge. We have transmitted currents over 300 nAmps into vacuum with no significant current being lost along the pathway. We can tune and step down the voltage along the path to vacuum to prevent breakdown at lower pressures (Fig 4).

Ion Selective Apertur

☑ **Why use aperture arrays** tubes eliminate rim losses very however, the ideal transmissio of an ion conductance device fr atmospheric pressure into vacu have the following characteristi

- Low throughput or gas load
- Low applied voltage
- Near ground potential
- Independence of flow & ion t
- No ion transmission losses

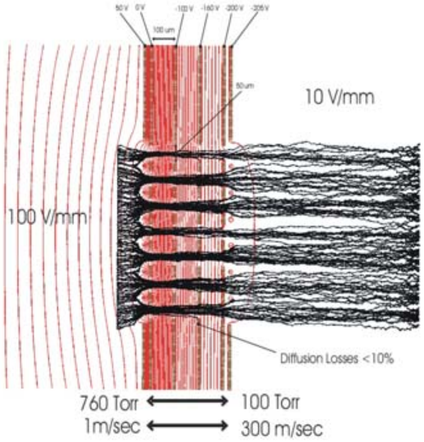

Figure 5- Simulation of ion trajectories for an Ion Selective Aperture Array (ISAA) showing the motion of ions under the influence of electric field and flow from atmospheric pressure into vacuum.

Single axis laminated at ca. 500 um diameter required thousands of volts to be applied in order to produce the electric fields required to focus and transmit ions along the axis. In addition, large diameter laminated tubes introduced "many" liters per minute of gas into vacuum with associated pumping costs and complexity. "Arrays" of laminated tubes are a viable alternative to single laminated tubes to address some of these limitations.

Figures 5 and 6 are simulations of parallel arrays of laminated tubes that have similar operating principals compared to single-axis tubes, but have unique advantages in that they allow us to reduce both gas load and applied voltage for a given amount of transmitted ion current (4,5). Gas through-put for a given sampling cross-section can be reduced by factors of 100 with laminated aperture arrays. Figure 6 is a potential surface showing how ions from a focusing region at AP are focused and swept through the conductance path into low field vacuum regions without significant losses.

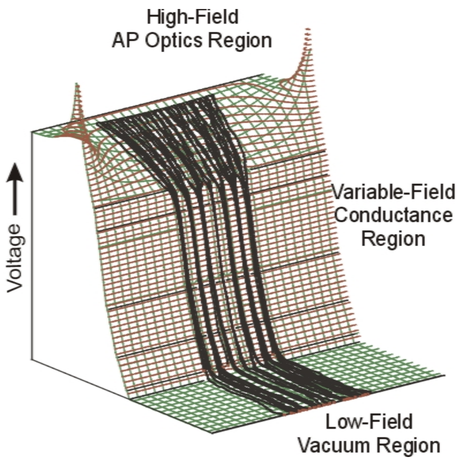

Figure 6- Potential surface of ion trajectories for an Ion Selective Aperture Array (ISAA) showing the motion of ions under the influence of electric field and flow from atmospheric pressure into vacuum. Ions flow down the potential surface like water over a waterfall. In high field, field dominates; in l field, flow dominates.

☑ **Ideal Dispersion Conditions-** One important consideration in sampling ions from relatively high fields from AP focusing regions is the requirement of matching the force vectors from both flow and field components of motion. Below we have the classic model of parabolic flow developmen in a cylindrical tube. The important point t be made when evaluating ion motion is the relative magnitude of flow and mobility components as ions move past each point along a tube. If we attempt to reduce the field as we traverse the tube, it is more favorable for ion transmission to allow dispersion downstream when fully develope flow has occurred. At this point, field dispersion can be minimized and flow dominated ion motion maximized.

A problem exists for larger diameter single-axis laminated tubes with delaying the field dispersion until fully developed flow has occurred because the distance can be significant (e.g. See Fig. 8: L(ent) is greater than 10 cm for 500 um diameter tubes). If we were required to maintain a 100V/mm field over 10 cm we would then require 10,000 volts along the tube. In contract, if we use a 100 um tube, the L(ent) is in the 100 um range. Under these conditions, a 100 V/mm field would require only 10 volts over the distance of L(ent). Having arrays of smaller diameter tubes allows us to optimized flow and field conditions with both lower throughput into vacuum and lower applied voltage.

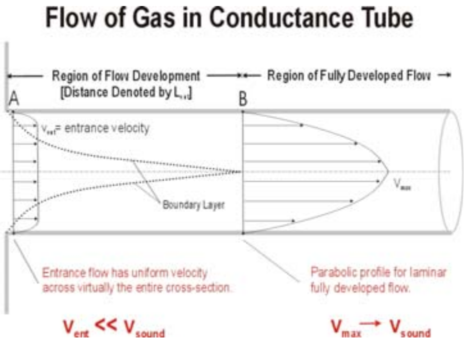

Figure 7- Diagram of the flow development in the entrance of a cylindrical tube showing planar entrance velocity profile and parabolic profile after accelerating to fully developed flow.

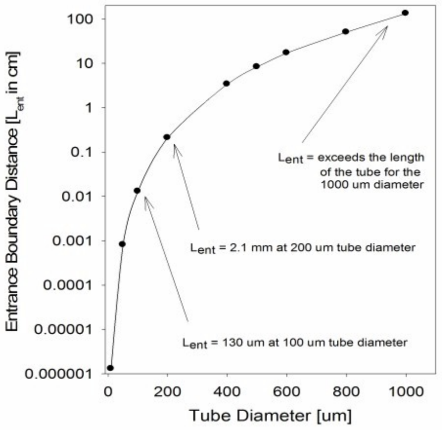

Figure 8- Plot of the distance to fully developed flow as a function of tube diameter. Note the significantly shorter distance at smaller diameter tubes.

Benefits of Aperture Arrays

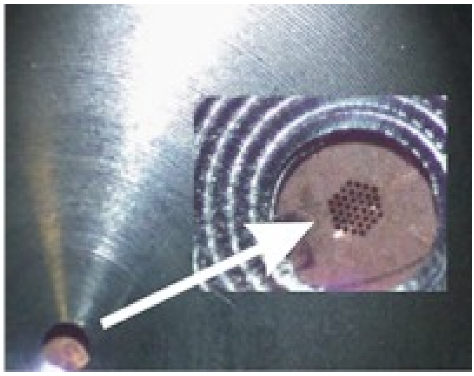

Figure 9- Photomicrograph of an ISAA assembly mounted on an electrospray inlet to a quadrupole mass spectrometer. This laminated array was fabricated with maskless photolithography using copper electrode material and liquid crystal polymer (LCP) as the insulating material.

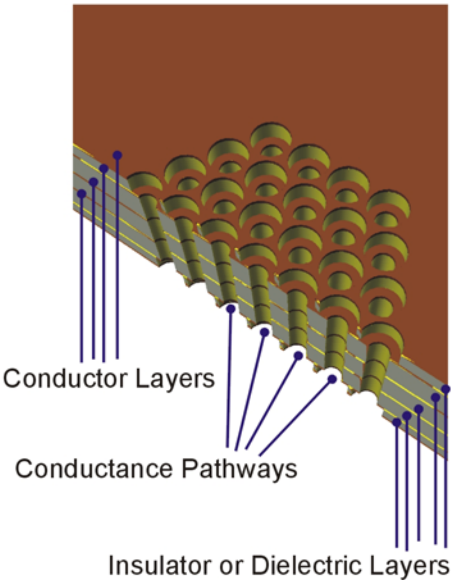

Figure 10- Cutaway image of an ISAA showing conductor layers, insulator layers, and conductance pathways. The particular design comprises inlet-tuning optics for more efficient collection of ions approaching the array front face and exit tuning optics for minimizing losses at the exit of the array where a molecular beam transports most of the ions into vacuum.

☑ **Control of Electric Field-** Ion Selective Aperture Arrays (ISAA) incorporate laminated tube technology into parallel and individually applied voltage to enable local and micro-dimensioned control of the electric field throughout the entire conductance pathway. Higher electric field optical regions can be sampled and higher current can be transmitted.

☑ **Control of Gas Load-** We are able to control flow into the vacuum region by using an array of tube limited flow pathways that have orders of magnitude less throughput than conventional tubes or pinhole apertures. More current, less gas.

☑ **Flow Independence-** Because we can sample large cross-sections of focused ion current onto a relatively low conductance tube array, we can effectively decouple gas throughput from ion transmission.

☑ **Minimized Voltage-** Miniaturization and micro-fabrication of critical features of aperture arrays have a significant advantage that we can gain precise control of the electric field, even to extremely high field strength, while only apply relatively low voltages. We envision that the laminates can be constructed with self-contained voltage dividers and simple (single-contact) connectors.

☑ **Matched Optics-** We are not limited to the traditional circular conductance pathway opening of tubes and pinholes. Rather, we are able to pattern our arrays to match any profile of ions emanating from source optics in constant or time-varying manner. Figure 11 shows an annular conductance opening that can be match to annular optics stacks.

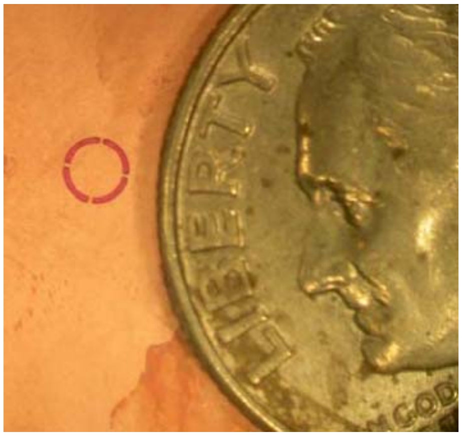

Figure 11- Photograph of an annular conductance opening fabricated using maskless photolithographic techniques to illustrate the ability to generate non-circular conductance openings that can be matched to source optics ion profiles.

☑ **Summary-** Aperture arrays offer significant advantages over field-free conductance paths for introduction of ions from atmospheric pressure into vacuum by eliminating rim losses and allowing close coupling with high compression [and high-field] optics. We are currently in the process of determining effective and affordable methods to micro-fabricate these devices. Standard and custom arrays and assemblies are available from Chem-Space Associates.

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