Taylor Cone Stability and ESI Performance for LC-MS at Low Flow Rates

Mike S. Lee¹, James P. Murphy III² and Gary A. Valaskovic²

¹Milestone Development Services, Newtown, PA 18940;
²New Objective Inc, Woburn, MA 01801-1023

With the advent of microspray and nanospray methods, there has been a return to “pure” electrospray methodology, in which no sheath gas or additional nebulization is utilized. It has been well established (1,2) that the liquid, and subsequent spray exiting the nozzle, may take on a wide variety of physical forms, or spray modes. Jaworek and Krupa (2) identified ten distinct spray modes, each with definable time-dependant morphological characteristics. The specific spray mode obtained depends strongly upon the geometry of the nozzle, the strength and shape of the electric field, and the mobile phase chemical composition. Specific spray modes yield different distributions of droplet sizes and charge-to-mass ratios (3). At low flow rates, the smaller, monodisperse droplets having a high charge-to-mass ratio, appear to offer analytical benefits including improved ionization efficiency (4,5) and a reduction in ion suppression (6). The most effective mode for producing such droplets is the cone-jet mode in which a stable, non-pulsating Taylor cone is observed (3).

We present here a system for the characterization of the different spray modes. For a mobile phase of fixed composition, flow rate and applied voltage are typically adjusted until a stable cone-jet mode is observed. For gradient elution chromatography however, the situation is complicated by continuously varying mobile phase composition. As a result, conditions for a stable cone-jet change during the run. Given the propensity of spray modes to pulsing phenomena (7,8), we have constructed an apparatus of high bandwidth (> 2 MHz) to characterize the pulsing electrospray modes. This has been combined with a phase variable strobe imaging system (1 µS pulse) for a non-ambiguous spray mode assignment.

A bench-top spray apparatus was constructed on an optical bread-board. A fused-silica electrospray PicoTip™ of either 10, 15, or 30 µm ID (New Objective, Inc.) was mounted on an X,Y,Z positioning stage. A CCD camera based microscope of 200x total magnification (PicoView, New Objective, Inc.) was mounted with its optic-axis perpendicular to the tip. The output of the CCD camera was connected to a PC with a frame grabber, running LabView 6.0 (National Instruments) for image acquisition. A 5 kV power supply (Stanford Research Systems Inc.) was controlled by the PC via GPIB interface bus. Reflected-scattered light illumination (150 W) was provided by a fiber optic bundle. Tightly focused light (< 5 µm beam waist) from a 10 mW diode laser (670 nm) was delivered orthogonally to the tip and spray plume in the cone-jet region. A PIN photo-diode with current amplifier (Thorlabs, Inc.) was positioned opposite the laser to detect interruptions in the beam caused by the liquid exiting the tip. The output of the photo-diode was delivered to a 100 MHz digital oscilloscope (Tektronix, Inc.) to determine the pulse frequency of the spray mode. For the acquisition of synchronous strobe images, free of blur, the photo-diode signal was fed to a home-built circuit to detect incoming pulses and control the phase and pulse width of a high intensity green LED positioned directly below the microscope. Typical pulse width (strobe time) of the LED was 1 µS. Mobile phase was delivered from a capillary HPLC (Agilent) with an additional flow splitter.

A 15 µm, coated, PicoTip™ was positioned 4mm in front of the counter-electrode. 50% Methanol, 1% Acetic Acid was delivered for a through-tip flow rate of 250 nL/min. Five distinct modes were observed, and pulsing frequencies were observed for all but the stable cone-jet mode. Pulsation/oscillation frequencies above 100 kHz were observed, two orders of magnitude higher than reported elsewhere (7,8). The results of the modes for various applied voltages is shown in figure 1. Figure 2 shows the pulsation frequency vs applied voltage for this tip, mobile phase, and flow rate.

The impact of these differing modes on ESI-MS issues such as charge state distribution, sensitivity, and ion suppression will be explored in further experiments. The use of both the imaging data and frequency data appear to be promising tools for the implementation of a “self tuning” electrospray system.
<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Mode</th>
<th>Oscilloscope Trace showing 102 kHz Pulse of Cone-Jet</th>
</tr>
</thead>
<tbody>
<tr>
<td>820</td>
<td>Dripping Mode</td>
<td>t=0, t=14 µs, t=33 µs</td>
</tr>
<tr>
<td>900</td>
<td>Spindle Mode</td>
<td>t=0, t= 5 µs, t= 20 µs</td>
</tr>
<tr>
<td>1300</td>
<td>Pulsed Cone-Jet</td>
<td>t=0, t= 2 µs</td>
</tr>
<tr>
<td>1500</td>
<td>Cone-Jet</td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>Multi-Jet</td>
<td></td>
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**Figure 1** Mode relationship for 15 µm ID Tip at 250 nL/min, 50% MeOH

**Figure 2** Frequency vs. Applied Voltage for the Above Tip

**References:**