

The Design and Performance of Polypropylene-based Nanospray Nozzle Chips

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Nanospray arrays can potentially dramatically increase the accuracy, efficiency and speed of high throughput screening operations when compared to existing electrospray technology. Arrays of three-dimensional plastic nanospray nozzles with micron-sized features have been successfully fabricated by microinjection molding. The insulating material for the nozzle body, and the relatively large dimensions of the nozzle are features not commonly found in traditional nanospray sources. The design, operation and performance of the new plastic nanospray nozzle array are presented.

The advantages of coating glass or silica nanospray sources with inert polymer layers or using plastic nanospray sources have been noted and individually tapered carbon-doped conducting polypropylene pipette tips have been successfully used as nanospray sources [1]. The process of tapering the conducting polypropylene tips is cumbersome and unreliable. Microinjection molding, however, is a low-cost way to produce plastic parts with small features uniformly. We have for the first time successfully micromolded plastic nozzles with features as small as 15 μm . Unlike the almost two-dimensional nature of nanospray chips fabricated from silicon, the three-dimensional molded plastic nozzles contain microscale as well as large features that enable the nozzle to be easily interfaced with essentially zero dead-volume with external sample input mechanisms such as capillaries from syringe pumps or liquid chromatography equipment, pipette tips from robotic liquid dispensing equipment, and eventually microfluidic devices designed to couple with mass spectrometry.

Each nozzle chip used in this study contains four nozzles with the spacing of the sample wells in a 384 microtiter-plate. Polypropylene is chosen as the base material because of its chemical purity and inertness, which minimizes undesired adsorption of analytes on its surface. The nozzles' inside diameters were 23 \pm 3 μm . The outside diameters of the nozzles range between 50 and 150 microns. Dependent on the placement of the counter electrode, which varied from 0.5 mm to 1 cm from the nozzle opening, the voltage used for a full spray plume ranged from under 2 KV to about 4 KV for a 50/50 methanol/water solution. The onset voltage is, however, relatively independent of the outside diameter of the nozzle. The voltage was applied to the sample liquid behind the nozzle since the nozzle itself is insulating. The mass spectra were taken with a triple quad mass spectrometer (Micromass Quattro) with the cone gas turned off. The voltage applied to the sample for spraying through the nanospray chip was supplied and controlled directly by the data system of the mass spectrometer.

The performance of these nozzles as nanospray sources has been demonstrated for gramicidin S. Figure 1 is a mass spectrum of 2 $\mu\text{g/mL}$ gramicidin S in 50/50 methanol/water showing the $(M+2H)^{2+}$ main ion peak. The voltage applied to the sample behind the nozzle was 2.6 kV. The flow rate was 190 nL/minute. The spectrum was from a single scan over a mass range of 100-1000 a.m.u. taken in 0.5 s. The highest ion count was in the low 10^7 range.

Our results show clearly that the performance and the operation voltages of the plastic nozzles as nanospray sources compare favorably with conventional nanospray sources. The dimensions of these nozzles, however, are substantially larger than those of the conventional sources. To understand the relatively low voltages needed to operate the plastic nozzles, it is useful to consider the following familiar equation [2] for the approximation of the onset voltage V_{on} , which causes spraying due to the instability of the Taylor cone:

$$V_{on} \sim \sqrt{\frac{r_c \gamma \cos \theta}{2\epsilon_o}} \ln\left(\frac{4d}{r_c}\right)$$

where r_c is often treated as the outside radius of the capillary used as the spray nozzle, ϵ_0 is the permittivity of vacuum, γ is the surface tension of the solution being sprayed, d is the distance between the counter electrode and the tip of the capillary, and θ is the half angle of the Taylor cone angle (49.3°). This equation has been adequate to describe qualitatively experimental observations. In the case of the nozzle in the polypropylene array chip, r_c cannot represent the radius of the nozzle since the nozzle is electrically insulating. In the derivation of the above expression [2] for the onset voltage, r_c is not the radius of the capillary, but rather the radius of curvature of the apex of an equipotential surface in the shape of a hyperboloid (see [3]). The electric field at this apex is matched to the field in the Taylor cone at the position where the radius of the cone is r_c . r_c in the present case is more appropriately related to the radius of the tip of the electrically charged liquid emerging from the nozzle opening. The onset voltage for spraying with the polypropylene nozzle can be approximated by assuming the liquid within and behind the nozzle to be described by the hyperboloid, and r_c is then related to the inner geometry of the nozzle. Figure 2 depicts schematically the region within the nozzle filled with an electrically charged liquid which approximates the hyperboloid. Indeed we have observed the spraying of the liquid at the tip of a liquid cone jet situated beyond the nozzle opening, as in conventional nanospray, and also sprays that appeared to originate from behind the nozzle opening with the visibility of the Taylor cone blocked by the nozzle opening. Factors affecting the dynamic radius of the liquid tip emerging near the nozzle opening may include its distance from the counter electrode, the dimension of the nozzle opening as well as the shape of the microfluidic channel leading to the nozzle.

While the details of the operational criteria of the insulating nozzle array await further investigations, the simple analysis presented here explains qualitatively how our plastic nozzle with a relatively large opening that minimizes clogging can generate a fine unassisted spray at a relatively low applied voltage.

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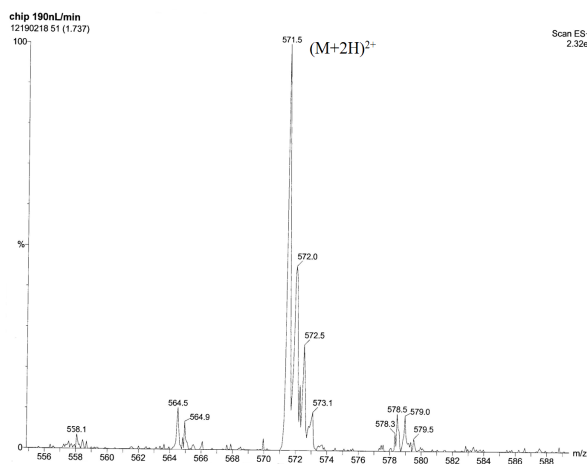


Figure 1: A mass spectrum of 2 $\mu\text{g}/\text{mL}$ gramicidin S obtained with the plastic nanospray chip. The flow rate was 190nL/minute. The scan time was 0.5 s over the full scan mass range of 100-1000 a.m.u.

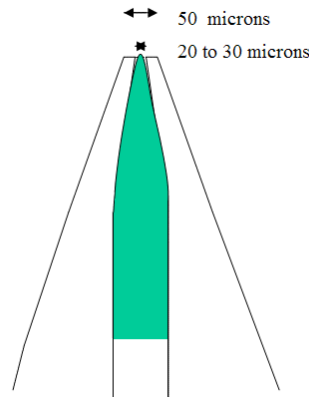


Figure 2: A schematic drawing showing the geometry inside the insulating nozzle filled with an electrically charged liquid (in green) that may influence the onset voltage for nanospray.

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