The Design and Performance of Polypropylene-Based Nanospray Nozzle Chips

Sau Lan T. Staats, Danny T. Chow and Andris Suna, Phoenix S&T, Inc., Elkton, Maryland 21921 U. S. A.

Overview

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.

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Introduction

Polypropylene Nanospray Sources

Coating glass or silica nanospray sources with an 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 contains 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.

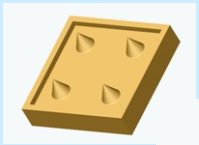
Methods

Nanospray Nozzle and Chip Design

- Conical nozzle structures 0.5 mm to 1.5 mm in height
- 20+/- 3 μm i.d., 50-150 μm o.d.
- A reservoir of a few microliters to milliliters connects directly to each nozzle
- Capillary from a syringe pump plugs directly to the nozzle without fittings
- Four nozzles per chip
- 384 microtiter-plate format
- Polypropylene and carbon-filled conductive polypropylene as base materials

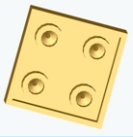
Methods

Polypropylene Nanospray Chip Design



Nanospray chip:
Nozzles side

Nozzle spacing:4.5 mm

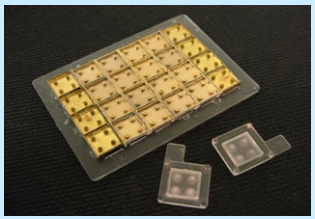


Nanospray chip: 3-D view showing nozzles and reservoirs

Nanospray chip: Reservoir side showing the entrance of each microfluidic channel leading to each nozzle

Nanospray nozzle: 50 μm o.d.

Nanospray nozzle: 150 μm o.d.



Nanospray chips arranged as an array for high throughput, and as individual chips for low through-put applications. The gold coating on the nanospray chip array is not used in normal operations.

Sample Input Mechanisms

Syringe-pumped sample through a capillary into the microfluidic channel leading to the nozzle

Plumbing-free, pipette-pumped. Sample is stored in reservoir behind the nozzle

Results

Spray Characteristics vs. Voltage

- The high voltage is applied to the liquid behind the nozzle since the nozzle is insulating
- For insulating nozzle, the spray can be tuned from droplets to an intense full plume from about 1.5 KV to 2.6 KV for ~50/50 Methanol/water mixtures.
- For a distance of a few mm to 1 cm between the nozzle tip and the counter electrode, the operating voltage is typically between 2 and 4 KV.
- Multiple plumes at higher voltages
- Negative spray voltage generates glow discharge as competing process at times
- For carbon-filled nozzles, the onset voltage for nanospray > 5KV

Nanospray of 40/60 Methanol/Water

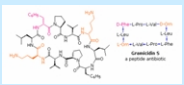
Nozzle o.d. ~ 80 μm

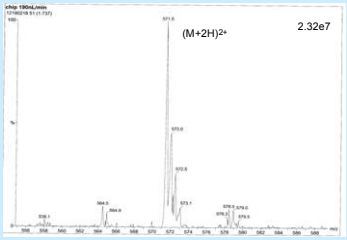
1.8 KV

2.4 KV

Nanospray-MS of Gramicidin S

Concentration: 2 μg/mL in 50/50 methanol water
Mass spectrometer: Micromass Quattro
Spray voltage:
2.6 KV
Flow rate:
190 nL/minute
Scan rate:
0.5 s/scan, 100-1000 a.m.u.





Summary of Observations

- Plastic nanospray nozzles with relatively large dimensions (up to 150 μm o.d., up to 30 μm i.d.) spray at under 4 KV
- Conductive plastic nozzles spray at much higher voltages
- The liquid Taylor cone is not always visible in the sprays
- Performance of the plastic nanospray chip as judged by the mass spectra of gramicidin S compares favorably with conventional nanospray sources

Discussions

Operation Voltages vs. Nanospray Chip Design

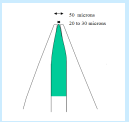
Our results show clearly that the performance and the operation voltages of the plastic nozzles as nanospray sources compare favorably with conventional nanospray sources. The dimensions of these nozzles, however, are substantially larger than those of the conventional sources.

Onset Voltage Based On Taylor Cone Instability

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

where r_c is often treated as the outside radius of the capillary used as the spray nozzle, ε_o 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 ? 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 an 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.



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.

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. The figure above 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.

Conclusions

- Plastic nozzles with nozzle openings from 15 μm to 30 μm have been successfully fabricated with micro-injection molding technology
- These nozzles perform excellently in nanospray-MS using gramicidin S
- The large nozzles with relatively large nozzle openings minimize clogging, and yet allow relatively low operation voltages to be used
- A simple analysis presented here based on the conventional Taylor cone instability as the spray mechanism points to the dynamic radius of the electrically charged liquid emerging from the nozzle opening to be the important parameter determining the spray onset voltage

Acknowledgements

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