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As shown in FIG. 2b, the electrodynamic Ion Funnel was operated in a vacuum produced by two root pumps, operating at 84 l/s and 110 l/s, respectively. The octapole was operated in a vacuum produced by a Turbo pump operating at 510 l/s. The Mass Analyzer was operated in a vacuum produced by a Turbo pump operating at 250 l/s. As will be apparent to those having skill in the art, the each of these pumps will generally create a successively larger vacuum as ions progress from the entrance of the instrument at the Multicapillary Inlet towards the Mass Analyzer.

The spray emitter array was positioned ~5 mm away from the multicapillary inlet. The high-voltage dc power supply and syringe pump described in FIG. 2a again provided electro-spray voltage and controlled liquid flow rate. Solutions of reserpine were used for evaluation of performance. The temperature of the heated multicapillary inlet was fixed at 200° C. A dc bias of 250 V was applied to the multicapillary block. The rf frequency and the amplitude applied to the ion funnel were 0.9 MHz and 130 Vp-p, respectively. The dc biases on the first ion funnel plate (25.4-mm i.d.) and the last ion funnel plate (2.3-mm i.d.) were 250 and 30 V, respectively, which resulted in an axial dc field of ~20 V/cm in the ion funnel. The mass spectrometer was operated in the positive ESI mode, and the selected ion monitoring (SIM) mode was used for the evaluation of sensitivity.

FIG. 3 shows a photo of nine electrosprays generated from the nine-emitter array using the arrangement shown in FIG. 1. The emitter array was operated at a total infusion flow rate of 3 μL/min using a solvent mixture of 50:50 methanol/water+1% acetic acid. A stable electro spray was established from each emitter without the assistance of any nebulization gas, as demonstrated by the nine stable Taylor cones evident in FIG. 3. Interestingly, each electro spray showed a much smaller spray dispersion angle compared to that from a conventional single-capillary-plate configuration, which is ascribed to the significantly less divergent electric field between the electro spray emitter array and the counter plane electrode. The result is better focused electro sprays although a higher than typical voltage (~7 kV for the electrode separation of ~5 mm) is required to establish the stable electro sprays.

After stable electro sprays were established with the emitter array, the total spray ion current was measured at different liquid flow rates. To establish a baseline for all the comparisons, the total ion currents for single electro spray generated from both a conventional fused-silica capillary (100-μm i.d. and 200-μm o.d. with the tip pulled down to 50 μm) and a microfabricated single-spray emitter were measured at different liquid flow rates. FIG. 4 shows the total ion currents measured at different flow rates.

The fact that the two sets of data in FIG. 4 correlate well indicates that the electro sprays had quite similar characteristics. It is also interesting to note from FIG. 4 that the total electro spray current fits a 0.44 power of liquid flow rate, very close to the theoretical prediction of de la Mora and Loscertales as described in De la Mora, J. F.; Loscertales, I. G. *J. Fluid Mech.* 1994, 260, 155–184. Their analysis concluded that, for electro sprays of highly conductive liquids, the dependence of the total electro spray current on the liquid flow rate could be formulated as,

$$I_s = f(\epsilon)(QKy/\epsilon)^{1/2} \quad (1)$$

where I_s is the total spray current from single electro spray, K is the electric conductivity of the liquid, y is the surface tension of the liquid, ϵ is the dielectric constant of the liquid, and Q is the liquid flow rate. Equation 1 was derived through

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a detailed dimensional analysis of the charge transport process through the Taylor cone and was verified by the authors experimentally using variety of liquid mixtures. Good agreement between the experimental results shown in FIG. 4 and equation 1 supported the optical evaluation indicating that stable cone-jet mode electro sprays were obtained in the present studies.

Next, multielectro sprays were generated from the micro-fabricated chip using different numbers of emitters. The total ion currents of the multielectro sprays were measured at different liquid flow rates. The experimental data shown in FIG. 5a clearly indicated that at each total liquid flow rate the total ion current increased as the number of the electro sprays increased. The results in FIG. 5a also show that the total ion current from eight electro sprays was ~3 times higher than from a single electro spray at the same total liquid flow rate. The reason for this is evident from equation 1. If one assumes that each electro spray in the array behaves identically to a single electro spray, then from eq 1,

$$I^* = f(\epsilon)(Q^*Ky/\epsilon)^{1/2} \quad (2)$$

where I^* and Q^* are the ion current carried by each electro spray and the liquid flow rate supplied to each emitter in the array, respectively. It is apparent that Q^* is smaller than the total liquid flow rate Q supplied to the emitter array. The total ion current of the multielectro sprays then becomes,

$$I_{Total} = \sum_{i=1}^n I_i$$

where n is the total number of electro sprays generated from the emitter array.

If we further assume that the liquid flow is distributed uniformly into every emitter, i.e., $Q^* = Q/n$, each electro spray in the array will then carry the same ion current. Equation 3 becomes

$$I_{Total} = nI^* \quad (4)$$

Substituting eq 2 into eq 4, we have

$$I_{Total} = \sqrt{nf(\epsilon)(Q^*Ky/\epsilon)^{1/2}} = \sqrt{n}I_s \quad (5)$$

total ion current from the multielectro sprays, compared to the ion current from single electro spray at a given total flow rate, is proportional to the square root of the number of electro sprays. To verify equation 5, the experimental data shown in FIG. 5a were normalized by the number of electro sprays in FIG. 5b. All the experimental data collapsed to provide a good fit by a single curve. These results support the assumptions used in the derivation of equation 5, i.e., that each electro spray carried approximately the same ion current in the multielectro spray and the liquid flow was distributed approximately equally to each spray emitter. Because of the higher ion current produced by the multielectro sprays, the potential of using multielectro sprays as an ionization source to enhance the sensitivity or dynamic range of mass spectrometry was further evaluated using the arrangement shown in FIG. 2b. Sensitivity comparisons between a single electro spray using a fused-silica capillary and multielectro sprays from a microfabricated emitter array were performed using a solution of 50 pg/μL reserpine in 50:50 methanol/water+1% acetic acid introduced at different infusion flow rates. While all the MS parameter settings were held constant, the single electro spray and multielectro sprays sources were interchanged. FIGS. 6a and b shows the SIM mass spectra obtained for single electro spray and