

Correspondence

Velocity Compression in Cylindrical Capacitor Electrospray of Methanol–Water Mixtures

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Phase Doppler anemometry was utilized to measure the >0.5- μm portion of the size distributions and the corresponding velocity distributions of methanol–water droplets generated by a miniature cylindrical capacitor electrospray (CCES) source. Droplets exceeding 1 μm in diameter were observed with the tail of the size distributions extending up to 5 μm . Droplets produced by this source displayed significantly narrower velocity distributions and smaller mean axial velocities relative to those generated by forced flow electrospray. In terms of flow rate, spraying voltage, droplet size, and axial velocity distributions, the CCES source represents a transition between conventional electrospray and nanospray sources. The CCES is quasi-monodisperse, and the droplets have close to uniform velocities. There is a significant effect of the spraying voltage on the width and mean values of the droplet size and velocity distributions for methanol solutions. Both mean diameters and average axial velocities are shifted toward larger values as the applied voltage is increased. The emission diameter predicted by Wilm and Mann provided a good lower estimate for the measured droplet diameters.

Recently, several groups have demonstrated the application of small inner diameter capillaries to produce cylindrical capacitor electrospray (CCES) ion sources.^{1–4} This miniaturized electrospray (ES) has generated interest and opened new avenues in the analysis of biomolecules. Distinctive features of this source include the omission of forced flow (i.e., there is no need for syringe pump or pressure differential to maintain the flow), the reduced incidence of corona discharge, simplicity, and ruggedness.¹ These sources can operate with an extremely wide range of flow rates (~1 nL/min to ~200 $\mu\text{L}/\text{min}$) utilizing moderate spraying voltages (1.3–3.5 kV). Both metal¹ and insulator^{2–4} capillary tips with 10–

25- μm i.d. have been used to generate stable spray without the application of a sheath gas.

Due to the importance of ES ionization (ESI) in mass spectrometry, there is a renewed interest in the characterization of these sprays. Although complete characterization—which would include the determination of droplet size, velocity, charge, and chemical composition distributions as a function of position with respect to the spraying device—is not available, several efforts have been made to obtain part of the information. Most recently, phase Doppler anemometry (PDA) was used to investigate the size and velocity distributions^{5,6} and laser-induced fluorescence was utilized to follow pH changes⁷ under spraying conditions typical in ESI mass spectrometry (ESI-MS). Identifying chemical composition (pH, etc.) changes within the spray can help in understanding the possible modification of analytes (e.g., protonation) during ESI.^{10,11} Droplet size and velocity information can support the design of ESI-MS and other interfaces responsible for the desolvation of droplets.

In this paper, we summarize our results on the size and velocity distributions of sprays generated by CCES. In this regime, the droplets produced in the >0.5- μm -diameter range were measured by PDA.⁸ Details of our setup have been described in an earlier publication.⁶ The investigations were conducted on methanol/water solutions using both ES and CCES sources. The 200- μm -wide probe volume of the PDA was positioned 1.5 mm away from the 5–10- μm -i.d. (25–50- μm -o.d.) tip of the tapered glass capillary. A grounded planar counter electrode was located at 22 mm from the tip. A thin platinum wire (o.d. 150 μm) was inserted into the capillary through which the high voltage was supplied. For the studied methanol–water mixtures, a spraying voltage of 1.7–2.4 kV was necessary to generate and maintain a stable spray.

- (5) Tang, K.; Gomez, A. *J. Aerosol Sci.* **1994**, *25*, 1237.
- (6) Olumee, Z.; Callahan, J. H.; Vertes, A. *J. Phys. Chem., A* **1998**, *102*, 9154.
- (7) Zhou, S.; Edwards, A. G.; Cook, K. D. *Anal. Chem.* **1999**, *71*, 769.
- (8) Based on light scattering, the PDA instrument simultaneously measures the size and the velocity distributions of the sprayed droplets. Each time a particle passes through the probe volume, a Doppler burst signal is generated with a frequency proportional to the particle velocity. The phase shift between Doppler bursts observed by different detectors is related to the size of the particle.
- (9) Wilm, M.; Mann, M. *Int. J. Mass Spectrom. Ion Processes* **1994**, *136*, 167.
- (10) Chowdhury, S. K.; Katta, V.; Chait, B. T. *J. Am. Chem. Soc.* **1990**, *112*, 9012.
- (11) Wang, G.; Cole, R. B. *Org. Mass Spectrom.* **1994**, *29*, 419.

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- (1) Wang, H.; Hackett, M. *Anal. Chem.* **1998**, *70*, 205.
- (2) Konig, S.; Fales, H. M.; Haegele, K. D. *Anal. Chem.* **1998**, *70*, 4453.
- (3) Hannis, J. C.; Muddiman, D. C. *Rapid Commun. Mass Spectrom.* **1998**, *12*, 443.
- (4) Fong, K. W. Y.; Chan, T.-W. D. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 72.

Table 1. Calculated Emission Diameter (d_e) and Measured Average Droplet Diameter (D_{10}) as a Function of the Spraying Voltage (U_a)

spraying voltage (V)	flow rate (nL/min)	d_e (μm)	D_{10} (μm)
1700	1990	0.88	1.43 ± 0.02
2000	3260	1.08	1.76 ± 0.02
2400	7310	1.63	1.90 ± 0.10

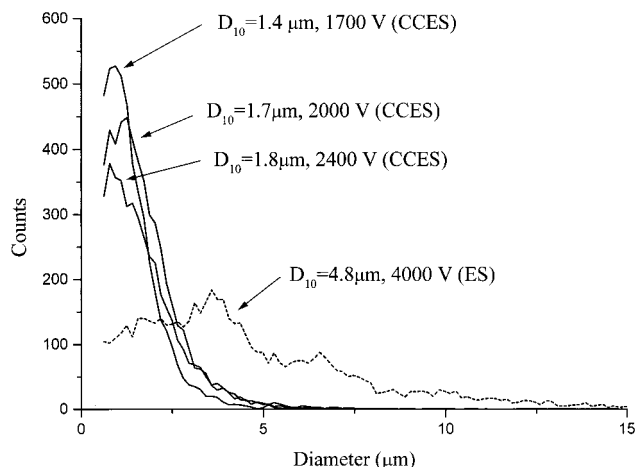


Figure 1. Size distributions of 90% CH_3OH droplets sprayed from CCES source at different spraying voltages showing large droplets with diameters extending up to $5 \mu\text{m}$. D_{10} values marked in the figure stand for the arithmetic mean diameter. For comparison, the droplet size distribution for ES from an i.d. = $150 \mu\text{m}$ capillary is also shown (dashed line).

Lowering the voltage led to pulsating spraying modes.

The flow rate was estimated by measuring the time necessary to transfer a certain amount of fluid from the capillary and the corresponding change in the mass of the capillary. The flow rate was determined to be a function of the spraying voltage and it varied between 1990 (at 1700 V) and 7310 nL/min (at 2400 V) (see Table 1). These values were significantly higher than the 1–500 nL/min used in nanospray (NS) sources but lower than typical flow rates generated in our previous study of droplet dynamics in ES ($\sim 20 \mu\text{L}/\text{min}$).⁶ Before and after the spraying experiment, the integrity of the capillary was verified by light microscopy.

Somewhat to our surprise, under most of the operating conditions, we were able to characterize the large-size portion of the droplet size distribution with PDA. In contrast to regular ES and also different from NS, the average droplet size was in the 1–2- μm range and the width of the distribution was less than 2 μm fwhm (see Figure 1). At higher voltages, the size distribution of the 90% methanol droplets extended up to $5 \mu\text{m}$. As the applied voltage was decreased, we observed smaller mean diameters (D_{10}). For example, spraying 90% methanol solution resulted in $D_{10} = 1.9 \mu\text{m}$ at 2400 V that decreased to $D_{10} = 1.4 \mu\text{m}$ as the applied voltage was lowered to 1700 V. Although the $<0.5\text{-}\mu\text{m}$ part of the CCES size distributions was not observed, these distributions showed substantially less spread than their ES counterparts.

Wilm and Mann calculated the emission diameter, d_e , at the base of the filament emerging from the Taylor cone:⁹

$$d_e = 2 \left(\frac{\rho}{4\pi^2 \gamma \tan(\pi/2 - \vartheta) [(U_a/U_T)^2 - 1]} \right)^{1/3} Q^{2/3} \quad (1)$$

where ρ and γ are the density and the surface tension of the liquid, respectively. The applied voltage, U_a , and the liquid flow rate, Q , are experimental parameters that have a direct effect on the emission diameter, whereas the threshold voltage, U_T , and the liquid cone angle, ϑ , are determined by the spraying regime. For classical Taylor cones, $\vartheta = 49.3^\circ$. According to the model of Wilm and Mann, at high flow rates the droplets are formed by the breakup of the filament and their diameter is larger than the emission diameter. In this high flow rate regime, the average droplet diameter is determined by the mean distance between filament breakup points and by the diameter of the filament. At lower flow rates, the filament becomes shorter and the droplet diameter approaches the emission diameter. Further lowering the flow rate can lead to direct emission of droplets from the tip of the Taylor cone. In this limiting case, the droplet diameter is equal to the emission diameter. Thus, we expect that the calculated emission diameter serves as a lower limit for the measured average droplet diameter.

On the basis of the PDA measurements presented above, we are in the position to compare the measured average droplet diameters with the emission diameters calculated using eq 1. For 90% methanol, $\rho \approx 790 \text{ kg}/\text{m}^3$ and $\gamma = 0.03536 \text{ N}/\text{m}$. Using the threshold voltage from ref 9, $U_T = 550 \text{ V}$, and the flow rate measured for our setup, $Q = 1990 \text{ nL}/\text{min}$ at $U_a = 1700 \text{ V}$, we arrived at $d_e = 0.88 \mu\text{m}$. Even though the threshold voltage in our case is probably different (due to the differences in methanol concentration and capillary geometry), this value gives a lower limit for the measured $D_{10} = 1.4 \mu\text{m}$ mean droplet diameter. Increasing U_T leads to higher emission diameter values. We evaluated the emission diameter as a function of the applied voltage based on eq 1. The results are summarized in Table 1 along with the measured arithmetic averages of the droplet size distribution. It is clear from the table that increasing the spraying voltage leads to larger emission diameters (because of the enhanced flow rates) and an increase in the average droplet size also takes place. However, the calculated emission diameter appears to be always smaller than the measured average droplet size. These findings support the predictions based on the model in ref 9.

The mean axial velocities of droplets from 90% methanol solution were in the 4.6–13.4 m/s range. For comparison, we also measured velocity distributions of droplets from the same solution produced by an ES system operated with a syringe pump at 24 $\mu\text{L}/\text{min}$ spraying at 4.0 kV through a stainless steel needle of 150- μm i.d. and 510- μm o.d.⁶ In contrast to ES, droplets generated by CCES had significantly smaller mean axial velocities and remarkably narrower velocity distributions (see Figure 2). This velocity compression may be attributed to the generation of more monodisperse droplets. To the best of our knowledge, this is the first report of measuring velocity distributions on droplets in sprays generated from narrow capillaries (i.d. $\leq 10 \mu\text{m}$) without forced flow.

As is clear in Figure 2, the average velocities scale with the applied spraying voltage; thus, the substantially reduced droplet velocities in CCES compared to ES may be the consequence of

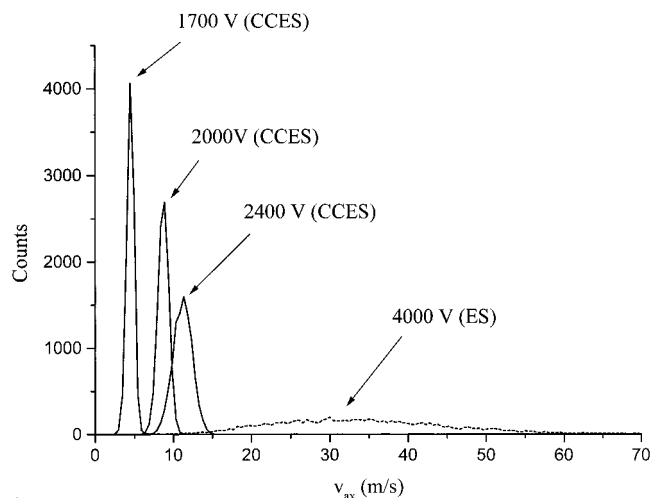


Figure 2. Comparison of velocity distributions of 90% CH₃OH droplets in CCES (solid line) and ES (dashed line) sources. The distances between the probe volume and the capillary for CCES and ES were 1.5 and 12 mm, respectively. Spraying voltages are indicated in the figure.

the significantly reduced spraying voltage. The onset of stable spraying voltages for 50 and 90% solutions was 1900 and 1700 V, respectively. In both 90 and 50% CH₃OH, an increasing trend of the axial mean velocities was observed when the applied voltage increased (see Figure 3). Figure 3 showed that the droplets from the 90% CH₃OH solution exhibited consistently higher axial mean velocities.

Based on our PDA measurements of the droplet size and velocity distributions from methanol solutions, the CCES is a regime that lies between regular ES and NS in terms of droplet size and velocity distributions, as well as spraying conditions (spraying voltage and liquid flow rate). A significant advantage of the CCES regime is that it can deliver droplets in the low-micrometer range with no need for forced liquid delivery. The CCES is quasi-monodisperse, and the droplets have close to uniform velocity. It is likely that at elevated voltages some NS ion sources work in this CCES mode. There is a significant effect of the spraying voltage on the width and mean values of the droplet size and velocity distributions. Both mean diameters and average axial velocities are shifted toward larger values as the applied voltage is increased.

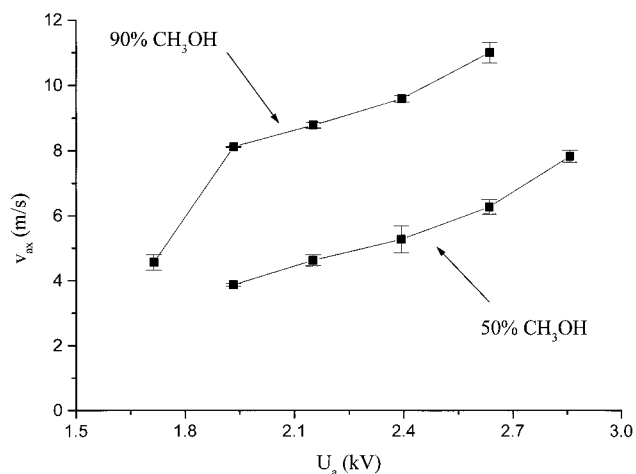


Figure 3. Increasing trend of the mean axial droplet velocities vs the spraying voltage (U_a) for 90 and 50% methanol solutions.

Clearly the slower moving, smaller droplets generated by CCES have a longer time to evaporate and desolvate in an ESI-MS interface. Moreover, since more of the droplets are within relatively narrower velocity windows (e.g., fewer in the high-velocity tail) as flow rates and voltages drop, once the distribution starts to fall into a velocity regime where droplet evaporation and desolvation is efficient on the experimental time scale, higher signal intensities will be observed. One can certainly imagine that, in normal electrospray, a large number of drops (those at the high end of a much broader distribution) are just too big and too fast to be effectively desolvated since they go blazing into the instrument too fast.

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