Optimizing Coaxial Sonic Spray Geometry for Generating Water Microdroplets

Maria T. Dulay, Christian F. Chamberlayne, and Richard N. Zare*

ABSTRACT: Sonic spray creates a stream of neutral and charged microdroplets without application of voltage, heating, laser irradiation, or corona discharge. The solvent of interest flows through an inner capillary (usually constructed of fused silica) that is surrounded by an outer stainless-steel tube through which a nebulizing gas flows under pressure. This technique has been widely used as the interface in mass spectrometric studies for chemical analysis and for understanding microdroplet chemistry. We have used light scattering to characterize the size distribution and density for water microdroplets as a function of several parameters, such as water quality, water flow rate, nebulizing gas pressure, and sonic spray geometry. We find that the size distribution of the microdroplets, which is critical to many applications, depends most sensitively on the distance between the inner and outer capillary outlets and the gas flow pressure. The best performance as measured by the smallness of the microdroplet diameters is obtained when the gas flow pressure is the highest and there is no separation distance, \(d\), between the two capillary outlets. In addition, at \(d = 0\) mm, the microdroplet diameter distribution is nearly independent of the water flow rate, indicating that studies under these conditions can be scaled up.

Sonicate spray and related variations have been widely used in many different mass spectrometric ionization methods for chemical analysis.\(^1\)\(^-\)\(^3\) The size of sprayed microdroplets plays an important role in mass spectrometry imaging, controlling chemical reactions inside the microdroplets,\(^4\)\(^-\)\(^6\) and analyte aggregation.\(^5\) For example, we have found that the size of the microdroplet in a coaxial sonic spray strongly influences the production of hydrogen peroxide in water microdroplets\(^6\) and the digestion of proteins in microdroplets containing a protease.\(^7\) In each case, when the average diameter of the microdroplets is reduced from 100 to 10 \(\mu\)m, product formation is accelerated by factors of 100 or more. This behavior has motivated us to examine how various factors of a sonic spray source might influence microdroplet size. For this purpose, we used a commercial light scattering device to record the microdroplet size distribution under various operating conditions.

**METHODS**

**Chemicals and Materials.** Biograde water (Corning) and ASTM Type 1 deionized water (ACS reagent) were purchased from Fisher Scientific (Waltham, MA, USA) and used without further purification. In-house distilled water and tap water from the laboratory were used. A fused-silica capillary (100 \(\mu\)m ID \(\times\) 365 \(\mu\)m OD) was purchased from Polymicro Technologies (Phoenix, AZ, USA).

**Microdroplet Size Measurements.** Scheme 1 illustrates the experimental setup. A HELOS 2750 particle size analyzer (Sympatec, Clausthal-Zellerfeld, Germany) was used to measure the size of the microdroplets produced from a coaxial sonic spray device. The device was composed of a 100 \(\mu\)m ID \(\times\) 365 \(\mu\)m OD fused-silica capillary (Polymicro Technologies, Phoenix, AZ) through which water flowed under ambient conditions (23 \(\pm\) 2 °C, 41–59% relative humidity). This capillary was positioned inside a stainless-steel (ss) tube (0.020 in. ID \(\times\) 1/16 in. OD) through which \(N_2\) gas flowed from a gas cylinder at varied pressures. The fused-silica capillary inlet was attached to a 10 mL syringe via PE tubing and driven with a Harvard Apparatus syringe pump (Holliston, MA). The coaxial tubes of the spray device were positioned in parallel to the base of the analysis chamber and within the laser beam where diffraction of light from the microdroplets was easily visible. The microdroplet spray head was positioned such that the microdroplet spray plume entered immediately into the measurement region of the particle size analyzer. The tip of the inner fused-silica capillary was maintained just outside the laser beam whose scatter was used for the measurement; thus, changes in \(d\) resulted in retraction of the outer capillary outlet away from the measurement region. To prevent any slight diffraction from the sheath gas from affecting the measure-
ment, the instrument was baselined with the nitrogen flow active but no liquid flow.

Data acquisition began approximately 2 min after the start of spraying to achieve spray equilibrium. The assumed measured height of the spray plume is consistent with the height of the coaxial tube position above the chamber floor; this measured height was adopted for all measurements.

PAQSOX 5.0.1 software (Sympatec, Germany) was used to acquire volumetric diameters (below which smaller drops represented 10% \(x_{10}\) and 90% \(x_{90}\) of the total volume), the volume mean diameter (VMD), where 50% of the droplet sizes are below and 50% are above this value, and the particle size distributions. The relative span factor (RSF) is a dimensionless factor indicative of the uniformity of the drop size distribution and defined by the following equation:

\[
RSF = \frac{x_{90} - x_{10}}{VMD}
\]

where \(x_{90}\) represents the microdroplet diameters where 90% of the droplet sizes are above this median and 10% are below and \(x_{10}\) represents the microdroplet diameters where 10% of the droplet sizes are above this median while 90% are below. Both \(x_{90}\) and \(x_{10}\) values were calculated by the PAQSOX software.

\section*{RESULTS AND DISCUSSION}

A laser diffraction approach was used to measure, in real time, nebulized microdroplet size distributions. In a coaxial spray device (see Scheme 1), the process of generating water

![Scheme 1. Experimental Setup for Water Microdroplet Generation and Measurement](image)

“Nitrogen gas is flowed through the stainless-steel tube of the spray device. The fused-silica capillary is attached to a syringe via PTFE tubing. Water flow rate through the capillary is controlled with a syringe pump. The water droplet spray plume is aligned within the laser beam of the particle size analyzer chamber. The inset shows a magnified illustration of the spray device where the fused-silica capillary (water) and the stainless-steel tube (gas) are in a coaxial arrangement.

**Figure 1.** Average volume mean diameter (VMD) measured as a function of the distance, \(d\), of the capillary outlet from the stainless-steel nebulizing gas tube outlet at Biograde water flow rates of (A) 100 \(\mu\)L/min, (B) 50 \(\mu\)L/min, and (C) 30 \(\mu\)L/min. Average relative span factor (RSF) as a function of \(d\): (D) 100 \(\mu\)L/min, (E) 50 \(\mu\)L/min, and (F) 30 \(\mu\)L/min. \(N_2\) gas pressure: 90 psi. Relative humidity range is 41–51%, and \(n = 3–4\) except \(n = 1\) at 30 \(\mu\)L/min, \(d = 0,2\).
microdroplets began by flowing water through a fused-silica capillary with applied N₂ nebulizing gas in the absence of an electric field. The flow of water breaks up into microdroplets as the stream emerges from the orifice (outlet) of the capillary. One method that has become prominent in analyzing the sizes of aerosolized or nebulized droplets is laser diffraction, which involves a volume-based measurement. The size of the water microdroplets is significantly influenced by the geometry of a coaxially arranged capillary and nebulizing gas tube (see Scheme 1), and a droplet size analyzer with laser diffraction was used to study the effect of the coaxial tube geometry under different operating conditions. Effects of nebulizing gas pressure and the type of water were also investigated. It has previously been established that microdroplets are formed with smaller diameters when the gas flow pressure is increased, but the variation with coaxial sonic spray geometry appears to have not previously been investigated. Many factors determine microdroplet size, such as surface tension of the solvent, spray pressure, and nozzle type. We limit our discussion to coaxial sonic spray sources with an emphasis on how this type of spray source is constructed.

**Effects of Coaxial Spray Geometry and Water Flow Rates on Microdroplet Size and Density (Biograde Water).** The geometry of the coaxial spray device, which is like two-fluid nozzles such as those used in coaxial atomizers, can dramatically influence the water microdroplet sizes. The volume mean diameter (VMD), which describes the microdroplet size in terms of the volume of liquid sprayed, is based on the volume where 50% of the total volume of the droplets has a diameter larger than the median and the other 50% has a diameter smaller than the median. VMD is a widely accepted measure of droplet size. The effect of the distance, d, of the outlet of the water flow capillary from the outlet of the nebulizing ss-gas tube (Scheme 1) on the microdroplet diameter and droplet distribution density were studied at constant N₂ pressure of 40 psi and Biograde water flow of 100 μL/min (Figure 1A), 50 μL/min (Figure 1B), and 30 μL/min (Figure 1C) at 41% to 51% relative humidity (RH). A general trend between d and VMD is apparent. A linear relationship within each data set is observed between the average droplet diameters and d at 0, 1, 2, and 3 mm for water flow rates of 100 and 50 μL/min and d at 0, 1, 2, and 2 mm for a 30 μL/min flow rate. At d values of 1, 2, and 3 mm, the capillary outlet extends outside the ss-gas tube while at d = 0 mm the capillary and ss-gas tube outlets were flush. In this d range, the average VMDs increased with increasing d. Positioning the outlet of the liquid-flow capillary away from the outlet of the ss-gas tube (in either direction) resulted in larger VMD values as compared to d = 0 mm.

At d = 0, 1, 2, and 3 mm, the water flow rate did not significantly affect the VMD values except for d = 0 mm at a 30 μL/min water flow rate (Figure 2). The smallest average VMDs are observed when d = 0 mm where the difference in the average VMDs at water flow rates of 100 and 50 μL/min is negligible: 11.96 ± 4.71 μm (n = 3) and 11.70 ± 2.63 μm (n = 3), respectively; however, at 30 μL/min, the average VMD is comparatively smaller in value by approximately 13%, 10.43 μm (n = 1). At d = 1 mm, the average VMDs are similar within error for all three water flow rates: 20.70 ± 3.68 μm (n = 4), 20.20 ± 4.22 μm (n = 4), and 18.80 ± 7.41 μm (n = 3) at 100, 50, and 30 μL/min, respectively. At d = 2 mm, the average VMDs are also similar within error for 100 and 50 μL/min water flow rates: 29.49 ± 3.46 μm (n = 3) and 29.85 ± 3.49 μm (n = 3), respectively, while a VMD of 28.86 μm (n = 1) is observed for a 30 μL/min water flow rate.

In Figure 1C, the largest average VMD in this d range is observed for d = 3 mm: 36.19 ± 6.17 μm (n = 3) at 100 μL/min and 34.69 ± 6.33 μm (n = 3) at 50 μL/min. At a d of −1 mm and the highest water flow rate (100 μL/min), the largest average VMD, 46.87 ± 5.84 μm (n = 3), is observed while the average VMDs at 50 and 30 μL/min are significantly smaller: 21.83 ± 6.65 μm (n = 3) and 27.71 ± 3.64 μm (n = 3), respectively (Figure 1C). The %RH in the lab frame was recorded at the time of the measurements. The small volume of water from the spray was observed to be insufficient to change the %RH. The variation in %RH was a result of measurements taken on different days. A slight shift toward larger microdroplets on the day with 51% RH, as shown in Figure 3, is not unexpected. In previous works, when gas is mixed with the wet aerosol, the VMD has been observed to increase.

The relative span factor (RSF) is a dimensionless factor that expresses the distribution width of droplet diameters measured under similar conditions, and it is a common value used in reporting laser diffraction data. Figure 1D–F shows the effect of d on RSF values at three different Biograde water flow rates. The RSF values for each d value are strongly affected by the water flow rate. When comparing the data acquired at different water flow rates, the RSF values are largest at the slowest water flow rate (30 μL/min) and smallest at the fastest water flow rate (100 μL/min) as shown in Figure 1D,F, respectively. RSF values have implications in spray drift. The lower the RSF value, the larger is the VMD, which results in a potential decrease in spray drift.

At constant water flow rate, the RSF values decrease with increasing d. The smaller the RSF value, the less variation there is between the sizes of the droplets within a given spray distribution. The set of RSF values measured at a water flow rate of 100 μL/min is the largest (1.69 ± 0.22 μm, n = 4) at a d value of −1 mm and the smallest (1.00 ± 0.08 μm, n = 3) at 3 mm as shown in Figure 1D. In Figure 1E, the set of RSF values at a water flow rate of 50 μL/min includes the largest RSF value (2.23 ± 0.28 μm, n = 4) at a d value of −1 mm and the smallest RSF value (0.91 ± 0.11 μm, n = 3) for d = 3 mm. In Figure 1F, a similar trend is observed where the largest RSF...
value (2.45 ± 0.43 μm, n = 4) was calculated for a d value of −1 mm and the smallest RSF value (1.29 μm, n = 1) was at d = 2 mm. No measurement was acquired for d = 3 mm at 30 μL/min as insufficient scattered light was detected to make a measurement of the microdroplet size distribution.

For each data set (constant gas pressure and constant water flow rate), the average VMD values are inversely proportional to the corresponding RSF values (Figure 1A−C). It seems reasonable that the RSF values would be the largest at d of −1 mm where the variability in the average VMD values at the different water flow rates is up to approximately 56%.

Figure 3 shows the microdroplet size distributions at different d values for three different Biograde water flow rates. When d is −1 mm, the distribution profile is generally bimodal with one droplet diameter maximum greater than 50 μm and the other maximum less than 30 μm (Figure 3A−C). The bimodal microdroplet distribution observed at a d of −1 mm may be caused by the deposition of water by the spray plume onto the inside of the outer stainless-steel sheath, where it is subsequently sprayed into microdroplets a second time off the inner edge of the outer sheath. On the contrary, at d = 0, 1, 2, and 3 mm, the distribution is monomodal (Figure 3D−M). At d = 0 mm, the measurements are highly reproducible at each water flow rate regardless of %RH. The plots are nearly symmetrical with slight tailing at the front end of the plot. While the plots are also nearly symmetrical for d = 1 mm at all water flow rates, the reproducibility of the measurements appears to be affected slightly by %RH as shown in Figure 3G−I. At d = 2 and 3 mm, the measured peaks become less symmetrical and less reproducible (Figure 3J−M).

Effects of Nebulizing Gas Pressure on Microdroplet Sizes. As shown in Figure 4A, an increase in the nebulizing gas pressure from 50 to 200 psi results in a decrease of the VMD by nearly 2-fold from 12.56 ± 1.45 μm (n = 4) to 6.36 ± 1.32 μm (n = 5). This observation is typical of other types of spray devices that involve aerosolization or nebulization. For a similar coaxial spray geometry, an increase in the gas velocity, which caused the shear effect of the gas on the droplet to increase, resulted in the decrease of the droplet diameters. In Figure 4B, the RSF values increase slightly at higher gas pressures, which indicates a slight decrease in spray quality.

Effects of the Type of Water on Microdroplet Sizes. Different types of water were studied, from ultrapure water (ASTM) to tap water and water with added NaCl as listed in Table 1. For all water types except for 25 μM NaCl in Biograde water, the average VMD values were similar within error, ranging from 10.13 to 10.57 μm. The type of water has no significant effect on the diameters of the microdroplets produced from the spray device at d = 0 mm.

CONCLUSIONS

The geometry of the coaxial sonic spray device, namely, the distance of the fluid-flow capillary outlet to the stainless-steel
A Technical Note

Table 1. Effect of Water Type on VMD and RSF at Constant N_2 Gas Pressure (90 psi), Constant Water Flow Rate (100 μL/min), and d = 0 mm

<table>
<thead>
<tr>
<th>Water Type</th>
<th>Avg VMD (μm)</th>
<th>Avg RSF</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biograde</td>
<td>10.40 ± 0.53</td>
<td>1.42 ± 0.12</td>
<td>3</td>
</tr>
<tr>
<td>ASTM</td>
<td>10.52 ± 0.4</td>
<td>1.41 ± 0.01</td>
<td>2</td>
</tr>
<tr>
<td>Distilled</td>
<td>10.22 ± 0.01</td>
<td>1.41 ± 0.01</td>
<td>2</td>
</tr>
<tr>
<td>Tap</td>
<td>10.57 ± 0.22</td>
<td>1.43 ± 0.03</td>
<td>2</td>
</tr>
<tr>
<td>26 μM NaCl in Biograde</td>
<td>8.80 ± 0.02</td>
<td>1.37 ± 0.02</td>
<td>2</td>
</tr>
<tr>
<td>257 μM NaCl in Biograde</td>
<td>10.13 ± 0.16</td>
<td>1.40 ± 0.04</td>
<td>2</td>
</tr>
</tbody>
</table>

gas tube outlet, is very important to the generation of small diameter water microdroplets with a narrow distribution of diameters. The smallest droplet sizes achieved were at d = 0 mm. As expected, an increase in the nebulizing gas pressure resulted in decreased diameters of the microdroplets. For a given d in the range of 0 to 3 mm, the water flow rate has a negligible effect on the microdroplet diameters with the smallest diameter at d = 0 mm. It is suggested that future sonic spray studies need to pay close attention to the separation between the inner and outer capillary outlets so that others can reproduce the results obtained. This information on microdroplet diameter distribution can also be used to optimize product yield in microdroplet chemistry experiments.

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**Author Contributions**

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**Notes**

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