SYRINGE PUMP SAMPLE DELIVERY ELECTROSPRAY AEROSOL GENERATOR MODEL 3482

APPLICATION NOTE AG-001 (A4)

Introduction

The Advanced Electrospray Aerosol Generator (EAG) Model 3482 produces high concentrations of quasi-monodisperse, submicrometer particles from 2 to 150 nm (initial droplet diameter of 150 nm, nominal). A liquid sample is delivered to the electrospray generator and forced through a capillary. The capillary extends into a chamber where a negatively charged orifice plate creates an electric field that draws the liquid sample into a Taylor cone. Uniform, charged droplets are drawn off the tip of the cone and mixed with air and CO_2 to dry the droplets. During the drying process, the droplets and particles resulting from the evaporated droplets are charge reduced by exposing them to bipolar ions generated by a soft X-ray neutralizer.

This application note outlines the method of using a syringe pump to deliver a liquid sample to the EAG as well as a basic procedure and example results for determining the initial diameter of the droplets generated by the EAG. An image of the basic setup used in this procedure is shown in Figure 1. For general EAG operating instructions, reference the Advance Electrospray Aerosol Generator Model 3482 Instruction Manual (TSI PN: 6007732).

Figure 1: Model 3482 Electrospray Aerosol Generator (EAG) used with syringe pump and Model 3938 Scanning Mobility Particle Sizer™ (SMPS™) Spectrometer

Delivering a Sample to the EAG

Figure 2 shows an operating schematic of the EAG. To generate aerosol using the EAG, a liquid sample must be delivered to the microcross where the flow is split between the waste line and the capillary. The flow rate through the capillary directly controls the size of the initial droplets generated.

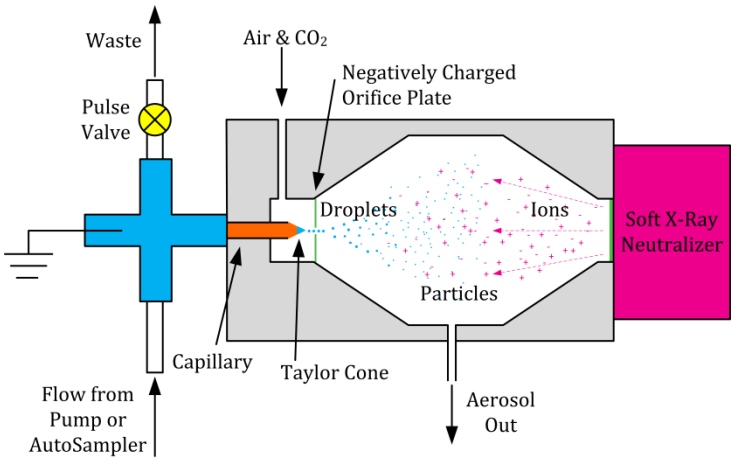

Figure 2: Schematic of 3482 electrospray aerosol generator

The ratio at which the flow is split between the waste line and the capillary is determined by the pressure in each line. The pressure in each line is determined by several variables including:

1. The flow rate of CO_2 and air through the EAG.

   These two flows affect the pressure at the outlet of the capillary. Increasing the air or CO_2 flow will increase the pressure in the chamber, thus decreasing sample flow through the capillary.

2. The diameter and length of tubing between the waste line and the pulse valve.

   The diameter and length of this tubing affects the pressure in the waste line. A longer length of tubing or smaller diameter tube will increase the resistance to flow through the waste line, increasing the sample flow through the capillary.

3. Height of opening of drain line (downstream of pulse valve).

   When the drain line (downstream of the pulse valve) becomes full of waste sample, the height of the outlet can affect the pressure in the waste line. If the drain line opening is higher than the capillary, the pressure in the waste line will be higher, increasing the capillary flow. Likewise, if the drain line opening is lower than the height of the capillary, the pressure in the drain line will be lower, decreasing the capillary flow.

By setting the above parameters, the sample flow rate delivered by the syringe pump can be used as the controlling variable for flow through the capillary and therefore droplet diameter.

While the EAG will function in a wide variety of configurations, this configuration described in this example has been used successfully to generate stable aerosols with the EAG.

Syringe Pump Operation

Materials

The materials used in the following setup are listed in Table 1. In this setup a Harvard Apparatus Pump 11 Plus syringe pump is used. This model was selected due to its flow rate accuracy (±0.5%), reproducibility (±0.1%), and range (0.0041 µl/hr-26.55 ml/min).

Table 1: Syringe pump sample delivery materials

Item Number (In Figure 3)	Material Description	Manufacturer	Model	Part Number[1]
1	Syringe pump	Harvard Apparatus	Pump 11 Plus	**3482-SPump**
2	Plastic syringes	Henke Sass Wolf GmbH	1 mL NORM-JECT® syringe	4010.200V0
Not Pictured	Glass syringes	Hamilton	1 mL 1000 series GASTIGHT syringe	81320
3	Syringe to tubing fitting 1	Upchurch	Female lock to 10-32 coned	P-659
4	Syringe to tubing fitting 2	Upchurch	10-32 coned to 1/16" OD tubing	F-120
5	Syringe to microcross, supply tubing	Upchurch	0.005" ID PEEK tubing	**3482793**
6	Microcross to pulse valve, waste tubing	Upchurch	0.0025" ID PEEK tubing	**3482922**

Setup and Configuration

Figure 3 shows the parts (listed in Table 1) used in this configuration.

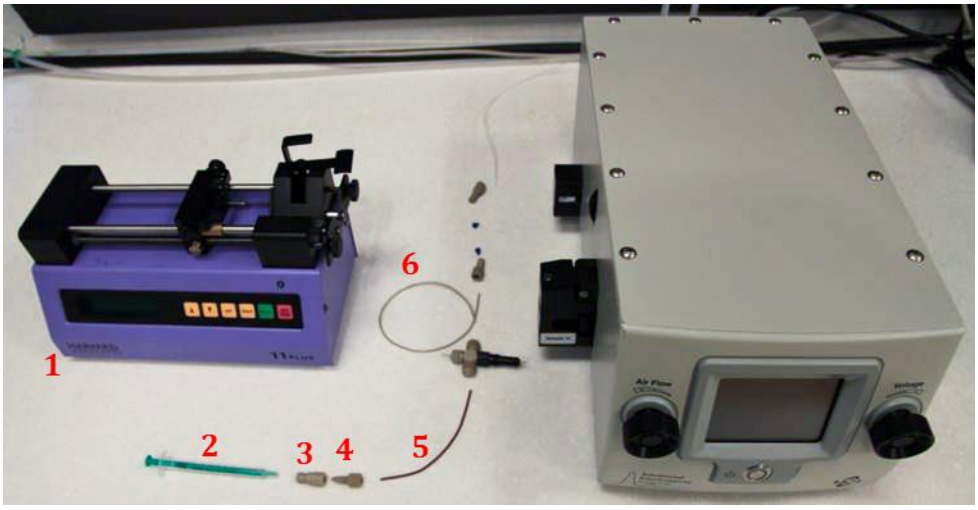

Figure 3: Materials used to operate EAG with syringe pump

[1] Bold part numbers indicate TSI part numbers. All other part numbers indicate manufacturer part numbers.

The microcross and waste line fittings are not numbered as they are part of any standard configuration using the EAG and are included with the EAG. The supply and waste tubing (items 5 and 6 respectively) are also part of any EAG standard configuration; however, the lengths of these components are variable and will affect system setup. The length of the supply and waste tubing and approximate syringe pump flow rates used are listed in Table 2.

Table 2: Sample configuration parameters for operating EAG with syringe pump

Parameter	Dimension/Setting
Air flow rate	1.4 SLPM
CO_2 flow rate	0.1 SLPM
Waste line length	10 inches
Supply line length	4 inches
Drain line opening height	Level with capillary

The general setup procedure is outlined below. For more detailed instructions for steps 1-6, reference the EAG instruction manual. For instructions on how to mix 20 mM ammonium acetate in water buffer, and for information regarding typical solutes or solids to add to the buffer, refer to the EAG instruction manual. For instructions on how to mix 67 mM ammonium acetate in isopropanol and ethanol (50/50) buffer, reference application note EM-004 located at www.tsi.com.

General Setup

1. Connect power and power on the EAG.
2. Connect the drain line from the waste reservoir to the pulse valve.

Note
Note: In this configuration, the drain line opening was kept at capillary height by inserting the drain line into a much larger diameter tube leading to the waste reservoir. As shown in Figure 4.

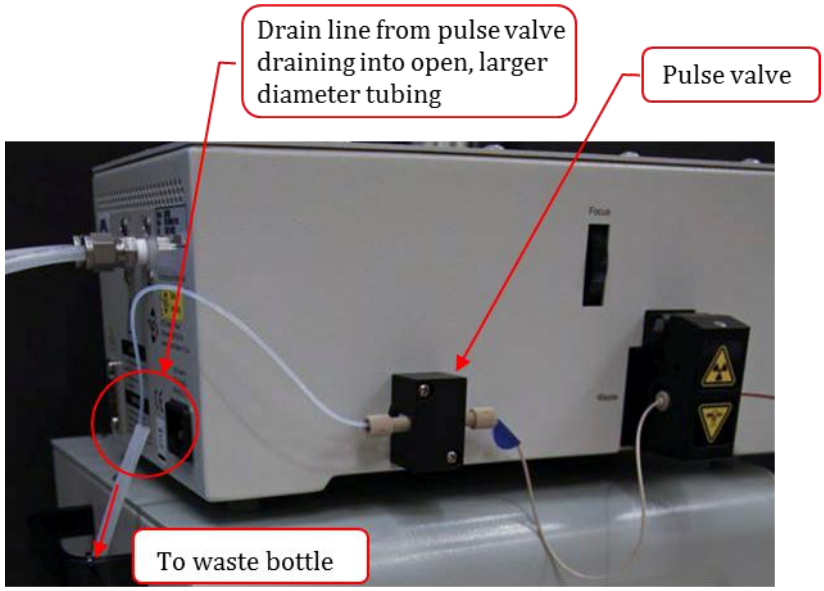

Figure 4: Maintaining constant pressure in the drain line by venting the drain line tube

3. Connect the waste line from the pulse valve to the microcross.
4. Install a capillary in the microcross and insert the microcross in to the EAG.

5. Connect the filtered air supply and CO_2 to the EAG and set the proper flow rates.
6. Connect the aerosol outlet of the EAG to a downstream device or chamber, if applicable.

Note
Keeping the pressure at the EAG outlet constant is critical as it directly affects the flow through the capillary, and therefore the droplet diameter. It is often convenient to attach a filtered vent on the aerosol outlet to maintain ambient outlet pressure, as shown in Figure 5 and shown installed in Figure 1.

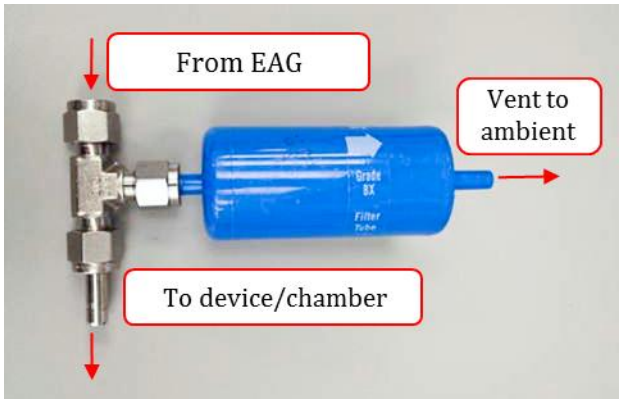

Figure 5: Filtered vent for pressure relief at outlet of EAG

Syringe Pump and Flow Setup

7. Fill a clean syringe with buffer solution and expel any air in the syringe.
8. Connect the syringe to the sample line using the two Luer-to-PEEK fittings as shown in Figure 3.
9. Install the syringe in the syringe pump. Refer to the syringe pump manual for instructions on how to load a syringe and set the limit switch and flow rate. The internal diameters for the syringes used in this example are listed in Table 3 below.

Table 3: Syringe diameters

Syringe	Internal Diameter
Plastic Henke Sass Wolf GmbH 1 mL (PN: 4010.200V0)	4.66 mm
Glass Hamilton 1 mL (PN: 81320)	4.61 mm

10. Purge the sample line, microcross, and capillary until all of the air bubbles in the system have been expelled from the sample line using one of the following methods:
    a. Setting the syringe pump to the operating flow rate and allowing the sample to flow through the system.
    b. Increasing the syringe pump flow rate to roughly 10 to 20x the operating flow rate.
    c. Manually injecting buffer into the system using the syringe by hand prior to installing it in the syringe pump as shown in Figure 6.

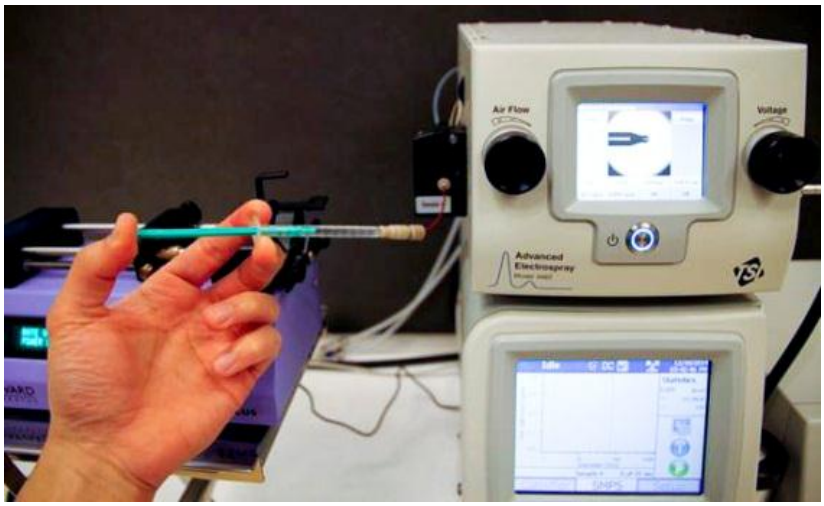

Figure 6: Manually purging the 3482 EAG with buffer

Firmly tapping the syringe, sample line, and microcross during the purging process can help expedite and ensure the removal of air bubbles. Figure 7d shows a bubble in the capillary. Air bubbles in the microcross can prevent the sample from grounding as shown in Figure 7c.

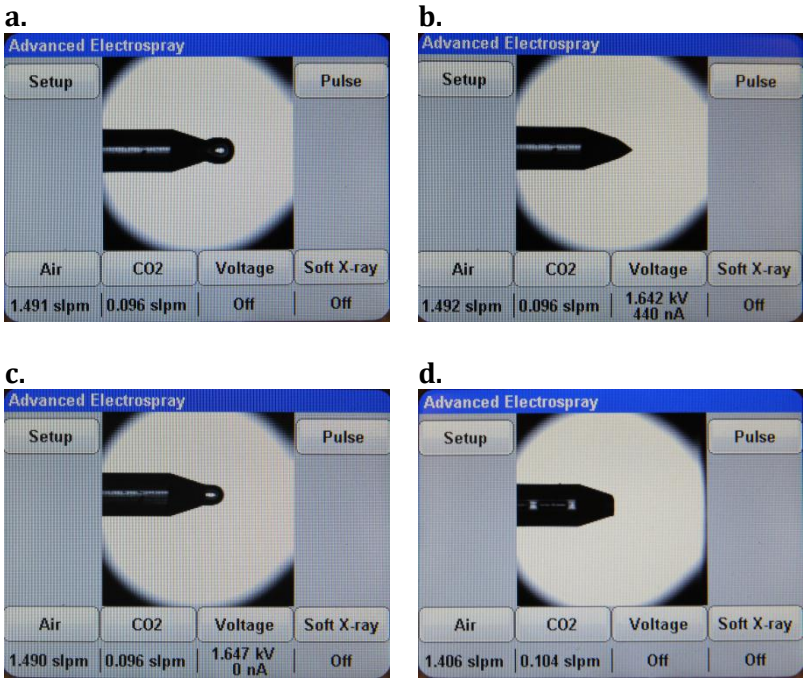

Figure 7: Common capillary states. a. Dripping mode, b. Ideal Taylor cone, c. Ungrounded buffer, d. Bubble in capillary

11. Set the syringe pump to the desired sample flow and allow the dripping mode to stabilize. In this configuration stabilization should take approximately 1 min. Figure 7a shows an ideal dripping mode.

    The flow rate values listed in Table 4 are values used in this example, for reference. It may be necessary to use values outside this range depending on the particular setup. Ideally, drops will form and release from the capillary tip at a frequency of approximately one drop per second.

    If purging at an increased flow rate (step 10b), it may be helpful to allow built-up pressure in the system to dissipate by setting the desired sample flow, stopping the syringe pump until flow through the capillary ceases, then immediately restarting the syringe pump at the desired sample flow.

Table 4: Typical syringe pump, voltage and current settings for the buffers used in this example

Buffer Type	Syringe Pump Flow Rate	Voltage	Current
20 mM ammonium acetate in water	3.0–4.5 µL/min	1.5–1.7 kV	420–570 nA
67 mM ammonium acetate in isopropanol and ethanol (50/50)	2.0–3.0 µL/min	0.9–1.0 kV	50–100 nA

Electrospraying

12. Turn on the voltage and soft x-ray.
13. Increase the voltage until the fluid at the capillary tip forms a Taylor cone as shown in Figure 7b. If the current does not increase with the increase in voltage and a Taylor cone is unachievable, as shown in Figure 7c, it is likely that the sample is not grounded. This can be caused by air bubbles in the microcross.

    The required voltage will depend on the conductivity of the sample and the flow rate of the sample through the capillary. Typical voltage settings and the resulting current values for the samples used in this example are shown in Table 4.

Changing Syringes

When changing syringes, it is important to prevent bubbles from entering the sample line.

14. Fill a clean syringe with the sample to be electrosprayed and purge any bubbles from the syringe.
15. Turn off the high voltage and soft x-ray on the EAG.
16. Turn off the air and CO_2 on the EAG.
17. Stop the syringe pump.
18. Remove the Luer-to-PEEK fitting from the end of the syringe and attach it to the new syringe.
19. Turn on the air and CO_2 on the EAG.
20. Repeat steps 10-13 to begin spraying.

Cleaning the Sample System and Capillary

Between samples, and after any sample in the electrospray, flush the capillary with buffer solution to remove any material that has deposited on the walls of the sample tubing or capillary. More rigorous cleaning procedures can be found in the EAG Instruction Manual.

Example: Determining Droplet Diameter as a Function of Sample Flow Rate

Using the procedure described above, a 1% solution of sucrose was sprayed at several different sample delivery flow rates. The size and concentration of the resulting sucrose particles were measured using a 3938 SMPS spectrometer. Figure 8 shows an example of the size distribution of electrosprayed 1% (by volume) sucrose in 20 mM ammonium acetate buffer.

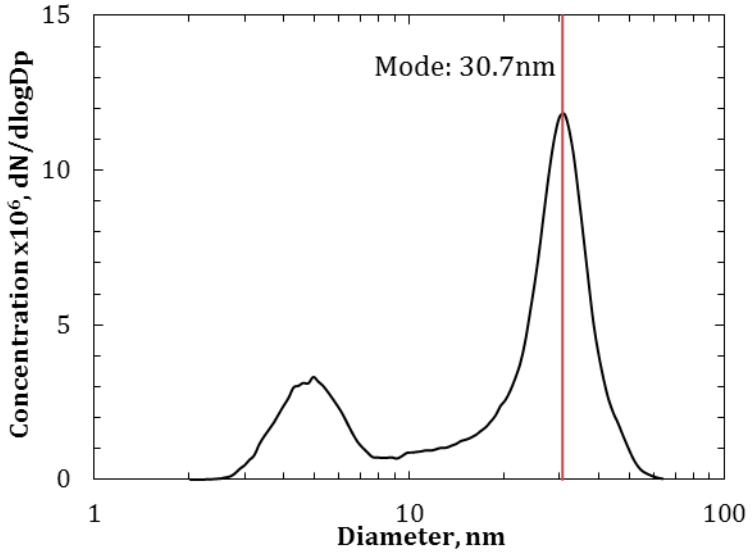

Figure 8: Example electrosprayed solution, 1% Sucrose, 3.5 µL/min, 1.65 kV, 422 nA, 1.4 LPM Air, 0.1 LPM CO_2

As shown in Figure 8, at 3.5 µL/min the mode particle diameter is 30.7 nm. Using Equation 1, where d_D is the initial droplet diameter, d_P is the particle diameter (30.7 nm) and C is the solution volume concentration (1%), the initial droplet diameter for 3.5 µL/min in this configuration is calculated to be 142 nm.

$$\frac{\quad}{\quad} \qquad \text{Equation 1}$$

To determine the effect of syringe pump flow rate on initial droplet diameter, the syringe pump flow rate was varied from 3 to 4.5 µL/min and the droplet diameter calculated at each flow rate. Above 4 µL/min, while the mode diameter continued to increase, the monodisperse peak began to broaden into a much more polydisperse distribution. The effect of syringe pump flow rate on initial electrosprayed droplet diameter can be seen in Figure 9.

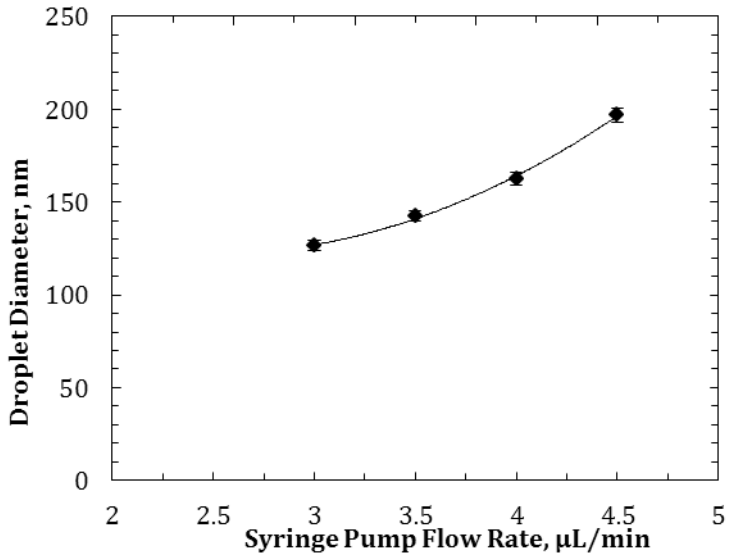

Figure 9: Effect of syringe pump flow rate on initial electrosprayed droplet diameter

The EAG is often used to generate monodisperse particles. As indicated by Figure 9, as the sample delivery flow rate is increased, the initial droplet size, and therefore the final residue particle size, increases. As such, it is critical that the syringe pump used be able to maintain a stable, accurate, and reproducible flow rate throughout the course of testing.