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Nanoparticle Electrospray Apparatus Manual

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Contract Scientific Authority: D. Pedersen, DRDC Suffield

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Nanoparticle Electrospray Apparatus Manual

Prepared by Adam Malcolm at Trent University, 2009

Table of Contents

1. Schematics and Part Description

The following figure shows the side profile of the electrospray apparatus, with the major areas labeled. Each area will be expanded and explored hereafter.

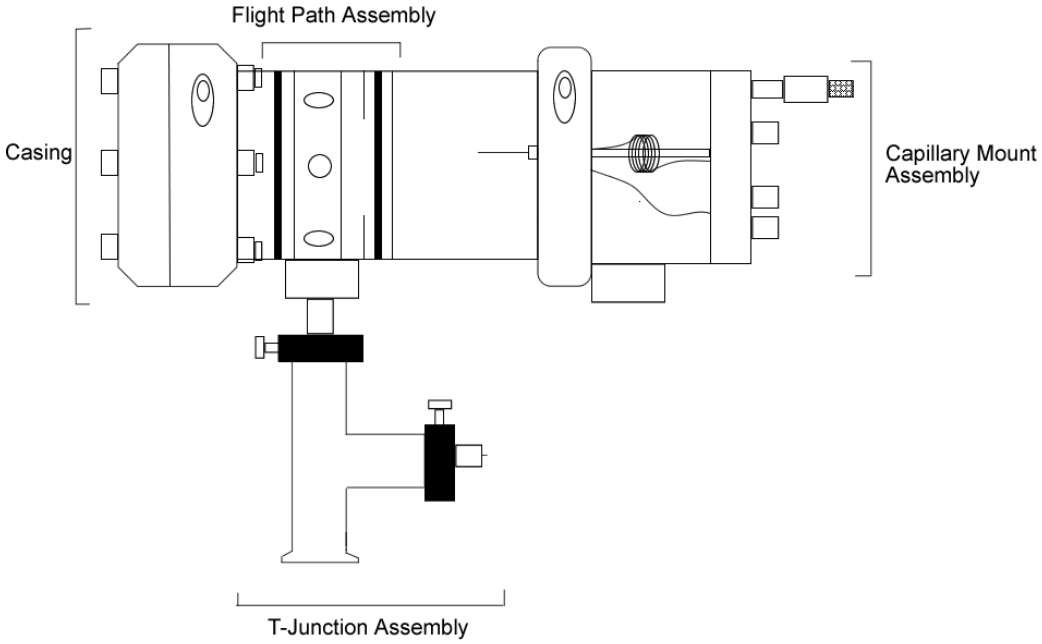


Figure 1.1: Side profile of the apparatus. The casing end is hereafter referred to as the front end, and the capillary mount assembly end is referred to as the rear end. Note that this is merely a simplified representation of the apparatus, and is not to scale.

The ***capillary mount assembly*** is where the analyte is injected, and fed through a series of tubes to reach the nickel capillary tip. The ***flight path assembly*** is the section that contains the skimmer cones, rubber o-rings, and spacer disks that ions will have to pass through in order to reach a detector or spectroscopic window on the other side. The ***T-junction assembly*** is a front-port mounted adapter where BNC cables can be attached and more importantly where rough or turbo differential pumping is attached. The ***casing*** refers to the round plexiglass housing where everything is attached.

1.1 – Casing

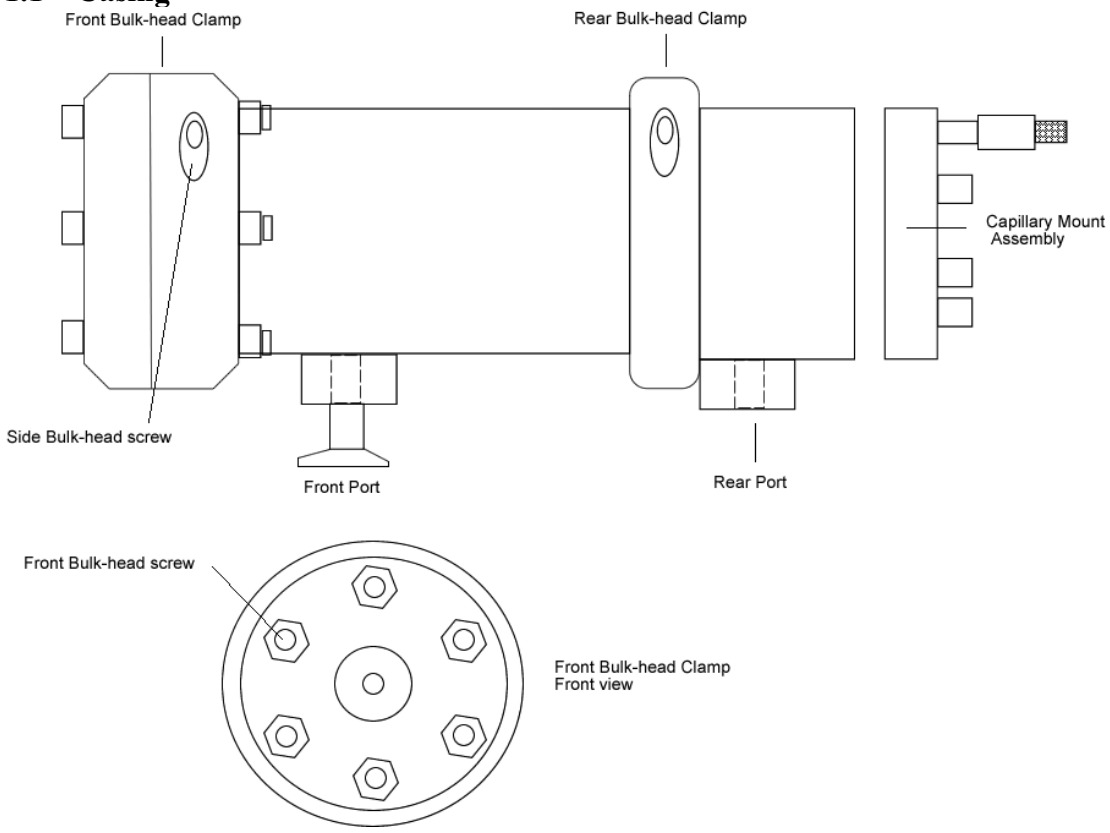


Figure 1.2: Plexiglass casing with its attached ports and clamps.

The electrospray casing is composed of 2 fitted plexiglass tubes with two bulkhead clamps, and 2 ports for pumping. It is also capped by the capillary mount assembly, thereby creating a contained environment for the electrospray. The front bulk-head can be removed so that the flight path assembly can also be removed. The rear bulk-head can be taken off to separate the two fitted tubes. The front port is adapted to the T-junction where pumping can be attached. The rear port can also have a pump fitted to it, however it is currently left opened in order to feed a N_2 curtain gas flow.

1.2 – Capillary Mount Assembly

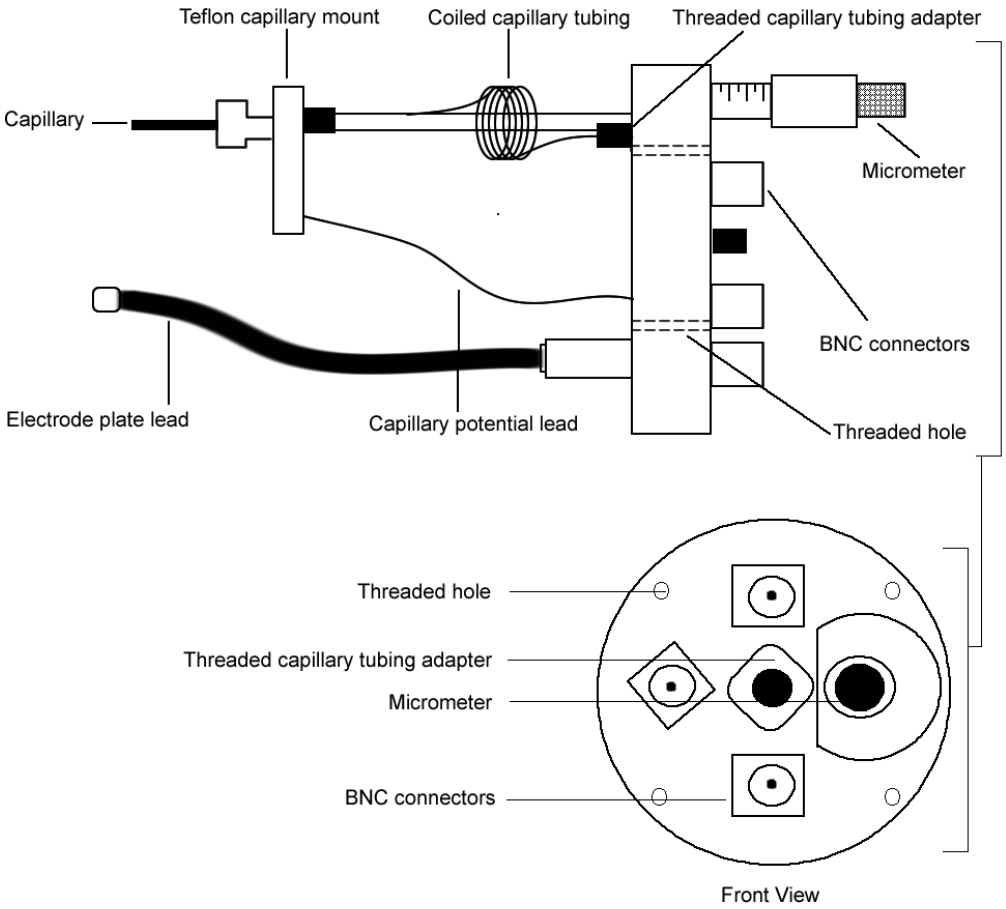


Figure 1.3: Capillary mount assembly detailed view

The capillary mount assembly is the place where liquid samples begin before being electrosprayed. Fluid is pumped from a mechanical syringe pump to the first threaded capillary tube adapter (the black squares in the above figure) and then through the coiled capillary tubing and out of the capillary. The micrometer can be used to move the capillary mount back and forth. The capillary is charged via a BNC connection on the front end of the assembly (see front view). Similarly, the electrode plate from the flight path assembly is charged via a lead attached to a BNC connector here as well. Because the orientation of the apparatus can vary it is difficult to discuss references to the top and bottom of the apparatus, so the front view in the above figure is the standard reference point.

The BNC connections are as follows:

Bottom: Electrode plate
Left: Capillary potential
Top: N/A

The top BNC connection is empty.

1.3 – Flight Path Assembly

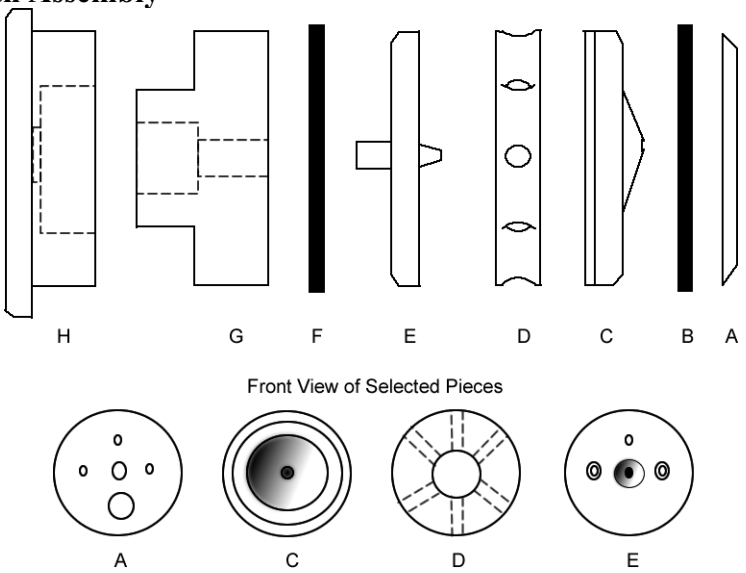


Figure 1.4: Flight path assembly pieces in the order they are placed inside the apparatus.

The flight path assembly is the set of plates, skimmer cones and spacers the ion beam must fly through in order to make it through the apparatus to a detector or window. The flight path consists of the following:

A – Electrode plate
B – O-ring (rubber)
C – Skimmer cone A (large)
D – Pump adapter disc
E – Skimmer cone B (small)
F – O-ring (rubber)
G – Flight path spacer
H – Front bulk-head plate

Also see the selected front view of some pieces for standard orientation.

This series of parts can be changed and altered to suit the desired modifications of the apparatus, as long as the pump adapter disc lines up with the front port of the casing (for pumping purposes). The electrode plate must also be first as it is required to be next to the capillary in order to form a Taylor cone for electrospray. It is charged via the electrode plate lead on the capillary mount, which inserts into either the left or right small holes (see A front view). Whichever hole the lead is inserted into, the other hole will have a small rubber tube for the curtain gas. The second skimmer cone can be charged to keep ions on course by putting it in contact with a small copper flat from the T-junction assembly. The front bulk-head plate is also the same front bulk-head labeled on the casing diagram. It serves to cap the front end and attach to the other half of the bulk-head clamp via 6 hex nut screws (see front view of casing, figure 1.2).

1.4 – T-Junction Assembly

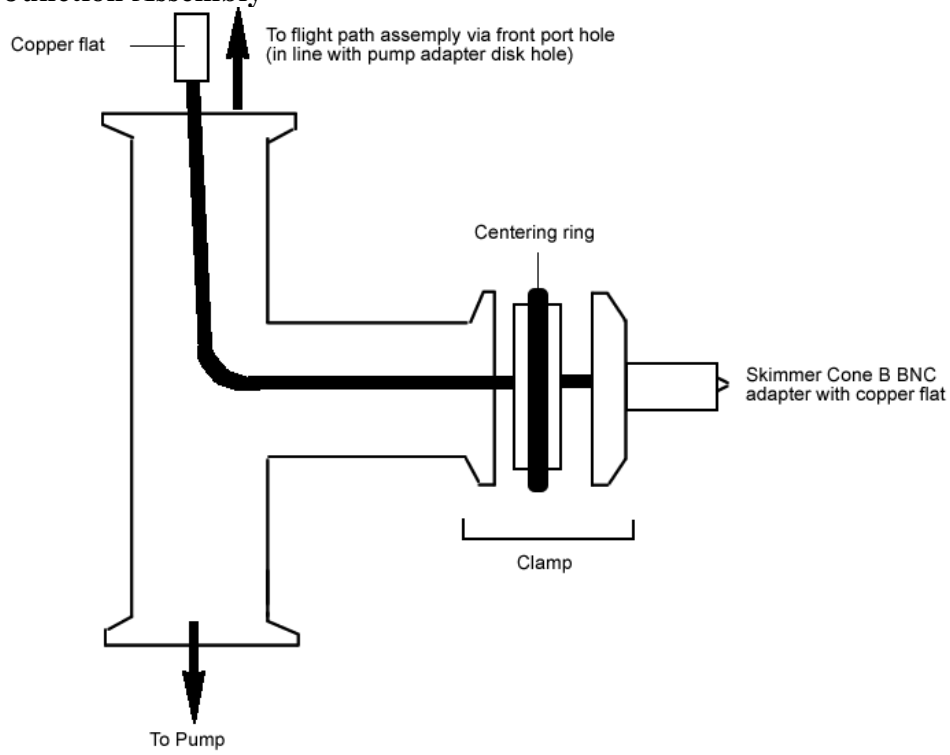


Figure 1.5: Cross section of the T-junction assembly; a 4-way junction can also be used.

The T-junction assembly is a 3-way (or 4-way) chamber which attaches directly to the electrospray casing at the front port, and is directly in line with the pump adapter disc of the flight path assembly. The copper flat is attached to Skimmer Cone B BNC adapter. The copper flat is fed through the T-junction, into the front port and through holes of the pump adapter disc, where it can then be in contact with skimmer cone B to apply a potential. Centering rings are necessary for all ends of the T-junction as they keep the vacuum from the pump, but only the one between the junction and the BNC adapter is explicitly shown here.

2. Assembly and Disassembly

2.1 Assembly

This section will discuss how to assemble the apparatus, however since the apparatus will likely be first used assembled, you may wish to skip to Disassembly (2.2) if you are disassembling it for the first time.

1) In order to reassemble you should have all of the pieces removed and laid out from steps 1 though 10 in section 2.2 Disassembly.

2) Place the two halves of the casing back together, gentle heating may be used to make the fit smoother.

3) Replace both halves of the rear bulk-head clamp and ensure they are snuggly secured. Fasten the two halves together with the side bulk-head screws, fastening each a little bit at a time, until both fasten tight at the same time.

4) Place the flight path assembly in the front end so that they stop at half way through where the other half of the casing has a smaller diameter. Place the pieces in the order shown in figure 1.4, starting with A through to C. Make sure the tapered end of the electrode plate is facing towards the rear, as are the skimmer cones. When placing the o-rings, be sure to apply a small amount of vacuum grease so they form a good seal.

5) When you get to the adapter disc (D), you will need to reattach the T-junction in order to feed the copper flat wire through the port hole and the disc itself. Once the wire is through the disc, screw the T-junction assembly into the front port hole. Re-tape the threads of T-junction with Teflon tape to ensure a tight fit.

6) Take the copper flat wire, and make sure it is wrapping around the circumference of the inner diameter, not obstructing the centre as to block ion flow. Bend the copper flat so that it lies flat on top of the gas adapter disc. The black wire should be wholly in the centre around the circumference of ID; only the copper flat should be on top of the disc.

7) Place skimmer cone B on top of the adapter disc with the copper flat. The copper flat should make electrical contact with the skimmer cone. Place the remaining flight path assembly pieces in the order shown in figure 1.2.

8) Place both the front bulk-head plate and the two halves of the bottom bracket on tightly. Fasten the bottom bracket with the two side bulk-head screws using an Allan key. Make sure the red dots on the front bulk-head plate and the bottom bracket are aligned otherwise the holes on each will not line up enough to fit the screws through.

9) Place the 6 bulk-head screws in the holes, each with their own washer. Then hand-fasten the 6 nuts onto each screw each with its own washer. From here, using an Allan key and small wrench to hold the nuts in place, tighten pairs of screws 180 degrees from

each other, a little bit at a time. Due to the tight fit of the internal pieces, tightening one pair too much before another can cause the bulk-head plate to simply shift in place. Tighten one pair a small amount, then move on to the next pair, repeating this process until all 6 screws are tight and the bulk-head clamp fastened. Note: this may take some time as pairs of screws tend to loosen as others become tightened, due to the shifting of the bulk-head plate.

10) Turn the apparatus on the front end. Place the capillary mount assembly into the top with its rubber o-ring. Ensure the red markers on the casing and the mount are aligned. As well, be sure to insert the electrode plate lead into one of the holes of the front electrode plate (either the left or right hole, using figure 1.4 front view A for reference, whichever isn't occupied by the curtain gas tube). Place the four silver screws in and tighten in pairs exactly as in step 9.

11) Re-tape the threaded hose adapter with Teflon tape, and screw into the front end. The apparatus can now be attached to a vacuum system. When ready, re-attach pump hose to T-junction and BNC connectors. Pull the curtain gas tube through the front port hole.

2.2 Disassembly

1) In order to disassemble the device, you will first need to disconnect all BNC wires if attached, and any pumping hoses. The following instructions will go through step by step how to take the apparatus apart, with individual sections for the section specific parts.

2) Before beginning, identify the markers on the bulk head. These are two dots (coloured red if the colour hasn't worn off) that should be aligned. There should also be a set of similar dots on the rear end, on the capillary mount. When the apparatus is reassembled, these must line back up.

3) Stand the apparatus on the front end so that the capillary mount is on top. Unscrew the four silver screws on the capillary mount. The threading is a tight fit, so it may feel stiff at first.

4) Remove the capillary mount assembly by lifting it out, bringing the sealing o-ring with it.

5) Now that the capillary mount is out of the way, turn the apparatus on its rear end so the front bulk-head clamp is facing up. Using an Allan key and small wrench, hold the nuts underneath and unscrew each bolt. There are six in total that must be removed, and each should disassemble into 1 nut, 1 bolt, and 2 washers.

6) Using a smaller Allan key, remove the 2 side bulk-head screws.

7) The bottom portion of the bulk head should now split into two halves and come off with relative ease. Next use the threaded hose adapter that screws into the front face of

the apparatus to pull the front bulk-head plate out. If the plate feels stuck, it is because the ID of the casing is exactly matched to the OD of the flight path assembly pieces. You should use a heating gun to heat the plexiglass casing. Once heated, the bulk-head plate should slide out with almost no effort.

8) Remove the flight path assembly pieces, remembering which order they go in. You should use the heat gun method from step 7 to do this, as well use a flat ended rod to push gently from the rear end. The pieces can only slide out the front end. For ease of reassembly, note the position of the front electrode plate with respect to the red markers on the casing. This will make it easier to reposition the attached rubber hose which must come out of the rear port hole.

As you remove the flight path pieces you'll come to the pump adapter disc, which should have the copper flat on top of it. At this point, remove the T-junction by unscrewing it from the front port – this copper flat should come out with it, through one of the gas adapter holes.

9) With everything removed, remove the rear bulk-head clamp by removing the two screws with an Allan key. The two halves should again split relatively easily.

10) Grasping both ends of the casing, gently twist until the two halves separate. **However note**: unless you need to polish or modify the casing, these should not be separated. Separation causes some wear and tear scuffing, which makes it difficult for the microscope camera to focus on the capillary through the casing.

2.2.1 Notes on the T-Junction

1) The wire connecting the copper flat and the skimmer cone BNC adapter is long, and will need to be coiled up inside the junction.

2) Flange clamps and centering rings are required at all ends of the junction.

2.2.2 Notes on the Capillary Mount

1) The capillary can be removed or replaced by unscrewing the yellow holder half-way, and then pulling it out.

2) The white wire connecting the BNC to the capillary is held on to the Teflon mount with solder. The wire itself is stiff, thus making it easy to crack the solder. Be gentle!

3) The metal bushings holding the Teflon mount can be loosened and removed for maintenance or cleaning by using a small Allen key to undo the two small screws on its side.

4) There is currently a vanadium shim underneath the washer between the Teflon mount and the yellow capillary holder. This is to ensure the capillary lines up with the centre of

the flight path assembly. This is required due to a small defect in the apparatus that causes the capillary to be aligned off-centre.

5) The capillary tubing adapters fit snug with the capillary tubing, so it is normal for them to be very stiff when trying to remove them.

3. Operation and Operating Conditions

3.1 – Operation

Experimental Preparation

Prior to any experiment, be sure to pump the flight path region for 5 or more minutes via the T-junction. Even though this area is still open to atmosphere in front of skimmer cone A, the influx of air through the small hole is slower than a rough pump can pump it away, so it will pump down. Keep the electrospray apparatus quarantined with a ball or needle valve attached to the front end, so that air doesn't leak into any vacuum system it's connected to.

Liquid Sample Injection

Liquid samples should be low in concentration (below 0.1 M) otherwise you risk altering the surface tension to the point where Taylor cone formation may be difficult or impossible with this apparatus. Surface tension is difficult to predict as it isn't affected exclusively by any single parameter. Literature estimates 10 – 20 mM to be the most efficient working range for electrospray apparatus.

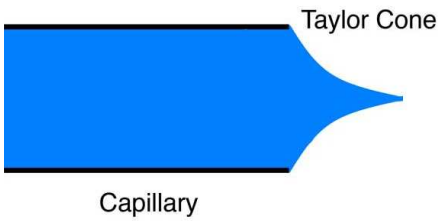
To inject a liquid into the capillary, draw about 5 mL of your solution into the syringe, and attach it to the syringe adapter with capillary tubing. This is connected to the capillary tube adapter on the rear end of the apparatus itself. Place this syringe into the syringe pump, select the flow rate you need and switch it on. Let this run for a few minutes, it will take some time for the liquid to reach the tip of the capillary.

At this time it would also be beneficial to set up the nitrogen counter flowing curtain gas. From the rubber tube coming out of the rear port hole, attach a nitrogen line, flowing between 400 – 500 L/hr to minimize the passage of air into the vacuum.

The Taylor Cone and Electrospray

Once liquid is flowing from the capillary at a regular rate, switch the power supplies connected to the electrode plate and capillary. To run in positive ion mode, the capillary should be positively charged, and the plate should be negative. For negative ion mode, the capillary is negative and the plate is positive. Keep the plate voltage fixed at some low negative or positive number, and change only the capillary voltage.

If running in positive ion mode, for example, set the plate to -400 V and begin with a capillary voltage of 1200 V. At this point, the liquid should seem to be drawn towards the plate. Increase the potential of the capillary in 100V increments until the liquid begins to be drawn in a steady stream towards the centre hole of the plate. Now increase the potential in 50 V increments until the stream collapses into a cone. At this point a Taylor cone has formed, and while small, should have the following general shape.



Matrix Isolation

With the Taylor cone formed, prepare your system for flowing of matrix gas, and set the flow rate to 10 sccm (optimal flow). At this point the nitrogen curtain gas should be flowing, the Taylor cone constantly spraying, and your matrix gas ready to flow. Simultaneously flow the matrix gas (Ar) and open the ball/pin valve between the cold, high vacuum matrix isolation and electrospray apparatus. Let this run for 2 - 5 minutes. Anymore than 5 minutes is unnecessary as the vacuum will draw in too much material, and the thermal load will overwhelm the cold window. A lot of background solvent vapour will also be drawn through, which should be minimized as much as possible. Record a spectrum. A spectrum without electrospray (liquid flowing, but no applied voltage) should also be taken for background solvent comparison.

Post-experimental Procedure

When all experiments are completed to ones satisfaction, the power supplies to the capillary and electrode plate should be shut off first. Close the ball/pin valve, and shut the nitrogen curtain gas off. Turn off the syringe pump, and remove the syringe. Empty the solution from the syringe and clean the syringe with methanol by drawing in a small amount, and letting it clean the inside before purging it. Then draw up a few mL of methanol again, and place it back on the syringe pump; turn the pump on. Let the syringe pump purge the capillary and capillary tubing with 1 – 2 mL methanol. With such a small bore of tubing, analyte residue easily forms clogs, requiring total replacement of the capillary tubing. By purging with methanol, residues are removed and the combination of high vapour pressure and capillary action let the tubing dry out overnight.

3.2 – Operating Conditions and Equipment Use

Electrode Potentials and Flow Rates

The electrode plate and capillary potentials for Taylor cone formation are different for every solvent and analyte system used. This potential difference is known as the onset potential (V_{on}), and its general value is determined by the solvent used, but can deviate depending on the dissolved analyte. Again, high concentrations of analyte greatly affect this number, so stay within the 10 – 20 mM range. The following table lists some common solvents and solvent systems that have been used for electrospray testing.

Table 1: Onset potential differences for different solvent and solutions

	MeOH	CH_3CN	DMSO	Water	MeOH/Water (60/40)	Au NP Solution
V_{on} (V)	~2300	~2500 V	~3000 V	~4000 V	~2400 V	~4000 V

In terms of flow rates throughout the apparatus, nitrogen curtain gases should be kept between 400 – 500 L/hr, and any matrix gas should flow at ~10 sccm. Liquid flow rate through the capillary should be kept low however, between 3 – 6 uL/min. These conditions have been tested to obtain the optimal spectrum in a matrix isolation experiment.

Notes on Solvents

A) Background solvent vapour is a fact of life with this apparatus. Every experiment will contain significant quantities of the solvent from simple vaporization of the sample. To minimize this, a curtain gas of nitrogen is flowed, and a high flow of matrix gas is used.

B) Water is almost always a less than ideal solvent to use for this apparatus as the potential required for Taylor cone formation verges on the limits of the power supply, and at very high potentials, static discharge inside the apparatus begins to occur. Static discharge will disrupt any Taylor cone formation and likely require a reboot of the power supply itself. To lower the required potential, something with a greater vapour pressure is used, like MeOH, acetonitrile, etc. However, often times an analyte will not dissolve in great quantities unless a solvent mixture is used. In the testing of the apparatus, a 60/40 $MeOH/H_2O$ solvent mixture was found to work most efficiently for the desired experiments.

Syringe Pump

Using a mechanical syringe pump means the flow rate of the liquid depends on the speed of the plunger and volume of the syringe. The supplied syringe pump has a calibration wheel that will tell you how fast liquid will flow based on the volume of the syringe and the setting of the pump. For most the work done so far, a 5 mL syringe is used, and the speed of the pump is kept at 1.5 (arbitrary units). This results in a flow rate of ~6 uL/min. Since the pump is measured in units of cc/hr, a conversion factor must be applied as scientific literature typically cites uL/min. There are 1000 uL in 1 cc, thus the number on the pump is multiplied by 16.7 to get a number in uL/min.

Micrometer

The micrometer on the capillary mount assembly moves the capillary to and from the electrode plate. However the scale on the micrometer knob itself is no way correlated to the distance from the capillary to the plate, so readings of the micrometer must always be made in relation to other micrometer readings. In tests that changed the capillary-plate distance, the required V_{on} was approximately the same regardless of the distance, though

at very close range discharge is more common, again depending on how high the potential is set.

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This is a user's manual describing components, assembly, and operation of an electrospray-type source. The apparatus was designed to allow nanoparticles from solution to be sprayed into a high vacuum environment and deposited into solid rare-gas matrices. It was fabricated at Trent University.

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nanoparticles, aerosol, electrospray, matrix solution

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