# Ion and Droplet Mass Measurements of an Electrospray Emitter using an ExB Filter

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**Abstract: Ion and droplet mass-to-charge measurements of electrospray from a single emitter tip were taken using an ExB type filter. The propellant used was the ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMI-$BF_4$), which has three distinct anion species, $BF_4^-$, $[EMI^+]$ $[BF_4^-]_2$, $[EMI^+]_2$ $[BF_4^-]_3$ during electrospray operation. Theoretical calculations show that the ExB filter would be able to resolve three anion species and the coincidently extracted droplets during a voltage sweep of the electrodes. The results from the experiment show peaks corresponding with the theoretical values of 87, 287, and 485 amu/e for the three $BF_4$ anion species, respectively, within experimental error. A broad peak was also observed at 6258 amu/e with a width of 6487 amu/e that corresponded to the range expected for droplets emitted at varying charge. Varying systematic errors were observed during the experiment, but remained consistent within a given test. Therefore, calibration factors based on the difference in the measured and theoretical potential on the ExB deflection electrodes for a given mass-to-charge ratio was determined for each test, which reduce the disagreement to within ±3% of the theoretical values. Proportional trend between the magnitude of the current peaks and the flow rate of the supplied EMI-$BF_4$, and the magnitude of the current peaks and the extraction voltage were also observed. Based on the number of peaks observed during operation at various flow rates, it was also found that the electrospray was operating in both the pure ion and ion-droplet regimes.**

## Nomenclature

| | | |
|---|---|---|
| amu | = | Atomic mass unit ($1.66\times10^{-27}$ kg) |
| $B$ | = | Magnitude of magnetic field (Tesla) |
| d | = | Distance between ExB electrodes (m) |
| $d_{col}$ | = | Distance between emitter tip and collimator opening (mm) |
| $d_{cp}$ | = | Distance between emitter tip and the collection plate (mm) |
| $d_{ex}$ | = | Distance between emitter tip and the extraction electrode (mm) |
| $D_{col}$ | = | Diameter of ExB collimator opening (mm) |
| $D_t$ | = | Diameter of emitter tip (μm) |
| $e$ | = | Elementary charge ($1.6\times10^{-19}$ C)) |
| $\varepsilon_o$ | = | Vacuum permittivity ($8.854\times10^{-12}$ F/m) |
| $\varepsilon$ | = | Relative permittivity of a liquid |
| $E$ | = | Magnitude of electric field (V/m) |
| $f(\varepsilon)$ | = | F. de la Mora's factor for electrosprays |
| $\gamma$ | = | Fluid surface tension (N/m) |
| $I_{emis}$ | = | Electrospray emission current (nA) |

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$I_{sp}$ = Specific impulse (sec)
K = Fluid conductivity (S/m)
$M_p$ = Mass of particle (amu)
$\eta$ = Non-dimensional flow parameter
L = Length of ExB filter that acts on a particle (m)
$q_p$ = Charge of a particle
$q_{D,max}$ = Maximum possible charge of a droplet
$Q$ = Flow rate (nL/min)
$\rho$ = Density (kg/m$^3$)
$r_D$ = Droplet radius (m)
$r_j$ = Taylor jet radius (m)
$u_p$ = Particle velocity (m/s)
$u_{p,min}$ = Minimum particle velocity that can pass through ExB filter (m/s)
$u_{tuned}$ = Tuned particle velocity in ExB filter (m/s)
$V_{ex}$ = Extraction voltage (Volts)
$V_{ExB}$ = Potential on ExB deflection electrodes (Volts)
$V_{corr}$ = Voltage peaks from CEM output after applying correction offset (Volts)
$V_{meas}$ = Measured voltage peaks from CEM output (Volts)
$V_{theory}$ = Theoretical voltage peaks expected in CEM output (Volts)
$V_{accel}$ = Particle accelerating voltage (Volts)
$V_{start}$ = Starting voltage for ion emission (Volts)

## I. Introduction

ION and droplet mass distribution in the beam of electrospray thrusters has been measured and characterized by Chiu[1,2], Lozano[3] and Gassend[4] using stopping potential devices, TOF spectrometers, and quadrupole mass spectrometers. Stopping potential devices are a simple way to measure potential distribution within an electrospray beam, but cannot discriminate droplet or ion mass, while TOFs and quadrupole spectrometers can measure mass, but are usually complicated instruments, and the fabrication and testing of custom spectrometers is a significant undertaking. Therefore, though these studies provided valuable results, there is motivation to develop a simple and effective way to obtain similar results. A Wien filter, otherwise known as ExB filter, may provide an inexpensive and simple method for measuring particle mass in electrospray beams. Unlike spectrometers and stopping potential devices, ExB filters distinguish different species of charged particles based on their velocities. If the accelerating potential is known independently due to extraction electrode settings it should be possible to derive mass information within the beam from a simple ExB device.

## II. Goal of Reaseach

The goal of this research was to determine whether an inexpensive and simple ExB filter can be used to measure the mass distribution of particles emitted from electrospray thrusters operating in both ion and droplet mode. Background covering electrospray thrusters and the theory behind the ExB filter's operation and resolution capability will be presented. This will be followed by the results recorded during the filter's experimental operation within the ion beam of an electrospray emitter operating on 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF4).

## III. Background

### A. Electrospray Thrusters

Electrospray thrusters can be manipulated to operate in pure ion, pure droplet, or mixed mode, which opens up the possibility of operating over a broad range of $I_{sp}$'s. For a given beam power, droplets would provide a larger thrust due to their size, which would have the thruster operate at a lower $I_{sp}$. Ions exit at much higher velocities but provide less thrust due to their size, thus they have very high $I_{sp}$ for a given beam power. A balance between ion and droplet emission would therefore provide a means to optimize an electrospray thruster for a given propellant and mission.

**B. ExB Filter Theoretical Operation**

As ExB filters are typically used to measure variations in ion species fractions by their velocities, theoretical calculations were done to prove that the filter would be able to discern the mass distributions of ion and droplet emission of an electrospray emitter.

*1. Traditional Operation*

For an ExB filter to detect ions or charged droplets the particles must travel through the electric and magnetic fields, undeflected, to reach the charge-exchange multiplier (CEM), shown in Figure 1. Therefore, the net Lorentz force acting on the particle within the filter section must be zero. This criterion is met if the particle velocity is equal to E/B. By using permanent magnets in the filter the magnetic field is a constant, leaving the electric field as the controllable variable in the device. By varying the voltage on the two deflection electrodes, and consequently the electric field acting on charged particles, the filter will allow particles of differing 'tuned' velocities to travel through the device. While strictly only a velocity filter, ExB filters have also been used to measure variations in ion species fractions based on an a priori knowledge of the ion accelerating voltage[5,6].

*2. Measuring mass-to-charge ratios of ions*

Although an ExB filter is strictly a velocity selector, if the accelerating voltage for the ion beam is known then the ExB filter can detect the charge-to-mass ratio in the beam. The equation for the kinetic energy of a particle can be rearranged, with the electric field inside the filter defined as $E = V_{ExB}/B$, to give the mass-to-charge ratio distribution as a function of the accelerating voltage of the electrospray beam and the potential on the ExB electrodes. This is shown in Eq. (2).

$$\frac{\mathrm{M_p}}{q_p} = 2eV_{accel}\left(\frac{\mathrm{d}\cdot B}{V_{ExB}}\right)^2 \tag{2}$$

Along with measuring the mass-to-charge ratios of particles passing through the filter, the resolution of the filter must be such that it is possible to discriminate the particles of interest within the beam. Often this condition is easily met. For instance, ExB filters used within the plume of a Hall thruster need only discriminate between Xe+, Xe2+, and Xe3+ and these peaks are widely separated. However, in an electrospray beam there may be a number of ions with similar mass-to-charge ratios and/or droplets with a near continuous distribution of mass. For the diagnostic to be useful it must be capable of resolving the relevant species. The primary limit on the velocity-resolving capability of the filter is the imperfect collimation of the entrance beam.

The entrance aperture and collimating aperture have a finite diameter and thus admit particles into the filter that have trajectories other than directly down the filter midline; because of this, for a given velocity selection (value of E/B) particles that are slightly above and below the corresponding velocity will still pass through the filter, as shown in Figure 1. If the different species of ions and particles have masses that differ too little then they cannot be resolved from the measured output of the ExB filter.

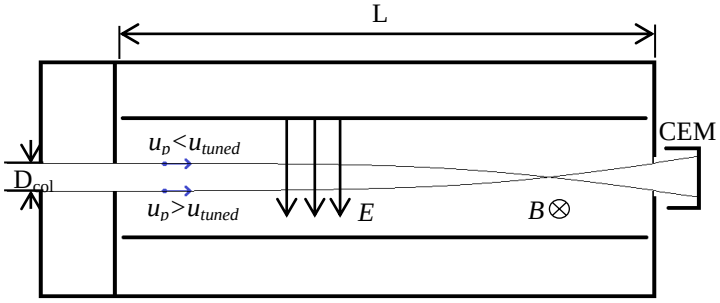


**Figure 1. Trajectory of particles with velocities slightly above and below the tuned velocity yet can still pass through the ExB**

Therefore, the variations of the mass-to-charge ratios for particles with off-axis trajectories that would pass through the collimator were estimated. The mass-to-charge ratio of a particle passing through the ExB filter is defined as seen in Eq. (3).

$$\frac{\mathrm{M_p}}{q_p} = \frac{2\mathrm{D_{col}}u_p^2}{eL^2(E-u_pB)} \tag{3}$$

In this equation the 'tuned' velocity of the ExB filter is $u_p = \frac{V_{ExB}}{\mathrm{d}\cdot B}$, $\mathrm{D_{col}}$ is the diameter of the collimator, and L is the length of the filter that acts on a particle. To find the mass resolution of the filter Eq. (3) was solved using the minimum and maximum velocities that can pass through the ExB filter, which were then subtracted from the mass-to-charge ratio at the tuned velocity, and then the difference was divided by the mass-to-charge ratio at the tuned velocity, shown in Eq. (4).

$$\frac{\delta\mathrm{M_p}}{\mathrm{M_p}} = \frac{\left(\frac{\mathrm{M_p}}{q_p} - \left(\frac{\mathrm{M_p}}{q_p}\right)_{min}\right)}{\frac{\mathrm{M_p}}{q_p}} \tag{4}$$

The minimum velocity shown in Eq. (5) was derived using a combination of the equation of motion and the Lorentz force as they apply to a particle being accelerated prominently by either the magnetic or electric fields across a distance equal to the diameter of the collimator. The maximum velocity is the same as Eq. (5) with the exception of the first term being negative.

$$u_{p,min} = \left(\frac{\sqrt{B^2\mathrm{L}^4(eq_p)^2 + 8\mathrm{M_p}eq_p\mathrm{D_{col}}E}}{4\mathrm{M_p}\mathrm{D_{col}}}\right) - \left(\frac{Beq_p\mathrm{L}^2}{4\mathrm{M_p}\mathrm{D_{col}}}\right) \tag{5}$$

A graphical representation of the mass resolution for the ExB filter was produced using a range of particle masses from 50 to 2100amu for an extraction voltage of 1732 V and is shown in Figure 2. 1732 V was calculated to be the starting voltage for the electrospray beam using Eq. (6) in Section IV. This plot shows that the filter will have a mass resolution of ±10.4 %, ±8.4%, ±7.2% and ±4.9% for any particles with mass-to-charge ratios greater than 1000 amu/e, 482 amu/e, 285 amu/e and 87 amu/e, respectively. The latter three correspond to the three lightest, singularly charged EMI-$BF_4$ anion species; any peaks above 1000 amu/e would correspond droplet emission as the probability of singularly or doubly charged anion species at or above this mass-to-charge ratio is very small.

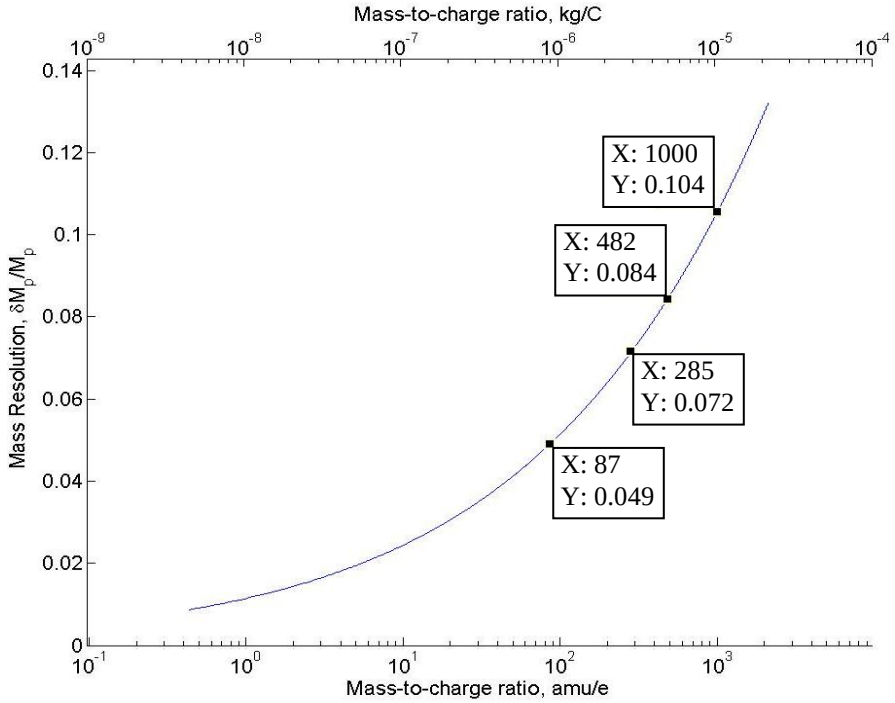


**Figure 2. Mass resolution of the ExB filter at an extraction voltage $V_{ex}$=1732 V.**

## IV. Experimental Methods and Apparatus

An electrospray emission source was fabricated from commercially available capillary tubes and a syringe pump. The source was affixed to the entrance aperture of the ExB filter at a distance of $d_{col}$ = 23 mm and operated at different values of extraction voltage and flow rate. The velocity selection criteria of the ExB filter was swept by varying the plate voltage while the output of the CEM was recorded to obtain a velocity spectra. The overall setup is shown in Figure 3.

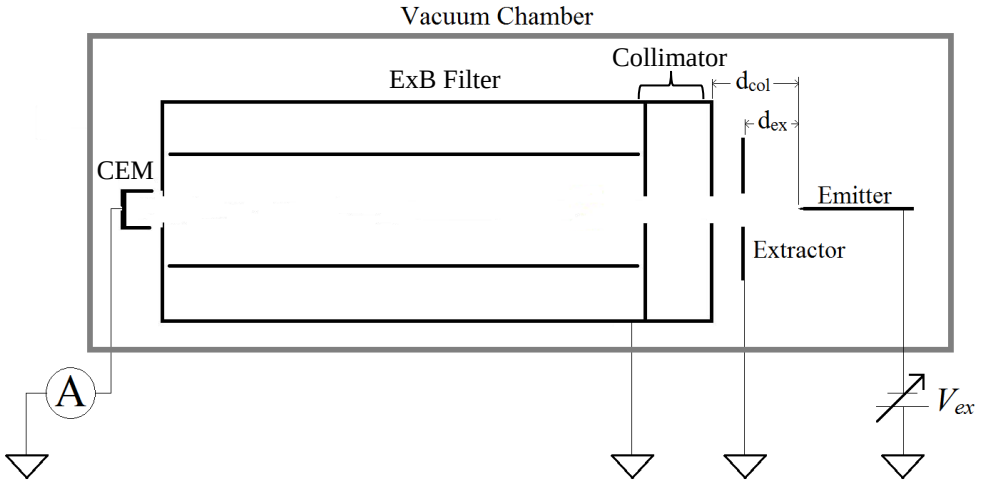


**Figure 3. Setup for measuring the mass-to-charge distribution of the electrospray emitter using the ExB filter.**

### A. Electrospray Emission source

The emitter and feed system to produce the electrospray beam was based off of that used by Lozano[3]. It consisted of a 5.0 µL syringe, a nano syringe pump, 20 µm ID fused-silica capillary tubing, 20 µm ID fused-silica needle emitter with a tip diameter of 10µm, a PicoClear conductive union, and an extraction electrode. The nano syringe pump fed the EMI-$BF_4$ from the syringe through the capillary tubing to the emitter tip, where it was extracted by the electrode. The conductive union was used between the emitter tip and capillary tubing and was held in by set screws in Teflon block. The emitter tip was also inserted through a Teflon plate to ensure concentricity between the tip and the opening in the extractor electrode. 0.04 in Al 3003 was used for the extraction electrode which was positioned at $d_{ex}$ = 3 mm downstream from the needle tip. The extraction potential was applied to the supplied EMI-$BF_4$ via the conductive union by a Glassman ±10 kV power supply. Due to difficulties in floating the ExB filter, the filter was grounded, thus, the extraction electrode was grounded as both the extractor and filter need to be at the same potential.

### B. ExB Filter

The Isp Lab's ExB filter, can be seen in Figure 4 and is composed of a collimator at the entrance to the device to filter divergent particles, Grade N42 Neodymium Iron Boron rare-earth magnets, stainless steel electrodes embedded in blocks of Teflon to produce the electric field, and a Ceramic Charge Exchange Multiplier (CEM) located at the collection end of the filter. The magnetic field produced by the magnets was measured using a gaussmeter to be 0.362 Telsa. The electrodes are held in place by threaded studs which pass through the casing of the filter and also serve as electrical connections.

The CEM input potential was biased using a Glassman high voltage power supply, which was set to a constant value of $V_{CEM}$ = -2300 V for all tests. The

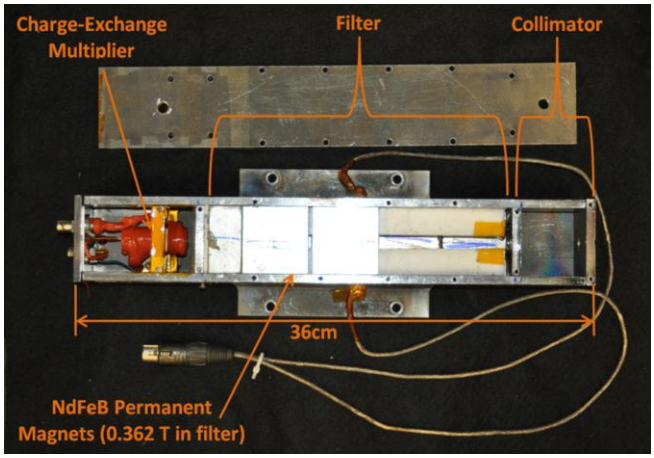


**Figure 4. ExB filter in Michigan Tech's Isp Lab (Open).**

gain of the CEM is proportional to the supply voltage, and is equal to $1x10^8$ for $V_{CEM}$ = -2300 V. The output of the CEM was measured using a Keithley 485 Picoammeter. The deflection plates in the ExB filter were powered by a Keithley 2410 Sourcemeter, which was capable of sweeping the ExB plate potential from zero to 500 V. The output of the Keithley was passed through a voltage divider with a grounded center tap, which forced one plate to be at half the total electrode voltage above ground and the other to be forced to an equal potential below ground. This is done to prevent any effects of deceleration within the filter, as explained in detail by Kieckhafer.[7]

### C. Facility

The vacuum facility uses a Varian Turbo-V 301 attached to an Ideal XDS 5 dry scroll pump to reach a chamber pressure of around $7.0x10^{-6}$ Torr with no instruments inside, and $1.0x10^{-5}$ Torr with the experiment setup. This is below $3.0x10^{-5}$ Torr, the maximum operating pressure that ensures there are little effects from particle collisions between the electrospray beam and the surrounding gases, and below $5.0x10^{-5}$ Torr, the maximum operating pressure of the CEM.

### D. Operating Conditions

The extraction voltage and the flow rate were chosen with the goal of providing a mixed beam of ions and droplets. Equations for both the starting extraction voltage and the non-dimensional flow parameter are given in Ref. 3, and are shown in Eq. (6) and Eq. (7), respectively.

$$V_{start} = \sqrt{\frac{D_t \gamma}{2\varepsilon_o}} \ln\left(\frac{4d_{ex}}{D_t}\right) \tag{6}$$

$$\eta = \sqrt{\frac{\rho K Q}{\gamma \varepsilon \varepsilon_o}} \tag{7}$$

The chosen propellant EMI-$BF_4$ has $\gamma$ = 0.05281 N/m, $\rho$ = 1294 kg/m$^3$, K = 1.15 S/m, and a relative permittivity of 71.48[8]. For the tip diameter and extraction distance used in this experiment, the starting voltage was calculated to be 1732V. The flow rates were chosen based on the non-dimensional flow parameter ($\eta$). In previous works[3,9] it was found that electrosprays emit both ions and droplets for $\eta$ = 1and greater. For EMI-$BF_4$, $\eta$ = 1 translates to 1.348 nL/min. A flow rate 40 nL/min was chosen to ensure the electrospray beam comprised of both ions and droplets. The experiment also encompassed runs that varied both parameters to observe any effects they might have on the mass distributions.

## V. Results

Several experiments were performed using the described apparatus while operating at varying flow rates and extraction voltages. Each test included several voltage sweeps of the potential difference applied to the ExB plates of 0-450 V, with the measured CEM output current recorded simultaneously. The following subsections outline the results from three of these tests.

### A. ExB Voltage Sweeps

*1. Preliminary ExB Sweep (Test A)*

A preliminary ExB voltage sweep test, Test A, was done using the base parameters of 1732 V and 40 nL/min for extraction voltage and flow rate, respectively. The ExB plates were swept from zero to 450V and the CEM output measured. The voltage sweep produced peaks at ~100 V, ~125 V and ~230 V, but also a fourth peak at ~40 V, and is shown in Figure 5.

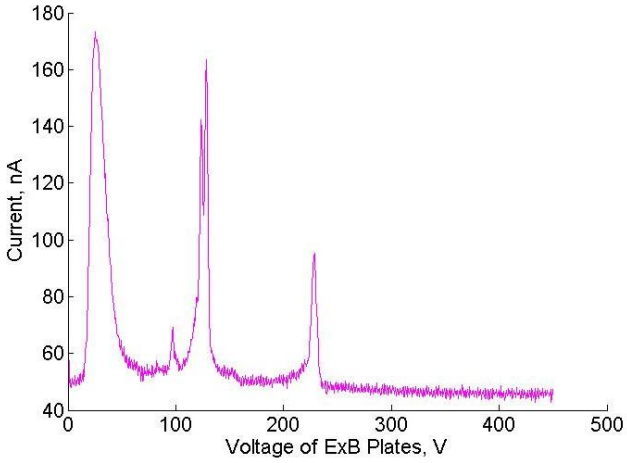


**Figure 5. CEM output current profiles for the ExB voltage sweep Test A. The extraction voltage and flow rate are Q = 40 nL/min and $V_{ex}$ = 1730 V, respectively.**

The potential on the ExB electrodes are proportional to the mass-to-charge ratio given in Eq. (2). Using this definition for the mass-to-charge ratio as a function of ExB potential and assuming the charged particles were accelerated through the full extraction voltage, the sweep in Figure 5 was converted to a CEM output current profile as a function of mass-to-charge ratio, shown in Figure 6.

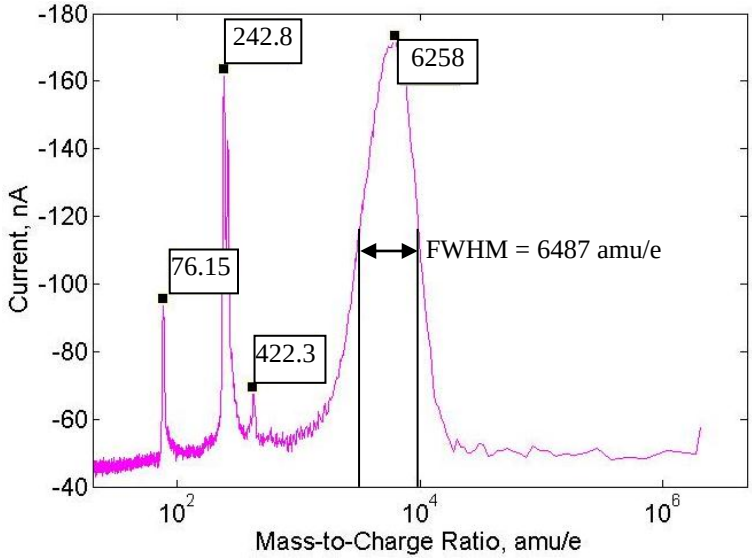


**Table 1. Mass-to-charge ratios corresponding to anion species that would be expected in a electrospray beam, using the ionic liquid [EMI][$BF_4$].[2]**

| Anion species | M/q (kg/C) | M/q (amu/e) |
|---|---|---|
| $BF_4^-$ | $8.996 \times 10^{-7}$ | 87 |
| $[EMI^+][BF_4^-]_2$ | $2.95 \times 10^{-6}$ | 285 |
| $[EMI^+]_2[BF_4^-]_3$ | $5.0 \times 10^{-6}$ | 482 |

**Figure 6. CEM output current profile for the ExB Test A plotted against Mass-to-charge ratio in amu/e.**

Figure 6 clearly shows four distinct peaks that occur at mass-to-charge ratios equal to 76.15, 242.8, 422.3, and 6258 amu/e. The three narrow peaks correspond with acceptable agreement to the expected location of the emitted ions from EMI-$BF_4$ as shown in Table 1. The wider peak at the highest mass-to-charge ratio is likely a continuous distribution of droplets.

*2. ExB Sweeps varying flow rates (Test B)*

With the preliminary test verifying that the ExB filter was able to resolve three anion species and droplets during electrospray emission, another test was performed in which the flow rates were varied to observe any effects there might be in the distribution. Three flow rates of 25, 30, and 40 nL/min were used, with an extraction voltage of 1730 V. The results are shown in Figure 7. Mass-to-charge ratios are calculated assuming the ions were accelerated

by the full extraction potential.

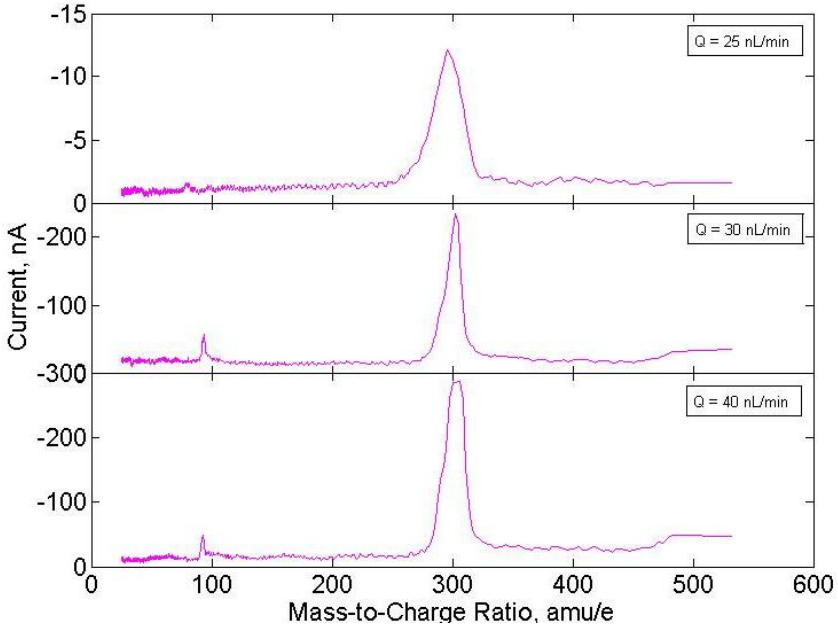


**Figure 7. CEM output current profiles for Test B. The extraction voltage is 1730 V for all runs and the flow rates for each run are labeled.**

*3. ExB Sweeps varying extraction voltages (Test C)*

A test was done using varying extraction voltages to observe any effects in the distribution. All runs had a flow rate of 24 nL/min with an extraction voltage varying from 1730 to 3000 V. The results for Test C are shown in Figure 8. It should be noted that both Figure 7 and Figure 8 are limited to 600 amu/e on the x-axis as no features existed above this point in any sweeps in Tests B and C.

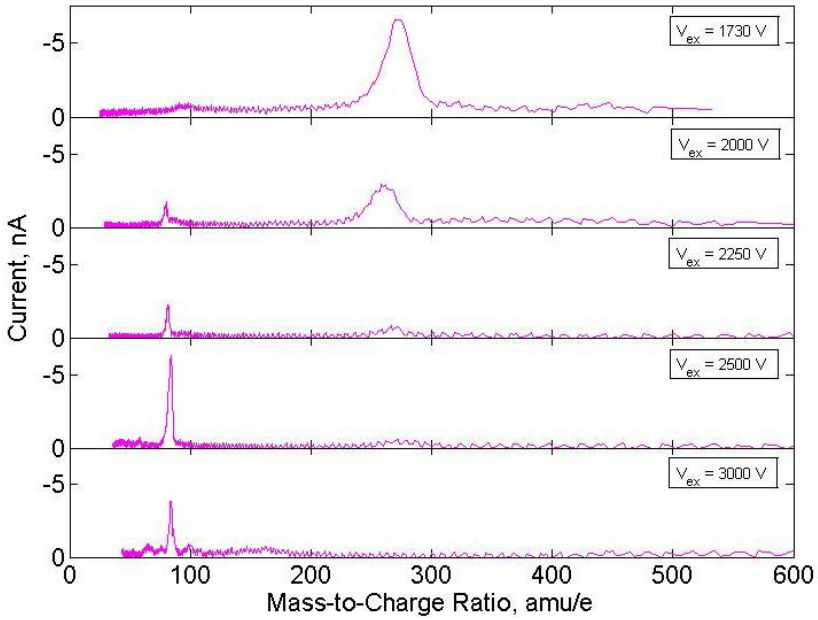


**Figure 8. CEM output current profiles for the ExB Voltage Sweep Test C. The flow rate was set to 24 nL/min and the extraction voltages for each run are labeled.**

## VI. Discussion

The results from these experiments gave conclusive evidence that the setup produced electrospray emission and the ExB filter produce discernable peaks at specific mass-to-charge ratios. Along with the verification of the ExB filter's new capability, several observations were made dealing with the operation of the electrospray thruster and ExB filter.

### A. Droplet Emission

A fourth peak at a mass-to-charge ratio of ~6200 amu/e continued to appear in some test conditions, but remained absent in the other conditions. The apparent width of this peak is ~6500 amu/e, which is far too broad for an atomic or molecular ion, thus the peak is very likely composed of a continuous distribution of droplets.

*1. Expected Droplet Mass-to-Charge Ratio*

Droplet emission has been analyzed is previous works[3] and follows the physics of Taylor cone-jet structures. Droplets form with a surface charge based on the Rayleigh limit, which is estimated by balancing the internal pressure of the droplet and the electric pressure at the droplet surface. At the equilibrium condition the maximum charge is then found by Eq. (8).

$$q_{D,max} = 8\pi\sqrt{\gamma\varepsilon_o r_D^3} \qquad \text{(Ref. 3)} \tag{8}$$

The jet radius, shown in Eq. (9), and the droplet-to-jet ratio of 1.89 are also derived in Ref. 3. The jet radius derivation uses the F. de la Mora's factor for electrosprays, $f(\varepsilon)$, which is about 2.86 for liquids with $\varepsilon > 40.9$.

$$r_j = \frac{1}{1.89}\left(\frac{6}{f(\varepsilon)}\sqrt{\frac{\gamma}{\rho}}\frac{\varepsilon\varepsilon_o}{K}\eta\right)^{\frac{2}{3}} \qquad \text{(Ref. 3)} \tag{9}$$

Knowing the properties of the liquid that makes up the droplet, the mass, maximum charge, and from that, the mass-to-charge ratio of the droplet can be derived. With set operating parameters, the theoretical velocities of emitted droplets can also be calculated. For a range of flow rates the mass-to-charge ratios for droplets holding charges of 50%, 75% and 100% of the maximum surface charge of an emitted droplet are shown in Figure 9.

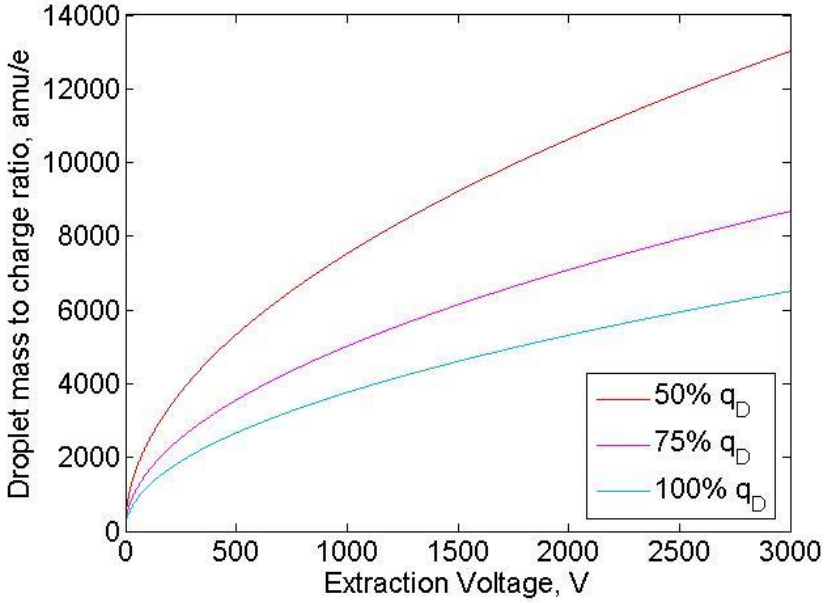


**Figure 9. Emitted droplet mass-to-charge ratios as functions of the Extraction Voltage for an emitter using EMI-BF4; γ=1.15 N/m, ε=71.48, ρ=1.294 kg/m$^3$, K=1.15 S/m.**

From these calculations it was found that any emitted droplets would peak between 4946 to 9892 amu/e and 5941to 11880 amu/e for extraction voltages of 1732 V and 2500 V, respectively. The respective range of masses for each of these theoretical peaks is 4946 amu/e and 5939 amu/e. This means that the spectrum of droplet mass-to-charge ratios should be seen as a wide peak in an ExB voltage sweep. As seen in Figure 6, the peak at 6258 amu/e

has a full width at half maximum (FWHM) of 6487 amu/e. This range of masses cannot represent a single ion species, but instead has a wide range of masses similar to the range seen for theoretical droplet peaks. Therefore, these peaks correlate with droplet emission.

*2. Absence of Droplet Peaks*

The absence of the wide droplet peak was observed in Test B and C and should also be discussed. The likely cause is that during this test there was no droplet emission. This is an unexpected phenomenon as previous works found that operating at flow rate greater than that corresponding to $\eta = 1$ places the electrospray beam in the ion-droplet regime[3]. However, the flow rates for all tests ranged from $\eta = 4.2$ to 5.5. This was intentional as ion and droplet emission was desired, but droplet emission was only observed in the Test A. Droplet emission hasn't fully been characterized, however, two possible reasons have been developed for the absence of emission below $\eta = 1$, which are related to the specific charge of the emitted droplets and the surface tension wave propagation. These are detailed by Lozano in Ref. 3. Therefore, it is possible that another phenomenon has an effect on droplet emission and produced the results seen here.

### B. Relative Magnitudes of Mass-to-Charge Ratio Peaks

Throughout the tests the relative magnitudes of the anion peaks have a consistent trend; the less massive $BF_4^-$ anion peak is smaller in than the peak corresponding to $[EMI^+][BF_4^-]_2$, when operating at lower extraction voltages, while the peaks corresponding to $[EMI^+]_2[BF_4^-]_3$ anions were the smallest in magnitude when observed, and only seen in Test A. This suggests that the mass distribution of the electrospray beam was largely composed of $[EMI^+][BF_4^-]_2$ anion species, with a smaller fraction of the $BF_4^-$ anion species, and occasionally a fraction of the $[EMI^+]_2[BF_4^-]_3$ anion species. This is different than the expected trend, as seen in Ref 2, where the electrospray beam was largely composed of $BF_4^-$ anions, with decreasing fractions of $[EMI^+][BF_4^-]_2$ and $[EMI^+]_2[BF_4^-]_3$, respectively. The difference in the trend seen in this experiment could be related to specific operating conditions, similar to the trends mentioned in the following paragraph.

Trends in the magnitude of the current peaks were also seen with varying flow rates and extraction voltages. As the extraction voltage was increased, the beam became comprised solely of the $BF_4^-$ anions as seen in Figure 8. This phenomenon could be due to the increase in electric stress seen on the Taylor cone which acts more heavily on particles with smaller mass-to-charge ratios. An increase in the flow rate produced a proportional increase in the magnitude of the current as seen in Figure 7. Physically this means that an increase in flow rate forces more propellant into the electrospray beam, and subsequently, ions that enter the filter and the CEM.

### C. Error in Mass-to-Charge Ratio Peaks

The final observation seen in all tests was an error in the measured values when compared to their theoretical values. Table 2 shows the measured mass-to-charge ratios during sweeps in Tests A-C and the error in these peaks compared to the theoretical values. The error in the mass-to-charge ratios for the tests is about -12% for Test A and +5% for Test B and -5% for Test C.

**Table 2. Measured mass-to-charge ratio peaks for Tests A-C, and the error in the measured peaks relative to the theoretical mass-to-charge ratios for expected anion species.**

| Theoretical | | Test A | | Test B | | Test C | |
|---|---|---|---|---|---|---|---|
| Anion | M/q (amu/e) | M/q (amu/e) | Error (%) | M/q (amu/e) | Error (%) | M/q (amu/e) | Error (%) |
| $BF_4^-$ | 87 | 76.15 | -12.47 | 88.86 | 1.84 | 82.54 | -5.12 |
| $[EMI^+][BF_4^-]_2$ | 285 | 242.8 | -14.47 | 300.7 | 5.51 | 269.13 | -5.57 |
| $[EMI^+]_2[BF_4^-]_3$ | 482 | 422.3 | -12.39 | | | | |

Within each test, the error is consistently above or below the expected mass-to-charge ratios calculated in Section III. Thus it is believe that different systematic errors within in each test are responsible for the deviations. These systematic errors can range from an inaccuracy in the recording of the CEM output, an inaccuracy in the electric and magnetic fields produced within the ExB filter, or some similar testing condition. However, because the error is consistent within each test, a calibration factor was used in the processing of the voltage data to compensate for the error. The calibration factors are DC offsets applied to the raw current vs. voltage profiles. The calibration factors for Test A, B, and C are equal to -6.5%, 3.2% and -4.7% of the expected voltage applied to the ExB deflection

electrodes: $V_{corr} = V_{meas} - 0.065 \cdot V_{theory}$ for Test A. When applied to the voltage sweeps, the final mass-to-charge ratios become those seen in Table 3.

**Table 3. Mass-to-charge ratios of all tests with the correction factor applied. The error is within the resolution of the ExB filter.**

| Theoretical | | Test A | | Test B | | Test C | |
|---|---|---|---|---|---|---|---|
| Anion | M/q (amu/e) | M/q (amu/e) | Error (%) | M/q (amu/e) | Error (%) | M/q (amu/e) | Error (%) |
| $BF_4^-$ | 87 | 87.1 | -0.03 | 90.9 | 3.8 | 89.1 | 3.29 |
| $[EMI^+][BF_4^-]_2$ | 285 | 277.7 | -0.59 | 288.4 | 1.32 | 284.3 | -.95 |
| $[EMI^+]_2[BF_4^-]_3$ | 482 | 483.1 | 1.60 | | | | |

## VII. Conclusion

A method to measure the mass-to-charge ratio of an electrospray emitter using an inexpensive and simple ExB type filter was devloped using the ionic liquid EMI-$BF_4$ as the propellant. The emitter was operated such that it would only extract the $BF_4$ anion or negatively charge droplets of the IL. The resulting measurements proved that such a device could discern these ion species from one another. These raw measurements did show several systematic errors, but calibration factors determined for each test were used to compensate for them, which reduced the error to ±3% of the theoretical mass-to-charge ratios for the anions in the electrospray beam. The electrospray was also seen to be operating in the ion-droplet regime. Droplet emission could be discerned from ion emission due to the wide range of M/q, which is too broad for a single anion peak. However, unexpectedly, such peaks were only observed during certain operating conditions. The reason for this is still unknown, though the theory could be similar to that which Lozano described on findings he made while running at lower flowrates. There appears to be trends between extraction voltage and the beam ion distribution, and the flow rate and beam current as well, though reasons for these are only speculations.

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