Low-Pressure ICP-MS for Planetary Trace Elemental Analysis

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Motivation

Techniques available for in situ chemical analysis for planetary exploration:

- Evolved Gas Analysis (EGA; e.g., SAM on the Curiosity rover),
- Laser Desorption Mass Spectrometry (LDMS; e.g., MOMA on the ExoMars rover)
- Laser-Induced Breakdown Spectroscopy (LIBS; e.g., SuperCam on the Mars 2020 rover)

Existing methods fail to meet the limits-of-detection required to accurately quantify trace element concentrations.

Project: Mission-enabling ICP-MS system (Goal: TRL1 → 4)

Supported by:

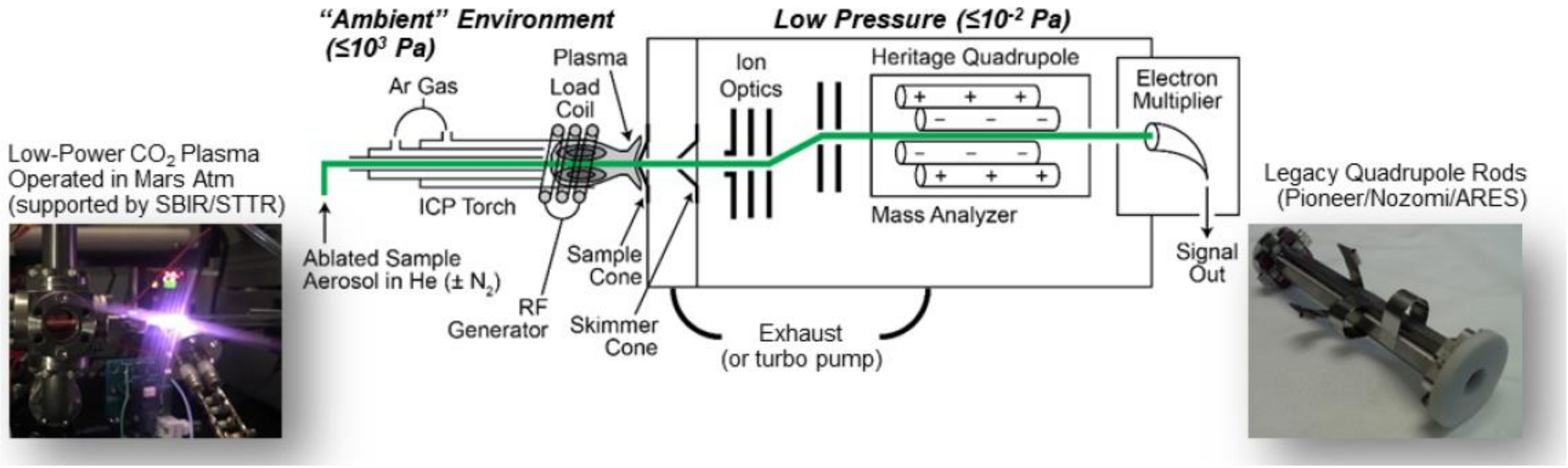
- NASA PICASSO Program grant number 80NSSC18K0932
- MassCEC AmplfiyMass program

Outline

Preliminary Studies

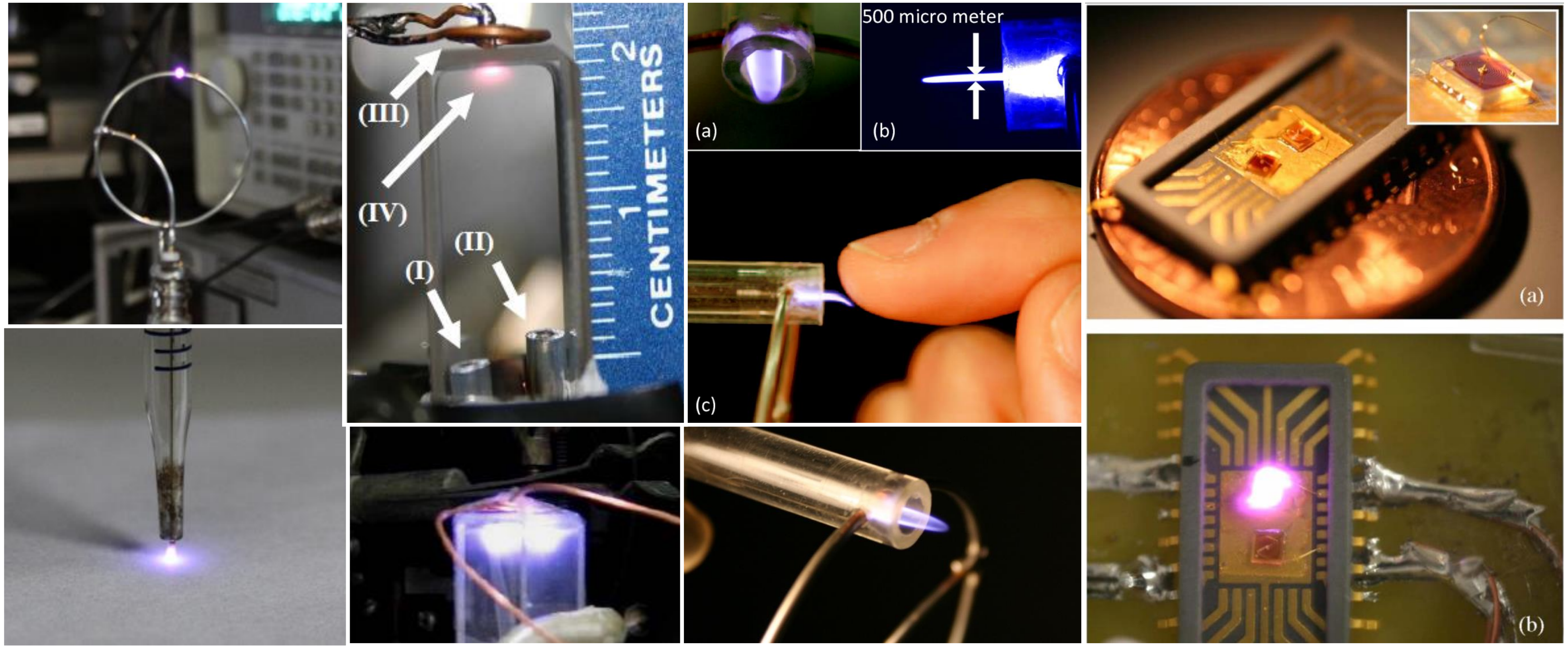
PICASSO Project

1) <u>Characterization of plasma capabilities</u>
2) Interface Design
3) Test and Characterization



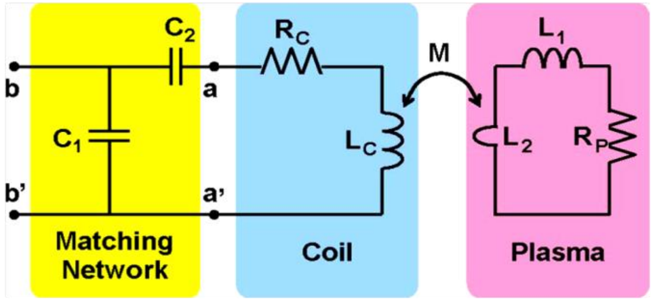
Miniature Plasma Ionization Sources

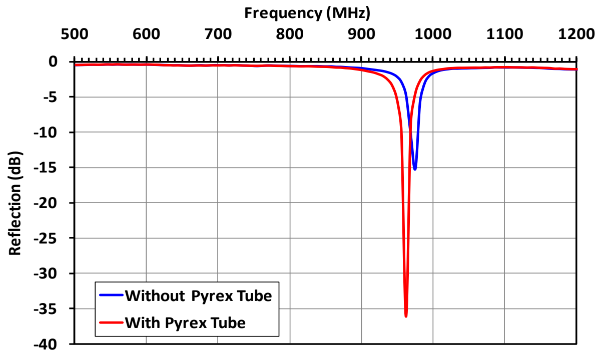
- Miniature Inductively Coupled Plasma on a Chip
- Pulse-Modulated Plasma with a Magnetic Loop Antenna
- Plasma Needle
- Reduced-Pressure Inductively Coupled Plasma
- U-Shaped Argon Plasma Jet

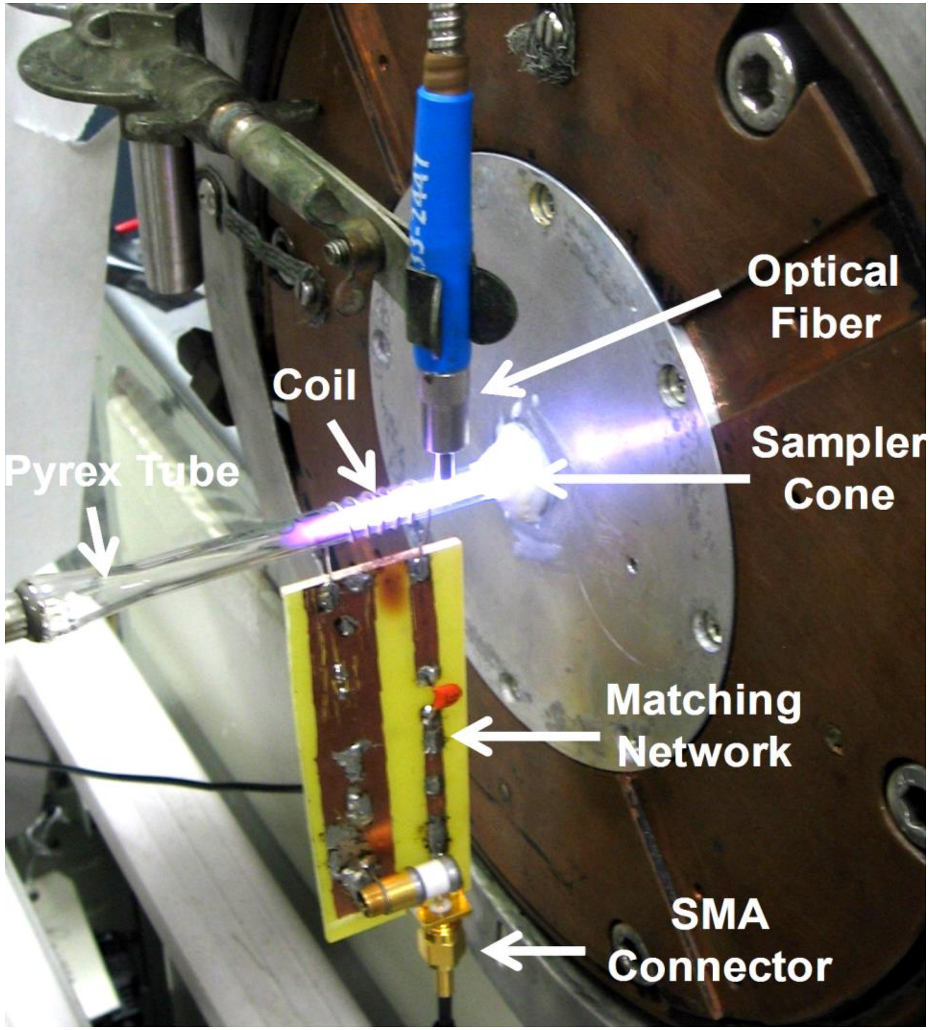


Plasma Under Simulated Ambient Mars Conditions

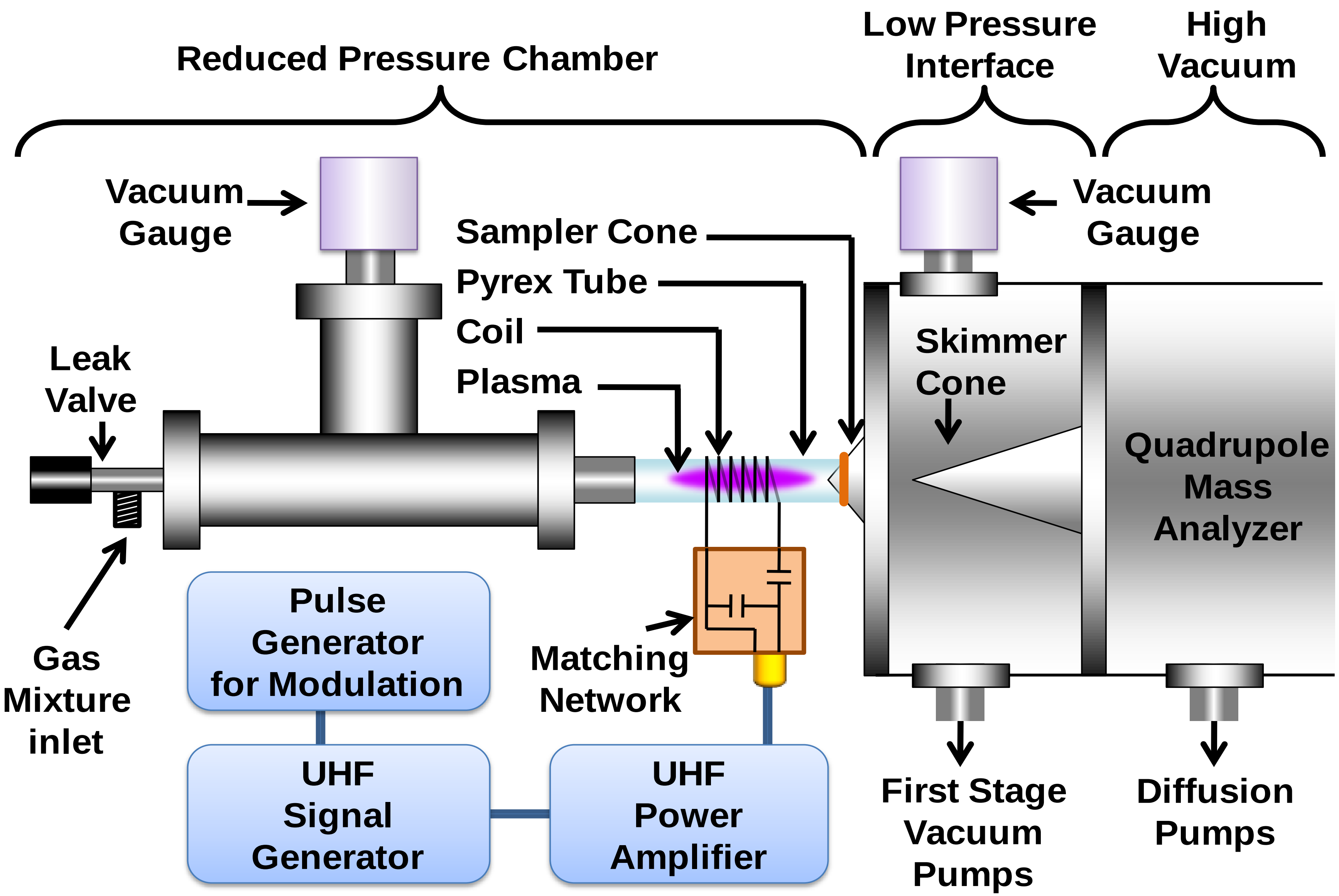
- **Atmospheric Pressure on Mars ranges from 0.2 Torr to 8.7 Torr**
- **Average pressure on Martian Surface is ~4 Torr**
- **Atmospheric Composition of Mars:**
  - 95.3% Carbon Dioxide
  - 2.7% Nitrogen
  - 1.6% Argon
- **Methane as analyte of interest**
- **Miniature ICP Generation**
  - Higher Frequency (~800 MHz)
  - Lower Power (<5 W)
  - Non-thermal







Experimental Setup



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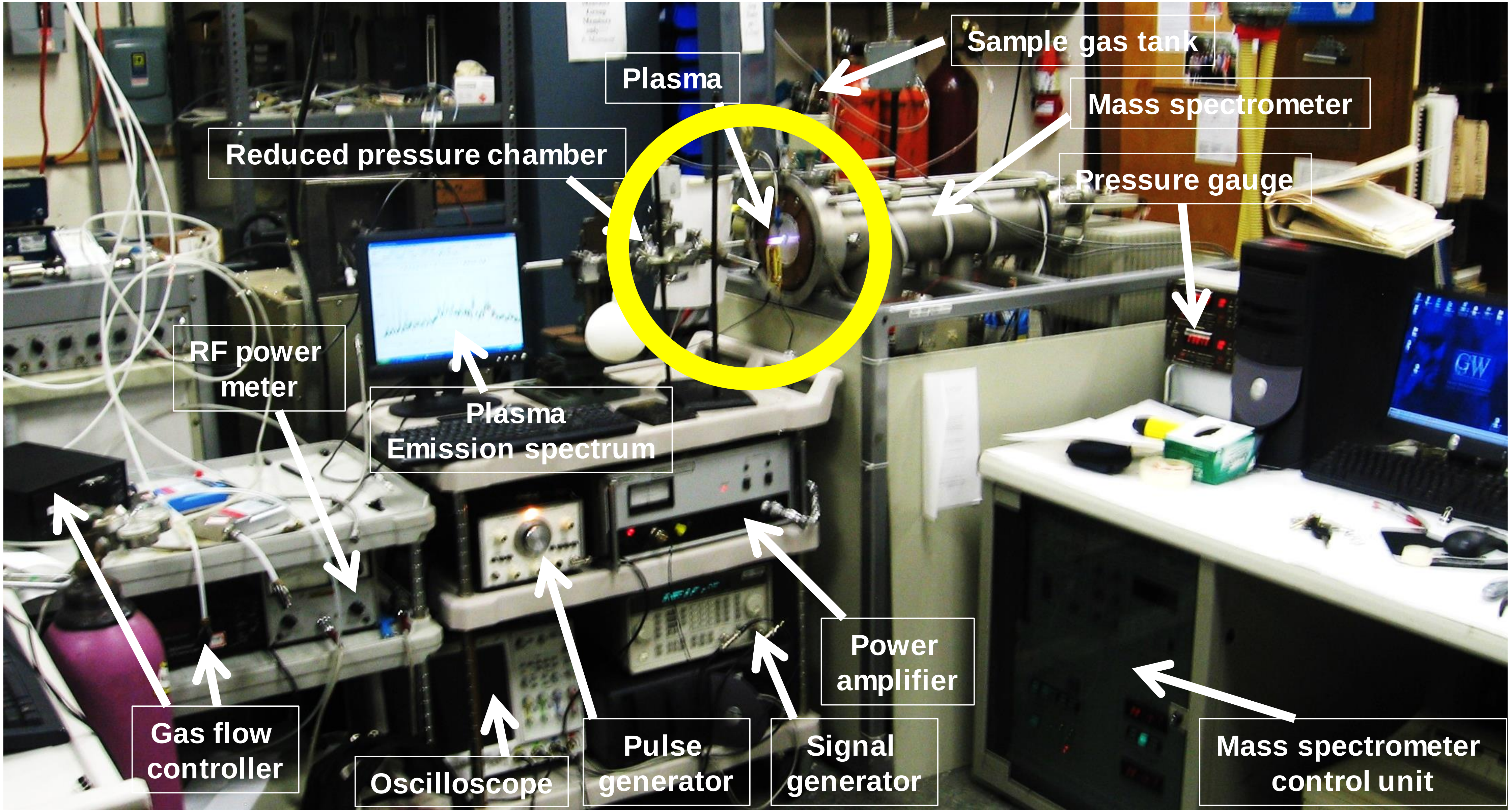
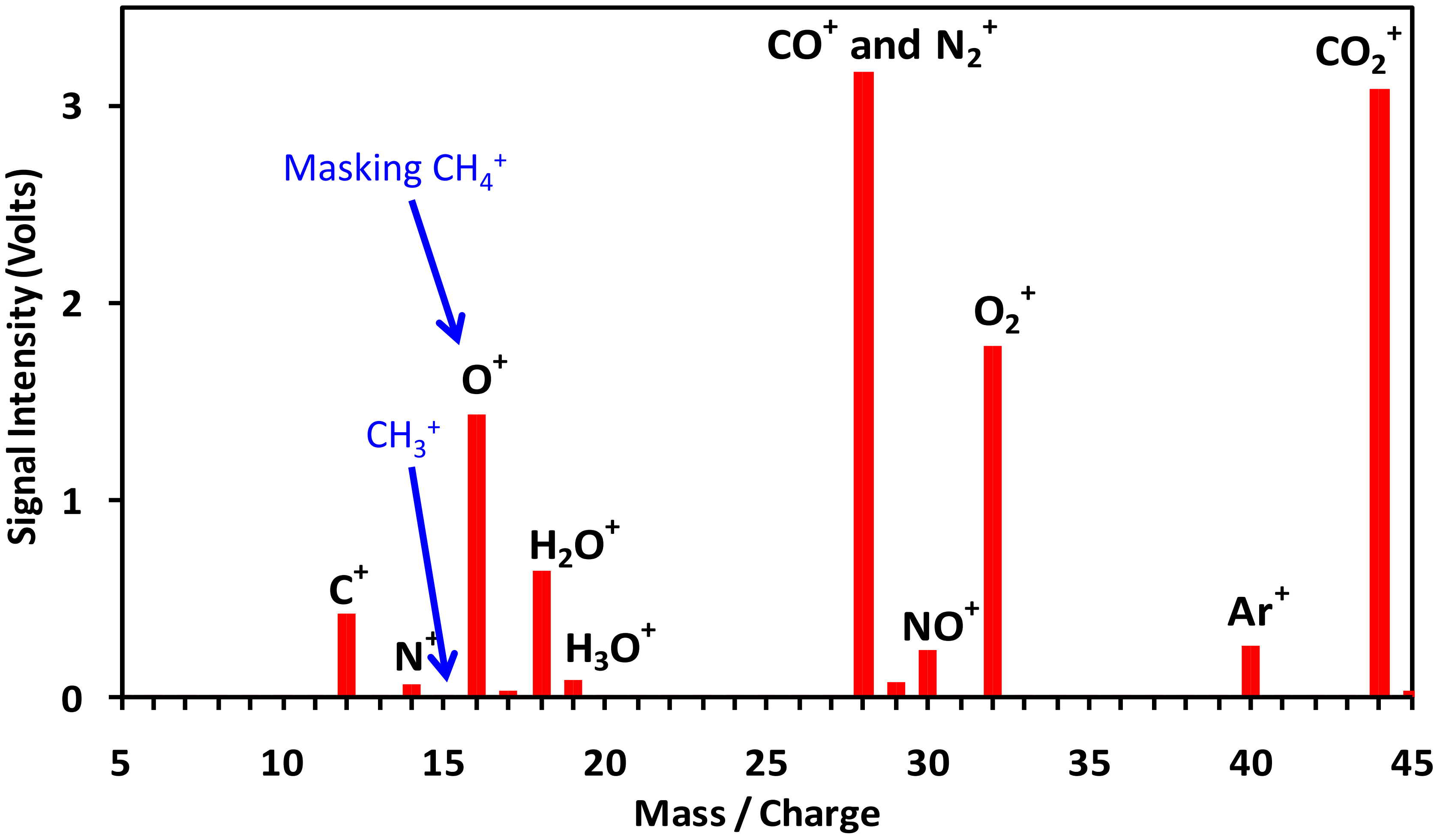


Background Mass Spectrum



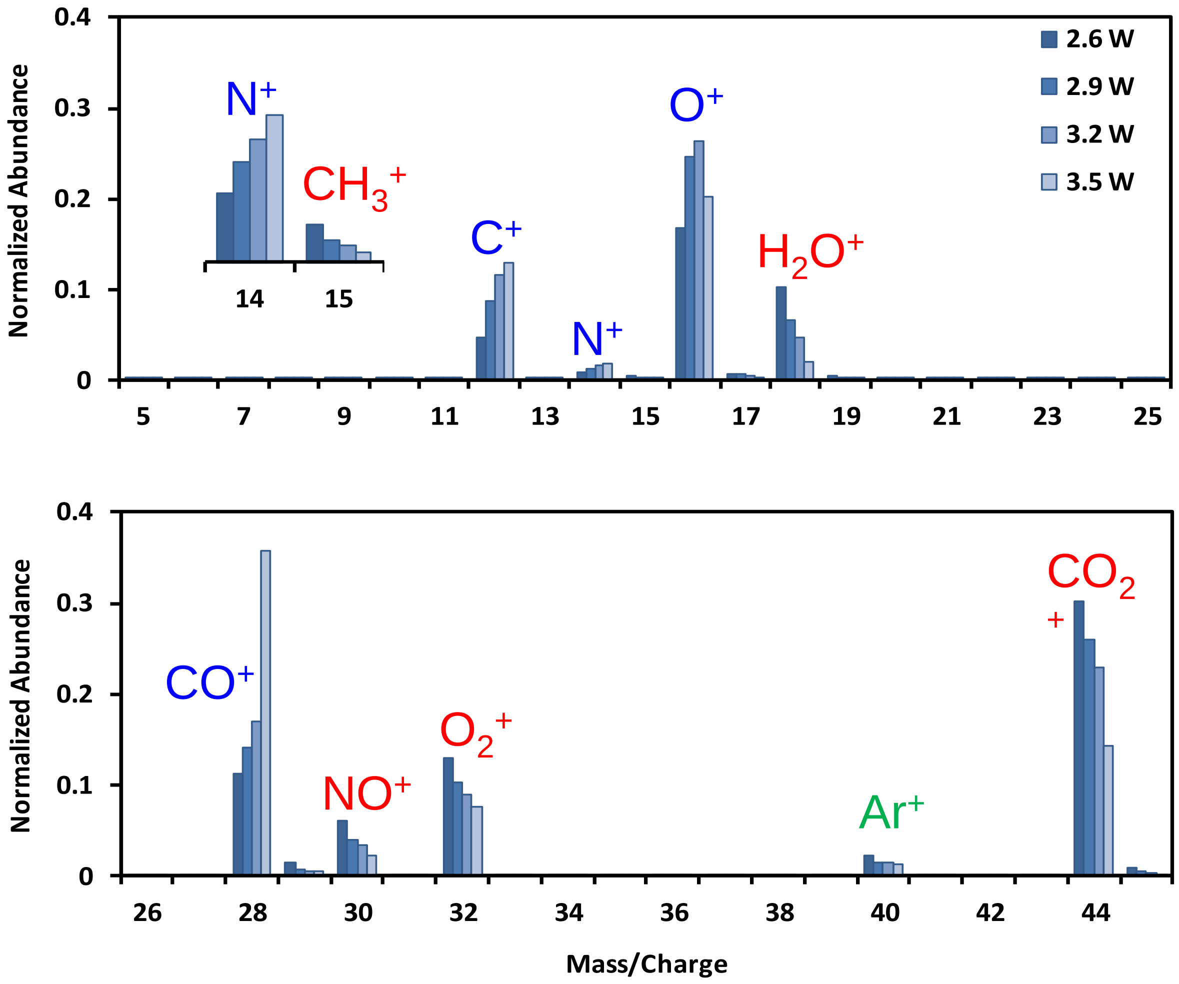
Effects of Plasma Power

Increasing Plasma Power:

Increase in relative abundance of the **fragment** ions:
C^+, N^+, O^+, and CO^+

Decrease in relative abundance of the **parent** ions:
CH_3^+, H_2O^+, NO^+, O_2^+, CO_2^+

No significant change:
Ar^+



The spectra are normalized by dividing the signals by the total sum of signal intensities in the spectrum. The detector voltage was set to -540, -520,-500, and -480 V for plasma power of 2.6, 2.9, 3.2, and 3.5 W, respectively. The skimmer voltage was -100 V. Pressure was 4 Torr.

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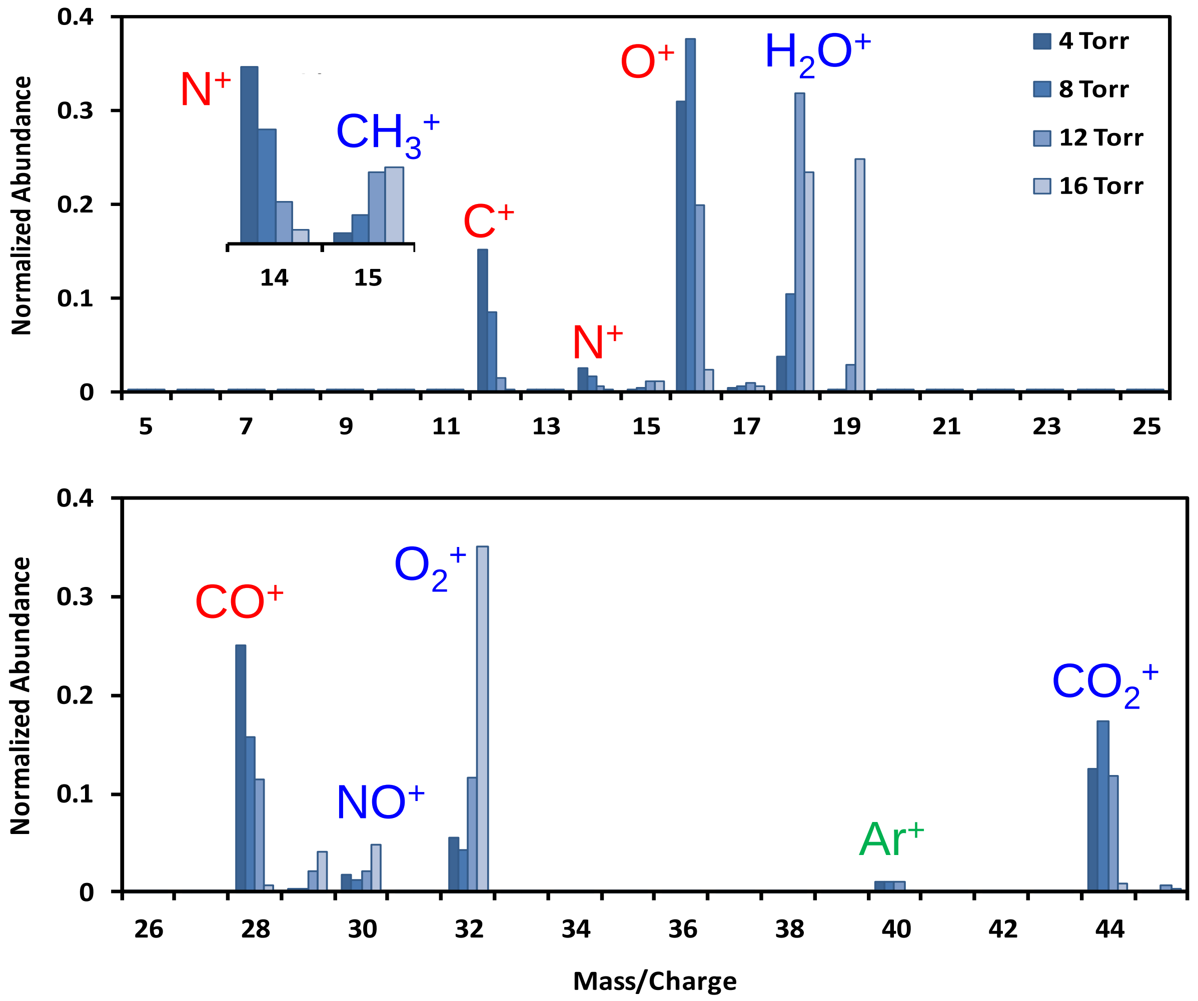


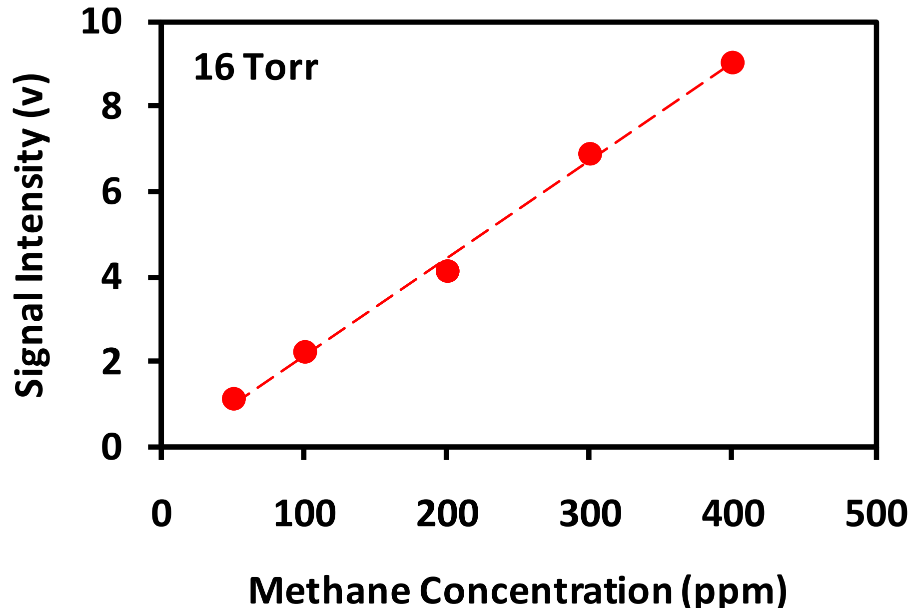
The spectra are normalized by dividing the signals by the total sum of signal intensities in the spectrum. The detector voltage was set to -460, -480, -540, and -610 V for the plasma pressures of 4, 8, 12, and 16 Torr, respectively. The skimmer voltage was -100 V.

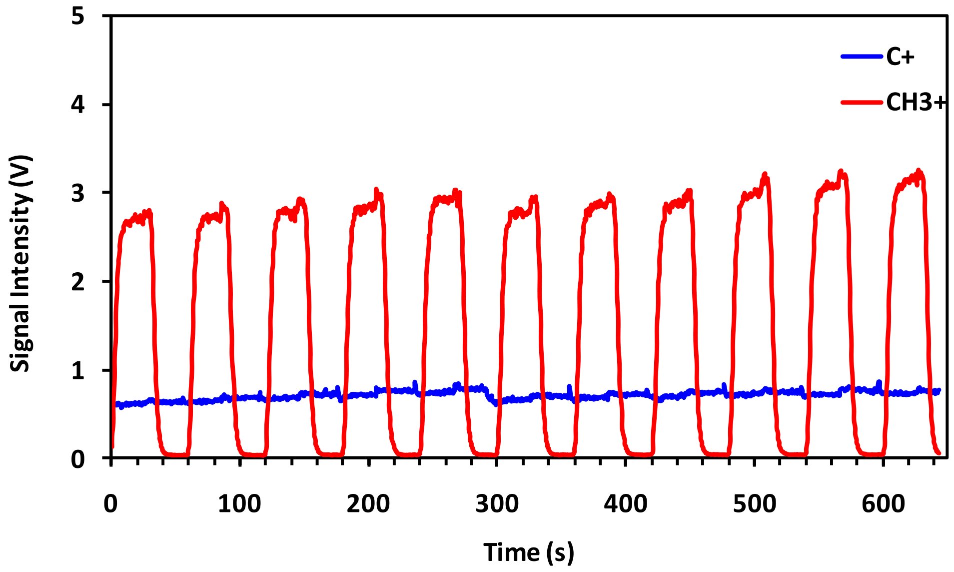
Analytical Figures of Merit

- Detection limit: 150 ppb
- Excellent repeatability and reproducibility
- No cross-contamination
- Simplicity and low cost
- Emission Spectroscopy

Pressure	Detection Limits* (ppm (v/v))	Sensitivity (V/ppm)
4 Torr	0.78	0.0062
8 Torr	0.93	0.0064
12 Torr	0.28	0.0121
16 Torr	0.15	0.0229

* Based on 3σ of blank signal at 15 amu

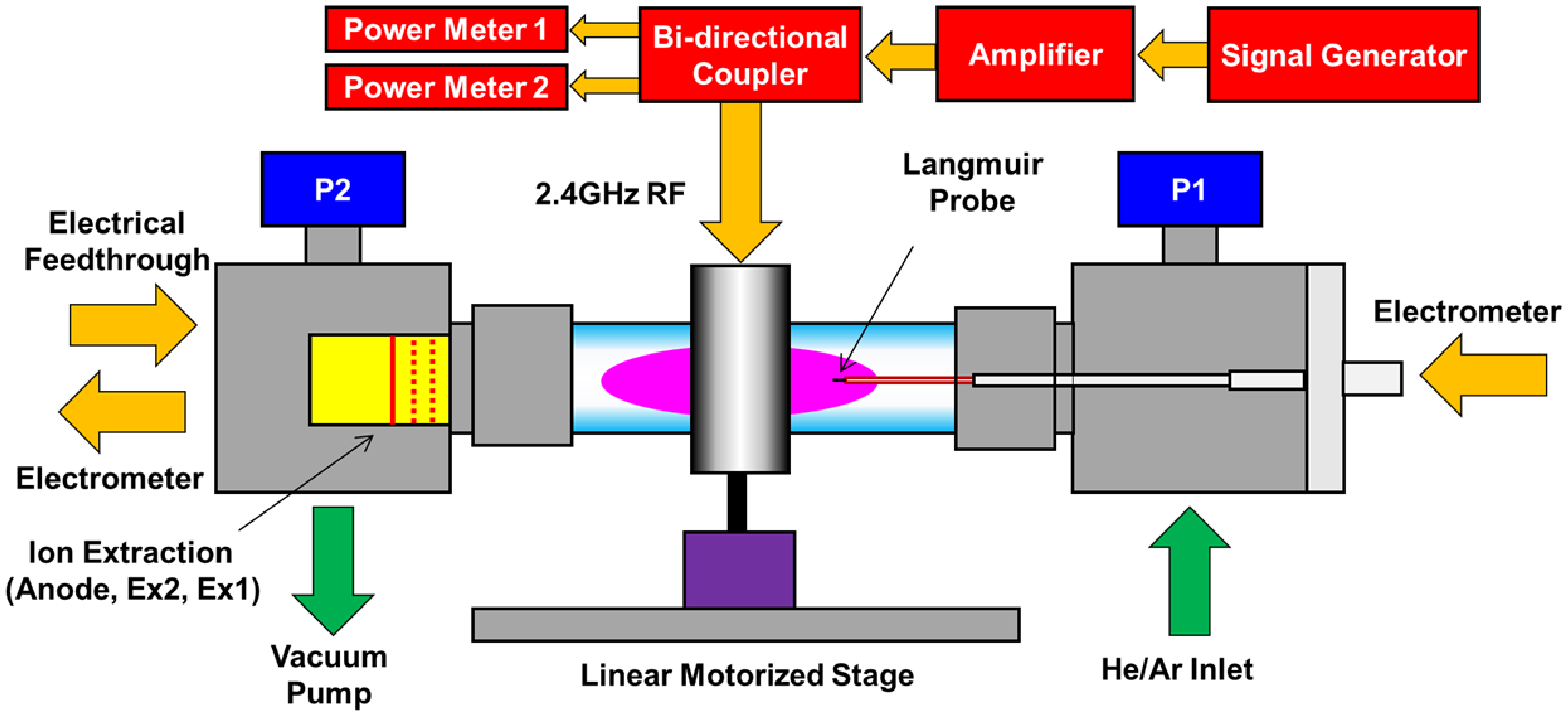




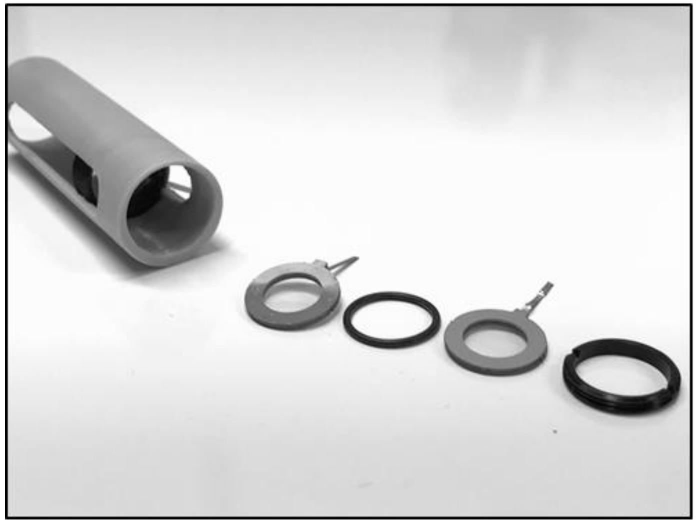
PICASSO Project

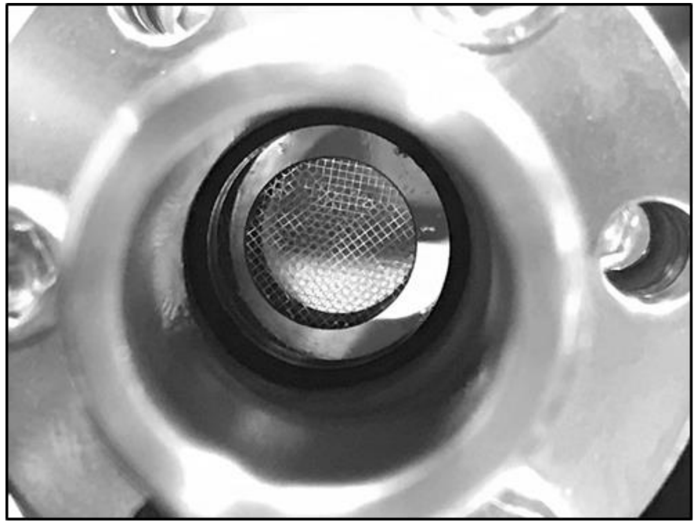
Fundamental Plasma Studies

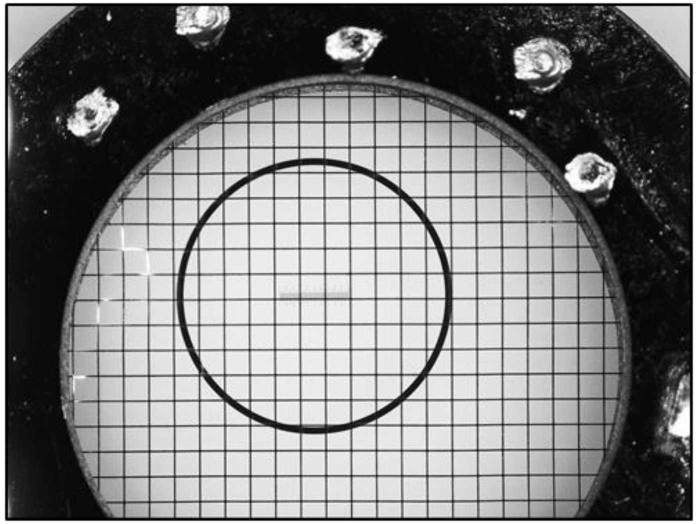
PICASSO: Experimental Setup

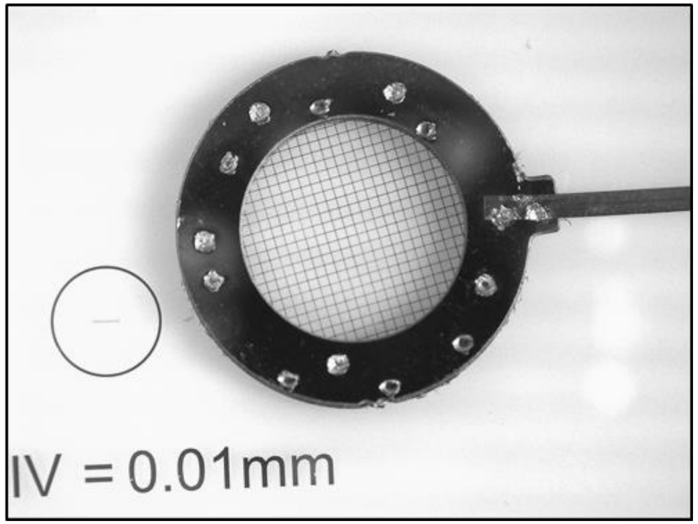


Extraction Lens Design

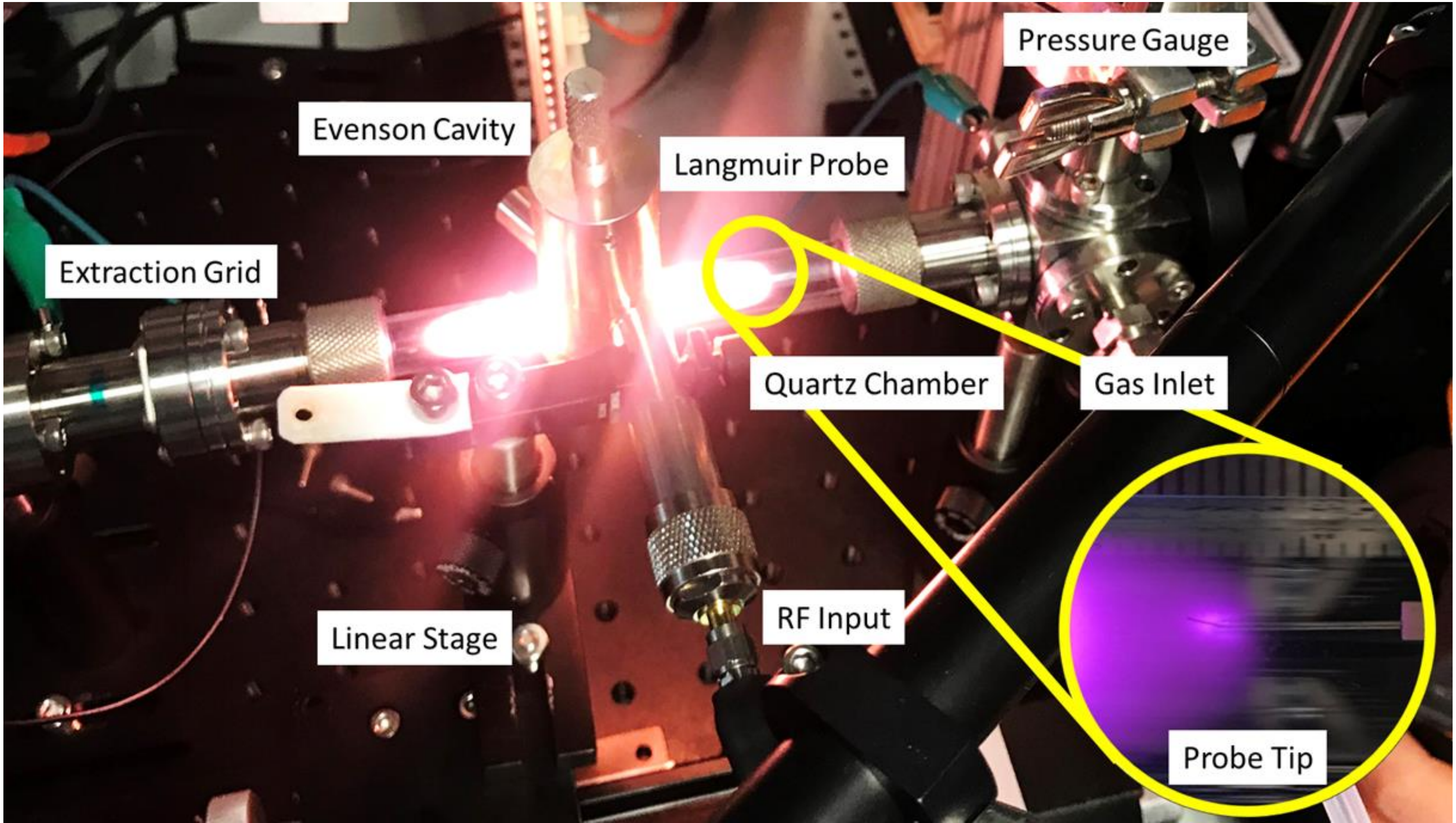








Experimental Setup

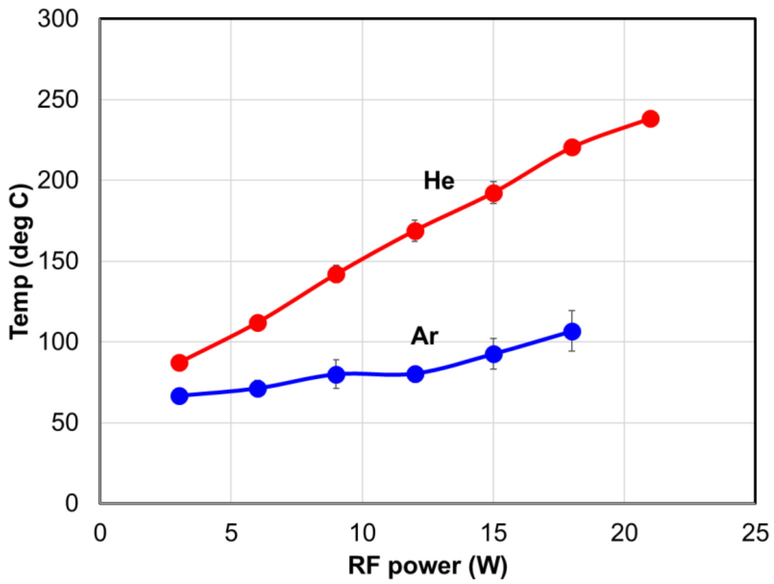


Thermal Imaging

Temperature measurements were conducted by a Keysight thermal camera.

Generally, He produced “hoter” plasmas than Ar.

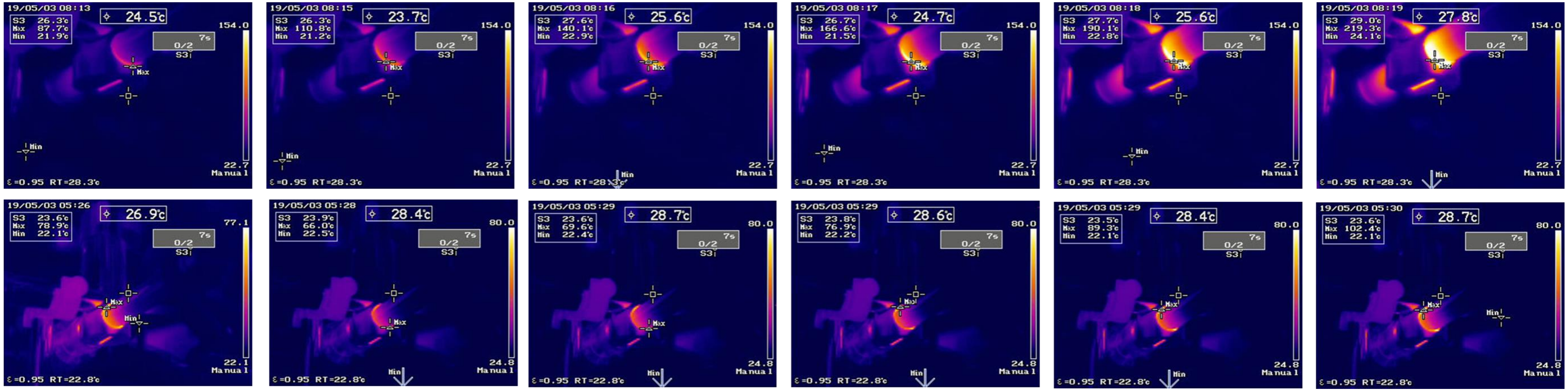
For He, temperatures reached as high as ~240C while for Ar, the maximum recorded temperature was 100C.



3W 6W 9W 12W 15W 18W

He

Ar



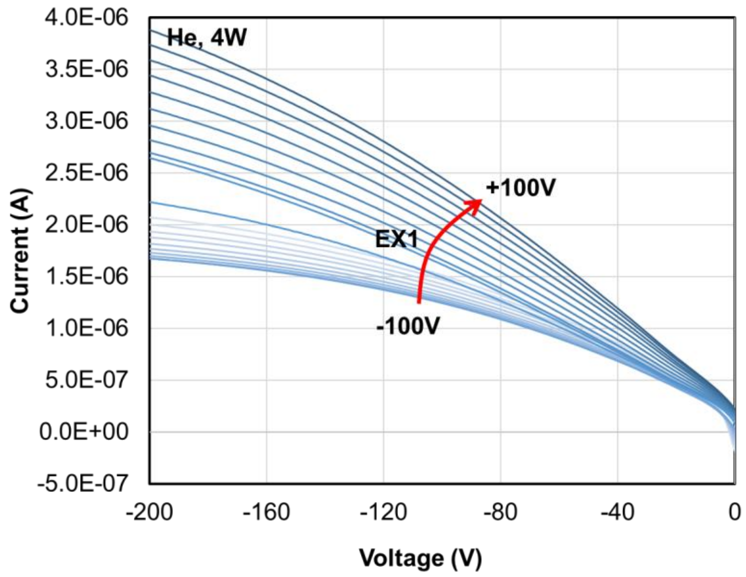
Ion Extraction Measurements

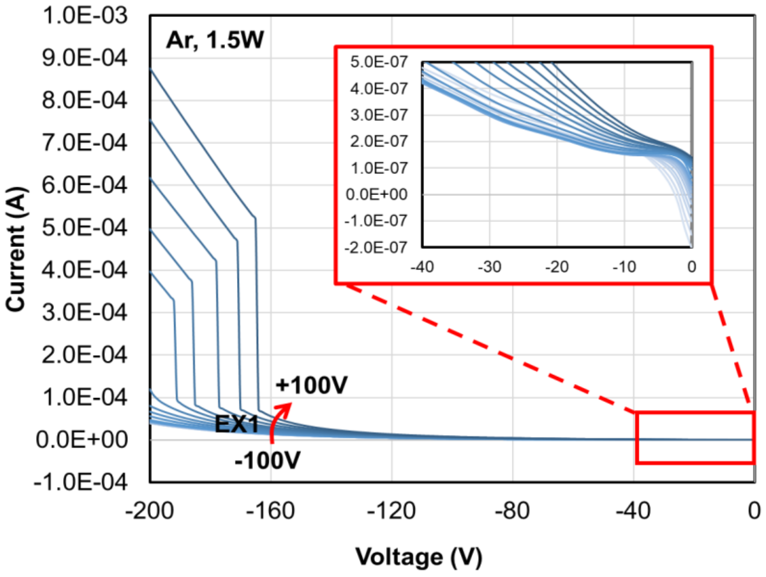
For EX1 sweeps (EX2=0):
both He and Ar, the voltage on the CP had a much greater impact on ion extraction than the voltage on EX1.

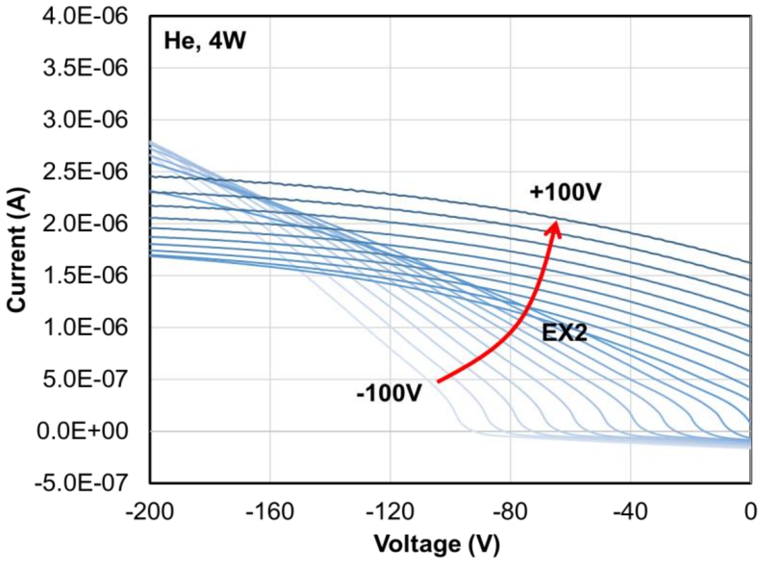
For EX2 sweeps (EX1=0):

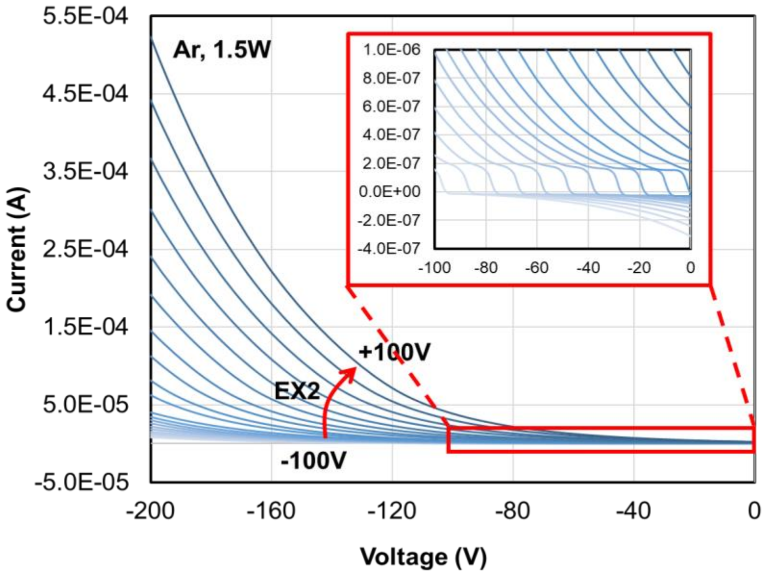
- In case of He, the voltage on the EX2 had a much greater impact on ion extraction than CP.
- In case of Ar, the voltage on the CP had a greater impact on ion extraction.

These may be explained by the X10 mass difference between Ar and He ions.



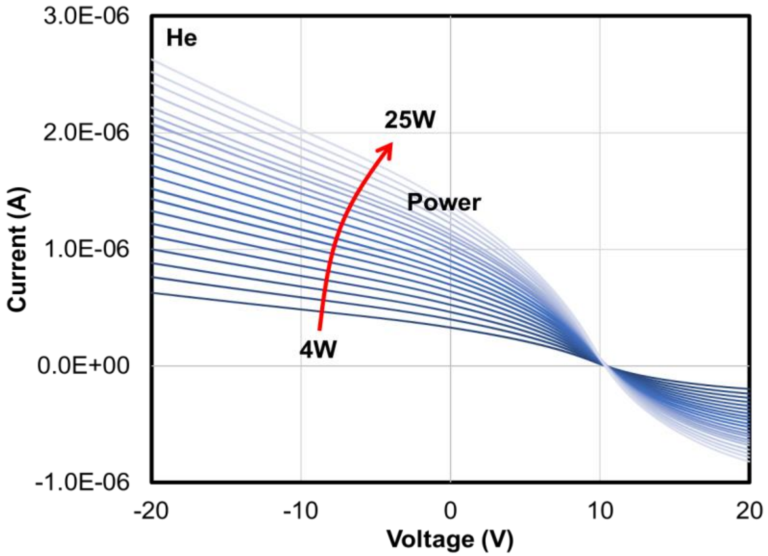


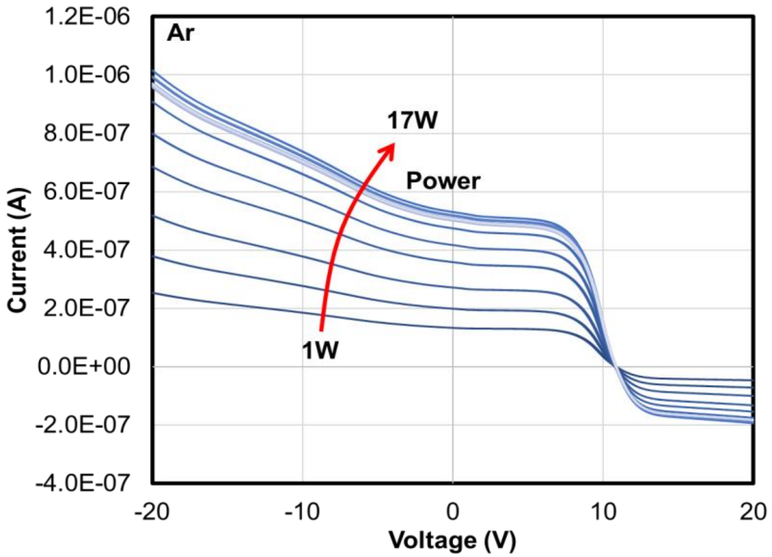




Effects of Plasma Power

- The extraction voltages were set at EX1=0, EX2=10V.
- For He, the electron and ion currents were equal.
- For Ar plasma, ion currents were more (>2x) than the electron currents.
- As anticipated increasing power increased ion current for both He and Ar.
- Ar plasma was saturated at 7W and could not produce any more ions. This was not the case for He.
- Further, the zero-crossing of current at +10V indicates that ion motion is predominantly controlled by the potential barrier on EX2 (and not the gas flow).





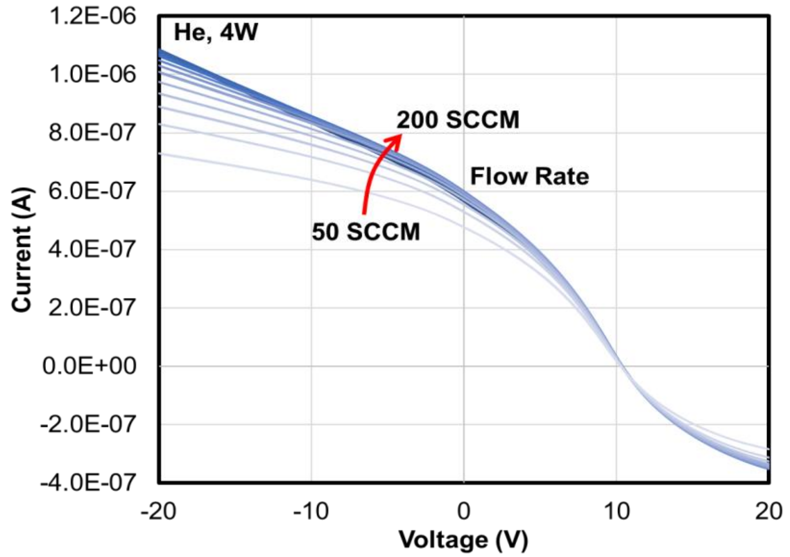
Effects of Gas Flow

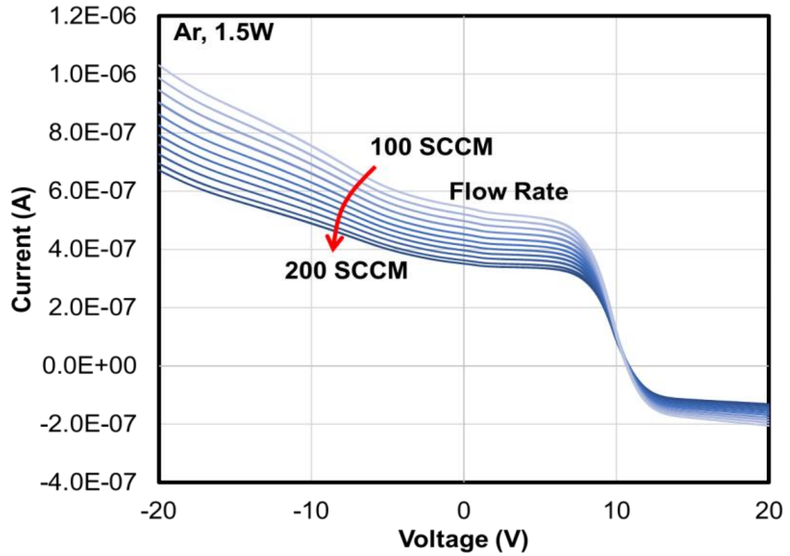
- The general shape of IV curves for the CP are similar with those shown for power sweeps, but the trends were opposite for He and Ar.

- Increasing the flow rate for He increased the ion current for He but decreased for Ar.

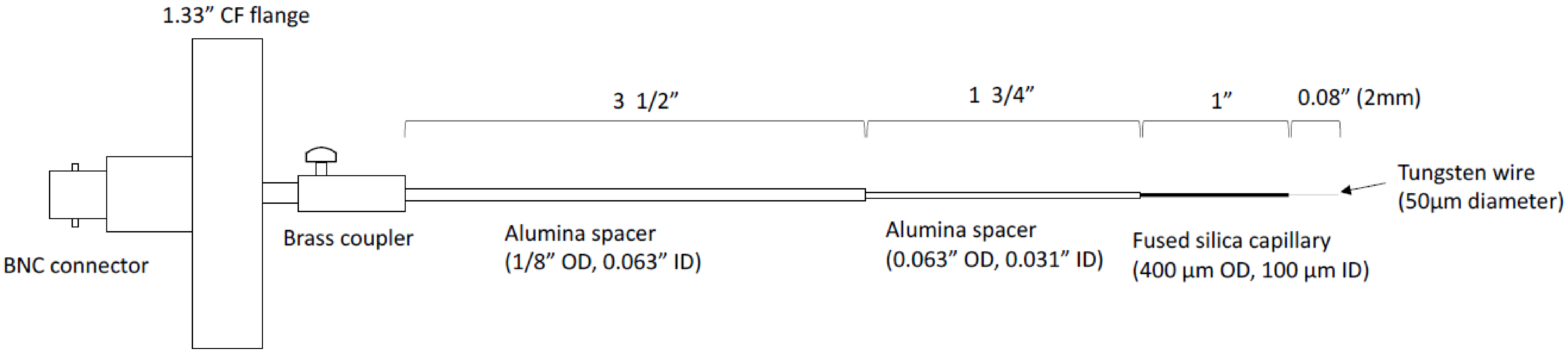
- Further, for Ar, the extracted ions show a knee at around 8V. This is not present in the He curves. The difference in the trends observed may be correlated to the Paschen curves of He and Ar for which the minimum breakdown voltage occurs as 5 and 1 Torr respectively.

- Because the pumping speed is constant, the pressure of plasma gas is increased by increasing the flow rate.



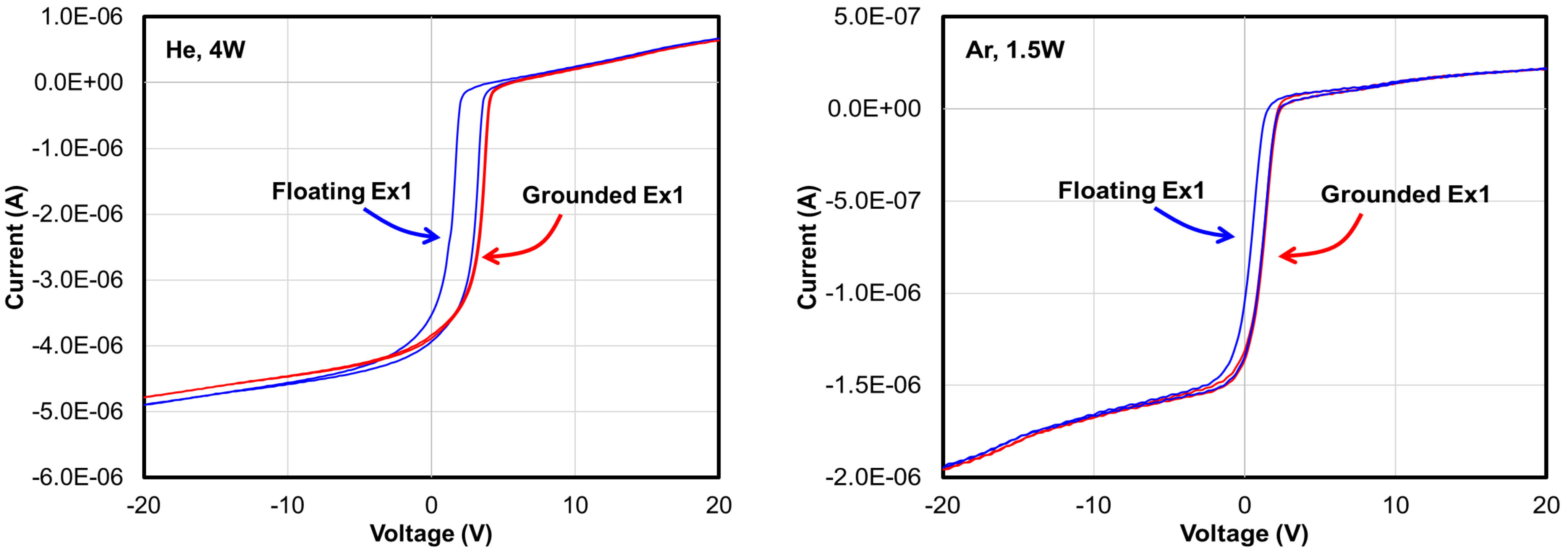


Langmuir Probe Measurements



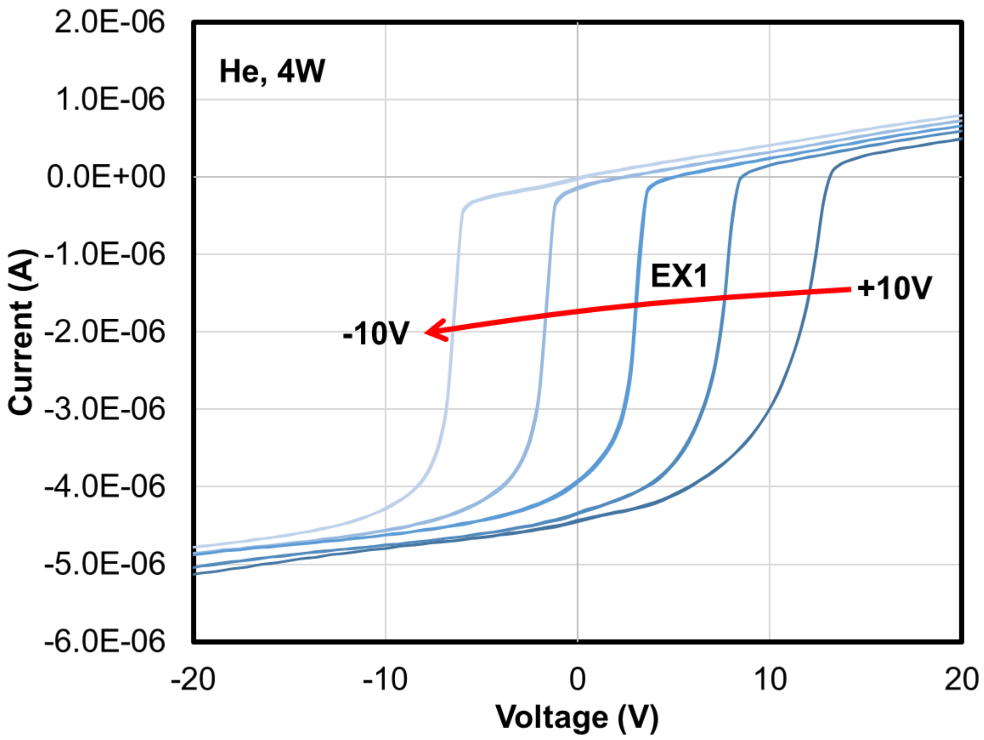
Hysteresis with Floating Extraction Grid

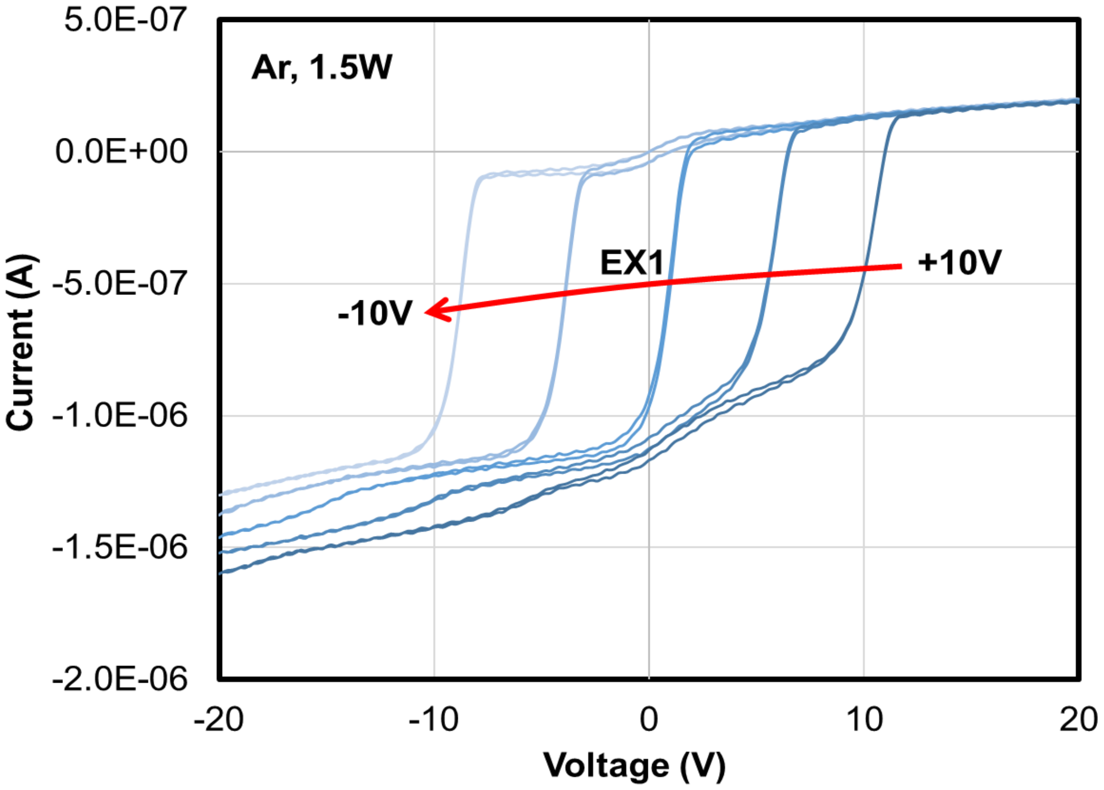
The voltage on EX1 affected the IV curve measurements. When EX1 was floated, the IV curves show hysteresis (normally correlated to tip contamination). Grounding EX1 removed the hysteresis.



Voltage on First Extraction Grid

To further investigate effect of voltage on EX1 on the plasma potential, +10, +5, 0, -5, and -10V were applied to EX1 which is facing the plasma without visibly contacting the plasma. It appeared that the plasma picked up the EX1 voltage, as its potential.



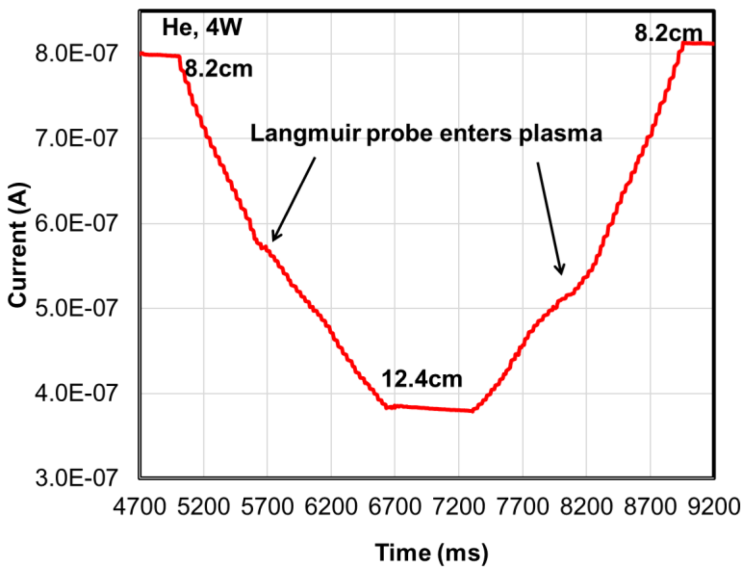


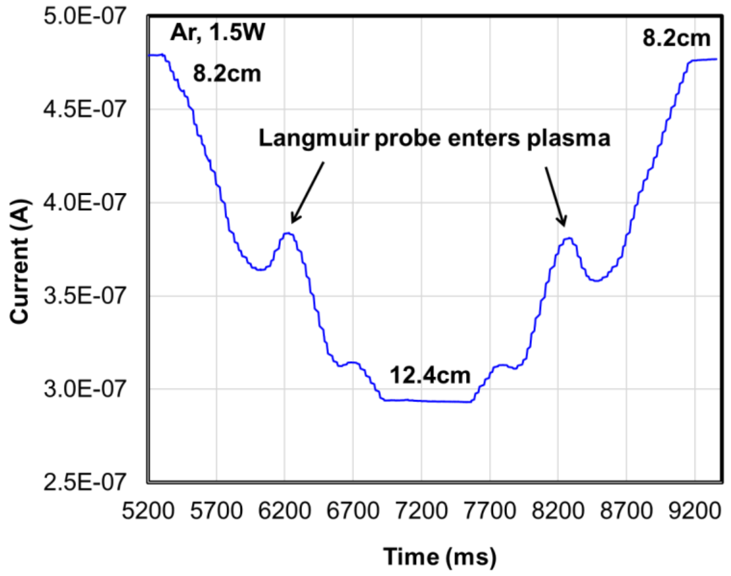
Effects of Plasma Position (Loading)

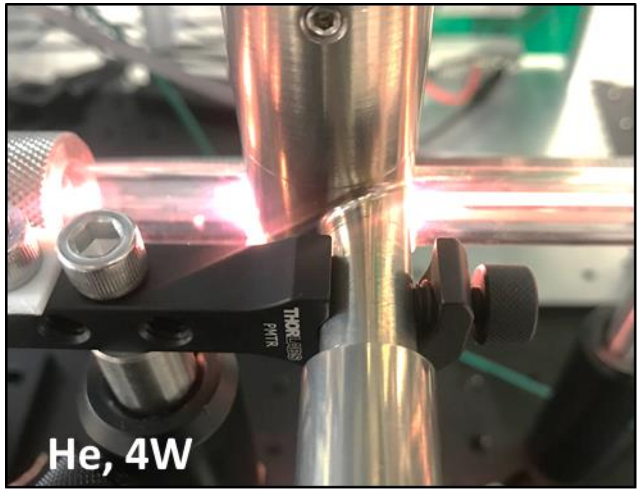
The location of the center of cavity was changed from 8.2-12.4 cm with respect to the CP using the linear stage. The ion currents on the CP were recorded with at -20V, EX1=0V, and EX2=+10V.

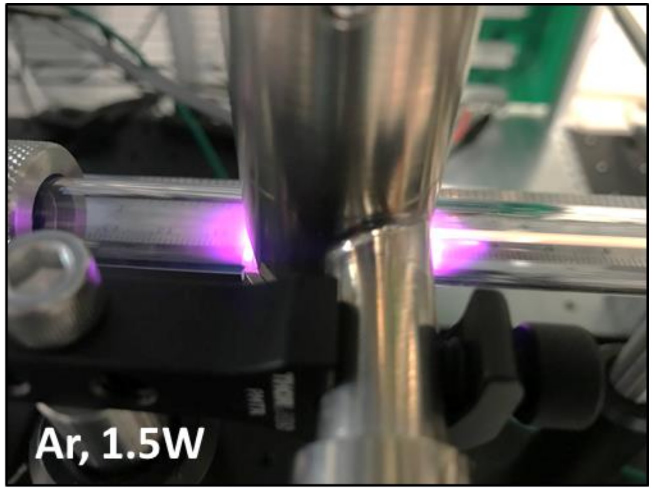
Sweeping the position for Ar and He resulted in ~1.6- and ~2-fold change in ion current.

The relative maximum occurred when the Langmuir probes entered the plasma, increasing the recorded current on the CP.



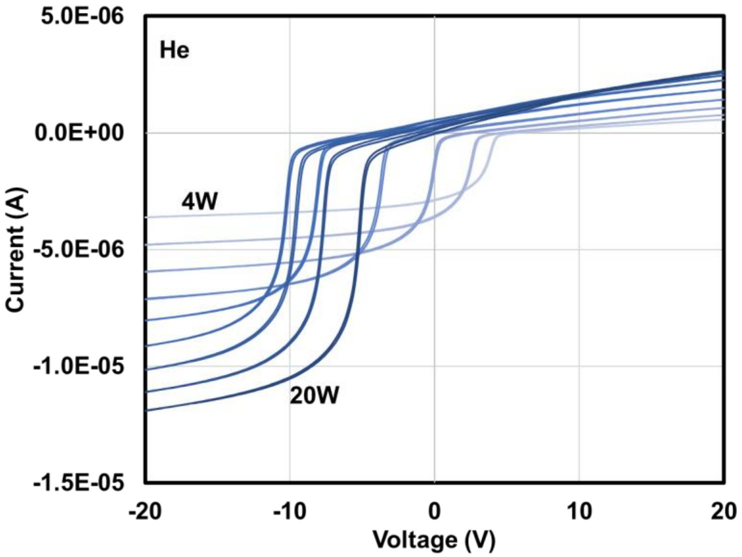


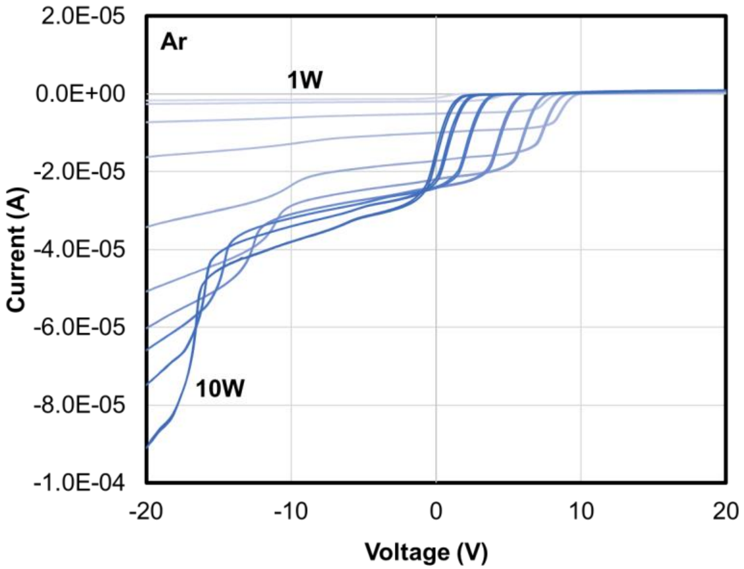


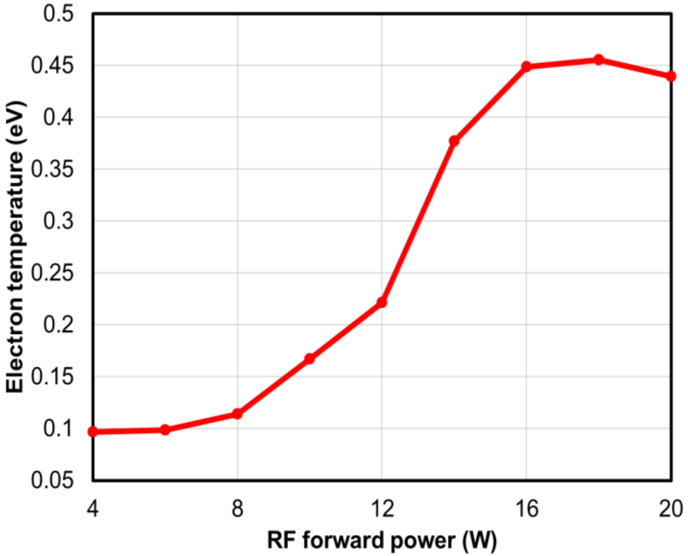


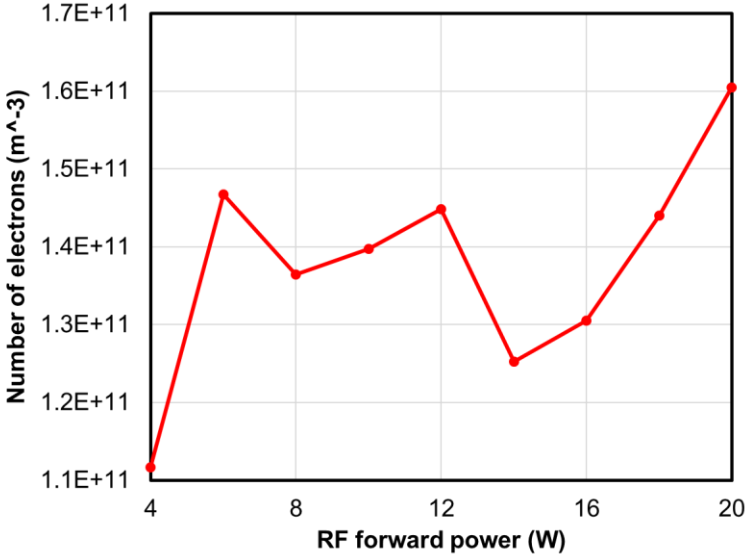
Effects of Plasma Power

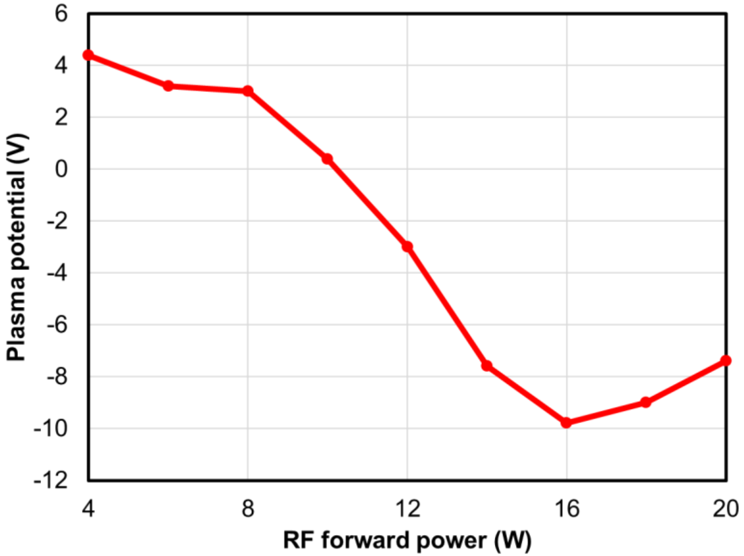
RF power increase resulted in a decrease in plasma potential but an increase in number of electrons and electron temperature. More high energy electrons are produced, which derived down the overall plasma potential.



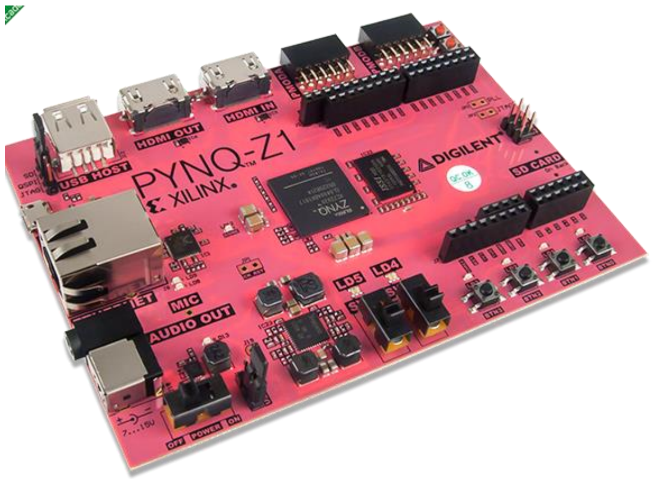


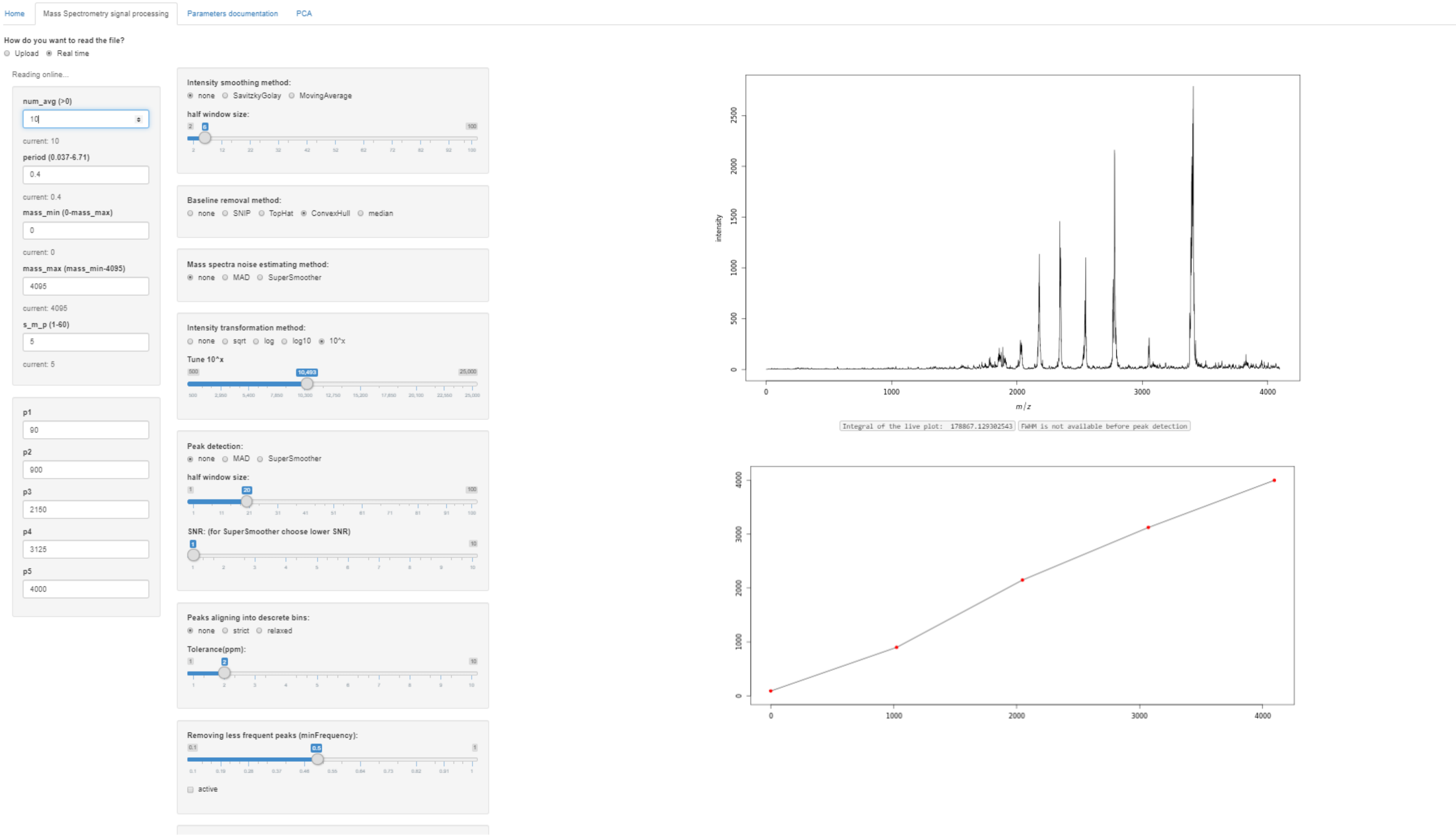






Custom Low-Cost Quad Electronics





Future Work

– Characterization of plasma capabilities

– **Interfacing the plasma with a mass spectrometer**

– **Test and Characterization**

Acknowledgement

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- Greentown Labs

Questions?