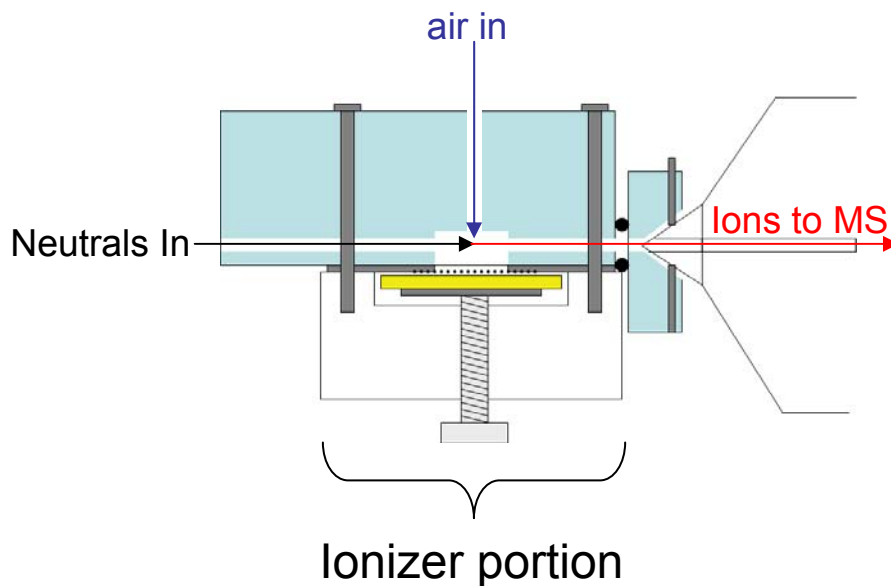


Switched Ferroelectric Plasma Ionizer (SwiFerr): A robust source for ambient mass spectrometry in Harsh Environments



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Switched Ferroelectric Plasma Ionizer

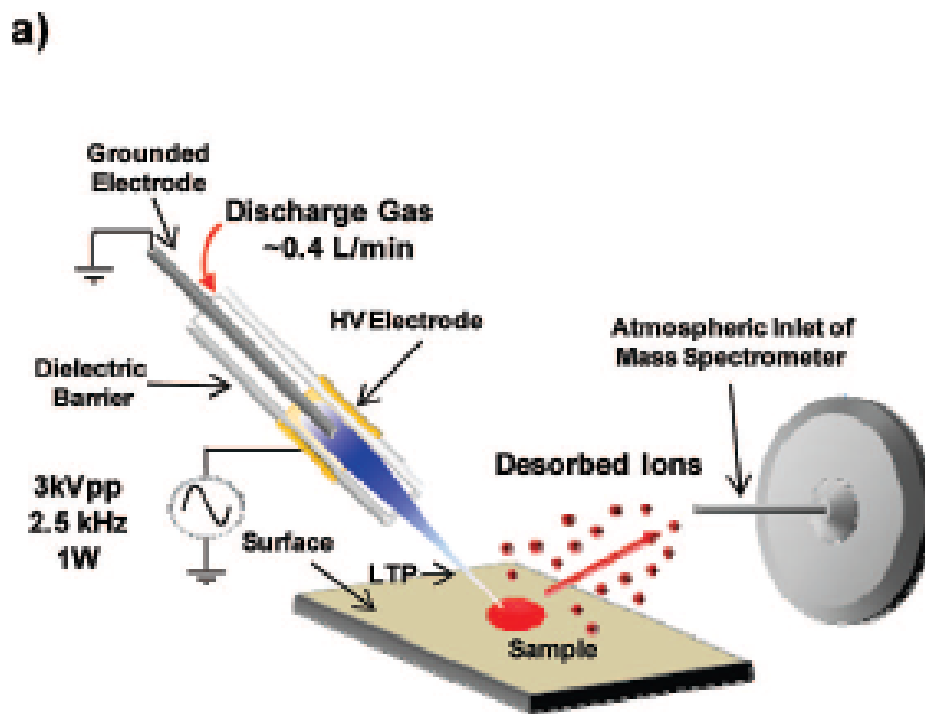
- A novel ionizer for ambient mass spectrometric analysis developed at Caltech.^{1,2}
- In this presentation
 - Plasmas in ambient mass spectrometry and previous work with ambient pressure plasmas
 - Design and Operating Principles of SwiFerr
 - SwiFerr used for organic vapor analysis
 - Pharmaceuticals analysis

1) Neidholdt, E.L.; Beauchamp, J.L. Manuscript in Preparation, 2009.

2) Neidholdt, E.L.; Beauchamp, J.L. Provisional Patent Application, 2009, Caltech.

Plasmas in Mass Spectrometry

- Techniques include DART, DAPCI, dielectric barrier discharge, etc.
- Example at right, Low temperature plasma probe (Cooks)
- Hollow Cathode (JPL)
- For ambient mass spectrometry: **analysis without advance sample preparation, at ambient pressure**

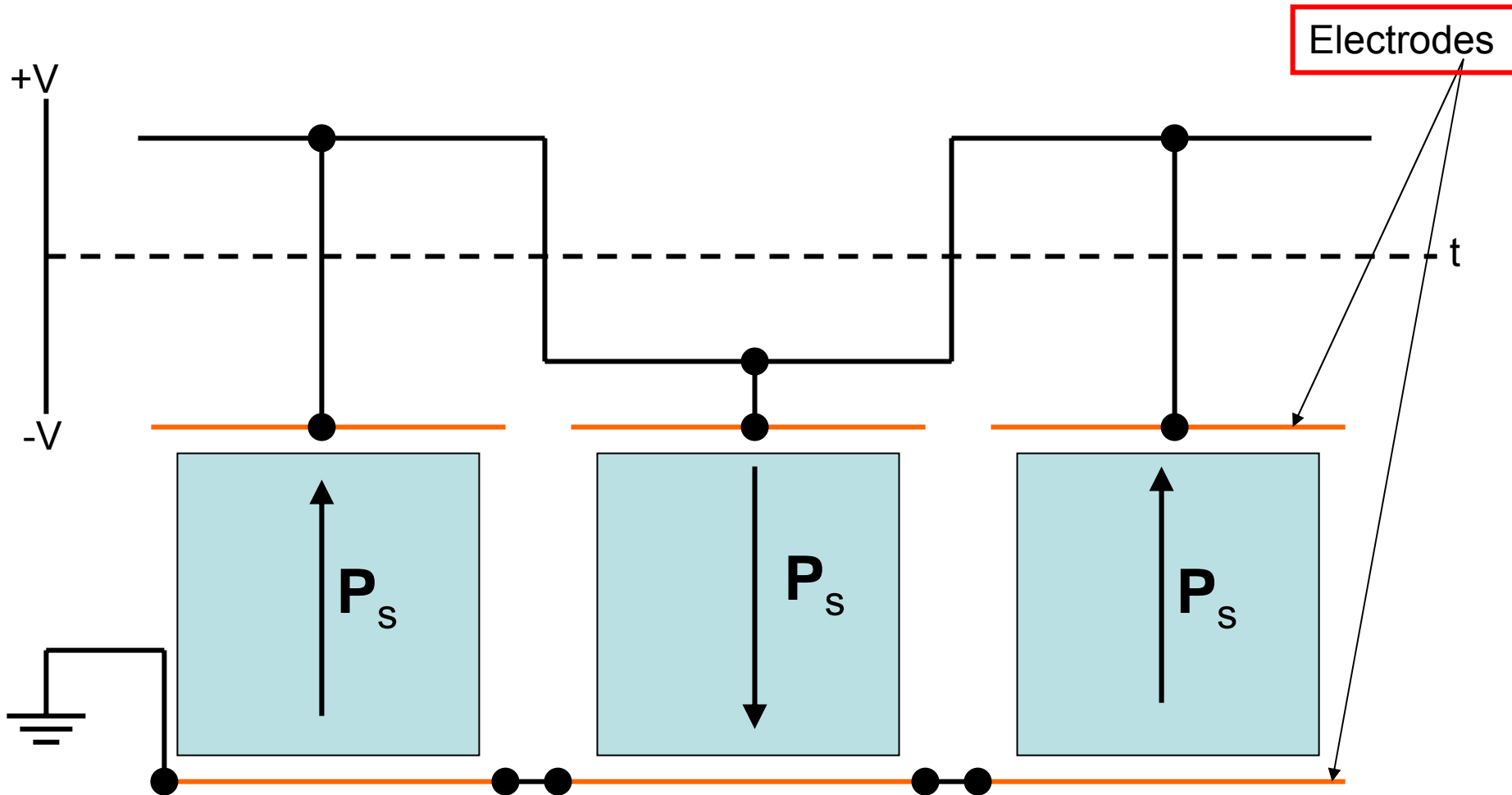


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SwiFerr is a plasma based ionizer for ambient mass spectrometry which relies on the ferroelectric properties of barium titanate to produce the plasma.

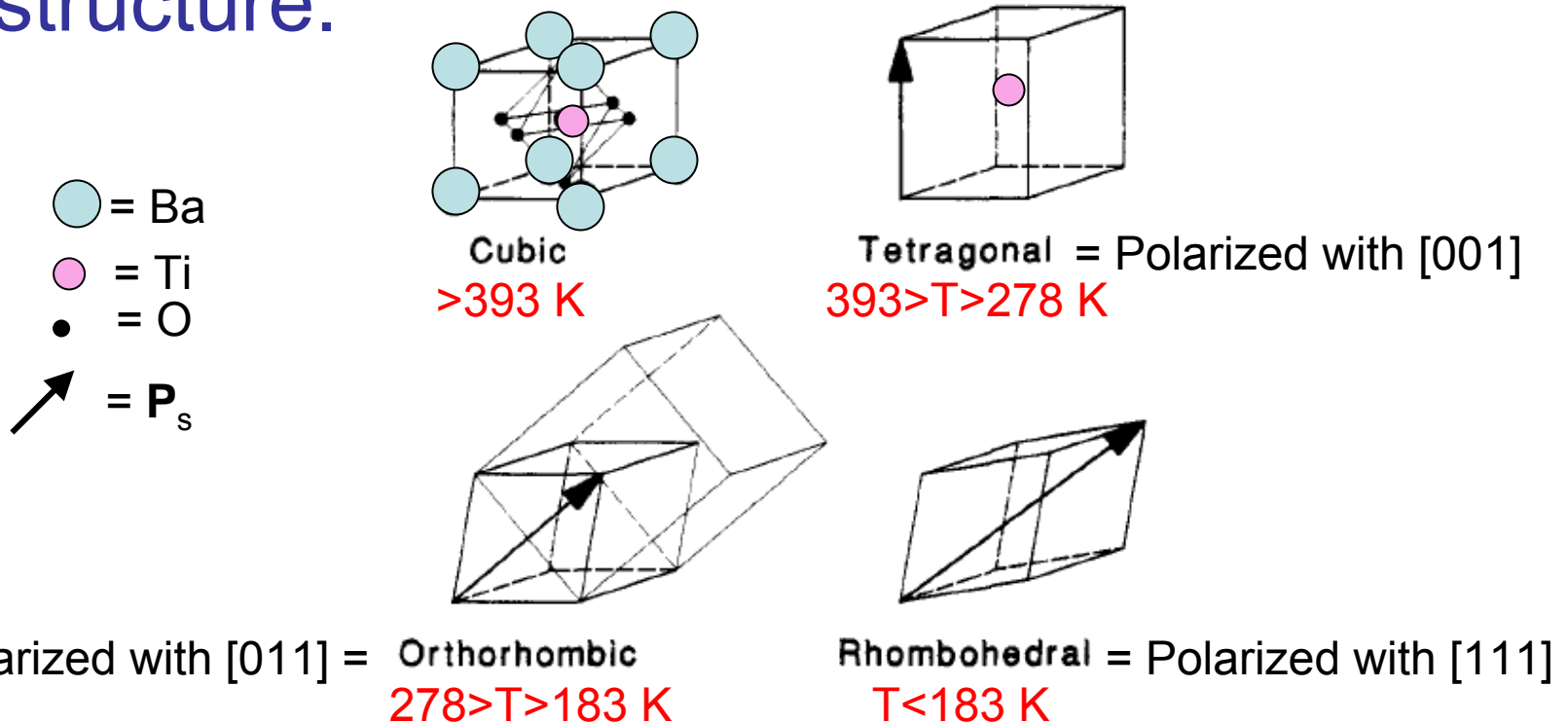
Ferroelectric Materials

- Asymmetric crystal structure of the material defines a net dipole in the **unit cell**, which imparts a spontaneous polarization for the bulk crystal.



Details on Polarization for BaTiO₃ (Unit Cell)

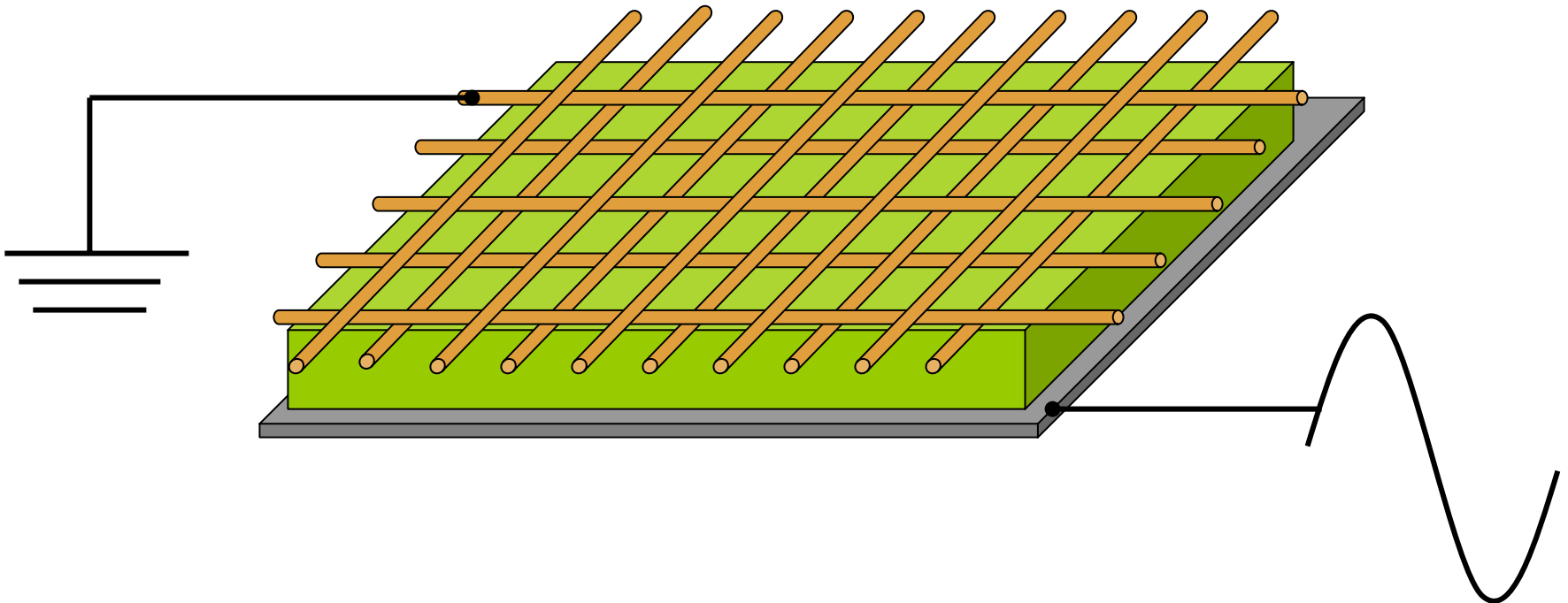
- Orientation of \mathbf{P}_s is dependent on crystal structure.



Structures¹ of the 4 different phases of BaTiO₃ and the phase transition temperatures. Position of O and Ti atoms defines polarization. Must choose phase according to experiment to be performed.

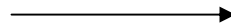
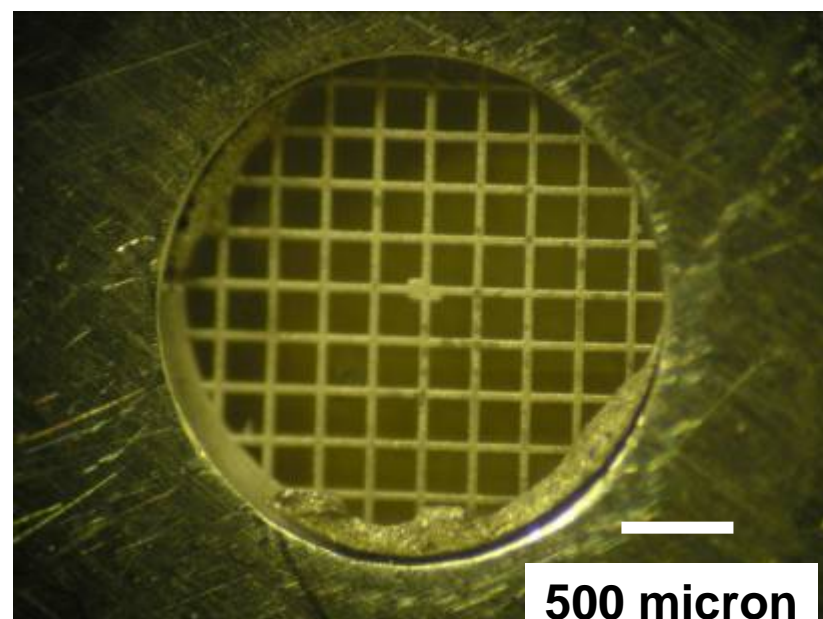
Achieving Polarization Switching (Electrodes)

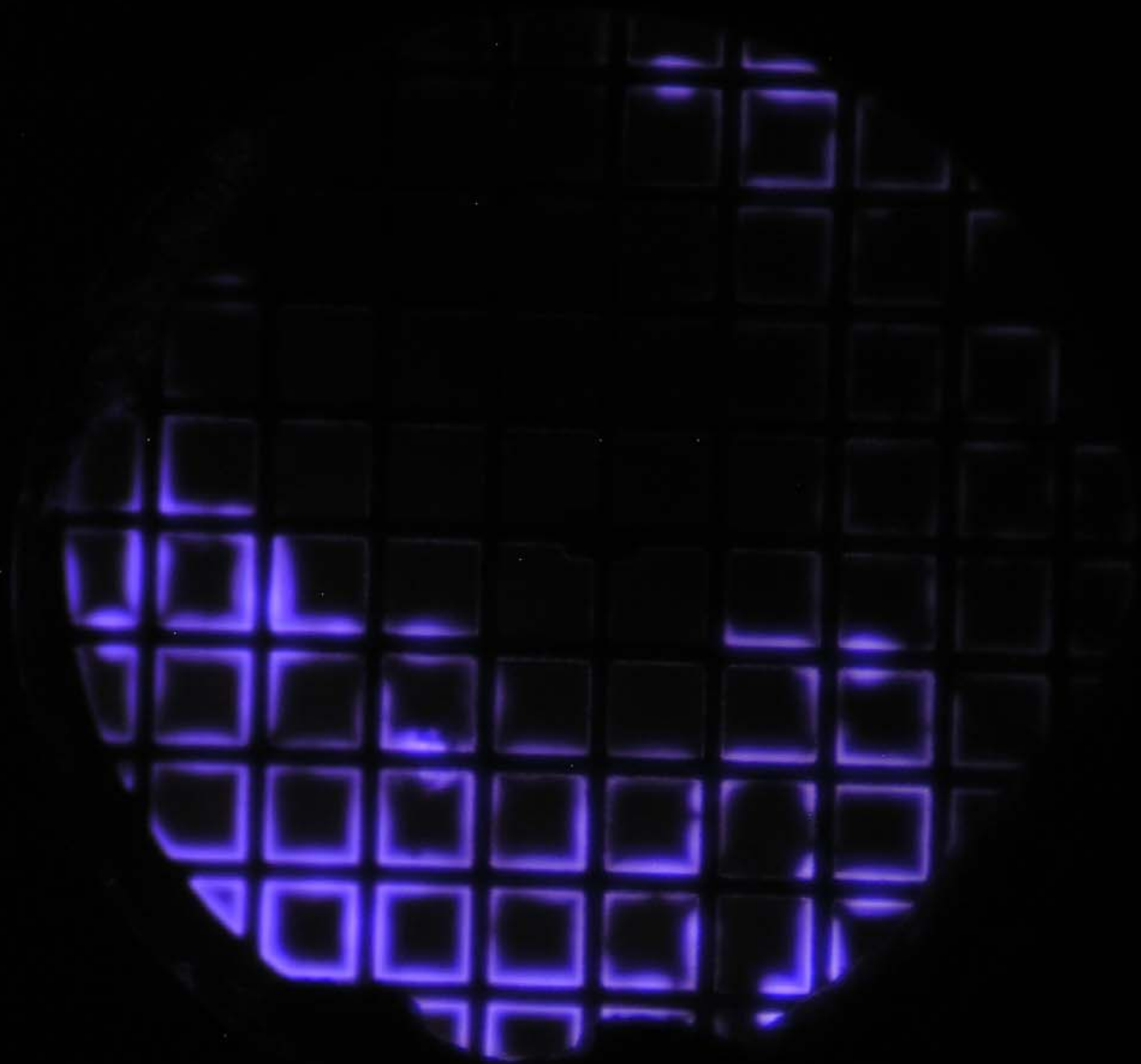
- Electrode arrangement varies by experiment; we use a solid electrode on the back side and a grid for the front electrode.



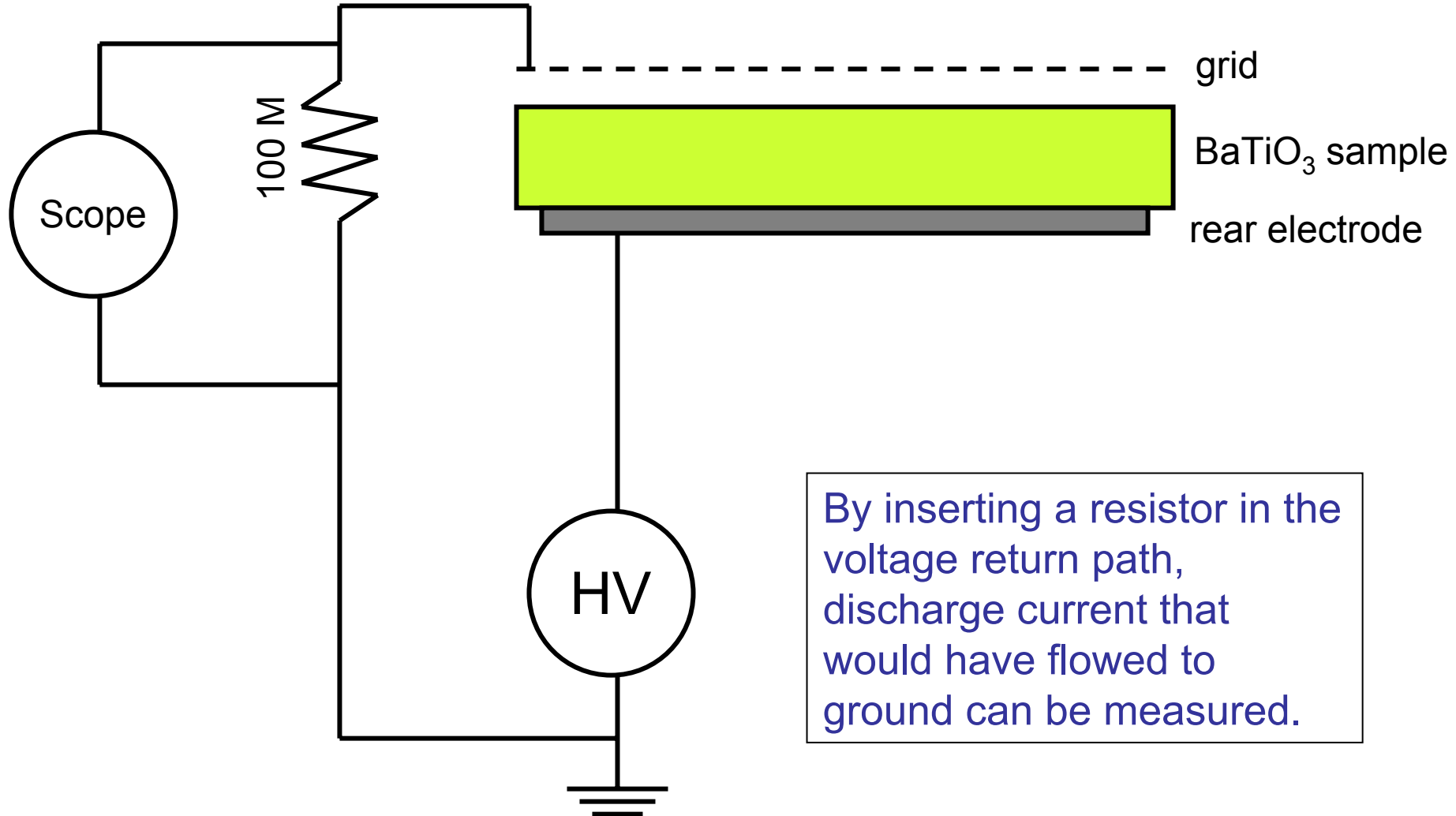
Plasma Formation in SwiFerr Ionizer

Plasma arises due to the electric fields created by the presence of a grounded grid in close proximity to the charged crystal face. Low light photography shows the plasma occurring most strongly near the grid wires.



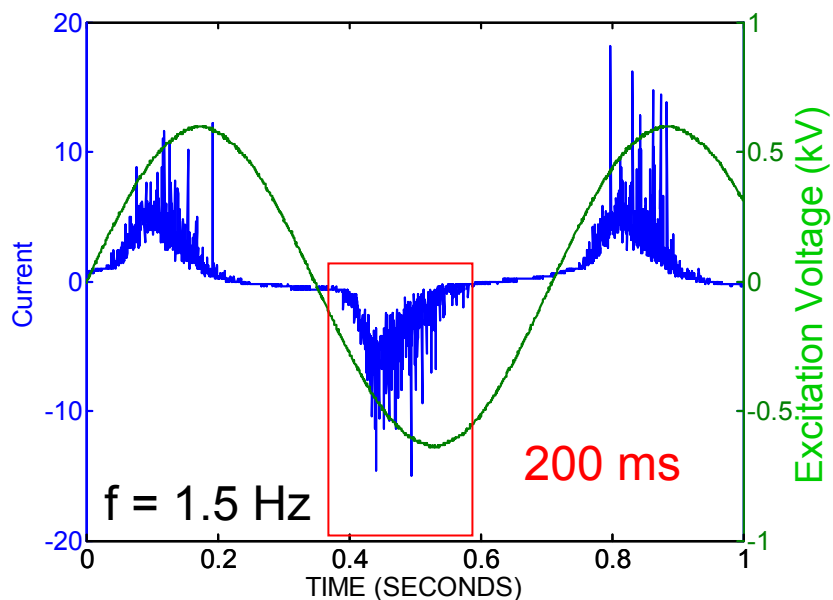


Electrical probing of plasma/discharge

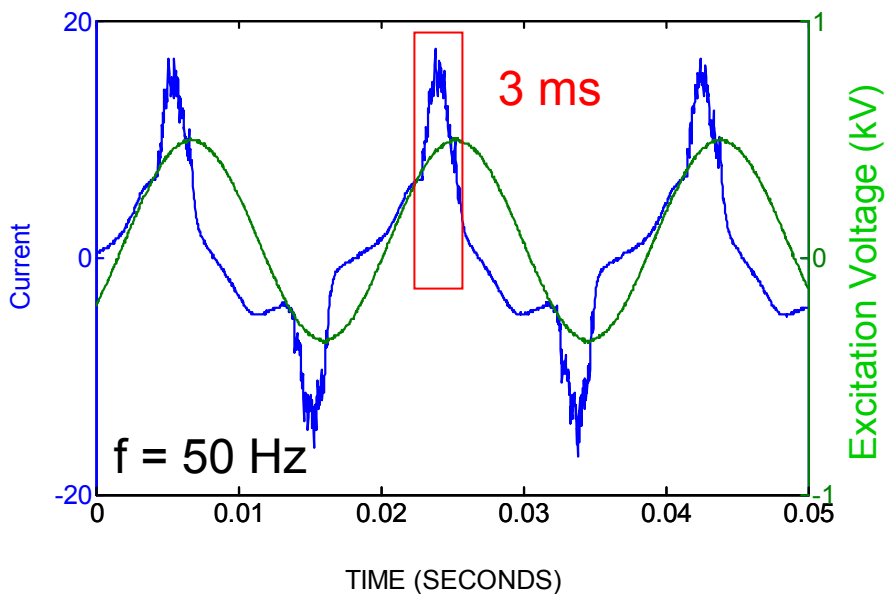
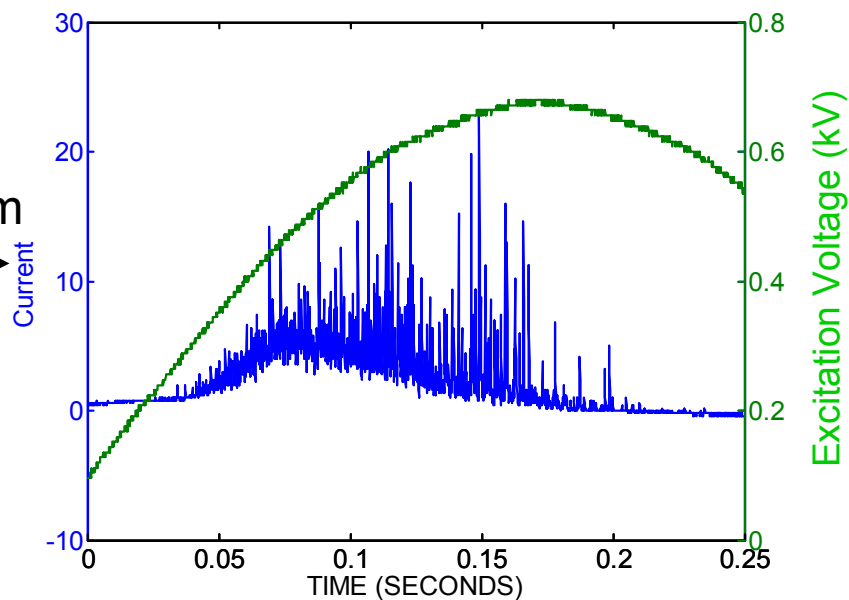


By inserting a resistor in the voltage return path, discharge current that would have flowed to ground can be measured.

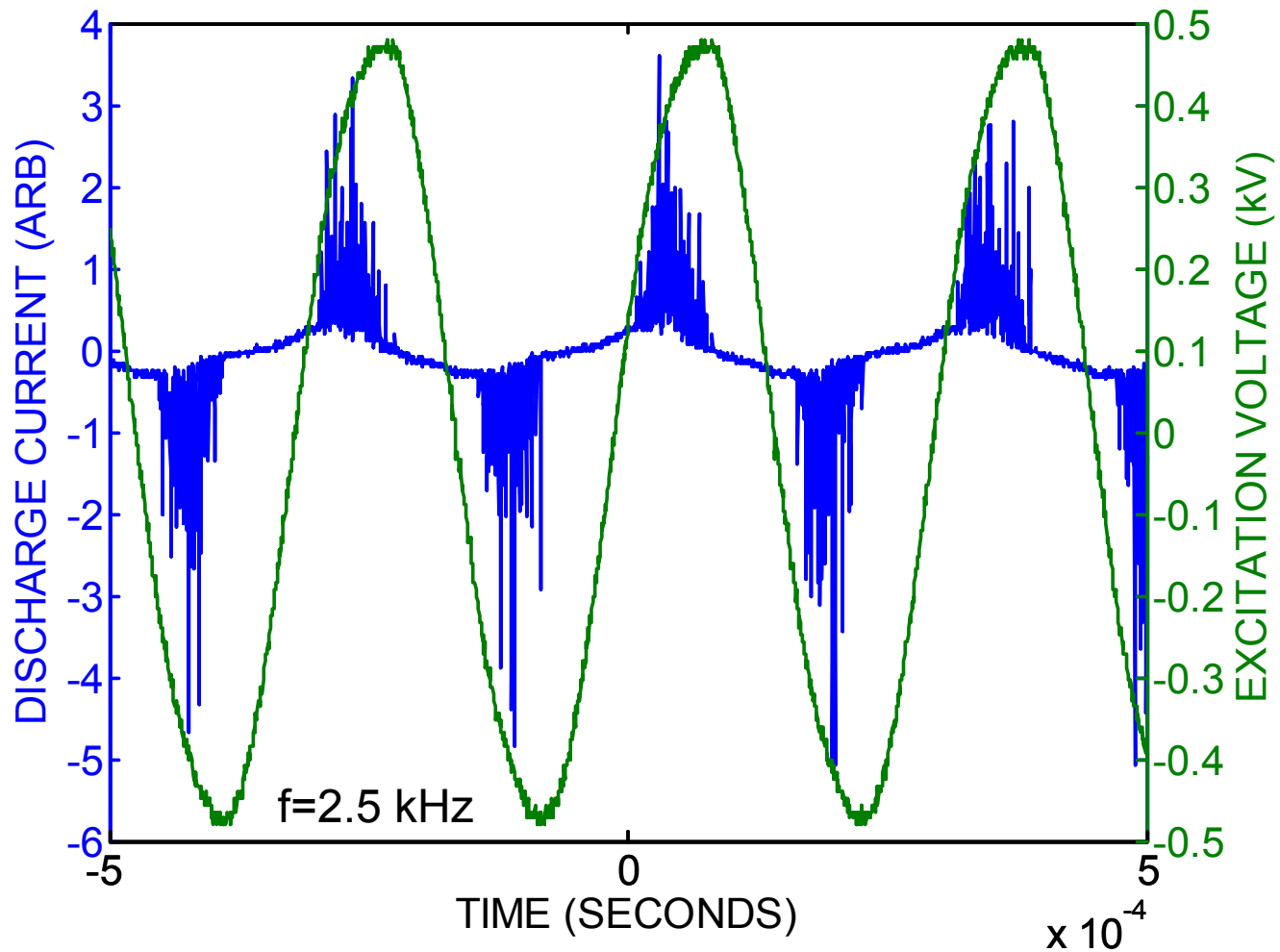
Timescale of Discharge



Zoom



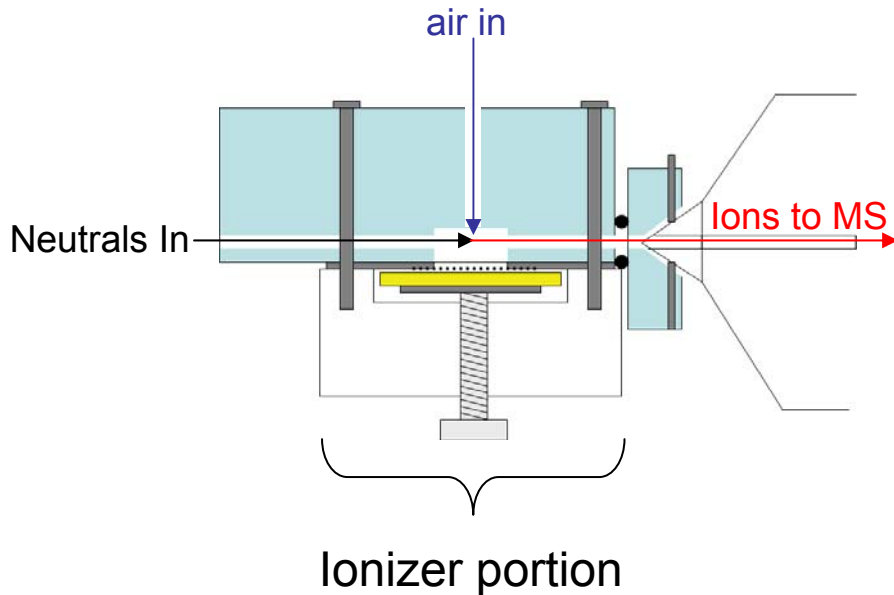
The discharge occurs during a half period of the excitation voltage, and is usually shorter than $\frac{1}{4}$ period. Thus, the timescale is proportional to the drive frequency. At this juncture, the source is not continuous.



$$T_{\text{discharge}} \leq \frac{1}{4f_{\text{excitation}}}$$

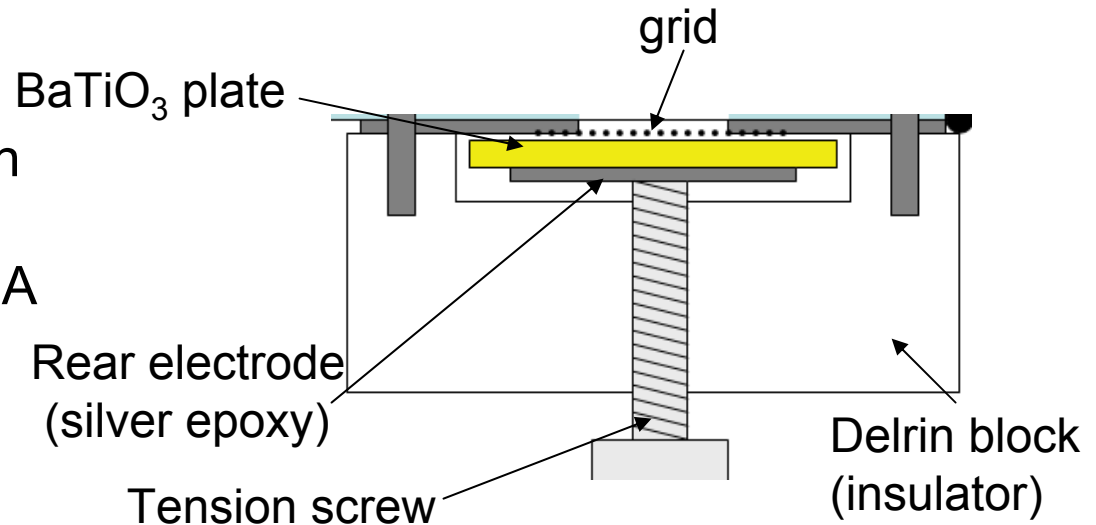
$$f_{\text{discharge}} = 2f_{\text{excitation}}$$

Switched Ferroelectric Ionizer

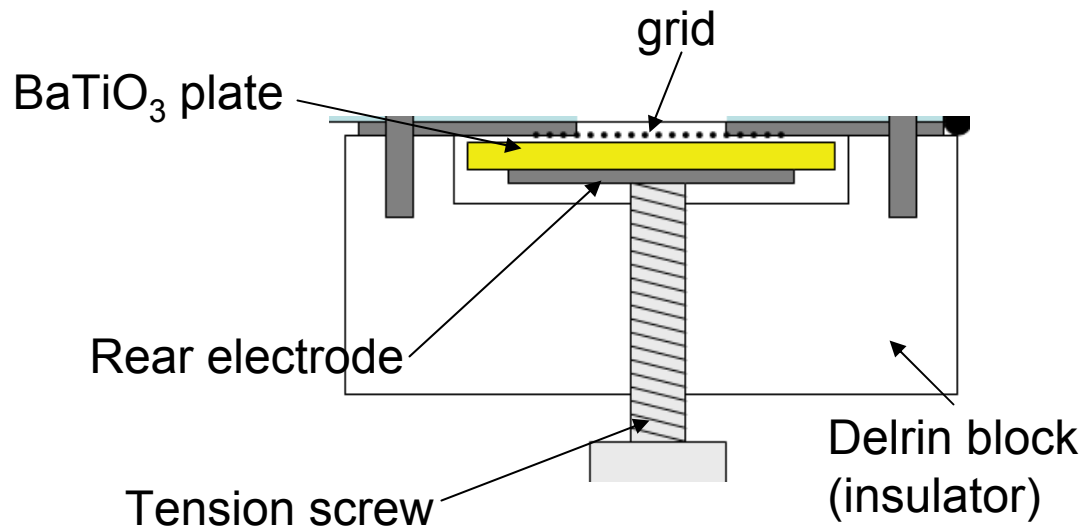


Neutrals are introduced into the reaction volume, where a plasma creates reagent ions that ionize trace species. Ions then flow into the inlet of an ion trap mass spectrometer.

Detail of ionizer region. A high voltage AC waveform is applied to the rear electrode. A plasma forms around the grid, held at ground potential.

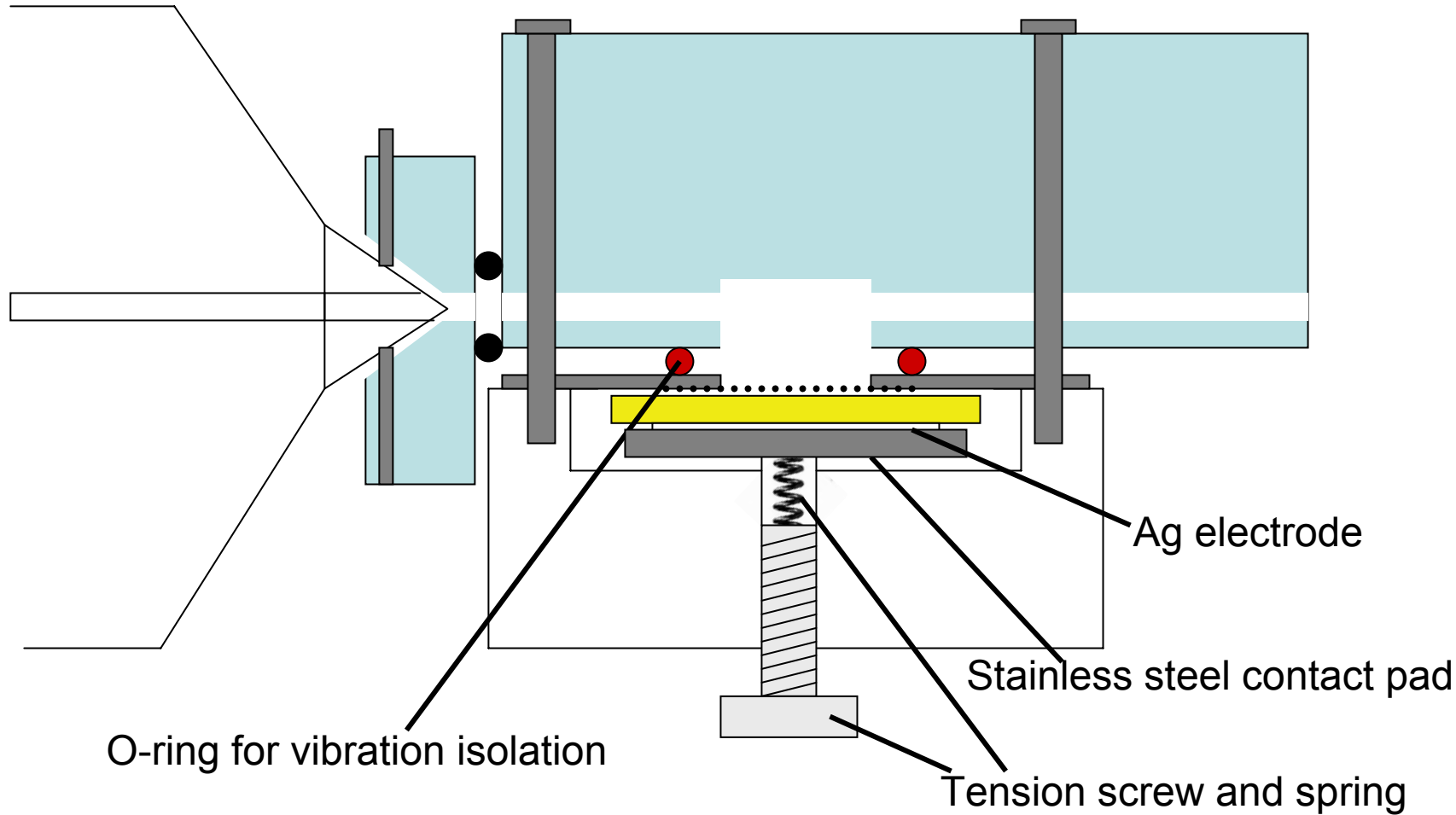


Details on source ruggedization



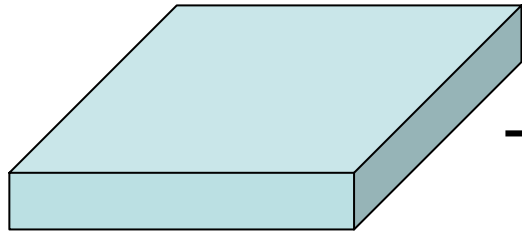
- Initial constructs of the device suffered from sample cracking. Cause of this was determined to be a non-rigid rear electrode as well as rigid clamping of the sample; piezoelectric vibrations caused mechanical stress.

Version 2

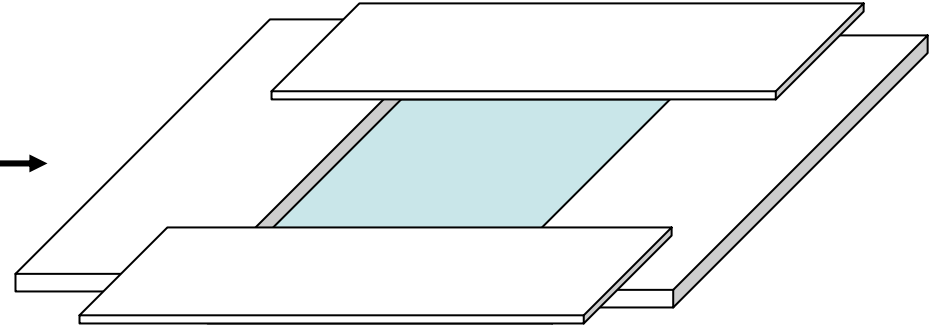


- The addition of the tension screw and spring, as well as the contact pad and o-ring contribute to rigidity and vibration isolation in the source.

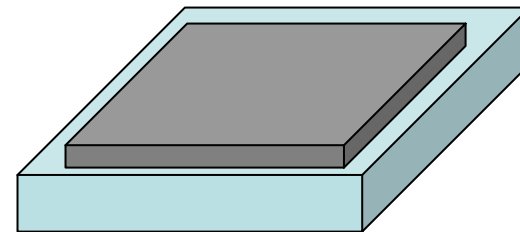
Fabrication sequence



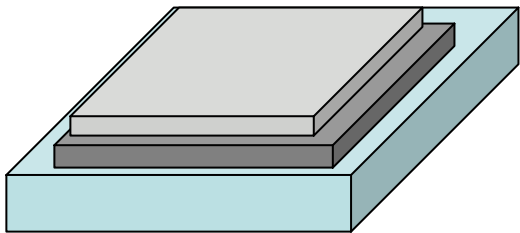
[001] BaTiO₃ (MTI Crystals)



Apply Scotch tape mask

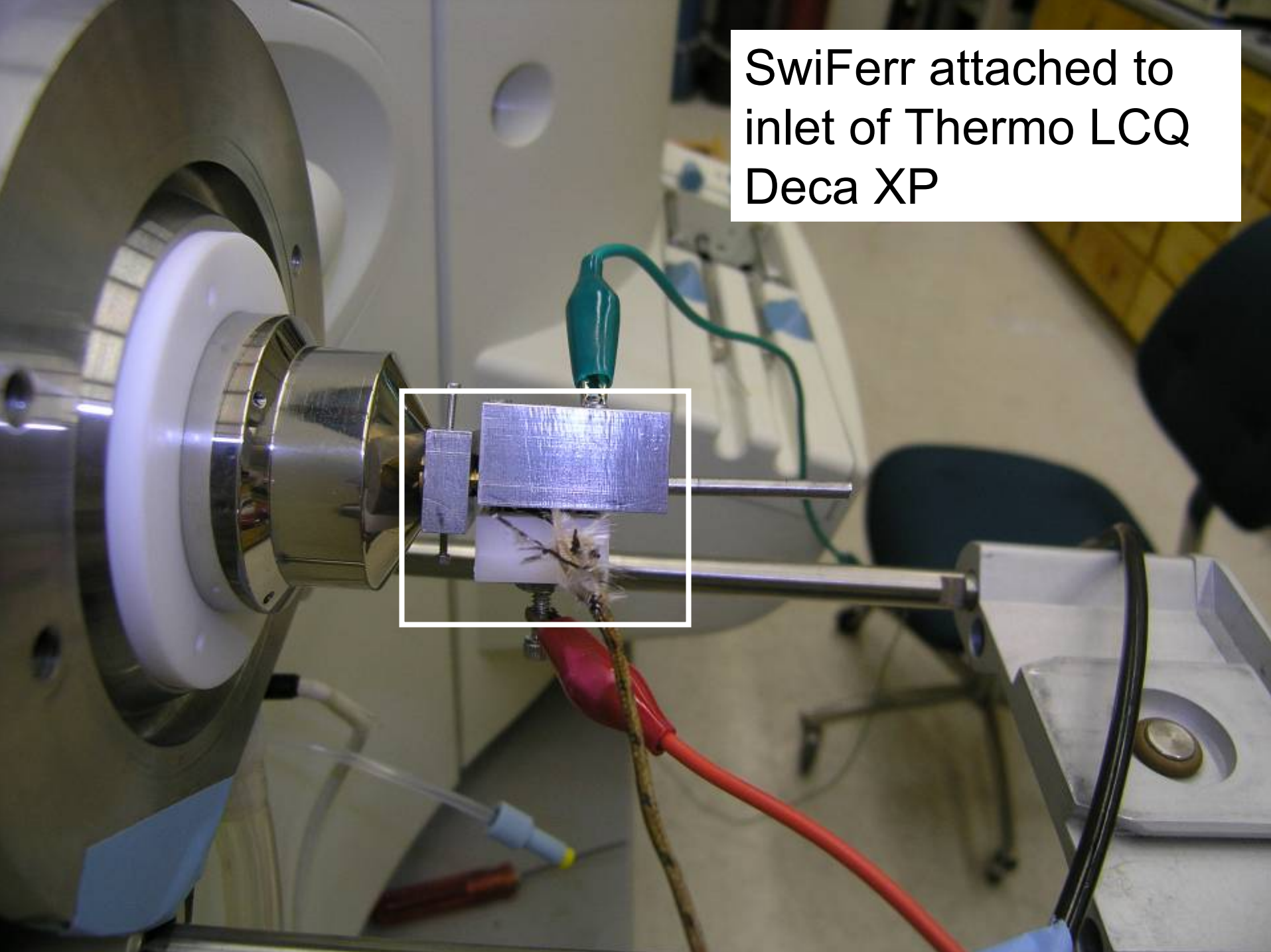


Application of silver epoxy
and mask liftoff

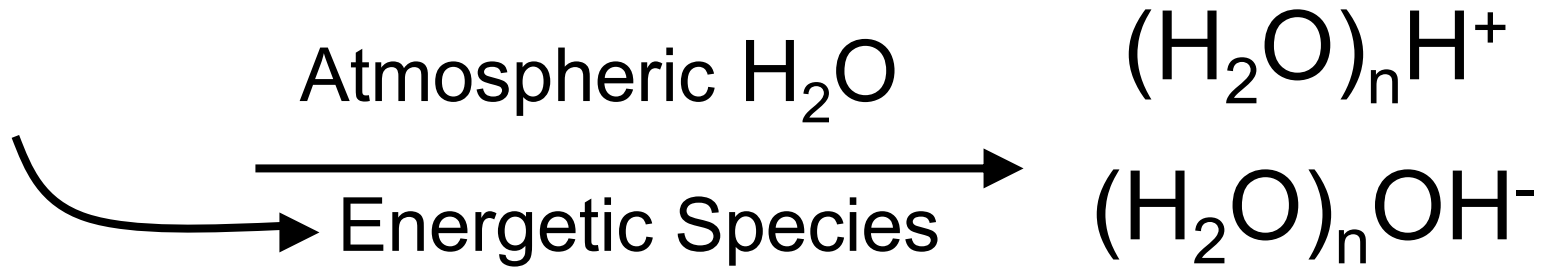
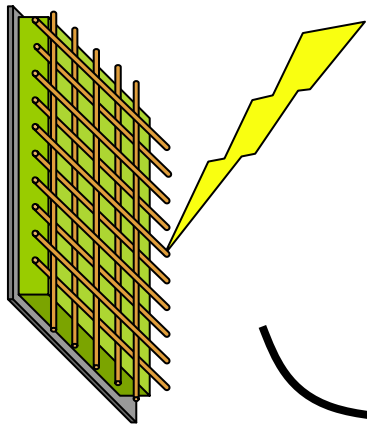


Application of contact pad on top
Of silver epoxy.

SwiFerr attached to inlet of Thermo LCQ Deca XP

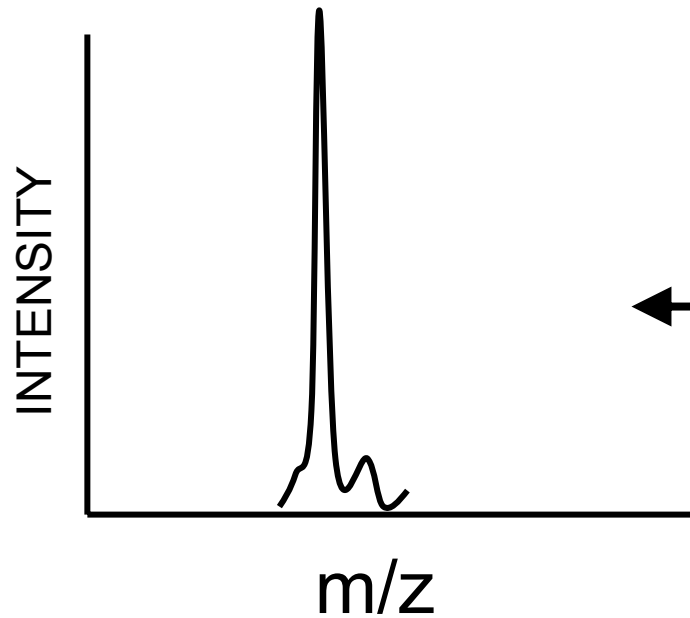


Proposed SwiFerr Ionization Mechanism:

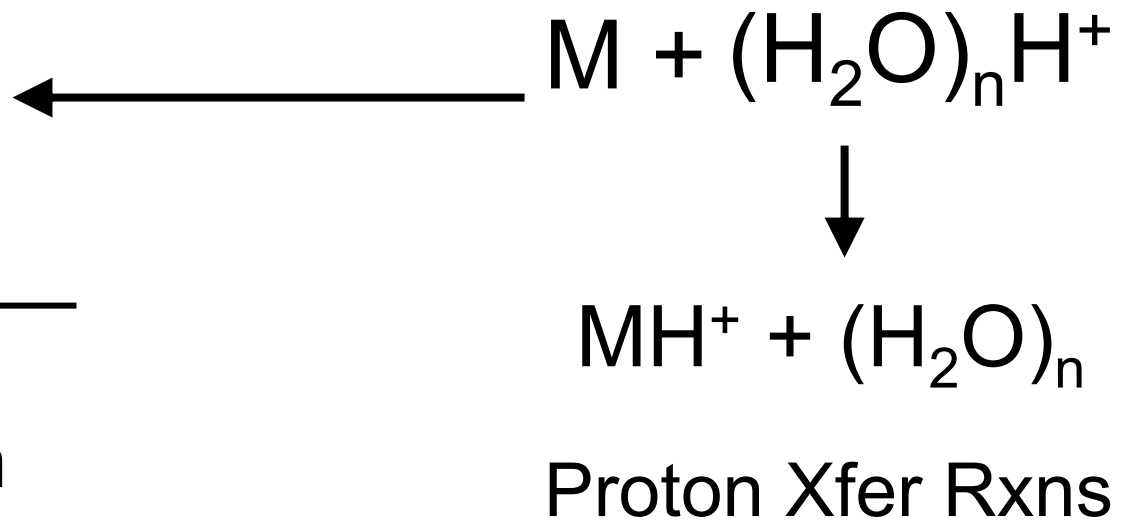


Switched Ferroelectric Plasma

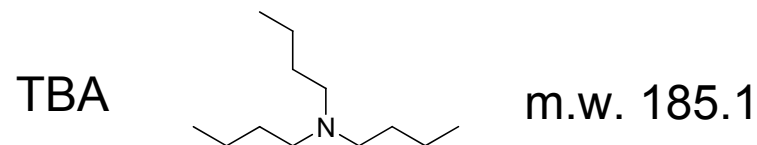
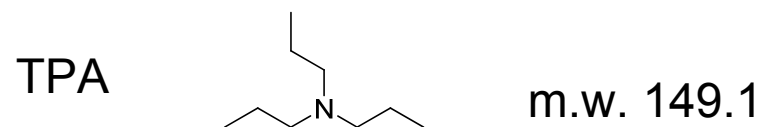
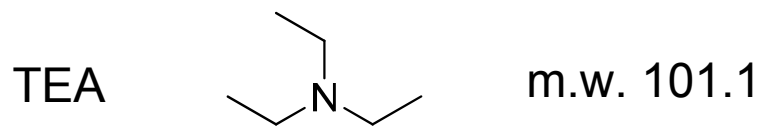
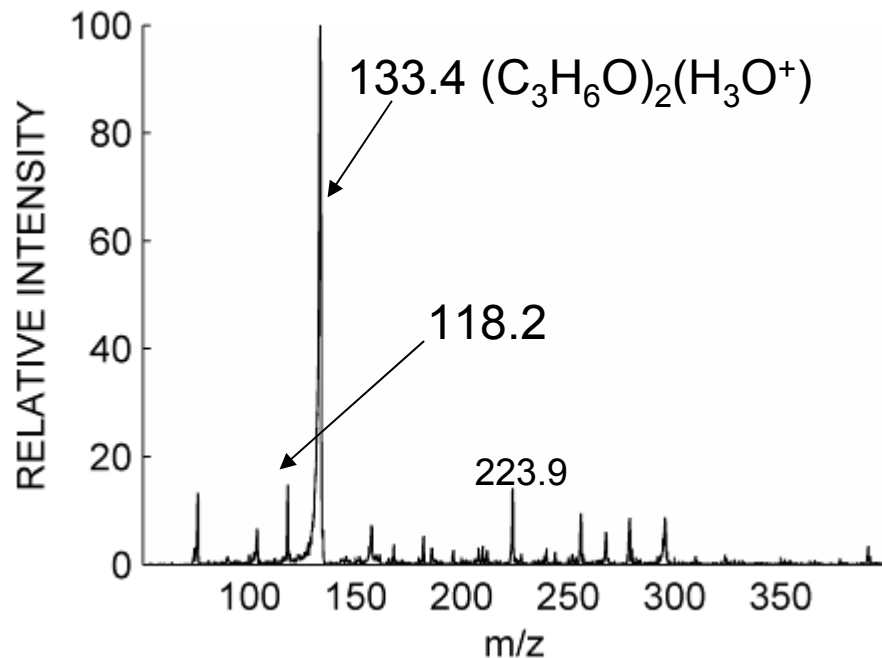
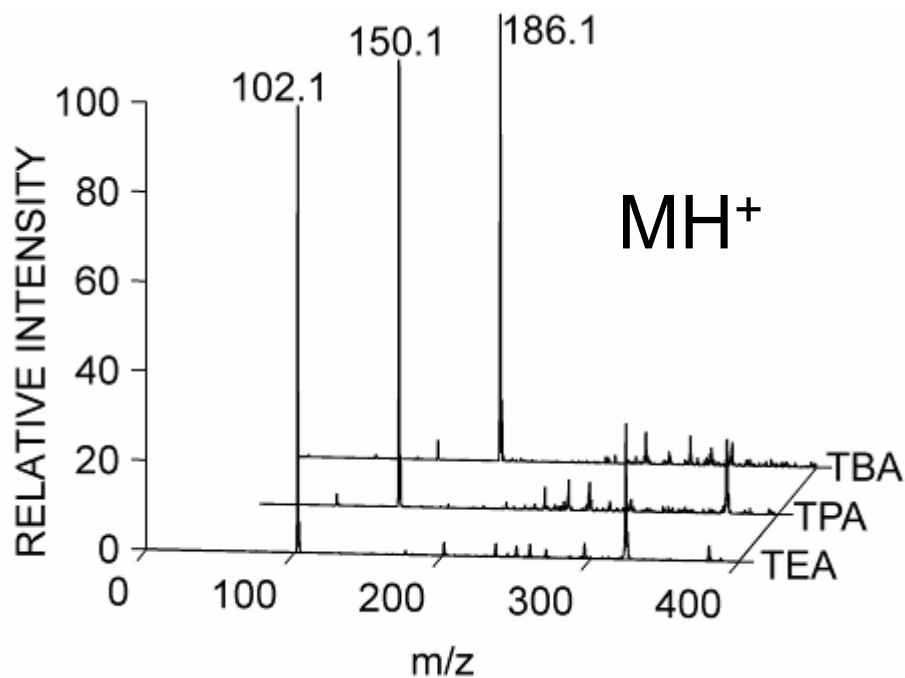
Chemical Ionization!



Mass Spectrum



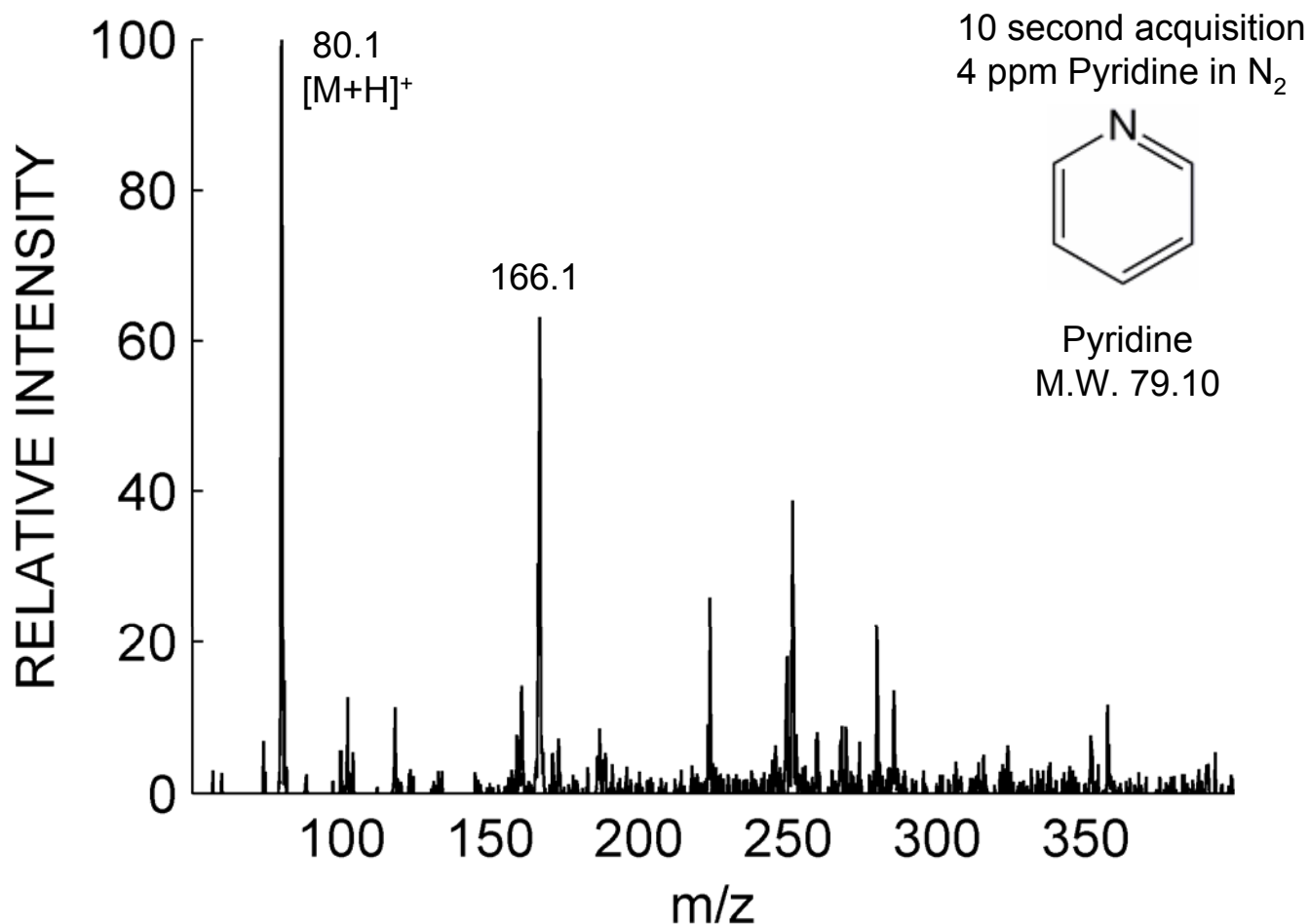
SwiFerr Organic Vapor Analysis



Acetone

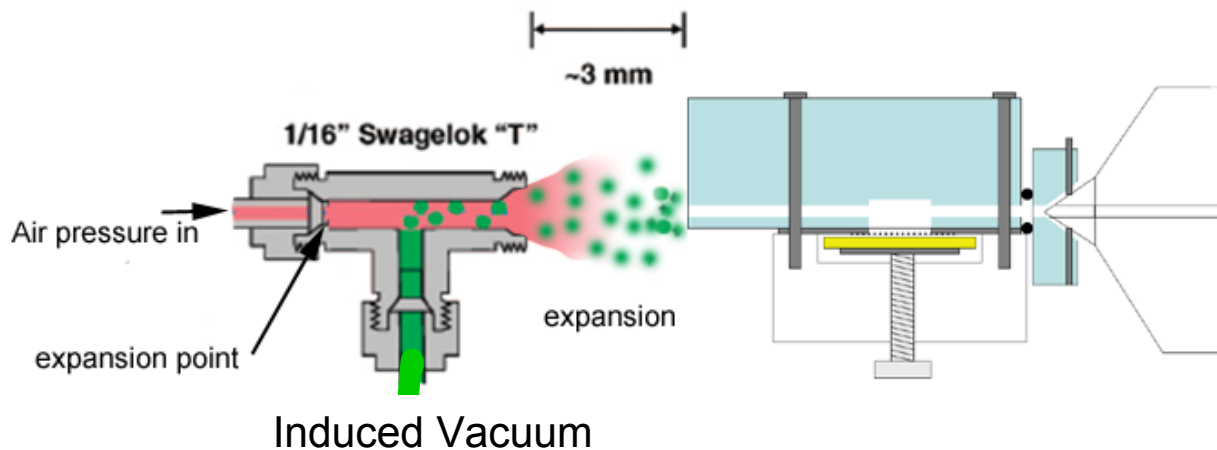


Vapor Detection at Low Concentrations

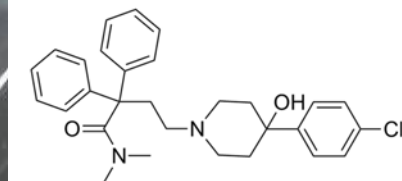
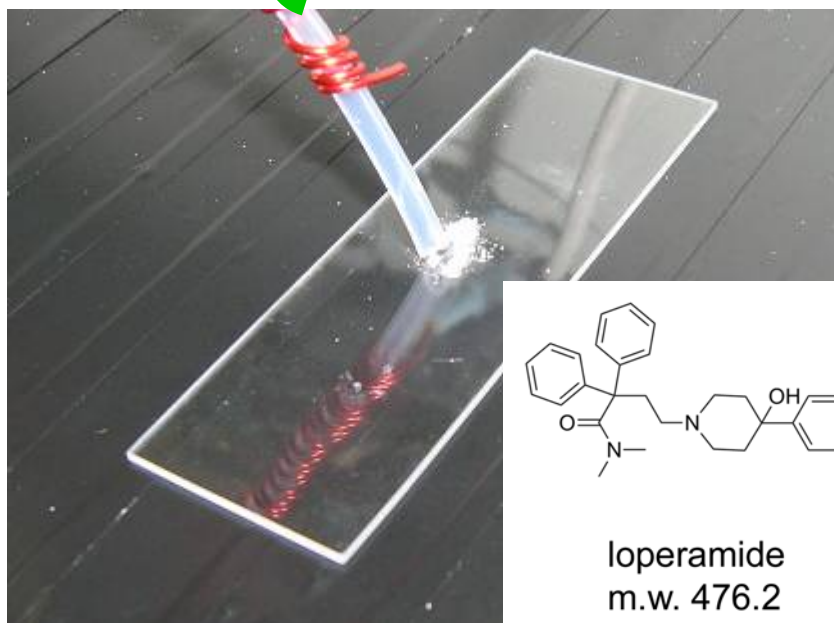


Pyridine was detected at concentrations approaching part-per-billion levels, suggesting ultimate sensitivity for SwiFerr to be in that range.

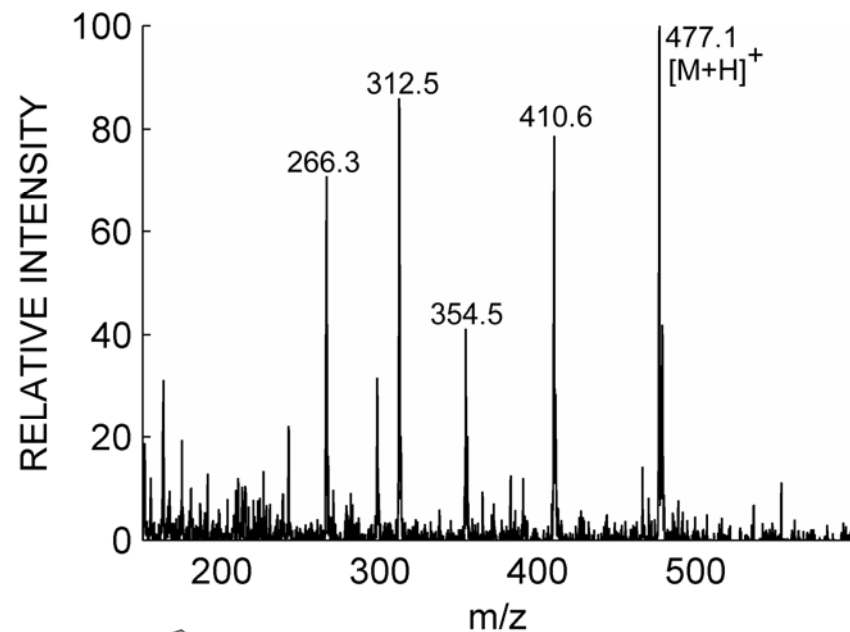
Aerosol Sampling and Analysis with SwiFerr



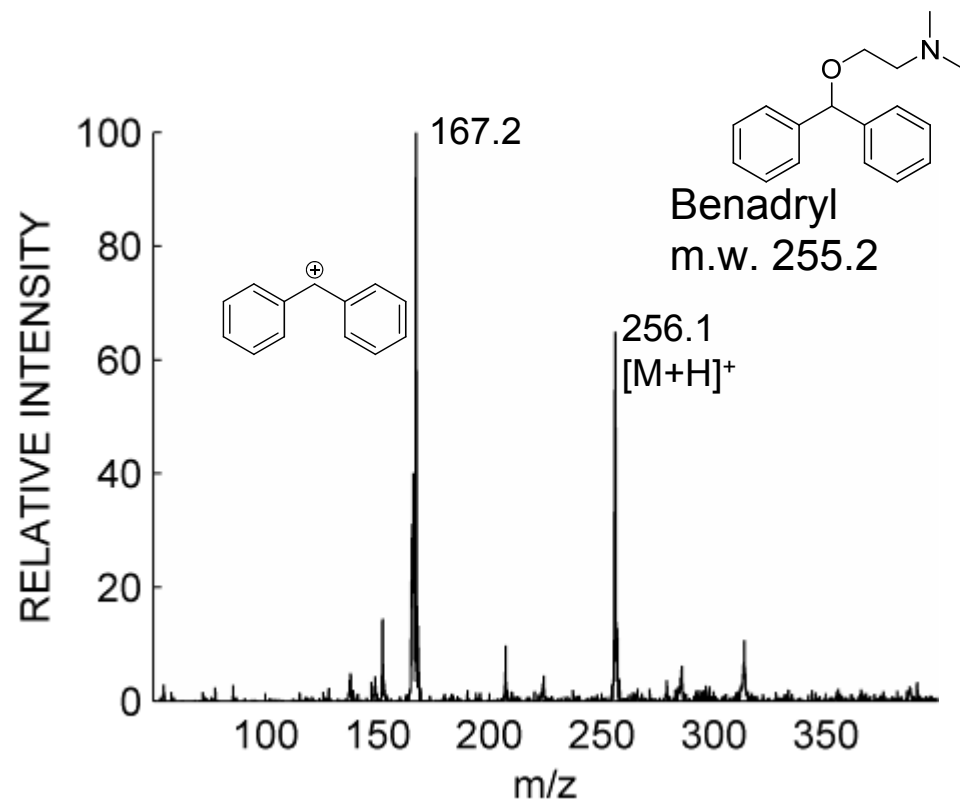
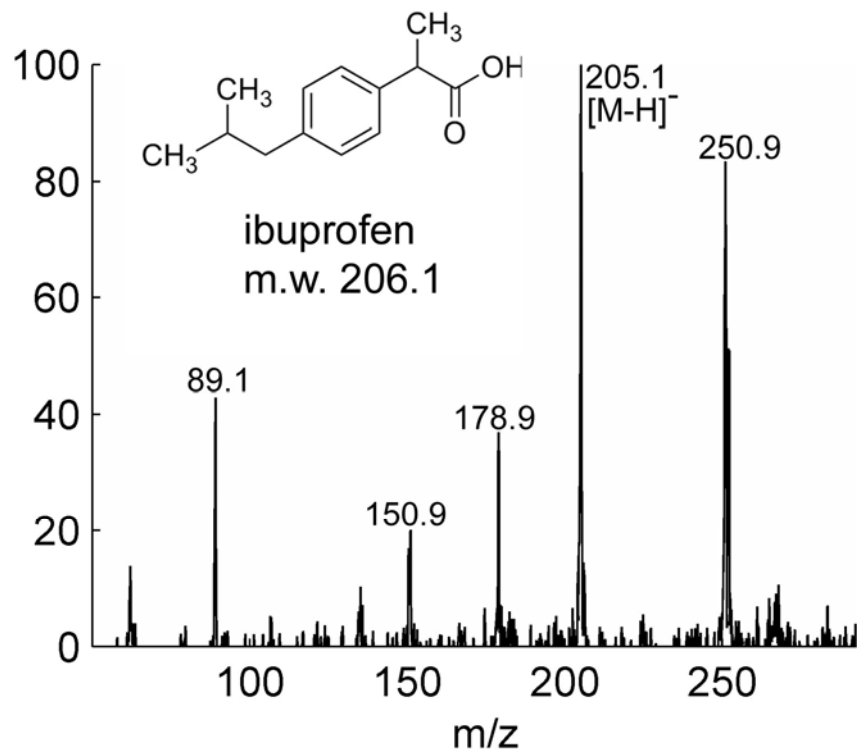
Pneumatic sampler used for sampling solids aerodynamically, injecting and then ionizing using SwiFerr.



loperamide
m.w. 476.2

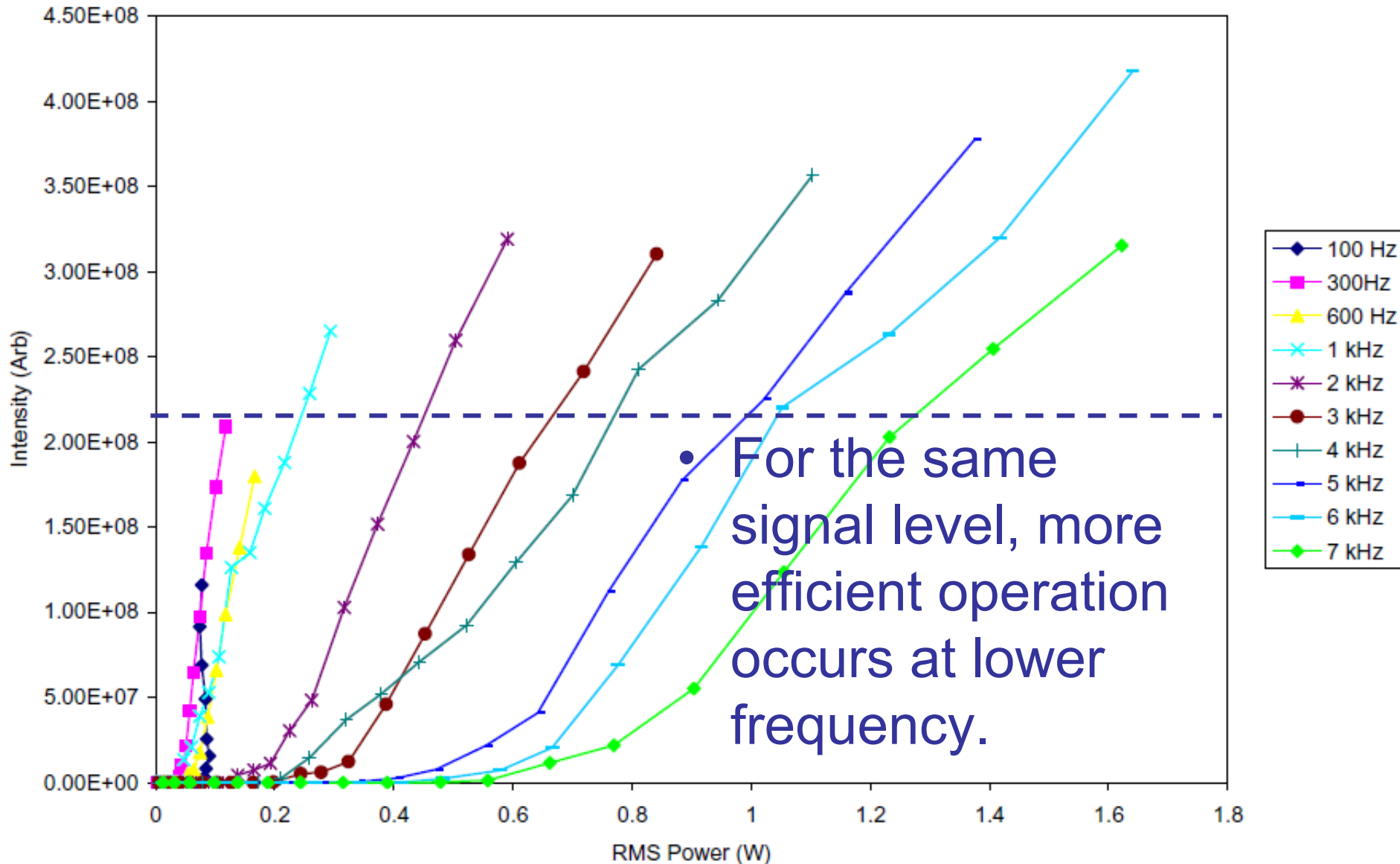


Pharmaceutical Analysis with SwiFerr



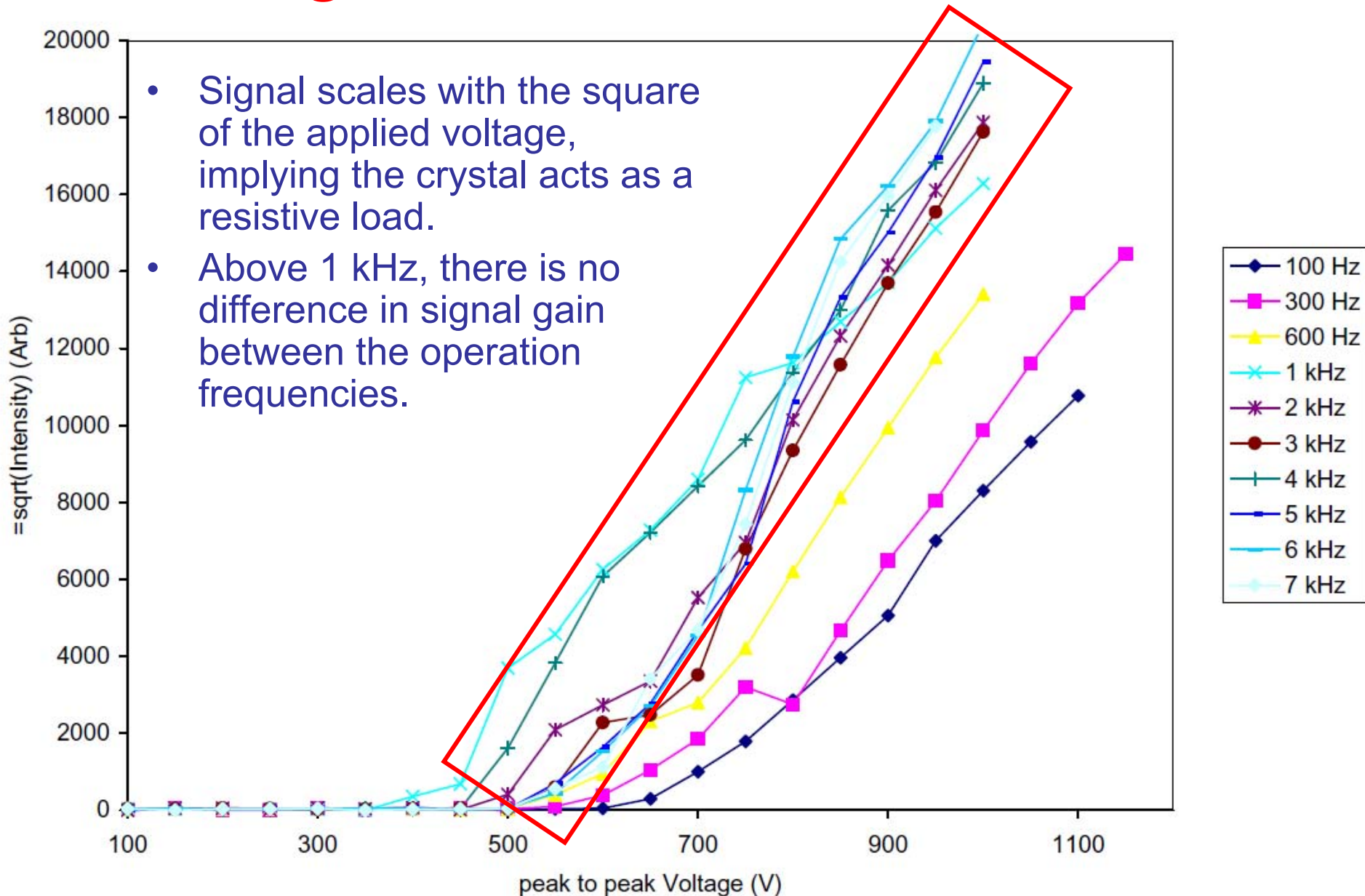
- Neat powder is introduced to the source as the crudest approximation of sampling.
- Versatility!

Power consumption of SwiFerr



Voltage threshold of ionization

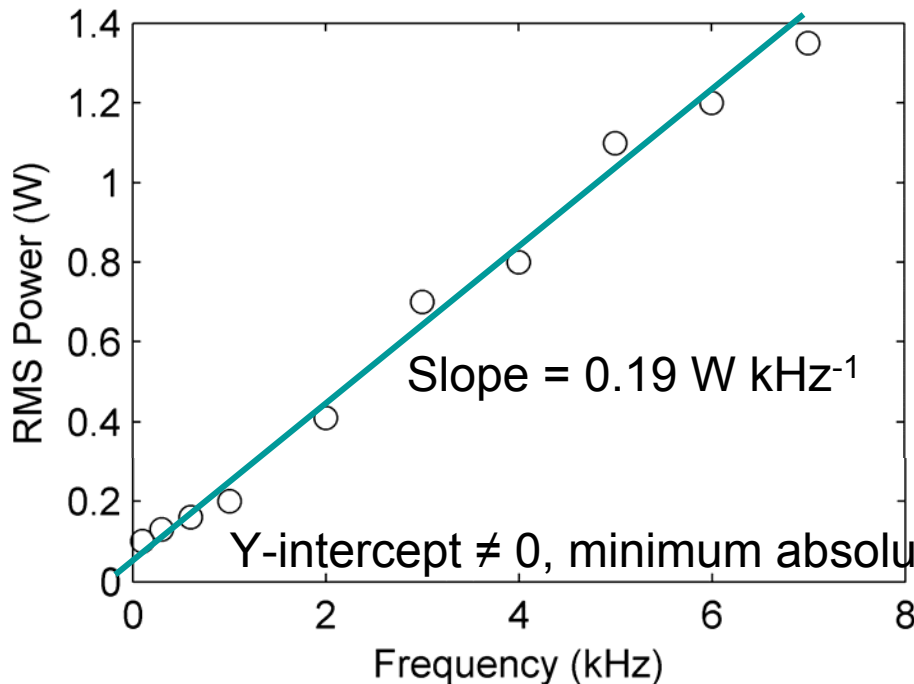
- Signal scales with the square of the applied voltage, implying the crystal acts as a resistive load.
- Above 1 kHz, there is no difference in signal gain between the operation frequencies.



Optimal Operation

- Minimum operation frequency determined by power budget and detector duty cycle

Range: 0.1 W and up



LCQ: Duty cycle: 3 scans / sec.
IMS: Dependent on ion gating
DMS: Low detection duty cycle-
higher frequency operation
may be required.
TOF: Synchronization of pulsing
with pusher

Summary: SwiFerr Ion Source

- Able to analyze a variety of substances with minimal sample preparation
- Low power consumption and simplicity of design
- Ease of miniaturization
- No consumables
- Long term autonomous operation
- Applications: Harsh environments, hazmat detection, illicit drug detection, CBW analysis

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Beckman Institute at Caltech

