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PLASMA ION SOURCE FOR ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETRY

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BACKGROUND

Jim Alberti – MSEE from the University of South Florida in Tampa, FL. and a BSEE from the Illinois Institute of Technology in Chicago, IL. 30+ years in R&D, product development, and systems engineering of instruments for industrial, medical, space, marine, and government applications, including instruments used in chemical analysis (both DMS and mass spectrometers) and systems utilizing DMS as a pre-filter for mass spectrometers. Co-author on several peer reviewed publications in journals such as Analytical Chemistry. Co-founder of MicroPlasma Systems.

Erkin Nazarov – Ph.D. from Ioffe Physical Technical Institute in Leningrad (1982) and Doctor of Physical – Mathematical Sciences from St. Petersburg Polytechnic University (1992, Russia). Pioneer and respected expert in DMS technology and developed DMS instruments at the Uzbek Academy of Sciences in the former Soviet Union and at New Mexico State University where he was an Associate Professor in Chemical & Biological Sciences. Chief Scientist and R&D manager at Sionex Corporation (2002 – 2010) and Senior Scientist at the Draper Laboratory at the University of South Florida 2010- 2016. Co-founder of MicroPlasma Systems.

Peter Fowler - Ph.D. from New Mexico State University (2021). Demonstrating new capabilities for molecular identification out of his doctoral research on multi-stage DMS instruments with several published papers, Peter is currently PI for an NSF SBIR to commercialize his doctoral research as CEO and co-founder of GP Ionics LLC.

Gary Eiceman - Ph.D. from UC Boulder (1977) Prof. Gary Eiceman has a 40+ year career in gas ion chemistry and is head of one of two historic research centers for Ion Mobility Spectrometry and allied techniques. He continues contributing research internationally in both fundamentals and applications of gas ion measurements through key government, academic, and industrial partnerships, including his role as President in GP Ionics LLC.

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Objective:

Develop a dual polarity, non-radioactive ion source replacement for existing ion sources with comparable or improved performance.

Why?

Existing ion sources for volatile organic compounds:

- Need longer operational lifetime with high efficiency of ion formation
- Need ability to ionize difficult ionization molecules
- Need enhanced efficiency of negative ion formation
- Can be cumbersome, complex and expensive to use
- Radioactive ion sources require regulatory oversight due to health and safety concerns, which is expensive and burdensome to the user
- Minimize power consumption (preferably < 5 Watts) if used in portable instruments

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Goals:

Ion source should provide:

- Dual polarity effective ion species generation
- Intensity of generated ion species comparable with existing ion sources, including radioactive
- Provide stability and longevity of operation in gasses at ambient pressure with enhanced gas flow streams
- Ease of use
- Total power consumption < 5 Watts
- Low cost
- Life-time operation of at least 1500 hours

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Plasma Gas Phase Chemistry Considerations

Plasma ion sources are not new and have been used successfully in positive polarity ionization. However, previous implementations of these sources in atmospheric conditions were not successful ionizing analyte in negative polarity due to ineffective removal of non-desirable ion complexes (**O_3^-, NO_x^-, CO_x^-**), formed due to plasma chemistry.

In **positive polarity operation**, positive ions are not affected by non-desirable ion complexes and are, therefore, available for ionization of analyte molecules with high efficiency.

In **negative polarity operation**, ion species with high electron affinity (EA) are formed in plasma and reduces (and can even prevent) efficiency of ionization of analyte molecules. Therefore, analyte ionization in negative polarity is difficult.

The goal of a dual polarity plasma ion source (NRIS) is to eliminate the presence of non-desirable ion complexes (**O_3^-, NO_x^-, CO_x^-**) when operating in negative polarity.

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First Test of the Non-radioactive Capacitive Discharge Plasma Source (NMSU, 1999)

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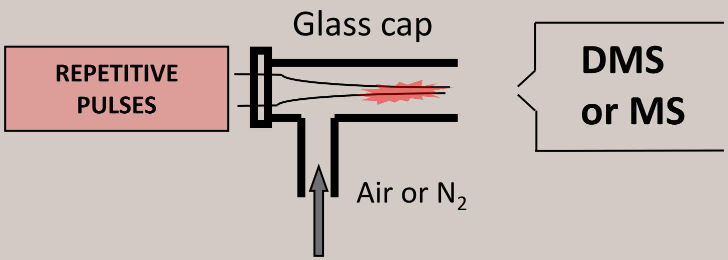
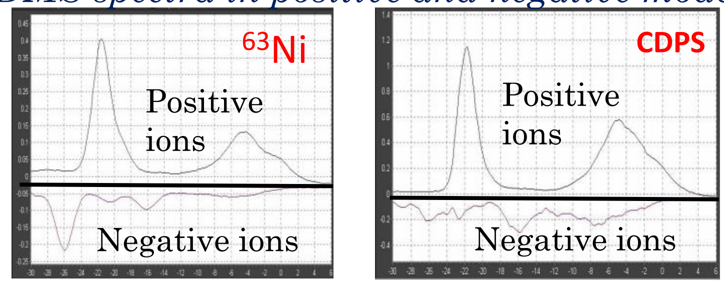
Plasma ion identification



DMS spectra in positive and negative mode



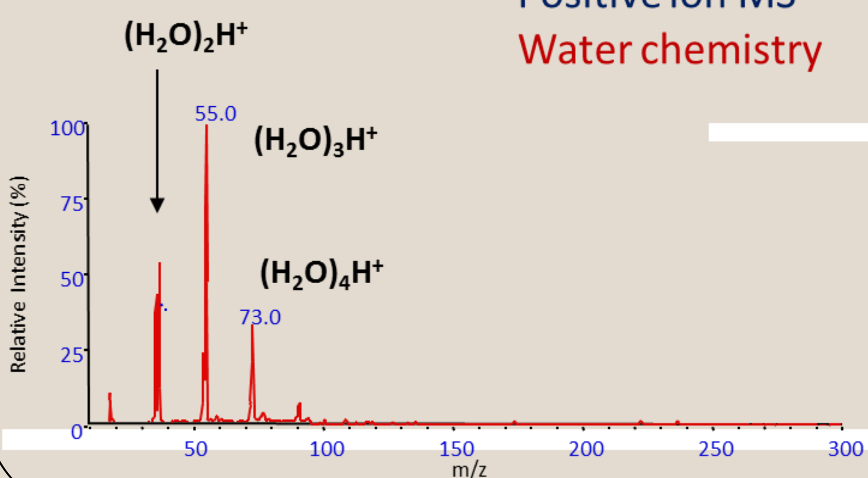
- No issue in positive mode.
- Issue with negative ions due to No_x generation.

Maximal ion current is 4 pA

Mass spectra in positive and negative mode

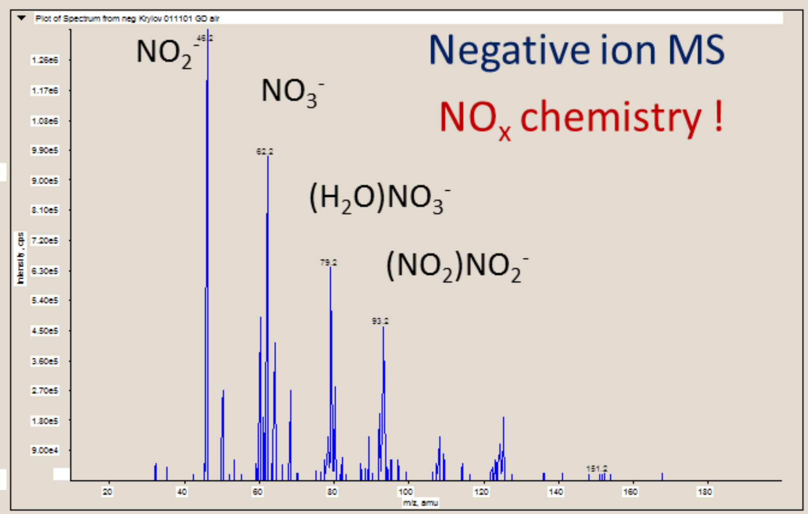
Positive ion MS

Water chemistry



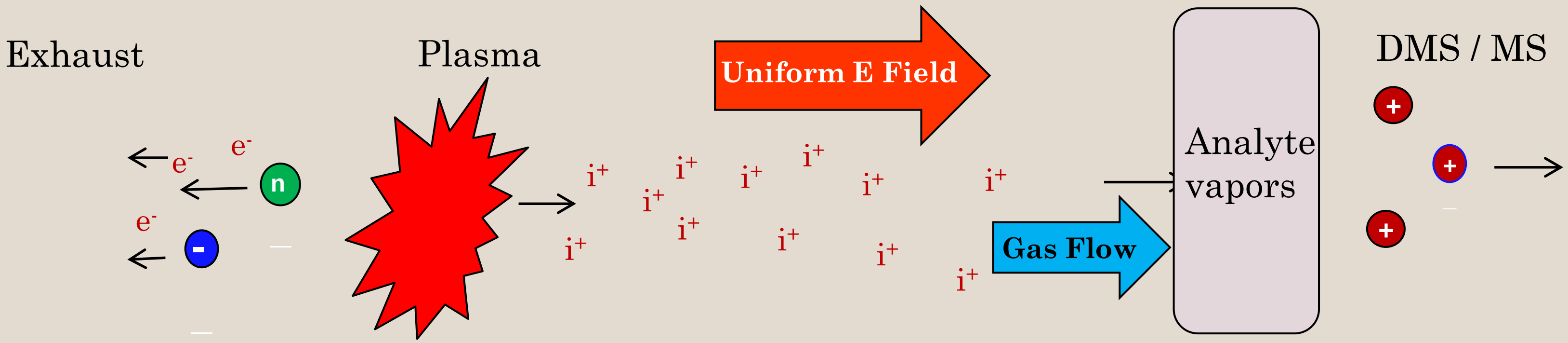
Negative ion MS

NO_x chemistry !

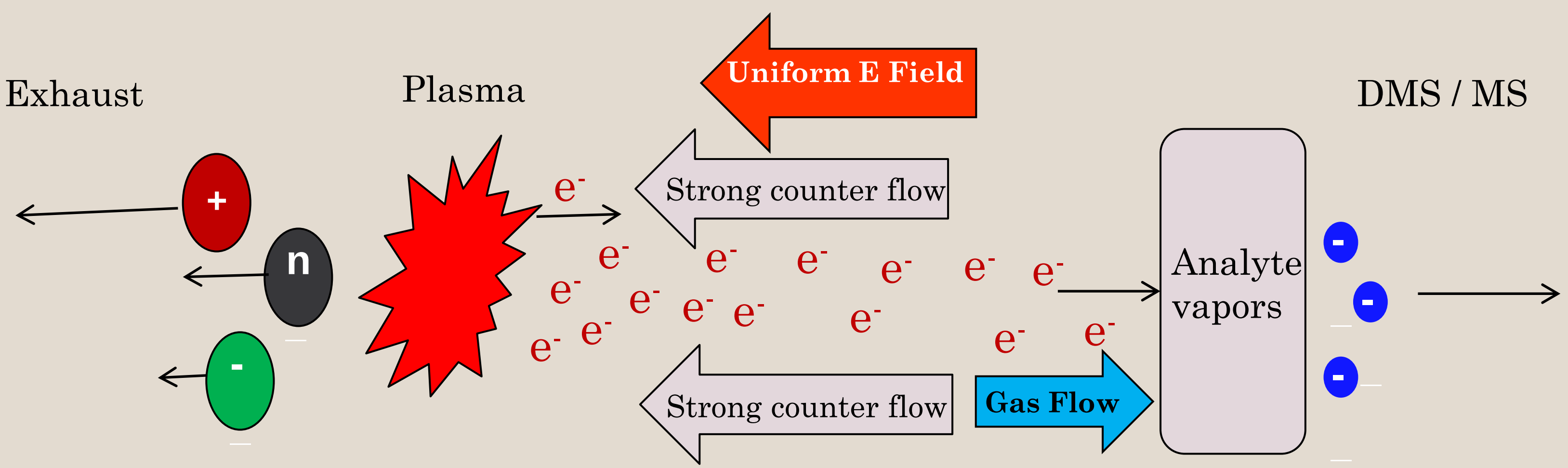


Our Concept for Positive and Negative Polarity

In <u>positive mode</u>: a uniform electric field directs the positive ions towards the reaction chamber to ionize analyte vapors. No counter-flow gas is required.



In <u>negative mode</u>: because undesirable ion complexes are larger in size than the desired electrons, clean the plasma with a strong counter-flow gas, then extract only the electrons from the plasma with a moderate, uniform electric field to direct them into the reaction chamber and ionize the vapors of analyte. With this design approach, sample ionization occurs comparably to a ^{63}Ni ionization source.



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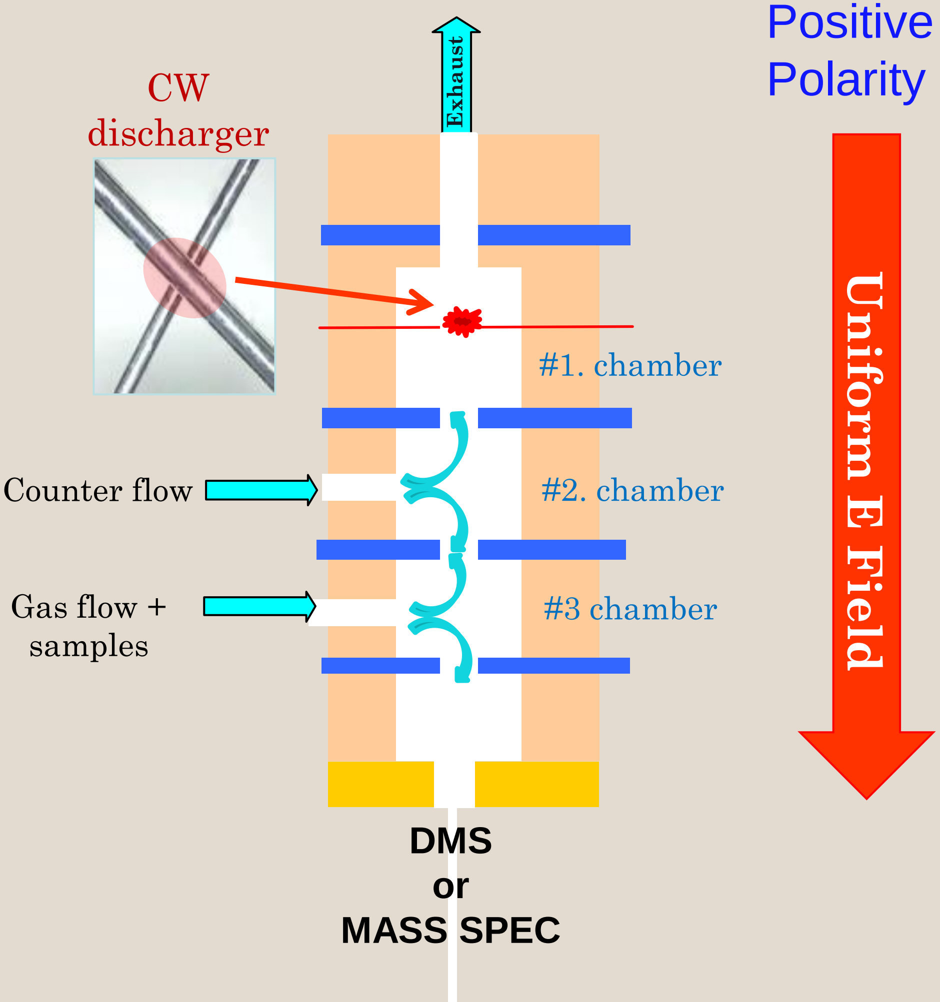
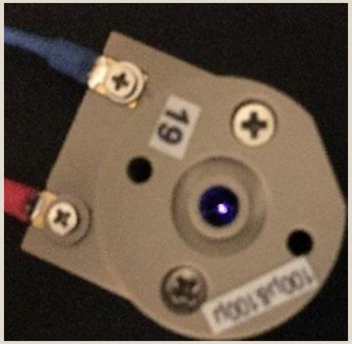
Draper Ion Source Design – Crossed Wire, Single Point

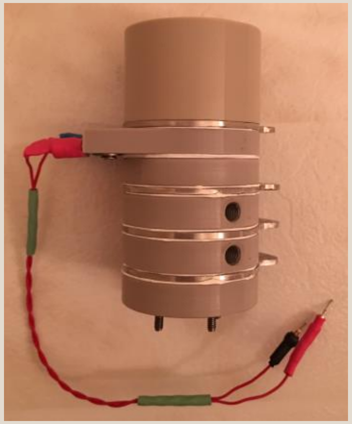
Dual Polarity Ion Source



PLASMA



DRAPER DESIGN



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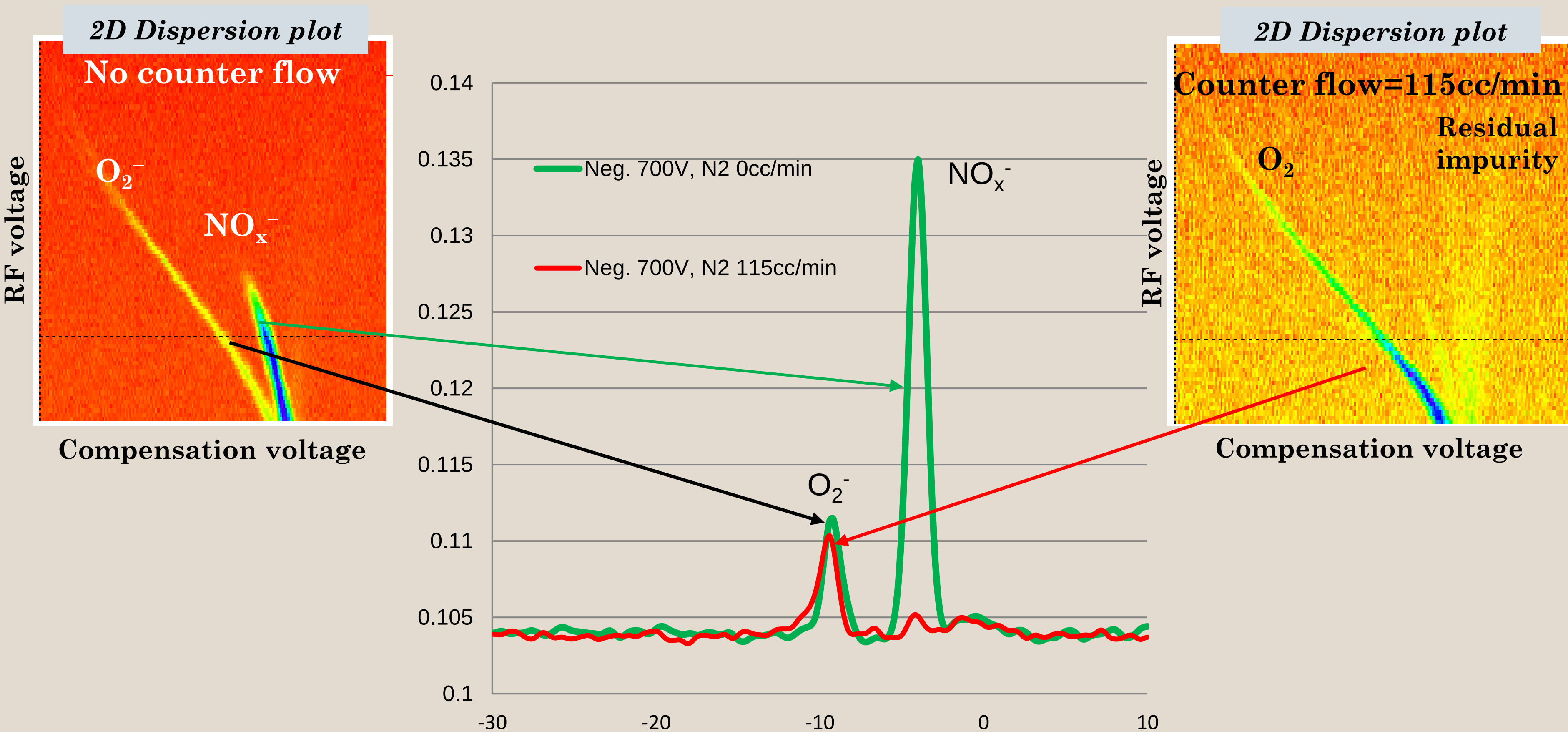
Effect of Counter Flow on Background Negative Ion Spectra using DMS

Direct experimental result for elimination negative NOx ions



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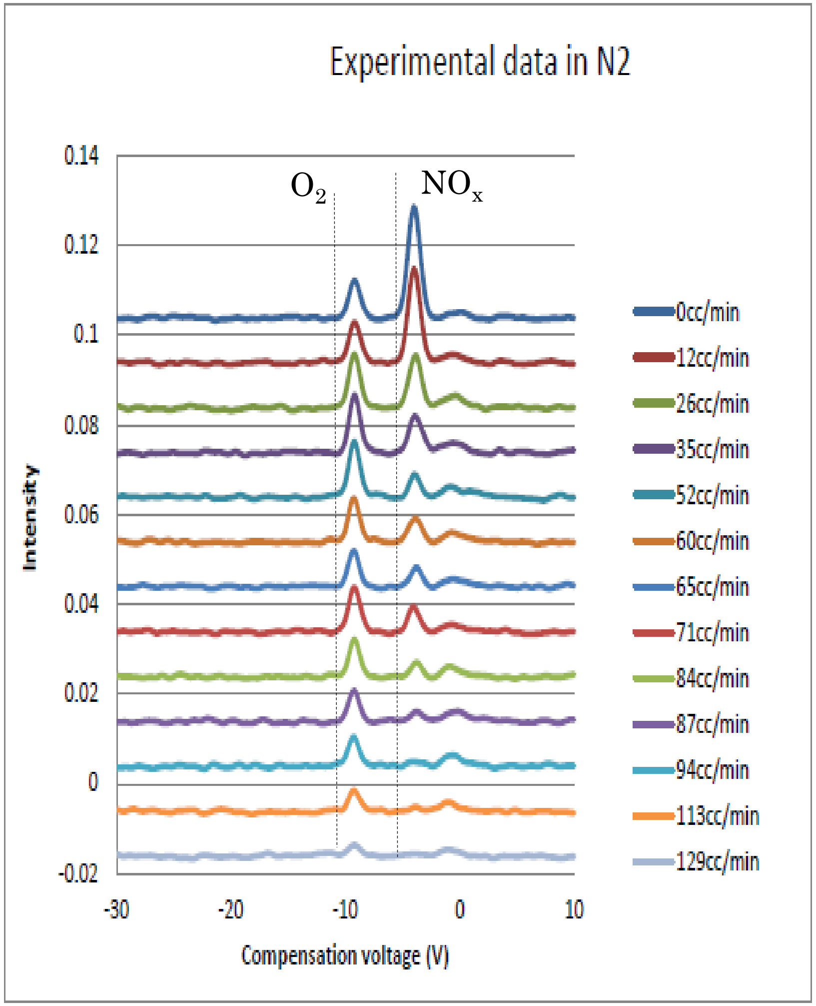
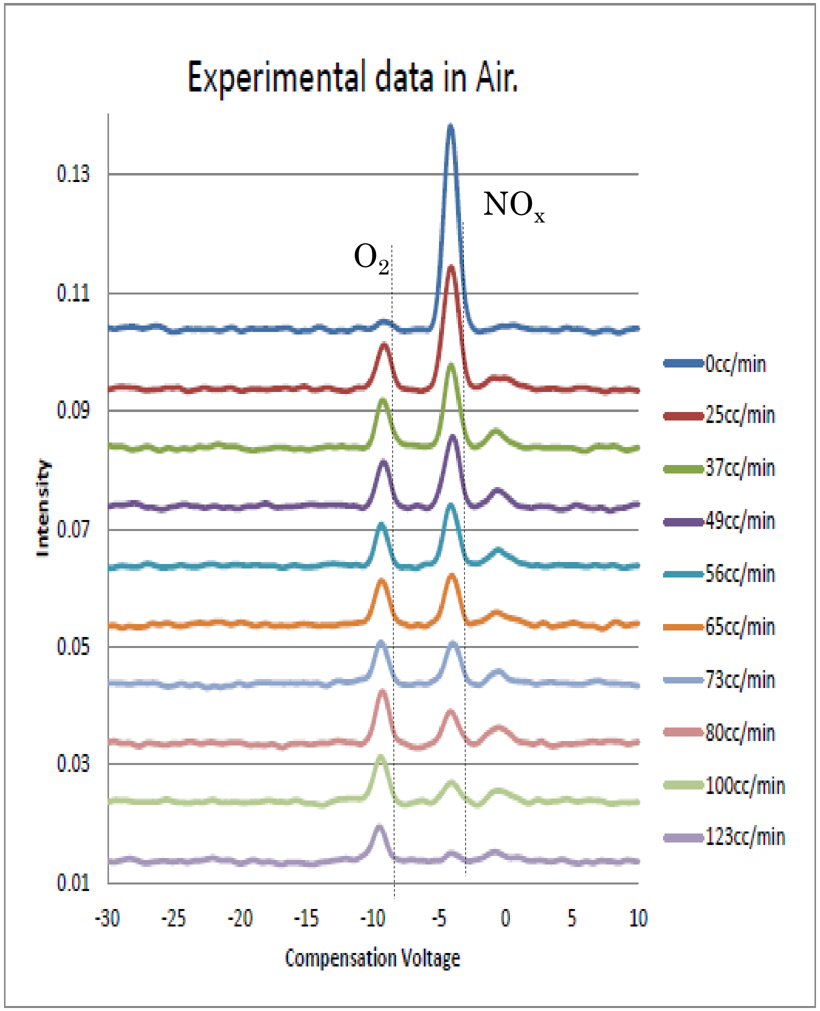
Effect of Counter Flow Rate on Background Negative Ion Spectra

Operation with N_2 and Air Transport Gases, DMS Instrument RF=700V





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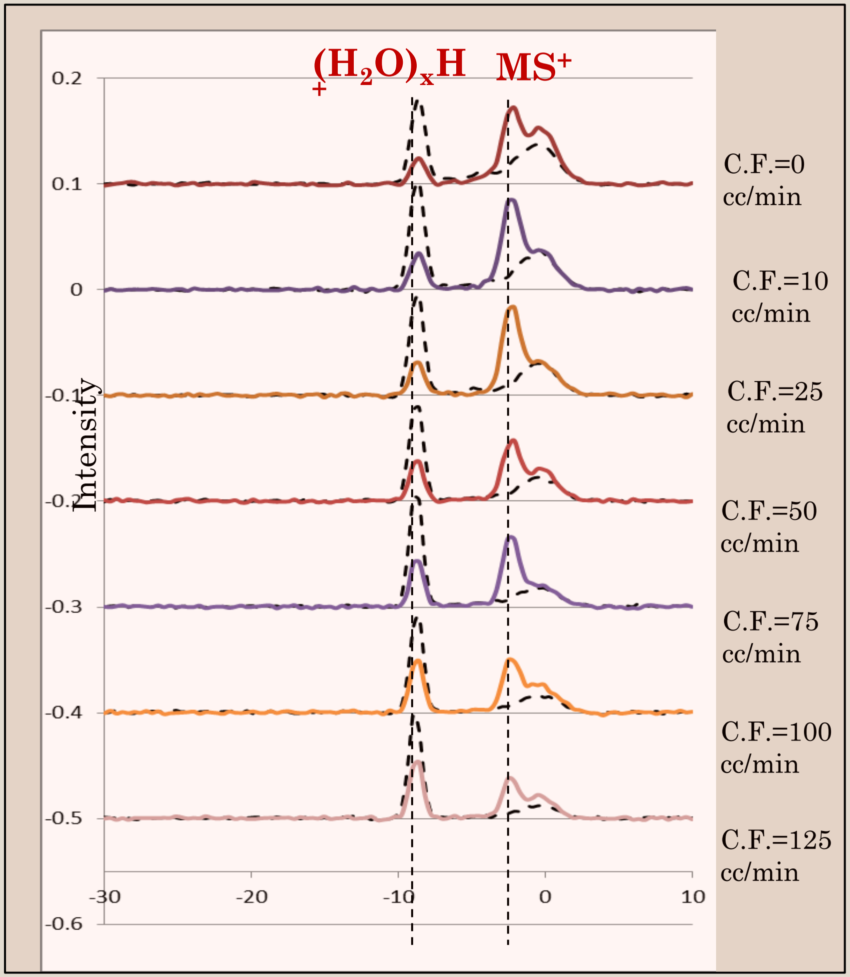
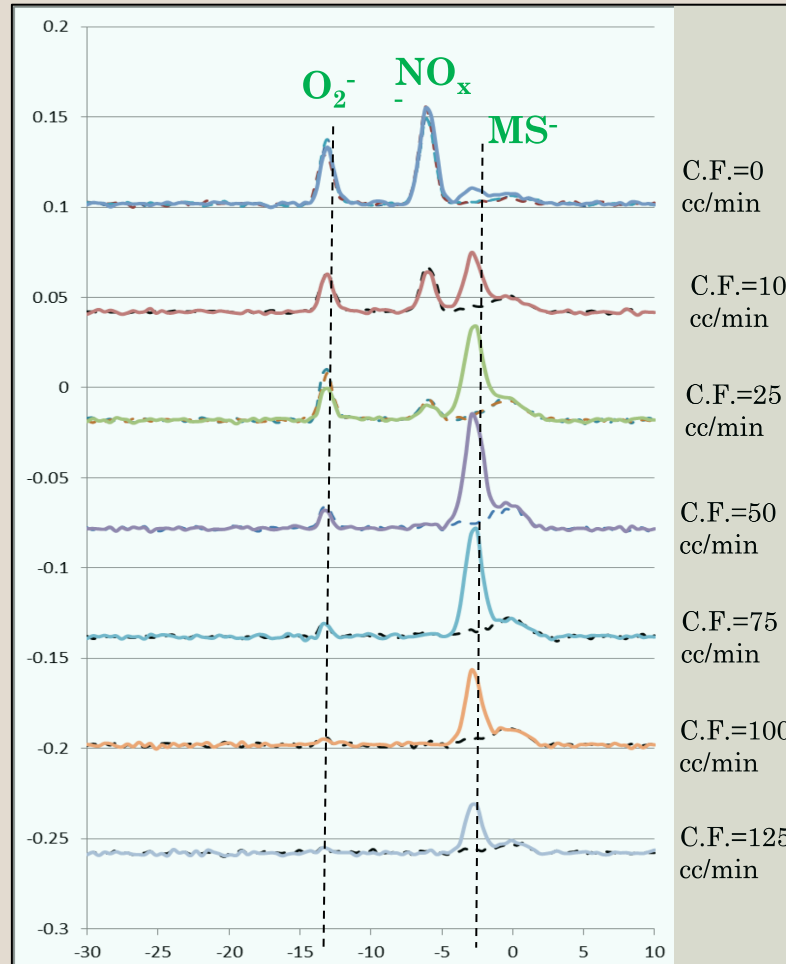
Effect of Counter Flow Rate on Methyl Salicylate (MS) Spectra

Positive ions



Compensation voltage

Negative ions



Compensation voltage

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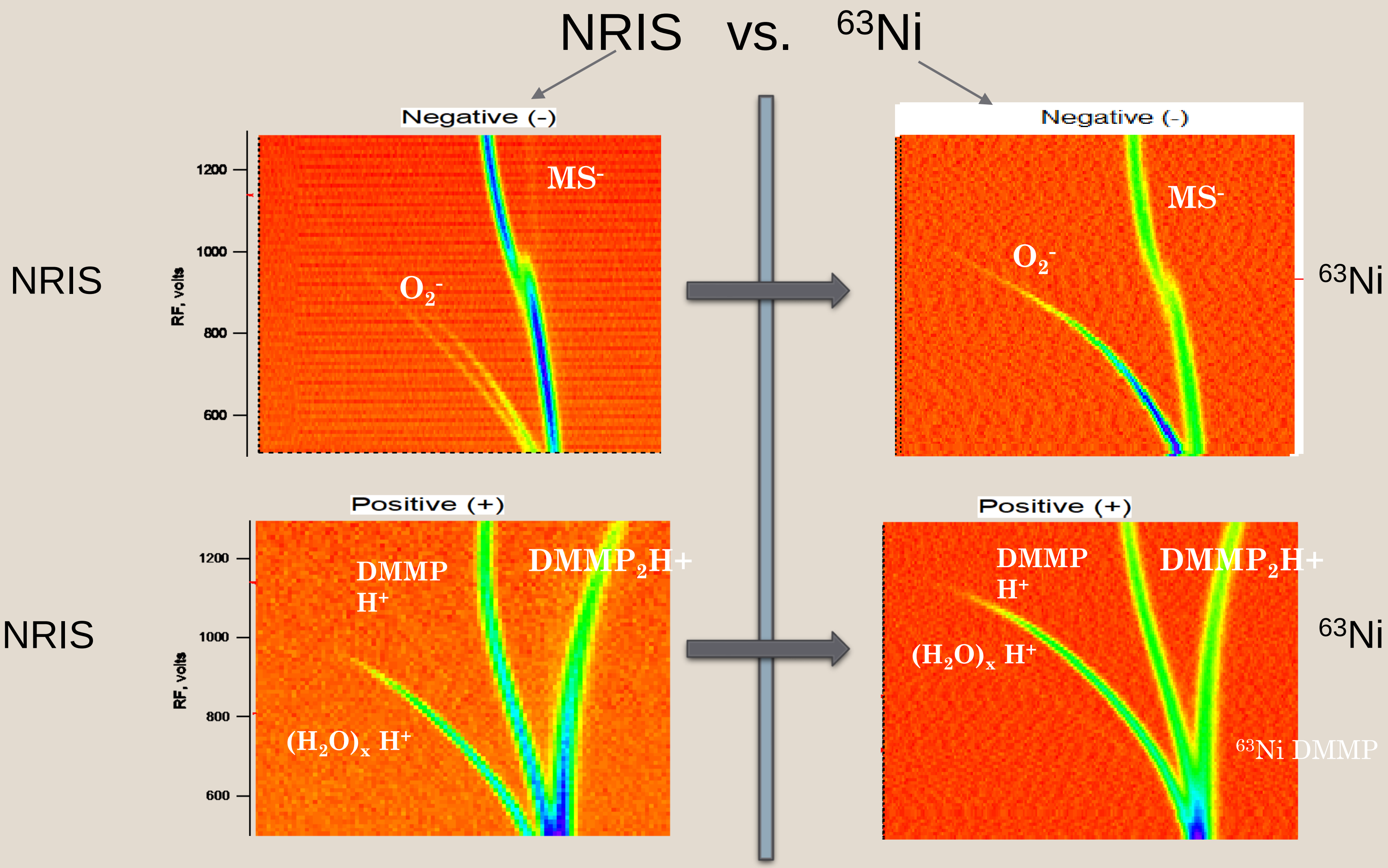
Dispersion Plot Comparison of Negative and Positive Ions for CWA Simulants Obtained with ^{63}Ni (radioactive) and with Non-radioactive Ion Source (crossed wires)



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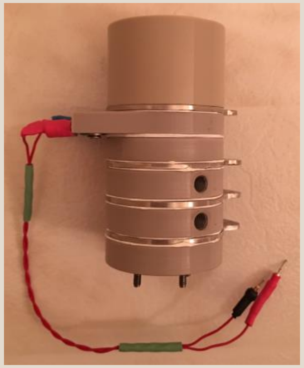
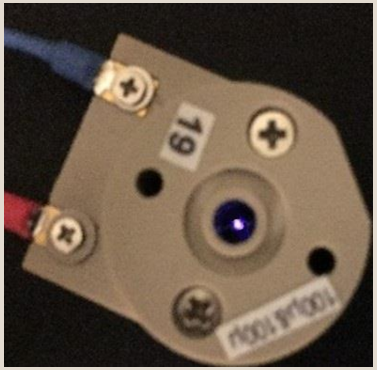
Draper Ion Source Design Disadvantages

Ion Source



Plasma Source

Plasma



CON's

- Oxidation and erosion of wire, over time, requires higher ignition voltage, which also increases plasma temperature and NOx production
- Single point of failure reduces reliability; Continuous use ~ = 500 Hours
- Small plasma spot minimizes volume of generated ions / electrons
- Plasma (contact point) not always located at center of air flow (could be improved with redesign)
- Additional chambers and electrodes increases manufacturing cost
- Machined design is high cost and difficult to assemble
- Drive electronics based on resonance, limiting ignition voltage. Plasma sometimes does not ignite under varying environmental conditions (i.e., humidity, temperature, etc.)
- Higher power consumption required for drive electronics; Power > = 8W

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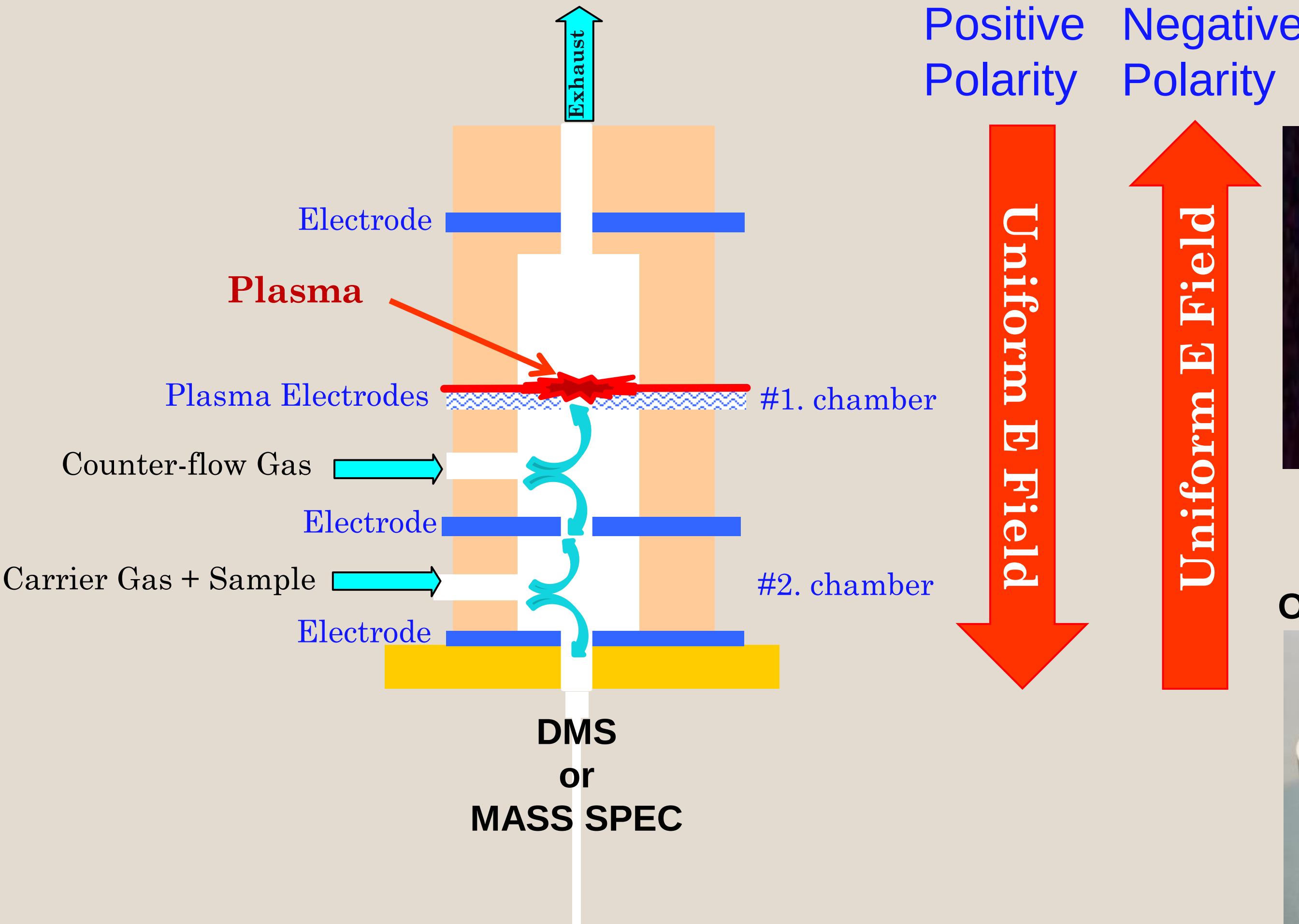
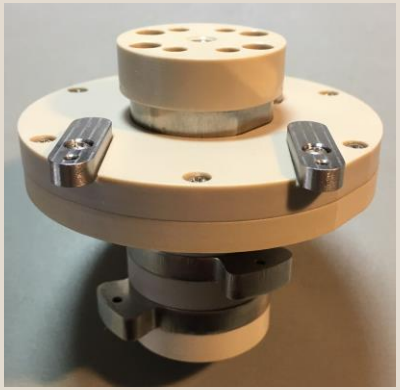
MicroPlasma Systems Ion Source Design (Proof-of-Concept)

Dual Polarity Ion Source



PLASMA

MPS GEN 1 PROOF-OF-CONCEPT DESIGN



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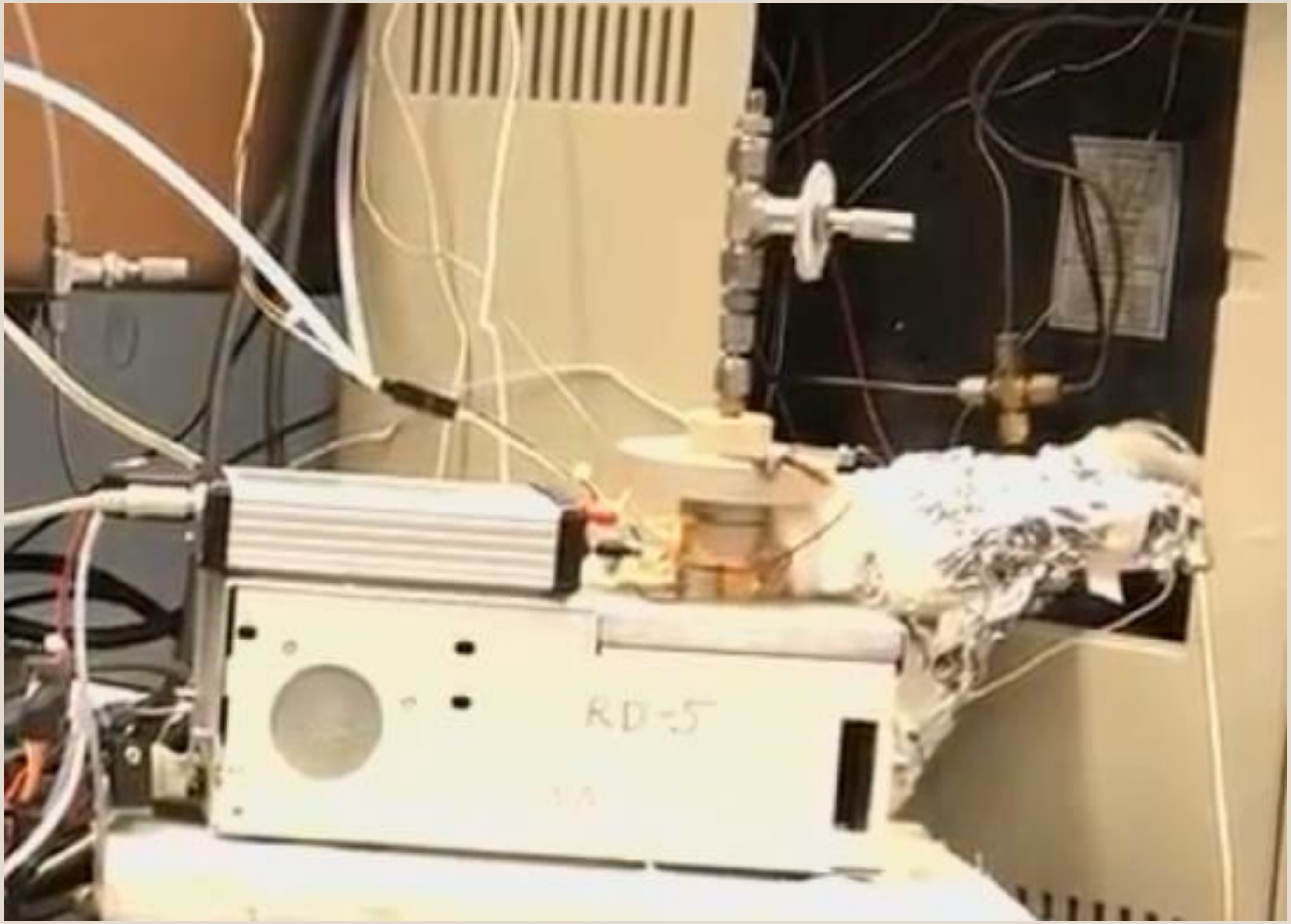
MicroPlasma Systems Ion Source Design
(Proof-of-Concept)

TEST SETUP USING SIONEX DMS SVAC



(Picture courtesy of G. Lee, P. Fowler, J. Lee, and G.A. Eiceman
Department of Chemistry and Biochemistry, NMSU, Las Cruces, NM 88003)

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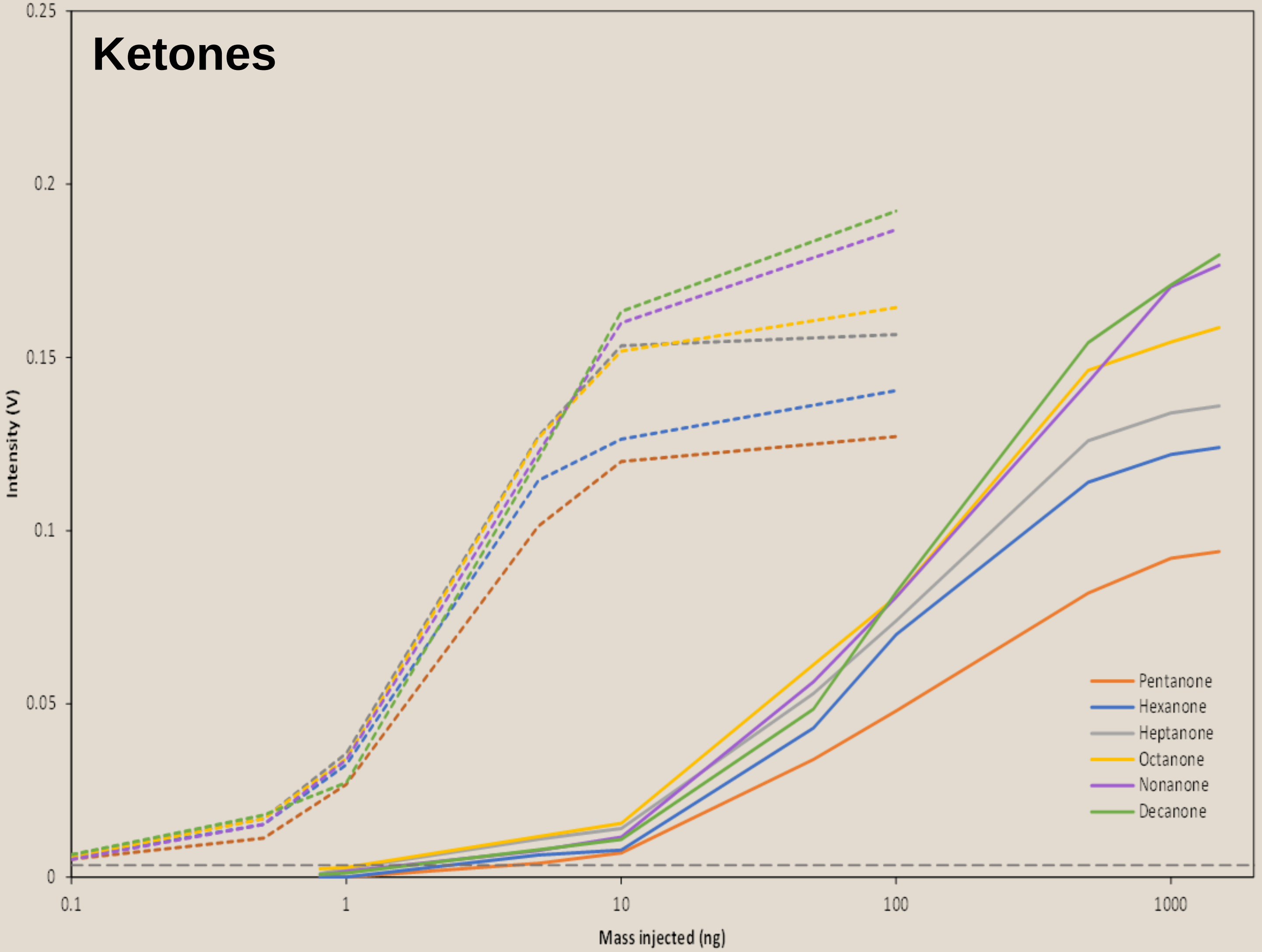
Response Curves: Gen 1 Ion Source (dotted) and ^{63}Ni Ion Source (solid) (Positive Polarity)



(Test data courtesy of G. Lee, P. Fowler, J. Lee, and G.A. Eiceman
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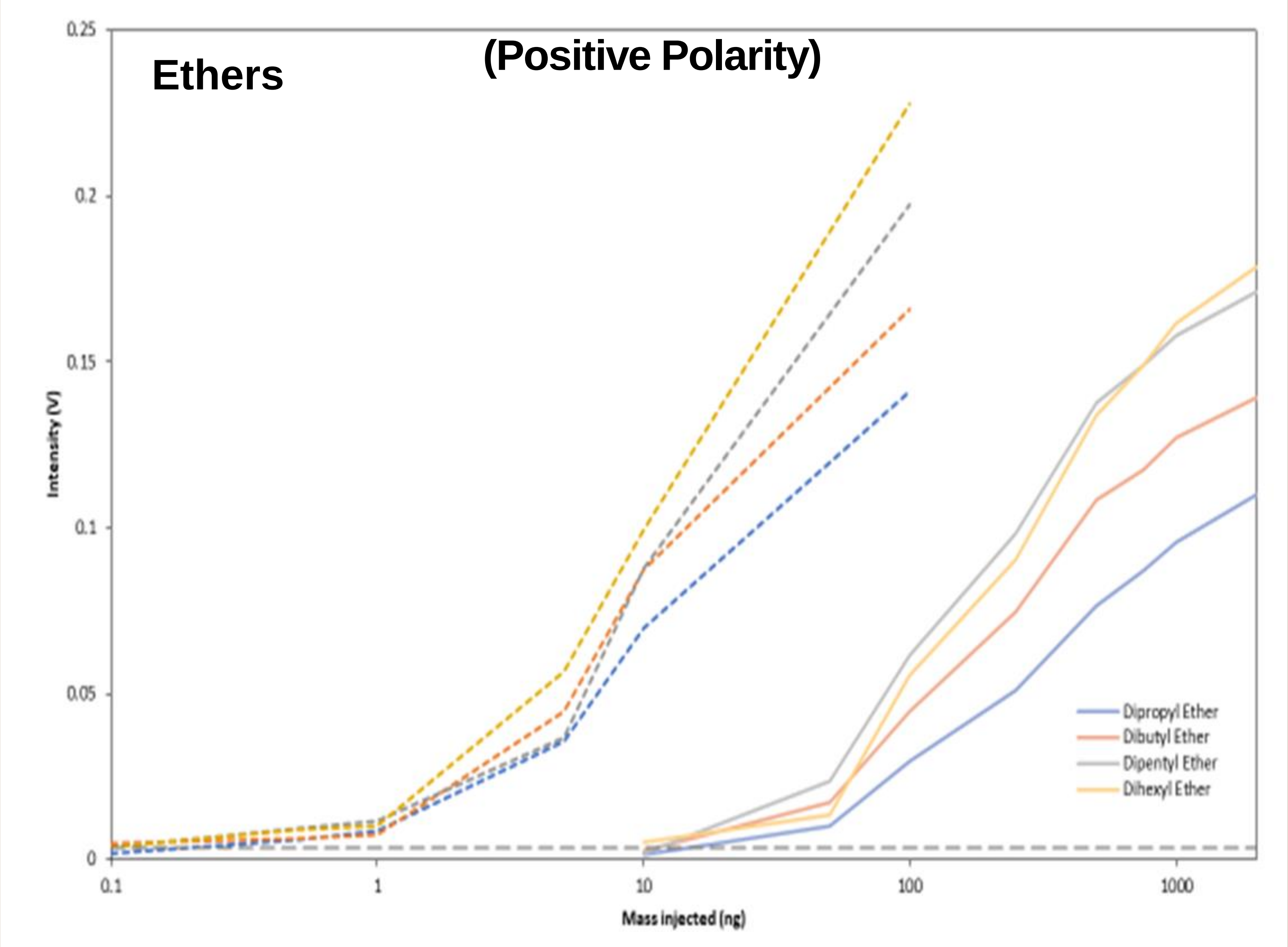

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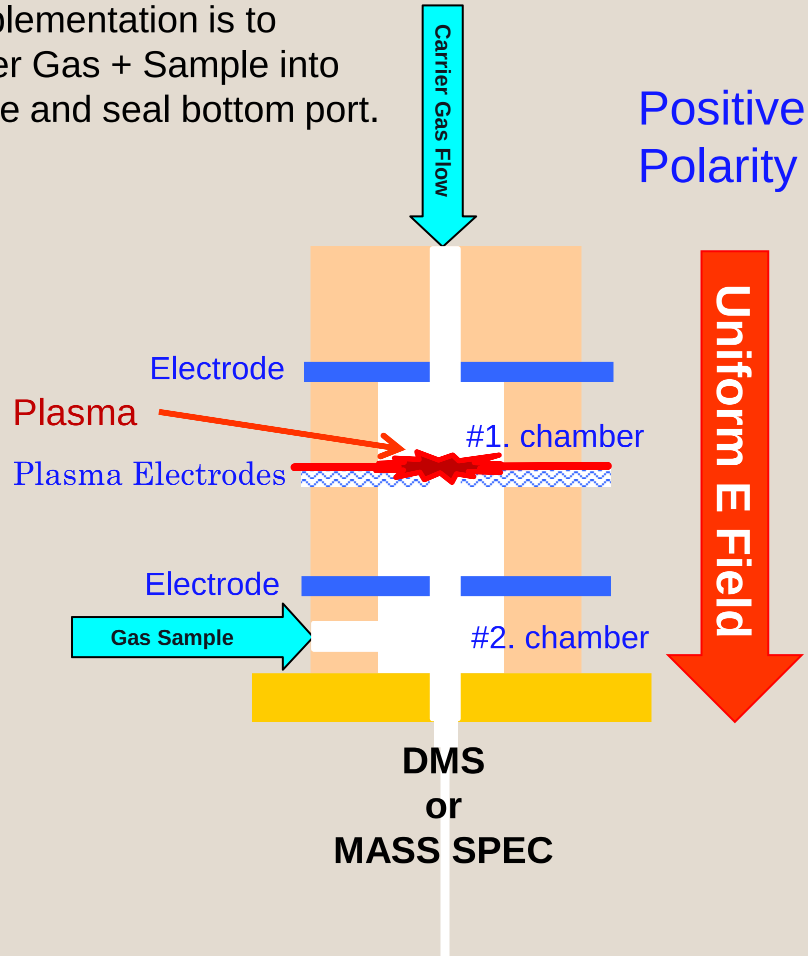
MicroPlasma Systems Ion Source Design
Gen 1 – Positive Polarity

Positive Polarity Ion Source

*Alternative implementation is to introduce Carrier Gas + Sample into top of ion source and seal bottom port.



GEN 1 DESIGN
POSITIVE POLARITY

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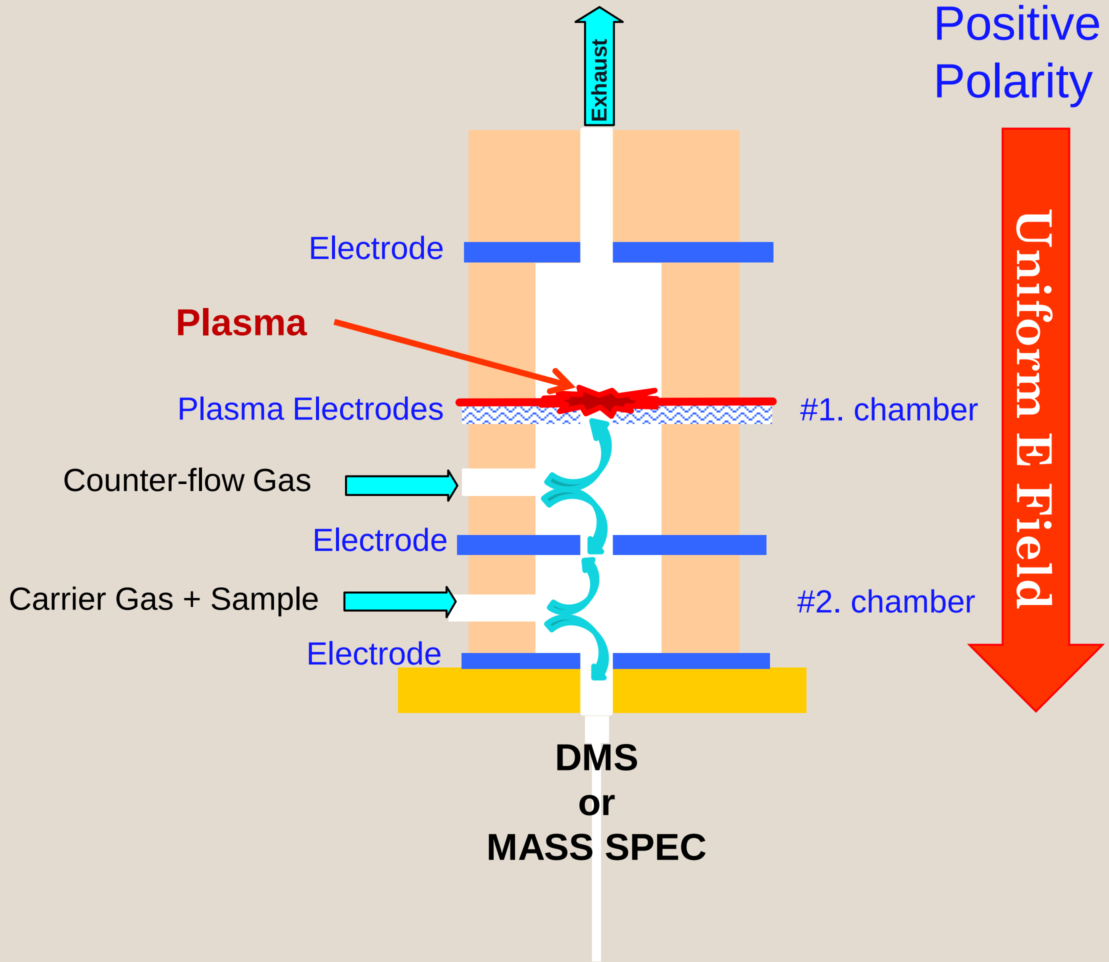
MicroPlasma Systems Ion Source Design
Gen 1 – Dual Polarity (Under Development)



WILL BE:
POSITIVE POLARITY DESIGN WITH ADDED CHAMBER #2

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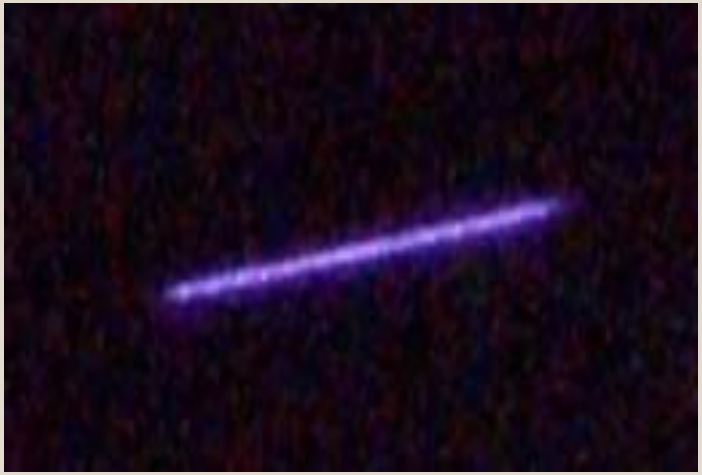
MicroPlasma Systems Gen 1 Design Advantages

Ion Source (machined)

Plasma Source



PRO’s

- Multi contact design reduces susceptibility to oxidation, generates homogeneous plasma that lowers plasma temperature, and minimizes NOx production
- Multi contact design increase's reliability; (conservative est.) 3x > single point
- Regulate volume of generated ions / electrons via drive electronics
- Design locates plasma in center of air flow
- Fewer chambers and electrodes reduces manufacturing cost of assembly
- Ion source operationally tested at 200°C with no issue.
- Plasma Generator electronic drive method less susceptible to environmental changes.
- Low power consumption drive electronics: < 1.5W (typical), allows use in portable battery applications
- Next Gen will be over-molded for reduced manufacturing cost and size

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MicroPlasma Systems Ion Source System

SPECIFICATIONS

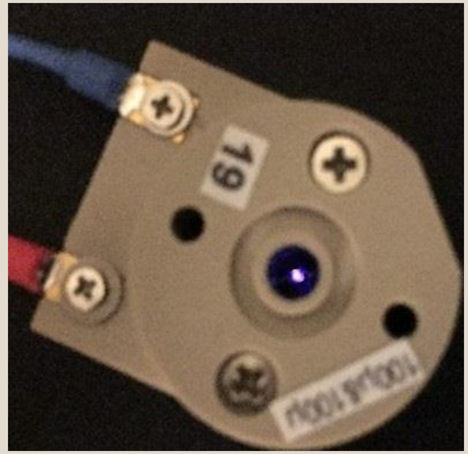
Ion Source (Pos Polarity)

Dimensions:	1.25 (L) x 1.25 (W) x 2.0 (H) in., (3.2 x 3.2 x 5.1 cm)
Weight:	1.4 oz. (39.7 g)
Material:	PEEK

Plasma Generator

Dimensions:	5.5 (L) x 3.0 (W) x 1.0 (H) in., (14 x 7.6 x 2.54 cm)
Weight:	8.5 oz. (241 g)
Voltage Input:	+10V to +14VDC, (+12VDC Typical)
Power In:	1.5W (typ), 3.6W (max)
Serial Com:	USB
HV DC (adj):	0 to ±1KV (Dual Polarity E-Field Drive)
Plasma Freq (adj):	488 Hz to 65.535 KHz
Plasma Duty Cycle:	1% to 10% in 0.1% increments

COMPARISON SUMMARY



PROPERTY	SINGLE-POINT CROSSED WIRES	MPS MULTI-CONTACT
Ion Generation	Lower	Higher ✓
Undesired NOx	Higher	Lower ✓
Plasma Temperature	Higher	Lower ✓
Reliability	Lower	Higher ✓
Environmental Changes	Higher	Lower ✓
Power Consumption	Higher	Lower ✓
Manufacturing Cost	Higher	Lower ✓

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Questions ?

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