Recent Developments with the Rotating Field Mass Spectrometer (RFMS) and Nanospray Ionizer”

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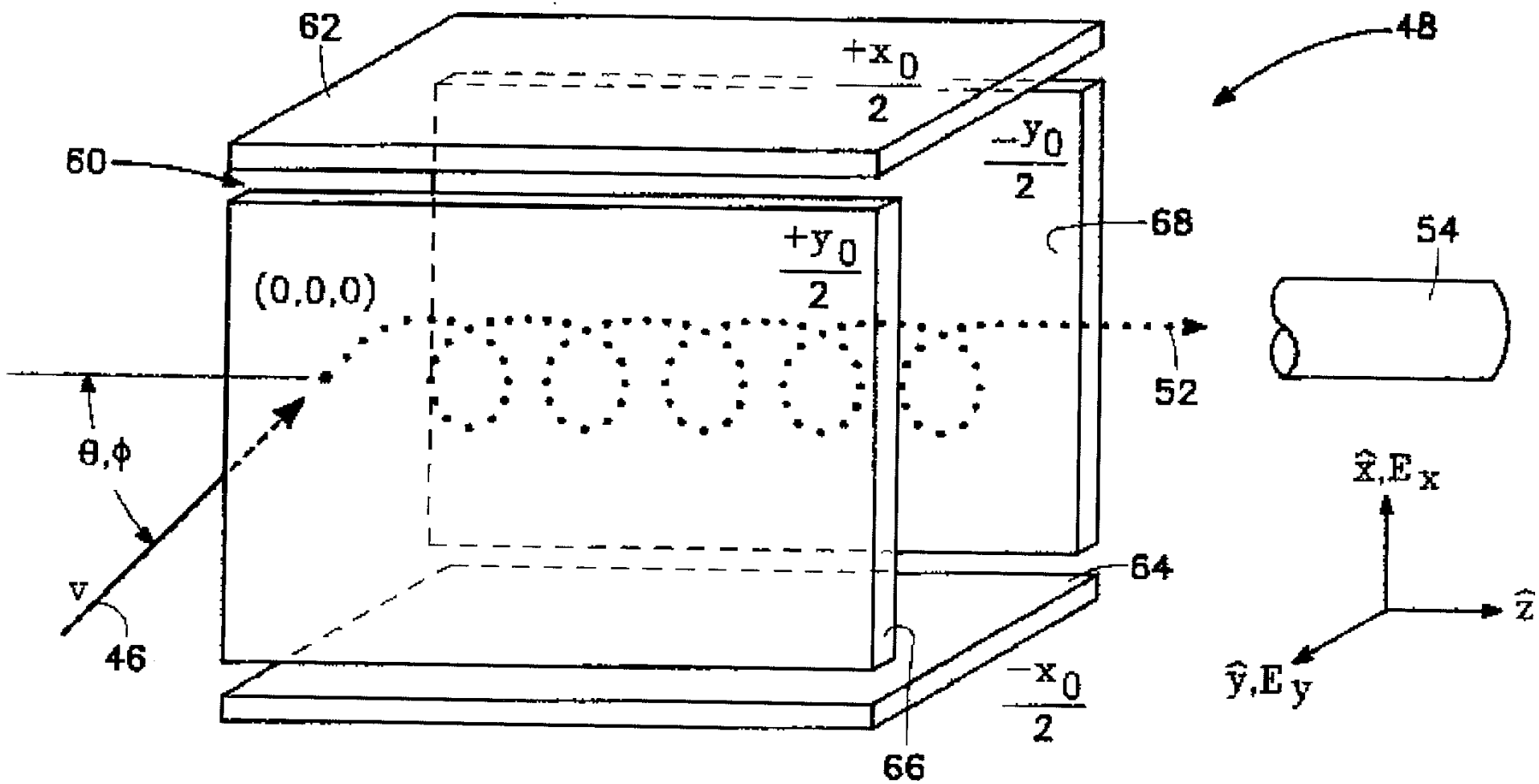
Current State-Of-The-Art Mass Spectrometer Performance Metrics

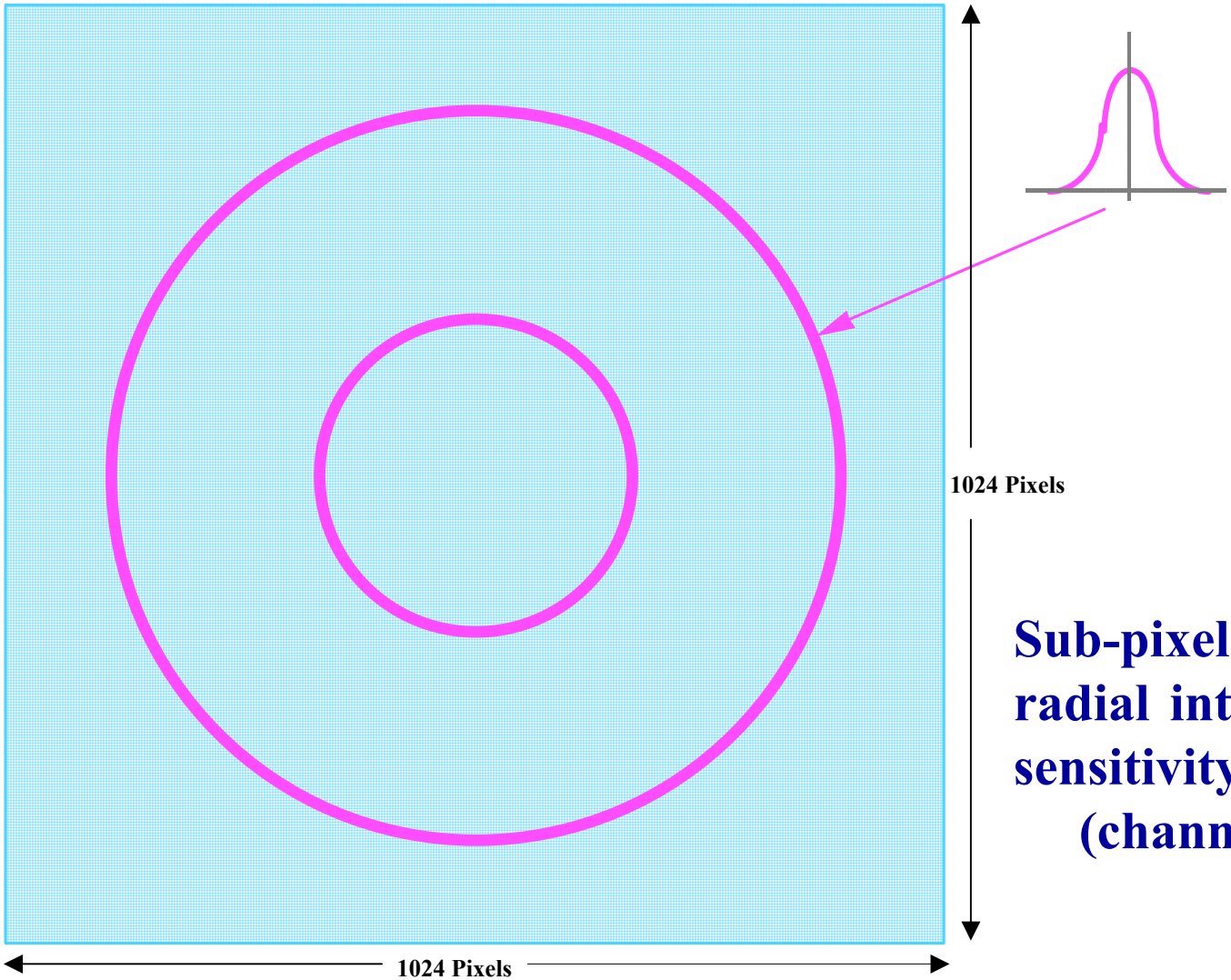
	Field Ionization/RFMS	Electron-Bombardment	Radioactive Ionization
Operating domain	**Torr - NanoTorr (10^{1}:<10^{-9})**	**MicroTorr (10^{-6} Torr)**	**Millitorr (10^{-3} Torr)**
Power requirements		**Quadrupole or Magnetic sector**	
Vacuum pump	**None (0)**	**Turbo : 20 Watts**	**Membrane : 10 Watts**
Operating Temperature	**-100 _200 C**	**Only at high temp**	
Ionizer	**Field : 0.1 Watt**	**Electron : 5 Watt**	**Source (0)**
RF/DC	**5 Watts @ 5Mhz**	**5 Watts @ 10Mhz 1 Watt (no RF)**	**5 Watts @ 10Mhz**
Ion sensor & computer	**0.7 Watt**	**0.7 Watt**	**0.7 Watt**
Total	**6 Watts**	**31 Watts**	**16 Watts**
Size	**100 cc**	**3500 cc**	**1500 cc**
Mass	**0.4 Kilogram**	**10 Kilograms**	**2 Kilograms**
Efficiency	**High** (100% ionization nanoamps/Torr gas load)	**Poor** (Ionization cross section of sample gas and total hot filament electron emission current) - fractions of nanoamps.	**Inefficient** (Ion depends on radioactivity of source - typically ^{210}Po 5 mCi providing 10^{7} alpha particles/sec) – picoamps at millitorr pressures
Cost	**Very low** ($100 per membrane)	**High - $5.5K** for turobopump, controller and roughing pump. Filaments inconsequential	**High - $6K** (ion pump $1K and source$5K)
Unique feature	**Operates at low pressure and any temperature. Ionization is 'soft'** (molecules are not fractured). **Membrane uniquely suited to generating and focusing ion beams.**	**Filaments relatively easily fabricated and built redundant. Filaments are fragile and burn out in moderate vacuum Beam focusing required. Ionization is 'hard'** (molecules fractured – produce ambiguous source mass/charge distributions).	**Needs millitorr pressure for largest efficiency. Source is robust. Beam focusing required. Ionization is 'hard'** (molecules fractured – produce ambiguous source mass/charge distributions).
Major constraints	**Dust filter required to prevent blocking of membrane pores.**	**Filaments have short life. Emission current related to filament temperature, condition and changing resistance.**	**Radioactive source introduces environmental problems and aggravates detection noise.**

Schematic of rotating field spectrometer



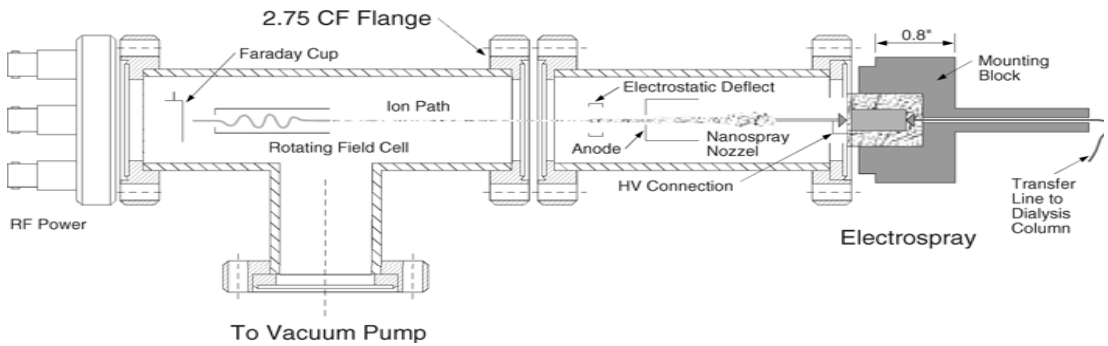
Active Pixel Detection - Enhanced M/ΔM

APS pixel 10^{-17} Amps

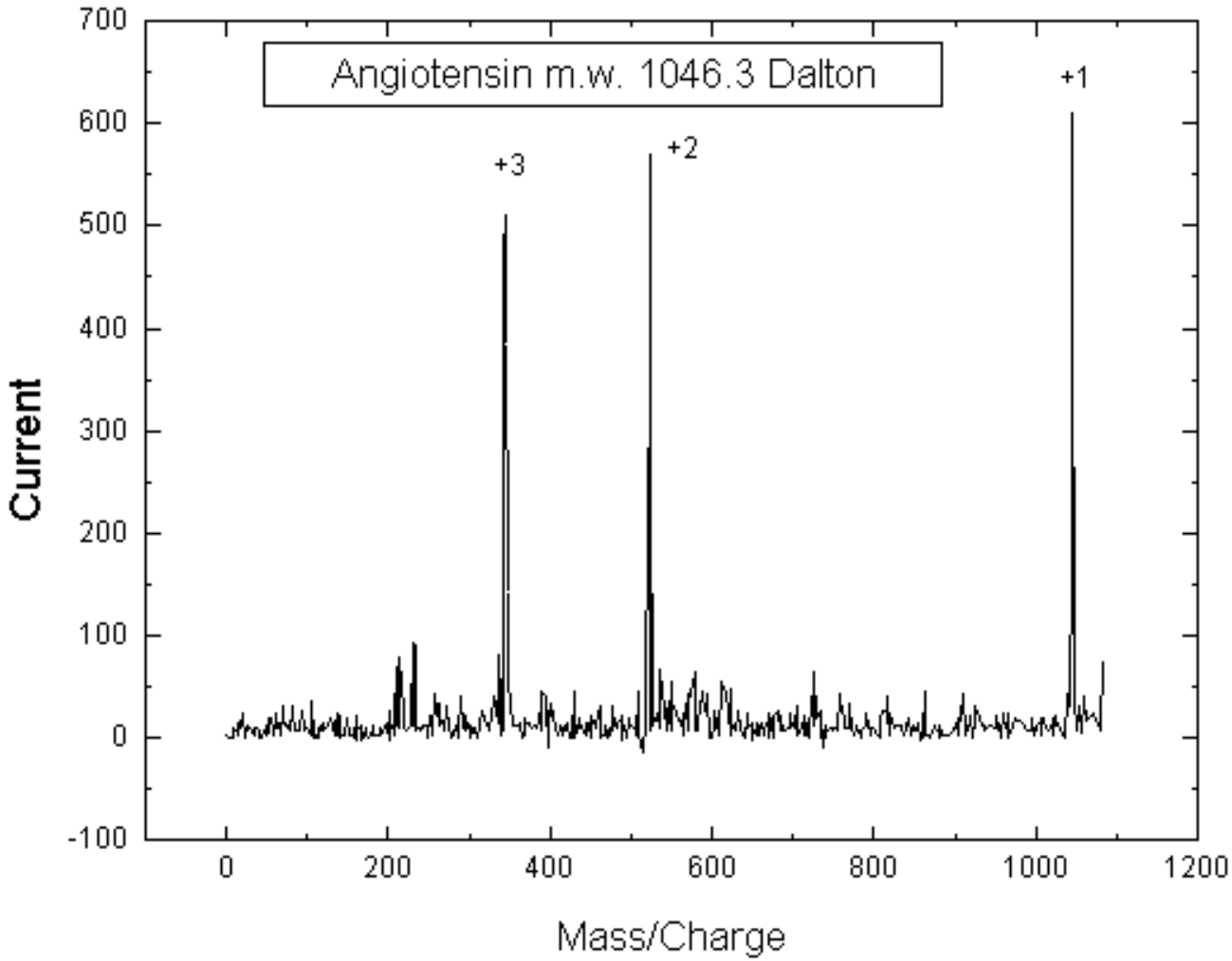


Sub-pixel centroiding and radial integration will have sensitivity of < 10^{-17} Amps (channel plate ~10^{-19} A)

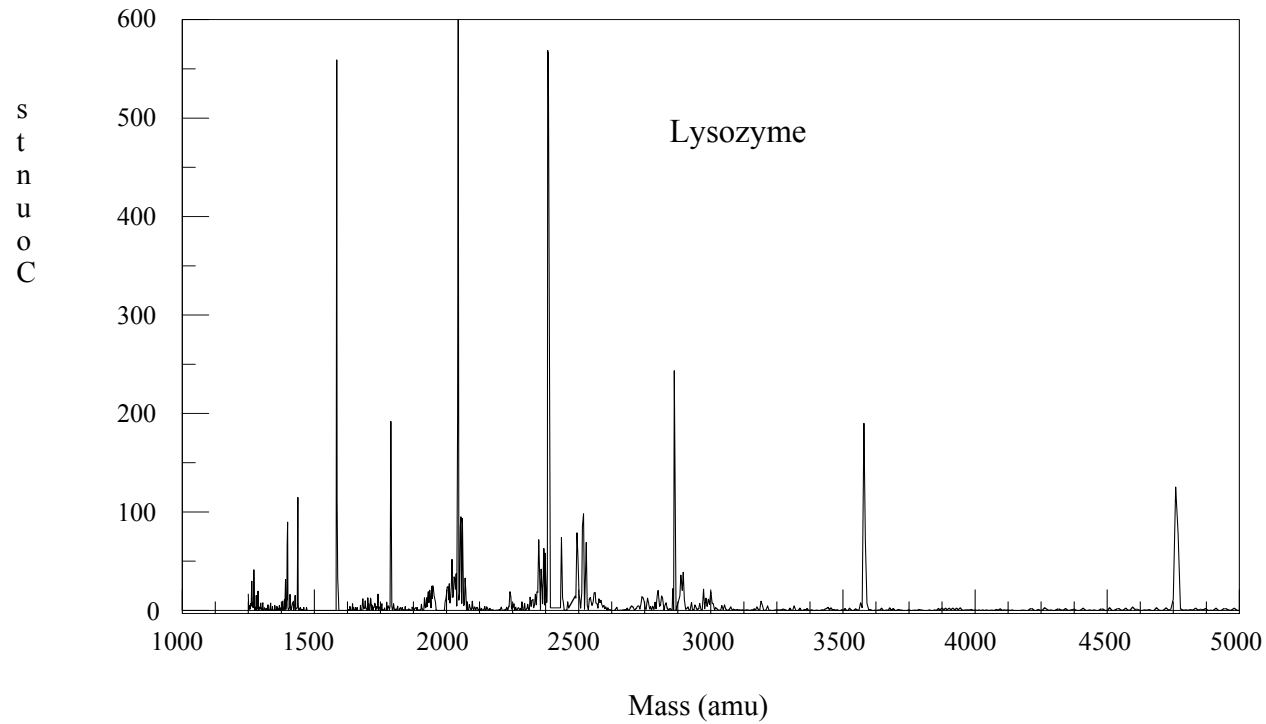
Nanospray Layout



Angiotensin /nanospray

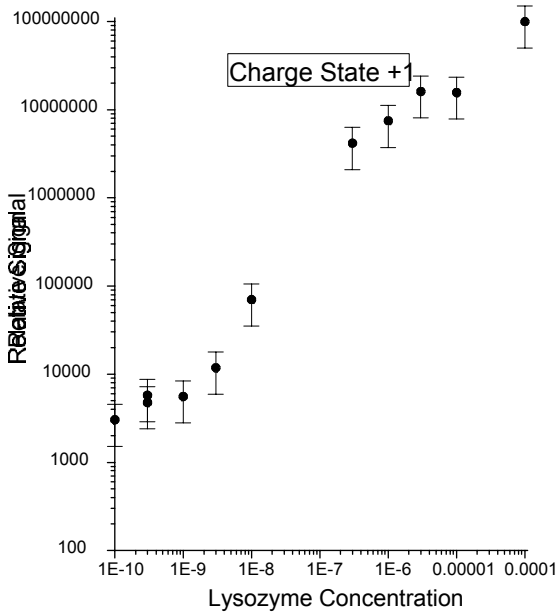


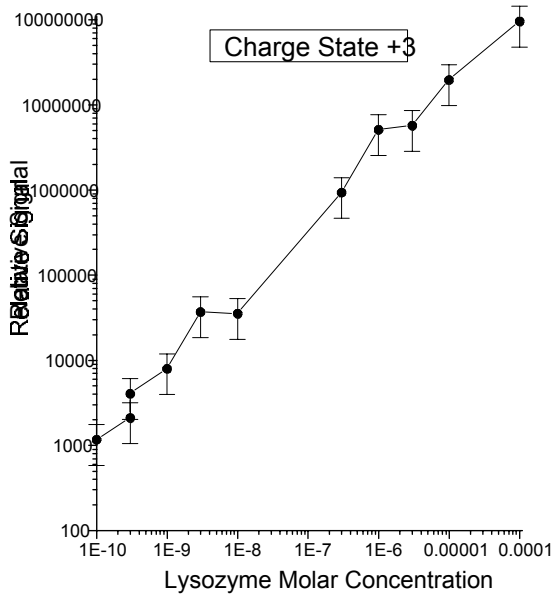
Lysozyme

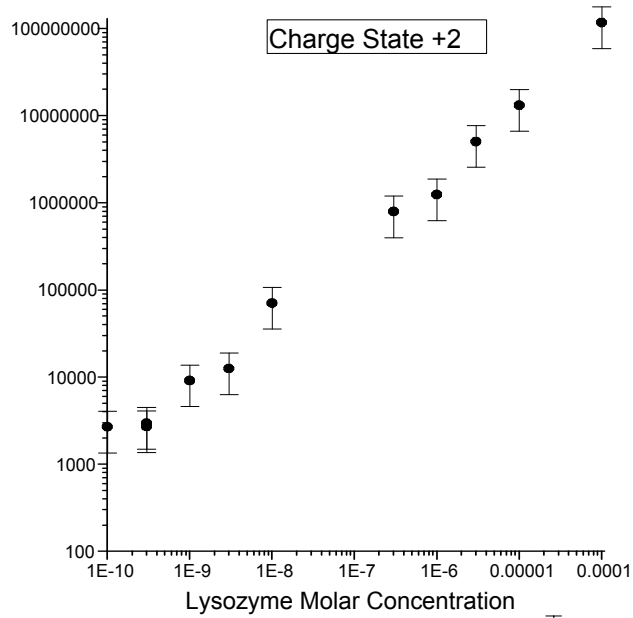


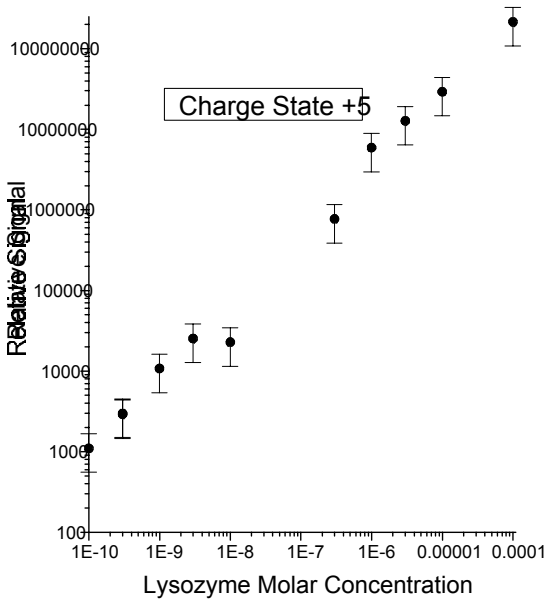
Beckman Coulter -JPL Task

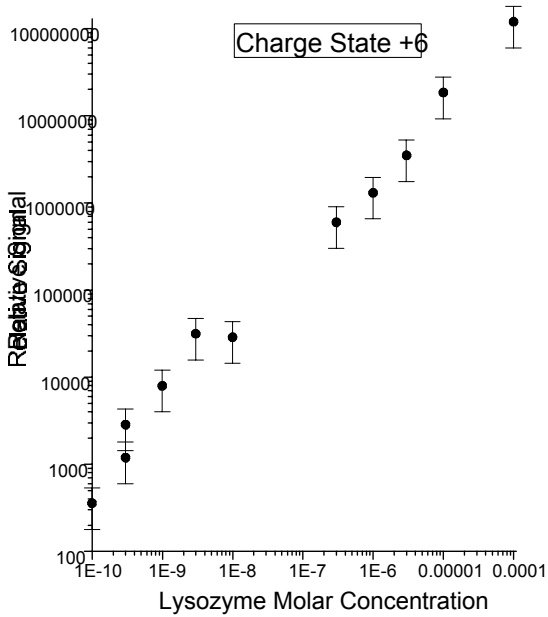
Lysozyme charge state peaks at various mass to charge ratios

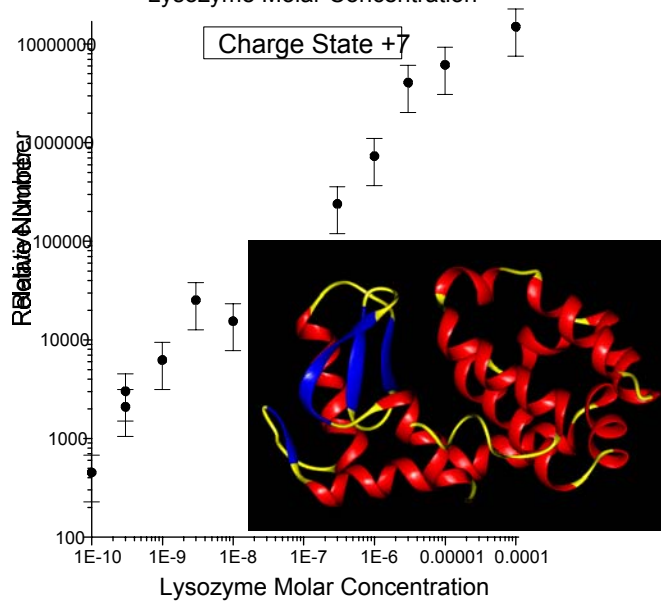












Lysozyme in ethanol at 10^{-3} - 10^{-10} Mol range with raw signal counts from each of the charge peaks

Summary of DNA Samples

Mass Analyzied to Date

Sample Types: These have included 10^{-4} to 10^{-10} molar lysozyme, angiotensin, adenosine, both positive and negative electrospray of seawater, and most recently, large DNA fragments and 10 micromolar solutions of oligonucleotides etc. Working with samples obtained from the CITY of HOPE Medical Center, courtesy Dr. Ted Krontiris. the following DNA samples have been injected into the device.

Name	#	length (mer)	[ ] micromolar	MW
P21E3AS	2	20	10	6173
60P21E3	6	60	10	18283
F-N1C80	7	80	10	24253 + FAM (600) total = 24853
GMS2S2	8	102	4.15	31257

High Throughput Genotyping, Microbial and Biological Genotyping.

Some samples to be analyzed would contain mixture of 4-50 polynucleotides closely grouped in size from 20-100 nucleotides (6600-33000 Dalton) and would require 1 nucleotide resolution. In the past such analyses have been done with large state of the art MALDI-TOF instruments costing $200,000. This compact field instrument could obtain comparable performance. Multiple RFMS systems could be built and would be ideal in this application since the number of components in the mixture can typically be pre-identified, the mass values for the components of interest are known, and there is no requirement for MS/MS analysis. The potential exists to develop a low cost system suitable for clinical or research applications.

60 mer DNA Fragment

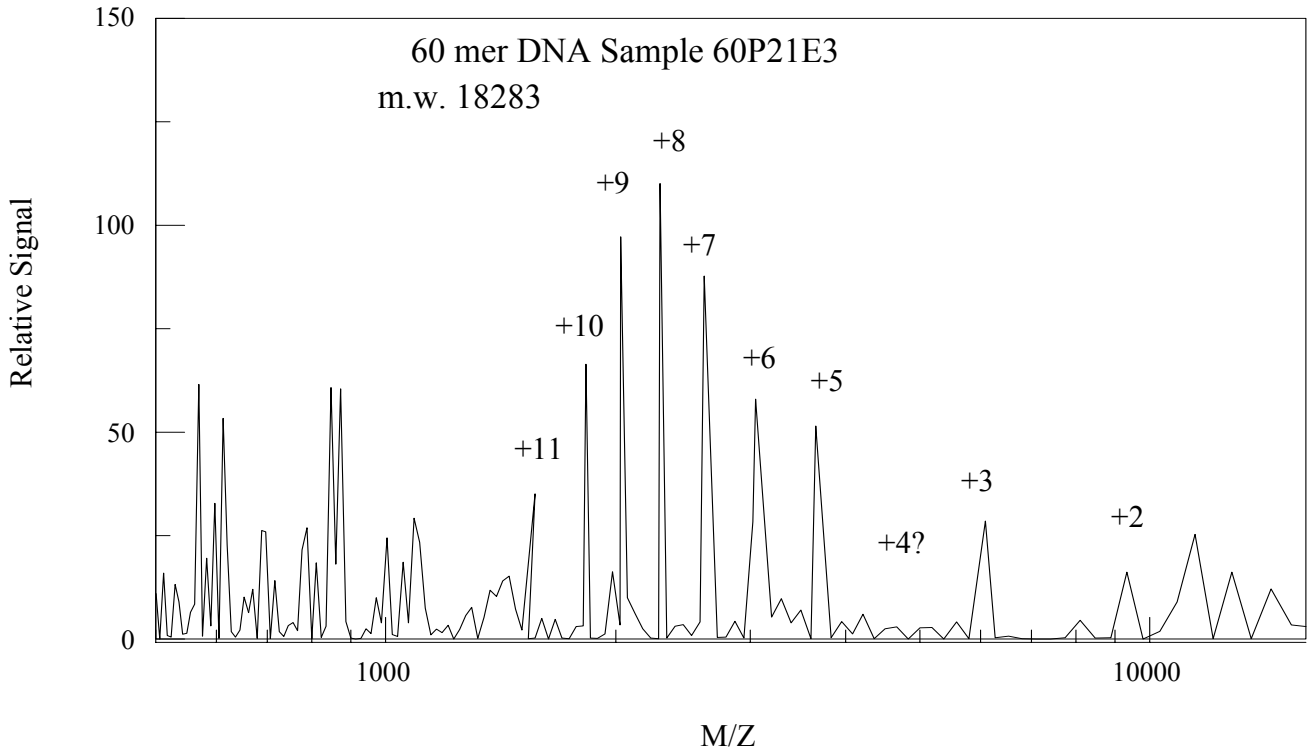
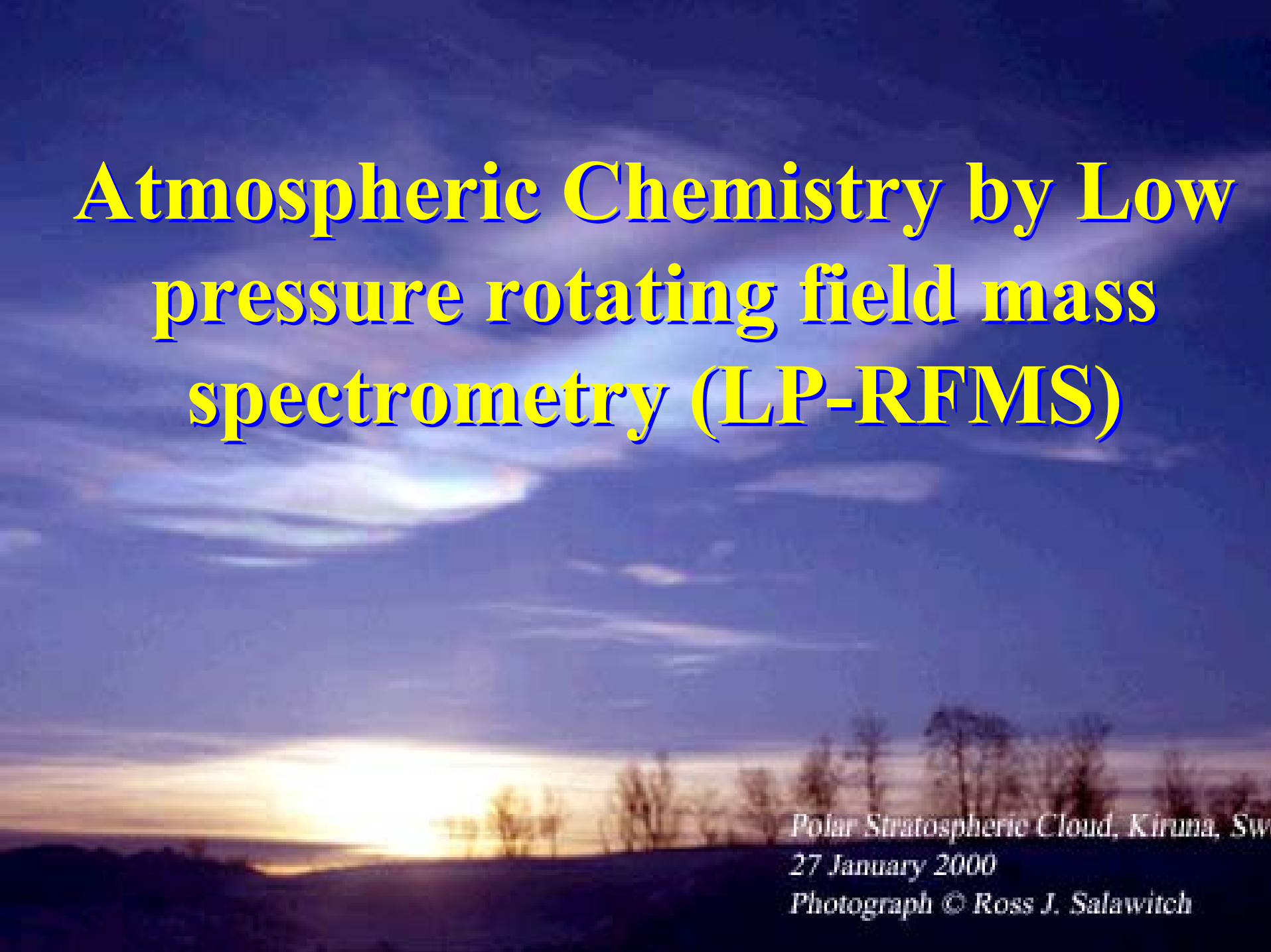
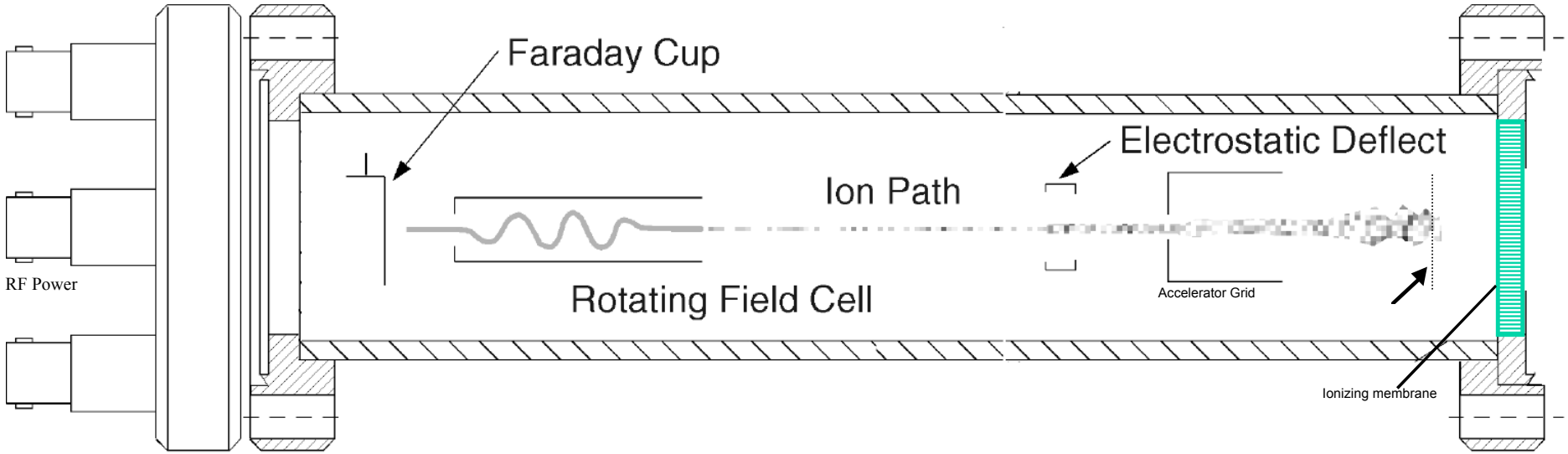


Figure 1 *A JPL mass spectrum of the 60 mer DNA Shown is the various m/z charge states arising from electrospray ionization. As can be seen, the RFMS is capable of measuring mass over an extremely large dynamic range.*

Atmospheric Chemistry by Low pressure rotating field mass spectrometry (LP-RFMS)



Low Pressure - Rotating Field Mass Spectrometer (LP-RFMS)

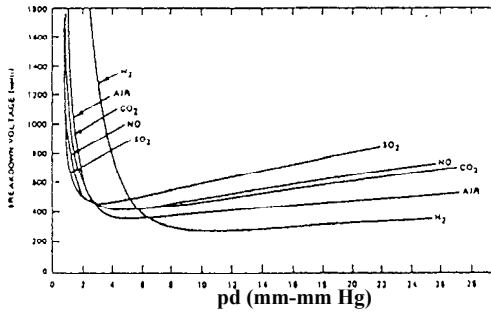


- **Unique mass spectrometer consisting of the field ionizer array, simple ion beam accelerator and lens optics, Rotating Field Mass Spectrometer (RFMS) and an ion detector**
- **Field ionizer array completely ionizes transit gas:**
  - **ionization is 'soft' - no species fragmentation**
  - **operates under Paschen curve - no plasma breakdown at any gas pressure**
  - **ion currents great enough to accommodate beam attenuation at pressures > 7 Torr**
  - **operational at both high and cryogenic temperatures**
- **Mass spectrometer has no vacuum pump, no filaments or radio active source**
- **'On resonance' ions (selected mass/charge) pass through the mass spectrometer in well defined helix trajectories to impinge upon the faraday cup ion collector**

Confidential

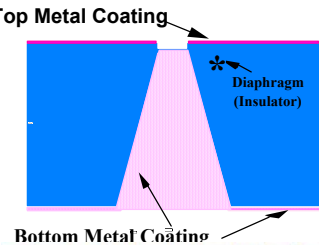
'Soft' Ionization Membrane

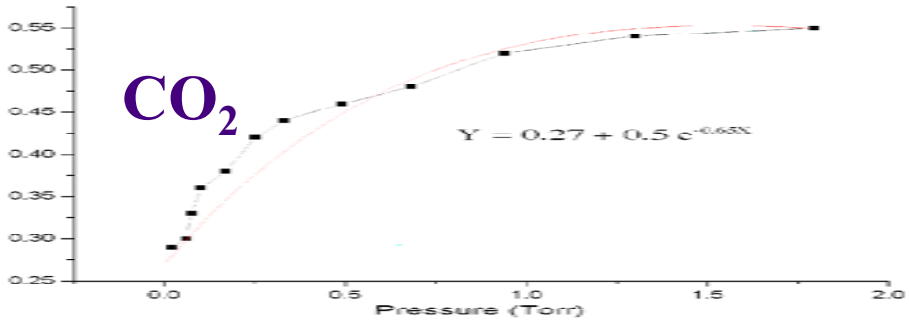
Avalanche arcing is the general out come of gas ionization in a high electric field. However, when the mean free path length between ionized molecules is greater than electrode separation – on the left of the Paschen curve - only ionization occurs.

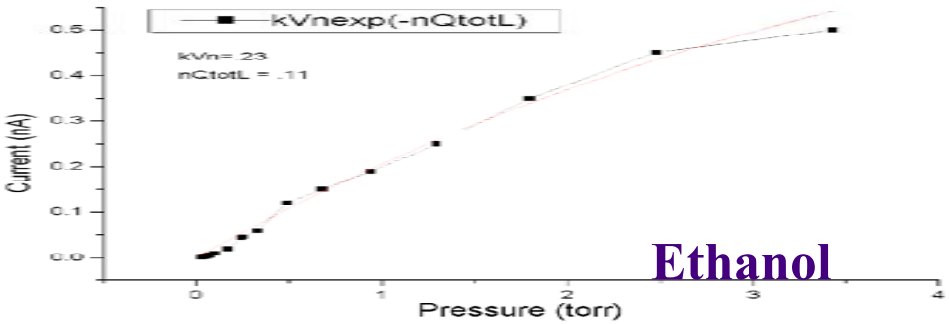


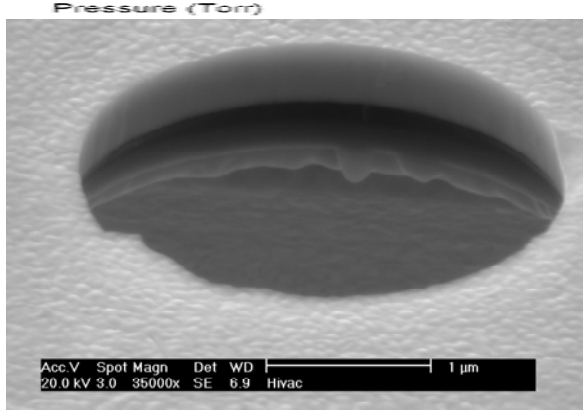
Paschen Curves for Various Gases

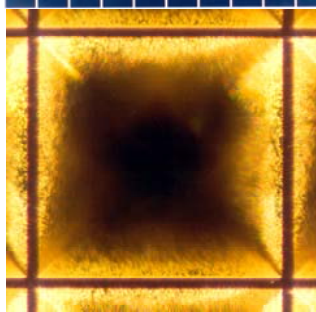
A miniature ionization device is best realized by micromachining small holes through a thin (sub-micron) membrane that has metal electrodes on each side of it. Electric field strengths in the megavolts/meter are, at sub-micron electrode separation, generated for each volt of potential difference between the metal electrodes. With electric field strengths in the tens to hundreds of MV/m any gas passing through the perforations and thus between the electrodes is totally ionized. Sub-micron thick membranes of moderate area are too fragile to sustain any pressure difference across them or to survive minor mechanical shock. A 0.1 mm thick substrate backing, back etched through to membrane, resolves these problems. The photographs present a 10x10 matrix of anisotropically etched pits, a single gold plated pit, gold covered membrane at bottom of pit, and FIB eroded hole (~2µm dia.) through 300nm Nitride membrane gold coatings (top and bottom).





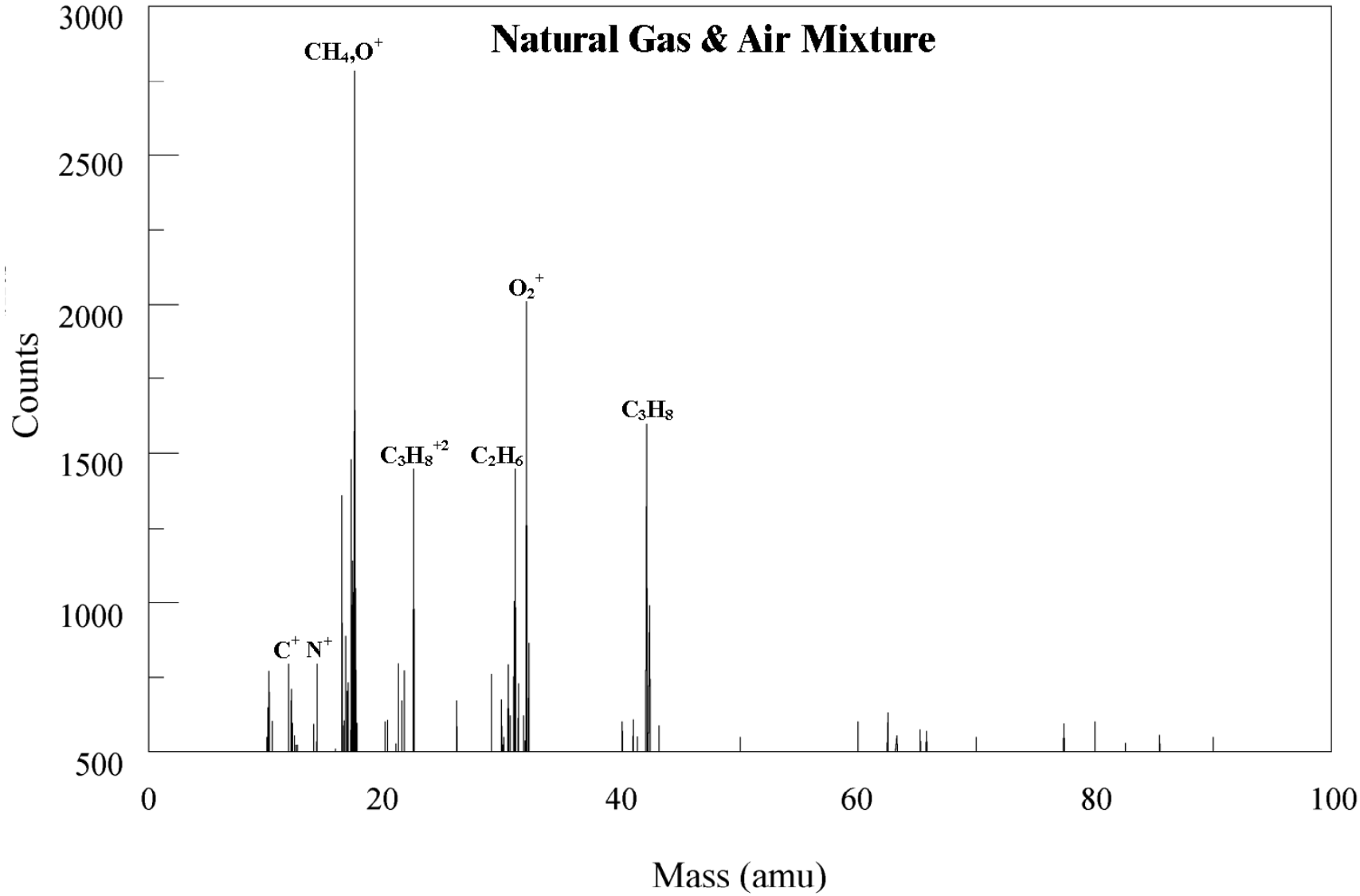




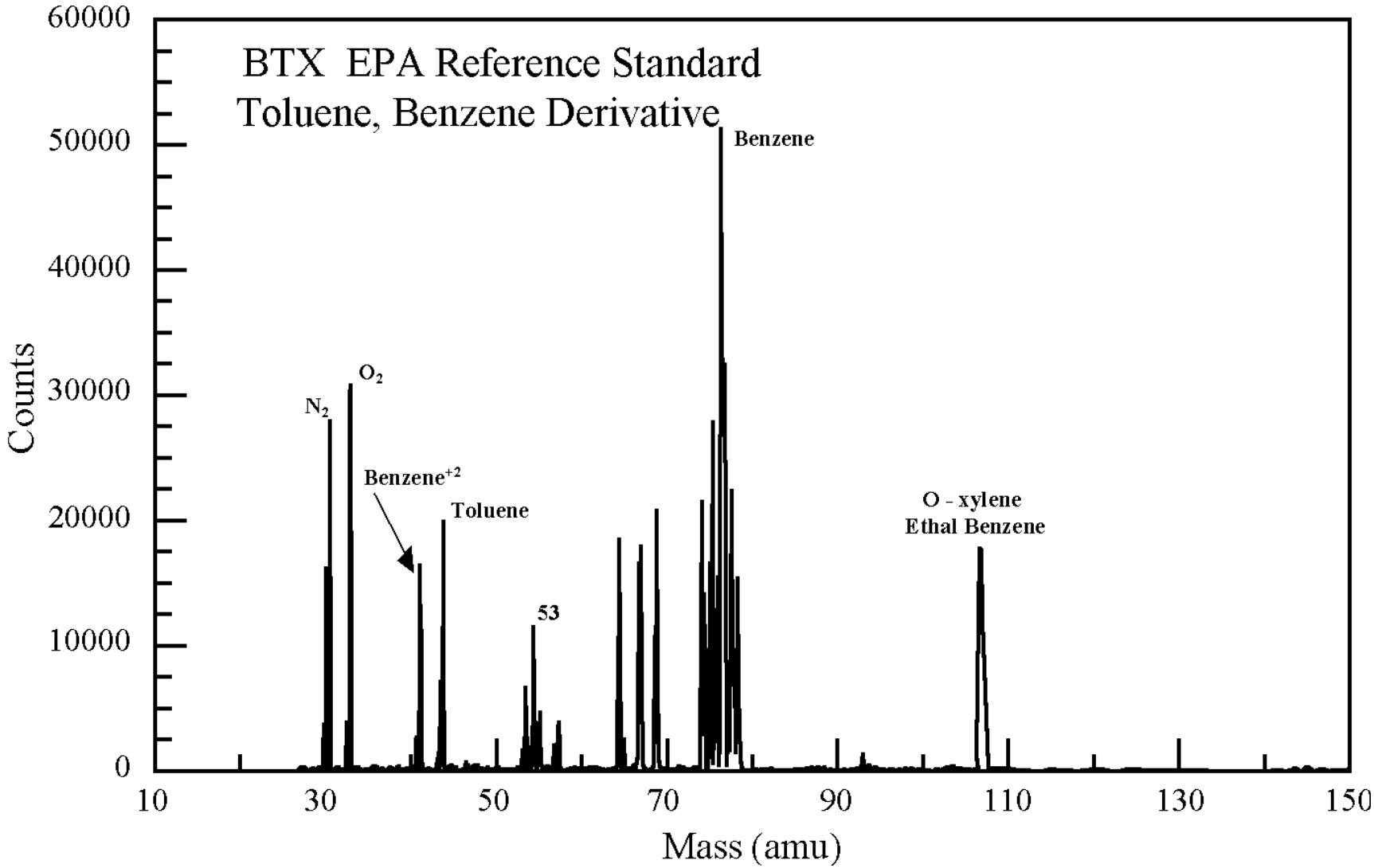


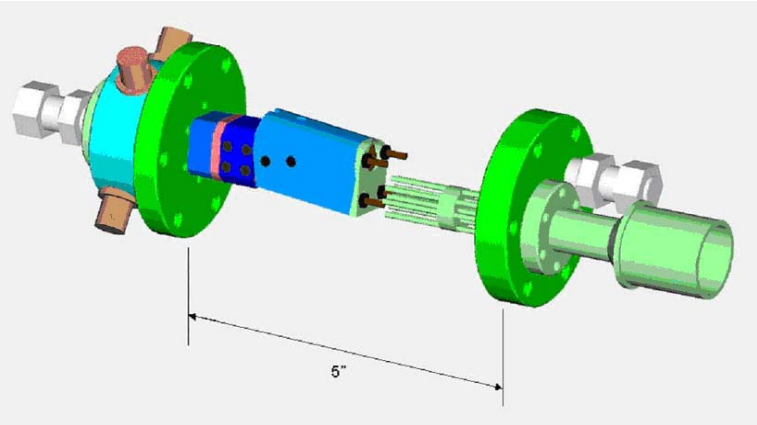
- Demonstrated mass range from 1 > 360,000 AMU {1200 MER DNA}
- Sensitivity of > 1 PPB or 10^{-11} Molar
- Mass resolution with cup > 400, with probe wire > 1000, and with APS > 10,000 M/ΔM
- Accuracy < 1% of reading for PPM and < 5% for PPB
- Electronic sensitivity - channel plate 10^{-19} Amps - APS pixel 10^{-17} Amps
- No sensitivity drift over time (with reference gas sampling or in-situ ratiometric comparisons with 'known' gas concentrations)
- Temperature range - Dew point (sampling pressure) : 200°C
- Maximum chamber pressure ~ 35 Torr (5% atmos. @ Sea level)
- Response time (dependant on sampling transport delays) < 60 sec.
- Sensor life expectancy (porous membrane) > 6 months (with filters) ce impervious to species complement

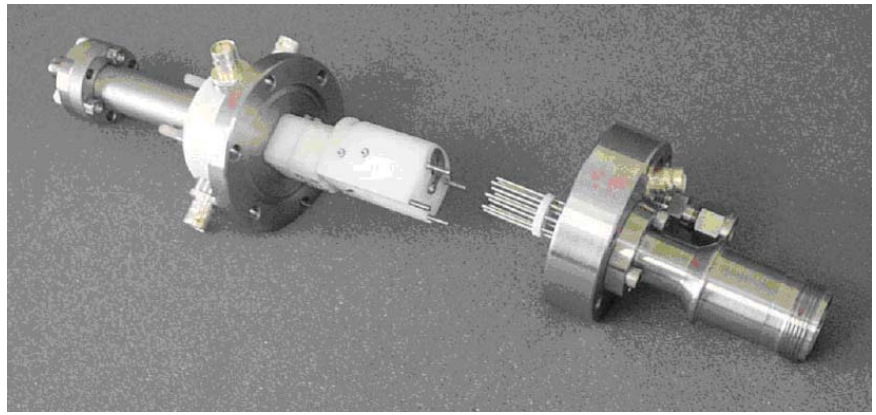
FIRMS spectra of Natural Gas & Air



FIRFMS spectra of EPA standard







. . The solid model design and picture of the actual Rotating Field Mass Spectrometer (SIM/RFMS) are shown below in Figures 7 and 8 which shows that the sensor is small enough to fit in the REMUS payload

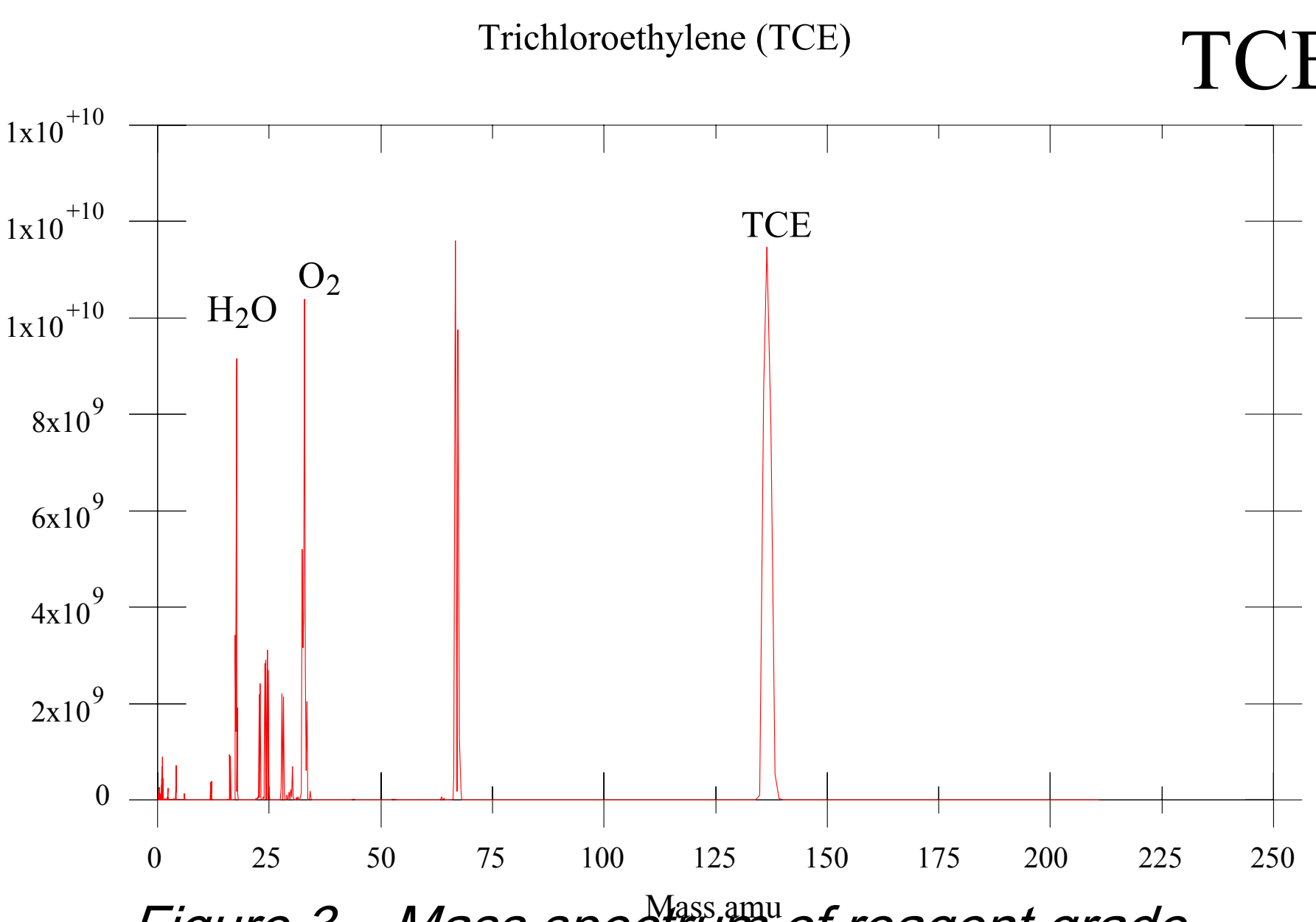
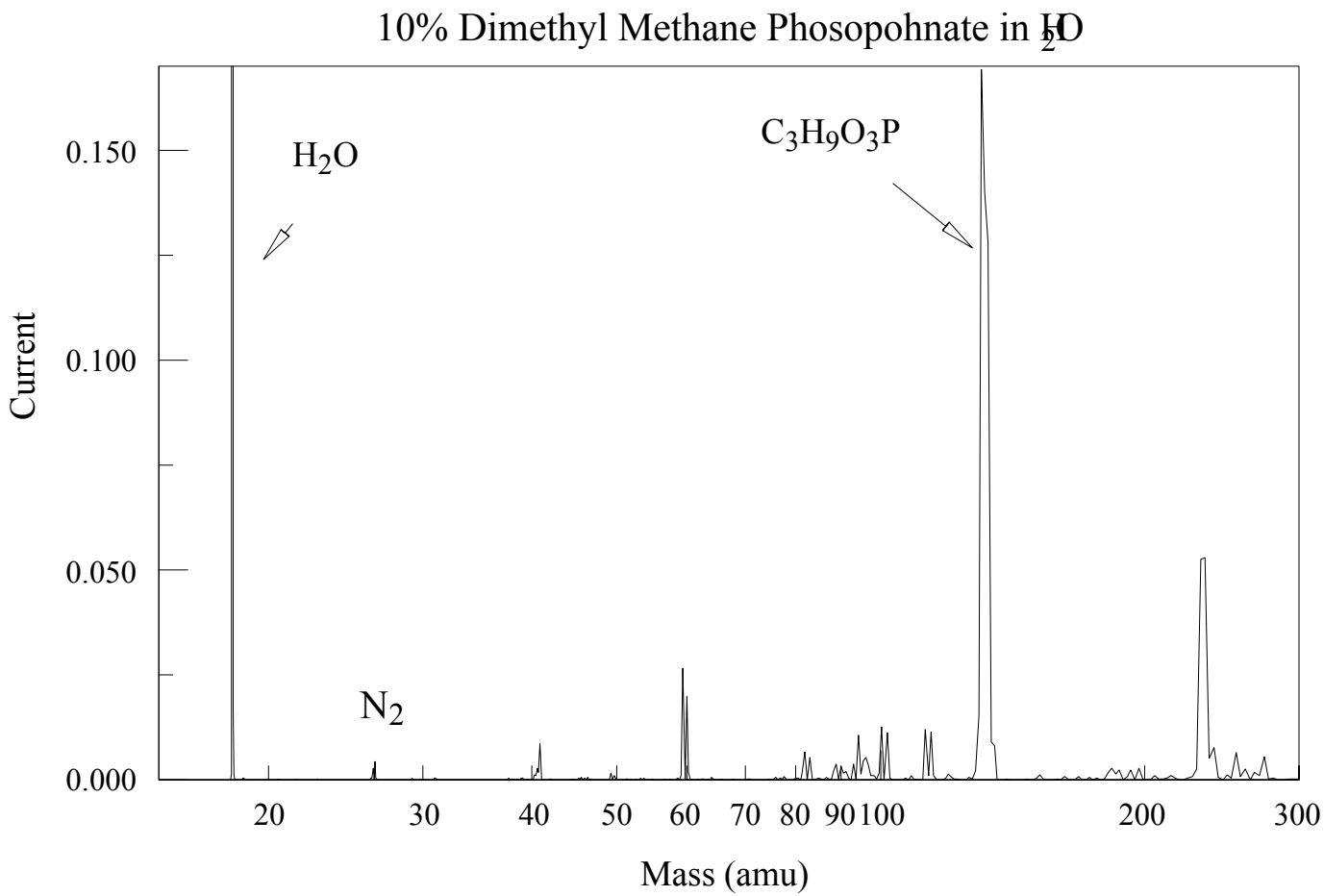
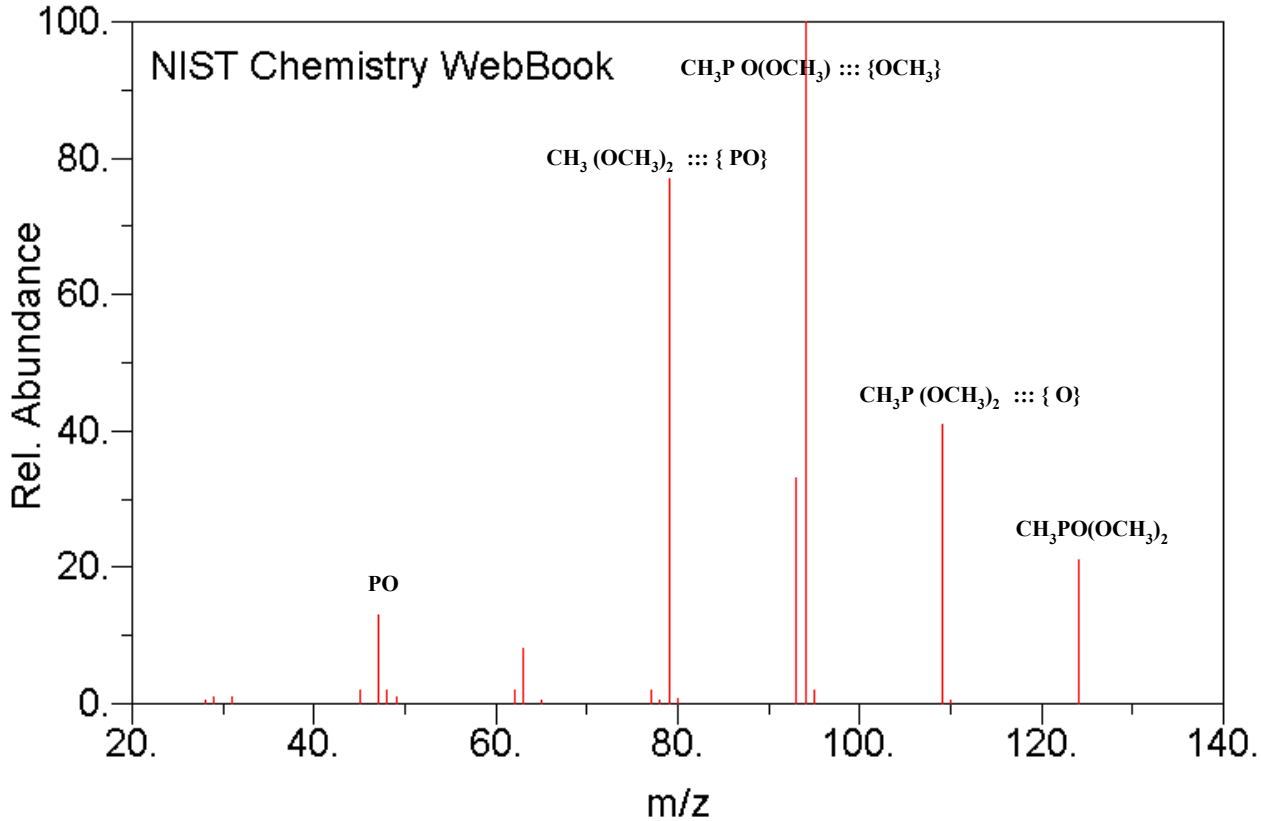


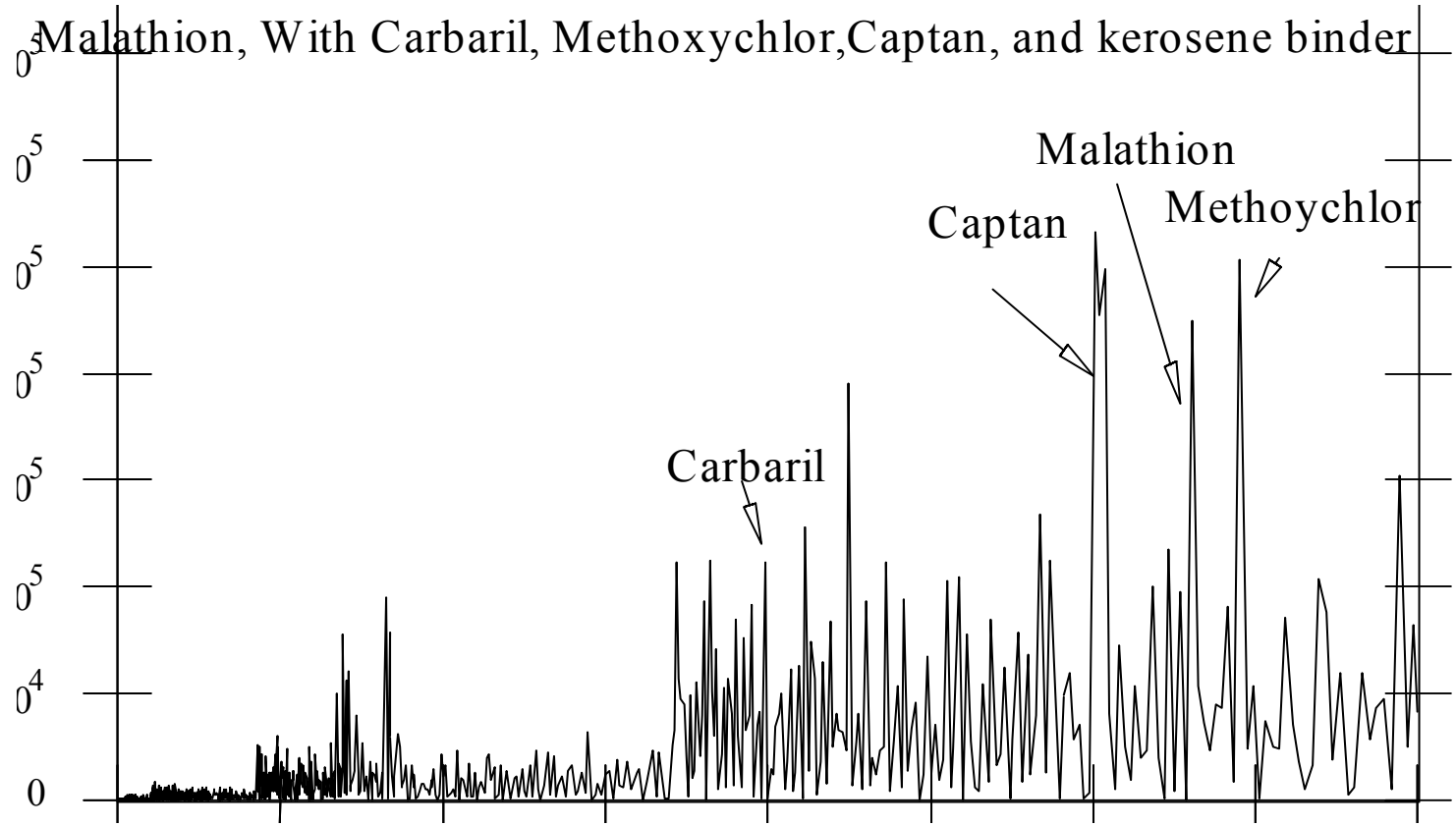
Figure 3 – Mass spectrum of reagent grade trichloroethylene.

DMMP Solution

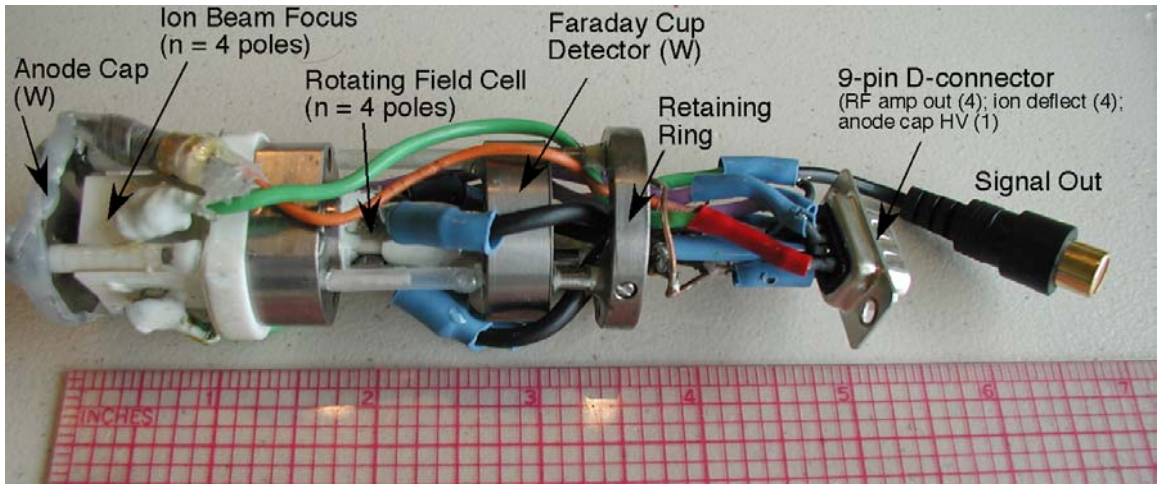




– NIST mass spectrum of pure DMMP in high vacuum. The unfragmented peak at 124 amu is smaller than those of many fragments.

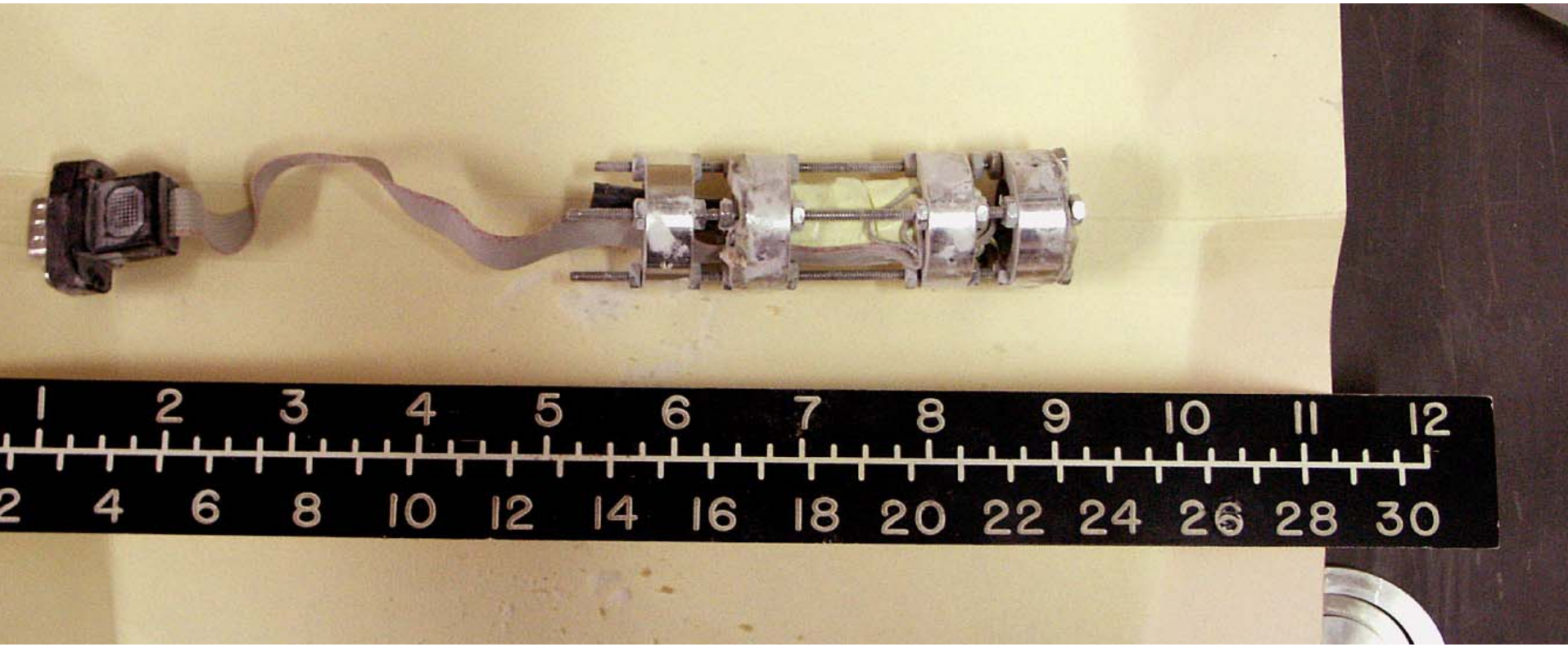


– Mass spectrum of "Liquid Fruit Tree Spray" containing neurotoxins which are readily identified in the spectrum.



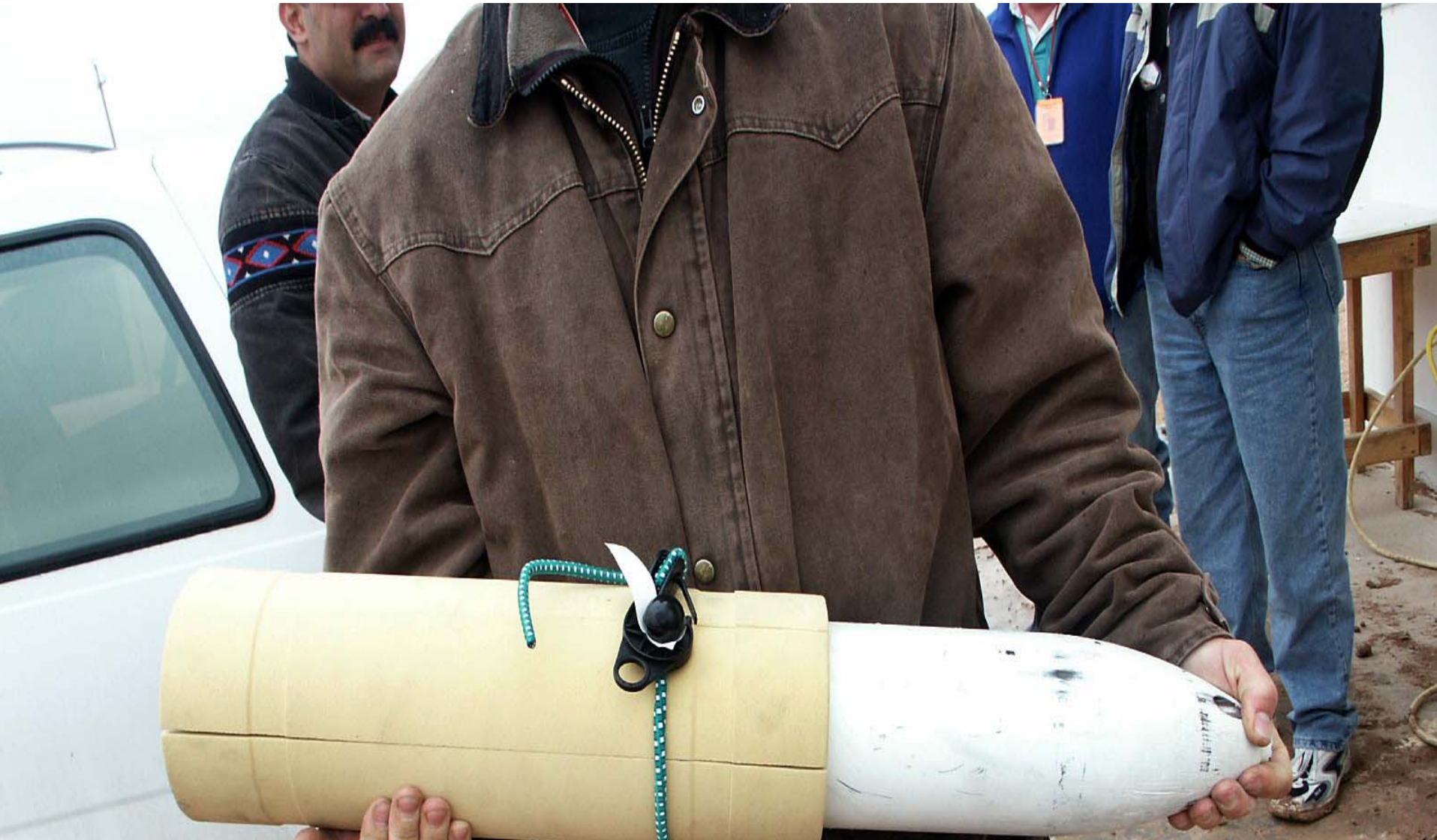
Photograph of the JPL Rotating Field Mass Spectrometer, showing major components (labeled) made primarily of 304 stainless steel and ceramic. Components labeled W are made of tungsten metal.

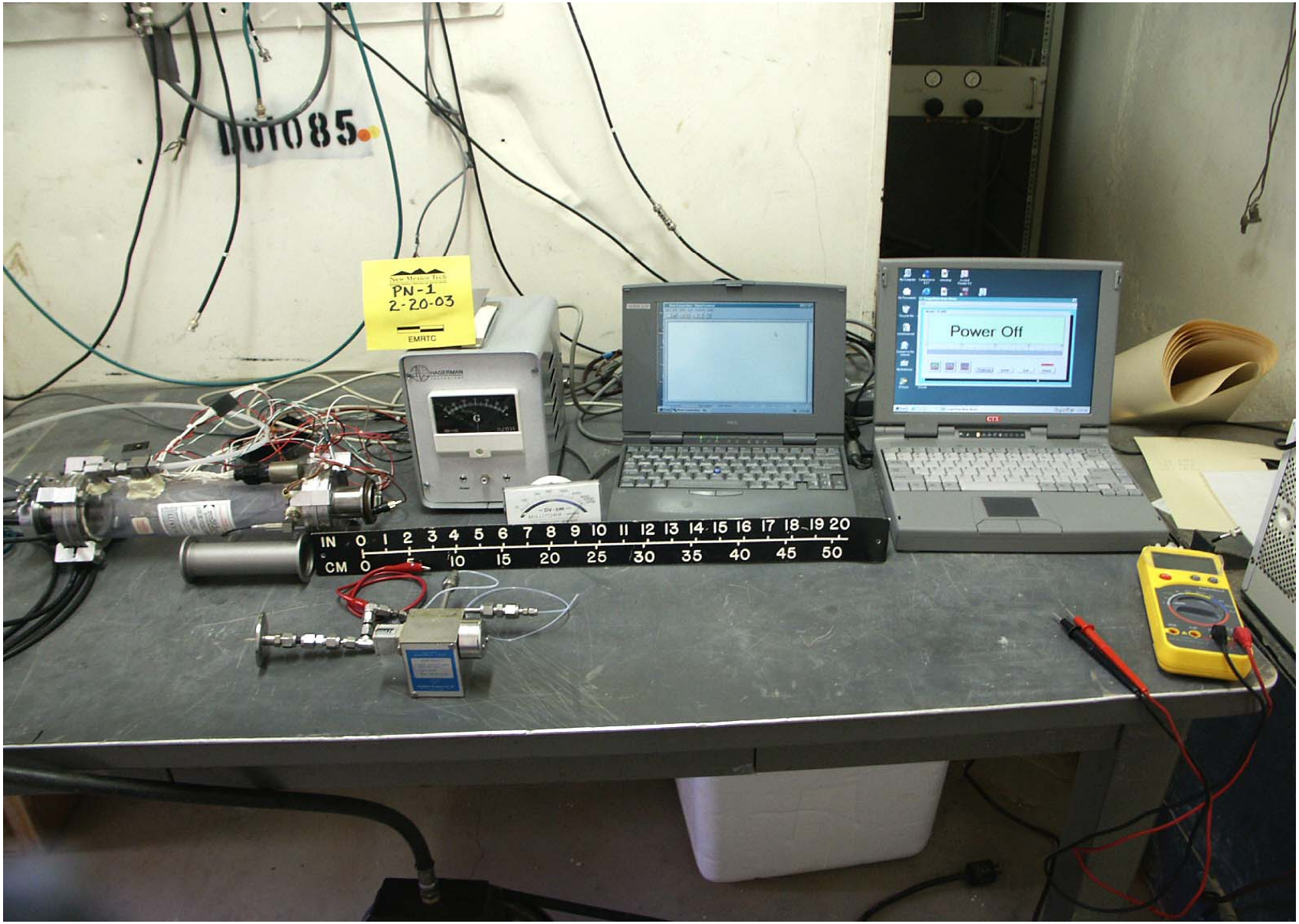
RFMS addapted for high g (2400g) impact, with glass bead “poweder” support



Sandia High –g Impact

Impact Shell Side View

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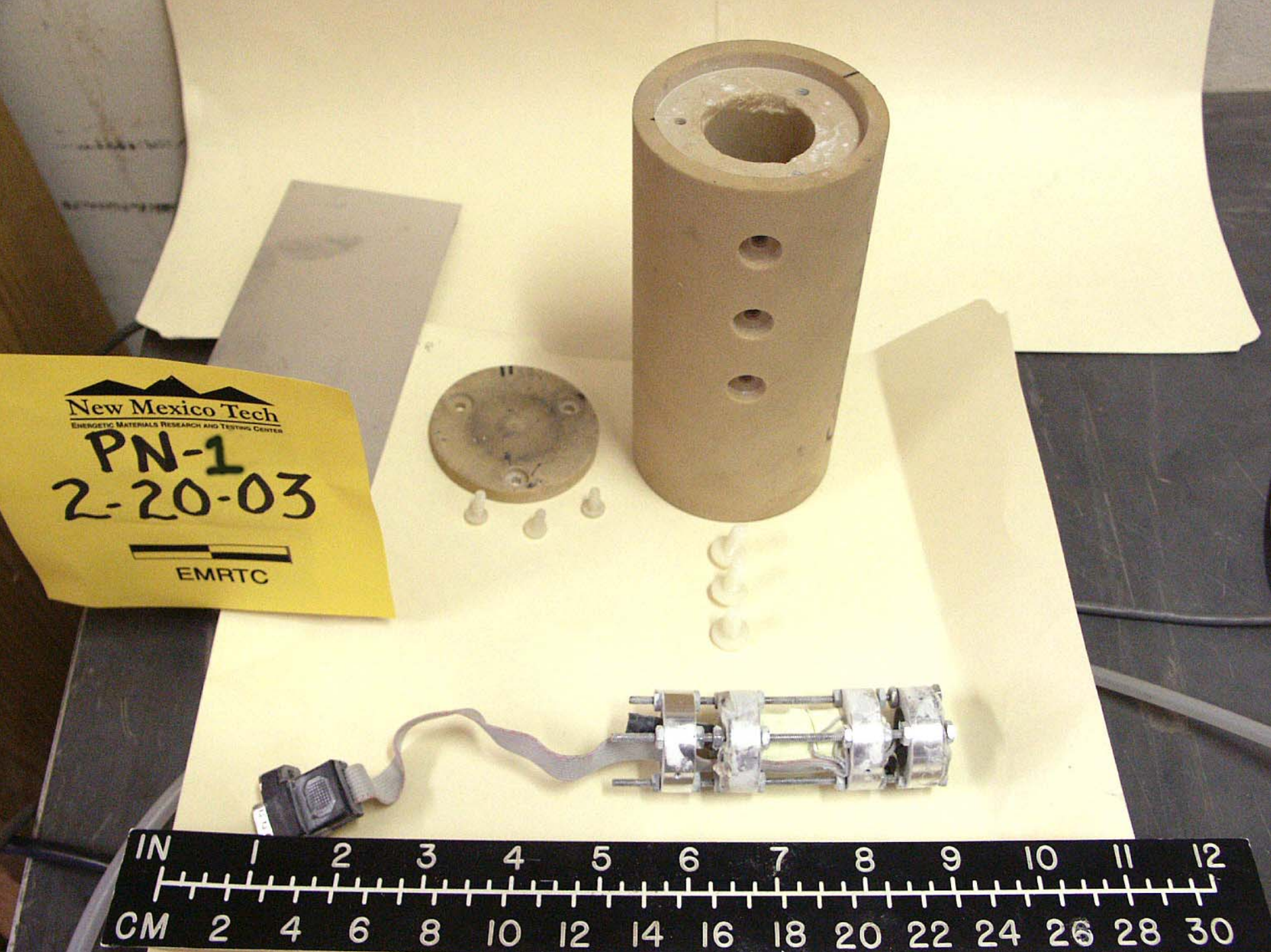
GRAND CANYON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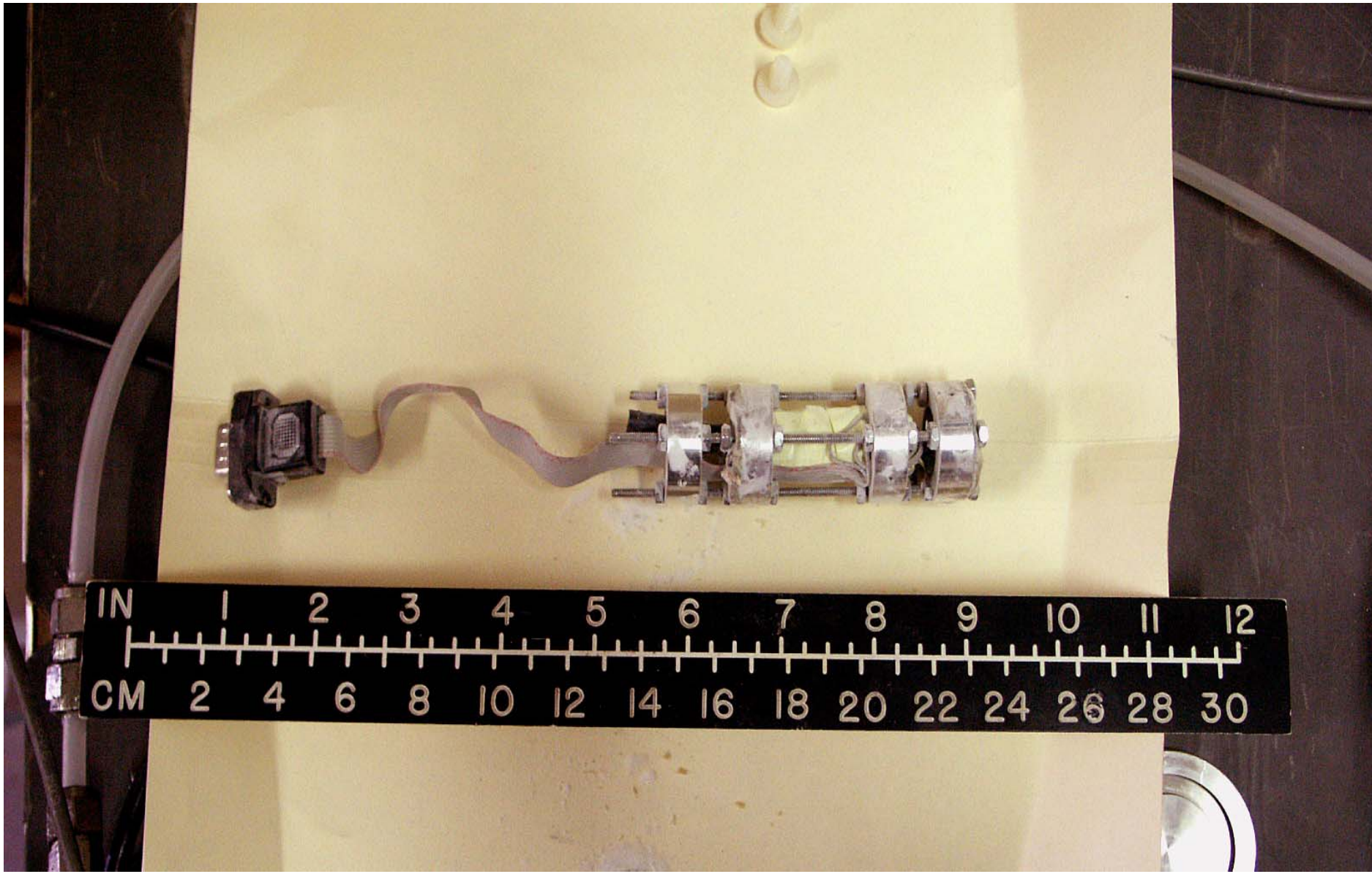
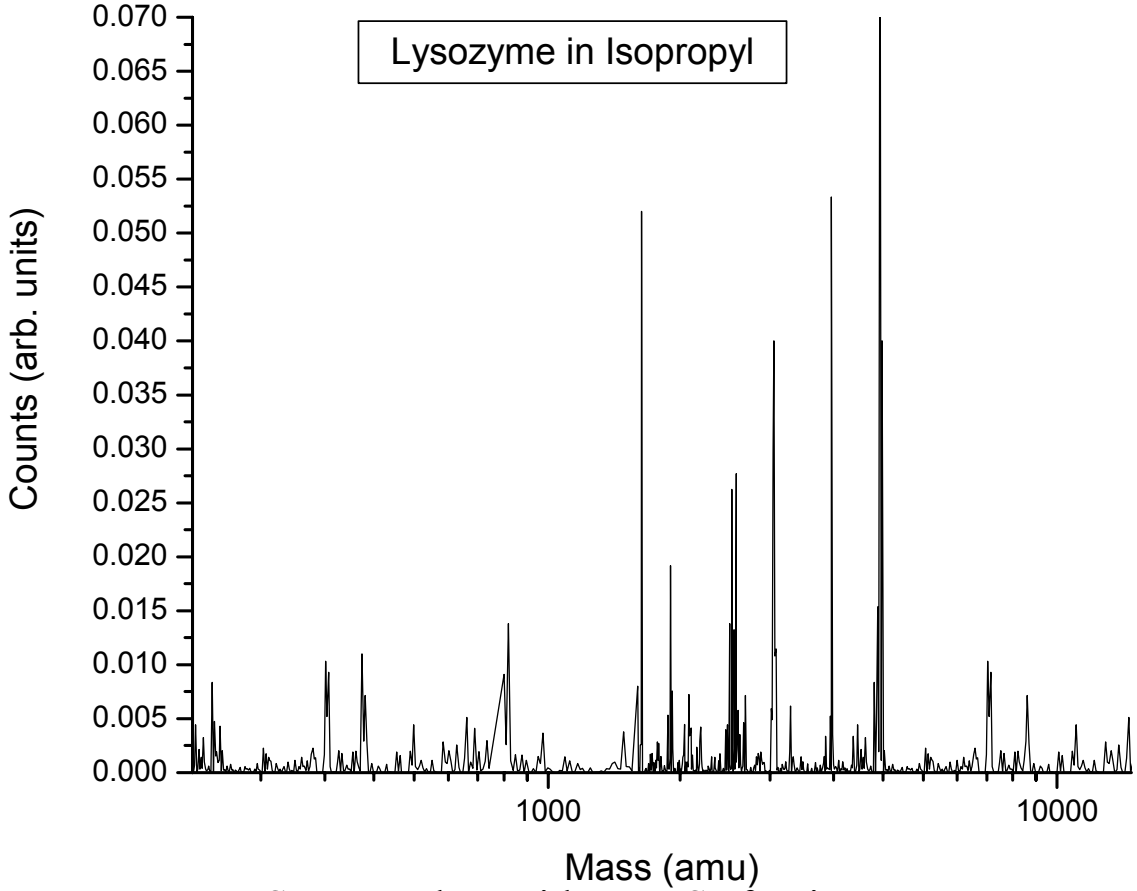
CUT INTO SIXTHS

Plywood Target Stack

RFMS after impact test, removed from glass bead support





Mass Spectra taken with RFMS after impact

Seawater Samples, Positve and Negative Electrospray