Redesign of the VAPoR Miniaturized Pyrolysis TOFMS for Improved Sensitivity

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Goddard Space Flight Center

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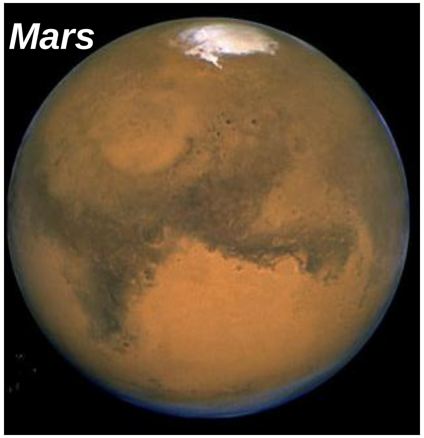
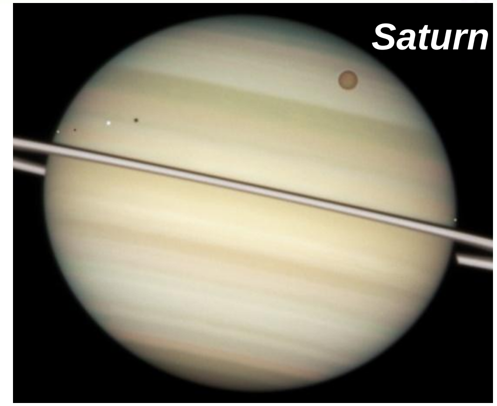
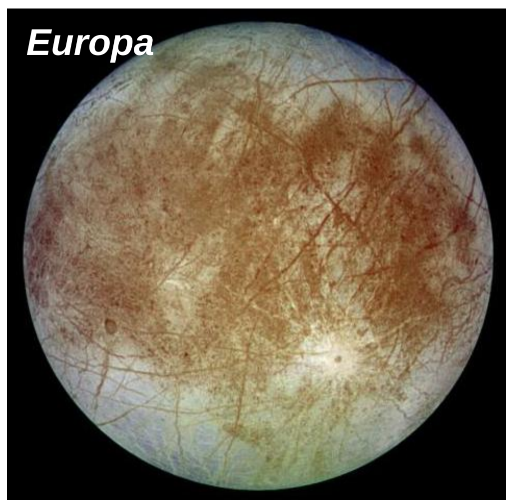
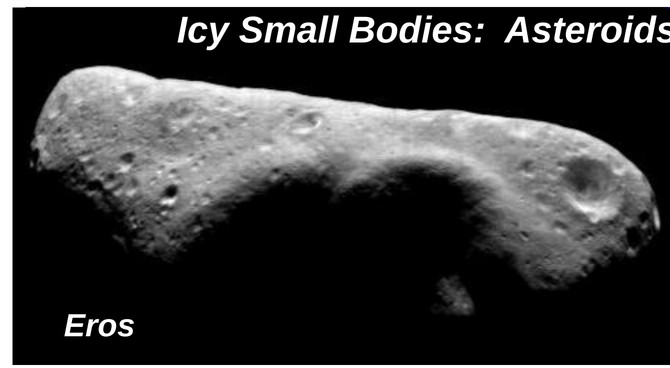
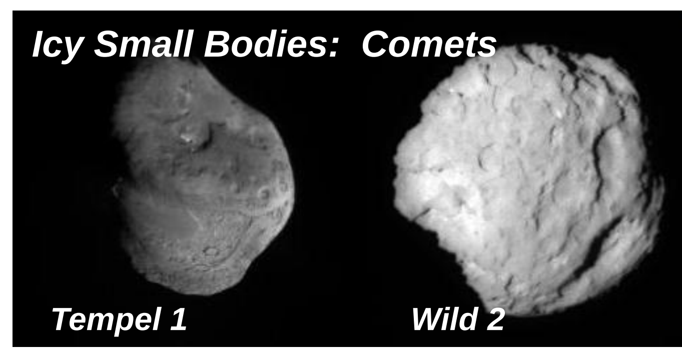
Planetary Targets for *In Situ* Instruments











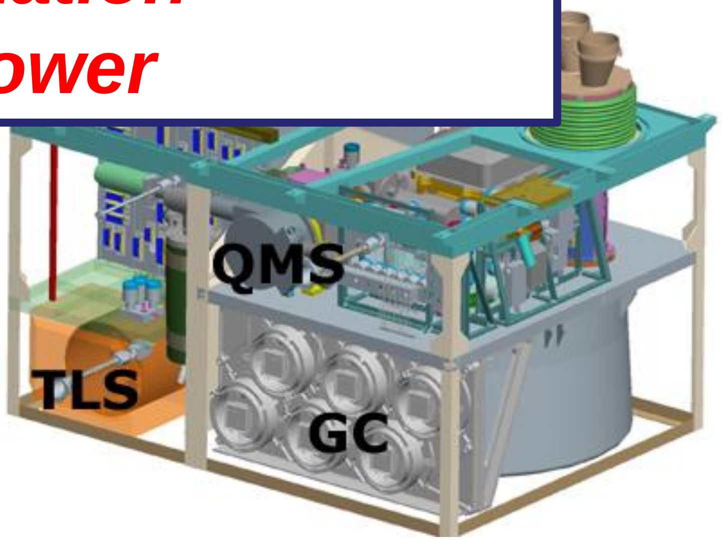
Planetary Mass Spec: State of the Art

Pyrolysis Gas Chromatograph Quadrupole Mass Spectrometer

- part of Sample Analysis at Mars Instrument Suite
- rover

Opportunities for improvement:

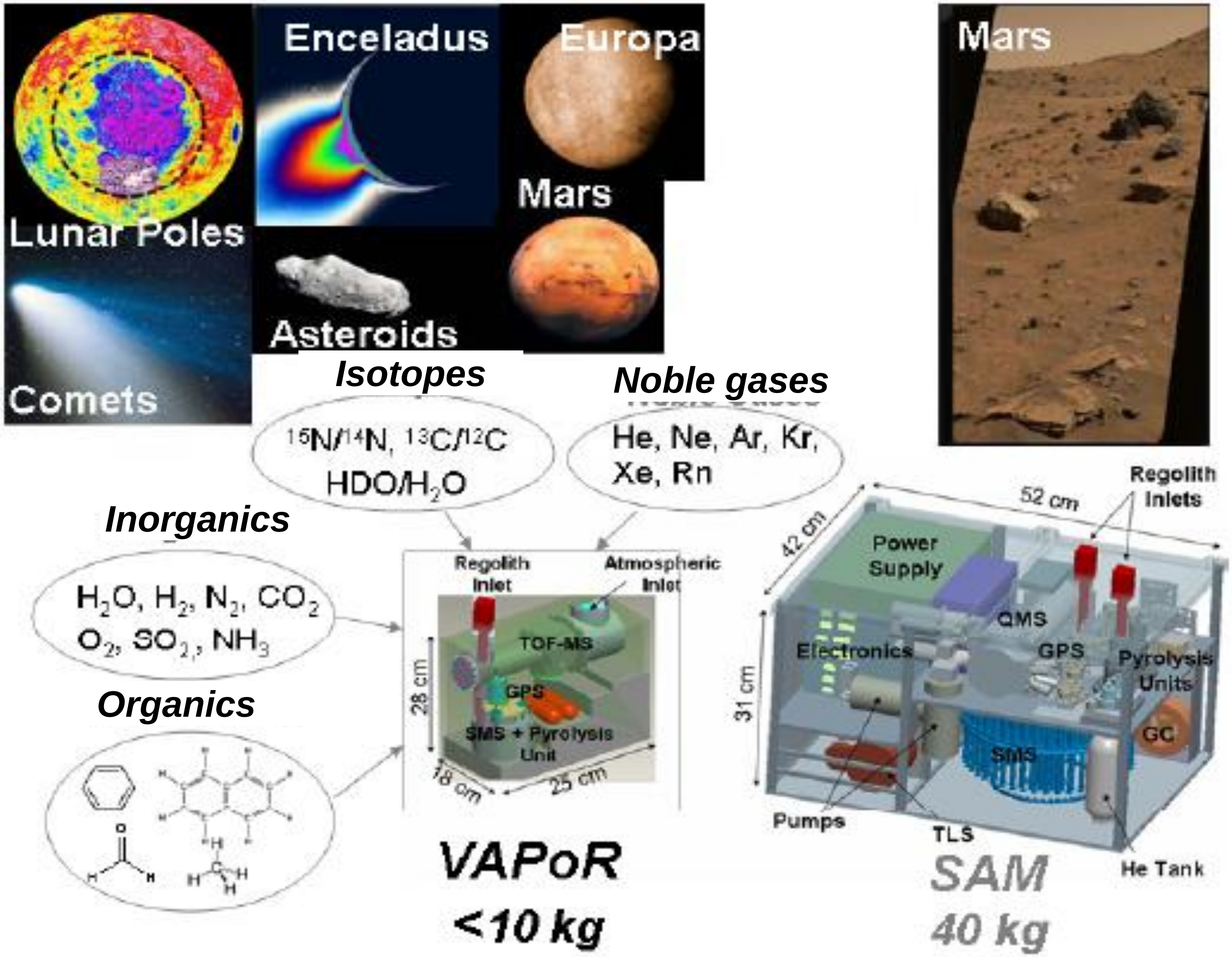
1) **Miniaturization**
2) **Lower power**



- QMS similar to Huygens
  - m ~ 1.3 kg, P ~14.5 W
- Thermionic filaments are used to ionize pyrolysis products or atmospheric gases

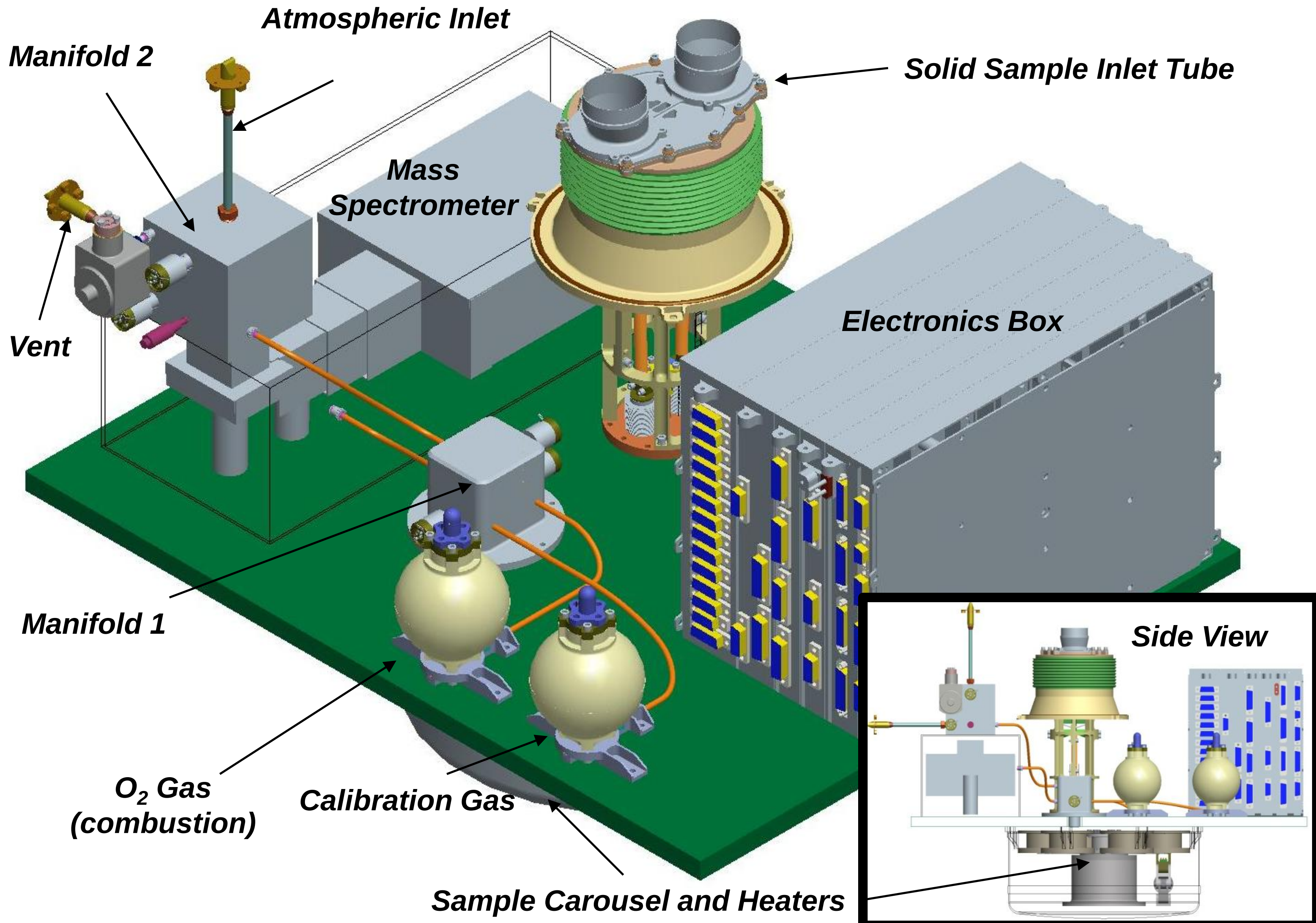
VAPoR

VAPoR – Volatile Analysis by Pyrolysis of Regolith



VAPoR Key Components

V. Holmes (Mechanical Design)

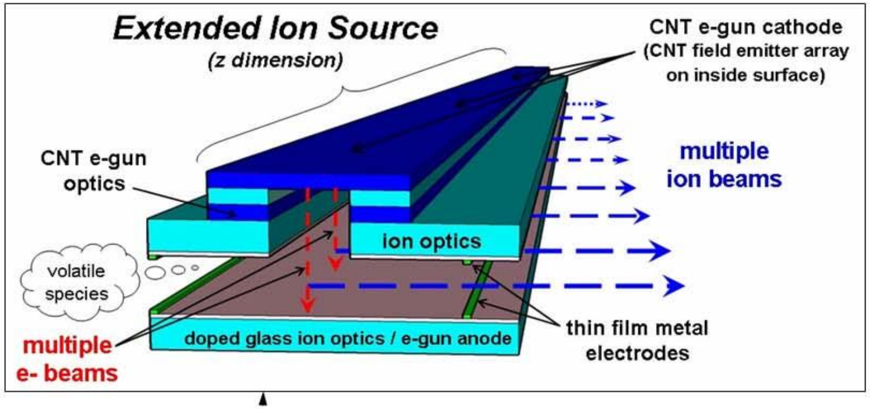


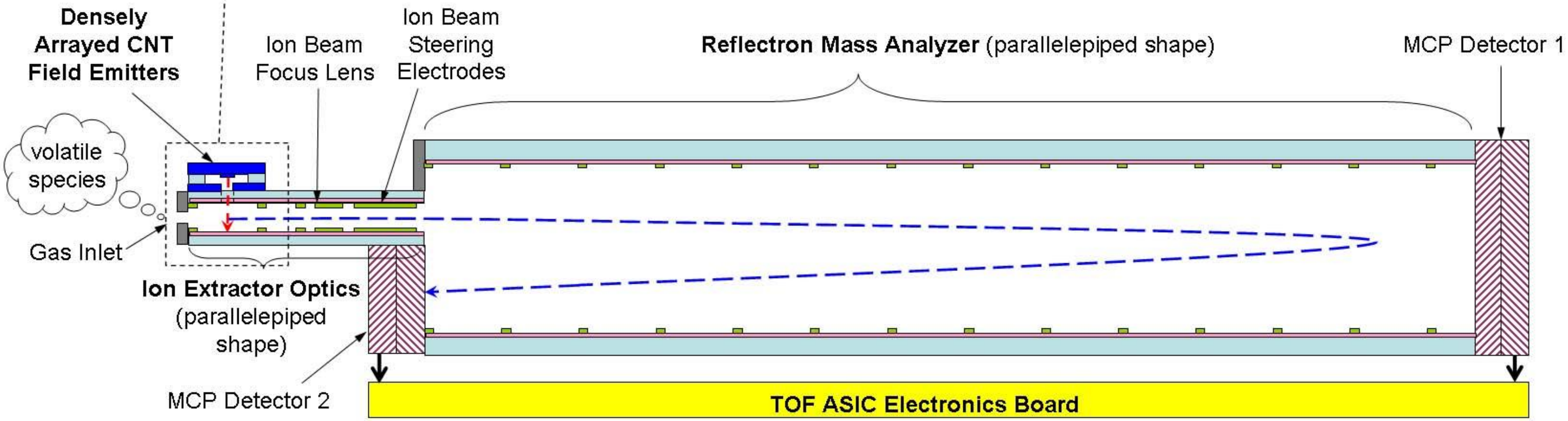
VAPoR Measurements of Lunar Atmosphere and Regolith

Objective		Instrument Target Measurements	Temp. Range (°C)
Origin of Volatiles	*C,H,O,N,S-Volatiles*	Atmospheric volatiles	n/a
		H_2O, H_2, CO_2, CO, N_2, SO_2 from regolith	100-1200
		D/H ratio in H_2O	0-800
		$^{13}C/^{12}C$ ratio of CO_2	100-1200
		$^{15}N/^{14}N$ ratio in N_2	600-1200
	Noble Gases	He, Ne, Ar, Kr, Xe, and Rn	300-1300
		Isotope ratios ($^3He/^4He$, $^{36}Ar/^{40}Ar$, $^{129}Xe/^{136}Xe$)	He: 200-500 Xe/Ar: 300-1300
	Organics	$^{13}C/^{12}C$ ratio in CO_2 from organics combustion	400-500
		Volatile hydrocarbons: methane, ethane, benzene, amines, alcohols, formaldehyde	300-1000
Resources (ISRU)		Water-ice in regolith	0-100
		O_2	1100-1300
		Reduced gasses such as HCN, NH_3, and H_2S	HCN/NH_3: 100-900 H_2S: 700-1300
		^3He relative abundance	He: 200-500

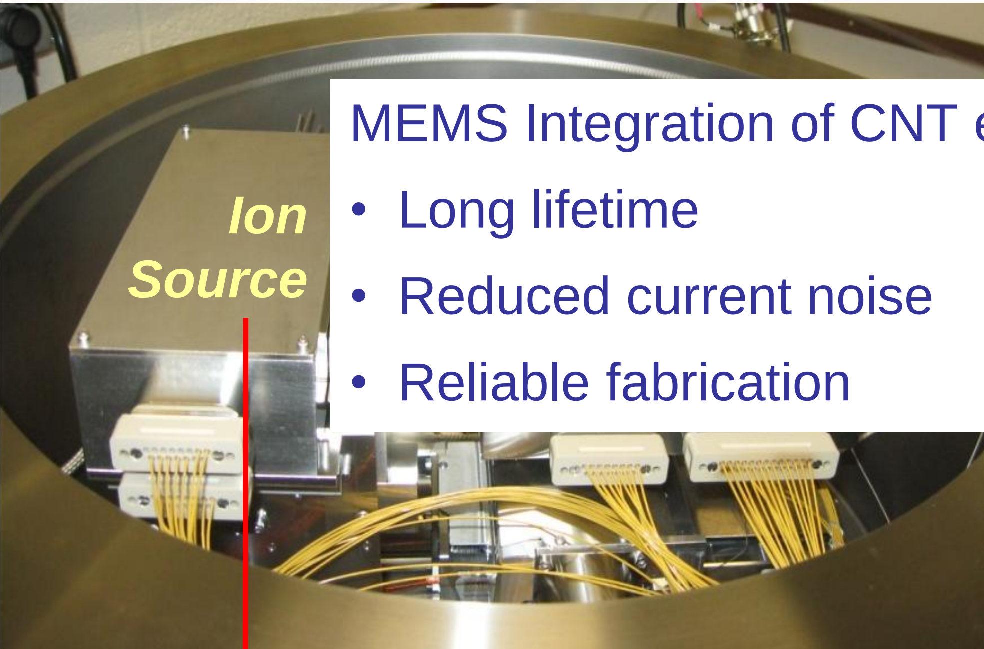
How the TOFMS works (old design)

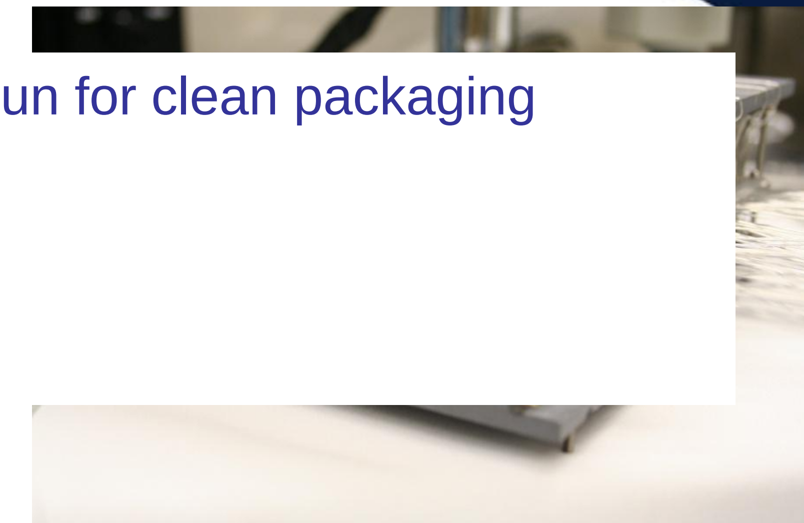
Electron impact ionization of volatile species followed by ion acceleration through reflectron.





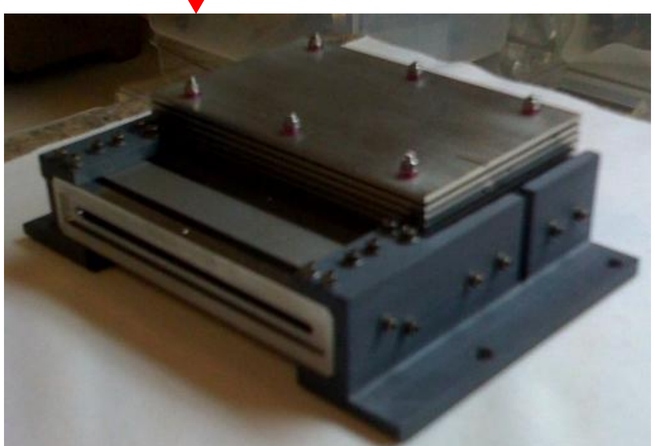
Miniaturized Time-of-Flight Mass Spectrometer



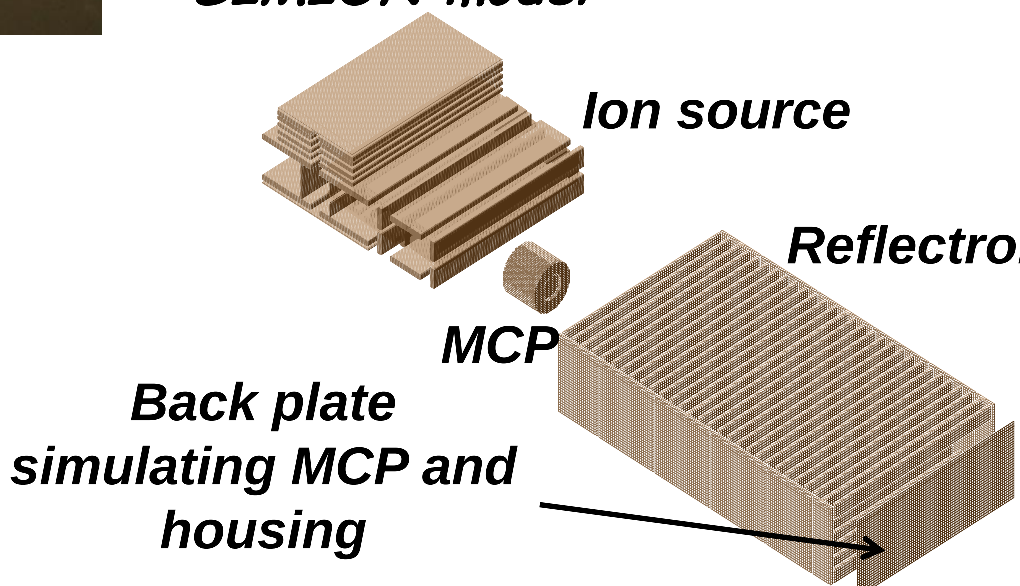


MEMS Integration of CNT e-gun for clean packaging

- Long lifetime
- Reduced current noise
- Reliable fabrication

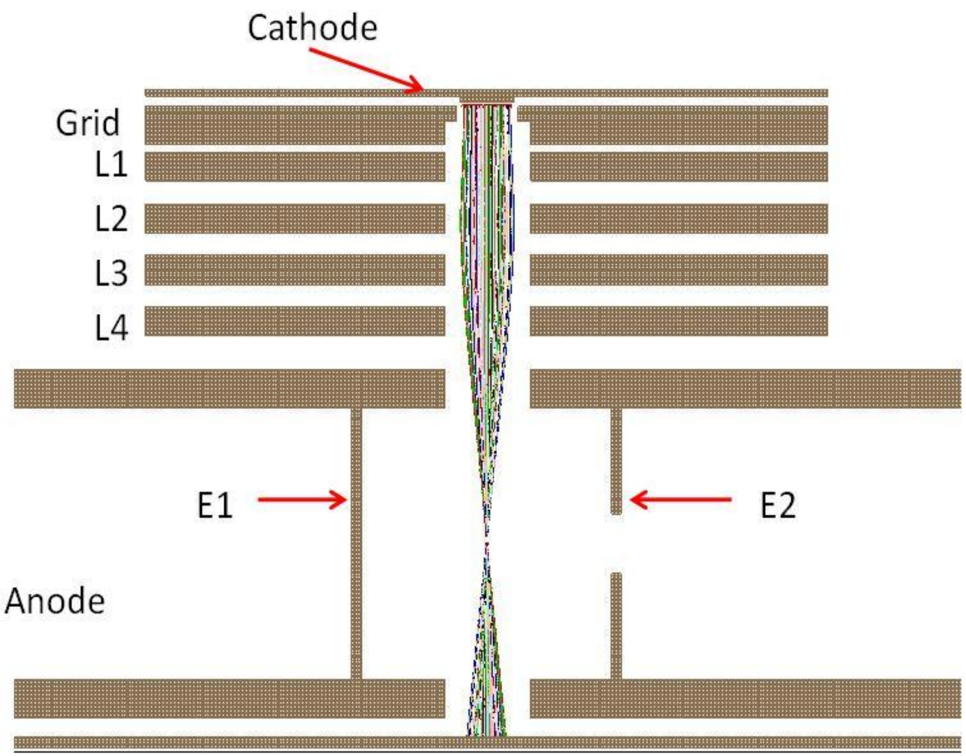


SIMION model

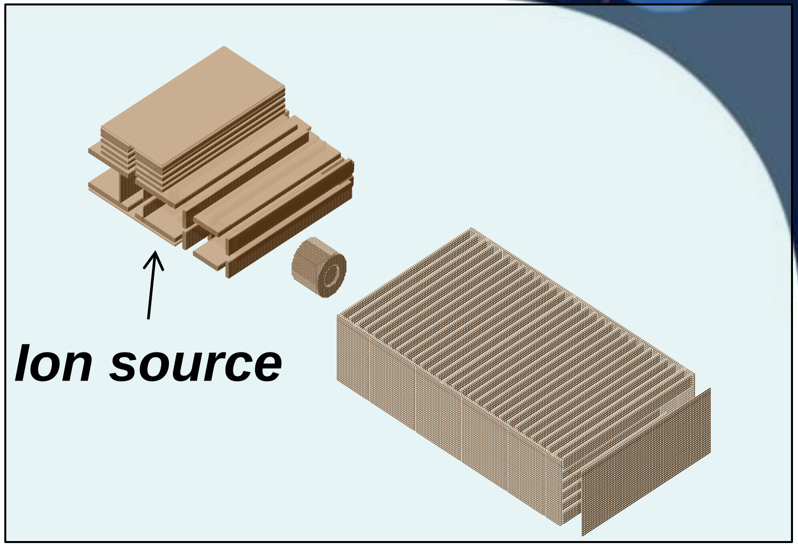


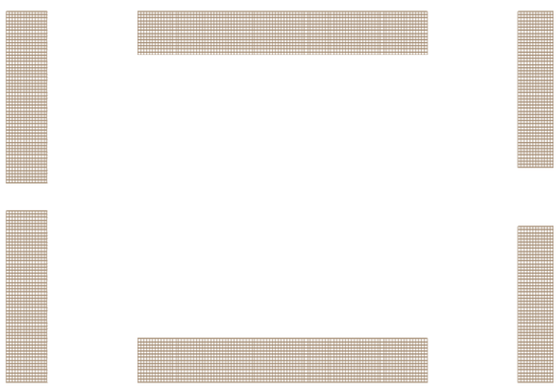
NEW DESIGN with cross section

Ion source cross-section



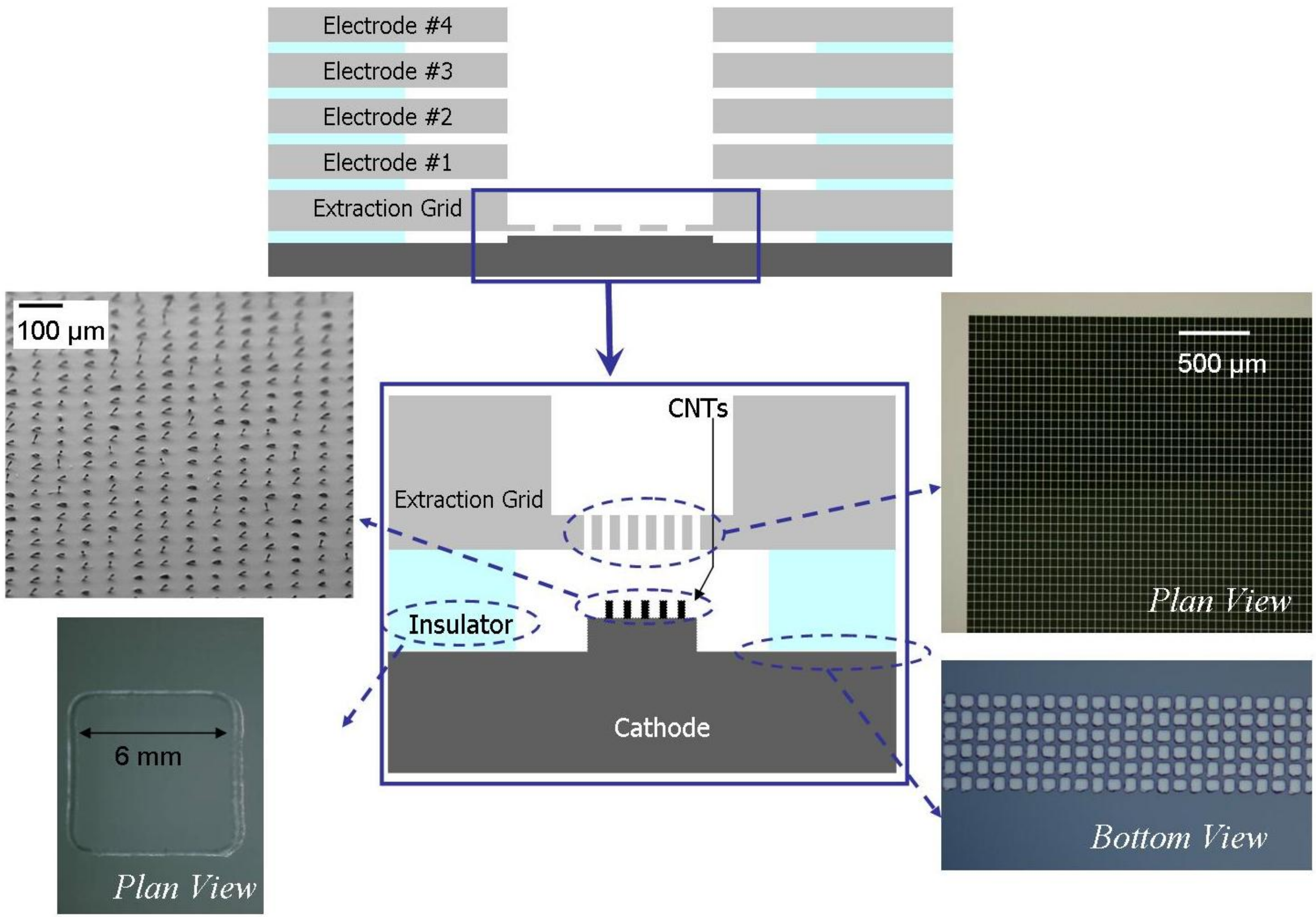
Electron beam



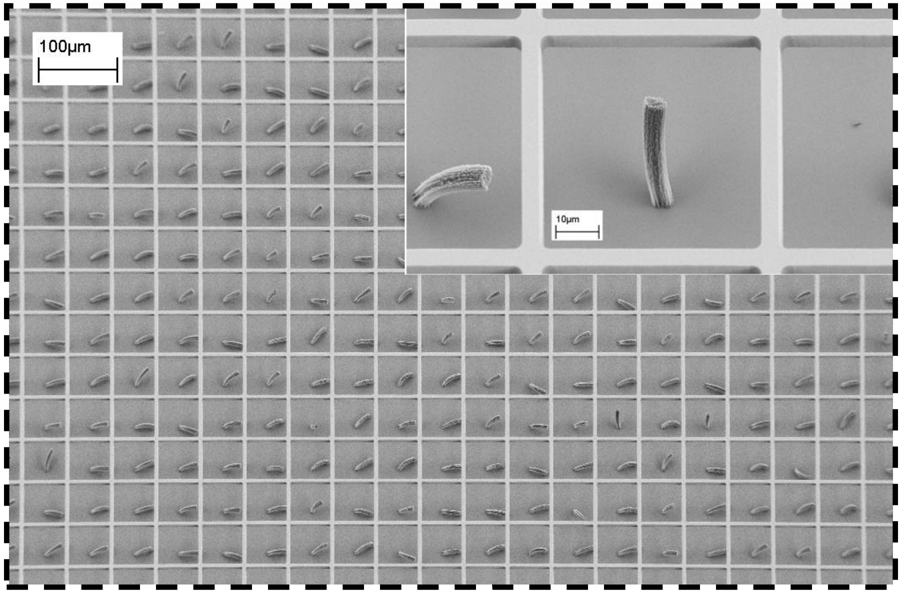


Recent Work: Assembly and Integration

Cathode-grid integration

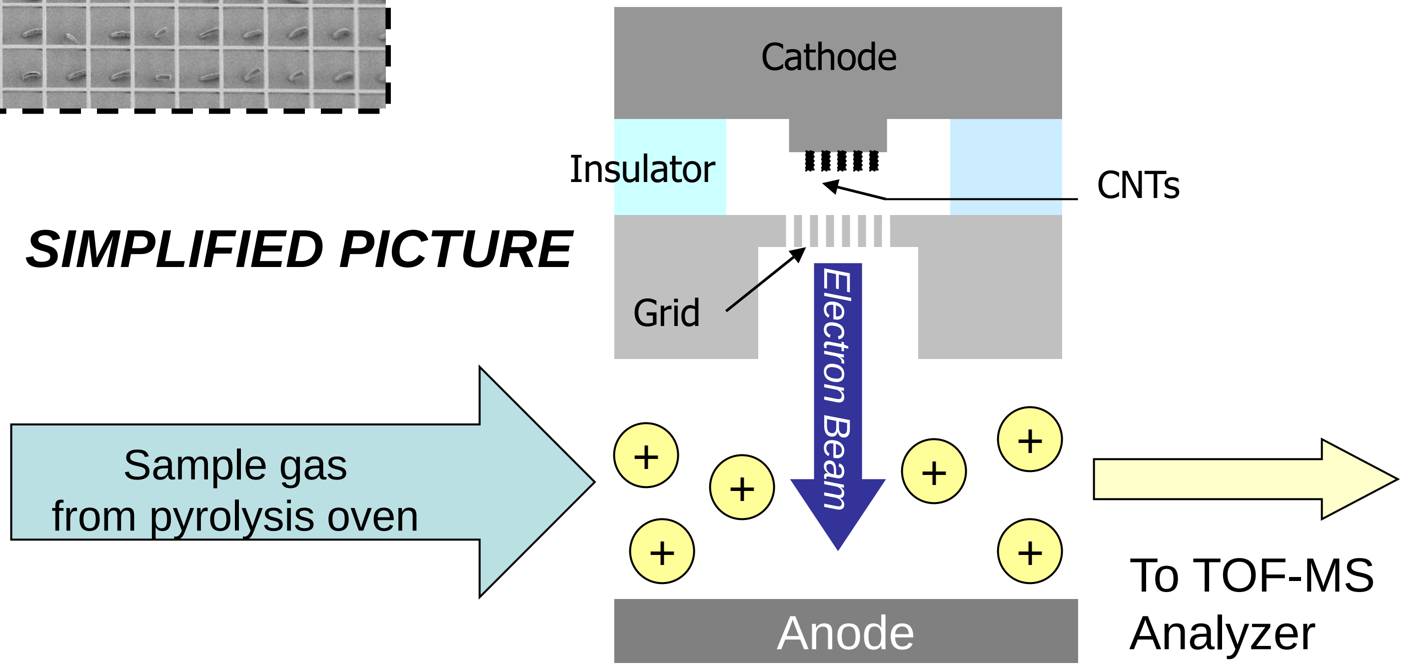


Carbon Nanotube Electron Gun



Carbon Nanotube field emitters
- Low power (100x < thermionic)
- Scalable for high sensitivity, redundancy
- Efficient ionization of the parent species
- Challenges: Lifetime and stability

SIMPLIFIED PICTURE

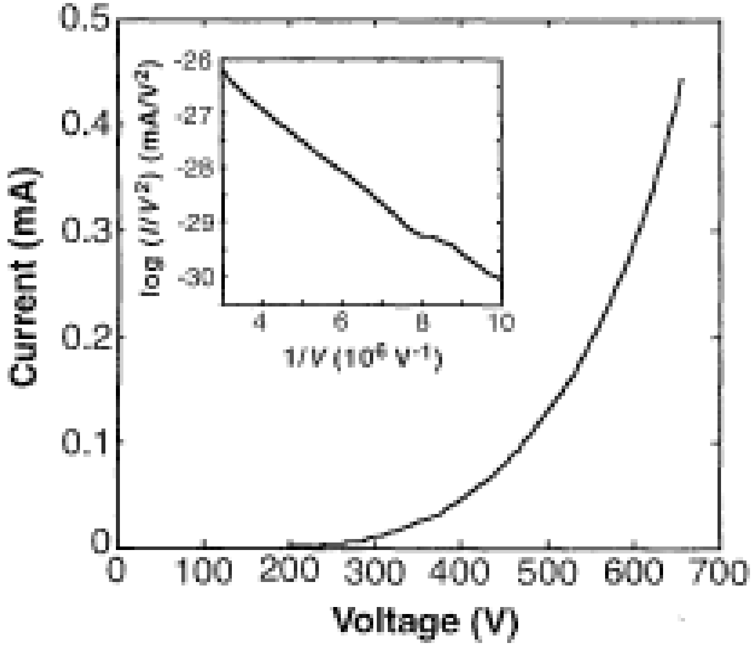


Previous Work: Field Emission in CNTs

- Fowler-Nordheim Tunneling
  - –β =Field enhancement factor
  - –Reported values of β vary from 400-1200 (for MWCNTs)

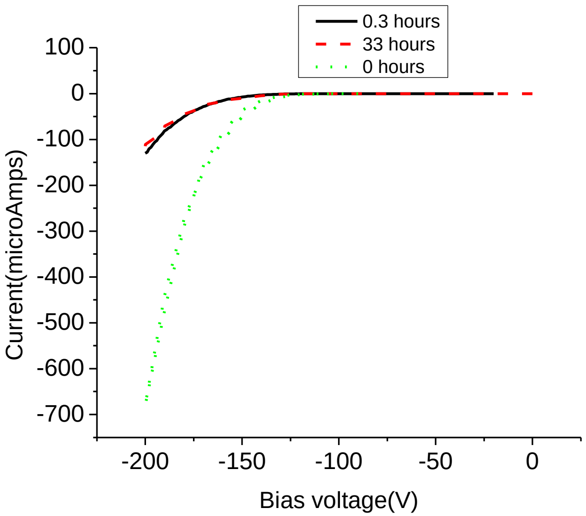
$$I = K_1 E^2 \exp\left(-\frac{K_2}{E}\right) \quad \beta = \frac{B\Phi^{3/2}}{K_2}$$

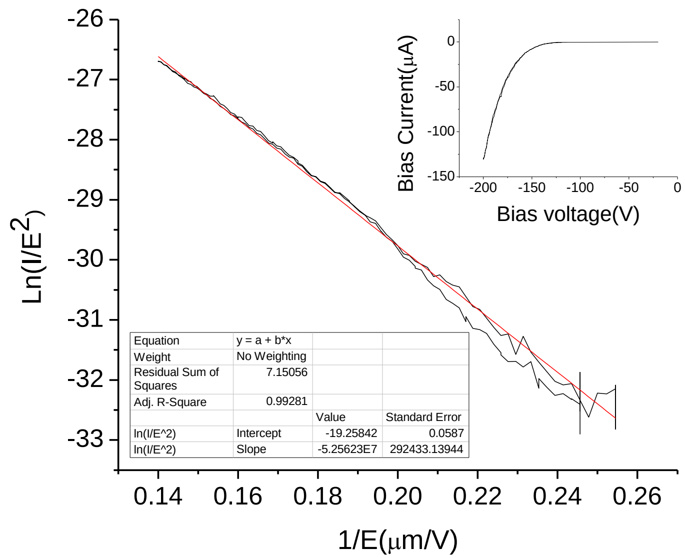
W. A. de Heer, A. Chatelain, D. Ugarte (1995)



CNT E-gun for Mini Mass Spec

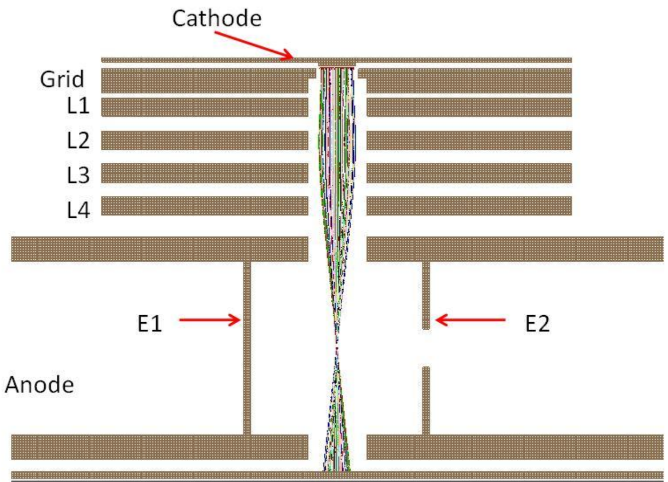
- Fowler-Nordheim behavior confirmed
  - β~1500
- 100s of microamps of emitted current
- Recent tests show current persists after initial drop off and other devices have persisted for several hundred hours in high vacuum[1]

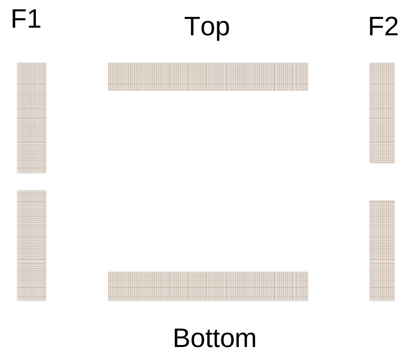




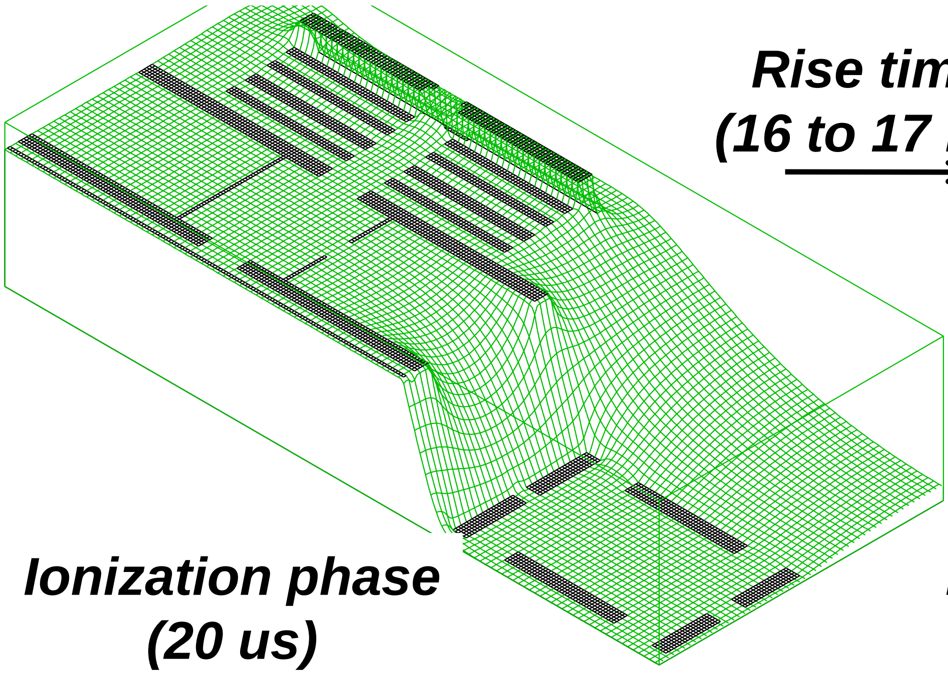
[1]S. A. Getty et al., "Effect of nitrogen gas on the lifetime of carbon nanotube field emitters for electron-impact ionization mass spectrometry, " 2008, vol. 6959, pp. 695907-695907-10.

SIMION Ion source simulation

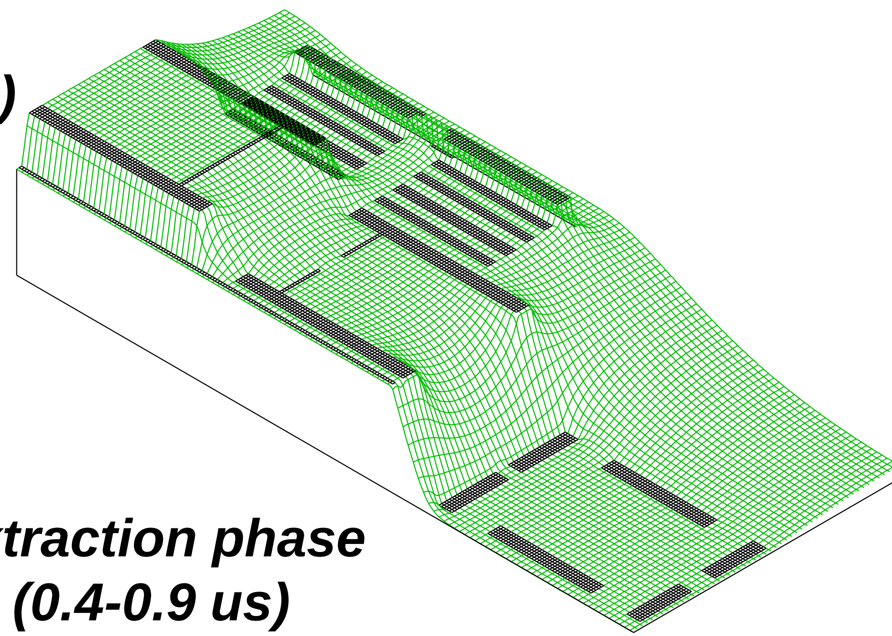




Electrode	Ionization	Extraction
Anode	650	650
Cathode	580	580
Grid	780	780
L1	735	735
L2	670	670
L3	660	660
L4	650	650
E1	650	950
E2	650	650
F1=F2=Top=Bottom	0	0



Rise time (16 to 17 ns) →

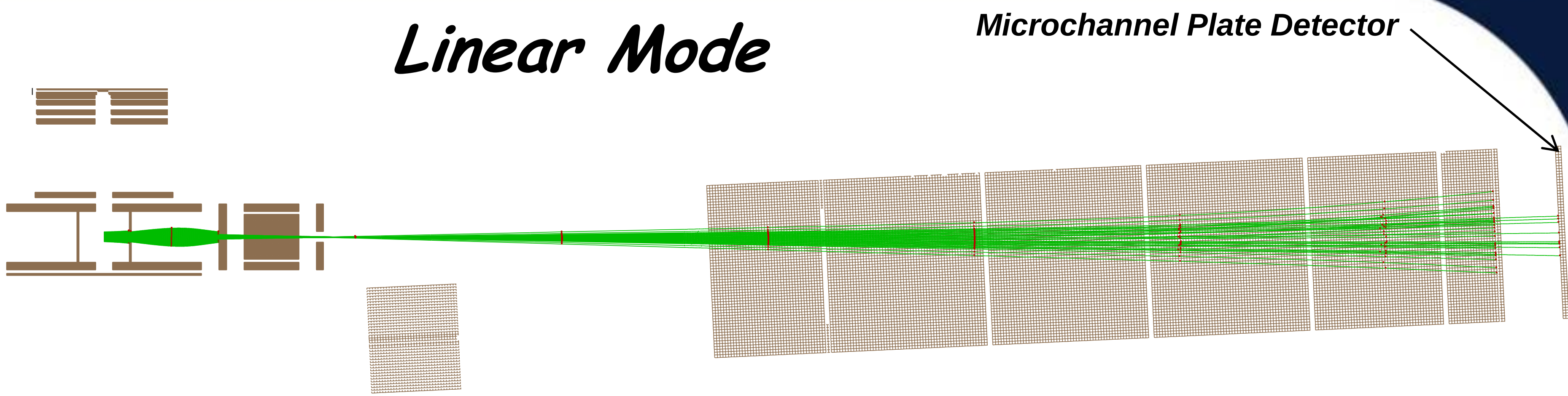


Ionization phase (20 us)

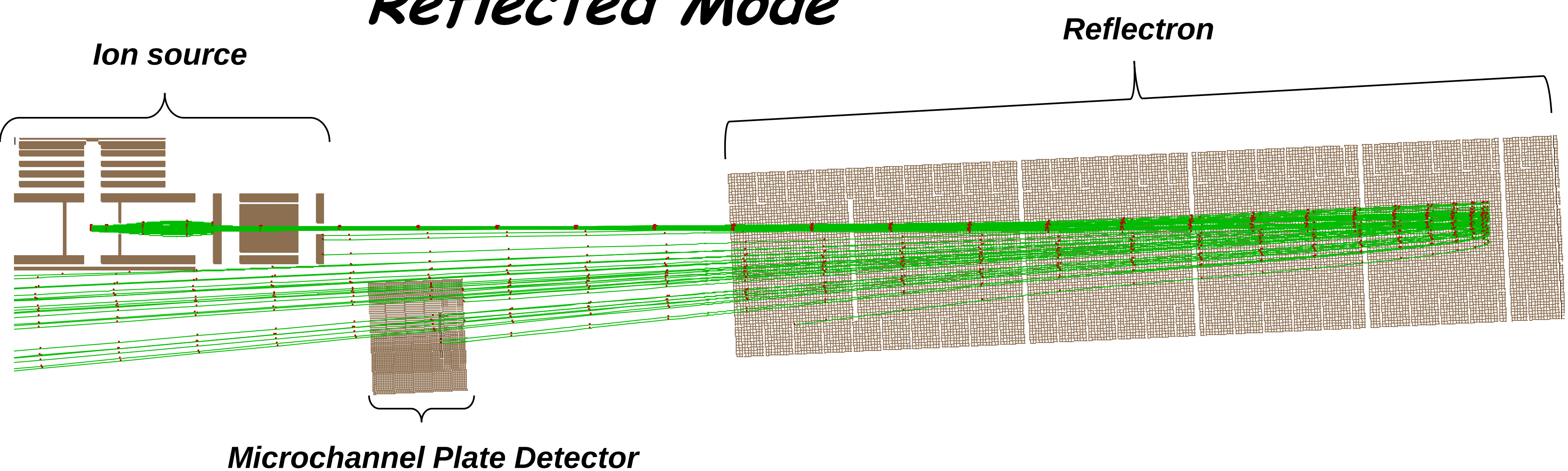
Extraction phase (0.4-0.9 us)

Reflectron operation modes

Linear Mode

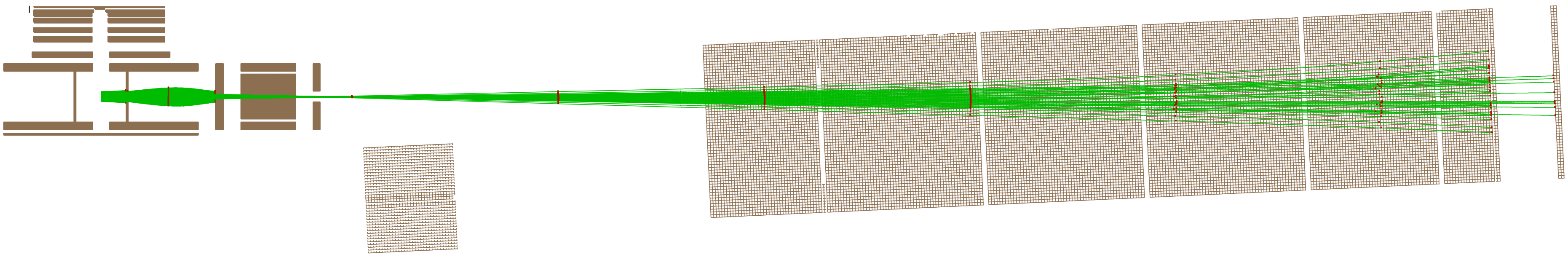


Reflected Mode



SIMION vs. experiment

Simulated vs. experimental TOF

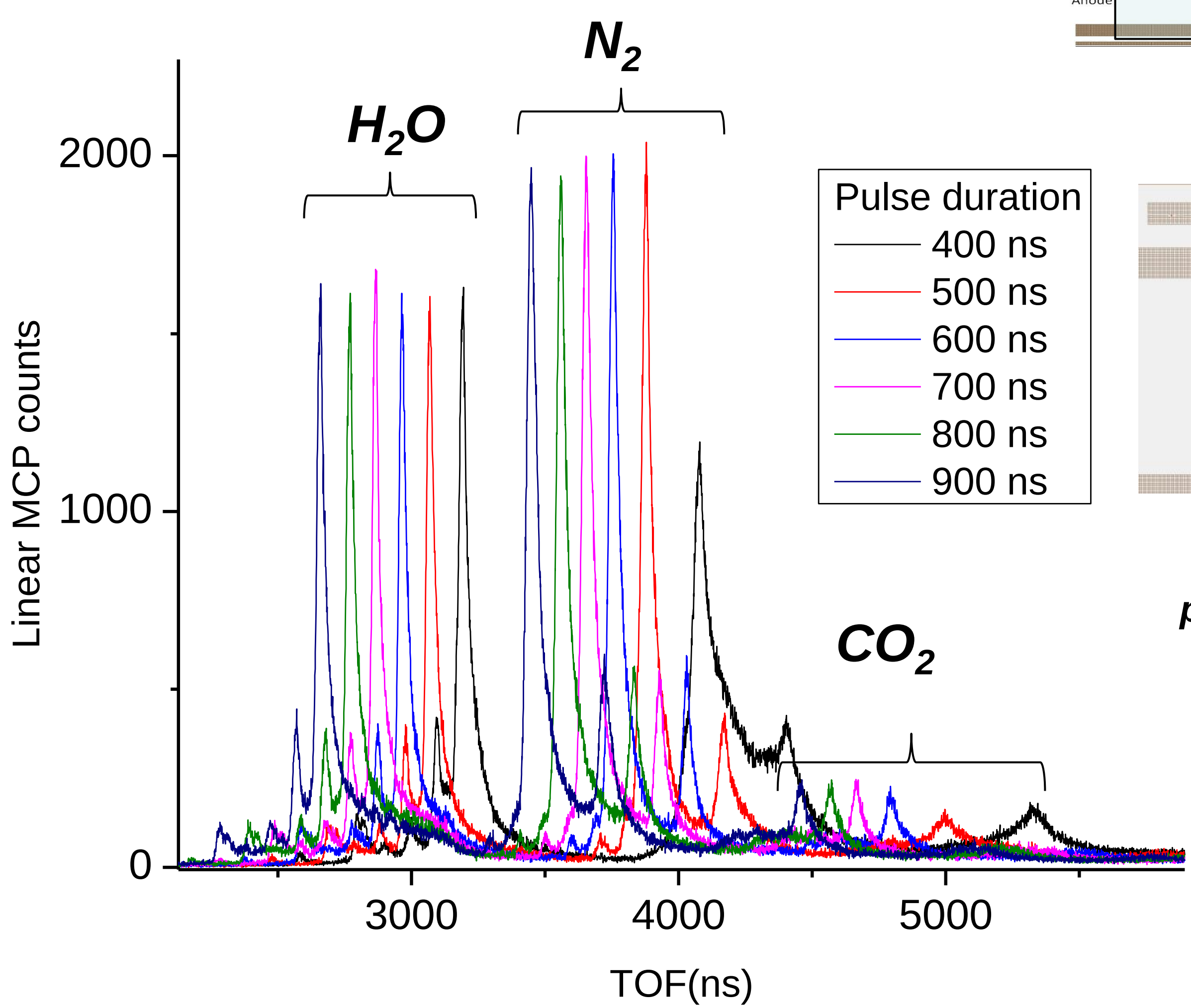


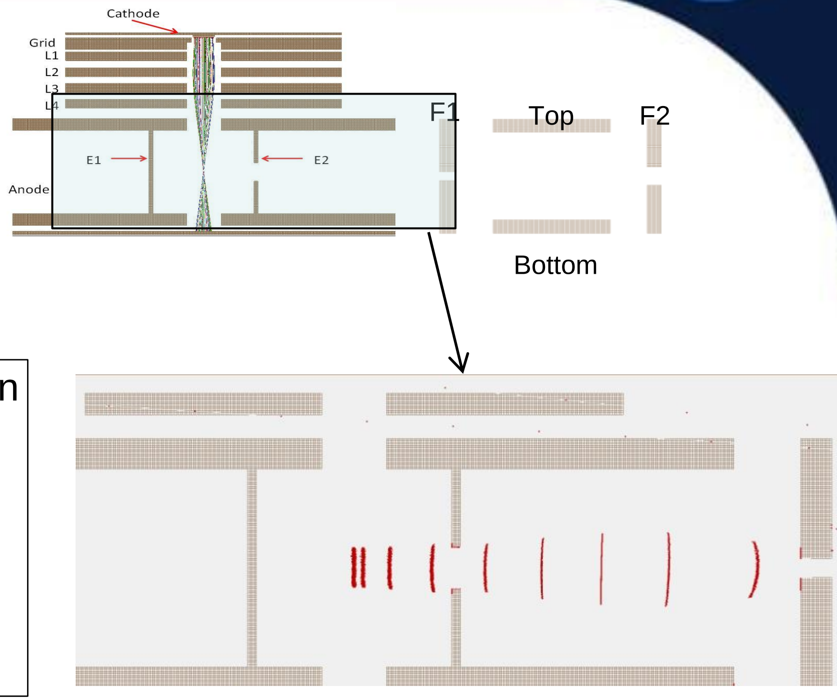
	H2O peak (µs)	N2 peak (µs)	CO2 peak (µs)
SIMION	3.15	3.91	4.91
Experiment	3.168	3.944	4.96

SIMION model and experiment deviate by <50ns

Optimization of pulse duration

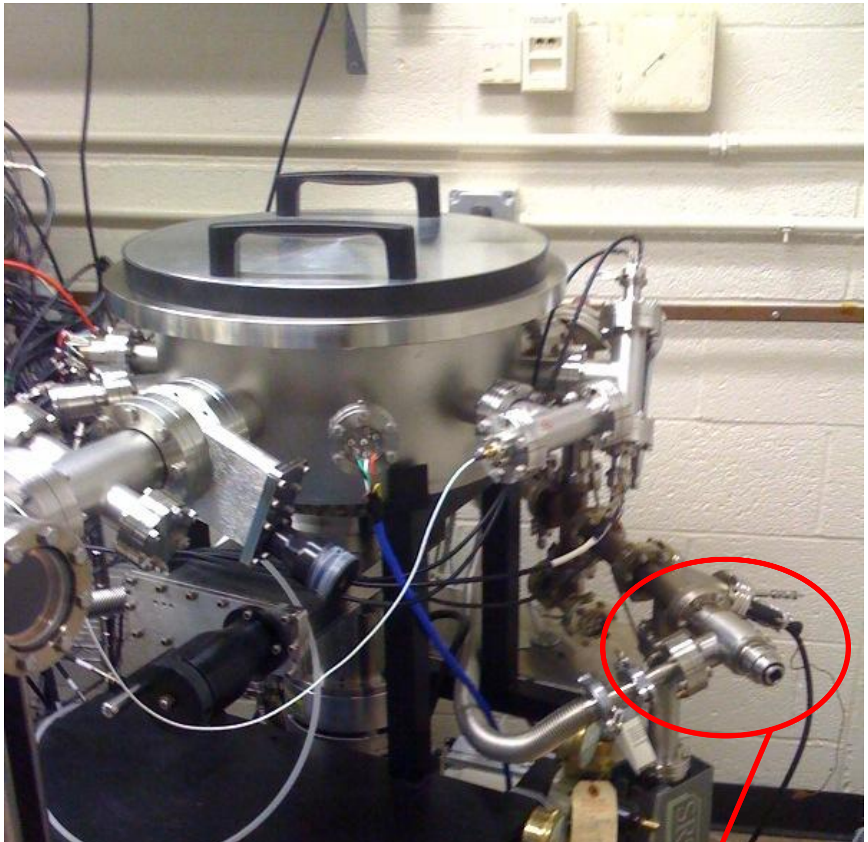
300 V pulse





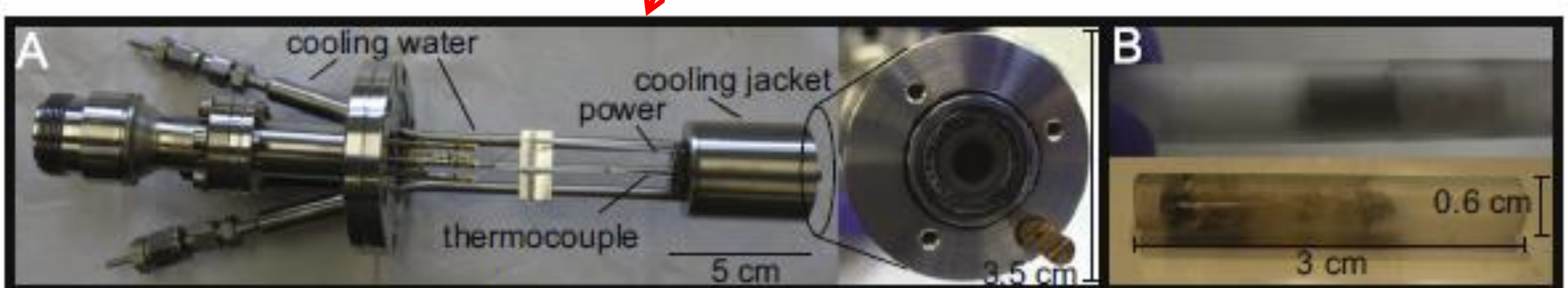
Red time markers indicate CO_2 ion position every 100 ns starting at t=0

Knudsen cell

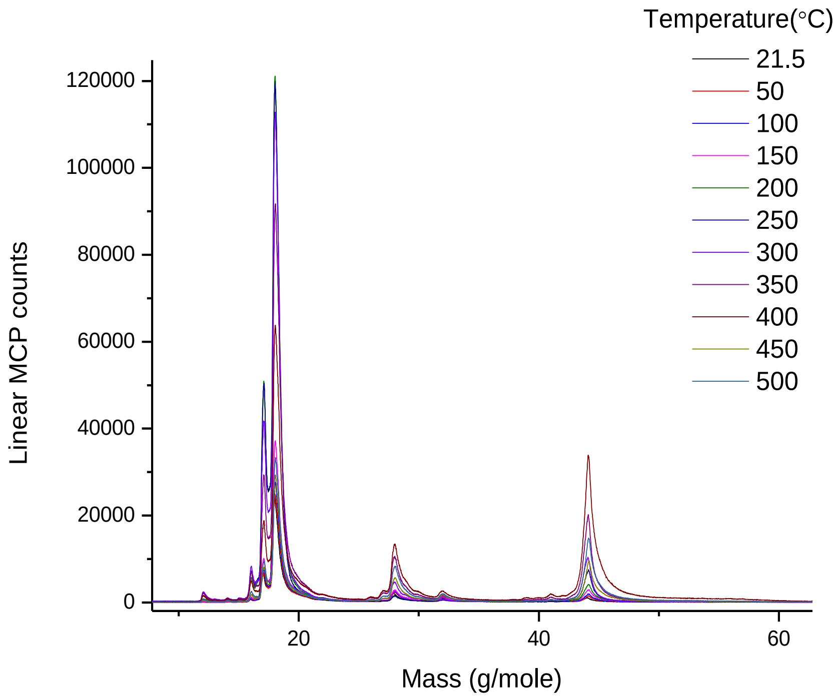


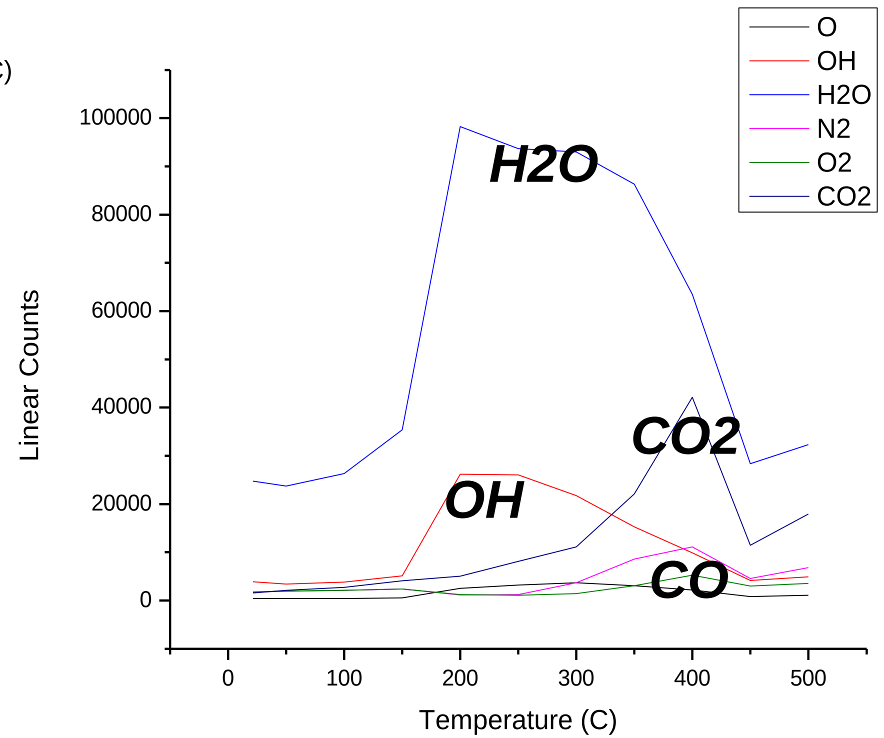
Knudsen cell testing:

- ***Used for preliminary testing***
- ***Heated up to 500 ℃***
- ***Sample packed into quartz tube***



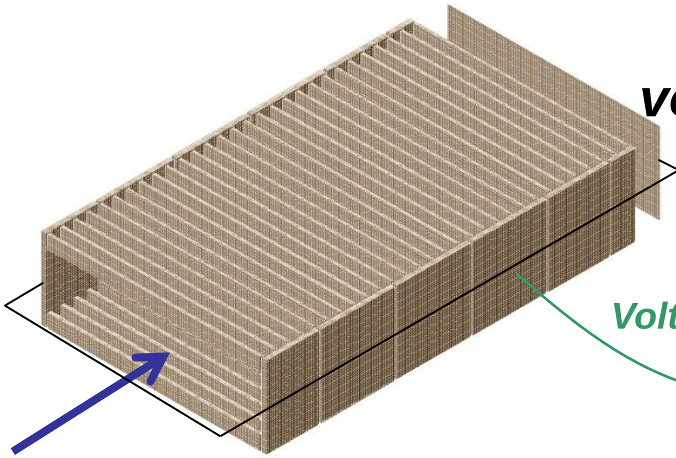
MARS simulant heated to 500 °C using a Knudsen cell





- ***Mass accuracy to within 0.2 Daltons via calibration to H_2O and CO_2***
- ***OH, H_2O evolved at 200 ℃ while N_2/CO, O_2, CO_2 evolved at 400 ℃***

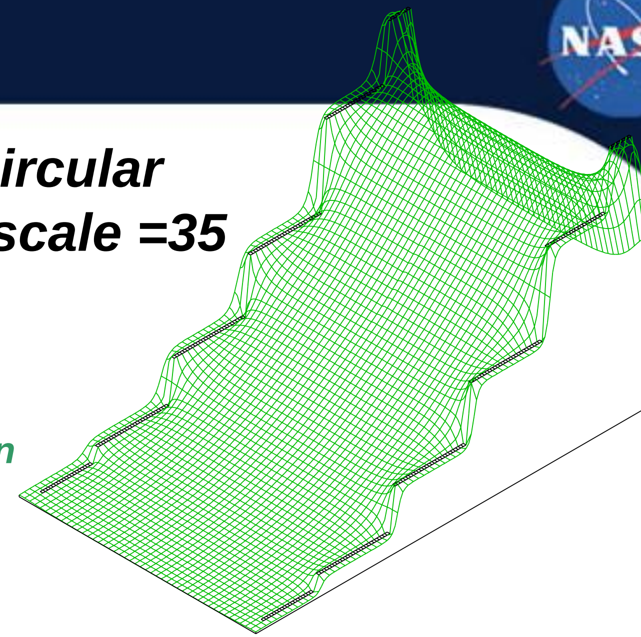
Reflected mode spectra



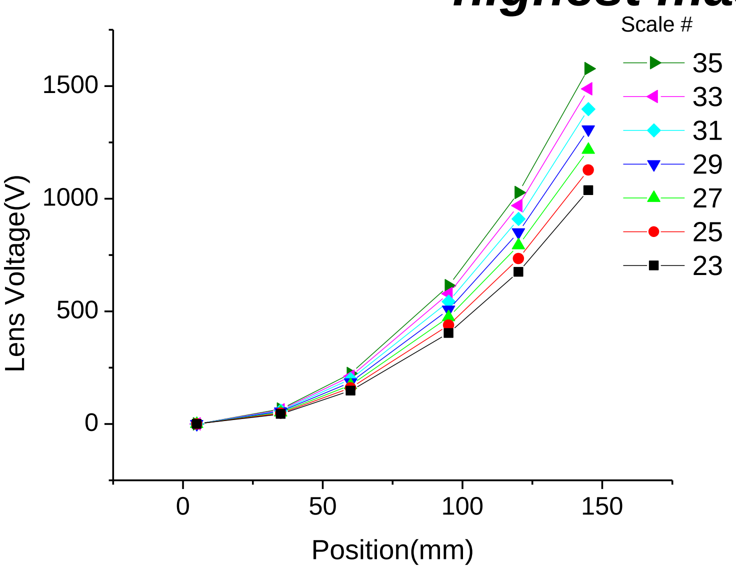
Ion flight direction

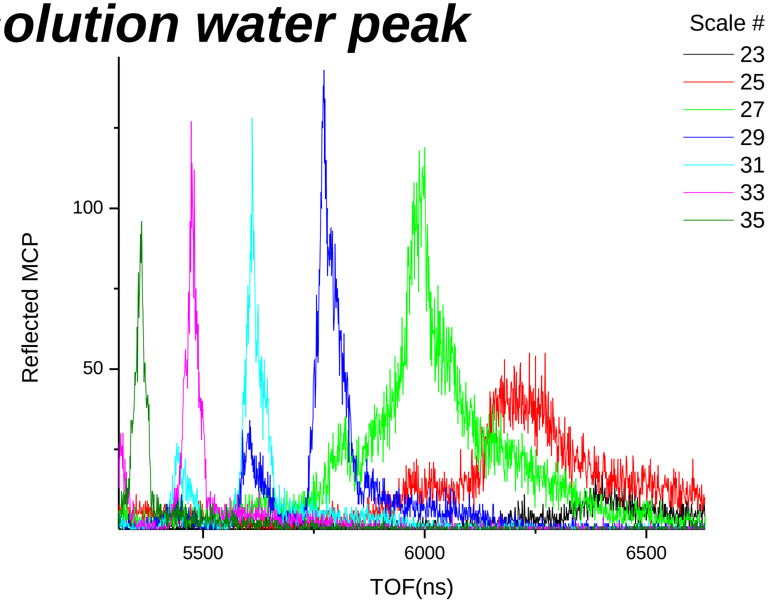
Non-linear circular voltage ramp, scale =35

Voltage variation within plane

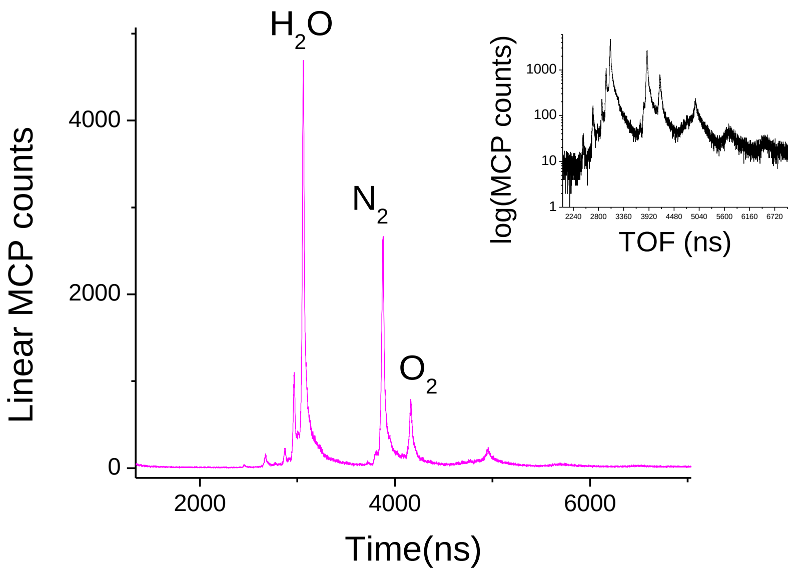


Higher scales -> Steeper voltage ramp -> highest mass resolution water peak

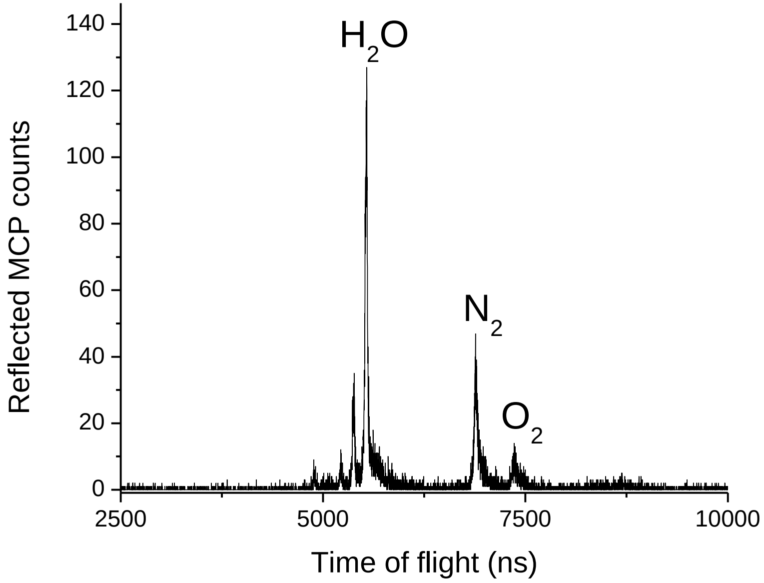




Comparison between linear and reflected mode



Mass resolution (H_2O)= 130
Sensitivity 3 counts per pulse
7% transmission (SIMION)



Mass resolution (H_2O)= 130
Sensitivity 0.1 counts per pulse
0.3% transmission (SIMION)

Opportunities for TOF performance improvement:

Change	PROS	CONS
•Optimize emitter/grid geometry (increased current) •Vertical pillar growth (increased current) •Wider MCP detector under ion source	Increase sensitivity	
•Increase apertures in ion source		Decrease resolution
•Modify geometry of ion source	Increase mass resolution	
•Time lag focusing through pulsed e-gun •Improve field definition in reflectron w/ plates and fewer floating electrodes		Decrease sensitivity
Use of other carbon based emitters	Improve emitter lifetime	
•Static →Dynamic •Refine initial kinetic energy distribution	Better simulation	
Replace Knudsen cell with VAPoR oven	Integration with VAPoR	

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