Isotope Ratio Analysis of Xenon with a Digital Ion Trap (DIT) and Improved Precision Data Acquisition System

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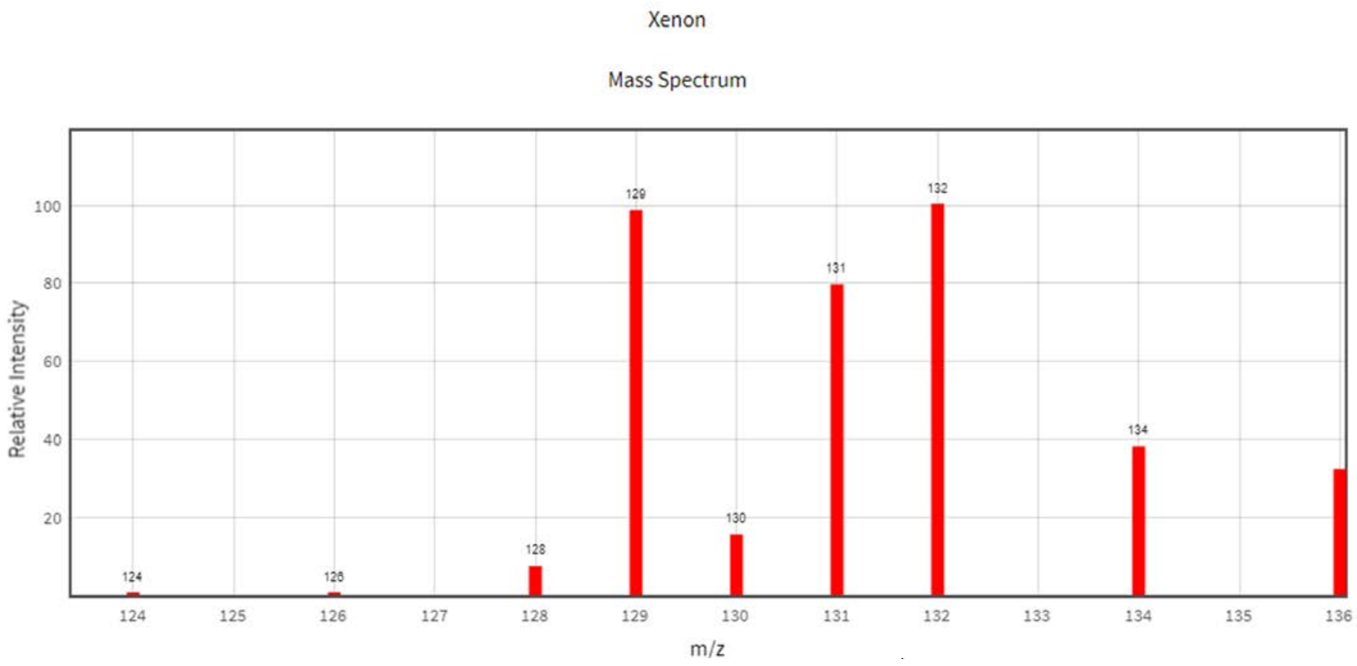
Why Study Xenon?

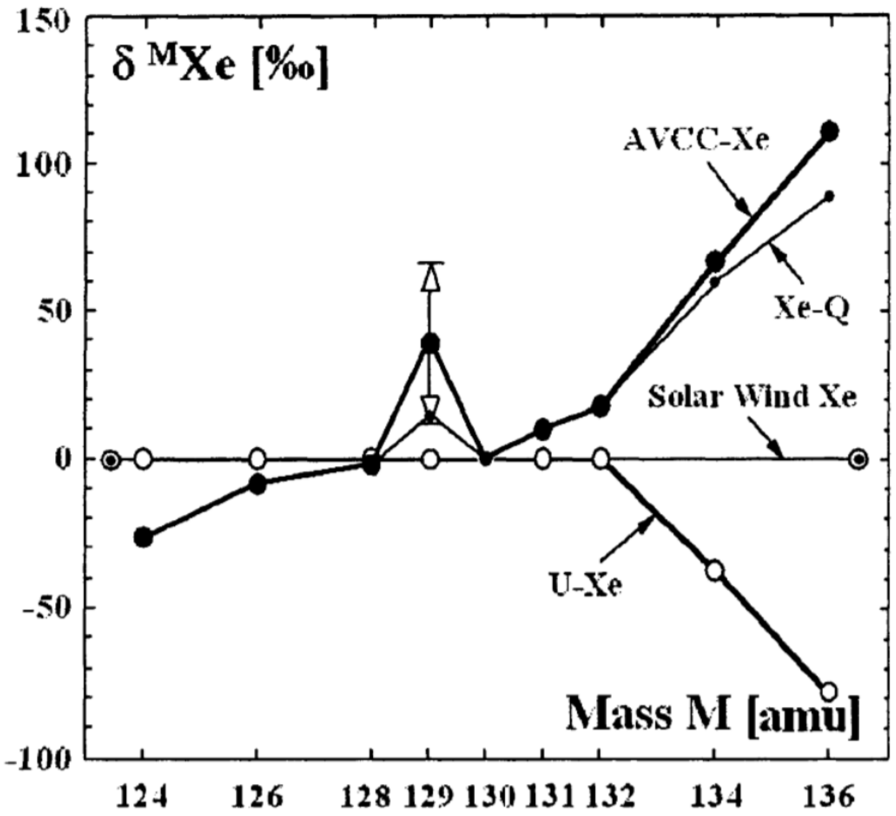
How did earth-like planets form?

How did the atmosphere of a planetary body evolve?

Where did an isotopic distribution of Xe originate?



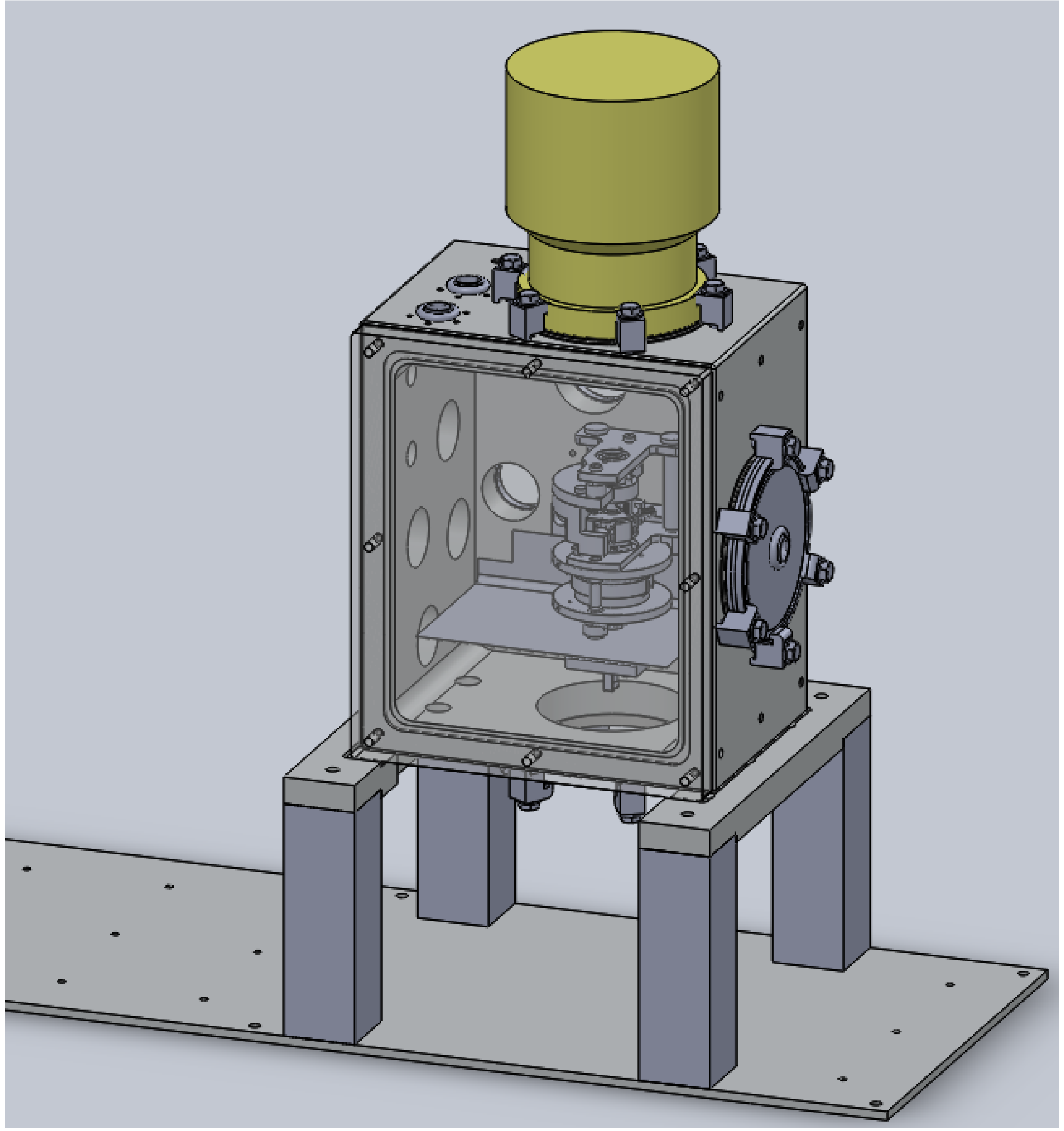
NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)



Pepin, R. O. On the Isotopic Composition of Primordial Xenon in Terrestrial Planet Atmospheres. In *From Dust to Terrestrial Planets*; Space Sciences Series of ISSI; Springer, Dordrecht, 2000; pp 371–395.

Why use an ion trap / digital ion trap?

- Advantages:
  - Higher pressure / lower power
  - Small physical size
  - Flexible operation
- Disadvantages:
  - Limited Trapping Capacity
    - Pusled buffer gas introduction (*Anal. Chem.*2018, 90, 17, 10600-10606)
  - Limited Mass Range
    - Theoretically unlimited mass range w/ DIT
  - Higher order secular frequencies
    - Yet to investigate



Isotope Ratio Measurement Improvements Utilizing an Improved Data Acquisition System

Why look at the data acquisition system?

Orbiters and rovers: Designed to perform IRMS

- Measurement precision is poor

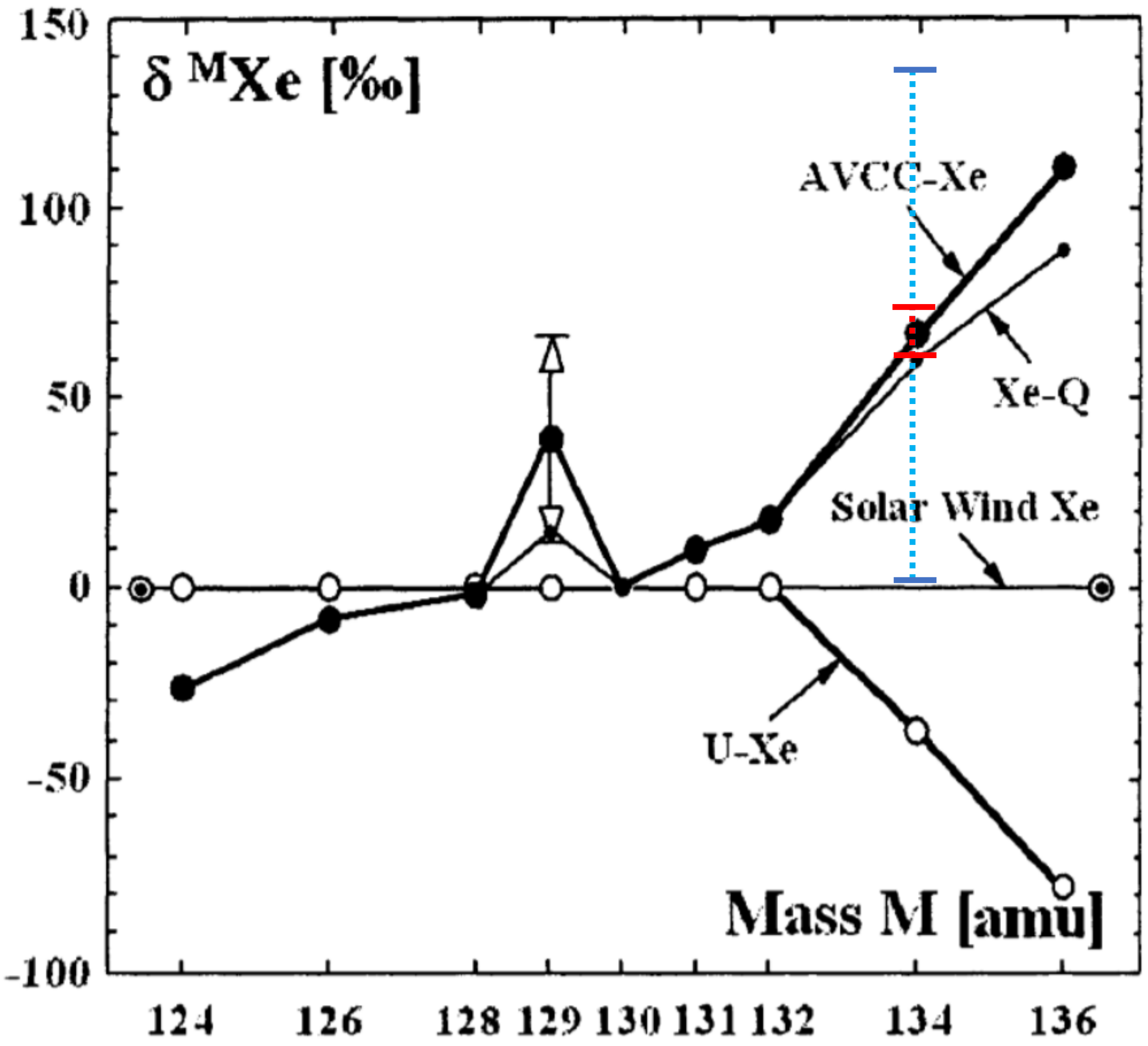
Curiosity MSL: Measurement errors from ±15 to ±150 $^0/_{00}$

Utilize Pepin's per mille deviation equation:

$$\delta^M Xe = 1000 \times [(R_M/R_{ref}) - 1]\ ^0/_{00}$$

- $R_M = {}^MXe/{}^{130}Xe$
- R_{ref} = Corresponding ratio from reference

m/z 134 and 136 show greatest variability



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Data Acquisition Systems

Data acquisition system

Two dimensions of precision

- X-axis resolution

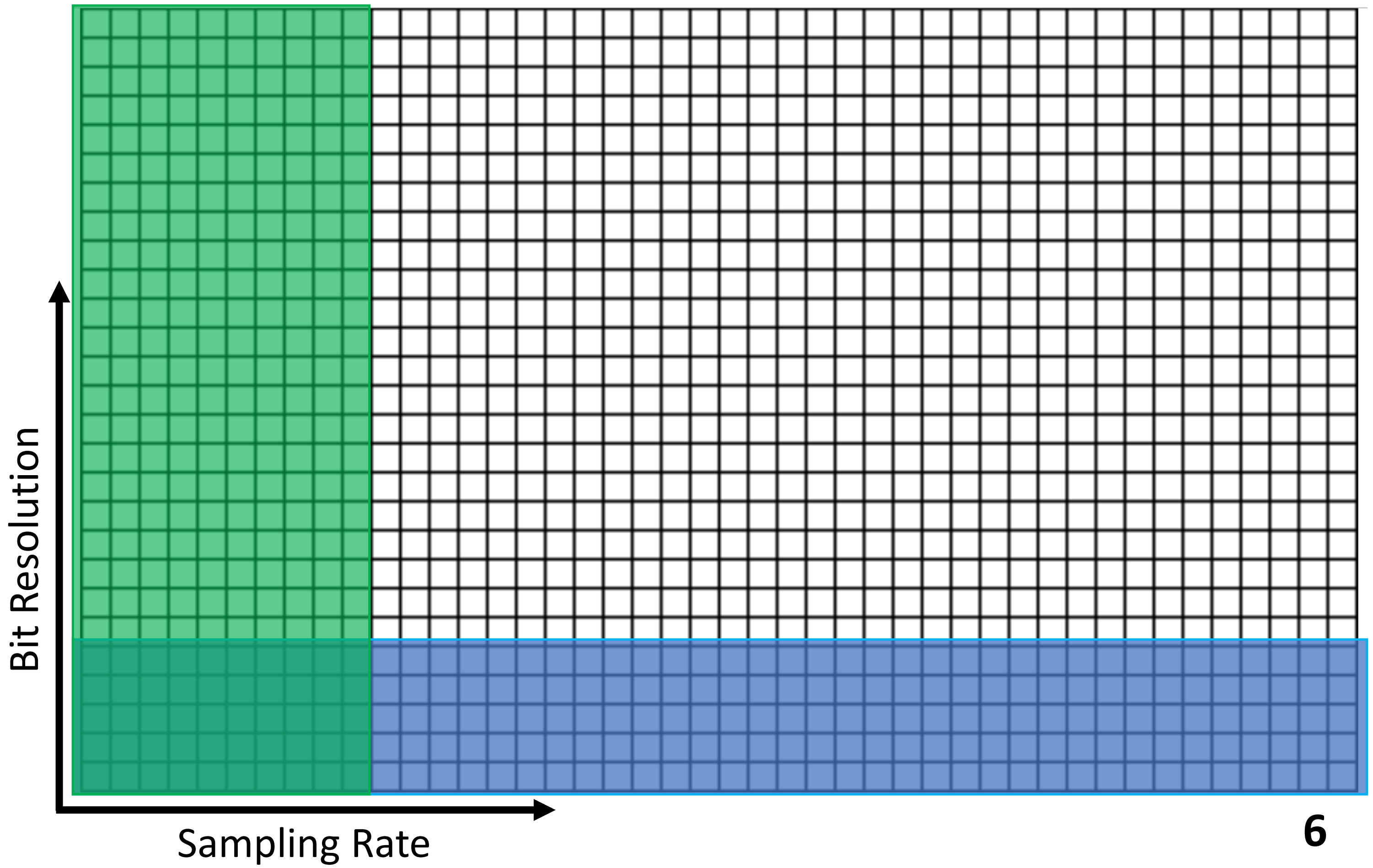
Sampling rate (Sa/s)

Rovers and probes: exceed requirements

- Y-axis resolution

Bits = 2^n

Rovers and probes: fixed at 8-bits



Data Acquisition Systems

LeCroy 7200 A:

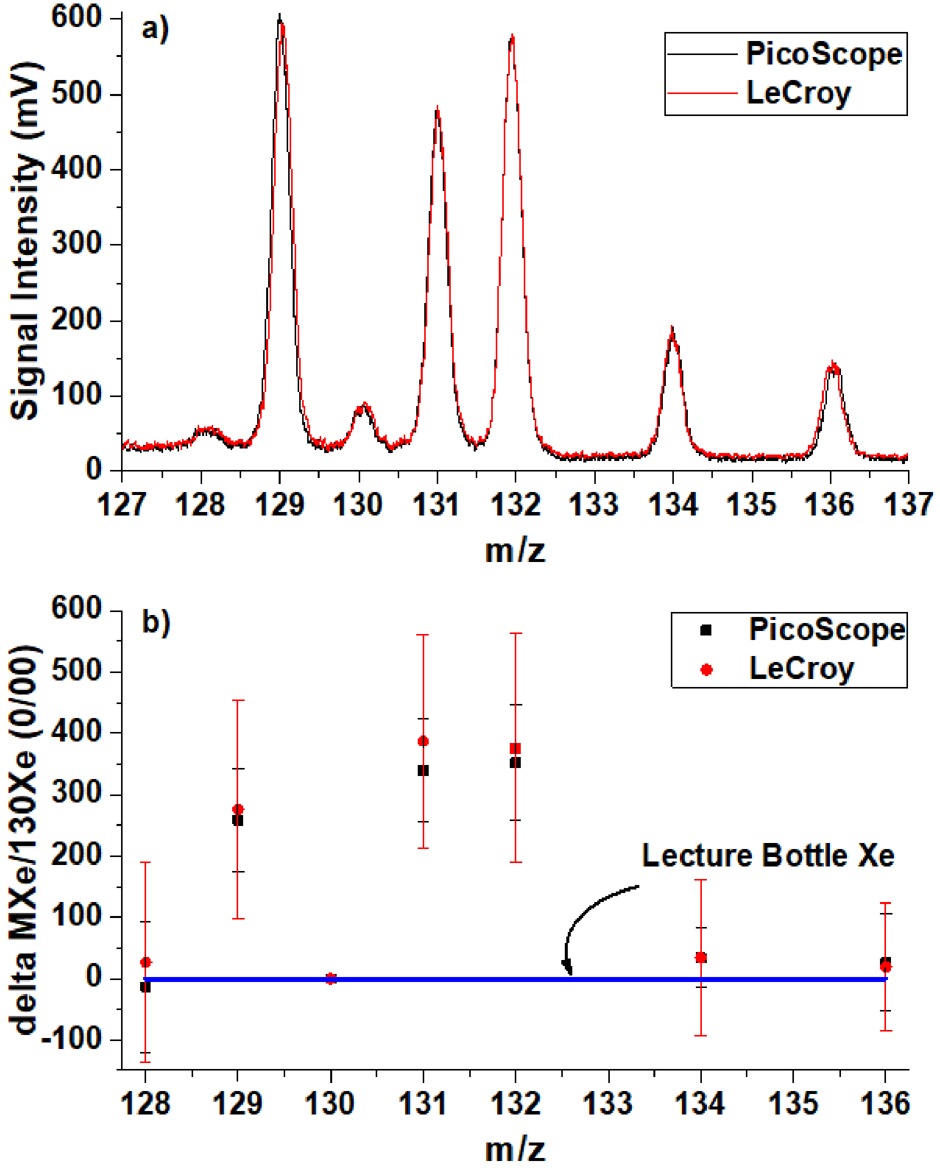
- X-Resolution: 50 kSa/s – 200 GSa/s
- Y-Resolution: 8-bit only
- No low pass filter (LPF)

Picoscope 5244D:

- X-Resolution: 5 kSa/s – 62.5 MSa/s
- Y-Resolution: 8, 12, 14, 15, & 16-bits
- Programmable LPF

LeCroy and PicoScope Comparison

- X-axis res: 10 MSa/s
- Y-axis res: 8-bits

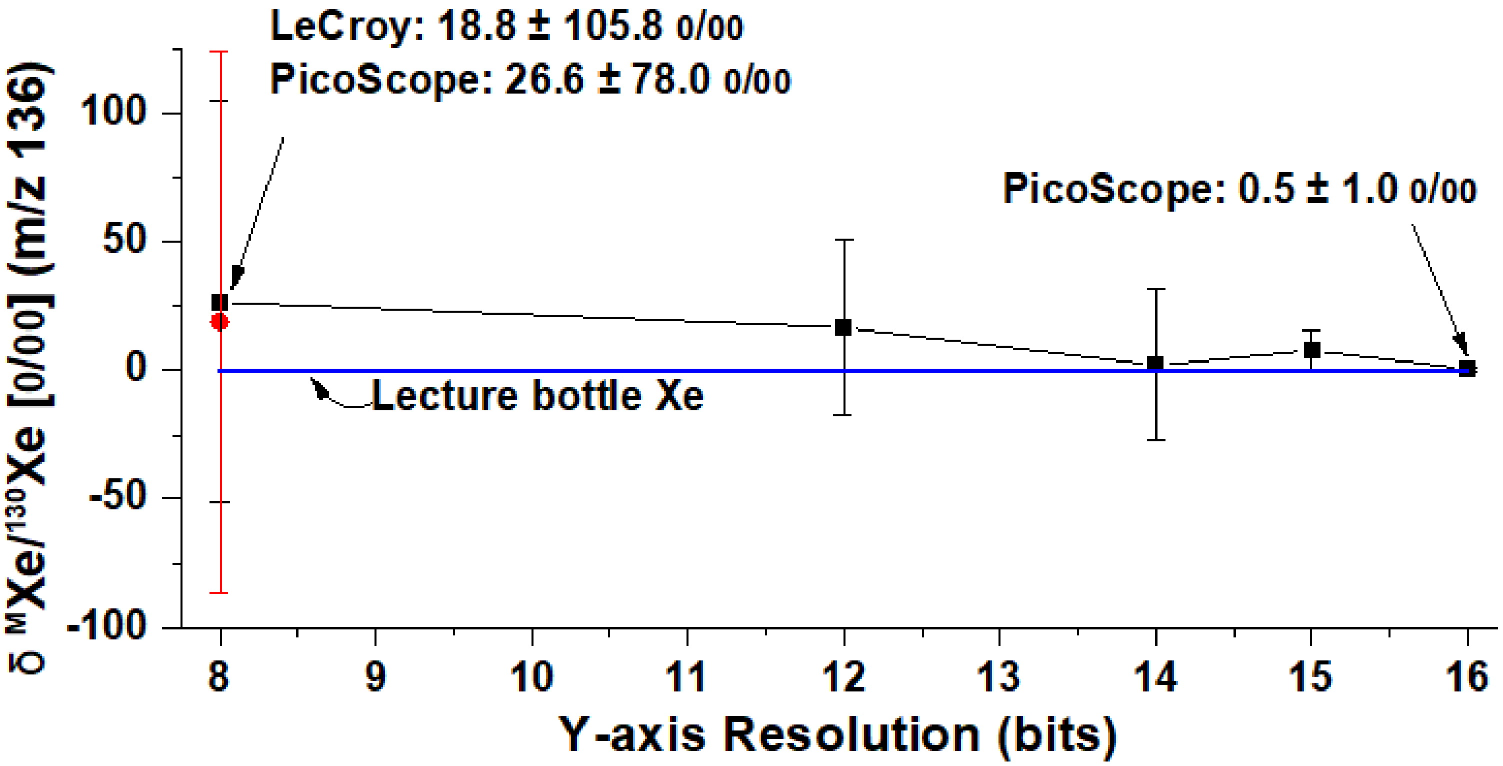


Y-axis Resolution Study

- X-axis res: 5 MSa/s
- Y-axis res:

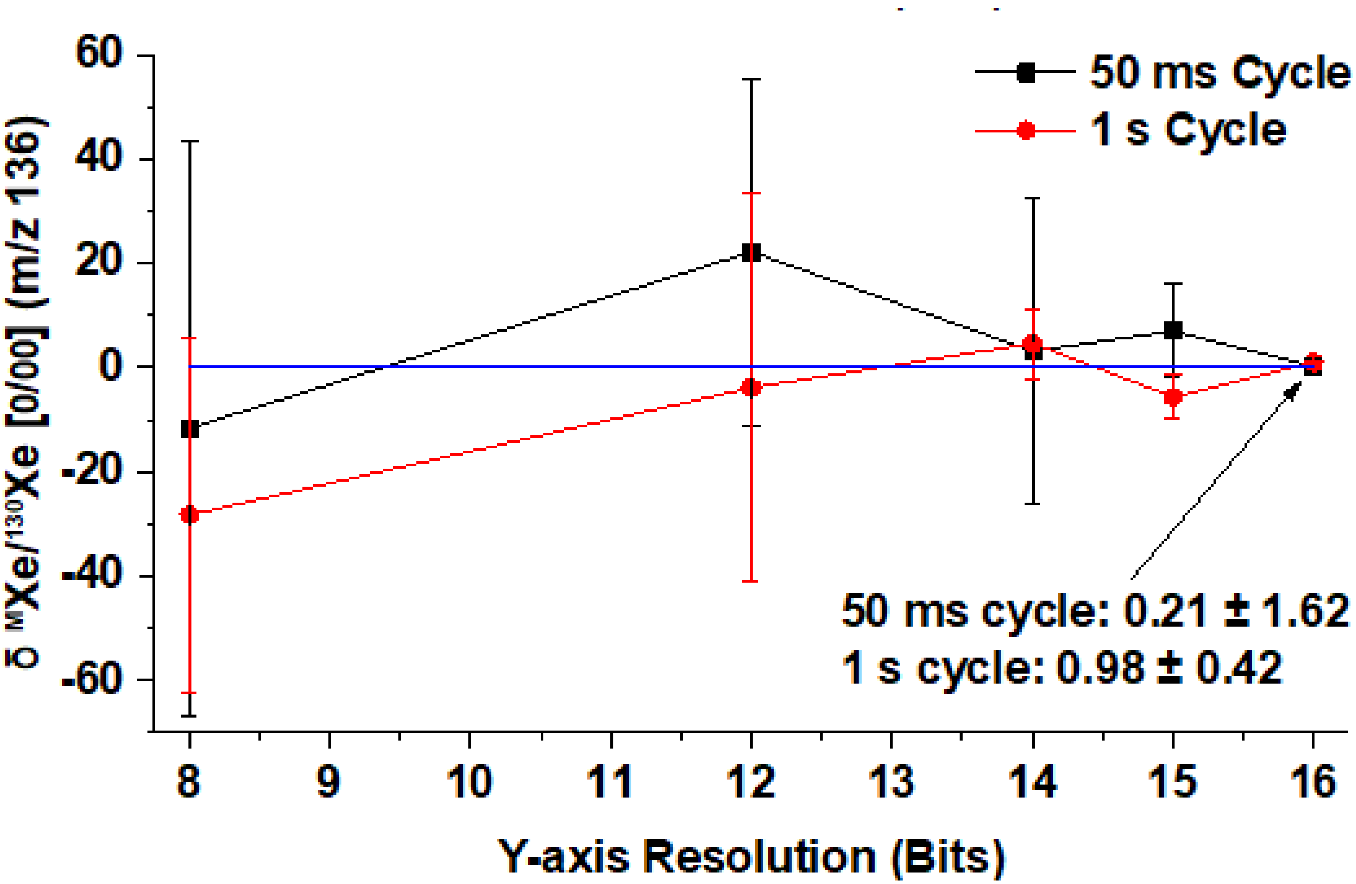
  8-16-bits PicoScope

  8-bits LeCroy



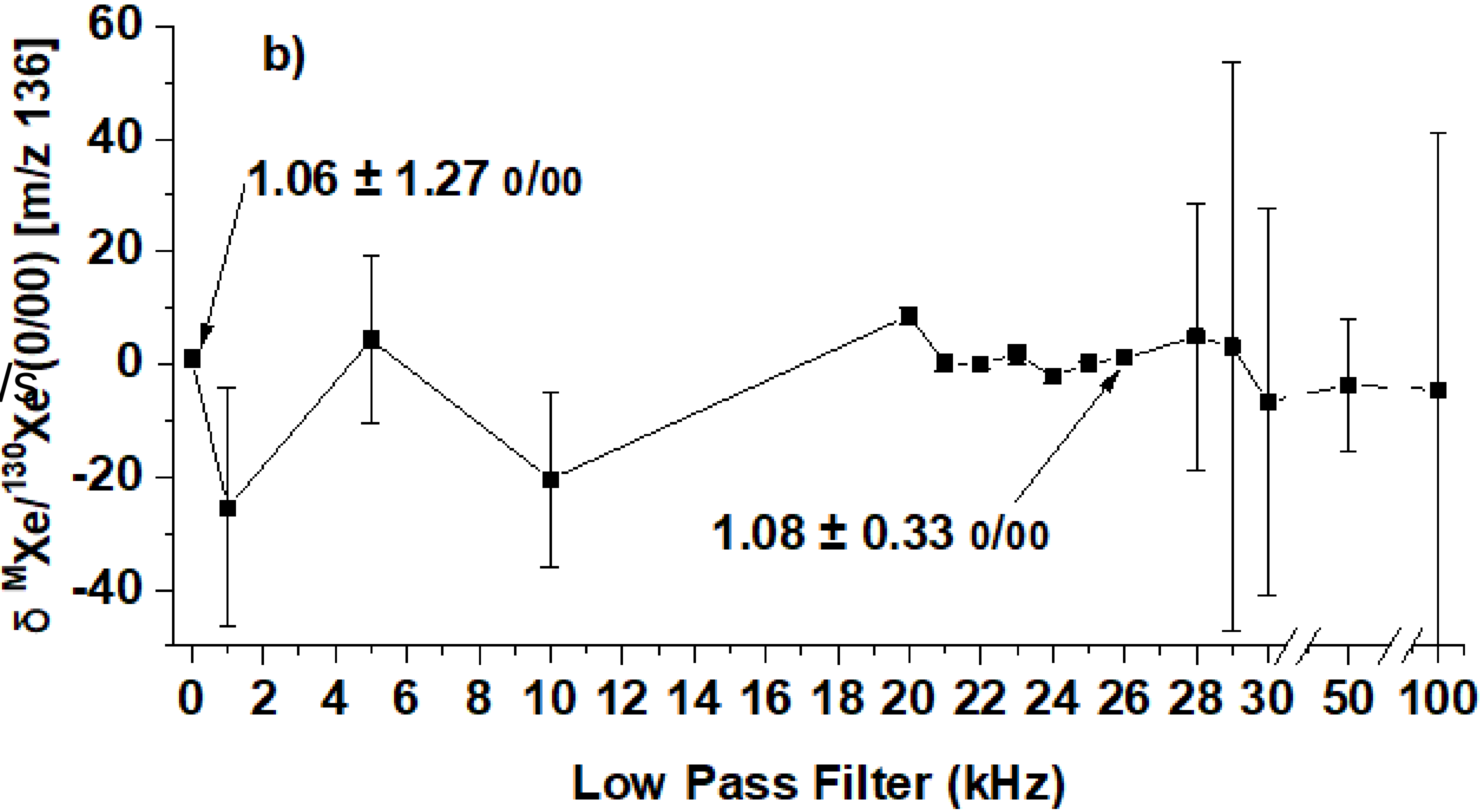
Data Acquisition Rate Comparison

- X-axis res: 5 MSa/s
- Y-axis res:
  8-16-bits PicoScope
- Data Acquisition rates:
  20 Spectra/s (black)
  1 Spectra/s (red)



Low Pass Filter Study

- X-axis res: 5 MSa/s
- Y-axis res: 16-bits PicoScope
- Data Acquisition rate: 1 Spectra/s
- Low Pass Filter: 1 – 100 kHz



Xenon Enrichment and Chemical Ionization Utilizing DIT

Selective Xenon Enrichment

Earth Xe conc. = 0.087 ppm Mars Xe conc. = 0.87 ppb

Enrichment Methods

Cryodistillation (Not SW&P friendly)

Enrichment (SW&P friendly)

- Zeolites and getter pumps

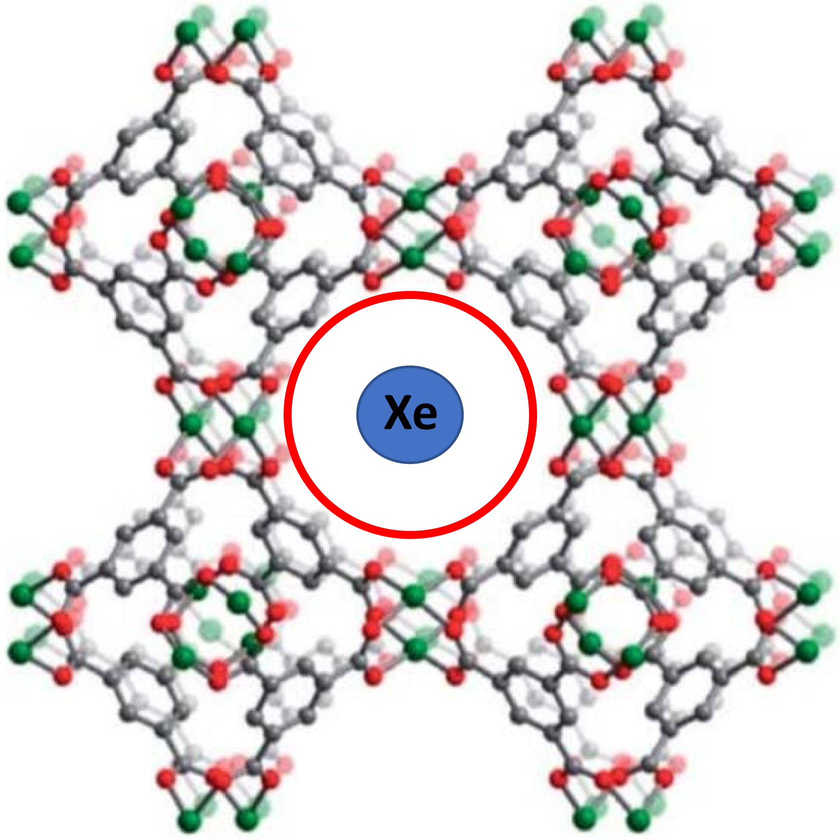
Selective Enrichment

- Metal Organic Frameworks (MOFs)

  Tunable structures

  Highly porous

MOF Material	Xe Uptake (mmol/g)	Xe/Kr Selectivity
HKUST-1	3.3	8.4
CROFOUR-1-Ni	1.8	22
SBMOF-1	1.4	16
Activated Charcoal	**4.2**	**8**



$Cu_3(btc)_2$
HKUST-1

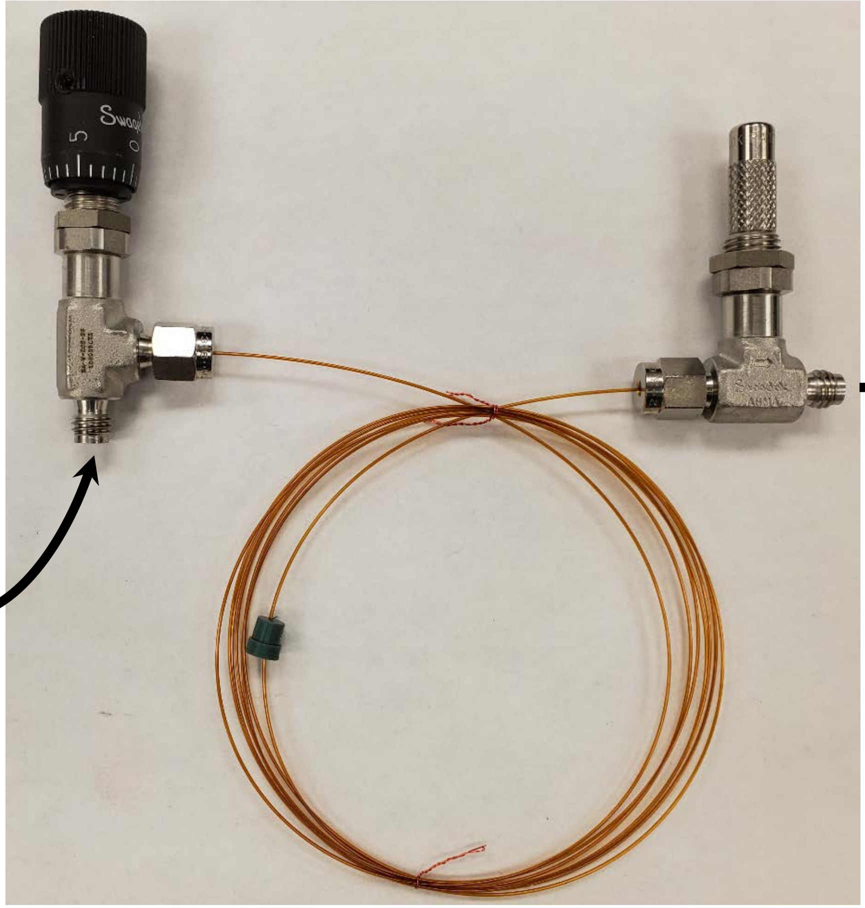
Mason, J. A. et al. Evaluating metal organic frameworks for natural gas storage. In *Chemical Science*, 2014; pp 32-51.

Selective Xenon Enrichment (Preliminary Setup)

Cryotrap Column:

- Restek PLOT column particle trap
- Length 2.5 m
- Column ID: 0.53 mm
- Coolant: Dry Ice (-78 °C)
- Bakeout: Hot water bath (~60 °C)

Conductance Issues



Selective Xenon Enrichment (Preliminary Results)

Cryotrap column timing:

- Loading time = 20 mins
- Dead volume evacuation = 60 mins
- Heated time = 20 mins

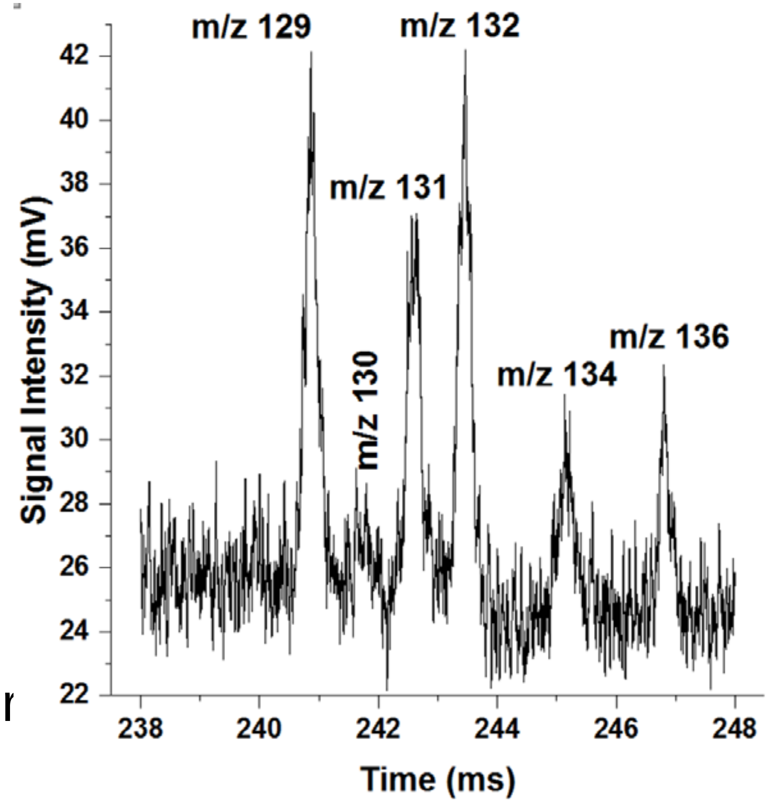
Results:

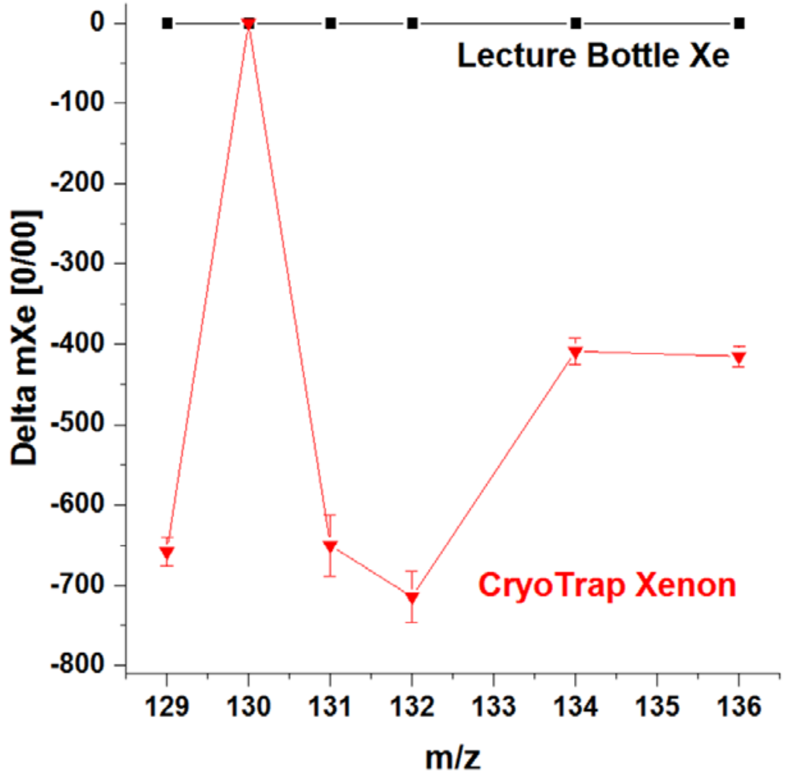
- Slow evacuation time

  Trapped xenon signal still observed after 1 hour

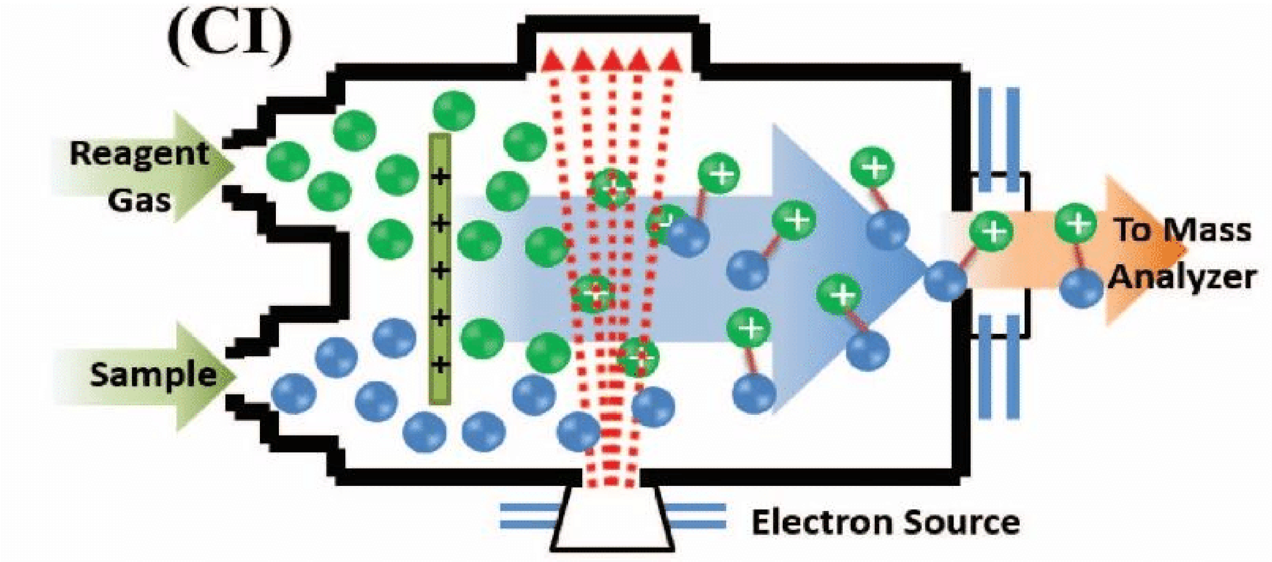
  Conductance to small to be efficient

Performed with Electron Impact Ionization





Chemical Ionization (CI)



https://www.researchgate.net/figure/Schematic-diagrams-showing-the-ionization-process-in-both-a-electron-ionization-b_fig15_312664731

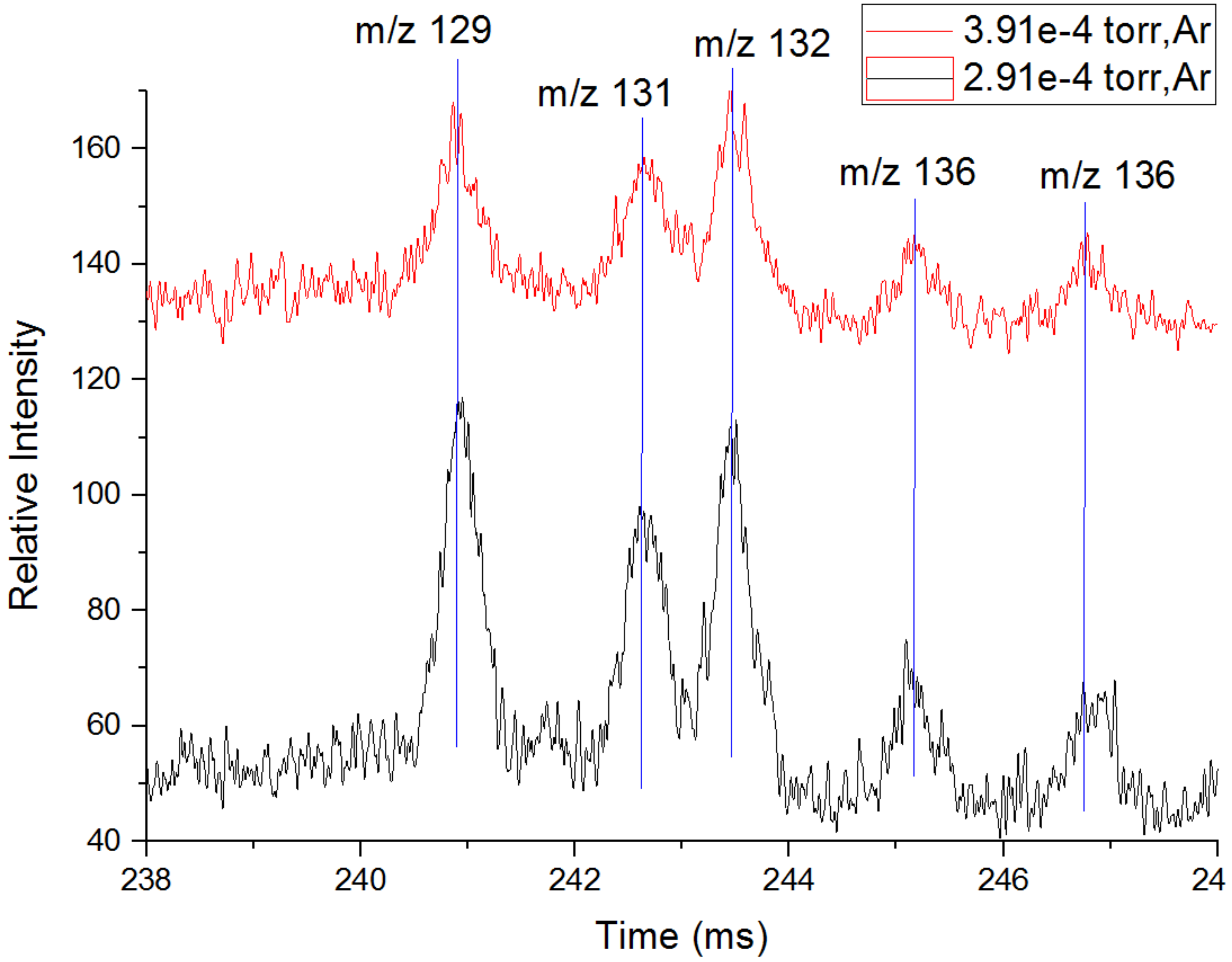
Chemical Ionization:

- $Ar + e^- \rightarrow Ar^{+\bullet} + 2e^-$

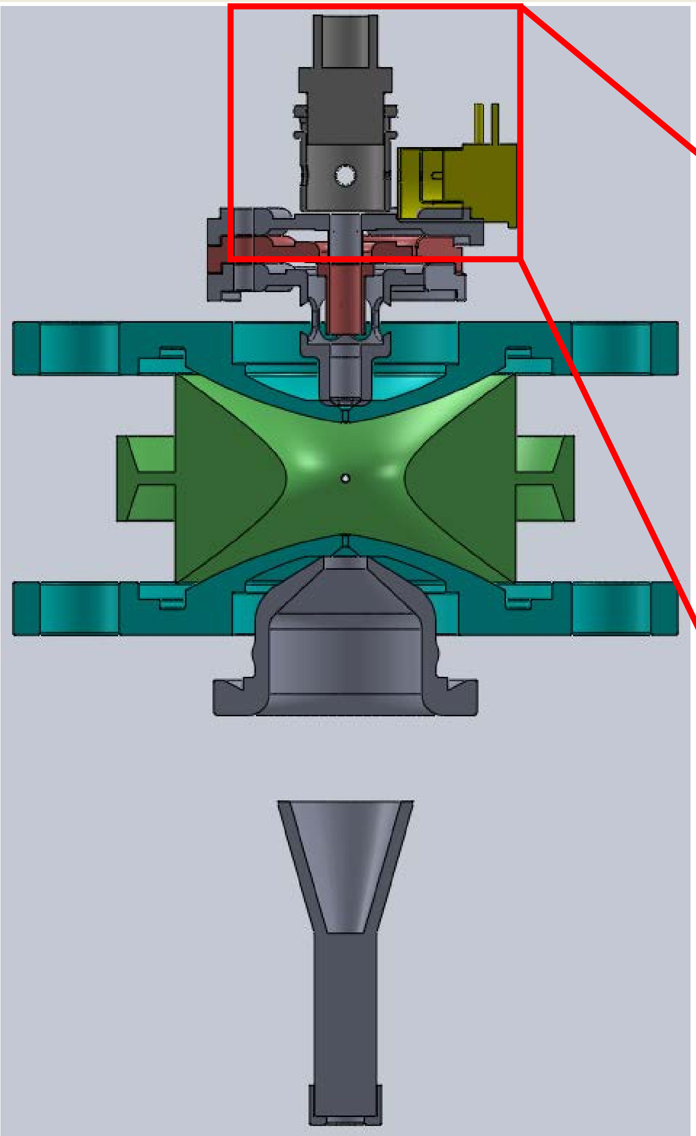
  $Ar^{+\bullet} + Xe \rightarrow Ar + Xe^{+\bullet}$
- Larger collision cross section
- Theoretically 100% ionization efficiency

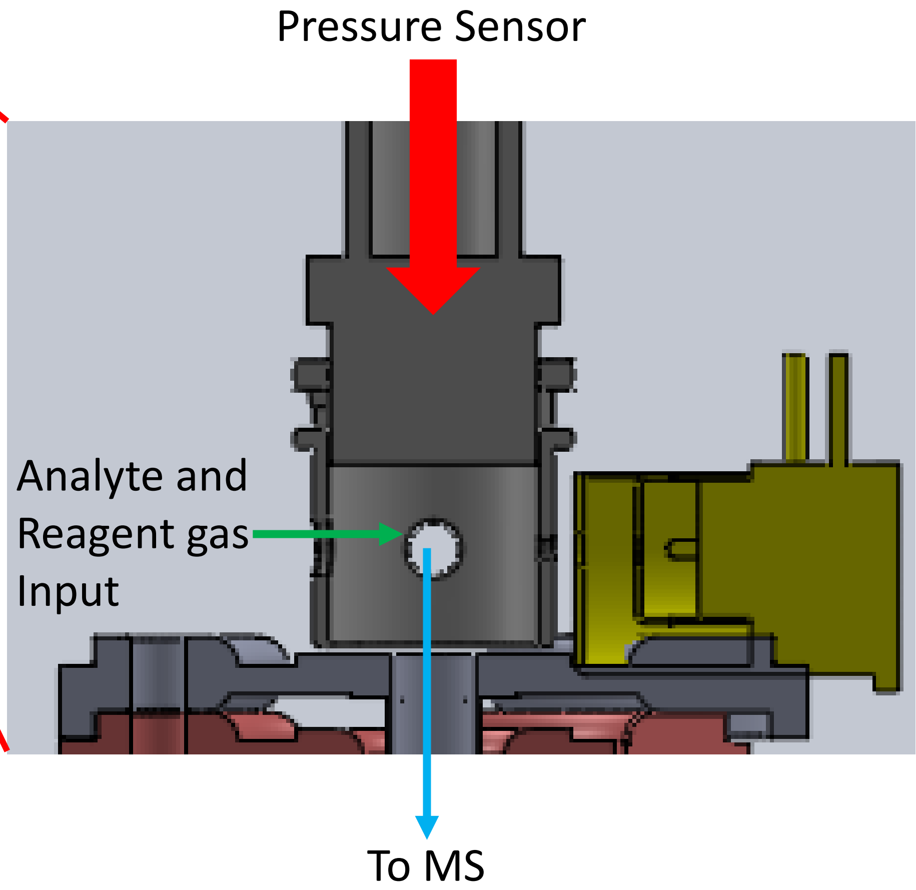
  1000x concentration of reagent species (~1 mtorr) to analyte (~1µtorr)

Argon CI

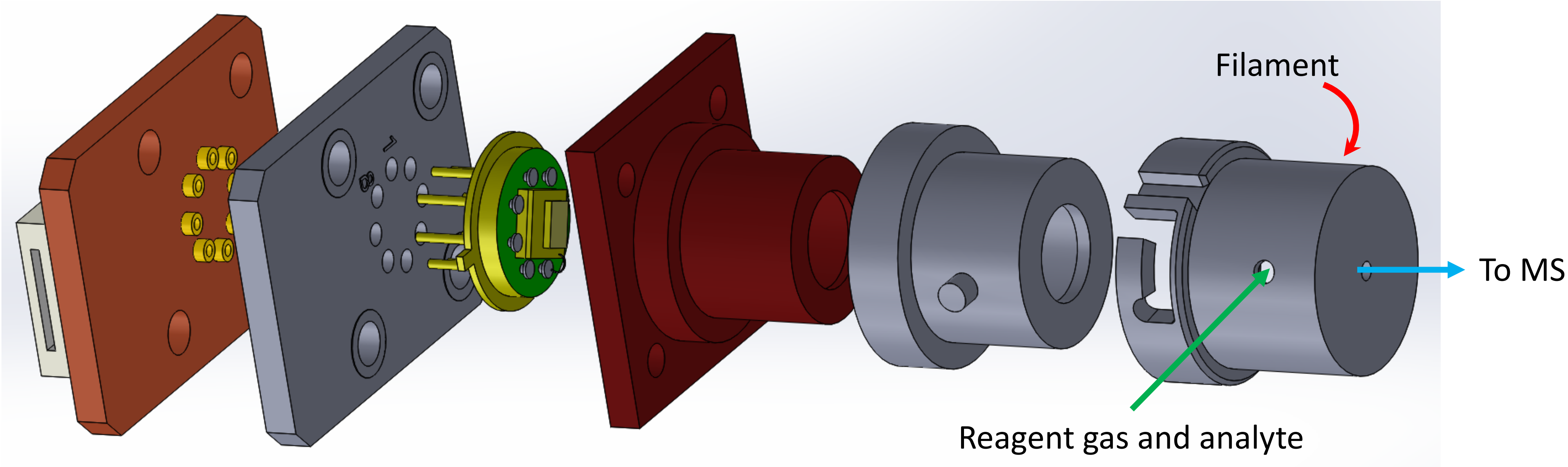

m/z 129
m/z 131
m/z 132
m/z 136
m/z 136
3.91e-4 torr,Ar
2.91e-4 torr,Ar
Relative Intensity
160
140
120
100
80
60
40
238
240
242
244
246
24
Time (ms)

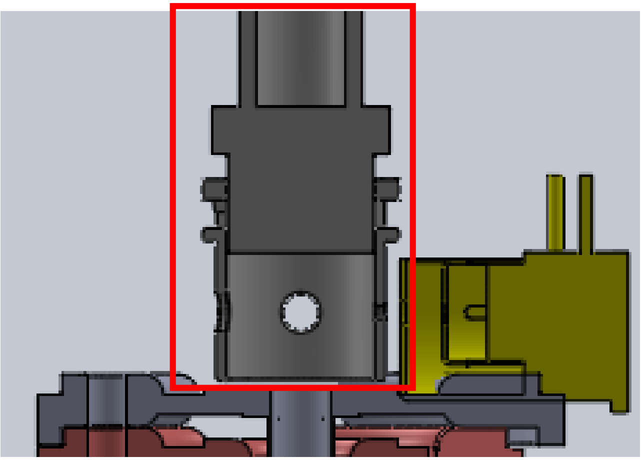
Chemical Ionization Pressure Measurements





Ion Volume Pressure Sensor Design





Summary

Isotope Ratio Measurement Precision and Accuracy

- Y-axis (bits) resolution: 3 orders of magnitude improvement in both precision and accuracy

    LeCroy @ 5 MSa/s and 8-bits: 18.8 ± 105.8 $^{0}/_{00}$

    PicoScope @ 5 MSa/s and 16-bits: 0.5 ± 1.0 $^{0}/_{00}$

- Data acquisition rate increase: ↓ precision by a factor of 2
- Low pass filter: ↑ precision by a factor of 10

Xenon Enrichment and Chemical Ionization

- Incorporate pressure sensor in ion volume
- Optimize chemical ionization setup
- Obtain enrichment materials and test

Acknowledgments

Advisor: Dr. Theresa Evans-Nguyen

Post Doc

Graduate Students

Undergraduates

Thank You

Questions?