Enrichment of Xenon Gas for Targeted Isotope Ratio Mass Spectrometry Utilizing a Digital Ion Trap

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Overview

Purpose: Study enrichment effects of xenon through the use of a cryotrapping column into a digital ion trap mass spectrometer operating in resonance ejection mode while also utilizing an improved data acquisition system.

Methods: Interfaced a custom built ion trap mass spectrometer with a PLOT column particle trap (Restek). Cryotrapping is performed by cooling the column using dry ice while xenon gas is introduced from one end of the column and evacuated to the chamber through the other end of the column. Enrichment occurred over 25 mins followed by purging of residual xenon left in the dead volume by way of vacuum drag. Upon achieving high vacuum conditions and no longer observing residual xenon, the column was isolated in line by way of shutoff valves and heated using a hot water bath followed by introduction into the mass spectrometer (MS). Electron impact ionization is performed external to the trap and ions are gated into the trap through an einzel lens. The trap is operated by frequency scanning the supplemental and holding the fundamental frequency constant utilizing function generators in a resonance ejection mode. Operational conditions were varied to measure the precision and accuracy improvements of the data acquisition system (DAQ) and the trapping ability of the column towards xenon.

Results: Incorporated a variable y-axis resolution data acquisition system and studied measurement improvements. Design, fabrication, and interfacing of cryotrap to the quadrupole ion trap.

Introduction

Xenon plays an important role when informing planetary atmospheric evolution models. During hydrodynamic escape of primordial planetary atmospheres, noble gases are fractionated resulting in heavier isotopes remaining in the atmosphere while lighter isotopes are ejected into space[1]. These models can then be used to determine probable sources of atmospheric xenon such as from the fission product of ^{244}Pu. Each source of xenon generates isotope ratios which normally present smaller isotopes with relatively the same abundance while the larger isotopes; specifically m/z 134 and 136; show the greatest variability. Instrument precision compromises experimental accuracy which can result in the misidentification of the source of xenon. Through the use of a cryotrapping column and an improved data acquisition system, enrichment of sample can be performed to improve measurement precision in in situ space applications.

Herein, the quadrupole ion trap MS is operated in resonance ejection mode using digital frequency scanning[2]. Interfacing a variable y-axis resolution DAQ and cryotrapping column to the custom built digital ion trap MS is also studied.

Methods – Instrument Setup

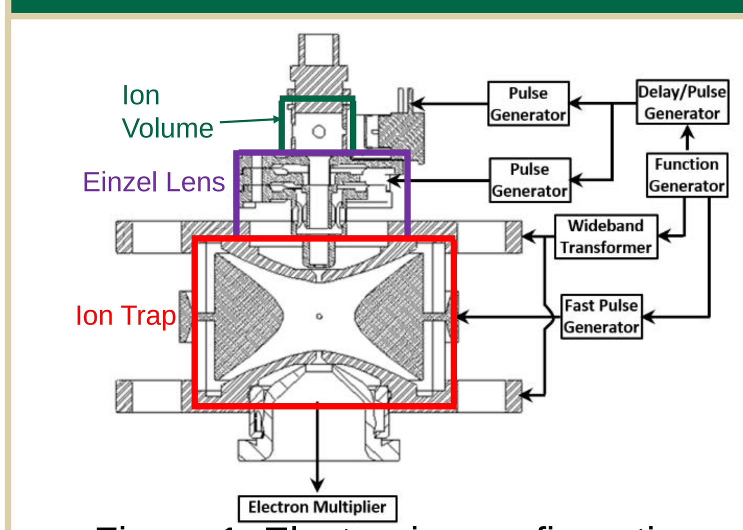

Figure 1: Electronics configuration for ion trap

- Ion trap electronics setup for resonance ejection mode shown in figure 1.
- Instrumental setup of digital ion trap (DIT) can be seen in figure 2. DIT electrodes were re-purposed from a Finnigan GCQ Plus.

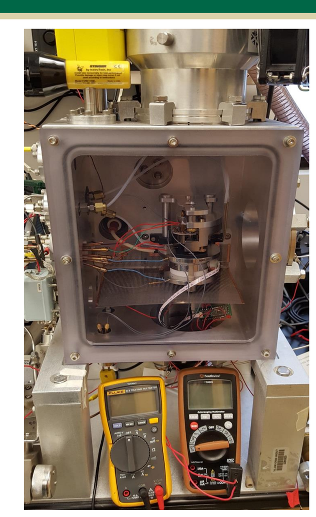

Figure 2: Quadrupole Ion Trap Setup

Constant Operating Parameters			
Supp. Sweep: 1 MHz – 15 kHz	Supp V: 2 V_{p-p}	Detector: 2000 V	Cycle Rate: 1 Hz
Fund. Sweep: 600 – 525 kHz	Fund V: 600 V_{p-p}	P_{Xe}: ~1 x 10^{-7} $torr_{Xe}$	P_{He}: ~7 x 10^{-4} $torr_{He}$

Methods – Oscilloscopes (DAQ) & Cryotrap Column

Figure 3: LeCroy 7200A

Figure 4: Picoscope 5244D

LeCroy 7200 A:
- X-Resolution: 50 kSa/s – 50 MSa/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

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)

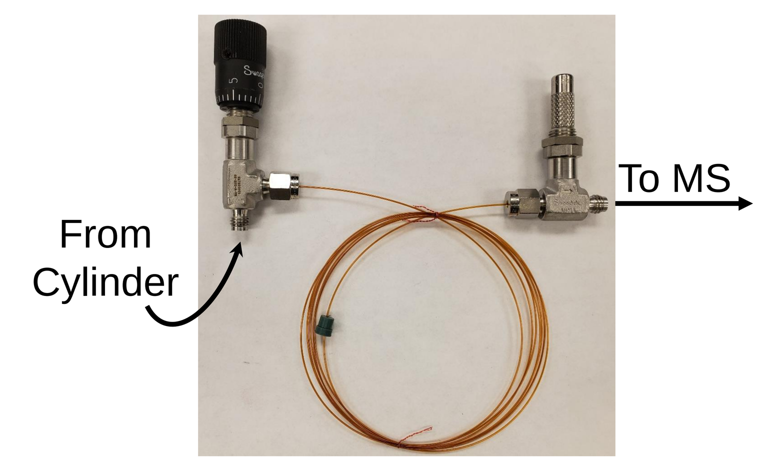

Figure 5: Trapping column coupled to ion trap

Methods – Xenon Standardization

- A lecture bottle of xenon was calibrated using an Agilent 7200 Q-TOF as seen in Figure 6.
- Calibrated abundances were then used as our references values for testing on our ion trap configuration utilizing the per mil difference equation provided by Pepin *et al*[1]:
  - $\delta^{M}Xe = 1000*[(R_M/R_{ref})-1]^0/_{00}$
    - R_M is $^{M}Xe/^{132}Xe$ for expt data.
    - R_{ref} is $^{M}Xe/^{132}Xe$ for ref data.

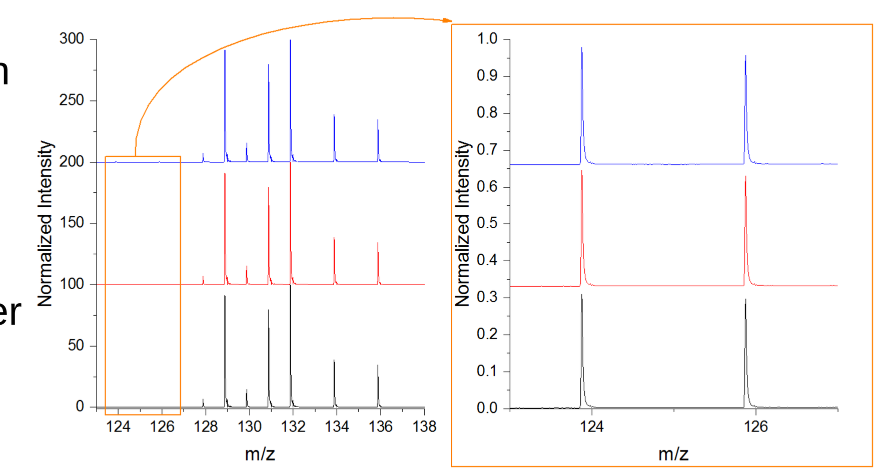

Figure 6: Xenon spectra obtained on an Agilent 7200 Q-TOF at USF-CPAS.

Results – DAQ Modifications (X-Resolution)

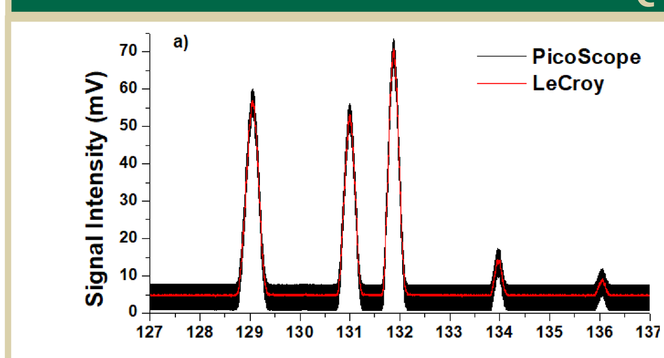

Figure 7: Xenon spectra at fixed x-axis (5 MSa/s) and y-axis (8-bit) resolutions

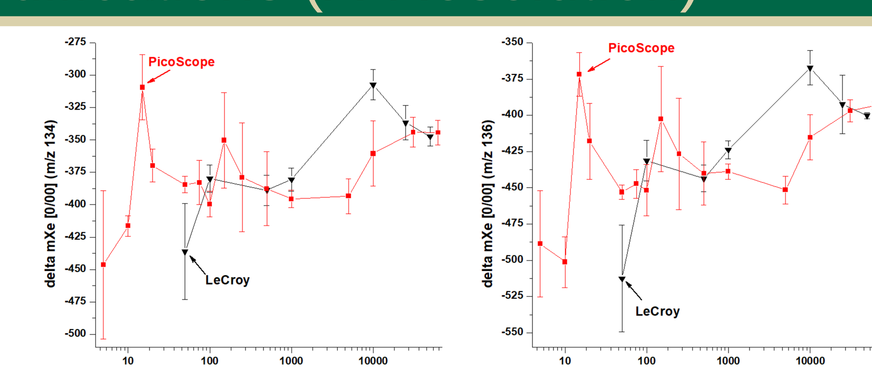

Figure 8: Sampling rate (x-axis) study on xenon isotopes m/z 134 and 136 for each DAQ system

- Initial testing found that the variable y-axis resolution DAQ measured significantly higher under the same operational conditions as seen in Figure 7.
- Triplicate error was reduced at sampling rates above 1 MSa/s but no other observable trend could be inferred as seen in Figure 8.

Results – DAQ Modifications (Y-Resolution and LPF)

Low Pass Filter:
- Introducing a LPF improves measurement precision for m/z 134 and 136 by a factor of ~8 and ~7, respectively.

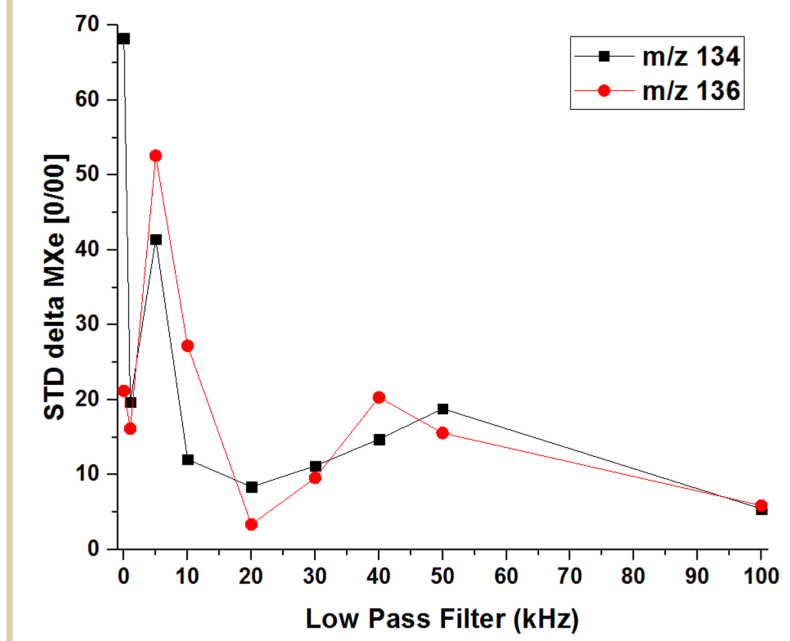

Figure 10: Standard deviation with respect to m/z 134 and 136 at varied LPF settings for m/z 134 and 136

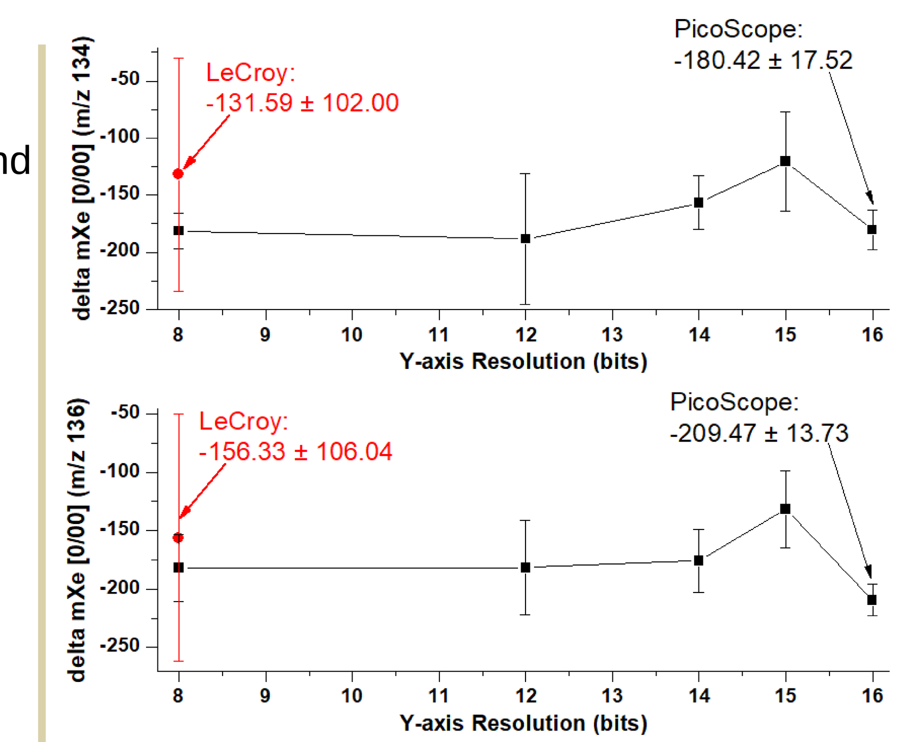

Figure 9: Per mil difference at varied bit resolutions for m/z 134 and 136

Y-axis Resolution:
- As can be seen in Figure 9, increasing the bit value improves measurement precision by approx. an order of magnitude for both m/z 134 and 136.

Results – Cryotrap Column

- Cryotrap column timing:
  - Loading time = 20 mins
  - Dead volume evacuation = 60 mins
  - Heated time = 20 mins
- Conductance limitations resulted in a slow bleed out of trapped xenon upon introduction into the trap at heating as seen in figure 11.
  - Occurred for over 1.5 hours before trial was discontinued.

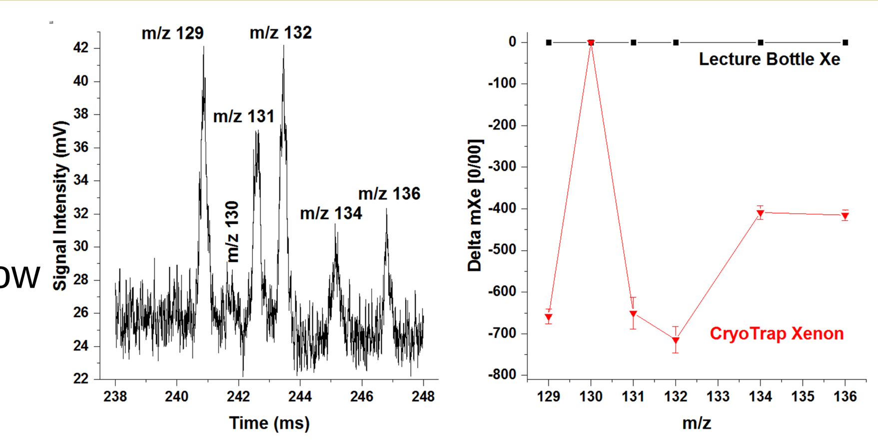

Figure 11: Cryotrap column xenon spectra averaged over 250 scans and 3 trials.

Conclusions & Future Work

While x-axis (sampling rate) resolution changes were found to not be beneficial to measurement precision; it was observed that both y-axis (bits) resolution and the introduction of low pass signal filtering improved measurement precision by factors of 10 and ~7, respectively.
Implementing a cryotrap column was found to enable xenon trapping but requires further development to allow faster release into the ion trap. Faster release times will enable the study of trapping capabilities of different trapping materials such as metal organic frameworks (MOFs).
Future Work:
- Implement pulsed buffer gas introduction utilizing higher precision DAQ.
- Investigate different cryotrap geometries and trapping materials.

Acknowledgements & References

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(1) Pepin, R. O. On the Origin and Early Evolution of Terrestrial Planet Atmospheres and Meteoritic Volatiles. *Icarus* **1991**, *92* (1), 2–79. https://doi.org/10.1016/0019-1035(91)90036-S.

(2) Vazquez, T.; Evans-Nguyen, T. G.; Shelley, J. T. Buffer Gas Concentration Effects on Collisional Cooling in a Digital Ion Trap. In *Proceedings of the 65th ASMS Conference on Mass Spectrometry and Allied Topics*; San Antonio, TX, 2017.