

CHARACTERIZATION OF A LINEAR ION TRAP MASS SPECTROMETER FOR NOBLE GAS MEASUREMENTS OF TITAN'S ATMOSPHERE. J. D. Graham¹; A. Grubisic¹; R. M. Danell^{1,2}; D. A. Kaplan^{1,3}; F. H.W. van Amerom^{1,4}; M. E. Castillo^{1,5}; W. B. Brinckerhoff¹; M. G. Trainer¹, ¹NASA Goddard Space Flight Center, Greenbelt, MD, ²Danell Consulting, Inc., Winterville, NC, ³KapScience, LLC, Tewksbury, MA, ⁴Mini-Mass Consulting, Inc., Hyattsville, MD, ⁵ATA Aerospace, Greenbelt, MD.

Introduction: Titan has a dense atmosphere primarily composed of nitrogen (95%), with a small amount of methane (~5%), and trace amounts of noble gases, larger hydrocarbons, nitriles, amines, and oxides. Open questions persist regarding the origin of Titan's atmosphere and the source of its methane. [1,2] Noble gas (NG) abundances can distinguish a chondritic or solar nebular origin for the atmosphere and inform methane outgassing properties. The only primordial NG ratio measured by Cassini/Huygens, a tentative $^{22}\text{Ne}/^{36}\text{Ar}$ value, was challenged by ^{22}Ne signals near the limit of detection, after correcting for the isobaric interference between $^{22}\text{Ne}^+$ and CO_2^{++} . [1] A $^{20}\text{Ne}/^{22}\text{Ne}$ measurement was precluded on Huygens due to large isobaric interferences from (radiogenic) $^{40}\text{Ar}^{++}$ while both Kr and Xe were below detection limits.

Dragonfly is a rotorcraft lander mission that will investigate the surface and atmosphere of Titan. The Dragonfly Mass Spectrometer (DraMS) will perform chemical analyses of the Titan surface and atmosphere at multiple landing sites. The primary science goals for DraMS center around analysis of the rich organic chemistry products found on and near the surface of Titan. [3] The DraMS mass analyzer is a linear ion trap (LIT) based on the Mars Organic Molecule Analyzer (MOMA) design. [4] While the MOMA LIT-based architecture is particularly suitable for organic analysis, its capability for NG analysis and isotope abundance determination has been less studied. This work is motivated to characterize and refine an operational approach for LIT-based measurements of Titan's atmospheric NG constituents.

Prototype Instrument: NG measurements were performed on a breadboard LIT instrument with dimensions and operational characteristics matching the future DraMS flight unit. The gas composition in the LIT was prepared to match the expected output of a precursor enrichment cell. Vacuum conditions of a static (fixed NG sample) measurement were replicated with active getter pumping.

Operational Characteristics Relevant to Noble Gas Measurements:

Ion-buffer gas charge transfer reactions. Helium buffer gas (3×10^{-3} Torr) is used for collisional cooling and trapping of ions within the LIT. Charge transfer from an ion to the neutral helium buffer gas is possible for any species with an ionization energy greater than that of helium. Such a transfer suppresses the detection

of many doubly charged ions and eliminates some isobaric interferences including $^{20}\text{Ne}^+$ and $^{40}\text{Ar}^{++}$. While quadrupole-based mass spectrometers may detect up to 15% of argon as Ar^{++} , LIT prototype spectra under present test conditions have never exhibited Ar^{++} . An upper limit of 0.004% of the total argon signal may be detected as Ar^{++} in LIT under typical operating conditions, effectively eliminating the isobaric interference.

Ion-molecule charge transfer reactions. Charge transfer can also occur between trapped rare gas ions and a neutral background molecule. Methane and water are the most significant expected contaminants within the LIT that have lower ionization energies than Ne, Ar and Kr, and are of most concern. This charge transfer results in both reduced NG sensitivity and higher instrument backgrounds as shown in Figure 1. At the shortest required ion trapping times (i.e. charge transfer reaction time), a maximum tolerable pressure for these contaminants was determined to be 3×10^{-7} Torr.

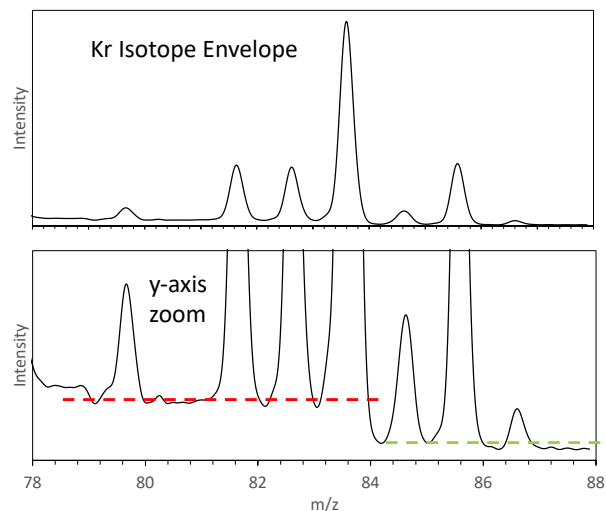


Figure 1 - Elevated background levels (dashed lines) arising from charge transfer to untargeted neutral species. Many such lower mass contaminant ions are not sorted by mass-to-charge ratio (m/z), but are rather immediately ejected from the trap and detected – raising backgrounds at masses below very intense peaks in the spectrum.

Isotopic fractionation through intraspecies charge transfer. At elevated partial pressures of a given NG, charge transfer is also observed between trapped NG

ions and NG neutrals present in the LIT. Due to the non-equilibrium conditions of these reactions, minor isotopes can lose charge to major isotopes resulting in fractionation as shown for neon in Figure 2. The partial pressure at which this fractionation is observable depends on the relative abundances of the major and minor isotopes. To mitigate this issue, maximum permissible operational partial pressures were established in the LIT of 1×10^{-5} Torr and 2×10^{-6} Torr for neon and argon, respectively.

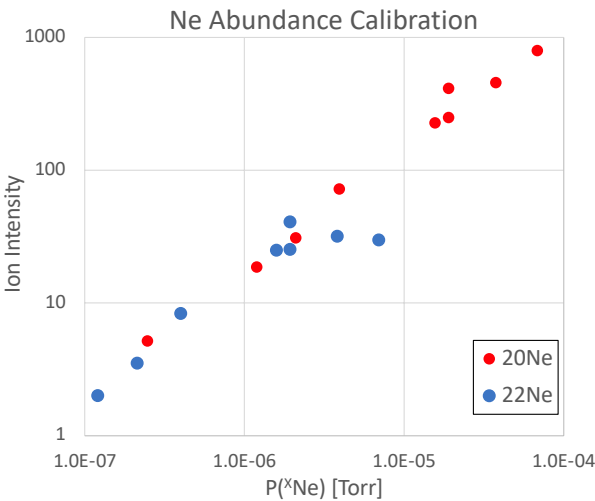


Figure 2 - Isotopic fractionation observed due to intraspecies charge transfer among neon isotopes. X = 20 or 22 (nominal isotopic mass).

Summary: Once the operational characteristics affecting the accurate measurement of noble gas intensities in the LIT were identified, the DraMS LIT was established to have the NG sensitivities and constraints as summarized in Table 1. With these characteristics of the LIT now understood, a detailed performance specification and a concept of operations for the complete end-to-end DraMS atmospheric mode experiment is being finalized.

Table 1 - Performance summary of the prototype LIT for NG measurements.

Absolute Limit of Detection	Ne: 600 fmol Ar: 200 fmol Kr: 40 fmol Xe: 12 fmol
NG Isotope Abundance Ratio Accuracy:	< ± 10% with in-situ calibration
NG Interspecies Abundance Ratio Accuracy:	< ± 20% with in-situ calibration
Maximum tolerable P(NG) to avoid intraspecies charge transfer	Ne: 1×10^{-5} Torr Ar: 2×10^{-6} Torr
Maximum tolerable P(CH ₄ + H ₂ O) to avoid loss of NG sensitivity	3×10^{-7} Torr

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References: [1] Niemann H. B. et al. (2010) *J. Geophys. Res.*, 115, E12006. doi: 10.1029/2010JE003659. [2] Glein C. R. (2017) *Icarus*, 293, 213-242. doi: 10.1016/j.icarus.2017.02.026. [3] Barnes J. et al. (2021) *Planet. Sci. J.*, 2, 130. doi: 10.3847/PSJ/abfdcf. [4] Goesmann F. et al. (2017) *Astrobiology*, 17, 655-685. doi: 10.1089/ast.2016.1551.