

A NEW QUADRUPOLE ION TRAP MASS SPECTROMETER FOR MEASURING NOBLE GASES IN PLANETARY ATMOSPHERES. G. Avicé¹, A. Belousov², S. Madzunkov², K. A. Farley¹, J. Simcic², D. Nikolic², M. R. Darrach², C. Sotin². ¹California Institute of Technology, GPS division, 1200 E. California Blvd, Pasadena, CA 91125, USA, gavice@caltech.edu, ²Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, USA.

Introduction: Noble gases are powerful tracers of physical processes such as the delivery of volatile elements to planetary atmospheres through meteoritic/cometary bombardment [1,2], atmospheric escape, degassing from the silicate parts of planets, etc. In this context, understanding the isotopic composition of Xe in planetary atmospheres is a high priority since Xe isotope ratios can answer fundamental questions such as i) What is the delivery mix (Chondritic/Solar/Cometary) to planetary atmospheres?; ii) To what extent is the silicate portion of a planet degassed?; iii) How much of the atmosphere was lost through atmospheric escape and what is the timing of this process? While recent results from space missions contributed substantially to our knowledge of the elemental and isotopic composition of noble gases on Mars [e.g. 3] and in comets [e.g. 4], some planetary reservoirs remain to be sampled and analyzed. For example, the composition of the atmosphere of Venus is still a missing piece of the noble gas puzzle [5]. Compact mission concepts to sample the Venus atmosphere below the homopause and to measure noble gases with the JPL Quadrupole Ion Trap Mass Spectrometer (JPL-QITMS) have recently been proposed [6].

QITMS or Paul traps were invented 6 decades ago [7], but their potential use as a mass spectrometer for noble gases was explored only recently. For example, in the 1990's, a team at JPL developed a QITMS and demonstrated its ability to measure the abundances and isotopic composition of noble gases [eg. 8]. Another study demonstrated the ability of the JPL-QITMS to measure at high precision the composition of various artificial isotopic mixtures of Xe in dynamic mode [9]. In many mission scenarios, a dynamic measurement is not envisageable. For example, a mission to the Venus atmosphere would collect a sample below the homopause (where gas atoms are well mixed) with ppm to ppb levels of noble gases and measure it only afterwards. Ability to measure gas in static mode would thus be required. Here we show that recent developments of the instrument allow measurement of Kr and Xe isotopes in static mode with a sensitivity and precision meeting the analytical requirements for characterization of the Venus atmosphere.

Instrumentation and calibration:

Description of the QITMS. The JPL-QITMS consists of three electrodes. In the current configuration, the top and bottom (end-cap) electrodes are grounded whereas the ring electrode receives a high-voltage radiofrequency signal (1-2 kV). Gas neutrals are ionized by electron-impact in the mm-sized space between electrodes via a side-mounted electron gun composed of a Ta cathode and an Einzel lens. A voltage ramp applied to the ring electrode ejects ions along the z-axis (Fig. 1). Ions are detected with a MAGNUM Channeltron electron multiplier operated in pulse-counting mode. The whole system is placed in a vacuum chamber permanently pumped via a turbomolecular pump (pressure lower than 10^{-9} torr) except when a sample of gas is to be analyzed. During "static mode" analysis the chamber is isolated from the turbopump and a SAES NP10 getter in the chamber removes residual gases and reduces the partial pressure of hydrogen.

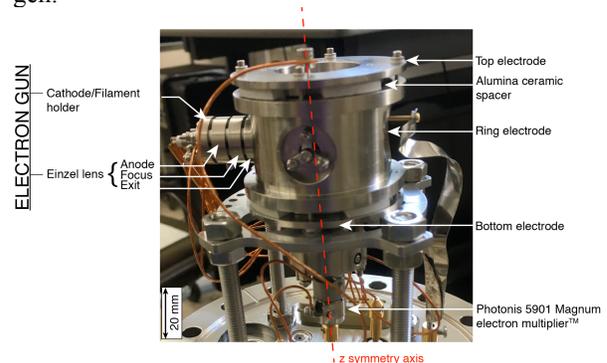


Fig. 1: Picture of the side-ionization JPL-QITMS

Analytical methods. A bottle containing a Kr/Xe gas mixture with atmospheric isotopic ratios was calibrated against a second tank filled with air at ambient pressure and measured at the noble gas laboratory (GPS division/Caltech) using classical sector instruments. Each aliquot taken from the bottle consists of 2×10^{-14} mol of ^{84}Kr and 8×10^{-16} mol of ^{132}Xe .

Aliquots of the gas mixture were first purified in a small vacuum line with a D-100 SAES getter. The resulting Kr/Xe mixture was then equilibrated with the trap chamber. A typical measurement cycle lasts between 25ms and 100ms. For a 25ms cycle, 15ms are dedicated to ionization and trapping of created ions. Two grids in front of the detector prevent positive charges (ions) and negative charges (electrons) from

entering the detector. A short ramp lasting about $80\mu\text{s}$ is then used to quickly eject masses lighter than about 60 a.m.u. A slower ramp (8ms) is then used to eject ions with masses of interest from ($m=60$ to >150). Every 1s, 40 frames containing up to 9000 channels are collected by the system. Many possible variations of this timing and of the shape of the RF ramp are possible and make this instrument very flexible. Changes mainly affect the sensitivity, mass range and resolution of the instrument.

Results:

Kr and Xe sensitivity. The sensitivity reaches 10^{13} cps/torr of Kr and Xe for an emission current of about $800\mu\text{A}$. The signal increases linearly with gas amount (over one order of magnitude range) and the Kr and Xe signals scale linearly with the emission current suggesting that no space charge limit is reached yet. Experiments show that this instrument is able to measure gas in static mode over durations as long as 16h, allowing high total counts and associated improved counting statistics uncertainties.

Isotope ratios. Because of RF instabilities, peaks have a tendency to "walk" over several channels with time. A mass spectra alignment procedure was thus applied [9] before computing isotope ratios by integrating the signal under each peak. With a partial pressure of 10^{-10} torr of Kr, major isotope ratios are determined with a precision better than 1% (Fig. 2).

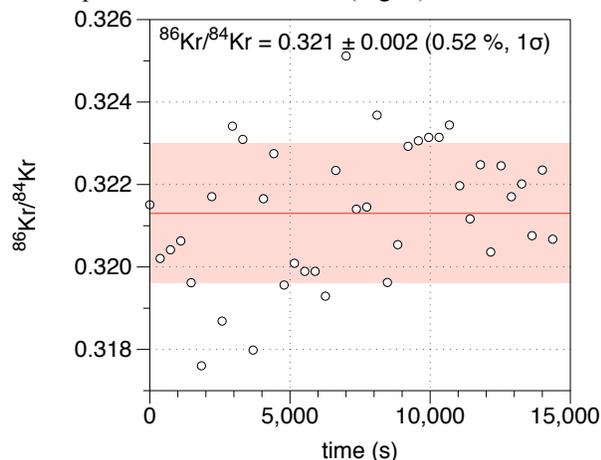


Fig. 2: $^{86}\text{Kr}/^{84}\text{Kr}$ ratio measured over 4h and with a partial pressure of Kr of 10^{-10} torr. The isotopic ratio is determined with a precision better than 1% meeting requirements for a measurement of the Venus atmosphere, for example [5].

Measuring Xe isotope ratios is more challenging for several reasons: i) Xenon in solar system reservoirs is often lower in abundance by about one order of magnitude compared to Kr; ii) higher voltage is required to eject Xe ions from the trap, putting the RF amplifier close to its operating limits; iii) ^{124}Xe and ^{126}Xe iso-

topes are rare (e.g. $^{126}\text{Xe}/^{132}\text{Xe} \approx 0.003$), a long measurement duration is thus required to obtain precise ratios. Results demonstrate the ability of the QITMS to measure major Xe isotope ratios with a precision better than 2% (Fig. 3).

Preliminary conclusions and future work:

In this study, we demonstrated the ability of the JPL-QITMS to measure the abundance and the isotope composition of the two rarest noble gases, krypton and xenon. Isotope ratios precise enough to answer fundamental questions in cosmochemistry can be obtained in a few minutes of analysis. Performance of the JPL-QITMS is capable of measuring the abundance and isotope composition of noble gases of planetary atmospheres in the context of missions carrying small payloads such as Cubesat missions.

Future investigations could involve testing new filaments to improve sensitivity and resolution through a better focus of the electrons and/or higher emission, improvements to the stability of the RF signal, potentially adding another electron multiplier to double sensitivity, and additional design efforts to further reduce the size of the system.

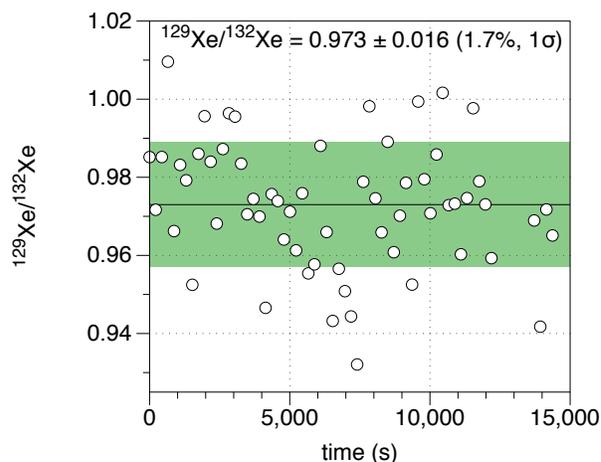


Fig. 3: $^{129}\text{Xe}/^{132}\text{Xe}$ ratio measured over 4h and with a partial pressure of Xe of 7×10^{-12} torr. The isotopic ratio is determined with a precision better than 2%.

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