

**A HIGH-PRESSURE HOLLOW CATHODE IONIZATION SOURCE FOR IN-SITU DETECTION OF ORGANIC MOLECULES ON MARS.** L. W. Beegle, and I. Kanik, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, Ca 91109, [Luther.Beegle@jpl.nasa.gov](mailto:Luther.Beegle@jpl.nasa.gov), [IKanik@pop.jpl.nasa.gov](mailto:IKanik@pop.jpl.nasa.gov)

We have designed, constructed and characterized a new high-pressure (1-5 Torr) hollow cathode discharge source (HCDS) that can be utilized as an ionizer in a wide variety of mass analyzers. It is able to function under ambient Martian atmospheric conditions without modification. The ionizer produces a stream of  $(\text{H}_2\text{O})\text{H}^+$  ions from pure water vapor ( $\text{H}_2\text{O}$ ) introduced into the ionizer from a small liquid water container. These ions react with air-borne samples and ionizes organic species present via proton-transfer-reaction (PTR) without ionizing the atmospheric components. PTR is a better choice for ionization over other conventional ionization techniques (i. e. radioactive  $\text{Ni}_63$  source, electron impact etc.) for *in-situ* detection of large organic molecules on Mars for two reasons: a) It utilizes a soft ionization technique so large organic species will not fragment, and b) the constituents of the Martian atmosphere and most non-organic species present on the surface will not react with  $\text{H}_3\text{O}^+$  as they have lower proton affinities than  $\text{H}_2\text{O}$  [1, 2].

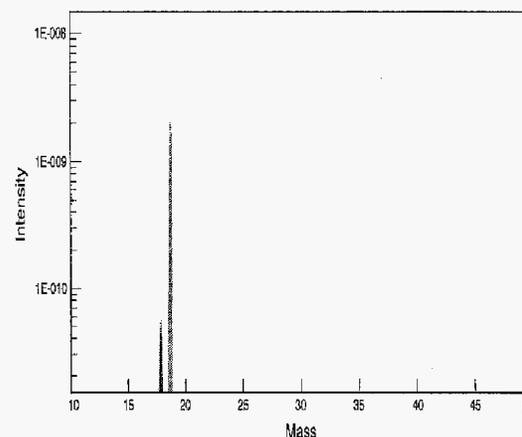
**Description of the Ion Source:** The ionizer consists of two major elements: The hollow cathode ionization source (HCIS) and the reaction chamber (RC).

*Hollow cathode discharge source:* The necessary density of reactant  $(\text{H}_2\text{O})\text{H}^+$  ions is provided by means of a HCIS which has recently been developed and characterized. Fig 1 shows that this source is capable of producing a beam consisting predominately of the reactant  $(\text{H}_2\text{O})\text{H}^+$  ions with the only other ion detected being  $\text{H}_2\text{O}^+$ . The spectra was obtained with quadrupole mass spectrometer (QMS) equipped with an SEM detector. The QMS was operated with the electron impact tungsten filament removed from the entrance so that only ions detected were the ions created with the HCIS.

The characteristic spectra shown in Fig. 1 is remarkably stable over the course of up to 7 hours and potentially much longer (see Fig. 2). Most of the fluctuations in the ion current as shown in Fig 2, was a due to the quadrupole mass spectrometer used to record the data, not the ionizer itself, since the ionizer discharge current remained stable during the time data was being collected. To obtain the spectra shown in Fig.1 & 2 water vapor supplied from a small container (~ 20 cc) was fed into the HCS used to create reactant ions [3]. The spectra shown were produced by a discharge operated at a pressure of 1 Torr in which the ions were fed through a 40 micron hole into a high vacuum region ( $\sim 10^{-5}$  torr) where a quadrupole mass spectrometer identified the ions. The cathode fall voltage was ~ 400 V and the discharge current was several mA.

The HCS consists of a coaxial cylindrical hollow cathode and anode. The discharge is not magnetized, and the cathode was specifically designed to operate with a cathode fall voltage ~ 400 volts at ~ 1 Torr. Electrons in the negative glow, located around the cathode axis, are therefore highly energetic. When the discharge is formed in the reactant gas, these conditions lead to the creation of a relatively dense plasma consisting mostly of energetic electrons and reactant ions. The distribution of ions is axially symmetric. Thus, the ions are easily extracted through a hole in the center of one of the enclosing plates, which is practically "on" the plasma potential, because the bulk of the potential is concentrated in the cathode fall region. The ions are extracted through a 40 micron extraction plate which is biased at -10 V. This type of ion source proved to be much more efficient in generating pure ions than electron impact ionization sources or discharges in mixtures of noble gases with reactant gas.

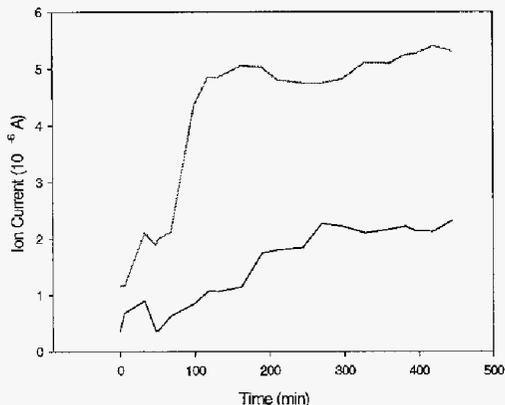
**Fig.1** Relative intensities of the ion beam produced by the HSC containing 98%  $(\text{H}_2\text{O})\text{H}^+$  (in red) and only 2% of  $\text{H}_2\text{O}^+$  ions (in blue) as shown in this mass spectrum.



*Reaction chamber:* To facilitate the ionization of target molecules through the proton-transfer-reaction (PTR) process [1], a beam of  $(\text{H}_2\text{O})\text{H}^+$  ions, generated by the HCS (see Fig.3), are extracted into the reaction chamber (RC). This is where the PTR occurs between the reactant ions and target molecules. Only the molecules with proton affinities larger than reactant gas will undergo the reaction. All the major atmospheric constituents of both the Earth and Mars have proton affinities lower than  $\text{H}_2\text{O}$ , none of the constituents reacts with  $(\text{H}_2\text{O})\text{H}^+$ . To test this we filled a section of the chamber with prime constituents of Martian air ( $\text{CO}_2$ ,

CO, N<sub>2</sub> and Ar) while the ionizer was on. No change in the resultant mass spectra was observed.

**Fig. 2** Relative intensities over time of (H<sub>2</sub>O)H<sup>+</sup> (in red) and H<sub>2</sub>O<sup>+</sup> (in blue).



This ionizer can be used with variety of mass spectrometers such as QMS, ion trap mass spectrometers and ion mobility mass spectrometers. However, IMS is the most promising one since it can be operated at 5 torr (Martian atmospheric pressure) and is capable of detecting and uniquely identifying organic molecules without the further need for a vacuum system with parts-per-billion sensitivity.

Sample extraction methods to release organic samples from rocks such as laser desorption and microwave heating are also being explored. IMS function analogous to a Time of Flight spectrometer except they can operate at high pressures including atmospheric pressure. [4,5].

#### Acknowledgment:

This research is funded by the NASA PIDDP office.

**References:** [1] Hansel A. et al. (1995) *Int. J. Mass Spect. Ion Process*, 149, 609. [2] Lindinger W. et al. (1998) *Int. J. of Mass. Spec. and Ion. Proc.*, 173, 191. [3] Beegle, L.W. et al. (2000) LPSC XXXI. [4] Beegle, L.W. et al. (2001) submitted to *Analytical Chemistry*. [5] Beegle, L.W. et al. Submitted to *Inter. J of Mass Spect.*

**Fig.3** Photograph of the Hollow Cathode Ionization Source capable of producing the (H<sub>2</sub>O)H<sup>+</sup> reactant ion (see Fig 1&2)

