

A HIGH-PRESSURE HOLLOW CATHODE DISCHARGE SOURCE FOR ION MOBILITY SPECTROMETERS FOR IN-SITU DETECTION OF ORGANIC MOLECULES ON MARS. L. W. Beegle, C. Noren and I. Kanik, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, Ca 91109, Luther.Beegle@jpl.nasa.gov, ikanik@pop.jpl.nasa.gov

Introduction: We have designed, constructed and begun testing of a new high-pressure (5-10 Torr) hollow cathode discharge source (HCDS) that can be utilized as an ionizer for ion mobility spectrometers as well as in a wide variety of mass analyzers. It is able to function under ambient Martian conditions without modification. The ionizer produces H_3O^+ ions from pure water vapor (H_2O) introduced into the ionizer from a small liquid water container. These ions react with air-borne samples which can contain a wide variety of organic species and ionizes them via proton-transfer-reaction (PTR). PTR is a better choice for ionization over other conventional ionization techniques (i. e. radioactive 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 H_3O^+ as they have lower proton affinities than H_2O [1, 2]. Moreover, if used in conjunction with an ion mobility spectrometer (IMS) which is under development in our laboratory, identification of organic species in the gas phase would be possible without vacuum pumps or differential pumping.

Ion Source: The ionizer consists of two major elements: The hollow discharge cathode source (HCDS) and the reaction chamber (RC).

Hollow cathode discharge source: The HCDS and water vapor are used to create reactant ions (H_3O^+). The reactant ions are then extracted into a short “drift region” by using ion optics. The HCDS electrode system consists of a coaxial cylindrical hollow cathode and anode whose dimensions are determined by the pressure of the discharge [3]. The discharge is not magnetized, and for pressures between 5 and 10 torr the cathode fall voltage is between 500 and 1000 volts which produces ~ 1 mA of discharge current. 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 extracted ions drift through the ion source drift chamber. This type of ion source has 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.

Reaction chamber: The RC is the second component where the PTR occurs between the reactant ions and target molecules present in the carrier gas. Present studies have included pure H_2O and trace amount of H_2O in Ar. For the case of simulated Martian “air” in the laboratory the carrier gas consists of 95% CO_2 , 2.7% N_2 , 1.6% Ar and trace amounts of O_2 and CO. The gas sample (common components of air or Martian air containing trace amount of organic constituents) to be analyzed is introduced into the reaction region by a leak valve where organic molecules will undergo proton-transfer reactions and form positive ions (product ions) with a high efficiency. The reaction chamber is essentially a modified drift tube with a slight electric field to de-promote water from clustering. In this section the PTR will occur between the ions, which are drifting in the electric field along the axis of the chamber, and target molecules present in the gas sample. The major constituents of the carrier gas (Earth/Martian air) will be simply flow through without reacting. As mentioned earlier, only the molecules with proton affinities larger than reactant gas will undergo the reaction and since all the major constituents in the Earth and Martian air have proton affinities lower than H_2O , none of the constituents reacts with H_3O^+ . The resonant proton transfer between H_3O^+ and H_2O does not alter the density of H_3O^+ ions either, thus it is not a loss term for H_3O^+ .

Table 3. Proton affinities (PA) and abundances of common components in Martian air and PA of some common organic molecules are tabulated.

Component	Abundance (%)	PA (kcal mol ⁻¹)
CO_2	95.46	130.9
N_2	2.7	118.2
Ar	1.6	88.6
O_2	0.17	100.9
CO	0.07	141.9
H_2O	0.03	166.5
HCN	Unknown	171.4
CH_2O_2	Unknown	177.3
C_6H_6	Unknown	181.9
NH_3	Unknown	204.1

Figure 1 shows a schematic of the laboratory HCDS which is presently undergoing characterization. The electrodes are made of molybdenum (shown in black) with the dielectric spacer constructed from Macor (shown in yellow). The Teflon block at both ends serves two purposes: A) The RC is made of Macor, which is a brittle substance, the Teflon allows for some give when tightening the IS. B) It ensures that the discharge is only in the gas discharge gap. That is the Teflon acts like an insulator allowing for only one possible path to ground: through the discharge gap.

Discussion: The sensitivity of this process can be described in terms of the ratio of the density of product ions $[MH^+]$ to the density of the reactant neutral molecule $[M]$ according to

$$[MH^+]/[M] \cong [RH^+] \cdot k \cdot t$$

where $[RH^+]$ is the density of RH^+ ions, k is the reaction rate constant of the proton transfer reaction, and t is the reaction time, which is the time that RH^+ ions take to drift through the reaction chamber [1, 2]. The density of RH^+ ions, $[RH^+]$, is defined by the generation capacity of the ion source. The reaction rate constant, k , is characteristic of the particular reaction. Of note, reaction times can be controlled through adjustment of the electrical field in the reaction chamber. An upper limit for the reaction time is defined by the cluster formation dynamics. When the drift velocity of RH^+ ions is too low, they may form $RH^+(H_2O)_n$ clusters, and these would introduce detection artifacts in the ion mobility spectra. Therefore, the drift time has to be regulated through judicious adjustment of the electrical field in the reaction chamber.

The HCDS was primarily designed for use as an ionization source for an Ion Mobility Spectrometer (IMS). The resulting instrument would be highly selective and sensitive to specific organic compounds. Furthermore it will be suitable for *in situ* detection of large organic molecules of biological importance (i.e., ones which would be suggestive of biochemical activity) and would do so at a greater sensitivity level than is now possible (low ppb). Because (a) the sensitivity is higher in comparison with conventional mass spectroscopy, and (b), the absence of the fragmentation problem of large organic species, this novel instrument should be able to reliably detect organic compounds, amino acids and possibly bacteria even in a complex chemical environment. The organic compounds to be detected on Mars might have been trapped in rocks, adsorbed on soils, or condensed as ices on and/or beneath the Martian surface. Laser desorption is now being tested in conjunction with the HCDS and an IMS to release the organic molecules from the environments mentioned above. The discov-

ery of such an organic compound would be an indication that life might actually have existed or still exists on Mars today [4]. More importantly, these trace components could identify samples of exobiological interest that could be cached for a later return to Earth for further study.

Acknowledgment:

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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] Schoenbach K. H. et al. (1997) *Plasma Sources Sci Technol.* 6 468. [4] Owen, T., (1997) *LPI Technical Report*, no. 97-01, 11.

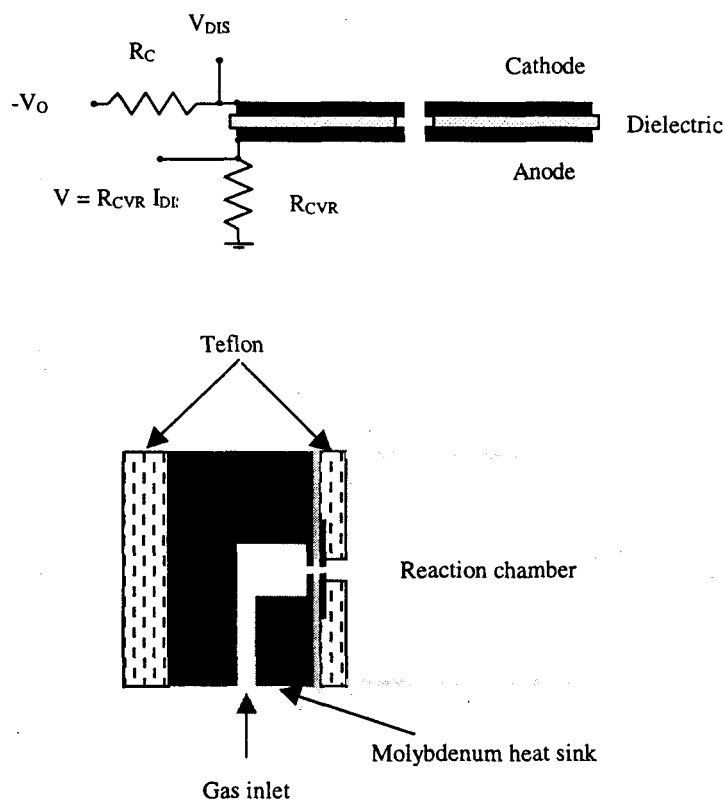


Fig 1- *top*: Schematic representation of the hollow cathode source (HCS), suitable to produce H_3O^+ ions in the ambient Martian environment. *bottom*: Schematic of the Ion Source (IS) including the reaction chamber (RC) and gas inlet. Teflon is utilized to isolate the discharge to the gap region. Not shown is the ion optics which is easily placed in the RC to focus ions onto a suitable detector.