

A VERY MUCH FASTER AND MORE SENSITIVE IN SITU STABLE ISOTOPE ANALYSIS

INSTRUMENT. M. Coleman^{1,2}, L. E. Christensen¹, J. M. Kriesel³, J. F. Kelly⁴, J. J. Moran⁵, S. Vance^{1,2}. ¹NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA, max.coleman@jpl.nasa.gov. ²NASA Astrobiology Institute, USA. ³Opto-Knowledge Systems Inc., Torrance, CA 90502, USA. ⁴J. F. Kelly, Pasco, WA, 99301, USA. ⁵Pacific Northwest National Laboratory, Richland, WA 99354, USA.

Introduction: We are exploiting an emerging infrared absorption spectrometry technology to develop an in situ measurement system which should offer at least four orders of magnitude improvement in sensitivity relative to currently operating systems. Although the approach eventually will have many applications, we are focusing initially on isotopic analysis of hydrogen and oxygen in water ice and hydrated minerals, sampled at high spatial resolution by laser.

Why start with water analysis: The search for life outside the Earth remains a very high-profile topic. For a planet or moon to be habitable requires availability of volatile materials. Water is a key ingredient for life, and a mediator of geophysical processes on Earth such as mantle convection and atmospheric chemistry. The solar system's store and distribution of water constrains planetary evolution and habitability. Water makes up much of the mass in the outer solar system, including primordial meteorites and comets that might have formed our oceans [1]. Spectroscopic observations and rare sample analyses show considerable heterogeneity of D/H ratios of comets [2] and while it is likely that cometary cores are primordial [3], it is not clear if the surface material observed remotely has been reworked. Processes such as weathering, evaporation, precipitation, freezing, radiolysis, etc., affect the isotopic compositions of ices. Furthermore, comet samples returned by the Stardust mission [4] showed both large and small isotopic variations and also extreme differences between grains. Therefore, there is a need for multiple in situ isotopic analyses of comets and asteroids with high resolution sampling.

Analytical method: IR absorption spectrometry with a tunable diode laser source is well-established for stable isotope analysis for many gaseous compounds, whether directly in a Herriot cell with an extended path length after many bounces between opposing mirrors [5] or by cavity ring down spectroscopy [6]. The spectrum for water offers good expression of all relevant isotopologues (Fig. 1).

While using the same spectral features for analysis, our instrument utilizes a hollow optic fiber instead of a chamber, greatly reducing the sample volume [8] (Fig. 2).

The fiber is a waveguide, enhancing the laser-water-vapor interaction. A longer fiber would give a longer

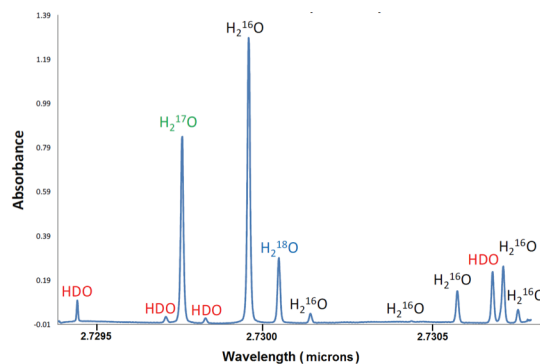


Figure 1. IR absorption spectrum for water isotopes [7].

path length, more absorption and thus more sensitivity. However that would also increase sample volume. Initially, we have chosen a 2 meter fiber length, which should give sufficient absorption. With a 2 m long fiber, we estimate that we will be able to analyze a 5 nanomole water sample to precision of 1‰ in 1 seconds and 0.1‰ in 10 seconds. This is a more than four orders of magnitude increase in sensitivity, despite a shorter optical path length.

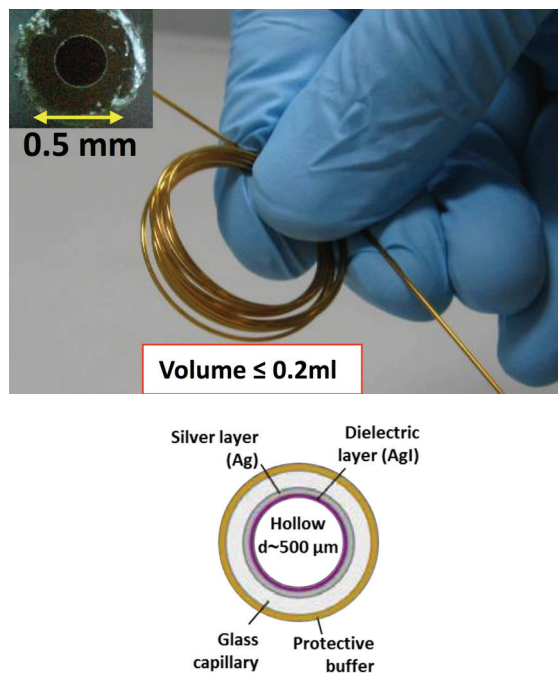


Figure 2. Hollow optic fiber, the absorption chamber.

Laser sampling: The wavelength of IR laser light chosen for spectrometry clearly is strongly absorbed by water vapor. Therefore our plan is to use the same wavelength, and indeed the same laser, for vaporizing water for analysis. This is shown in Fig.3, a schematic view of the three units that comprise the complete instrument. Although not shown in detail here, we have designed the sampling head so that it would make a sufficient seal to the surface being analyzed, being deployed on a simple arm. The sampling beam is intended to have just sufficient power to volatilize ice or release water from hydrated minerals without causing ablation and ejection of particle that might obstruct the camera or enter the hollow fiber. However, to avoid that unlikely possibility, we have designed the head to have an oblique sampling incidence and have included baffles to impede particle movement.

Conclusion: We have chosen water analysis as the first attempt to use this very sensitive analytical technology for a flight instrument because of the magnitude of the scientific problem. However, having established this way of measuring, we can envision many other applications for astrobiology and planetology. CO₂, SO₂ and CH₄ are routinely analyzed by laser absorption spectrometry and this approach would be amenable to undertaking such analyses in situ, either directly or after a simple sample processing front end.

References: [1] Javoy M. (1998). *Chem. Geol.* 147, 11-25. [2] Bockelée-Morvan D. et al. (2015) *Space Sci Rev* 197, 47–83. [3] Davidsson B. J. R. et al. (2016) *A&A* 592, A63. [4] McKeegan K. D. et al. (2006) *Sci.*, 314, 1724-1728. [5] Wahl E. H. et al (2006) *Isotop. Env. Health Stud.*, 42, 21–35. [6] McManus J. B. et al (2010) *Isotop. Env. Health Stud.*,46, 49-63. [7] Chen P. et al. (2011) NASA PIDDP Final Report, JPL Project/Task Number: 103957. [8] Kelly J.F. et al. (2012) *Rev. Sci. Inst.* 83, 023101.

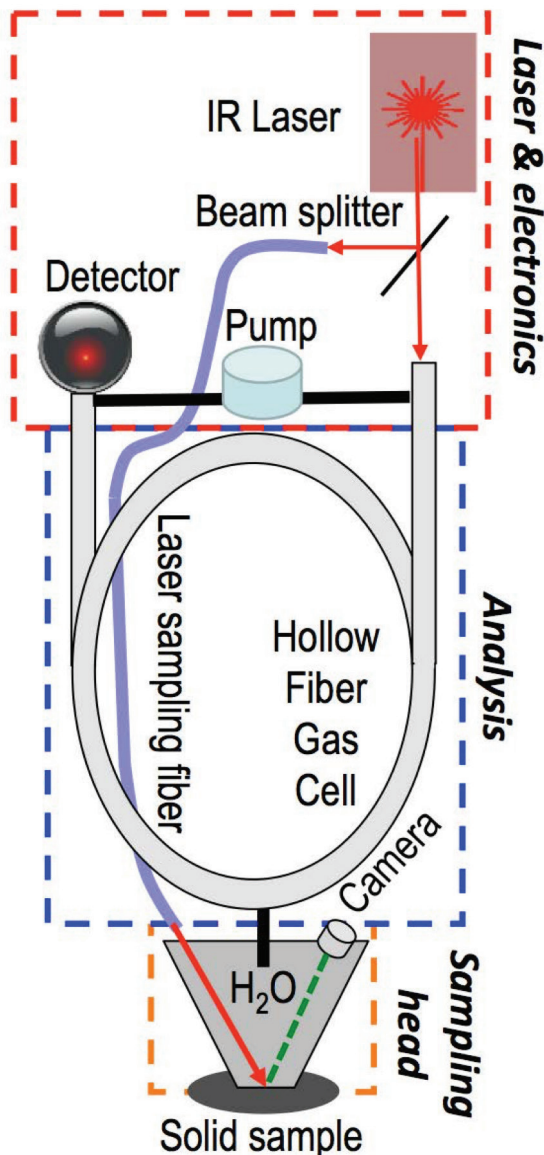


Figure 3. Schematic of the complete instrument.