Capillary Absorption Spectrometer (CAS), a compact, low-sample-volume isotope analyzer for planetary applications

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Abstract— **Isotope-ratio analysis is a powerful tool to elucidate planetary systems. Isotopic data can provide information on potential sources of water in the solar system (e.g., D/H ratio), as well as evidence for life beyond Earth (e.g., 13C/12C and 34S/32S). We describe a trace-gas and isotope analyzer that utilizes a low-volume (~ 1 ml), compact gas cell, in a concept we refer to as a Capillary Absorption Spectrometer (CAS). An analyte is drawn into a hollow fiber, which has a reflective inner coating that guides a tunable laser beam to a detector. There is near unity overlap between the laser beam and the gas sample in the fiber, leading to a highly sensitive system with an ultra-compact size. The measurement approach is similar to the Tunable Laser Spectrometer (TLS) aboard the Curiosity Rover, with the difference being that the CAS can perform measurements with orders of magnitude less sample. The CAS on missions to the Moon will help better understand Lunar water sources, or the CAS on an Enceladus plume flythrough can provide insight into methane origins. With the CAS low SWaP, it is an appealing instrument for numerous missions to help answer pivotal questions.**

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1. INTRODUCTION

Water's origin in the solar system is still an open question that isotopic ratio analysis can help answer. Specifically, the source and cycle of lunar water is under debate [1] and a better understanding is important for planetary science and even future efforts to establish habitation. Water can be characterized by its oxygen (e.g., 18O/16O) and hydrogen (D/H) isotope ratios with the latter having large variations observable by astronomical spectroscopy. Asteroids are similar to Earth's ocean water, while comets show a range of values, mainly with much higher D/H ratios[2]. Furthermore, external fluxes (e.g., solar winds) are postulated as altering the D/H ratio[3]. Answering questions related to water origin and diurnal cycles will be difficult to achieve solely with returned samples and remote astronomical observations. In-situ isotopic instruments could allow for more detailed studies, in particular, one capable of being deployed on smaller vehicles and missions.

Another key focus of NASA planetary exploration is searching for life beyond Earth. Stable isotope analysis is a powerful tool employed in this search. Isotopic fractionation imposed by microbial activity produces a biosignature[4][5] that can be preserved in biomass or rock records[6]. Looking for such isotopic signatures requires fine-scale analysis using a tool capable of making in-situ measurements with minimal sample requirements.

Isotope ratio mass spectrometry (IRMS) has been the workhorse of light stable isotope analysis for multiple decades. However, these instruments are ill-suited for remote deployment due to their large size, high power consumption, stringent vacuum requirements, and measurement interferences from common molecular species with equal mass. Infrared (IR) laser spectroscopy systems have emerged to provide smaller, unambiguous measurement platforms for both trace gas sensing and stable isotope analysis. In particular, systems exploiting the "molecular fingerprint" region in the mid-infrared (Mid-IR) wavelength range, $\lambda \sim 2 – 16\ \mu m$, Figure 1, can uniquely identify molecular species and isotopologues with relatively high sensitivity.

For example, the Sample Analysis at Mars (SAM) system aboard Curiosity uses an IR tunable laser spectroscopy (TLS) instrument with a multi-pass Herriott cell. However, this gas cell has a sample volume of 400 ml, which can be a challenge to fill in sample-limited applications.

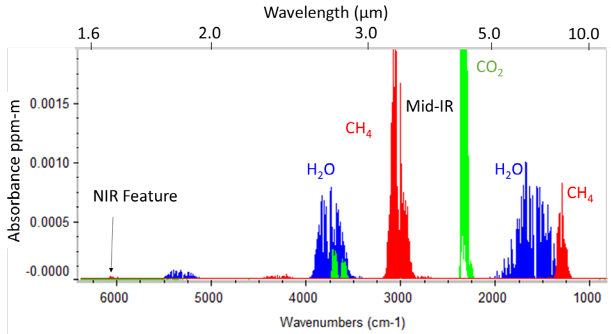


Figure 1. Absorption features of H_2O, CH_4, CO_2 for a concentration of 1 ppm and pathlength of 1 m. Features in the Mid-IR are significantly stronger than in the NIR.

2. CAPILLARY ABSORPTION SPECTROMETER

As an alternative to a multi-pass gas cell, the Capillary Absorption Spectrometer (CAS) uses a hollow core fiber optic waveguide, Figure 2. Gas under analysis is drawn into the fiber, which has a reflective inner coating that guides a tunable laser beam to a detector. There is near unity overlap between the laser beam and the gas sample, leading to a highly sensitive system with a relatively small cell volume (V = 0.03 to 9 ml). The hollow fiber length (L =1 to 5 m) can be coiled and other components (e.g., vacuum pump) are small, leading to a compact system with low total size, weight, and power (SWaP) requirements.

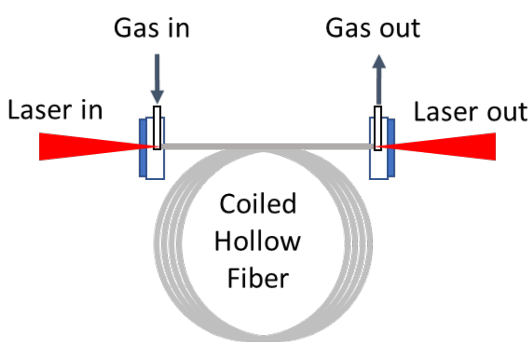


Figure 2. Diagram of Capillary Absorption Spectrometer (CAS), which uses a hollow fiber optic waveguide as a gas cell for laser spectroscopy analysis.

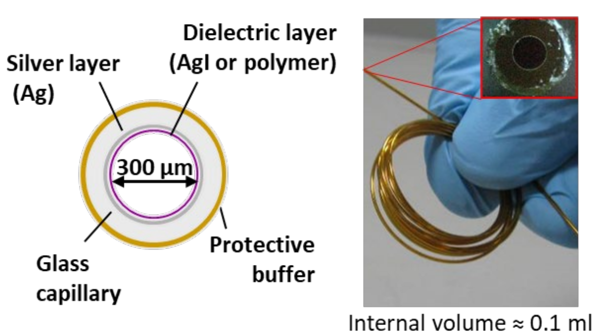


Figure 3. (Left) Diagram of hollow fiber cross section. (Right) Picture of coiled hollow fiber with inserted microscope image of fiber end.

Capillary hollow core fiber optic waveguides utilized for the CAS, were developed and pioneered by Jim Harrington [7], and transferred to OKSI in about 2010. OKSI continued to push the technology forward developing solutions for spectroscopy applications, including plastic hollow fibers to enable larger diameters with lower loss and faster gas flow rates, see Figure 4. In 2020, OKSI spun off a separate company, Guiding Photonics LLC, that now produces and sells hollow fibers and associated gas cells, while OKSI continues to develop spectroscopy solutions utilizing the hollow fibers.

The basic structure of the hollow fiber consists of a wavelength tuned dielectric mirror (silver + silver-iodide) deposited on the inside of a glass capillary tube, see Figure 3. These hollow fibers are highly effective for delivery of Mid-IR laser beams, and are particularly appealing for spectroscopy applications given that (1) there are no end reflections from the hollow core, which could potentially cause feedback to the laser, (2) broadband options enable coverage of essentially the entire Mid-IR wavelength range (e.g., $\lambda = 2\text{-}16$ µm), and (3) single-mode operation is possible with a relatively large core (200 - 500 µm) [8][9].

Figure 4. Picture of hollow fiber produced using a relatively large internal diameter (ID = 1500 µm) plastic capillary.

3. CARBON DIOXIDE ISOTOPE ANALYSIS

The CAS was initially conceived and developed by Jim Kelly and colleagues while at the Pacific Northwest National Laboratory (PNNL)[10][11]. OKSI began providing the hollow fibers to PNNL, and the relationship morphed into a collaboration to transition the technology, improve the performance[12], and increase the technology readiness level (TRL).

In one set of experiments, the sensitivity of the CAS was improved using OKSIs proprietary hollow fiber technology to enable δ13C measurements with as little as 25 femtomoles of carbon [13]. Following this, Jim Moran (now at Michigan State University), lead efforts to utilize the CAS technology for analysis of solids including plant and rhizosphere samples for biofuel applications, Figure 5. In this case, laser ablation (LA) sampling is used followed by combustion to convert reduced C phases in ablated particles to CO2. The CAS's ability to make measurement with minimal sample size (sub-picomole), equates to the ability to determine δ13C of solids with high spatial resolution (~ 10 microns). Additional work by PNNL developed continuous flow methods with the CAS enabling isotopic mapping of samples[14].

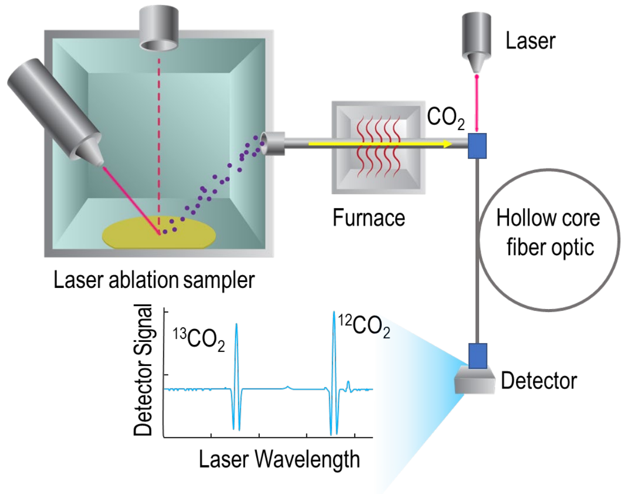
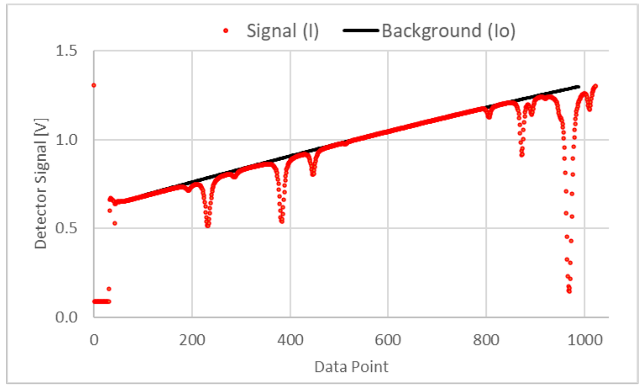


Figure 5. Diagram illustrating carbon isotope analysis of solids using laser ablation sampling, followed by combustion to CO2, and then analysis by a CAS.

4. Example Water Isotope Analysis

Currently OKSI is focused on developing water and methane isotope analyzers for planetary applications. An example detector signal taken with a water isotope CAS is shown by the red points in the top plot of Figure 6. To generate this scan, the current supplied to a distributed feedback (DFB) laser is ramped, which changes the wavelength over a relatively narrow range (this wavelength change corresponds to the x-axis in the plot). The measured absorbance is calculated from the natural log of the ratio of the signal to a background, where the latter represents the response with no absorbing molecules present. This measured absorbance is fit to a spectral model with known parameters (e.g., HITRAN), bottom plot of Figure 6, to determine the concentration of each species / isotopologue.

Calibration data for a prototype water isotope CAS system is shown in Figure 7, showing excellent linearity for both the deuterium isotope ratio (δD) and the oxygen-18 isotope ratio (δ18O). This data was collected by injecting isotopic liquid water samples into an evacuated, heated front-end, which produced dilute water vapor that was drawn into the CAS at reduced pressure, P ~ 10kPa. Note that our system also measures the 17O isotope ratio, but the liquid isotope standards are not characterized for 17O, so there is not a convenient means to test/calibrate this measurement. This is actually an example of how a laser spectroscopy system can provide more information than what is typical for other instruments, e.g., an isotope ratio mass spectrometer has difficulty making accurate 17O measurements of water due to the mass interference with HDO.



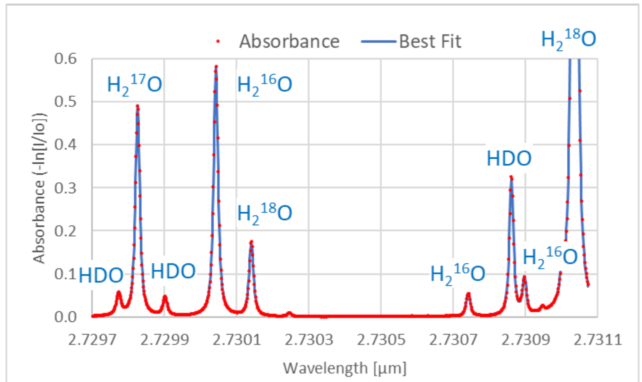
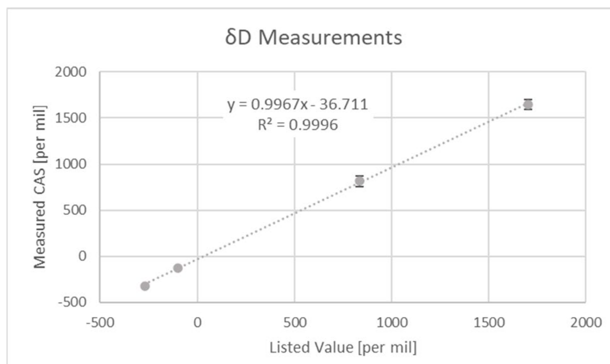


Figure 6. (Top) Measured detector signal (red points), along with background (black line). (Bottom) Calculated absorbance (red points) and spectroscopic fit (blue line) with features for different isotopologues labeled.



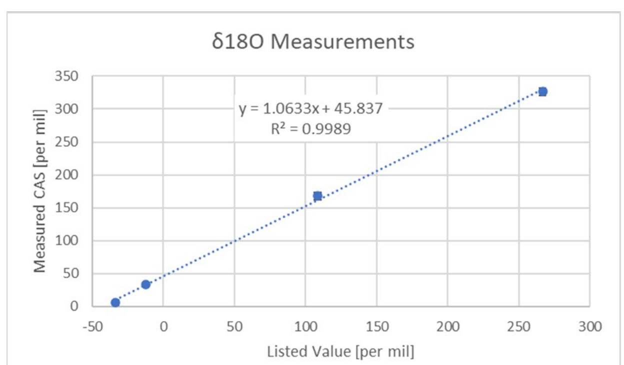


Figure 7. Calibration curves for (Top) deuterium and (Bottom) oxygen isotope measurements.

5. Methane Isotope Analysis

Multiple methane CAS analyzers have been developed by OKSI over the past few years. Examples include both an in-situ underwater version for analysis of hydrothermal vents, as well as a system for field measurements at coastal wetlands, Figure 8. The former includes a membrane-free degassing inlet, which was originally conceived by Max Coleman at JPL, and developed by OKSI to measure methane at the sea floor at depths down to 3000 m.

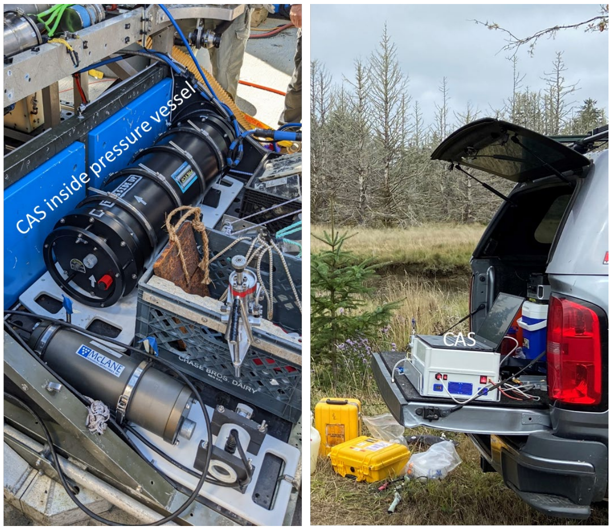


Figure 8. (Left) Picture of underwater methane CAS system mounted on a remotely operated vehicle prior to use for in-situ analysis of hydrothermal vents. (Right) Picture of field portable methane CAS being used to measure samples at a coastal wetland site.

Methane CAS sensors are now being developed by Guiding Photonics, a spin-off company from OKSI. A picture of a prototype sensor is shown in Figure 9, and an example spectral scan showing measurement of methane isotopes and ethane is shown in Figure 10. Performance of this system was characterized by collecting data over an extended period of time and calculating the precision of the determined isotope ratios as a function of averaging time, Figure 11. In this example, the precision for an averaging time was found to be δD ~ 4 ‰ and δ13C ~ 1 ‰ for an averaging time of 100 s. For longer averaging times, long-term drift degrades the performance.

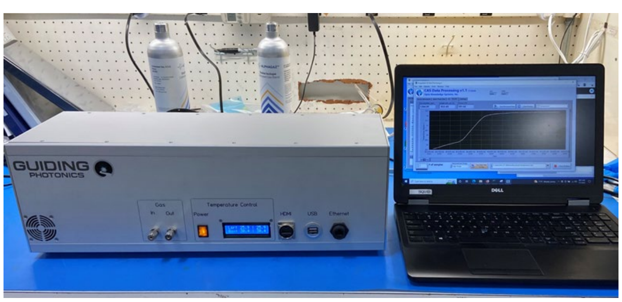


Figure 9. Methane isotope analyzer produced by Guiding Photonics.

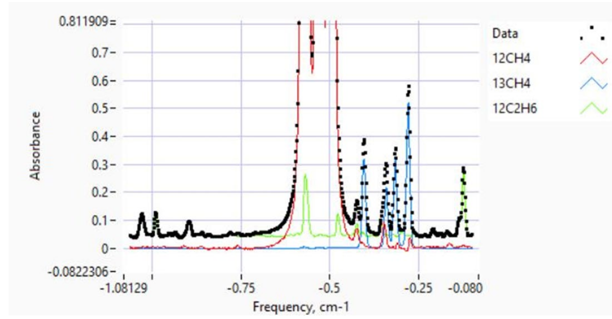


Figure 10. Spectral scan black points, along with fits for partial concentrations of methane isotopologues and ethane.

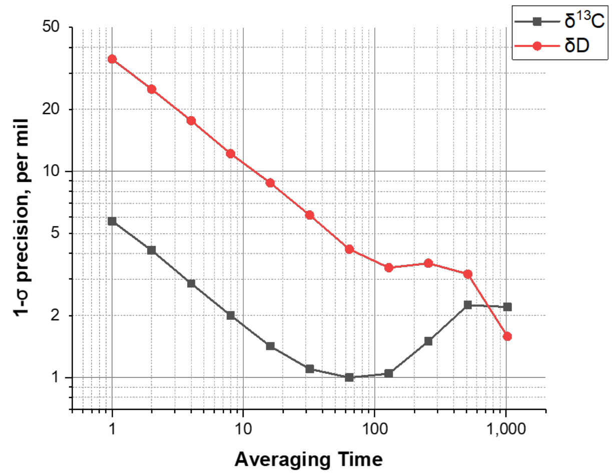


Figure 11. Allan deviation plot showing precision as a function of averaging time for a prototype dual-isotope methane analyzer.

6. Discussion / Future Work

The CAS technology is currently being pushed forward on two fronts: (1) OKSI is conducting research and development to raise the technology readiness level for planetary applications and (2) Guiding Photonics is developing fully packaged sensors for commercial applications.

For planetary applications we are collaborating with Honeybee Robotics to develop appropriate front end sampling systems. This includes separate, but related efforts, for systems designed to (A) analyze water in lunar regolith from a lander or rover and (B) analyze methane in Enceladus' plumes in a flyby. In this development, consideration is being given to prevent mass related effects in collection and transport through the system that may potentially bias the isotope ratio, i.e., "isotopic fractionation". This technology, with the low SWaP and low sample-size requirements, could also aid in numerous other planetary explorations. For example, on a DAVINCI-like mission, it could provide answers about Venus' greenhouse-gas composition, helping explain the runaway effect. Or, it could easily be placed on an Ingenuity-type Helicopter, to measure organic compounds in places Curiosity cannot take the SAM.

In addition to providing a device for in-situ planetary analysis, we have developed strategies to utilize the CAS for the laboratory analysis of returned samples, similar to the approach shown in Figure 5. Such a system could be used to measure both carbon and sulfur isotope ratios providing initial characterization (i.e., triage) with minimal sample, while preserving the bulk of the sample for other analyses.

7. Summary

We provide a brief summary of recent efforts to utilize the Capillary Absorption Spectrometer (CAS) for isotopic analysis. The concept provides a means to measure relatively small sample quantities in a low SWaP package. The CAS is an appealing solution for acquiring data in sample limited and/or SWaP limited applications.

Acknowledgements

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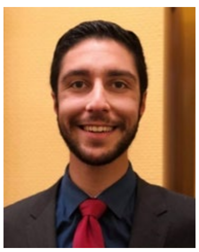
Biography

***Jason Kriesel** received a B.S. in Physics from the University of California, Irvine in 1992 and a Ph.D. in Physics from the University of California, San Diego in 1999. He was an NRC post-doc at NIST, Boulder from 2000 to 2002. For the past 20 years he has been at OKSI leading the development of sensor technology for a range of applications. He currently heads the Environmental Sensing group at OKSI, which is focused on utilizing Mid-IR spectroscopy for trace-gas, isotope analysis, and combustion diagnostics. Furthermore, he has led all of the hollow fiber optic work at OKSI, from initiating the technology transfer, to developing a commercial product line, to co-founding and leading a spin-off company, Guiding Photonics LLC, which is focused on producing and selling hollow fiber optic-based products.*

Andrew Fahrland *received an M.S. in Engineering from Stanford University in 2008. He has been building and testing field-portable laser spectrometers for environmental, defense, and industrial applications for 16 years. He worked as an R&D scientist for Los Gatos Research/ABB for 8 years, and has consulted extensively for OKSI, Picarro, and other prominent commercial vendors of laser instrumentation. He has built sensors for a wide range of harsh environments, including hypersonic test systems, combustion environments in rockets, gas turbine engines, and power generation equipment, deep-sea underwater systems, high-power laser systems, drone and aircraft-based airborne sensing, and in-field environmental sensing applications. He is an expert in design and development of miniature, ruggedized field sensors and integrated systems development.*

James (Jim) Kelly *received his Ph.D. in physics from University of Chicago in 1984. After a postdoc at JILA-Boulder, CO and an academic position, he moved to the Pacific Northwest National Laboratory (PNNL) to manage their Atomic-Molecular Spectroscopy Group. He was involved in the first demonstration of high-resolution Doppler-limited spectroscopy with cw-Quantum Cascade lasers and jointly published this work with researchers from Bell Labs in 1998. Kelly also formed a collaboration with Dr John Hall in 1999 to eventually demonstrate QCL intrinsic linewidths << 10 KHz. Germane to this paper, Kelly used the low noise current sources developed from his collaboration with Dr. Hall to demonstrate 1 ppm noise-equivalent absorbance (NEA) detection in multi-mode 1 mm ID capillary waveguides, thus allowing stable-isotope analysis of CO2 with pico-mole samples. Starting in 2009 he began a collaboration with OKSI using their proprietary fibers to further the performance of hollow fiber-based laser spectroscopy.*



Emre Ozen *received his B.S. in Aerospace and Mechanical Engineering from the University of California, Davis in 2019 and has been working at OKSI as a systems engineer since 2020. He has experience with operating various digital imaging systems and performing digital image processing. His experience in this field began at the Western Cooling Efficiency Center where he statistically analyzed high-speed video of ebullition dynamics in multi-phase heat exchangers. In addition, Emre has helped develop various trace gas sensors and isotope analyzers at OKSI. Examples of this include work developing instruments for in-situ methane, carbon dioxide and carbon monoxide measurements.*

Ilana Gat *is Vice-President at OKSI working to grow the space-based company technology. She received her Ph.D. in Aeronautics from Caltech in 2018 working under Professor Paul Dimotakis and worked at JPL as an A-team Core member and TeamX systems engineer. She has experience from fluid and gas dynamics at fundamental levels to mission formulation and systems engineering. Additionally, while at Caltech, Dr. Gat ran the 2017 Caltech Space Challenge which developed a mission, dubbed "Lunarport," to use Lunar in-situ resources for rocket refueling. This required investigations of low-g drilling, sample extraction, water sample conversion to LOX and LH2, and sample storage. Since joining OKSI, Dr. Gat has helped push OKSI technology to space-based applications, and co-founded the spin-off company, Guiding Photonics LLC to commercialize the hollow fiber products.*