In-situ, real-time methane sensor for vents and seeps

Jason Kriesel
OptoKnowledge Systems, Inc. (OKSI)
Torrance, CA, USA
jason.kriesel@oksi

Andrew Fahrland
OptoKnowledge Systems, Inc. (OKSI)
Torrance, CA, USA
andrew.fahrland@oksi.ai

Kaori Emerson-Shurilla
OptoKnowledge Systems, Inc. (OKSI)
Torrance, CA, USA
kaori.emerson@oksi.ai

Emre Ozen
OptoKnowledge Systems, Inc. (OKSI)
Torrance, CA, USA
emre.ozen@oksi.ai

Max L. Coleman
California Institute of Technology, Jet Propulsion Laboratory
Pasadena, CA, USA
max.coleman@jpl.nasa.gov

Tamara Baumberger
Cooperative Institute for Marine Resources Studies, Oregon State University
Newport, OR, USA
orcid.org/0000-0001-5920-6212

David A. Butterfield
Joint Institute for the Study of Atmosphere and Ocean, University of Washington
Seattle, Washington, USA
david.a.butterfield@noaa.gov

***Abstract*— To meet the need for better analysis of ocean methane, we have developed an in-situ gas sensor, that combines a novel laser absorption spectrometer with a membrane-free approach to water sampling. The sensor was designed for real-time measurements of methane concentration and isotope ratio at depths down to 3000 m and is useful for scientific studies as well as energy exploration. We describe the design, development, and utilization of the sensor. Including presenting data from measurements at deep-sea hydrothermal vents on two recent scientific research cruises: July 2022 and March-April 2023.**

Keywords—methane, isotope, energy exploration, ocean vent / seep, spectroscopy

I. Introduction

Methane in ocean environments has important implications for the global carbon cycle but determining relative contributions of specific sources is complex. Furthermore, determining potential locations for drilling as well as differentiating background methane in the water from methane due to production facilities is hampered by the current slow, time-consuming approach of extracting discrete water samples that are later analyzed in a lab. The lab approach is generally expensive and labor intensive and results in limited sample density over time and space. The sensor described here directly quantifies the methane concentration in the water column with the added capability to determine isotope ratio. This new tool can enhance efforts to quantify ocean methane, attribute its source, and improve fundamental understanding of biogeochemical processes.

II. Capillary Absorption Spectrometer (CAS)

The sensor concept is based on tunable laser absorption spectroscopy (TLAS) in the mid-infrared (Mid-IR) wavelength range ($\lambda \sim 2$ to 16 μm), which is a highly selective and sensitive technique that is able to differentiate AND quantify a range of molecular species, including greenhouse gasses, volatile organic compounds (VOCs), Toxic Industrial Chemicals (TICs), and combustion products. In many applications a gas cell is used to provide a defined volume and/or to enable measurements at reduced pressure. Companies such as Picarro and Los Gatos Research (LGR) typically target weak absorption features in the near-infrared (NIR) wavelength range and use cavities to increase the effective interaction with a sample volume ~ 100 ml.

We have been developing TLAS systems that utilize a hollow fiber optic waveguide as its central gas cell, in a concept we refer to as a capillary absorption spectrometer (CAS) [1]-[5]. The hollow fiber is glass or plastic capillary with an internal diameter ranging from ID = 0.2 to 1.5 mm that is coated on the inside with a reflective coating optimized for Mid-IR wavelengths [6]. The fiber contains the gas under analysis and guides the probe laser beam from source to detector with near unity overlap between the beam and the analyte. The small volume, high interaction between analyte and incident light (i.e., high analytical sensitivity), and overall physical flexibility of the waveguide confer reduced footprint, power, and sample size requirements over related techniques and are directly applicable to field deployments and portable operations.

The CAS concept is now being developed by Guiding Photonics [7] for lab-based analysis, see Figure 1. In this paper we describe a customized version of the CAS sensor for in-situ underwater analysis.

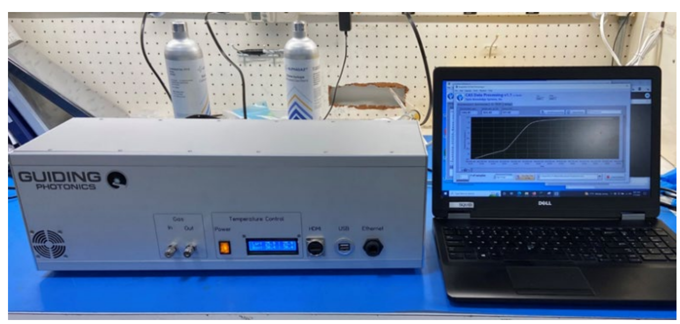

Figure 1. Example bench top CAS system developed by Guiding Photonics (a spin-off company from OKSI).

III. In-situ Underwater Methane Sensor

In general CAS sensor hardware consists of a tunable laser, a hollow fiber gas cell, a detector, electronics, and gas plumbing

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components. For in-situ, underwater methane analysis at depth, we also developed a novel sampling system and packaged the system in a pressure housing. The sampling approach enables measurement of dissolved gases without using a membrane, which are exceedingly difficult to calibrate. Instead, of a membrane the system conducts measurements by taking a discrete amount of water (~ 1 ml) into the pressure housing. This small "slug" of water is introduced into an evacuated chamber, which effectively "degasses" the methane and other volatiles (including water vapor). The small amount of evolved gas is sufficient to fill the hollow fiber gas cell of the CAS sensor, where a laser absorption signal is measured, see Figure 2. The whole system runs off of 24VDC and streams data in real-time via an ethernet connection to a remote operator.

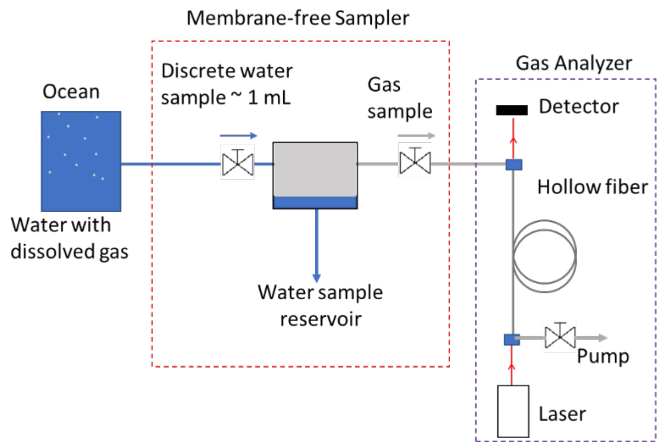

Figure 2. Simplified diagram of system. A membrane-free front end includes a pre-evacuated chamber in which gas is evolved from a water sample. The gas then travels to the CAS system and is analyzed utilizing tunable laser absorption spectroscopy.

IV. Field Testing / Utilization

The underwater methane CAS was first demonstrated on a CTD Rosette analyzing methane concentration in the water column, see Figure 3. The system ran off battery power and communicated with an operator aboard the host ship (Rachael Carson) via a custom 2-wire connection. The system was deployed over a two-day period in June 2021 with CTD casts to various depths at multiple locations in Puget Sound, Washington. A comparison between in-situ measurements and measurements of the head-space of returned water samples are shown in Figure 4. The measurements verified the basic "sea-worthiness" of the sensor, and demonstrated the ability to perform in-situ methane measurements.

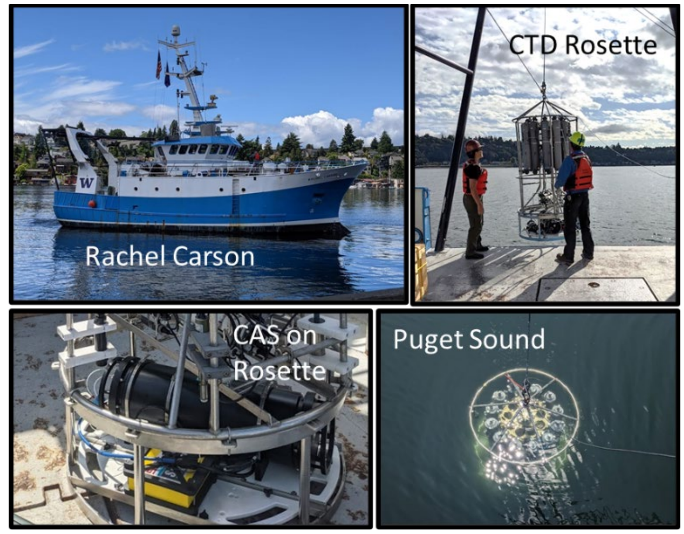

Figure 3. The underwater methane CAS was utilized to measure methane in Puget Sound, Washington in June 2021. The system was mounted on a CTD rosette with battery power.

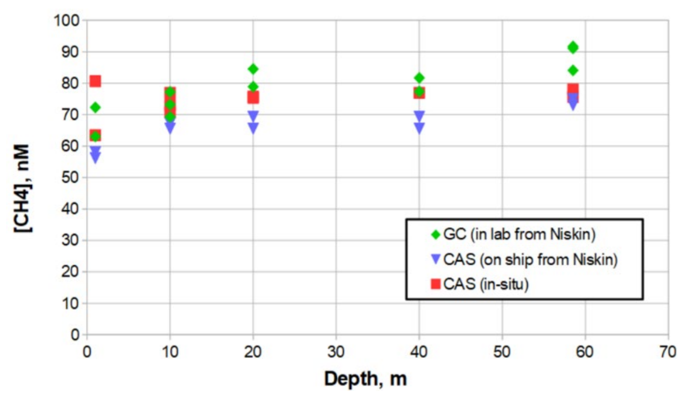

Figure 4. Measured methane concentration for samples at different depths comparing in-situ CAS measurements (red) with CAS measurements of head-space gas of returned samples (blue) and gas-chromatography (GC) measurements of returned samples (green).

Following installation on a CTD, the system was utilized on two different remotely operated vehicles (ROVs) on two different research cruises designed to study deep-sea hydrothermal vents.

For the initial ROV deployment, the CAS was installed on the Jason ROV utilizing on-board 24VDC power and an ethernet connection, see Figure 5. The system communicated directly with an operator aboard the host ship (R/V Thompson), which enabled control and real-time data visualization. In-situ methane measurements at vent sites taken with the CAS from an ROV dive are listed in Table 1. These measurements are shown along-side off-line measurements of returned samples conducted with a GC. The CAS enabled more measurements than was possible with the returned samples including additional samples at one location of interest ("Anemone"), as well as a measurement at an additional location ("Virgin Mound")

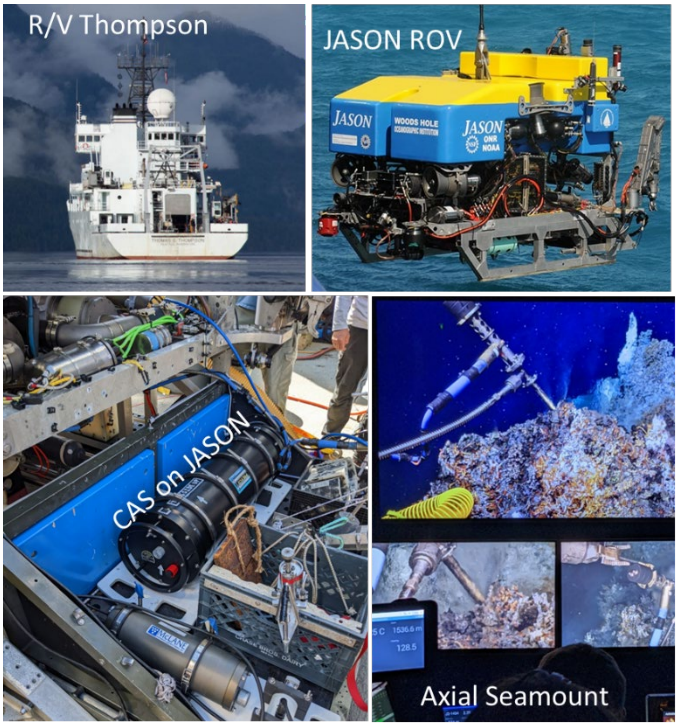

Figure 5. The underwater methane CAS was mounted on the Jason ROV and utilized to measure vents at Axial Seamount in the Pacific Ocean off the coast of Oregon / Washington in July 2022.

Table 1. Data from one ROV dive at Axial Seamount. Comparison of in-situ methane concentration measurements to measurements taken of returned water samples after the dive.

Time of Sample	Vent Name	Methane Concentration	
		CAS In-Situ	GC post dive
18:55	205 – Anemone	8.66 μmol	
19.38	205 – Anemone		4.59 μmol
19:44	205 – Anemone	7.37 μmol	
20:17	205 – Anemone	7.10 μmol	
22:38	Inferno	54.5 μmol	
22:41	Inferno		51.0 μmol
00:59	205 – Anemone	7.15 μmol	
01:11	205 – Anemone	6.72 μmol	
02:40	205 – Anemone		4.99 μmol
03:32	Virgin Mound	125.4 μmol	
04:42	Hell		50.4 μmol
04:42	Hell		96.4 μmol
04:50	Hell	85.6 μmol	

More recently, the CAS was installed on the Subastian ROV, again utilizing on-board 24VDC power and an ethernet connection, see Figure 6. An example, real-time, in-situ methane measurement taken at a vent site along the Mid-Atlantic Ridge is shown in is displayed in Figure 7. In this case, a multi-injection approach was utilized to "stack" methane in the gas cell and increase the signal to noise of the measurement.

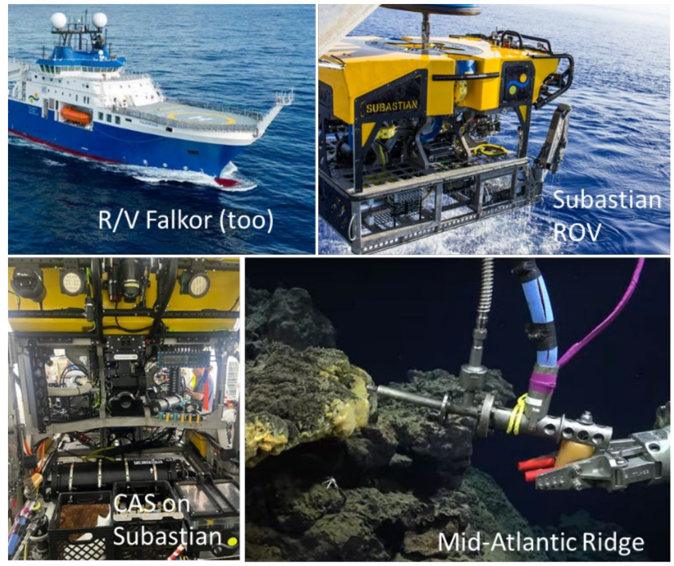

Figure 6. The CAS system was utilized on an ROV in a research cruise at the Mid-Atlantic ridge in March/April 2023.

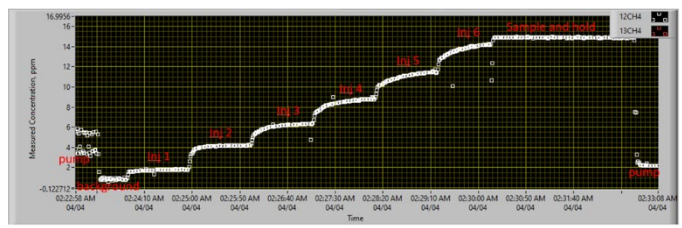

Figure 7. Measured methane concentration versus time at one vent site. For this case, multiple, sequential injections into the water sampling system were collected enabling quantification with each injection along with the ability to increase the amount of methane in the gas cell to improve the signal to noise ratio.

V. Discussion

In this paper we present example utilization of an in-situ methane measurement tool capable of real-time analysis of vents and seeps at depth, as well as the ability to perform measurements in the water column. The system is capable of isotope ratio analysis; however, these measurements are not presented here. We also note that similar concepts are being pursued by researchers at Woods Hole Oceanographic Institution (WHOI) [8].

Acknowledgment

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