First Expeditionary Deployments of the Deep Ocean Raman In Situ Spectrometer

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ABSTRACT

MBARI's *in situ* laser Raman spectrometer (DORISS – Deep Ocean Raman In Situ Spectrometer) was deployed at gas vents in Guaymas Basin, Gulf of California in 2003. The first *in situ* Raman spectra of natural gas venting from the sea floor were obtained. These spectra were compared to GC analyses of samples collected at the same vent and Raman analyses of pure methane deployed as a standard for at-sea testing.

Laser Raman spectroscopy is a powerful technique for analyzing the chemical composition and molecular structure of solids, liquids, and gases. The prototype deep-ocean Raman instrument is based on an off-the-shelf laboratory model from Kaiser Optical Systems, Inc. Engineering test deployments conducted over the past 1.5 years have shown that Raman spectra of high quality can be obtained in the deep ocean. We have acquired spectra from solid, liquid and gaseous specimens deployed as deep as 3600 m in the ocean. We are currently in the next phase of development which consists of using DORISS for exploratory measurements of natural targets in the deep ocean.

During an expedition to the Gulf of California on the R/V Western Flyer in 2003, DORISS was deployed successfully by the ROV Tiburon at natural gas vents on the sea floor (~1582 m depth). Spectra were collected of gas samples at the vent site and at depths above the hydrate stability zone. Bands for methane dominate the spectra. Attempts to collect spectra of natural gas hydrates at the vent were difficult in part due to the stringent positioning requirements of the probe head when analyzing solid, opaque targets. This problem has been addressed by the development of a precision underwater positioner (PUP) that provides a stable platform for analyses and precision movement of the probe head (see following poster OS32A-0236).

The DORISS instrument is divided into three pressure housings :

Spectrometer Housing — spectrometer, CCD and associated electronics

The two sampling optics were used during this expedition (both shown above left):

Stand-off optic – a 10X objective used behind a dome window
- ~3 mm depth of focus in water, 0-10 cm working distance in water
- larger depth of focus provides greater flexibility but lower power density

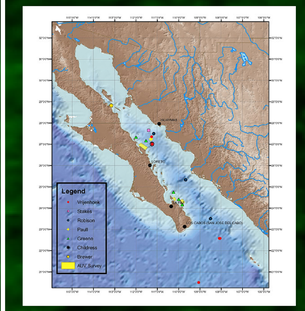
Immersion optic – 2 mm focal distance lens at the end of 10 in. long, 0.5 in. diameter metal tube with a plane sapphire end window protruding through a flat endcap with a gland seal (pictured at right)
- ~1 mm depth of focus, 1-7 mm working distance in water
- higher power density preferred when analyzing gases, but small depth of focus requires precision positioning when used on opaque targets

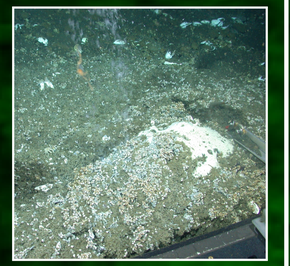
Calibration

DORISS was calibrated routinely during the cruise. The Kaiser calibration kit includes a neon source for wavelength calibration, a tungsten source for intensity calibration, and a cyclohexane standard for laser wavelength calibration. A diamond plate was installed in the laser path within the probe head but off focus. The strong, stable 1332 cm^{-1} line is superimposed on all spectra providing a calibration reference during deployment.

Instrument details can be found in Brewer et al., in press.

Gulf of California Expedition

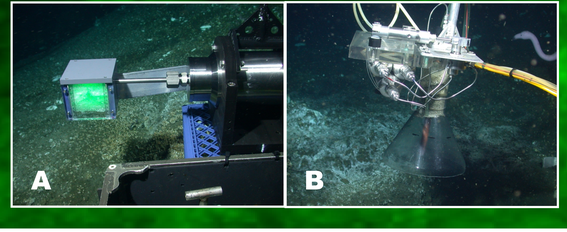




The preferred method of obtaining gas spectra was through use of the immersion optic protruding into an open-bottomed cube (picture A below). Gas was trapped in the cube forming a gas space around the immersion optic (i.e., no seawater was present in the beam path). Both configurations were successful for analyzing gas samples. The one problem was the formation of a partially-opaque hydrate skin on the window of the immersion probe and the glass top of the sampling funnel. This partially blocked both the exiting beam and the backscattered signal, thus greatly reducing the sensitivity. Once the sample was brought above the hydrate stability zone (~585 m depth, ~7.0°C) clean, high quality spectra could be obtained.

Gas Samples

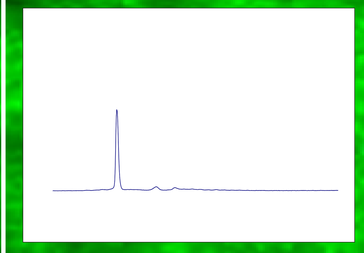
Gas samples for shore based analysis were collected in 150 ml stainless steel cylinders. Three evacuated cylinders were integrated into a sampling funnel with a heating element (picture B below). During sample collection gas hydrate formed in the sampling funnel which could clog the lines to the cylinders. The heating element was used to heat the sample and melt the hydrate. The gas could then be pulled into an evacuated cylinder by actuating a valve. Sixteen samples were collected in this manner. These samples include gas bubbling from the vent, gas bubbles captured above the vent, gas within the sediment, and melted hydrate from within the sediment.



Raman Analysis

Raman spectroscopy, which is capable of identifying covalently bonded gas species, can be used to determine the composition of natural gas [e.g., Diller and Chang, 1980]. The primary constituent of the vent gas was assumed to be methane which has a strong Raman peak at ~2917 cm^{-1} (, vibrational mode), and smaller peaks at 1535 ( ), 3020( ), and 3070 cm^{-1} (2). Non-methane hydrocarbons (NMHC) were also assumed to be present in measurable quantities. Raman spectra of the vent gas were obtained at the sea floor (1582 m, ~3.0°C) and at various depths in the water column using both sampling optics.

Data processing was performed with the GRAMS/AI spectral processing package from ThermoGalactic. The GRAMS peak fitting algorithm deconvolves the peaks, calculates and subtracts the baseline function, and determines peak positions (Raman shift), heights, widths and areas.



Conclusions & Future Work

DORISS successfully obtained *in situ* Raman spectra of natural gas emanating from a vent on the sea floor. As verified by shore-based GC analysis, the gas was composed primarily of methane (~97%). Trace constituents were not present in high enough concentrations to be detected by Raman analysis. Two significant lessons were learned from this expedition. 1) When analyzing gases within the hydrate stability zone, a heater can and should be used to remove hydrate skin formed during collection. This was successfully done for the gas sample collection and would have greatly improved the Raman data collected on the sea floor. 2) Precision position is necessary when collecting Raman spectra of opaque targets (such as solid hydrate, hydrate skin, or rocks). This requirement is dictated by the focal depth of the sampling optics. A new Precision Underwater Positioner (PUP) has been built for this purpose and is described in the following poster (OS32A-0236).

Raman spectroscopy is a powerful analytical tool that can now be used to analyze targets *in situ* in the deep ocean. We plan to continue expeditionary deployments of the DORISS instrument in 2004 during an expedition to Hydrate Ridge and the Cleft Segment of the Juan de Fuca Ridge. At these locations we will attempt to use Raman spectroscopy to analyze gas hydrates *in situ* (using the PUP positioner), and to analyze various targets in hydrothermal vent environments – vent fluids, bacterial mats, sulfides, etc.

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GC Analysis

Methods

Vent gases, some containing decomposed hydrate samples, were collected in stainless steel evacuated cylinders (right) for later analysis. In the laboratory we determined C_1–C_5 hydrocarbons and CO_2 concentrations using a Hewlett Packard, 5890 gas chromatograph with a flame ionization detector (FID) for hydrocarbons and a thermal conductivity detector (TCD) for CO_2. He was the carrier gas at a 36 ml/min constant flow rate. Samples were transferred to a calibrated volume loop (0.1 ml and 1.0 ml) at atmospheric pressure through a glass tube packed with Drierite for water removal before injection into the GC column (2 m Porapak-Q 60/80 mesh). Run conditions were 40°C for 2 min, increasing at a rate of 16°C/min to 200°C and held at this temperature. Calibration was performed using hydrocarbon gas standards of known concentration (Scotty IV calibration gas (HC-MIX #9)). Precision for replicate analyses was ± 0.33 mole% for C_1–C_5 and ± 1.5 mole% for CO_2.

Results

The hydrocarbon gas and CO_2 concentrations measured, and the $C_1/(C_2+C_3)$ ratios are listed in Table 1. The hydrocarbons detected consist of methane to iso-pentane. Methane is the major component (96.7 - 98.8%). NMHC are trace components (<0.28%). CO_2 is 2.7 - 3.2% except for sample T0578 (1.4%). The ratios of $C_1/(C_2+C_3)$ (<10^3) suggest the contribution of small amounts of thermogenic gases. In sample T0578, the material recovered contained both primary gas and hydrate fragments released by sediment disturbance. The hydrocarbon results are similar to the other samples. The presence of trace quantities of iso-C_5, and undetectable n-C_5 suggests some fractionation mechanism. We note that structure-H hydrate could provide this as iso-C_5 can be included in this structure but n-C_5 cannot. However, we have no direct evidence for the presence of this hydrate form. For T0563 and T0573, we see small changes in the concentration of C_1 and CO_2 gases near 5 m and 8-10 m above the vent. This may be controlled by bubble dissolution and rise rate, with the highly soluble CO_2 component (solubility ~10.5 greater than methane) being rapidly lost.

Table 1. Molecular compositions of vent gases and hydrates from the sea floor in Guaymas Basin, Gulf of California.

Dive #	Cylinder	C_1	C_2	C_3	i-C_4	n-C_4	i-C_5	CO_2	$C_1/(C_2+C_3)$	Description
		mole %								
T0563	Red	96.7	0.25	0.042	0.013	0.001	0.003	2.95	332	Main gas vent @ 1 m
	Blue	96.7	0.24	0.042	0.013	0.001	0.003	2.73	344	Main gas vent @ 5 m
	Black	97.3	0.25	0.042	0.013	0.002	0.003	2.88	333	Main gas vent @ 0 m
T0566	Red	98.0	0.25	0.041	0.013	0.002	0.003	2.91	337	Main gas vent @ 0 m
	Blue	97.6	0.25	0.269	0.062	0.052	0.009	2.94	188	Main gas vent @ 0 m
	Black	97.5	0.25	0.283	0.065	0.053	0.009	2.95	182	Duplicate of Blue
T0573	Red	97.4	0.27	0.078	0.017	0.002	0.004	3.15	283	Main gas vent @ 0 m
	Blue	97.0	0.26	0.077	0.017	0.002	0.004	3.06	290	Main gas vent @ 2-3 m
	Black	96.9	0.27	0.080	0.018	0.003	0.004	3.08	281	Main gas vent @ 8-10 m
T0576	Red	98.1	0.25	0.083	0.019	0.003	0.004	2.81	297	Sediment gas bubbles
	Blue	98.1	0.26	0.078	0.017	0.003	0.004	3.11	290	DORISS excavation vent
	Black	98.8	0.26	0.082	0.018	0.003	0.004	2.91	293	3rd sample from disturbed site
T0578	Red	98.4	0.26	0.077	0.016	0.002	0.004	3.04	295	Small vent as DORISS
	Blue	97.8	0.26	0.077	0.017	0.002	0.004	3.09	293	Main gas vent
	Black	98.4	0.26	0.077	0.017	0.003	0.004	3.03	294	Duplicate of Blue
T0582	Red	98.2	0.17	0.118	0.027	0.006	0.008	1.43	337	Sediment gas + clathrate

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Background Image: The 532 nm green laser of DORISS illuminates a cube filled with natural gas hydrate from a deep-sea gas vent at Guaymas Basin during the 2003 MBARI Gulf of California Expedition.