

**ABSTRACT**

MBARI’s new laser Raman spectrometer (DORISS) — Deep Ocean Raman In Situ Spectrometer — was deployed at gas vents in Guaymas Basin, Gulf of California in 2003. This spectrometer has a dual laser system with 532 nm (green) and 633 nm (red) lasers. Two laser beams with different frequencies were used to collect Raman spectra of gas bubbles and natural gas seeping from the sea floor. Laser Raman spectroscopy is a powerful technique for analyzing the chemical composition and phase changes of materials in a real-time and non-invasive manner. The DORISS instrument was designed and fabricated in-house at MBARI and includes a special design that allows for compactness and ruggedness. The instrument was deployed near a gas vent in the Guaymas Basin, and the spectra were collected using the 532 nm laser, while the 633 nm laser was used to collect spectra of natural gas venting from the sea floor. The instrument was successfully deployed on multiple occasions during the 2003 Expedition to the Gulf of California.

**Gulf of California Expedition**

During the Spring of 2003 on the RV Western Flyer and R/V Research Vessel in the Gulf of California, Mexico, we conducted Leg 5 of the expedition (April 21 – May 11). Several ROV dives to this site we attempted to analyze natural gas seeping from the sea floor. Methane which has a strong Raman peak at ~2917 cm⁻¹ is present at ~97%. Non-methane hydrocarbons (NMHC) were also assumed to be present in measurable amounts. Changes in the position and intensities of the gas bands correlate changes in gas composition. The report includes a list of all spectra obtained during the expedition and a discussion of the results.

The high intensity spectra were collected with the immersion optic after the sample was raised above the hydrate stability zone (such that the hydrate skin formed around the gas vent was digested). The optical path length of the immersion optic was ~2.5 cm. The spectra were collected in situ at the site where the two spectral windows are joined. There are three main observations for this data:

1. In situ analysis is the only technique that has been identified in the spectra to date. While other high-resolution technologies may be present, they may not be at high enough concentrations to be detected by Raman spectroscopy.
2. Changes in the position and intensities of the gas bands correlate changes in gas composition. The report includes a list of all spectra obtained during the expedition and a discussion of the results.
3. The high intensity spectra were collected with the immersion optic after the sample was raised above the hydrate stability zone (such that the hydrate skin formed around the gas vent was digested). The optical path length of the immersion optic was ~2.5 cm.

**Conclusions & Future Work**

DORISS successfully obtained signatures of trace gas composition in a high light or dark background. The spectrometer was successfully deployed on multiple occasions during the 2003 Expedition to the Gulf of California. The instrument was designed and fabricated in-house at MBARI and includes a special design that allows for compactness and ruggedness. The instrument was deployed near a gas vent in the Guaymas Basin, and the spectra were collected using the 532 nm laser, while the 633 nm laser was used to collect spectra of natural gas venting from the sea floor. The instrument was successfully deployed on multiple occasions during the 2003 Expedition to the Gulf of California.

**GC Analysis**

**Methods**

The specific Raman signature of pure components such containing decomposed hydrate samples, were collected in stainless steel evacuated cylinders (~2917 cm⁻¹ for hydrates, ~1332 cm⁻¹ for ethane, 3198 cm⁻¹ for methane). A gas chromatograph (GC) and mass spectroscopy (MS) were used to determine the composition of natural gas samples obtained from various sites. The GC-FID (flame ionization detector) and MS (mass spectrometer) were used for gas chromatography and mass spectrometry, respectively. MS was used to confirm the presence of methane, ethane, and propane. The GC was used to determine the presence of other hydrocarbons such as C4-C6 hydrocarbons. The GC was used to detect the presence of chlorinated compounds in the sample.

**Results**

The results were divided into two categories: primary and secondary. The primary results are based on the analysis of the sample gas venting from the sea floor. The secondary results are based on the analysis of the decomposed hydrate samples. The high intensity spectra were collected with the immersion optic after the sample was raised above the hydrate stability zone (such that the hydrate skin formed around the gas vent was digested). The optical path length of the immersion optic was ~2.5 cm. The spectra were collected in situ at the site where the two spectral windows are joined. There are three main observations for this data:

1. In situ analysis is the only technique that has been identified in the spectra to date. While other high-resolution technologies may be present, they may not be at high enough concentrations to be detected by Raman spectroscopy.
2. Changes in the position and intensities of the gas bands correlate changes in gas composition. The report includes a list of all spectra obtained during the expedition and a discussion of the results.
3. The high intensity spectra were collected with the immersion optic after the sample was raised above the hydrate stability zone (such that the hydrate skin formed around the gas vent was digested). The optical path length of the immersion optic was ~2.5 cm.

**References**


**Abbreviations**

GC: Gas chromatography

MS: Mass spectrometry

Raman: Laser Raman spectroscopy

GC-FID: Gas chromatograph - Flame Ionization Detector

MS: Mass spectrometer

GC/MS: Gas Chromatography/Mass Spectroscopy

GC/FID: Gas Chromatograph - Flame Ionization Detector

**Figures**

Figure 1: Schematic diagram of the DORISS instrument.

Figure 2: Spectra of natural gas venting from the sea floor.

Figure 3: Comparison of GC and Raman results.

Figure 4: Mass spectrometry results of gas samples.

Figure 5: Raman spectra of natural gas venting from the sea floor.

Figure 6: Gas chromatograph results of gas samples.