# Two Generations of Deep-Ocean Raman In-Situ Spectrometers

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Lessons Learned While Optimizing Instrument Robustness and Sensitivity

Geochemical explorations of the deep ocean have historically relied on samples recovered from surface ships, manned submersibles and remotely operated vehicles (ROVs). These samples are then processed using ship or shore-based analysis. During recovery, these samples are exposed to changes in pressure and temperature, which may alter their geochemical composition. Advances in scientific instrumentation, measurement techniques and deep-ocean submersibles now allow for in-situ detection and analysis. One such technique, Raman spectroscopy, has been successfully adapted to provide in-situ geochemical analyses in the deep ocean. Over the last several years, scientists and engineers at the Monterey Bay Aquarium Research Institute (MBARJ) have successfully developed and deployed two generations of deep-ocean (4,000-meter) laser Raman spectrometers. This article describes the engineering approach taken to build these systems, the challenges faced during development and solutions to these challenges.

## Raman Spectroscopy

Raman spectroscopy is based on the principle of Raman scattering. When light hits a target, most photons are elastically scattered. A very small fraction of the photons-about one in 10 -are inelastically scattered. The energy shift of the scattered photons is equal to the change in the vibrational energy of the target molecule. This shift provides both a "fingerprint" of the target and information about the molecular structure and atomic environment.

Raman spectroscopy is a rapid, nondestructive technique requiring little, if any, sample preparation. Most importantly, perhaps, is that it is effective for interrogating liquids, solids and gases. For deep-ocean studies, samples can be measured undisturbed by changes in temperature, pressure or redox (which commonly affect recovered samples). Raman spectroscopy provides new opportunities for advanced sensing of chemical processes in the ocean with applications to methane hydrates, hydrothermal vent minerals and fluids, and gas fractkmation studies.

There are several challenges to using Raman spectroscopy in the deep ocean. The first challenge is to package a spectrometer designed for lab use for deployment on a submersible-this includes both a durable pressure case and providing a watertight pass-through for the electrical and fiber optic connections. The optic bench of the spectrometer is precisely aligned. Thus, it is important to counteract the effects of changing pressure during deployment, which can alter the alignment if the optical bench is tightly coupled to the pressure case, Changes in temperature also cause spectral shifts, which will change the wavelength calibration, making it important to monitor and stabilize temperature as much as possible.

An additional challenge to using this technique in the deep ocean is maximizing instrument sensitivity. The Raman return signal is very weak. It can be easily drowned out by stronger signals, such as fluorescence. Increased instrument sensitivity allows for the detection and determination of trace components. MBARI's current ocean-going instrument can identify pure gases or liquids, but determinations of trace components in those gases or dissolved in liquids are limited. At present, only sulfate can be observed at natural concentrations in seawater. Unfortunately, the highly important carbonate system is below detection limits. A more sensitive instrument requires shorter acquisition times. Currently, Raman spectra are acquired by averaging multiple scans to increase the signal to noise ratio. The accumulation time per scan and number of replicate scans are balanced against the practical limits of detector saturation and time available to take measurements. ROV time is precious, so the faster that spectra are acquired, the more samples that can be analyzed.

## Deep-Ocean Spectrometer

The idea of developing a laser Raman spectrometer as an ROV-deployable instrument was first proposed at MBARI in 1999. In order to demonstrate proof-of-concept, the project team decided to convert a commercial laboratory instrument for use in the deep ocean. Based upon specifications of size, weight, spectral resolution and ease of use, a Kaiser Optical Systems Inc. (Ann Arbor, Michigan) spectrometer (Holospec f/1.8i) was chosen for this work. The instrument was repackaged into three separate pressure housings. The design of an Lshaped pressure case to house the optical bench and spectrometer camera provided the greatest engineering challenge.

The first Deep-Ocean Raman InSitu Spectrometer (DORISS) was operated for three years. The success of this original system provided the motivation to build a second-generation instrument (DORISS2). The project team established several re-design goals, including easy maintenance, robust operation, weight reduction and increased system sensitivity.

Like DORISS, DOR1SS2 is comprised of a commercial spectrometer (NRXN-E) from Kaiser Optical Systems, a laser, a local computer and a custom power supply-all of which are mounted in one titanium pressure housing. In addition, a separate titanium pressure housing holds the probe head, which consists of optics and filters and is mounted on a translational stage. Fiber optic cables connect the two housings. The system includes two fibers: an excitation fiber (which delivers the light from the laser to the probe head) and a collection fiber (which returns the scattered light collected by the probe head to the spectrometer).

The DORISS2 spectrometer is a U-shaped optical bench. The charge-coupled device (CCD) camera from Andor Technology (South Windsor, Connecticut) has a 2,048 x 512-pixel array and is back illuminated, which results in greater sensitivity. The excitation light is generated by a 532nanometer wavelength, 100-megawatt laser head from Coherent Inc. (Santa Clara, California). The laser and power supply are mounted on a large heat sink which is actively cooled. Environmental sensors (temperature and humidity) are mounted within the spectrometer, on top of the computer stack and near the laser head. A local (bottom-side) computer communicates with the laser, the CCD camera and a top-side shipboard computer via Ethernet through the ROV tether.

The spectrometer and other internal components are mounted on isolation pads and carried on a custom frame that reduces the possibility of physical distortion of the optic bench from vibration or dimensional changes caused by pressure effects on the main housing. The spectrometer's elongated U shape makes it possible to use a cylindrical pressure case design. This redesign led to a lighter 4,000-meter-rated pressure housing. The previous deep-sea spectrometer system, DORISS, consisted of three pressure housings, whereas DORISS2 requires only two housings. Reducing the number of pressure housings in the system results in a 90-pound reduction in weight. The system can now be deployed on vehicles that have a more restricted payload. The DORISS2 system mounts in the rear of the ROV, and the probe head is typically mounted forward of the vehicle in a horizontal or vertical orientation, depending on the target of interest.

The DORISS2 system corrected a number of technical deficiencies from the DORISS prototype, such as ease of maintenance and robustness. However, early tests of the DORISS2 system did not yield the expected gains in sensitivity and performance desired.

The lack of sensitivity measured in DORISS2 was quickly attributed to the custom fiber optic cables. A 100 micrometer multi-mode fiber is used to collect the returning scattered light. The 100 micrometer fiber is not currently an industrial standard and, thus, is unsupported by subsea connector and cable manufacturers. The original cables were comprised of two single fibers, each in an extruded plastic sheath for protection. The fibers were then bundled in a free-flooding harness. The fibers performed well when newly assembled, but were not robust enough to survive the rigors of long-term ROV work. The losses through the fiber appeared to be caused by uneven pressure effects on the protective sheathing. The lack of robustness, degrading performance and high maintenance cost, motivated the project team to pursue a new cable design.

Fiber Optic Cables

The next step was to build a seawater-tight, rugged, easily handled cable that had a depth rating of 4,000 meters. DORISS2 requires an excitation fiber of 62.5/125 um (fiber diameter/outer diameter with cladding) and a collection fiber of 100/140 micrometer. A rigorous vendor search yielded no such product.

Engineers and technicians at MBARI designed and fabricated a prototype oil-filled fiber optic cable. The cable consists of two sets of excitation and collection fibers for redundancy. During lab pressure testing of the oil-filled cables, the measured attenuation was less than three decibels at 4,000 meters, compared to attenuation of 25 to 30 decibels with the original cables. The prototype fibers performed well in sea trials, so the team started on a more robust, consolidated design.

The cable's final version is 10 meters long, has 12 copper conductors and two pairs of optical fibers. The fibers are protected by a flexible, half-inch-diameter, hydraulic hose of steel mesh outer and Teflon inner tubing, which withstands the rough handling it might see on the ship's deck or by the ROV's manipulator arm.

Cable Testing Results

The new oil-filled cables dramatically improved the overall system performance. The cables' performance was evaluated in the field by comparing acrylic spectra taken on two different ROV dives-one dive with the old cables and one with the new oil-filled cables.

By analyzing the collected spectra, the relative performance of the cables over a wide range of depths was determined. On both dives, spectra of an acrylic target were collected at multiple depths, including 500 and 1,000 meters. A majority of the signal loss occurs between 500 and 1,000 meters, although the performance continues to degrade with depth. In general, the performance does not degrade significantly between zero to 500 meters.

By comparing acrylic peak heights, it is apparent that 70 percent of the signal present at 500 meters was lost at 1,000 meters due to pressure-related attenuation in the original cables. By comparison, only 20 percent of the signal is lost between 500 and 1,000 meters with the new oil-filled cables.

Field Programs

For the initial field trials, transparent targets were selected that did not require fine focusing. In this way, disproportionate dissolution of artificial gas mixtures were observed versus time in the deep sea.

As the observational capabilities increased, more ambitious targets were pursued. Natural samples of methane hydrate were persued in situ at Hydrate Ridge (off the coast of Oregon), hydrothermal mineral formation on Gorda Ridge (also off the coast of Oregon) and at a barite formation in Monterey Bay. More recently, the fractionation of a complex mixture of hydrocarbons during the formation of methane clathrate have been investigated during a controlled seafloor experiment. In August 2006, scientists and engineers worked off the coast of Vancouver Island, Canada, in Barkley Canyon using DORISS2 and the oil-filled fiber optic cable assembly. Raman spectroscopy was used to identify the constituents of large hydrate mounds.

Conclusions

Following on the early success of DORlSS, the project team carefully considered the weaknesses, challenges and lessons learned using laser Raman spectroscopy on extended cruises and in the deep ocean.

The results of that effort led to the second-generation instrument (DORISS2) that improves upon the capabilities of DORISS. The changes included a new rugged optical bench on thermal and vibration isolation, a more sensitive camera and new oilfilled fiber optic cables.

Sea trials proved that the new cable assembly has very limited attenuation at depth. In the future, it is hoped that a new, smaller probe head will be incorporated to look at ways to extend the functionality to examine fluorescing media.

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