**Lessons learned while optimizing instrument sensitivity in deep ocean Raman spectroscopy**

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Over the last several years, scientists and engineers at the Monterey Bay Aquarium Research Institute (MBARI) have successfully developed and deployed two generations of deep ocean laser Raman spectrometers. Laser Raman spectroscopy, a type of vibrational spectroscopy based on Raman scattering, allows the non-invasive interrogation of geo-chemical targets *in-situ*. There are many advantages to this type of spectroscopy: it is rapid, non-destructive, and can be used to analyze solids, liquids and gases. Unfortunately, one of the disadvantages of using Raman spectroscopy is that it is a very weak signal, only 1 in 10,000,000 photons is Raman scattered. Thus, it can be very difficult to detect dilute chemical compounds in solution, such as bicarbonate and carbonate ions at natural concentrations. The Raman spectra can also be drowned out by other stronger signals such as fluorescence or ambient light. Once the project team had succeeded in building a spectroscopy system suitable for the deep ocean, the next challenge became improving the sensitivity of the instrument. This paper will discuss the efforts we have made to increase the sensitivity of our second generation Deep Ocean Raman In-Situ Spectrometer (Doriss2) and the lessons learned along the way.

Doriss2 consists of a commercial off-the-shelf spectrometer from Kaiser Optical Systems Inc. that has been re-packaged for use in the deep ocean. The instrument consists of a 532 nm (green) excitation laser, a holographically filtered probe head with interchangeable optics, a U-shaped spectrometer, and a CCD camera from Andor Technology. All of these components are mounted within a titanium pressure housing rated to a depth of 4000m. The pressure case and spectrometer is an appropriate size and weight to be carried on either of MBARI's ROVs.

In developing this second generation instrument, we incorporated new components which improved system performance. One such improvement was the use of a back illuminated CCD camera which is much more sensitive than the original front illuminated CCD camera. Additionally, we have tested a new probe head which is both smaller and has greater light throughput. However, the element which will have the most impact on system sensitivity is a set of new custom-made fiber optic cables. Due to the unusual size of our collection fiber optic cable (multimode 100/140 micron), we were unable to find a suitable off-the-shelf pressure rated cables or connectors. We built several sets of custom fiber optic cables, but despite our efforts, their performance degraded substantially over time. Furthermore, they were very fragile which made using them in a marine operations environment quite perilous. Recently, we have produced a new oil-filled pressure compensated fiber optic cable which performs far better in pressure testing and is much more robust. At 6000 psig, this cable shows losses of only 2-3 decibels versus previous cables where losses of 25-30 decibels was common. This new fiber optic cable will be field tested in May and the results of this test deployment will be presented.

The complete system will be deployed in August in Barley Canyon for the purpose of investigating exposed methane clathrate hydrate deposits *in situ*. The great advantage to studying these outcrops in situ is that we will be able to investigate the hydrates in their natural state without alterations caused by decomposition or degassing such as occurs when samples must be recovered for analysis in the lab.  Results from these studies will be presented as an example of the performance capabilities of the new instrument.