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Recent Advances in Deep-Sea *in situ* Geochemical Measurements by ROV Deployed Laser Raman Spectroscopy

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ABSTRACT

Raman spectroscopy is a valuable analytical technique for making *in situ* geochemical measurements.[1,2] It is applicable to liquids,[3] solids[4] and gases;[5] requires little or no sample preparation; and is rapid with typical analysis times of several minutes or less.[6] These features combine to make it an ideal technique for deployment and use on remotely operated vehicles (ROVs) in a variety of applications.[7]

We report here results from our second generation laser Raman spectrometer (DORISS2). Our new pressure compensated fiber optic cables have increased the signal intensity at 1024m depth from 8% of maximum signal intensity to 88% of maximum, greatly reducing the time required to acquire a sample spectrum and allowing detection of lower concentrations of sample components.

The development of a single axis positioner (SAP) has allowed us to use DORISS2 when the payload weight is an issue, in places where the seafloor is too steep to safely deploy our 3-axis precision underwater positioner[8] (PUP), or where operational conditions (such as an overhanging ledge) are too restrictive and PUP would not fit. The SAP adds a new degree of flexibility we have not had and has permitted the analysis of fish scale carotenoids in a live rock fish with no apparent harm to the organism.

HARDWARE DEVELOPMENT

The major engineering challenge was to build a single axis moving stage that was both light enough to be carried by the ROV manipulator and yet when held locked on target is also capable of moving along the laser axis in steps of 0.1 mm or less. Our previous experience with linear actuators when we built PUP[8] revealed that, after minor modifications for use in water, Exlar linear actuators would satisfy our motion specifications so the major portion of our efforts could be directed into the design of a well balanced cradle and handle for the laser Raman spectrometer probe-head. After several trials, we selected a design (see: Figures 1 & 2) that could provide multiple attachment points for maximum flexibility in a variety of applications.

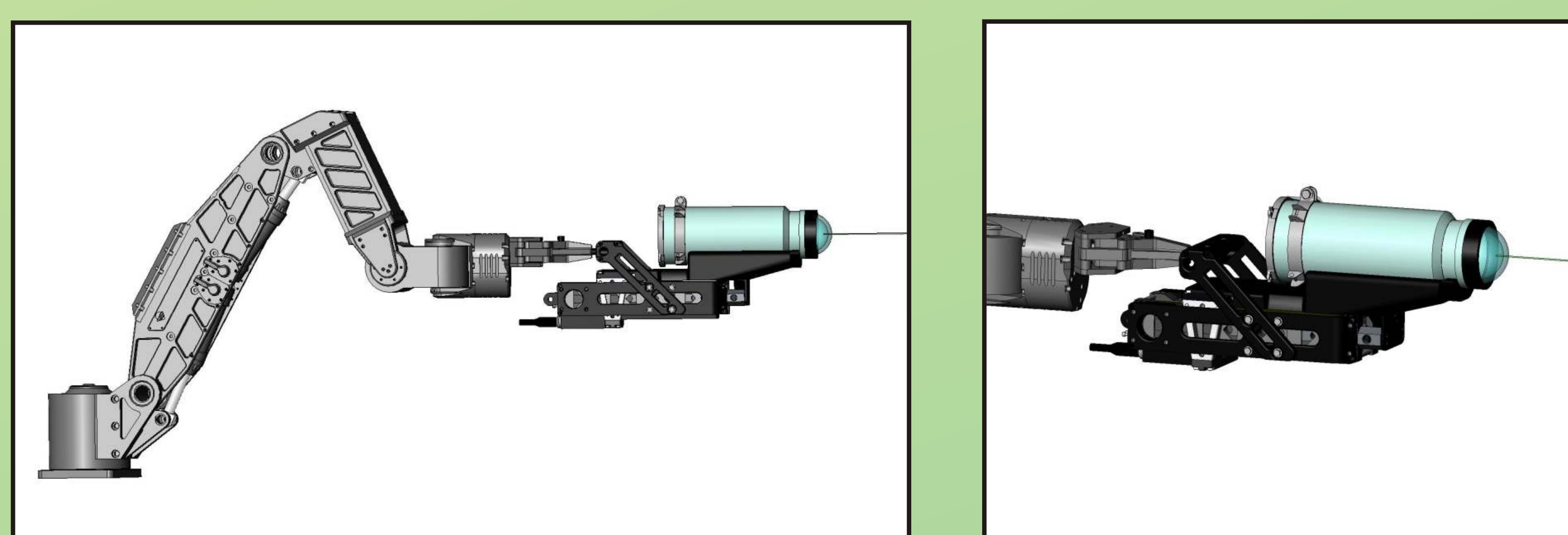


Figure 1. Side-view and close-up of the Single Axis PUP in the grip of the ROV manipulator arm using the “on-axis” handle. The “on-axis” handle provides the most linear arrangement of the several handle options. The manipulator grip is nearly in-line with the laser axis so that wherever the grip points, the laser will point as well. This design allows for a long reach but comes at the cost of a long moment arm which puts strain on the manipulator and when fully extended is sensitive to ROV vibrations.

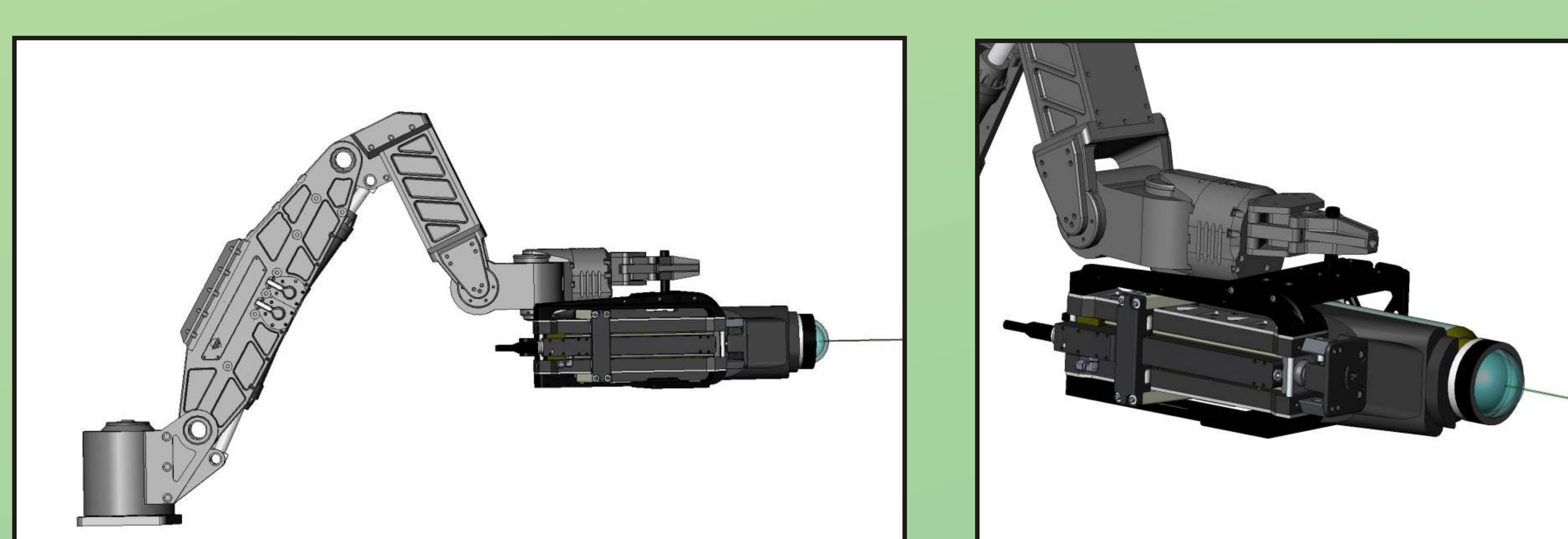


Figure 2. Side-view and close-up of the Single Axis PUP in the grip of the ROV manipulator arm using the "side-mount" handle. The "side-mount" handle provides a balanced arrangement for the probehead on the manipulator arm with the cradle positioned almost directly below the grip. This position has a shorter moment-arm and is less sensitive to vibration but does not have the reach of the on-axis mount. It also requires a somewhat wider approach to the target.

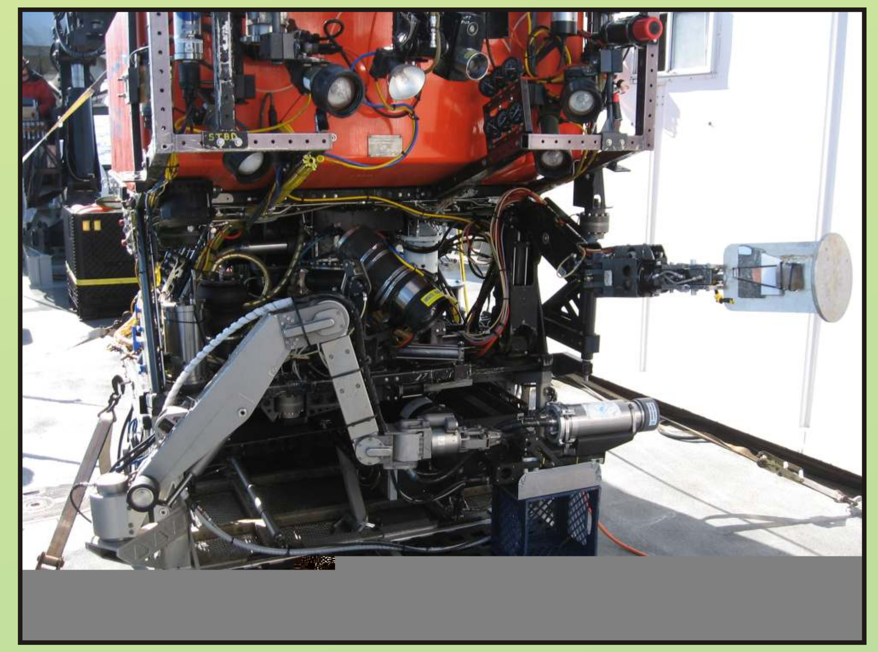


Figure 3. Front-view of ROV Ventana with the Single Axis PUP mounted in the starboard-side manipulator grip. A milk-crate with an aluminum tray provides a temporary saddle for the probehead and cradle to ride on while the ROV is diving to the sea-floor. This takes some of the mechanical load off the manipulator arm and provides a safe stowage position while on the sea-floor. The target tray is clearly visible in the grip of the port-side manipulator arm. Samples of several rock slabs and a silicon wafer are mounted on the target tray for in situ calibration.

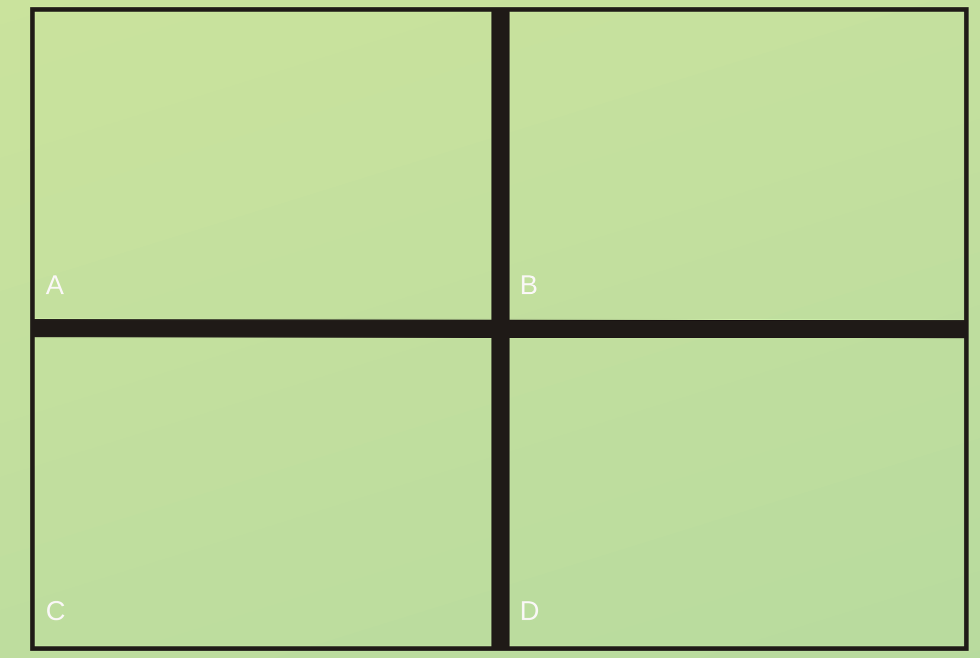


Figure 4. (A) Laser Raman probehead is approaching the silicon wafer specimen on the target tray. In this view the target tray is sitting upright on the sea-floor detached from the ROV to test the effect of ROV vibrations on spectra obtained while the probehead is held in the manipulator grip. (B) Same as figure A but with the ROV lights off so that a Raman spectrum can be collected without interference from the ROV lights. (C) Laser Raman probehead approaching a rockfish on the sea-floor. (D) Same as figure C but again with the ROV lights off.

IN-WATER TESTING

1. MBARI FIBER-OPTIC CABLES

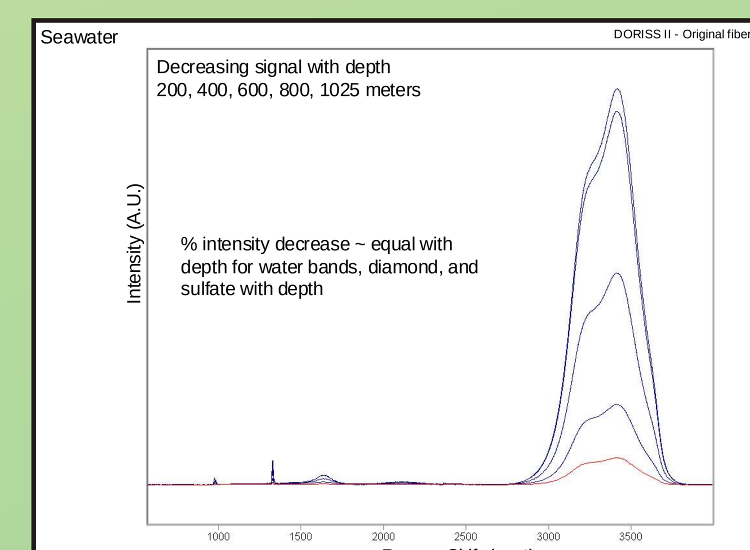


Figure 5. Sequential spectra obtained using DORISS2 with the original polyurethane clad fiber-optic cables showing the reversible attenuation effect of hydrostatic pressure. All spectra are plotted on the same scale.

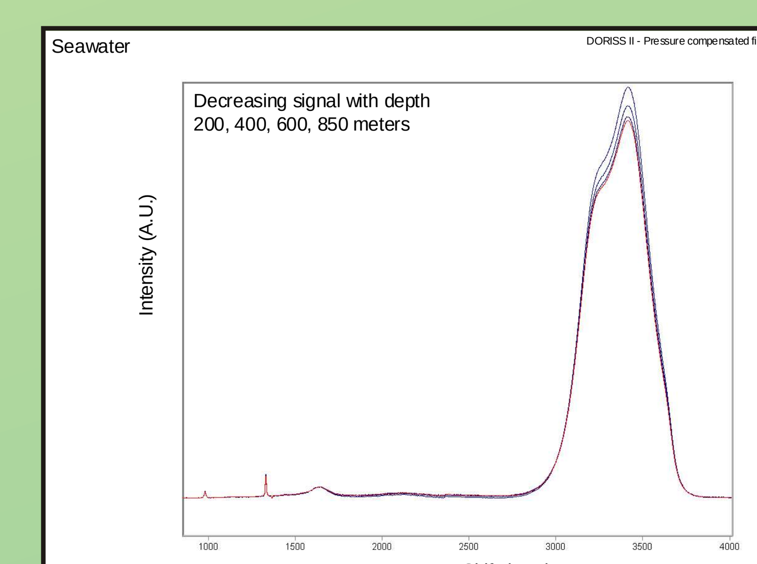


Figure 6. Sequential spectra obtained with DORISS2 using the new pressure compensated oil-filled fiber-optic cables assembled at MBARI that demonstrate only a minimal amount of signal attenuation due to the effect of hydrostatic pressure. All spectra are plotted on the same scale.

2. SINGLE-AXIS POSITIONER

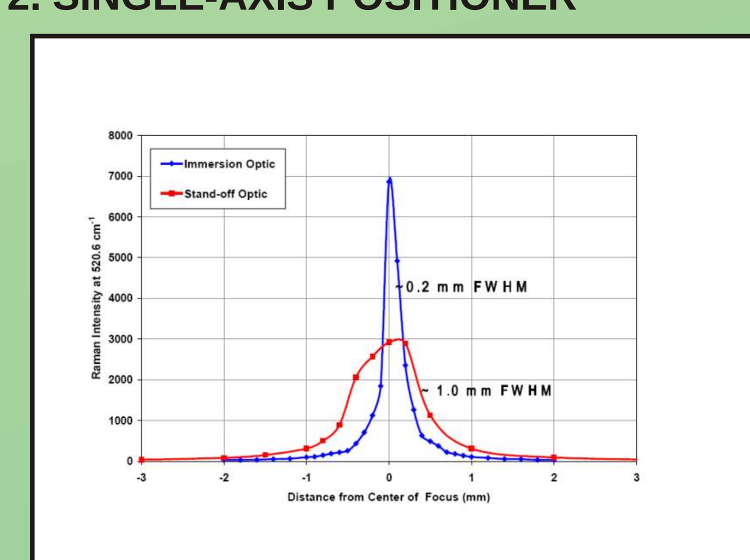


Figure 7. Plot of the depth-of-focus for two of the laser Raman probehead optics. In both cases the very shallow depth-of-focus is readily apparent. While the immersion probe has clearly a shallower depth-of-focus, the greater intensity of the light focused into this shallow volume generates a stronger signal. If focus on the specimen can be achieved this greater energy density yields a much stronger Raman effect and greater signal-to-noise ratios than obtained with the other probehead optic and similar exposure times. The broader depth-of-focus for the stand-off optic makes it easier to place a target in the focal plane but the compromise is the obvious reduction in sensitivity.

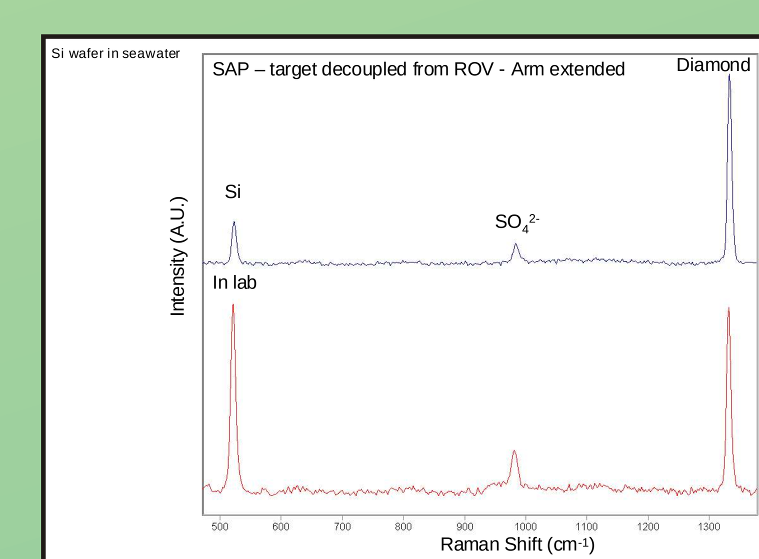
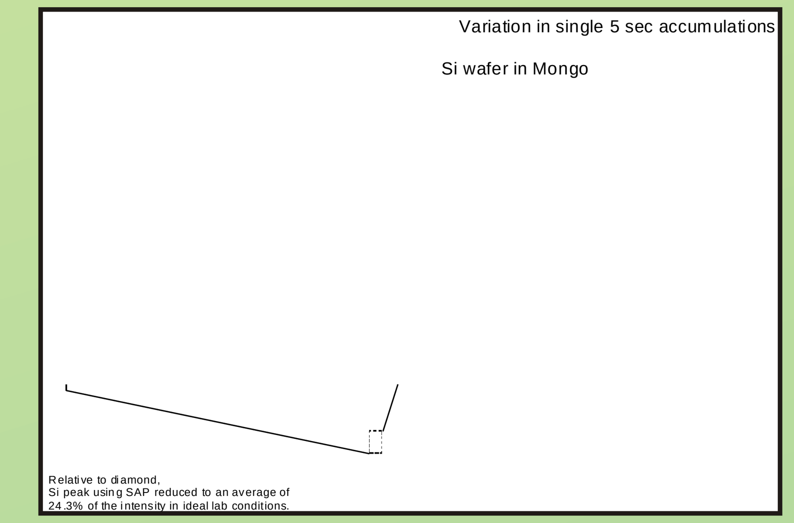
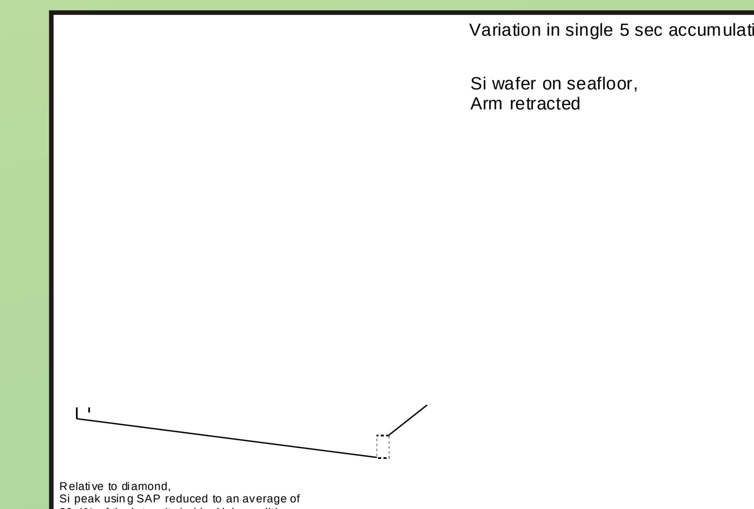
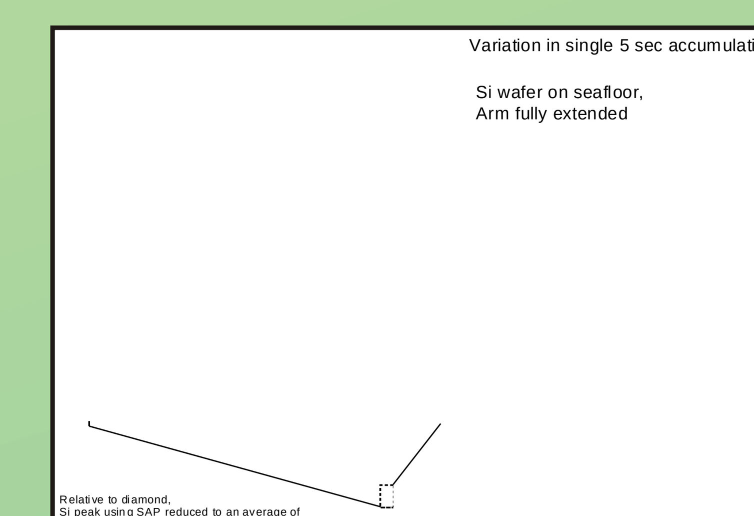


Figure 8. Comparison of two laser Raman spectra of the silicon wafer target. While both spectra were obtained in seawater, the red trace was collected in the lab where a precise placement of the target in the laser beam was easily achieved with a micrometer positioning stage. The blue trace shows the same target but this time the focus was achieved by pointing the laser with the ROV manipulator arm and focusing the target with the SAP at 1000m. The spectra have been scaled so that the peak for our diamond internal standard is the same. While the seawater sulfate peak is about the same the silicon wafer peak is diminished in intensity when the SAP is used to focus the laser on the target.







3. OPAQUE TARGET TESTING

Opaque targets provide the most sensitive test of our ability to focus the laser on the surface of an object. Whereas clear or translucent targets allow for a "soft" focus inside the target material, opaque targets require that the object be precisely within the depth-of-focus. Place an object too close to the probehead and the laser beam is too broad to provide a strong Raman signal and the scattered light is also not in focus for collection and return to the spectrometer. Likewise, place an object too far from the probehead and the laser beam comes into focus too soon and then broadens before reaching the target. Again the light is applied to too wide of a surface area to provide a strong Raman signal. Any scattered light is also not in focus and so it is not efficiently collected and returned to the spectrometer. These two effects work in concert to dramatically weaken the Raman signal when an object is out-of-focus and conversely to yield a dramatically stronger signal as the target is brought into the field of focus.

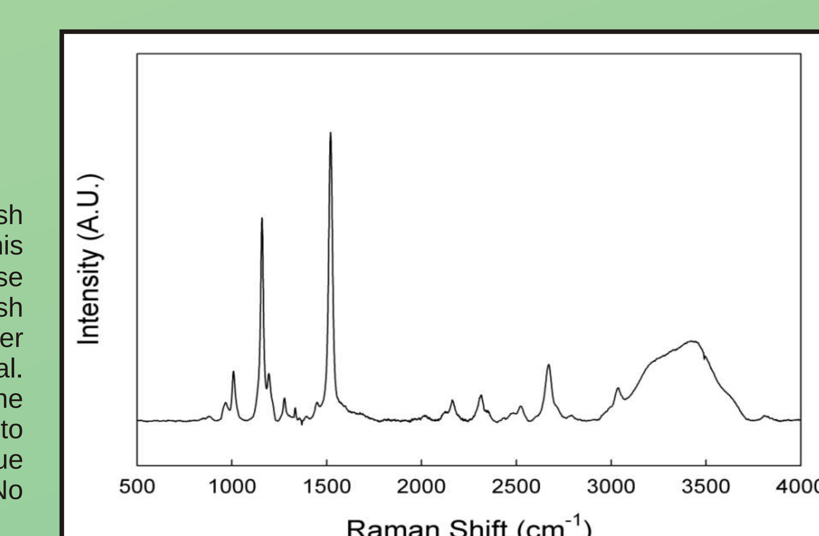
In the top figure at left, we see a spectrum of the silicon wafer target when the SAP is used to focus the laser with the target held in the port-side manipulator. In this position, both the probehead and the target are coupled to the ROV, so vehicle vibrations will tend to be in-sync and barring any resonance effects the probehead to target distance should be nearly constant.

In the middle figure at left, the laser target has been placed on the sea-floor and is de-coupled from the ROV. The target and probehead now move independently of each other. The SAP is used to focus the laser on the target, but the manipulator arm is kept close to the vehicle to minimize the de-focusing effects of ROV vibrations. Even so, we see an increase in scan-to-scan variability of the spectrum caused by vehicle vibrations.

In the bottom figure at left, we have backed the ROV away from the target stand and extended the manipulator arm to maximum reach. This position is a worse case scenario for sample interrogation as it amplifies the effects of ROV vibration. Again the SAP is used to focus the laser on the target and a spectrum is acquired. In this case, the scan-to-scan variability is prominent and visible even in the water Raman peak.

4. FISH SCALE SPECTRUM

This figure shows the laser Raman spectrum of the scale of a live Rockfish collected in situ at 1024m depth in Monterey Bay. The principal bands of this spectra (between ~1000-3200 cm^{-1}) are due to beta-carotene. The decrease in the intensity of the water Raman peak is due to the fact that because the fish scales are partially transparent, we can focus "inside" the scale and less water is in the focusing volume. Less water means less water Raman signal. Generally, the rockfish are quite skittish when approached and swim-off at the slightest provocation. The fact that this fish sat still long enough for us to collect a spectrum suggests that the Raman laser is a non-invasive technique for biological target interrogation that did not cause any discomfort. No rockfish were harmed in the preparation of this poster.



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