Project Number: 600045

Project START year: 2000 Project END year: 2002

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600045 Laser Raman Spectrometer For Deep-Sea Studies

1) Abstract

The proposed year 2002 LRS program is a continuing project to design, configure and field a Laser Raman Spectrometer for use by the MBARI science community in furtherance of their research efforts in the deep Ocean. Initially, the LRS will support the research initiatives of the Ocean Chemistry of the Greenhouse Gases Project. It is however a general purpose measurement tool for advanced ROV deployment allowing for the in situ molecular speciation of many types and forms of chemical and biological samples.

The year 2001 effort has so far resulted in the design, test, fabrication and integration of a state of the art LRS instrument obtained from Kaiser Optical Systems. The instrument was demonstrated to work well in its field configuration in the laboratory. However, on it's first test dive during the last week of July, the pressure vessel containing the spectrometer optical bench flooded causing damage to the lenses and to the CCD camera used to visualize the Raman spectra. This damage is currently being repaired and modifications to the pressure vessel are being made in preparation for a second engineering proof of concept dive, which is scheduled for the last week in October of 2001. Laboratory testing of the LRS has shown that the high pressure tolerant fiber optic interconnecting cables exhibit 5 dB more optical loss than their conventional counterparts, resulting in an in-water system level configuration reduction in detection sensitivity of 10 dB. These losses appear to be due to the pressure-tolerant in-line connectors. Additional work to obtain lower loss pressure tolerant fiber optic cables, connectors and penetrators is required.

The spot size of the probing laser beam is on the order of a fraction of a square millimeter (when using a 2.75 inch focal length set of relay optics) and J.Freeman at WU has determined that the depth of field for maximum sensitivity is on the order of one millimeter. Thus in order for the LRS to be truly usable in deep water research applications, a "through the lens" visualization capability and a precision XYZ positioning

capability are required. Provision of these functions was proposed and authorized for the year 2001 LRS effort. However, these tasks have not yet started and with the need to recover from the pressure vessel flooding incident we will not be able to start them until year 2002. As the LRS methods utilization and development tasks in science proceed, it is anticipated that new optical probe head requirements (different focal lengths and spot sizes) and different sampling techniques (a sampling configuration for determining the molecular composition of pore waters in sediments for example) will need to be designed, fabricated and integrated with the basic LRS.

Obtaining spectral data quality control information is an important part of the evolution of the LRS instrument capabilities if the resulting science data is to be ported/shared between MBARI and other scientific institutions. In situ instrument temperature and humidity measurements will be appended to the measured spectral data obtained from the LRS. Our WU collaborators have suggested that a diamond (insensitive to temperature and pressure) local standard (Zheng et al., 2001) be incorporated in the LRS optical head sensing path so that every spectrogram could have an internal standard for comparison. We will evaluate the feasibility and desirability of incorporating this function in the LRS and implement it if appropriate. Suppliers of fluorescence free diamond chips have been identified, and lab tests are already proceeding at WU.

2) Proposal

a) N/A - continuing project

b) Approach to the problem

The spectrometer components have been purchased from Kaiser Optical systems. MBARI has designed And built pressure vessels in which the spectrometer has been installed. Complete functionality of the spectrometer as installed in the pressure vessels has been demonstrated in the lab subject only to the optical losses mentioned earlier. External communications capability using ethernet communication protocols has been demonstrated. The LRS has been integrated with and been shown to be operational in dockside tests on both the Tiburon and Ventana ROVs. In-water functionality of the LRS at depth will be demonstrated with a scheduled end of October Western Flyer/Tiburon dive.

The major year 2002 new/continuing efforts will consist of:

1. Design, fabrication, test and integration of a "through the lens" white light video visualization system. This capability is necessary in order to identify the precise sample surface/volume being measured. White light illumination is necessary because the use of the already existing monochromatic laser illumination will create images consisting largely of fringe patterns which are very hard to interpret when looking at a video monitor.
2. Design/acquisition of a precision remotely controllable XYZ positioner for use with the spectrometer optical probe head. The spectrometer measurement field of view depends on the exit relay optics used and will generally be on the order of 1 mm or less with the corresponding field depth of focus also being on the order of 1 mm. Spectra acquisition times are on the order of 10s of seconds. Therefore, a capability to deploy the LRS optical head "off vehicle" remote from the ROV is desirable. It is proposed that this function be implemented using an independent free standing structure (so as to remove vehicle vibration and imprecise positioning capability) with a remotely controllable precision XYZ motion capability. It is intended that this positioner be "generic" in it's design so that it can for example support the needs of C. Sakamoto for micro profiling and K. Buck for microscope positioning. We will use as much of the micro-positioning

technology already developed for the semiconductor manufacturing industry as possible and repackage it to work in the deep ocean.

3. A 2 mm focal length pressure-tolerant immersion set of relay optics will be purchased from Kaiser Optical, and designed into a pore water sample cell configuration for insertion into sediments. This configuration will likely require that a new optical sensor head pressure vessel be designed to accommodate the unique mounting configuration of the immersion optic.
4. While it is anticipated that the temperature and humidity sensors will be installed in the optical bench pressure vessel and the electronics pressure vessel in time for the this year October dive, there will be additional software efforts required to present and archive this data for spectogram quality control purposes. An appropriate GUI for this data will need to be developed.
5. The feasibility of incorporating a diamond standard sample in the optical head optical path (Zheng et al., 2001) will be determined. If feasible, this capability will be implemented. There are known, and more importantly yet to be determined, pressure and temperature effects in the measured spectra of Raman active materials as well as anticipated pressure and temperature variations caused by the instrument itself. Fluorescence effects also contribute to the background. The diamond standard will allow these effects to be quantified and the data corrected if needed.
6. Since Raman spectroscopy is a relatively new measurement technique, large libraries of spectrograms currently do not exist. The "methods development" tasks will therefore consist of acquiring and/or measuring the spectra for molecular species of interest to the MBARI science community. In addition, MBARI analysis techniques for interpreting the spectra of multi molecular compounds will be developed in conjunction with outside collaborators.
7. It is anticipated that the spectrometer will be ready for use by the science community early in year 2002. Support for science use of the instrument will be provided and any upgrades needed for the year 2003 Gulf of California cruise designed, fabricated and tested.
8. The LRS configuration and operation will be documented.

All of the above efforts will run concurrently except for the documentation effort which will take place the last month of the year.

References Zheng X., W. Fu, S. Albin, K. L. Wise, A. Javey, and J. B. Cooper. 2001. Self-referencing Raman probes for quantitative analysis. Appl Spectr., 55, 382-388.

c) Specific deliverables

1. A completely packaged and tested LRS will be delivered to science.
2. The "white light" visualization system will be implemented.
3. The precision XYZ positioner will be designed, fabricated and tested.
4. A pore water optical sample head will be designed, fabricated and tested.
5. Fiber optic laser and collection cables with significantly reduced losses will be obtained.
6. Temperature and relative humidity measurement for spectra quality control will be implemented.
7. Incorporating a diamond spectral standard in the optical path will be evaluated and incorporated if it is feasible and desirable.
8. The design and operation of the spectrometer will be documented.

d) Project team

Science related tasks - Dr. Peter Brewer, PI, Dr. Ed Peltzer, Kurt Buck, Dr. Sheri White (organizational affiliation TBD)

Engineering related tasks - George Malby, Project lead, EE design and system integration, Danelle Cline, SE design, integration and test, Mark Brown, ME design, hardware fabrication integration and test.

Tiburon related tasks - Dale Graves and associates

Operations related tasks - Steve Etchemendy and associates

e) Project Lab Space

Integration and test of the LRS components and system is proposed to be carried out in the new ME lab in building B as is currently being done with the year 2001 tasks. The LRS lab area in building G will also be utilized for software development system level tasks and optical subsystem testing and validation.

3) Budget

The following material items will be purchased (buy because MBARI does not have the capability to produce these items in house) during year 2002.

1. 2 mm focal length immersion lens system from Kaiser Optical Systems - model number HPT-IO-D-VIS - $3570.
2. Small pressure vessel for immersion lens/pore water probe optical head from Deep Sea Power and Light - $5000
3. Video camera to interface with existing Holographic Probehead from Kaiser - model number HL5-MVA-532 - $11900
4. White light illumination parts (LEDs, power supply) - $500
5. 20 foot long pressure tolerant fiber optic laser cable and 20 foot long fiber optic collection cable - vendor TBD - $5000 per cable - $10000 total
6. Two bulkhead mounted high pressure fiber optic pigtail cables to mate with items in #3 above - vendor TBD - $3500 per cable - $7000 total
7. XYZ positioner parts (stepper motors, motor controllers, bearings, lead screws, etc) - $5000
8. Diamond for calibration standard - $1000

9 Misc raw stock and electronics parts - $3000

Total purchased items = $41970

Three trips to present TBD papers on the LRS to appropriate TBD symposia.

3 trips - 2 people per trip - $1500 per trip - $9000 total

Two trips to WU at St Louis for training in Raman spectrographic techniques

2 trips - 5 days per trip - 2 people per trip - $1500 per trip - $6000 total

4) Milestones

It is our intention in this early phase to dovetail the engineering and science milestones with the cruise schedule established for the Greenhouse Gases project. This will provide measurement opportunities for full water column profiling and for obtaining relatively simple spectra on CH_4 and CO_2 hydrates, and on saturated solutions. This will require close coordination of effort. Work on obtaining spectra in the presence of background fluorescence is proceeding with colleagues at WU.

	Visualization System	XYZ Positioner	Pore Water Sample Head	Quality Control Measures	Documentation	Total Resources [1] for each resource category for all milestones listed here
Milestone date	11/30/02	9/30/02	7/31/02	8/31/02	12/31/02	
Milestone description	Working System	Working System	Working System	QC Measures Available	Paper work done	
EE	15	30	10	20	15	90
SE	10	30		25	10	75
ME	20	35	15	10	10	90
IAG						
ME Technician	5	20	10	5		40

[1] This number should be same as the number you entered on the resource requests for this particular resource

EE Technician	5	7				12
Machine Shop	10	20	5	5		40