WHOI-88-53

Woods Hole Oceanographic Institution

In-situ Chemical Sensors for Detecting and Exploring Ocean Floor Hydrothermal Vents

Report of a Workshop

Edited by Remy J-C. Hennet
and Jean K. Whelan

November 1988

Technical Report

Support was provided from the Mellon Joint Initiative Award to
"The WHOI Friends of Vents" and from the NOAA, National Sea Grant Program to
The Woods Hole Oceanographic Sea Grant Program
through grant Number NA86AA-D-SG090.

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Approved for Distribution:

David A. Ross, Chairman
Department of Geology & Geophysics

TABLE OF CONTENTS

I. ABSTRACT

Researchers and engineers, from academia, government, and industry, met and discussed the feasibility of using state-of-the-art laboratory technology for in-situ chemical measurements in the deep ocean, in and around active submarine hydrothermal systems. The concept of an autonomous benthic explorer (SENTRY) was presented to illustrate some of the constraints which must be kept in mind when adapting laboratory analytical tools to the deep ocean. A concensus was reached that some existing technologies either are being, or can be, adapted for in-situ measurement, in the near future, at reasonable cost. For many analytical techniques, minimal basic research will be required, and laboratory and in-situ testing represent the bulk of the work to be performed. A selection of analytical techniques appear particularly ready to undergo testing and transformations for in-situ measurements, including: electroplating, voltametry, potentiometric glass electrodes, and fiber optic technologies. Other techniques, such as in-situ Mass Spectrometry, do not appear to meet the criterias of technological readiness for in-situ deployment. Some technologies already being utilized or under development for use in the deep ocean include, for example: CO_2, O_2, H_2, H_2S, CH_4 sensors, voltametry for the determination of sulfur chemical speciation, fiber optic sensors for pH determination, and automated chemical microlaboratories for a wide variety of applications. These techniques, however, require further research for long-term deployment and their ability to perform at high temperature, as encountered around submarine active hydrothermal systems.

II. ACKNOWLEDGEMENTS

This workshop would not have been possible without hard work and outstanding logistical support from Martha Tarafa and the enthusiastic exchange between the workshop participants.

We also thank Joe Cann and "The WHOI Friends of Vents" for their encouragement to organize this workshop, and John Tokar for allowing us to include his Report as an Appendix.

Financial support from the Mellon Joint Initiative Award to "The WHOI Friends of Vents" and from the NOAA National Sea Grant Program to the Woods Hole Oceanographic Sea Grant Program (Grant No. NA86AA-D-SG090) Project No. R/O-7-PD is gratefully acknowledged.

III. INTRODUCTION

The workshop was a successful meeting between academic and government scientists from diverse backgrounds, engineers having expertise in design and deployment of sophisticated instrumentation at the bottom of the ocean, and industrial scientists aware of the availability and cost of state-of-the-art technology. For many participants, the two days' meeting was their first encounter with oceanography. The general feeling at the end of the workshop was that the needs of the oceanographers are not so complicated; the in-situ species and quantities to be measured are generally trivial in the laboratory (pH, metals, non-metals, organics, gases, biological activity, temperature, etc.), and well within the detection limits of available technology. The problems, in further development for oceanographic research, are related to the pressure/temperature conditions, and the difficulty of controlling analytical procedures under water in completely remote areas. Oceanographers actively involved with in-situ measurements had a chance to present and discuss the capabilities and limitations of their pioneering work. Most interestingly, people, who probably would never have met otherwise, discovered they had some common interests and could help each other in resolving problems related to their respective work. It is our hope that these relationships will develop and lead to successful research projects in the near future.

The workshop consisted first of a series of oral presentations designed to bring the participants to a common ground for further discussion. Deployment technology, examples of pertinent previous work, and description of state-of-the-art technology, were presented. Spontaneous speakers volunteered their input which gave rise to lively and thought-provoking discussions. Five working groups were formed, based on a brief "democratic" discussion to select the technologies of greatest interest. Each working group had a leader whose task was to assemble the information discussed, and present it to the workshop at large. The participants were encouraged to contribute their input to more than one working group, and most did. Several participants also contributed additional personal reports to express their view outside the groups. The notes, viewgraphs and reports were collected at the end of the workshop and edited as the present report. The reports have not been reviewed and may contain some inaccuracies.

IV. LIST OF ORAL PRESENTATIONS

1. Introduction
   Remy Hennet

2. Technical Constraints in the Deployment of Sensor Technologies
   Albert Bradley

3. The State-of-the-Art in Sensor Technology: What is Generally Measured Today
   Peter G. Brewer

4. General In-Situ Measurement Needs for Biological Studies
   Craig Taylor

5. At Sea Calibration of ALVIN High-Temperature Probe
   Andrew Campbell

6. Fuel Cell H_2 Sensor
   Frank Sansone

7. Fiber Optic Sensors
   Tom Kulp

8. In-Situ Application of Basic Voltametry
   Donald Nuzzio

9. Electrochemical Applications
   George Luther

10. Oxygen and Sulfide and Other Ion Activity Measurements - A Submersible Chemical Laboratory
    Kenneth S. Johnson

11. Noble Gases/Mass Spectrometry In-Situ
    William J. Jenkins

12. Sensors, Sensor Arrays and Chemometrics
    James Callis

13. Spectroscopic Techniques
    Jeffrey Steinfeld

14. In-Situ Instrumentation for Measuring Primary Productivity and Chemical Species
    Craig Taylor

15. Microinstrumentation - Microelectronics
    David Edell

V. VENT SENTRY - AN AUTONOMOUS BENTHIC EXPLORER

Albert M. Bradley, Woods Hole Oceanographic Institution

Vent Sentry

An Autonomous Benthic Explorer

ABSTRACT: Sentry is an unmanned, untethered, autonomous vehicle for performing a variety of benthic survey experiments (such as vent monitoring). This self-propelled vehicle will be able to acoustically navigate over the bottom with accurate position (within centimeters) and orientation control. The initial vehicle will include digital video, 35mm photography, CTD data logging, and transmissometry, and will have 50-100km. of travel range.

USE CONCEPT: A study site would be surveyed and marked with one or more acoustic beacons. The beacons would have a known relationship to major features of interest. The survey would be done with a submersible such as DSV ALVIN or a tethered system such as ARGO/JASON. In areas of low topography, the site development might be done with a camera sled photo survey within a long baseline net. In flat areas where the study area does not need to be site specific, free drop deployment of the beacons would be sufficient.

After the survey is completed and beacons implanted, Sentry is deployed. Optionally, at a later date after the initial survey results had been carefully studied, the scientific team could return to the site and deploy Sentry. Sentry free-glides under its own control to a spot near the beacon but away from the area to be investigated and drops its "glide wing" descent weights. Sentry then maneuvers itself and latches onto the beacon, where it "sleeps" in a low power mode. At preprogrammed times, or due to event triggering such as an unusual water temperature change, Sentry would perform preprogrammed survey routines.

At a preset time, or on direct command, system failure, or pre-programmed trigger conditions, Sentry would move clear of the beacon and drop its ascent weights for recovery. A satellite transmitter would alert the user and provide a means of locating the Sentry for recovery. Another Sentry (or the same one after servicing) could be dropped to the same location to continue the survey work. The beacons would be designed for a longer deployment life than a single Sentry deployment. After servicing and possibly reprogramming, the recovered Sentry could then be deployed at another monitoring site, repeating a survey pattern it or another Sentry had done several months ago.

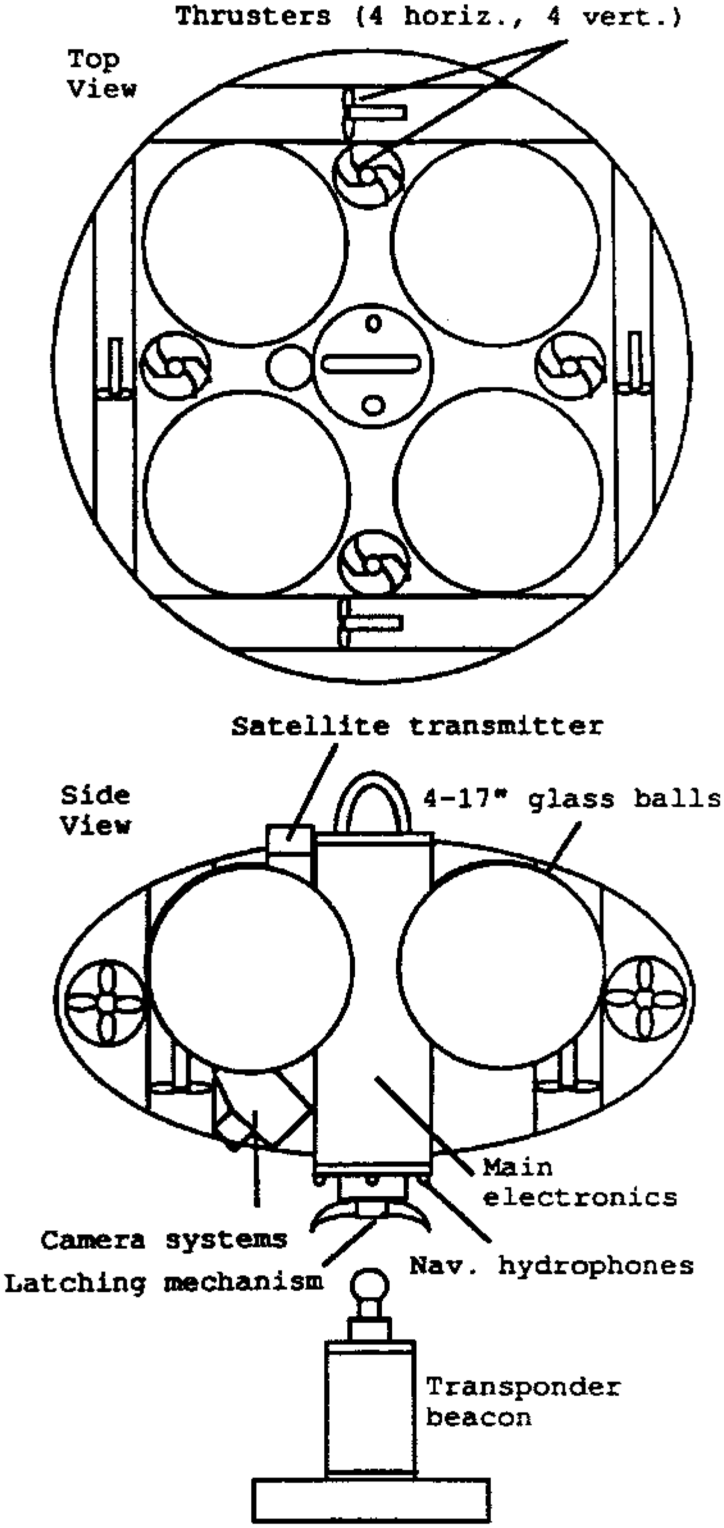
Two of the many possible scenarios for use are short term intensive, and long term overview. In the first type, ships of opportunity passing by the site would drop a Sentry at a pre-surveyed site. The Sentry would perform a fast, intensive survey for hours to days, only using the beacons for positioning information. It would be recovered during the same cruise. In the second type, ships would drop off the Sentry and continue on, with the Sentry being recovered months or years later. Trade-offs include power consumption (mainly distance covered), the amount of data collected, and available time.

POTENTIAL SCIENCE TASKS

Photographic Survey: The simplest yet possibly most valuable task Sentry will be able to perform is a repeated photographic survey of an area. While it is almost impossible to schedule ALVIN (and probably ARGO/JASON) to return to a site at regular intervals, Sentry could revisit sites by being deployed from ships of opportunity. From its "sleep" mode it could wake up at intervals and make repeated video and photographic surveys over a large area. For instance, it could circle a hot vent at intervals for several months to record development of physical structure.

Chemistry survey: With a long-term sensor package installed, the Sentry would be able to perform simple analysis at pre-specified locations within its survey area.

Plume Studies: Sentry could survey a vent plume and its evolution by periodically releasing from its bottom attachment point, adjusting to positive buoyancy, and slowly ascending as it follows the current. Using its navigation system, it would store the resultant near-bottom current profile. At a preset altitude it would then do a grid survey of temperature, conductivity, transmissometry, and possibly chemical content to outline the vent plume.



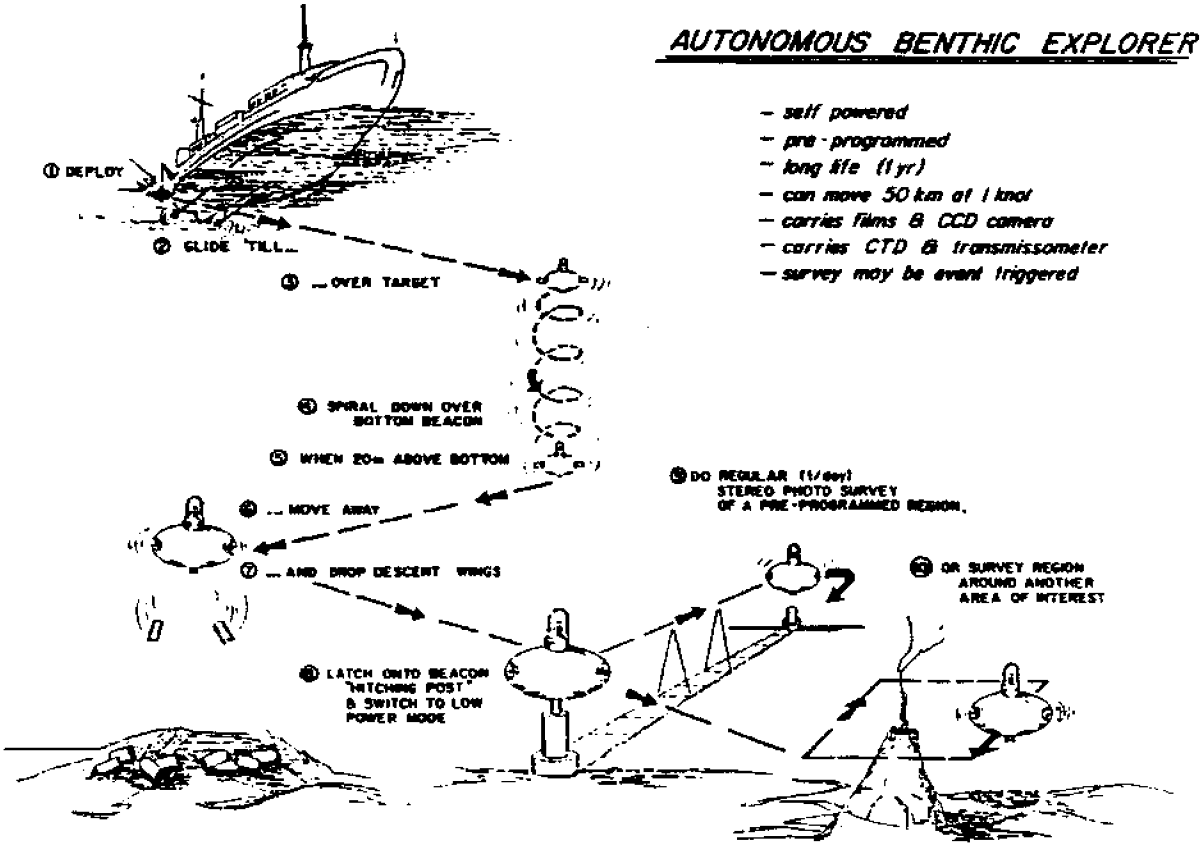
Preliminary design cutaway views

Waste Disposal Monitoring: The Sentry could be used to do long term photo and chemical surveys of existing disposal areas. With proper sensors it could check for release of undesirable chemical or radioactive products. If a release was detected, the vehicle could drop its ballast, head for the surface, and transmit warnings via satellite.

EXISTING TECHNOLOGY

Mechanical/Electrical: The primary electrical and mechanical (trim, variable ballast, hydraulics, compensation) systems will be designed and built by the ALVIN Group. Design constraints relating to weight, stability, power efficiency and operational considerations are similar to those of ALVIN despite the decreased size. Proven concepts with known reliability developed from years of experience with ALVIN will be used whenever possible.

Navigation and Control: The electronic control and navigation systems will be designed by the Advanced Engineering Laboratory. A modified short baseline navigation system developed for the "Pop-up" profiler will be used to navigate with one or more beacons. This concept is also currently being developed for use within ALVIN. The system is similar to the precision high frequency homing system employed for controlling accurate surfacing of the "Flying-Fish" profiler. Since Sentry is intended to be readily modifiable for future needs, a distributed processing system will be used. This allows the addition or removal of scientific subsystems with minimal impact on the high level control programming. The "top level" program used to control each deployment will be written in a simple, BASIC-like language to facilitate user modifications.



SCIENCE INPUT NEEDED

The design, construction and initial testing of this vehicle is expected to take two years. In order to gain the operational experience necessary to efficiently accomplish the expected tasks of the RIDGE program, funding must be obtained now to move beyond the concept stage. If you think your RIDGE program could use an instrument such as Sentry, **YOUR PROPOSAL INPUTS ARE NEEDED**. NSF funding for development cannot be obtained without a current scientific justification. If you are currently working on, or expect to have a program in the near future which could use Sentry, please contact us to discuss your needs. **We** are preparing a proposal, but need **your** input.

Send your proposals, ideas and needs to:

Barrie Walden
ALVIN Group, Smith 301
Woods Hole Oceanographic Institution
Woods Hole, MA 02543
(617) 548-1400 x2407
Telemail: B.WALDEN or ALVIN.OPS

Dr. Albert M. Bradley
Advanced Engineering Laboratory, Smith 201
Woods Hole Oceanographic Institution
Woods Hole, MA 02543
(617) 548-1400 x2448
Telemail: A.BRADLEY

Please note that the area code for Woods Hole will change to (508) on July 16, 1988.

SECTIONS VI to X: GROUP REPORTS

VI. REPORT GROUP 1

Electrochemical/Electroanalytical Techniques

Reported by
George Luther

The feasibility of electrochemical measurements in these unique ecosystems was discussed with regard to (1) the type of electrochemical measurement (potentiometry or voltammetry) and (2) the area near the vents [high temperature/high pressure vent or low temperature/high pressure plume].

The consensus was that voltametric methods should be the technique of choice for measurements at high temperature/high pressure as encountered in vent fluids (up to 350°C and 500 atm). The principal reasons for this are (1) the capability of using temperature resistant solid state electrodes; (2) the inherent ability to detect analytes at low concentrations (10-100 nM), and the rapidity of the analyses. For example, the use of Square Wave Voltametry allows rapid determination (1-10 seconds measurement time) of trace metals at the nM level.

At present, there are many materials available for possible in-situ electrodes for voltammetric analysis. These include Au, Pt, Pd, C, Ir-Hg, Ni, W, Ti, Ag, micro-Hg, etc. Such electrodes should be stable for short-term deployment (e.g., one ALVIN dive), and possibly long-term deployments in less hostile environments such as vent plumes, for example. The types of electrodes considered can detect and quantify a vast variety of oxidizable/reducible species and characterize key redox equilibria (e.g., H_2, H_2S, O_2, Fe^{2+}/Fe^{3+}, Ca^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, etc.). The in-situ chemical speciation of sulfur or iodine compounds is also feasible using this technique. In addition, it should be possible to observe and characterize in-situ metal complexes with inorganic and organic ligands, since complexation phenomena quantitatively affect voltametric measurements.

What remains to be worked out for in-situ deployment of voltametry are the details of constructing and characterizing working and reference electrodes for use under high temperature/high pressure conditions. The calibration of the electrodes will also have to take into account other parameters such as ionic strength, dissolved O_2, H_2S, electrode corrosion, etc.; note that some existing equipment can be made self-calibrating.

None of the potential technical problems seem to be insurmountable. For example, electrode corrosion by in-situ H_2S can be prevented by applying appropriate potential to the electrode system to inhibit perturbating sulfide formation. The power supply needed for voltametric measurement lies within the limits defined at the workshop (e.g., 100 or 1000 whr, at any desired volage for the SENTRY system). Furthermore, one advantage of voltametry is that filtering is not required prior to analysis because electrodes are responding to dissolved species only. Perhaps, the first stage of development for in-situ voltametry would be to simply electroplate analytes of interest onto an electrode (deployed in the vent fluid, for example) and analyze the plating in the laboratory (e.g., onboard surface vessel). Laboratory analysis would allow stripping of the electroplated species in selected matrices to enhance detection and/or sensitivity. Note that the amount of a species sampled by electroplating would be proportional to the vent fluid velocity (not diffusion). This simple sampling technique (electroplating) could thus provide valuable background information to help in calibrating and understanding the real-time data obtainable by voltametry. Furthermore, the electrode system to be used for voltametric measurements or simple electroplating could be replaced by an array of micro-electrodes having diverse properties.

Potentiometric glass electrodes were also discussed and can be regarded as an adequate in-situ technique for measurements below about 100°C. Glass electrode sensors for Li^+, pH, Na^+, Cl^-, F^-, and S^{2-}, could be easily constructed for oceanographic research (some of them already exist).

In conclusion, a consensus was reached that electrochemical techniques can be used to study the chemistry of submarine hydrothermal activity. Minimal effort (financial and research) would be required to deploy existing laboratory technology at the bottom of the ocean.

VII. REPORT GROUP 2

Optical and Spectral Techniques

Reported by
Tom Kulp

The diversity of optical and spectroscopic techniques suggests numerous applications to deep ocean measurements. A major limitation, however, is the reluctance of high pressure liquid water to transmit photons outside of a relatively narrow range of visible frequencies (the so-called "blue-green window"). This makes it impossible, for example, to work in the mid-infrared "chemical fingerprint" region unless the species to be analyzed can be removed from the liquid. Otherwise, one is restricted to visible-wavelength techniques. Optical-fiber techniques are generally advantageous for transmission between the sampled region and the detection electronics. Measurement techniques considered are summarized in Table 1.

The following techniques were considered:

1) Nondispersive Infrared
2) Raman Probes for Remote Sensing
3) General Light Scattering Techniques
4) Visible Fluorescence
5) Optical Fiber Sensors
6) Optical Fiber Array Multiplexing

Optical spectroscopy is a diverse field with wide application techniques with regard to their applicability to the following measurements in the deep ocean:

- Quantitation of dissolved gases (i.e., CH_4, CO_2, H_2S, H_2, O_2).
- Quantitation of ionic species at low concentration.
- Quantitation of various organic species.
- Quantitation of mineral species.
- Measurements of microorganisms.

Table 1. Optical and Spectral Techniques

Measurement	Typical Parameters	Technique	Comments
Dissolved Gases	CH_4, H_2S, NH_3, CO_2	Non-dispersive infrared with gas correlation filters	Applicable only to IR active gases, needs purge or membrane technique to partition dissolved gases.
Dissolved Gases	Above + H_2, O_2, $SO_4^=$	Raman Scattering	Requires visible laser, probably diode pumped solid state. Capillary geometry with dissolved gas separation may be necessary.
Particulates, Microorganisms	Bacterial number density; precipitate density	Light Scattering	Best done with laser.
Flow Velocities and Fields	Current speeds and direction	Laser Doppler Velocimetry	Requires visible laser, may have large Rayleigh scattering background.
Temperature	0 to 350°C	Fluorescent Optrode	Relative fluorescence from temperature dependent surface, e.g. Eu/Er - can be multiplexed to yield temperature field fluctuations.
Dissolved Chemicals	H_2, CO_2, O_2, Ionic species	Reactive Optrode with colorimetric or other detection method	Techniques under development - see "microlab" section for further discussion.
Conjugated Dissolved Organics	Metabolites and other biochemical traces	Visible Fluorescence	Limited to fluorescent species, not quenched by high pressure.

1) Nondispersive Infrared

Several dissolved, infrared active gases are thought to play major roles in the microbial metabolism critical to vent biology. These include methane (CH_4) and hydrogen sulfide (H_2S) which serve as major energy sources, ammonia (NH_3) which is a critical nutrient and carbon dioxide (CO_2) which may serve as a respiration tracer.

Nondispersive infrared absorption (NDIR) spectroscopy is a potential diagnostic for each of these IR active dissolved gases which can offer high selectivity at relatively low cost and power consumption. Specificity for individual species would be achieved by using gas correlation cells filled with the species of interest or equivalent spectral masks.

In order to effectively utilize NDIR it is almost certainly necessary to separate a portion of the dissolved gases from the liquid phase. This separation is necessitated by the relatively high infrared opacity of high pressure liquid water. Effecting this separation is the major technological challenge in implementing the NDIR technique. A high surface to volume sample cell with gas permeable walls is one potential solution, while an active inert gas stripping system is a second possibility.

The optical components of the system would include a small "Nernst glower" type infrared source, a small, purgeable infrared absorption cell (possibly multipass), gas correlation cells or equivalent spectral correlation masks, and a solid state, electrically cooled, infrared detector. The power necessary to operate the optical system will be less than the power required for sample handling. The only consumable would be high pressure inert gas (He, Ar or N_2) needed to purge the optical cell and possibly to strip dissolved gases from the water samples.

2. Raman Probes for Remote Sensing

An alternative approach to analyte separation and direct IR analysis is to shift the vibrational information into the "blue-green" window of the water transmission curve by use of Raman spectroscopy. In this technique, visible-wavelength laser pulses are propagated into the sampled region and the backscattered. Raman-shifted radiation is collected and detected. This technique permits IR-reactive species such as H_2 and O_2 to be monitored, as well as methane, CO_2 and H_2S. Dissolved ions such as $SO_4^=$ present at millimolar concentrations may also be detected. Fiber-optic probes could be used for optical pulse transmission, and the Raman bands isolated by means of interference filters.

There are several serious limitations which must be considered. The low sensitivity of Raman spectroscopy limits detectivity to species number densities not less than 10^{16} cm^{-3}. Sensitivity may be enhanced by several techniques, such as light-trapping in a capillary waveguide, use of stimulated, coherent, or surface-enhanced Raman techniques, or use of resonance Raman spectroscopy for species (other than those enumerated above) processing visible-wavelength chromophores. The degree of interference from broad and intense Raman bands of the water must be assessed (this can be done in preliminary laboratory studies). Power requirements for the laser source are not negligible, but diode-pumped solid-state lasers now becoming available may be practical for undersea applications.

3. General Light Scattering Techniques

Elastic light scattering is commonly used to measure a number of physical parameters, most notably flow velocity (Laser Doppler Velocimetry), particle numbers, and particle size. Commercially available Laser Doppler Velocimetry (LDV) systems can generally measure all three of these parameters. Because of its optical nature, LDV is an inherently non-invasive technique. Furthermore, the optical beams that make the measurement can be directed fairly easily to make measurements at multiple points. One can envision an application in which flow, particle size, or particle number were measured in a multipoint fashion to map a flow field in a plane - or an application in which these parameters could be monitored at a single point over a long time period to determine their temporal fluctuations. In conjunction with scaler concentrations, these flow measurements could provide chemical flux information.

There would be a considerable amount of engineering involved in the use of this technique. A laser would be required (that could possibly be a diode pumped solid state 2x YAG). Furthermore, data analysis electronics are required. Deep-sea applications of LDV are, however, being pursued. Thus, some of this engineering may have been accomplished already.

4. Visible Fluorescence

Visible fluorescence is a sensitive, although rather non-specific, technique that can be applied to the quantification of some inorganic and molecular organic species. Possible applications might include the quantification of biological molecules such as flavins, nucleotides, or pigments. If some of the mineral species found around a vent were fluorescent, they might be quantified in this manner as well. We simply state here that fluorescence can be used to quantify species such as those mentioned provided that they are fluorescent and that they retain this fluorescence at high pressures. However, the potential non-linearity of fluorescence as a function of concentration must be kept in mind.

5. Optical Fiber Sensors

Optical fiber sensors offer potential for sensing *in-situ* chemical events in real time. The sensors can be used as bare fibers for direct spectroscopy or be converted to a selective sensor with a reagent chemistry. The sensor reagent can be immobilized at the fiber tip or exist in solution, as in a flow cell device.

The advantages of the optical fiber (unattached to a flow-cell device) is the potential for inserting the probe into harsh regions or events, with an appropriate protective distance between the analyzer and the area probed. Due to the low cost of optical fibers, the probes can be disposable. They can provide information about physical properties (temperature and pressure) and reversible and irreversible chemistries. Numerous immobilization chemistries exist for designing sensors and the following list is an example of some approaches that have been successfuly used in preparing fiber optic sensors.

Some of the types of sensors currently available commercially are:

- pH Sensors

Reversible sensors made with immobilized fluorescent pH indicators; long-term stability possible with ratio measuring. Disadvantage: temperature dependence of fluorescence and limitation of the pH range.

pH Sensors can also be prepared by coupling a pH sensitive absorbing species to a pH insensitive fluorescor. Via an energy transfer mechanism the absorber will modulate the fluorescence of the donor. Numerous other sensing schemes can be adapted to this methodology.

- Gas Sensor

CO_2 detected with pH sensor enclosed with CO_2 permeable membrane. Long term stability possible with ratio measuring. NH_3 can be detected by a similar pH dependent sensor.

O_2 can be sensed by its quenching of fluorescent dyes. These dyes can be immobilized or supplied by a flow injection technology. O_2 has also been detected by chemiluminescence (Freeman, Seitz, Anal. Chem., 1981, 53, 98).

- Nonalkali Metals, Al(III), Re(II), Mg(II), Cd(II), Zn(II)

A variety of molecules become fluorescent when complexed with certain metals. This can be used in an immobilized or flow injection scheme. Limitations: selectivity and lack of reversibility.

- Na^+

A reversible Na^+ sensor has been prepared by R. Seitz through an ion-pairing scheme. An ionophore is immobilized on a solid substrate with an anionic fluorophore and a cationic polyelectrolyte that quenches fluorescence of the bound fluorophore. The presence of Na^+ displaces the cationic quencher resulting in increased fluorescence.

- Chemiluminescence (Bioluminescence) Sensors

Due to the existence of bioluminescence at aquatic depths it may be possible to take advantage of these chemistries for sensors. An example would be the photoprotein, aiquorin, which chemiluminesces when in the presence of Ca(II). This is irreversible, highly sensitive.

- Irreversible Fiber Optic Sensors for Harsh Environments

Where it is not feasible to use a flow injection analyzer, i.e., the middle of a plume, a disposable fiber optic sensor could be introduced. The sensor reagent would require immobilization. The durability of the sensor chemistries in these circumstances is unknown but the design of optical fibers offers a unique way of probing inaccessible regions. Given the low cost of the fibers the development of disposable sensors is not a limitation.

6. Optical Fiber Array Multiplexing

Fiber optics can serve to couple an array of optical sensors (coptrodes) to a central spectroscopic instrument. This allows rapid, multipoint measurements in a manner that may be more convenient than other similar techniques (electrical sensors for example). Furthermore, some of the direct spectroscopic techniques mentioned above may be performed through optical fibers to accomplish multipoint monitoring. Currently available multiplexers allow dwell times of 1 ms per optical fiber (with the possibility of addressing 32 fibers). Optical fibers transmit light signals with immunity to electromagnetic interference over long distances. One might imagine that data could be transmitted directly through a hull of a vessel without the noise that conventional electrical feedthroughs encounter. One could localize the spectral instrumentation within the hull and transmit light to make measurements through it.

VIII. REPORT GROUP 3

Microlaboratories for In-situ Chemical Analyses in Hydrothermal Vents

Reported by
Kenneth Johnson

The detection and exploration of hydrothermal vent systems requires the development of real time chemical analyzers that can be operated in-situ. Because of the variety of studies that can be envisioned, there is a need for many different types of chemical analyses to be performed, and a wide range of concentrations that might be encountered (i.e., Mn from 0.1 nM to 1,000,000 nM). Physical and chemical variability within vent systems requires a measurement time scale that may vary from seconds to years. Systems that can be adapted to a variety of conditions are necessary. While selective chemical sensor technology is an attractive tool for real time studies of vents chemistry, much of the technology remains to be developed. Chemical microlaboratories, on the other hand, provide a capability for in-situ chemical determinations that are adapted from proven methods and are available today.

We define 'microlaboratories' as systems that allow a series of automated manipulations, necessary for the determination of dissolved chemicals, to be performed with no intervention necessary from the operator. Such systems can be used to adapt existing methods of chemical analysis for use in-situ around hydrothermal vents. 'Microlaboratory' systems provide a technology that, in some cases, requires no, or relatively little, additional development to provide a working system.

The manipulations that are typically necessary to perform chemical analyses by a microlaboratory system in-situ can be divided into a relatively simple set of operations: the accurate delivery of fluids via an appropriate pump, directional control and mixing of fluids by valves, detection, and data storage and manipulation. These units may be reliably built in modular form, providing a high degree of user flexibility in the analyses that may be performed with minimal additional development of hardware.

Microlaboratory systems that perform these manipulations are usually designed around one of two modes of operation: continuous flow or batch mode. Batch mode operations, which are often thought of as robotic systems, are widely used in industrial and clinical laboratories. We believe batch mode operations would be impractical for in-situ use in the foreseeable future.

Continuous flow systems, on the other hand, have been widely used in oceanographic research both onboard ship and, recently, in-situ. These highly modular systems are easily adapted to a variety of conditions and analyses, which makes them well suited for vent research. At present the only example of a working microlaboratory for chemical determinations is based on flow injection analysis (FIA). FIA systems can be used to perform a complex series of chemical manipulations (solvent extraction, preconcentration, separations, multiple reagent additions, standardizations, etc.) and can be interfaced to a wide variety of existing chemical detectors. Furthermore, FIA systems are capable of operating in-situ and they have already proven to be useful tools for the study of hydrothermal vent systems.

FIA systems now in operation are suited for short term (< 1 day) deployments from submersibles and on hydrowires. In-situ chemical detection schemes are presently limited to colorimetry. With little additional engineering development the endurance of in-situ FIA systems could be greatly expanded. Additional sensor technologies implementing electrochemical, fluorescence, and chemiluminescence detection will permit multispecies analysis and greatly increase analytical sensitivity. With little additional engineering development the endurance of in-situ FIA systems could be greatly expanded. For example, major power consuming components involve the peristaltic pumping systems. Alternate low power means for fluid pumping are use of microgear pumps coupled to brushless DC motors and possible future application of piezo-electric pumping systems.

For long term deployments increased life time of labile reagents must be addressed.

IX. REPORT GROUP 4

In-situ Mass Spectrometer

Reported by
Kristin Orians

It was concluded that in-situ mass spectrometry would be possible, but only with great difficulty and expense. The species which could be analyzed by this technique include: gases (He-3, He-4, other noble gases, O_2, CO_2, CO, CH_4, C_2H_6, H_2O/D_2O, H_2, NH_3, H_2S), volatile organics, and selected isotopic ratios. All of these except for the noble gases can currently be measured by alternative (and more readily available) technologies as described in the reports for the other groups. Probably the greatest problems in trying to deploy a deep sea mass spectrometer are:

1) Operation of a high vacuum instrument in an intrinsically high pressure environment.

2) Power requirements and size.

3) Problems with need for eliminating water vapor.

In order to better document these difficulties with currently available technology, a "thought exercise" is outlined below which illustrates some of the possibilities and limitations of trying to deploy a mass spectrometer for underwater work.

Sampling mechanism: Hydrophobic membrane - possibly Teflon. Quartz would be a possibility if only helium was to be measured. The membrane must be able to handle high pressure gradients (for example, from 400 atm to vacuum). Additional selectivity might be added by using a small gas chromatograph as currently in use for various types of field work in non-oceanic environments.

Size: The vacuum space should be kept as small as possible (1 cm^3 or less, if possible) to minimize pumping energy. With such a small vacuum space, it might be possible to use an ion trap to detect single ions as an image charge (eliminating the need for an electron multiplier). The limitation of the "smaller vacuum space" approach is a density of less than $10E^6$ ions/cm^3 in order to minimize ion-ion interactions in the source which would lead to signal distortion.

Ion Traps are basically of two types:

1) Quadrapole. These have an advantage in having no magnet. Their disadvantage is that the ion source temperature must be maintained at about 500°C (if attempting single ion, or image charge, detection). Also, a complex signal detector is required to sort out the small signal which occurs on top of a large quadrapole V cycle signal.

2) Ion Cyclotron Resonance (Penning trap). The advantage is that no ion heating is required and that rapid FT signal processing is possible. The disadvantage is that a (large) magnet is required. In addition, tuning would need to be computer controlled and the whole system should be kept in a pressure casing. Most of these would require heating to about 150-250°C except for the RGA type.

Pump: Possibilities include Cryo and Penning pumps which have low power requirements, but can't pump He and H_2. For this purpose, pumps having higher power requirements (about 5 KV) would have to be used (i.e. turbo, Getter, ion, or diffusion pumps). An ion pump could be used after some sort of rough pump which is capable of achieving less than $10E^{-5}$ torr.

Ionization would be carried out either by an electron beam ($10E^{-4}$ amps/torr) or via photoionization.

Available technology includes residual gas analyzers ($5,000-$20,000) which have a mass range up to about 200 amu and generally come with quadrapole detector, turbo pumps, and a very sensitive electron multiplier. Sizes are generally in the range of about 1 ft^3, although the Nier NASA Mars lander probe was considerably smaller. However, it must be kept in mind that this probe was designed to operate in a vacuum rather than in a high pressure environment.

Calibration. FIA to pass standard, blank, and sample over sampling membrane. Drift would have to be monitored continuously in situ.

Other Considerations. Some thought was given to a system which could be pumped down onboard ship, sealed off, and then used in the vent area for only one dive, possibly with a smaller in-situ pump. However, since such a system would be unable to carry out measurements continuously or over any reasonable time period, it is hard to see the advantage of such a system over shipboard measurements.

X. REPORT GROUP 5

Microtechnology for Innovative Solutions to Chemical Sensor Needs

Reported by
David J. Edell

Microtechnology can be effectively applied to a small number of chemical sensing needs. Conceptually, large scale systems with integrated circuit signal conditioners and multiplexers can be developed, custom devices which involve non-standard microtechnology often require very expensive, time intensive developmental efforts. The most difficult problem with the use of microcircuit technology is the problem of protection of the circuits from saline environments. This problem is being addressed for applications of microcircuit technology for long term (decades) use in biological systems. At present it appears that microcircuits can be used in saline environments for at least months and perhaps years when appropriately designed and fabricated. It should be noted that standard silicon integrated circuit technology device performance is severely degraded at temperatures above 150°C.

Why would anyone build an integrated sensor for chemical oceanography? The need is not clear. Perhaps, there may be justification for an integrated system that measures many parameters at many locations (thousands) over relatively long periods of time. Such a system could conceivably measure temperature (stable resistance thermometry), conductivity (4 point measurement), and pressure/seismic, light and pH using relatively known and proven technologies. Since pH is a surface potential measurement, the effects of surface contamination on the sensor would be the most likely problem to be overcome. Many macroscopic amperometric or potentiometric methods that are acceptable could also be integrated on such a probe. One possibly useful technology is a multiple microelectrode system which enhances speed, sensitivity, and reduces stirring effects. Drive, sense, signal conditioning and multiplexing circuitry could be added to complete a sub-system which conceptually could be assembled onto a long cable system for deployment as a stationary or towed profilometer system. However, if the number of devices are not large, it is more economical and timely to use more standard technology.

Other sensors could be useful - such as hydrogen sensors, O_2 and O_2 sensors - but fabrication complexity (expense) and long term instability are major problems.

Other microfabrication technologies which may find use in the development of chemical analytical systems include various micromachined structures and membranes. Micromachined structures can take many forms, and there are numerous materials and geometrical limitations, but in general, structures can be made down to 0.1μ dimensions. Microtubules with 10^{-8} cm^2 cross section and centimeter lengths can be fabricated reproducibly. Microchannels with 200/1 aspect ratios and defect free, perfectly parallel monocrystalline silicon sidewalls can also be fabricated. One of the more intriguing aspects of microfabrication technology is the ability to fabricate planar optical waveguides. With microlithography one can etch into the layer various optical devices such as lenses and gratings. In addition, flow channels can be fabricated so that fluids can be continuously passed through the system. As an example, consider the recently developed integrated optical disk heads. These eliminate the need for hard fabrication and alignment of at least nine optical elements. We foresee the adaptation of this technology for production of particle counters and flow injection type detectors.

1000Å membranes supported with integrated silicon grids can be fabricated of silicon dioxide, silicon nitride or many other materials including metals and polymers. The support grid can have openings down to 1 micron to create membrane systems which are extremely strong.

A possible use for microchannel or microtube systems could be for rapid separation of gases from liquids using semipermeable membranes. If the tubes or channels were designed as light guides, it may be possible to construct an in-situ optical spectrometer for dissolved gases. Research would need to be done on choice of membranes and fabrication techniques for certain membrane materials.

In spite of all the potentially useful and certainly interesting concepts that could be developed, a cautious approach is advised since the technology is quite expensive and time consuming to develop. Perhaps, as a collaborative venture with a major university, or NASA, it would be a reasonable technology area to investigate for solutions to problems that cannot be solved other ways.

Where possible, standard IC's newly developed for consumer markets should be used. These are highly advanced, general purpose, low power subsystems which are low cost ($15-25). Three very useful IC's are femtoamp electrometers, instrumentation amplifiers, and icepoint compensated thermocouple conditioning circuits.

A novel biosensor concept, which would be worthwhile exploring in the context of research would be to develop biosensors based on transduction of information from living systems. For example, if a particular ecosystem is being investigated, identify a suitable animal with a reasonably-developed nervous system that could serve as host for a transducer for extraction of neural information related to particular chemicals of interest. An example might be to implant the olfactory systems of salmon, and transduce the information from their chemoreceptors which are known to be quite sensitive. The advantage of this system would be that the sensors would be maintained by the living system, so long-term stability would be assured. This same approach may be applicable to deep sea organisms if they could be brought to the surface, adapted to low pressures, implanted, then re-adapted to high pressures.

XI. ADDITIONAL COMMENTS

Comments by
Jeffrey Steinfeld

The conclusions reached during the workshop are pretty well incorporated into the report of the "Optical Sensors Technology" working group. While there are distinct possibilities for dissolved gas analysis by NDIR spectrophotometry following stripping from seawater (possibly *in-situ*, certainly following sample retrieval), and for Laser-based Raman (LIDAR) techniques, the approach which seems to have the greatest near-term potential is application of routine colorimetric and spectrophotofluorimetric measurements *in-situ*, most probably in conjunction with optical fibers and/or flow injection techniques.

Comments by
James Callis

The Sensor Hierarchy and Chemometrics

In thinking about chemical sensing the most obvious approach is to consider the analytes of interest one at a time. Thus, one would make a list of species to be elucidated and then obtain one sensor for each analyte. Unfortunately, this approach has the drawback that most chemical sensors are simply not selective enough and if they report only one parameter such as voltage or intensity then there is no way of confirming that the signal is actually measuring the desired analyte. On the other hand, if the sensors were perfectly selective, there would be no possibility of measuring unanticipated or adventitious components.

As an alternative to an array of perfectly selective sensors, consider an array of sensors of less selectivity, but each one possessing a differing selectivity for the various analytes. Under these circumstances each analyte will generate a pattern of responses across the sensor array. Mathematically the response can be expressed as a vector, and the discipline of linear algebra shows that much more powerful analytical methods are available for data reduction. In particular we need to consider the possibilities of multivariate calibration and pattern recognition that can be employed. Recent advances in the former will allow simultaneous multicomponent analysis with powerful methods for outlier detection and compensation for an unknown and/or variable background.

The recent work of Kowalski and colleagues shows the possibilities for unselective arrays. These workers investigated the use of an array of piezoelectric mass detectors, each coated with a different gas chromatography phase. By use of multivariate analysis this group was able to make a seasoned selection of 7 coatings from a menu of 100 which yielded an optimal analytical instrument for a pre-selected panel of 15 analytes.

At this juncture it is important to point out that the optical spectrum of an analyte can also be considered as multichannel response. In particular, vibrational spectroscopy has the advantages of universality of response, but the response is quite unique to specific analytes (i.e., selective). For example in the region 3500-1500 cm^{-1} one finds spectroscopic channels for functional groups while at lower frequencies the channels reflect the molecular structure and conformation (fingerprint). Here, there has been a great deal of activity in developing multivariate calibration methods for simultaneous multicomponent analysis.

A relatively neglected region of the spectrum of the near infrared from 600-2500 nm. Here one finds the vibrational overtones of OH, NH and CH groups. Although these bands are weak and relatively broad and overlapping, the measurements can be made with excellent signal to noise ratios (10^4/1 to 10^5/1) over long enough path lengths (100 microns to

1 cm) to preclude sampling difficulties. In addition, one can take advantage of the fiberoptics technology that has been developed for the communications market, miniature photodetectors, light emitting diodes and even lasers are readily available.

Many years ago it was pointed out to the oceanography community that the near infrared spectrum of seawater was remarkably sensitive to salinity and temperature. Unfortunately, little advantage could be taken of this phenomenon because the effects were subtle and confounded. Recent studies at the University of Washington show that with the aid of multivariate calibration and advanced spectral instrumentation the temperature and salinity of seawater can be simultaneously measured. With the advent of miniature spectrometers and diode arrays it is time to consider the possibility of NIR spectroscopy over fiber optics as a continuous means for seawater characterization.

While multichannel sensing will greatly advance the capabilities of in-situ analysis, there will undoubtedly remain a significant fraction of problems involving trace amounts of analytes in very complex matrices. For these problems, sample preparation will be required. Here, the rapidly evolving technology of flow injection analysis (FIA) can be used. Sampling, extraction, concentration, chromatography and detection can all be performed with very tiny modules. From the chemometrics standpoint, FIA is unique in introducing a new dimension to the analysis - that of time. When multichannel detectors are combined with flow injection techniques the resulting data is obtained in the form of a matrix. Linear algebra shows that such second order tensors provide even more powerful analytical methodologies. In particular, for linear systems the newly developed strategy of rank annihilation provides a way to obtain quantitative results even in the presence of an unknown and variable background.

In conclusion, we have seen that there is a hierarchy of chemical sensors ranging from simple one-channel/one-analyte sensors to multianalyte sensor arrays to ultraminiature instruments to chemical microlaboratories. Correspondingly we have seen how the data sets range from one parameter (scalar) to multiparameter (vector spaces) and with incorporation of the time dimension to multidimensional data sets (matrices). As the dimension of the data sets increase the computational requirements increase correspondingly. Fortunately the rewards are also commensurate - quantitation in the face of an unknown and variable background.

Comments by
Frank Sansone

1. Application of H_2 Sensors

Uses:

- mapping
- measurements of H_2 concentrations and transformation rates in fluids and plumes
- determination of Eh in vent fluids

Advantages of H_2 Sensors:

- high concentration in vent fluids and low concentration in ambient seawater

Sensors Available:

Fuel Cells:
- low cost (e.g., $10,000)
- currently available, although they need improvement in sensitivity and response time. Also, they cannot be used above 60°C
- low power requirement
- such sensors are currently deployed

Chemfets:
- small and easy to deploy; very low cost (less than $5,000)
- only available as laboratory prototypes - need research
- fast response
- cannot be used over 60°C
- probably unsuitable for high-sulfide vent fluids end-members

Ceramic oxides:
- small and easy to deploy
- can be used at high temperature and pressure
- not yet available - need 1-2 years of research
- low cost (less than $5,000)

2. A Special Sensor Needed for Large-Scale Mapping of Vent Plumes

Use:

Would be used to identify previously unknown site of hydrothermal activity. The sensor would be mounted on a towed or free vehicle.

Requirements:

- very high sensitivity
- very large dynamic range
- small size
- low weight
- low power consumption
- fast response

The value of such a sensor is indicated by the "usable dynamic range" (see Table 2 below). The chemical species measured must have very high concentrations in vent waters, and very low concentrations in ambient seawater.

Table 2. A comparison of the usable dynamic range of hydrothermal vent sensing systems. Usable dynamic range = (vent water composition - ambient water composition (or detection limit, if higher)) ÷ analytical precision. Vent water methane and hydrogen composition data are for the East Pacific Rise (Whelan and Craig, 1983).

Parameter	Vent Water Composition	Ambient Composition	Analytical Precision	Usable dynamic range
Temperature (low T vent)	30°C	4°C	0.005°C	5.2×10^3
Temperature (high T vent)	350°C	4°C	0.005°C	6.9×10^4
Methane	50-65 μM	1 nM	0.1 nM	$5.1\text{-}6.5 \times 10^5$
Hydrogen (present instrument)	360-1700 μM	5 nM (detection limit)	10 nM	$3.8\text{-}17 \times 10^5$
Hydrogen (optimized instrument)	360-1700 μM	0.3 nM	0.03 nM	$1.2\text{-}5.7 \times 10^7$

Comments by
Andrew Campbell

Suggestions for Microlaboratories (see Report Group III) for High Temperature Fluid Analyses

A. Requirements

1. Obtain relatively pure endmember samples (less than 2 nM Mg)

    - pump system with 2 thermocouples to monitor purity
    - cooling coil (to cut in on command)

2. Subsample cooled solutions

3. Direct samples of high temperature fluids

B. Analyses

1. H_2S + sulfide species

2. NO_3^-, NO_2^-, and NH_4^+

3. Dissolved silica

4. Mn, Fe, Cu, Zn, Pb(?)
    Contentration ranges:
    Mn: 100 uM - 3 mM
    Fe: 10 uM - 20 mM
    Cu: 40 nM - 40 uM
    Zn: 100 nM - 100 uM
    Pb: 50 nM - 500 nM

C. Field Studies and Engineering

1. Off shelf with currently available technology

2. Combine pump sampler with in-situ flow injection analysis system

3. Field studies of prototype

SECTIONS XII to XV: APPENDICES

XII. APPENDIX A: Viewgraphs Presented by the Different Groups During the Workshop

Group 1

Electrochemical Measurements at the Ocean Floor Hydrothermal Vents

1) Potentiometry vs. voltammetry
2) High T./High P. vent fluid vs. Low T./High P. Plume/SSW

Methods of Choice: High T./ High P. Voltammetry

a) Solid state electrodes - Direct
b) Square wave volt. (most sensitive)
   Linear sweep volt. (least sensitive)
   Both Fast!
c) Redox species - H_2, S, O_2, Fe^{2+}, Cu^{2+}, etc.
d) Speciation H_2S, $SO_3^=$ (metal complexes)

Plating Approach - Indirect

a) Plate metals
b) Plate non-metals
c) Measure in real time or onboard ship
d) [A] to vent fluid velocity not diffusion possible to calc. fluid velocity by varying deposition time
e) Vary plating potential for selectivity or electrode protection

Needs - Concerns

a) Best electrode material and construction for ref. and working
b) Stability of electrodes
c) Standard Calibration
d) Ionic strength adjustments?
e) T/P corrections
f) Single electrode vs. array of microelectrodes
g) Profiling possible?

High T/High P

Potentiometry

1) Electrode stability critical
2) Uses for Li^+, pH, Na^+, Cl^-, F^-, $S^=$

Low T/High P

Both Potentiometry + Voltammetry are Feasible

1) Potentiometry - major cations, anions
2) Voltammetry - trace, redox species

Approaches

1) Direct measurement *in situ*
2) FIA approach (if necessary)
3) Plating approach (voltammetry)
    - $\lesssim$ 30 sec deposition
    - $\lesssim$ 10 sec data acquisition

Conclusion

1) Electrochemical techniques are feasible
2) Lab studies
3) Field Studies
4) Adapted to Rosettes
5) LCEC
6) Cost

Optical and Spectral Techniques

Measurement	Typical Parameters	Technique	Comments
Dissolved Gases	CH_4, H_2S, NH_3, CO_2	Non-dispersive infrared with gas correlation filters	Applicable only to IR active gases, needs purge or membrane technique to partition dissolved gases.
Dissolved Gases	Above + H_2, O_2, $SO_4^=$	Raman Scattering	Requires visible laser, probably diode pumped solid state. Capillary geometry with dissolved gas separation may be necessary.
Particulates, Microorganisms	Bacterial number density; precipitate density	Light Scattering	Best done with laser (see above). Needs calibration.
Flow Velocities and Fields	Current speeds and direction	Laser Doppler Velocimetry	Requires visible laser; may have large Rayleigh scattering background.
Temperature	0 to 350°C	Fluorescent Optrode	Relative fluorescence from temperature dependent surface, e.g. Eu/Er - can be multiplexed to yield temperature field fluctuations.
Dissolved Chemicals	H_2, CO_2, O_2, Ionic species	Reactive Optrode with colorimetric or other detection method	Techniques under development - see "microlab" section.
Conjugated Dissolved Organics	Metabolites and other biochemical traces	Visible Fluorescence	Limited to fluorescent species, not quenched by high pressure.

Group 3

'Microlaboratory' - a system that performs one or more manipulations on the sample and which can operate automatically with no operator intervention. Provides results in 'real' time.

'Sensors' - require no sample manipulations

Microlaboratory types
1) Batch - robotic systems
2) Flow - FIA

What's feasible now
FIA - colorimetry

What's feasible soon
FIA - electrochemistry + ??

"'Thinkjet' pump!"

"Capillary pump!"

"Infusion pump!"

Requirements for Chemical Analysis

There are a wide variety of possible studies that require many different analyses over a broad concentration range, i.e., Mn: 0.1 to 1,000,000 nM.

Broad time scale - seconds to years

Variety of conditions - 2- 350°C

A single sensor for one element is not likely to span the range of concentrations and conditions.

NEED a modular, adaptable system for many analyses and detector types.

Group 4

In-situ Mass Spectrometry

Potential:	Sensitive technique to measure gases and volatile organics with isotopic selectivity. Multi-element sensor.
Components:	Sampling interface, ionizing beam, ion trap - mass selection, vacuum pumps, signal interpretation electronics.
Limitation:	Power requirements Size - ≤ 1 cubic foot, can scale down Pressure housing Heating - only for rough pump onboard ship

Sampling Interface

Hydrophobic membrane - Teflon?
  High pressure (300 atm to vacuum)

Ionizing Beam

Electron beam (or photoionization?)

Ion Trap/Mass Selection

Quadrupole
  Vacuum requirement not as strict
  No magnet
  Rapid mass scan capabilities

but - High ion temp (500°C)?

Volatile organics can be measured

Ion Cyclotron Resonance (Penning trap)

No ion heating
FT signal processing
but - Need magnet
Higher Vacuum?? (only need unit mass resolution)

Ion Detection

Electron multiplier
Single ion detection - image charge
  (small volume)
Faraday cup (sensitivity: 10^{-4} amps/torr)

Vacuum Pumps

Cryo	Small and cheap, but difficult to maintain in remote region over time. Need to clean up.
Getter Penning	To remove reactive gases - use in series with ion pump for noble gases
Turbo	High power, could use to rough pump onboard ship
Ion	Can be small with low power requirements if used to maintain existing vacuum with low load. Good for noble gases.

Rough pump onboard ship (with turbo pump and higher T)

Maintain vacuum <u>in</u>-<u>situ</u> (with Getter pump <u>and</u> ion pump)
Small volume, low load

Available Technology

Residual Gas Analyzer

Cost: $5K - $20K
Mass range: Up to 200 amu
Components: Quadrupole, turbo pump, electron multiplier
Size: 1 Cubic foot ?
Power requirements: Large ?

NASA Mars-landing Probe

??

Faraday Cup System

E-beam filament ionization
Quadrupole mass selection
Direct ion detection - Faraday cup
<u>Small</u> (3" diameter, 8" long)
2 amp, 110V power at max.

Group 5

Microtechnology for Chemical Oceanography

Non-standard technology is costly unless delivered in large quantities (10,000's).

Complex circuit systems no more expensive than simple ones.

Circuits limited by protective coating technology, but should last for 1 year, using special tech.

High temperature operation is a limitation (<150°C-200°C).

Why micro technology? Perhaps for multisensor, 3-dimensional monitoring of global system.

Micro-Machined Structure

Planar optical wave guides with lenses and gratings and flow channels.

Adaptation of optical disk heads for particulate counting and flow injection.

Membranes, membranes/light

SPM for H_2,
CH_4, H_2S

Light for spectroscopy

Argon purge gas

Possible Multisensor System

Temperature
- Diode
- Thin film resistance

Conductivity
- 4-Point measurement

Pressure/Seismic Sensor

Light
- Diode

pH
- Chemfet (surface problems)

Any other stable amp./volt. technique could probably be incorporated. Multiple microcathodes may be of some value.

Must be multiplexed, etc. and ordered in quantities of thousands; otherwise use standard technique.

Conclusions

1. Large number of possibles.
2. A few reasonables.
3. Each reasonable idea requires substantial investment in development and maybe some research time and money.
4. Without large quantity need, or very acute need for speed or small size, use more standard techniques.

   Neural sensors for use of marine animal biosensors?

XIII. APPENDIX B. Report No. NOAA-88-1: Development of Fiber Optic Chemical Sensors for the Measurement of pH, CO_2, and O_2 in Sea Water (with permission from Lt. Cmdr. J. M. Tokar, U.S. Dept. of Commerce).

Report No. NOAA.88-1

Biannual Technical Report

Contract No. 50-DMNA-7-00162

Development of Fiber Optic Chemical Sensors (FOCS) For The Measurement of pH, CO_2 And O_2 In Sea Water

Prepared by:

Kisholoy Goswami, Sr. Scientist
and
Stanley M. Klainer, Principal Investigator

ST&E, Inc.

1214 Concannon Boulevard
Livermore, California 94550

Prepared for:

Lt. Cmdr. John M. Tokar

U. S. Department of Commerce

National Oceanic and Atmospheric Administration
11400 Rockville Pike
Rockville, Maryland 20852

February 9, 1988

ST&E, INC.

ABSTRACT

Fiber optic chemical sensors (FOCS) are being developed for the measurement of pH and the detection and quantification of carbon dioxide (CO_2) and oxygen (O_2) in sea water. These sensors are being developed by ST&E, Inc. under a Phase II SBIR contract with the National Oceanographic and Atmospheric Administration (NOAA). Deliverables under this contract are the three (3) sensors, a 3-channel reader, participation in at-sea evaluations, R & D drawings, an operations manual, biannual technical reports and a comprehensive final report.

During the first six (6) months of this program, the following tasks were initiated:

(1) Recheck, upgrade or replace the individual FOCS chemistries developed during the SBIR Phase I program. This includes evaluating fluorescence vs. absorption vs. refractive index measurements, direct measurements vs. energy exchange and graft vs. dipped membranes.

(2) Evaluate other FOCS designs. The objective is to determine whether side coating the fiber optic has significant advantages over tip-coating. In addition, the possibilities of using a reservoir probe is being evaluated.

(3) Establish specifications for 3-channel reader. This will provide individual measurement systems for each type of FOCS thus making simultaneous readings possible.

(4) Develop testing procedures. These fall into two (2) categories: (i) laboratory evaluation and calibration and (ii) sea trials. In the laboratory, modifications of test procedures used to calibrate medical instrumentation is being considered. It is too early to consider the at-sea tests.

(5) Make, test and evaluate pH, CO_2 and O_2 FOCS based on (1-4) above.

(6) Protect the FOCS from fouling by sea water constituents.

In addition, the Principal Investigator presented a seminar at NOAA summarizing the Phase I SBIR program and discussing the goals and focus of the Phase II effort. Furthermore, the NOAA Technical Officer and the Principal Investigator are preparing a technical paper based on the Phase I research for publication in a peer reviewed journal.

I. INTRODUCTION

The first six (6) months of this program were devoted to the transition from a Phase I to a Phase II SBIR effort. In doing research and development under the SBIR setup there is an abrupt change in focus between phases. Phase I is a feasibility study. The objective to covert and idea or concept into something that works. Phase II is to develop an operating prototype, i.e. the precursor to a commercial product. The goal is not only a device that works, but one that performs well and meets specifications under in-situ conditions. In the present program this means converting fiber optic chemical sensors (FOCS) for pH, CO_2 and O_2 from laboratory demonstration units to practical probes which can make measurements in sea water from shipboard.

During this reporting period six (6) tasks were initiated:

(1) Reevaluate the chemistries developed for Phase I and based on this critique use the existing reagents, modify or replace these.

(2) Appraise existing FOCS designs and choose one (1) {or, perhaps two (2)} that best meet NOAA's requirements for in sea water measurements.

(3) Establish the specifications for the 3-channel reader and initiate performance tests on individual sub-assembly concepts.

(4) Develop test procedures, including calibration, for both laboratory and sea trials use.

(5) Continue test and evaluation of design and chemistry selection using breadboard FOCS until final selections are made (before end of first year of program and after initial sea trials).

(6) Determine how to protect the FOCS chemistry from fouling by sea water constituents.

In addition, selected support functions were/are being performed:

(1) The Principal Investigator presented a seminar at NOAA on August 6, 1987 during which he discussed the results of the Phase I effort and the Phase II goals.

(2) NOAA, ST&E and Tufts University personnel are preparing a series of technical papers, for peer reviewed journals, on the monitoring of sea water using FOCS. The first article will be on pH of sea water.

(3) A subcontract was signed with Tufts University (per the ST&E Phase II proposal) for a cooperative effort on the CO_2 FOCS.

II. ACCOMPLISHMENTS

During this six (6) months the following seven (7) specific tasks have been addressed and conclusions drawn:

(1) Two (2) FOCS designs have been agreed on: (i) side coating (Section III.A.1) and (ii) a reservoir at the distal end of the fiber (Section III.A.2).

(2) Several dyes will be used to cover the complete pH range. No final selection has been made but preferences are beginning to develop (Section III.B.1) and no decision has been finalized between direct fluorescence and energy exchange techniques (Section III.B.1).

(3) The use of hydroxpyrenetrisulfonate and a gas permeable membrane has been selected for the analysis of carbon dioxide (Section III.B.2)

(4) The ruthenium tris-bipyrazyl complex has been selected for the detection of oxygen (Section III.B.3).

(5) The use of branched polyethylene glycols has been selected for immobilization of the sensing reagents (Section III.C).

(6) Initial laboratory procedures for standardizing calibration and test of the FOCS have been established (Section III.F).

(7) Preliminary designs for the 3-channel reader have been discussed and selected, and the parts for breadboarding critical subassemblies ordered (Section III.E).

The results discussed above are based on controlled laboratory experiments using test FOCS or test pieces (usually microscope slides).

III. TECHNICAL DISCUSSION

The purpose of the present research and development is to produce fiber optic chemical sensors (FOCS) for the measurement of pH and the detection and quantification of CO_2 and O_2 in sea water. The effort can be divided into three (3) components: (i) the three (3) different FOCS, (ii) the reader (filter fluorimeter) and (iii) laboratory calibration and test and in sea evaluation from shipboard. The technical effort during this reporting period has progressed smoothly and significant in roads have been made towards reaching the goal of preliminary sea trials in the summer of 1988.

A. FOCS DESIGN

The FOCS developed during Phase I [1] were all tip coated using acrylamide-based surface amplification techniques [2,3]. During this Phase II effort three (3) alternative designs have been evaluated: (i) side coated [4], (ii) sample flow through [5] and (iii) a reservoir at the distal end. At this point in the investigation the tip coated has been rejected because of poor reproducibility between sensors (it is <u>very</u> difficult to get the same amount of material on a small surface area, i.e. 10^{-5} cm^2). The flow through sensor has also been put aside because the development of this type of sensor would be disproportionate to the rest of the program. Thus side coated and reservoir FOCS are being pursued.

A.1 Side Coated FOCS

The side coated or "sandwich" FOCS is based on the same physical principles that cause light propagation through an optical fiber. In this case a pseudo fiber optic is the sensor. To explain this requires that a basic fiber optic be described.

Light transmission through a fiber optic is an evanescent wave (Figure 1). If the refractive indexes of air, the core and the clad are N_0, N_1 and N_2 respectively, then the angle at which the light enters the clad, φ_c, is defined as:

$$\varphi_c = \sin^{-1} N_2/N_1 \qquad (1)$$

and the numerical aperture, NA, is dependent on the entrance angle of the light, α_m through the relationship:

$$\sin\alpha_m = NA = (N^2{}_1 - N^2{}_2)^{1/2}/N_0 \qquad (2)$$

Furthermore, for light to propagate the fiber, it is required that $N_1 > N_2$. If this requirement is not met then the light exits the sides of the fiber and not the tip.

For the sea water sensors where longevity is a key requirement, there is a need for "large" reaction volumes. Furthermore, for good reproducibility it is

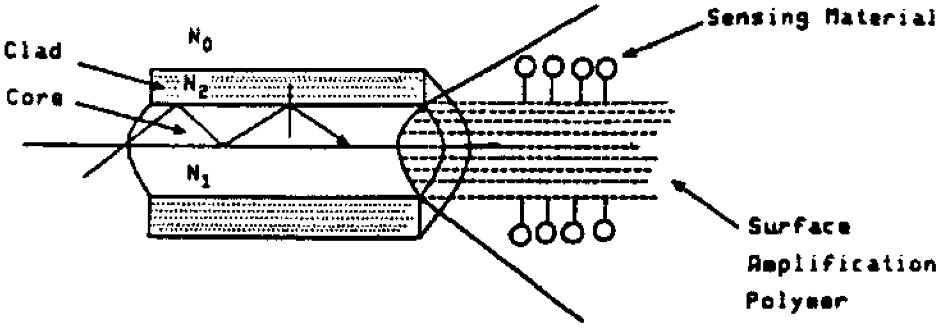


Figure 1: Light Propagation Through A Fiber Optic

necessary for the sensing reagents which are deposited with the same thickness each time. This is best done on the sides where there are large surface areas (as compared to the tip) and the sensor is less sensitive to small anomalies in the coating. Figure 2 shows a side coated approach where the reacting chemistry is "sandwiched" between the core and the clad. The objective is to make the refractive index, N_3, of the reacting medium greater than N_1 and N_2 while keeping N_1 greater than N_2. Thus, because N_3 is greater than N_1 the light passes through N_3 and is sent back to the core when it reaches N_2. At this point the core also looks like a clad because N_3 is larger than N_2. Thus there is the equivalent of a "multipass reaction volume" along the surface of the fiber which gives a multifold increase in sensitivity. Any reactions or interactions that do occur in the reactive layer will change the angle and amount of light that passes through the fiber. In addition, for fluorescent reactions, the added sensitivity will permit small changes in emitted light intensity to be monitored. In order to get the proper N_2 a polymer clad will used. In addition, polymers are desirable because the clad must be sufficiently porous so that the species to be monitored have access to the sensor chemistry. The porous clad can also act as a membrane and protect the chemistry. It should be noted that the light coming out of the tip of the sensor will be an annulus with a dark center because the light never enters the core in this design.

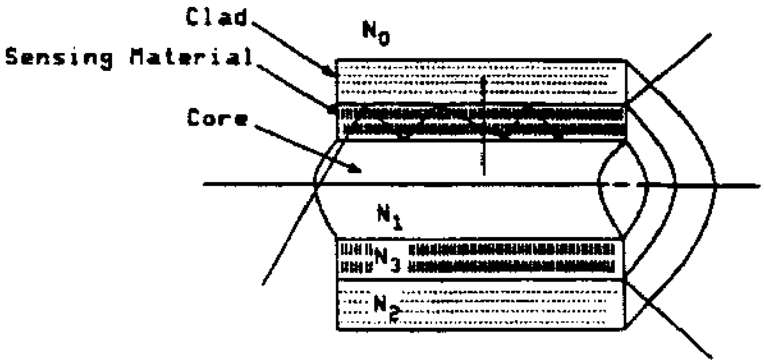


Figure 2: A Side Coated FOCs

By immobilizing (Section III.C) the reactants to the core, any chance of losing the sensing material by "leakage" through the porous polymer clad is obviated. It may also be possible to make multiple sandwiches by coimmobilizing several sensing materials (N_3 has several different active sites) or layering several reagents between the core and the clad (where $N_3 < N_4 < N_5$, etc.).

For the sea water sensors the species specific fluorescent reagents are placed in the "sandwich". For pH a porous clad is used while for CO_2 and O_2 the clad is a gas permeable, liquid impermeable, membrane.

A.2. Reservoir FOCS

The need for high resolution, long active lifetimes and good reproducibility between sensors for a particular species has resulted in the reevaluation of the reservoir sensor concept for CO_2 and O_2. In this design (Figure 3) the sensing reagent are in liquid form and kept in the sensor by the gas permeable membrane. Using this approach all of the key elements of the sensor can be very accurately controlled. The reagent solution can be made with a very high degree of repeatability, the active volume can be precisely controlled, the field-of-view of the fiber is accurately known and the size of the membrane can be held to good tolerances. The one question yet to be answered is the dissimilarity between gas permeable membranes. This will be evaluated during the next reporting period. The big drawback of the reservoir FOCS is size. It is about 1 cm in diameter compared to the solid state (sandwich) sensors which are 400 to 600 µm. On the other hand, the reservoir CO_2 sensor should be able to measure changes of $<\pm 2$ ppm at an abient CO_2 concentration of 2450 ppm, a requirement for in sea measurements of CO_2. The performance of the solid state vs the reservoir FOCS will be fully evaluated during the next six (6) months.

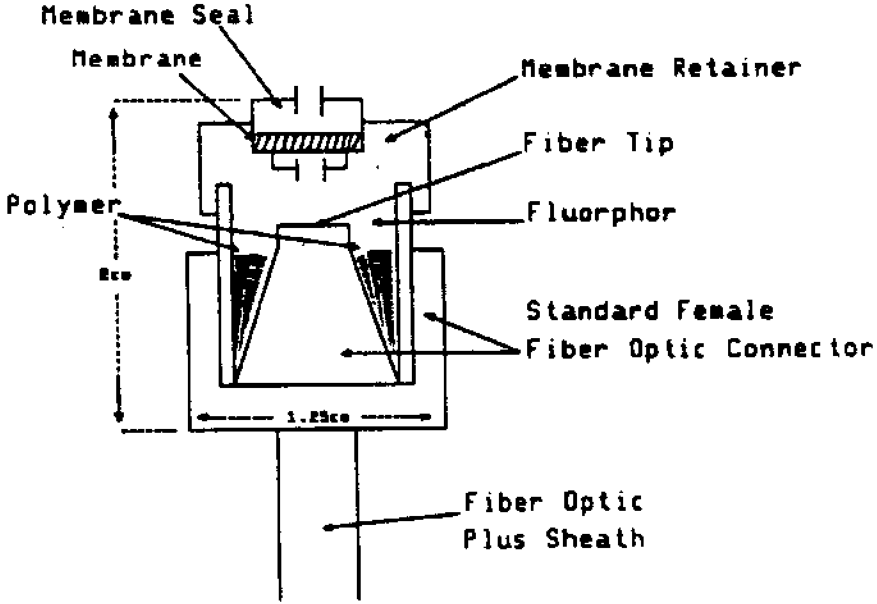


Figure 3: Reservoir FOCS

B. FOCS CHEMISTRY

Development of the chemistry for the fiber optic chemical sensors (FOCS) for the measurement of pH, CO_2 and O_2 has been the prime research objective for the past six (6) months. Research strategies have been developed, materials and equipments necessary for the project have been selected. Efforts have been devoted toward the pH, CO_2 and O_2 probes. The initial findings are summarized in this section. In particular emphasis has been placed on fluorophor stability and the ability to make reproducible sensors with very similar performance characteristics.

B.1 pH Chemistry

The "trade offs" between energy exchange and direct fluorescence will continue to be investigated because each has very interesting merits. The advantages of energy exchange include: (i) good sensor stability, i.e. limited to negligible effects from bleaching and (ii) limited dynamic range which can be translated into excellent precision. The biggest drawback is the possibility of non-uniformity between sensors, i.e. the inability to make many sensors which all behave similarly. Direct fluorescence has the advantages of (i) simple chemistry and (ii) easily detected and quantified signals even when analyte concentrations are very low, i.e. sub part-per-million. The present obstacle, for direct fluorescence is "bleaching" which may be solvable using the proper immobilization chemistry.

The variation of fluorescence intensity of a fluorophor with pH is the basis of this sensor. During the Phase I effort [1], direct fluorescence was used and a pH probe based on fluorescein amine as the pH sensitive fluorophor was demonstrated. The principal drawback of this sensor, as mentioned previously, was "bleaching" of the fluorophor when it was exposed to the excitation light. To overcome the "bleaching effect" a different type of immobilization polymer system is being explored for attaching the sensing reagent onto the side of the fiber optic. The new chemical system uses branched polyethylene glycols (B-PEG's) (Section III.C). These contain "ether" (-O-) and "hydroxyl" (-OH) functionalities which are inherently poor electron donors as opposed to the nitrogen containing functional groups in the acrylamide polymer used during Phase I. The postulation is that the weaker the electron donor the more stable the fluorophor. During the next six (6) months, a comparison of the stability of fluorophors using different immobilization polymers will be completed.

In the case of energy exchange, the initial research included a selection and evaluation of absorption indicators. These are being looked at from two (2) aspects: (i) the use of absorption obviates the bleaching problems observed with fluorescence dyes and (ii) absorption dyes give more precise coverage of the pH range thus making a broader coverage possible which is more responsive to NOAA's needs. This system can still made use of the high sensitivity associated with fluorescence by coimmobilizing a fluorophor with no pH sensitivity at the pH's of interest, i.e. eosin, with the pH sensitive dye and measuring the change in fluorescence intensity as the absorption characteristics of the system change with pH [6].

Table I shows the pH sensitive reagents being investigated. Only one (1) or two (2) will actual be made into a FOCS.

The pH FOCS will use the side coated design only. This is dictated by the fact that the sea water itself must come in contact with the sensing material. Since effective unidirectional membranes do not exist, it is not possible to use a liquid system such as would exist with a reservoir, i.e. a membrane does not exist which would reliably keep the fluorophor in while allowing the sea water to enter and exit the sensor at will.

TABLE I

pH Range	Direct Fluorescence	Energy Exchange With Eosin
2.4 to 4.0		2,6 Dinitrophenol
3.1 to 4.4	Morin	
4.0 to 5.8		2,5 Dinitrophenol
5.2 to 6.6	Acridine	
5.6 to 7.2		Dibromophenoltetrabromophenolsulfonthalien
6.0 to 7.0	Luminol	
6.0 to 8.0		Curcumin
6.5 to 8.0	Orcinourine	
7.2 to 8.8		Cresol Red
7.4 to 9.0		Metacresol Purple

B.2 CO_2 Chemistry

The detection of CO_2 is accomplished by taking advantage of the equilibrium:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \qquad (3)$$

In this system the concentration of H_2CO_3 is directly related to the amount of CO_2 present. In sea water CO_2 is the only gas present capable of forming an acid with the water and thus a pH measurement can be a direct measurement of the CO_2 concentration.

In practice the pH FOCS chemistry is separated from the sea water by a gas permeable, liquid impermeable membrane. Thus no liquid reaches the sensing reagents and the pH measured is for the H_2CO_3 only!

The key to good CO_2 sensitivity is to choose either a fluorophore or energy exchange system whose pKa is close to that of H_2CO_3 at the concentrations expected (pKa ~ 7.2). HPTS (hydroxypyrenetrisulfonate) is being considered as the pH sensitive fluorophore for the detection of CO_2. It is water soluble (before immobilization), has good stability (better than fluorescein) and has a pKa of 7.3 which is close to the $H_2O + CO_2 \longleftrightarrow H_2CO_3$ equilibrium at the anticipated CO_2 concentrations. In addition, several of the compounds listed in Table I are likely candidates.

For the CO_2 FOCS either direct fluorescence or energy exchange can be used to measure pH. In addition, for the sea water application either the side coated design or the reservoir FOCS can be used. At this juncture in the program the desire is to focus on the solid state sensors (the HPTS immobilized on the sides of the fiber using B-PEG's) while, realistically, developing the reservoir system (HPTS in solution in the reservoir) as a back up for the initial sea trials.

The membrane is a key component of the CO_2 FOCS. It is an area of focus because placing the membrane on a FOCS needs more research and development.

For the side coated design, emphasis continues to be placed on the gas permeable graft polymer membrane used to separate the CO_2 from its liquid matrix. The characteristics of the membrane for the CO_2 sensor are being defined. The yet to be answered question is: "Is a gas permeable, liquid impermeable, membrane sufficient or does the membrane have to be proton impermeable as well?". One method of grafting the membrane to the B-PEG's is discussed in Section III.C.

For the reservoir FOCS it is planned to use commercially available gas permeable membranes. This is possible because: (i) the minimum size is well within existing technology and (ii) the membrane mechanically fits into the FOCS and no grafting is needed.

B.3 O_2 Chemistry

Luminescence quenching is the basis for the oxygen sensor development efforts. Two oxygen sensitive fluorophores, ruthenium tris-bipyridy complex [$Ru^{II}(bpy)_3$] and ruthenium tris-bipyrazyl complex [$Ru^{II}(bpz)_3$], have been chosen. Their structures are shown in Figures 4 and 5.

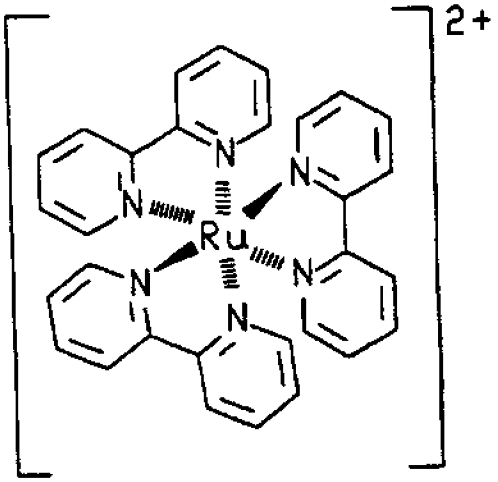


Figure 4: Ruthenium Tris-Bipyridyl Complex

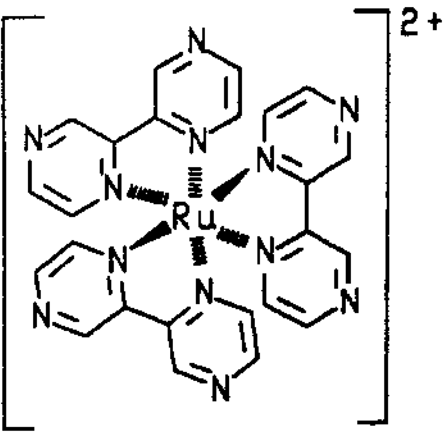


Figure 5: Ruthenium Tris-Bipyrazyl Complex

The tris-bipyridyl complex of ruthenium (Figure 4) can be excited between 430 and 490 nm and its emission peak appears at 610 nm. This is an ideal wavelength range to work in. This compound exhibits a very large strokes shift and this makes the "clean" separation of the excitation and emission signals possible. It's first excited triplet energy of 217 kj/mole and triplet lifetime of 670 ns makes it a very interesting choice. Its luminescence is very efficiently quenched by oxygen as evidenced by the high magnitude of the quenching rate constant (k_q = $3.3X10^9$ $M^{-1}sec^{-1}$). Figure 6 shows the luminescence quenching of $Ru(bpy)_3^{2+}$ by oxygen present in the atmosphere.

The second oxygen sensitive fluorophore, the tris-bipyrazyl complex of ruthenium, $Ru(bpz)_3^{2+}$ (Figure 5) appears to show a better oxygen response as shown in Figure 7.

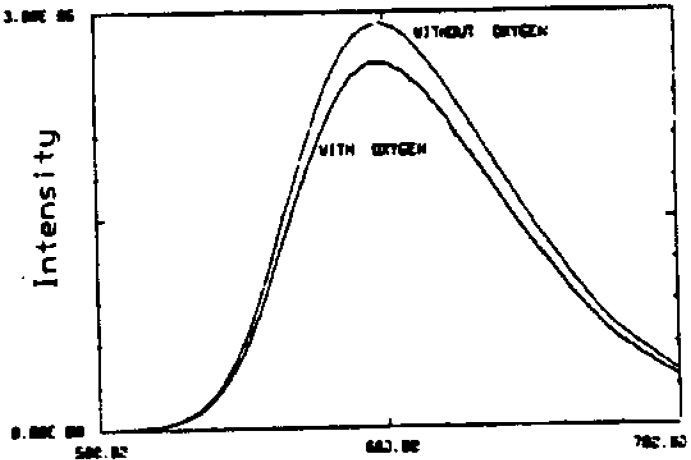


Figure 6: Spectrum Showing O_2 Quenching for $Ru(bpy)_3^{2+}$

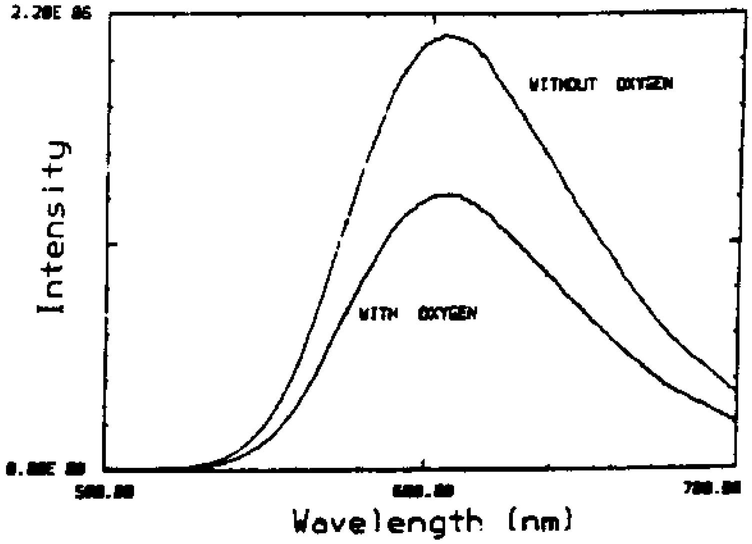


Figure 7: Spectrum Showing O_2 Quenching of $Ru(bpz)_3^{2+}$

The data shown in Figures 6 and 7 is for oxygen quenching experiments performed in solution phase. The next logical step was to put the oxygen sensitive fluorophor on a flat glass surface. The attachment has been achieved via physical adsorption. Figure 8 shows the resultant oxygen quenching data.

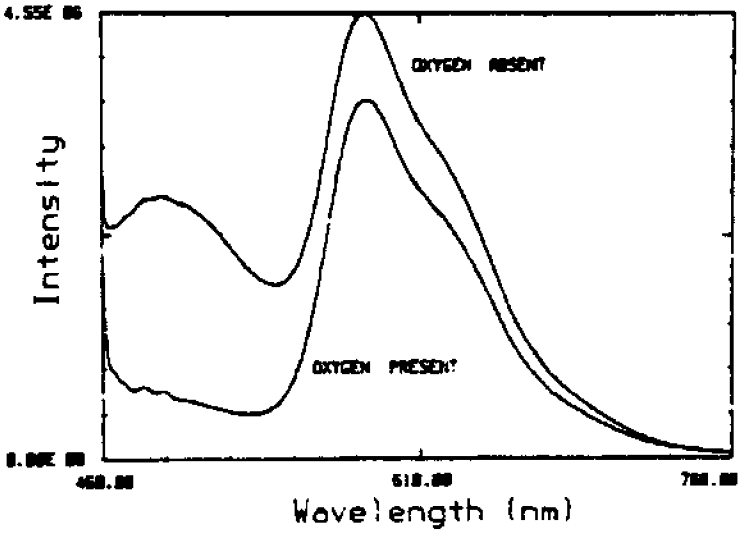
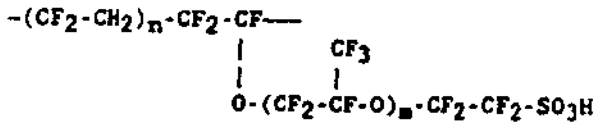


Figure 8: Emission spectra of $Ru(bpz)_3^{2+}$ deposited on flat glass plate.

The research now focuses on the immobilization of the oxygen sensitive complex onto fiber optic core. Currently, the possibility of attaching $RU^{II}(bpz)_3^{2+}$ onto glass core having a cation exchange capacity is being explored. The glass surface is silanized and made into amino glass (Section III.C Equation 5). Then the silanized glass is soaked in nafion solution. Nafion has a perfluorinated backbone and pendant sulfonic acid groups (Figure 9) which make it an attractive cation exchanger.



$$-(CF_2\text{-}CH_2)_n\text{-}CF_2\text{-}CF\text{—}\ ;\ \text{O-}(CF_2\text{-}CF(CF_3)\text{-}O)_m\text{-}CF_2\text{-}CF_2\text{-}SO_3H$$

Figure 9: Nafion

The plan is to attach the nafion polymer to the silanized glass by electrostatic interaction between $-NH_3^+$ and SO_3^- groups. There would be still plenty of anionic SO_3^- groups left on the nafion for the uptake of cationic $Ru^{II}(bpz)_3^{2+}$ moieties. This work will be completed in the next three (3) months.

The O_2 FOCS, like the CO_2, can be of either side coated or reservoir design. For this FOCS, the membrane is not critical because separation of the gas from the liquid (sea water) is not essential for specific, sensitive analyses.

C. IMMOBILIZATION

Immobilization is the general terminology used for attaching chemistry to a solid. It covers all aspects from the formation of covalent chemical bonds, to electrostatic bonding to mechanical entrapment. Immobilization is a necessity when the objective is a solid state sensor.

C.1 Attachment With Acrylamides

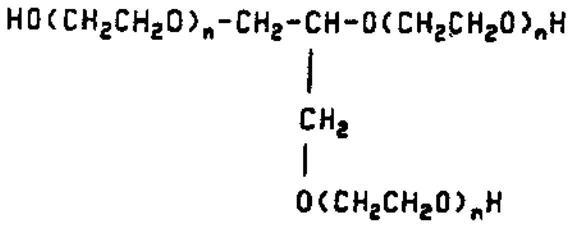
During the Phase I contract, acrylamides were used to attach the chemistry to the fibers. This is described, in detail, in the final technical report [1].

The use of acylamides have two (2) major drawbacks: (i) they are strong electron donors and thus reduce the stability of the fluorophor and enhance "bleaching" and (ii) they have no anti-fouling properties. It was, therefore, decided to look at the polyethylene glycols to obviate these problems.

C.2 Attachment With Branched Polyethylene Glycols (B-PEG's)

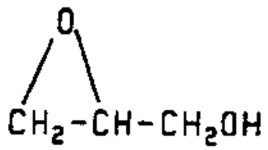
The use of B-PEG's is being considered because: (i) they are weak electron donors and should improve the stability of the fluorophor, (ii) their use in immobilization is well-documented [7-10], (iii) they are known to have biocompatible (anti-fouling) properties and (iv) the number and types of active sites can be controlled.

The final method used to prepare the FOCS is as follows: (i) aminopropyl glass/quartz is made, (ii) cyanuric chloride-activated polyethylene oxide [poly(ethylene glycol)] is prepared, (iii) the activated polymer is attached to the fiber optic and (iv) fluorophor is bound to the polymer.

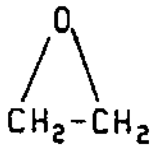


$$HO(CH_2CH_2O)_n-CH_2-\underset{\underset{O(CH_2CH_2O)_nH}{|}}{\underset{CH_2}{\underset{|}{CH}}}-O(CH_2CH_2O)_nH$$

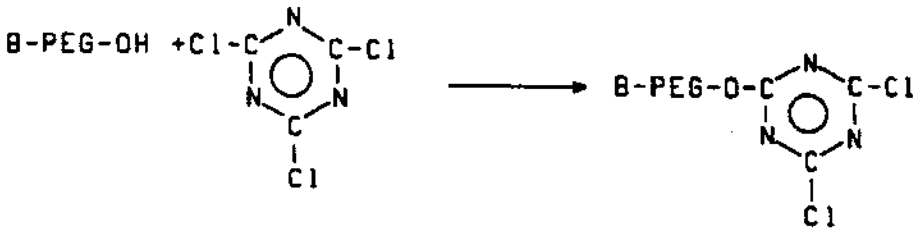
Here the degree of branching is controlled by the amount of glycidol



included in the polymerization of ethylene oxide.



The B-PEG is electrophilically activated as follows:



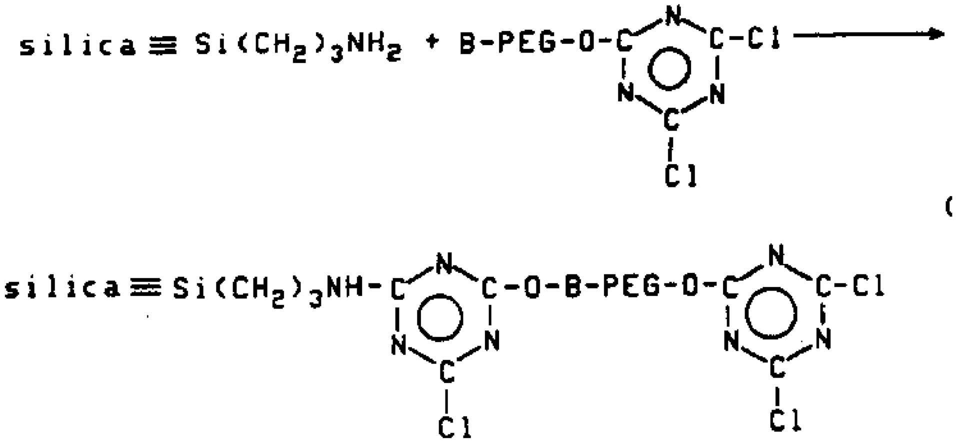
(4)

It should be noted that each OH on the B-PEG can be so activated, thus providing numerous attachment sites for each B-PEG.

The glass or silica fiber optic is nucleophilically activated using a silyl compound:

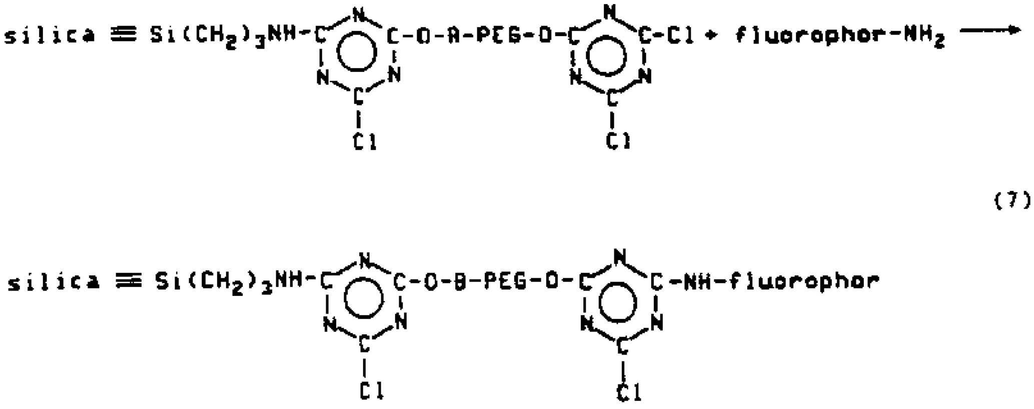
$$\text{silica} + (MeO)_3Si(CH_2)_3NH_2 \longrightarrow \text{silica} \equiv Si(CH_2)_3NH_2 \qquad (5)$$

The activated B-PEG is then attached to the glass:



(6)

The activated B-PEG is then reacted with the fluorophor:

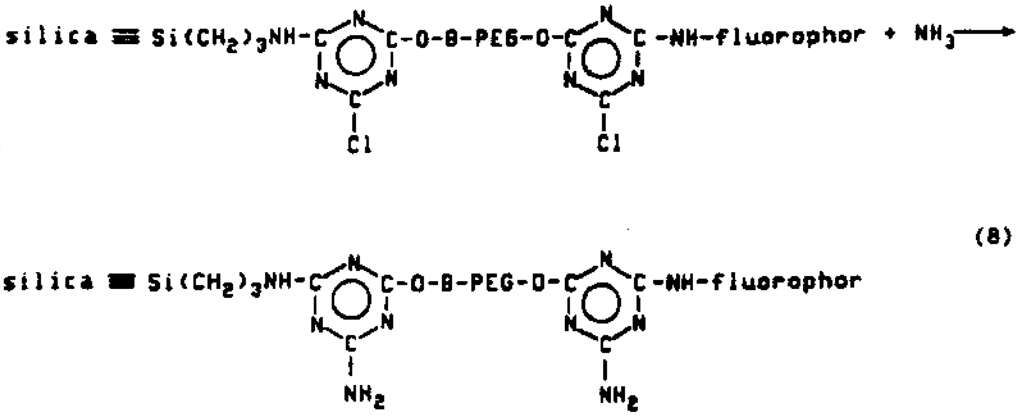


(7)

C.3 GRAFT MEMBRANE

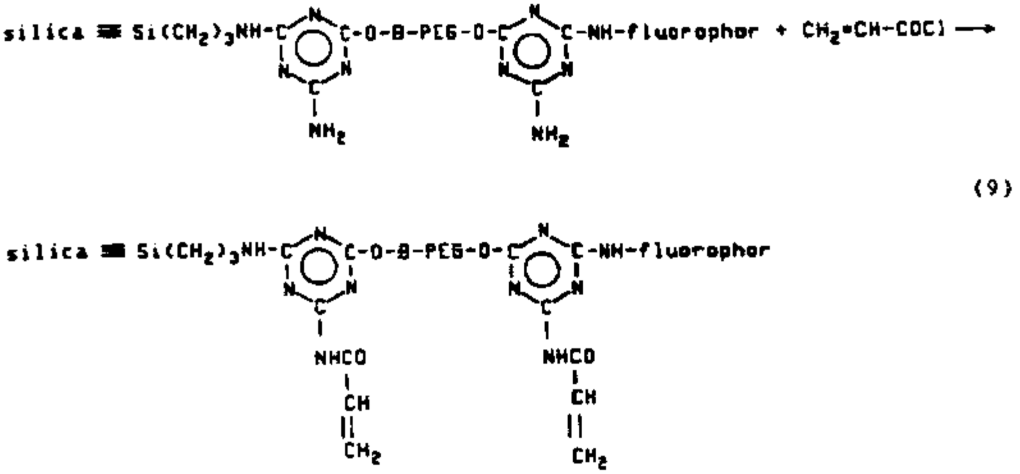
The development of the graft membrane is at a very early stage. To do this properly requires that the membrane be "hung" on the polymer. This can be done after B-PEG immobilization of the fluorophor. The chemistry under investigation proceeds as follows:

Treatment with NH_3 puts a $-NH_2$ group on the B-PEG.



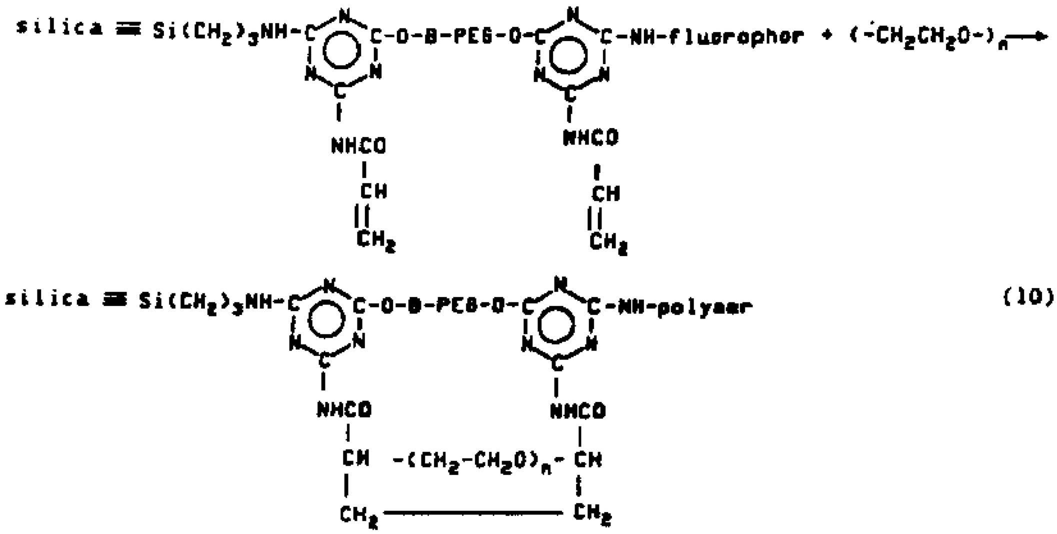
(8)

Reaction with acryloyl chloride then introduces a polymerizable chain.



(9)

The polymerizable chain is then converted to a membrane using a polyether.



(10)

Pore size can be manipulated by employing polyethers of different chain lengths why physical properties by possible branching.

D. ANTI-FOULING PROTECTION

As the program progresses and the FOCS are defined, the uses for sea water sensors become more clear. One thing that has become obvious is that making measurements with FOCS hanging over the side of a vessel, as defined in the Phase II proposal, is only one of many applications. To be truly versatile the FOCS must be stable, in sea water, for at least six (6) months and be capable of making measurements during that time. Since it is ST&E's objective to give NOAA the best FOCS possible, it has been decided to address the longevity problem as part of the reevaluation of the FOCS development although it is not a requirement under the Phase II statement of work.

There is a continued awareness that FOCS active lifetime could be reduced by fouling of the chemistry by the constituents normally present in a sea environment. Possible approaches to protecting the sensor are being investigated. These include (i) controlled pore size membranes and (ii) a "kelp-bed type" "waving" polymer to "wipe" the sensor surfaces clean. Most important, however, is that previous experiences have shown that polyglycol polymers are extremely good in environments, such as the sea, where fouling is caused by biological materials. These will be examined first for the side coated FOCS since B-PEG's are already part of the immobilization procedures. Other types of membranes are also being evaluated for both the side coated and reservoir FOCS.

To assure the long term performance of the FOCS, therefore, requires that the chemistry be protected both from the sea water and from the biological materials that are also present. For the CO_2 and O_2 sensors a gas permeable protective membrane appears feasible. Silicone should provide excellent protection. It has high gas permeability and is not attacked by fungi or bacteria provided a biocide is added. Moreover, it is a commonly available material.

Silicone cannot be used with the pH sensor because a gas permeable coating would convert it to a pCO_2 FOCS. Porous polycarbonate may be a good protector but this could increase the response time of the sensor to 10 to 20 seconds. This will be evaluated as the program progresses.

E. INITIAL "READER" DESIGN

The reader design is underway. The engineer has been instructed to package nearly three (3) completely redundant systems into a single box. Where appropriate, certain subsystems will be common to all three (3) channels, i.e. batteries, computer, etc. Several critical requirements have been identified for shipboard use: (i) temperature compensation for the optics and electronics, (ii) maximum light output from the miniature tungsten source, (iii) optimum transmission of the excitation and return (signal) light, (iv) low noise, high gain amplifiers and (v) a large number of dynamic range selections. At the present time parts have been ordered so that breadboards can be made and tested for these important subassemblies.

F. CALIBRATION AND TEST PROCEDURES

The focus during the first six (6) months has been on developing calibration and test procedures to be used in the laboratory. No effort has been expended to date on preparing for the sea trials.

The primary activity in developing laboratory protocol has been to contact the manufacturers of medical CO_2 and O_2 measuring equipment for catalogs and specifications. The possibility of using this type of approved equipment for an independent reference is very attractive. One question that is being addressed is the effect of sea water salinity on these apparati. It also has been decided to use commercially available calibration solutions. Corning offers such solutions (in pressure cans) for use with blood gas analyzers and these should be apropos.

pH will be calibrated using a buffer set which has been modified with the appropriate salt concentration.

Copenhagen sea water will also be used as a basic standard.

G. BIBLIOGRAPHY

[1] Klainer, S.M., Principal Investigator; "Development of Fiber Optic Chemical Sensors (FOCS) for the Measurement of pH, CO_2, and O_2 in Sea Water"; Contract No. DOC/NOAA 50-DMNA-7-00162, Phase II SBIR; August 1987 to August 1989.

[2] Munkholm, C.; Walt, D.R.; Milanovich, F.P.; Klainer, S.M.; "Polymer Modification of Fiber Optic Chemical Sensors as a Method of Enhancing Fluorescence Signal for pH Measurement"; Anal. Chem., 1986, *58*, 1427.

[3] Klainer, S.M.; Walt, D.; Gottlieb, A; Amplification of Signals from Optical Fibers; Patent Pending (004,339).

[4] Klainer, S.M.; "Fiber Optics which are Inherent Chemical Sensors", Patent Application Pending (#046986).

[5] Klainer, S.M.; Harris, J.M.; Goswami, K.; "Modular Fiber Optic Chemical Sensor", Patent Pending (125,259).

[6] Jordan, D.; Walt, D.; Milanovich, F.; "Physiological pH Fiber-Optic Chemical Sensor Based on Energy Transfer," Anal. Chem., 1987, *59*, 437.

[7] Harris, J.M.; Yalpani, M.; Van Alstine, J.M.; Struck, E.C.; Case, M.G; Paley, M.S.; Brooks, D.E.; Synthesis of Polyethylene Glycol Derivatives," J. Poly. Sci., Poly. Chem. Ed., 1984, *22*, 341.

[8] Shafer, S.G.; Harris, J.M.; "Preparation of Cyanuric-Chloride Activated Poly(Ethylene Glycol), J. Polym. Sci. Polym. Chem. Edn., 1986, *24*, 375-378.

[9] Paley, M.S.; Harris, J.M.; "Synthesis of the Aldehyde of Oligomeric Polyoxyethylene," J. Polym. Sci. Polym. Chem. Edn., in press.

[10] Harris, J.M.; "Synthesis of Polyethylene Glycol Derivatives," J. Macromol. Sci.-Rev. Macromol. Chem. Phys., 1985, *C25*, 325-373.

IV. SUMMARY

The program is proceeding as planned. It is on schedule and within budget. Most important is that significant scientific advances have been made during the first six (6) months. In particular:

(1) The chemistry for CO_2 has been selected.

(2) The chemistry for O_2 has been chosen.

(3) The decision on pH chemistry will be finalized within two (2) months.

(4) Two (2) FOCS designs have been picked.

(5) Laboratory calibration and test protocols will be completed in three (3) months.

(6) Research and development has begun on protecting the sensors from the sea water environment to assure long active lifetimes.

(7) Design of the 3-channel "reader" is underway and critical sub-assemblies are being breadboarded.

XIV. APPENDIX C. Charge to Group - Material Distributed Prior the Workshop.

Charge to Group - Information Distributed Prior to Workshop

June 20, 1988

Introductory note:

Chemical Sensors for Detecting and Exploring Ocean Floor Hydrothermal Vent Systems

Organization

The workshop will consist of a presentation of the technical constraints surrounding the deployment of in-situ chemical sensors in the ocean, followed by an overview of the present situation, and a series of more specific actual or potential in-situ sensor applications.

(Note: Every participant is invited to make a short presentation, if desired - 10 min. of any work related to the workshop; for this, prior notice and a title should be given to the organizers.)

Next a general discussion will be held to identify the most promising potential sensor technologies. Small working groups will be formed to further discuss a limited number of sensors defined by the general discussion as being the most promising. The results of the working group deliberations will be presented the second day of the workshop and short written reports from each participant and working group will be assembled to be edited later as the final workshop report. During the afternoon of the second day, participants will have an opportunity to tour the Woods Hole Oceanographic Institution, including some of the laboratories which are developing the technology which might be used in sensor deployment.

Constraints to keep in mind

The sensors to be deployed have to be sensitive and accurate enough to record at least the lowest concentrations (usually values for seawater) shown in the table attached to this note. Furthermore, they must be developed to work in-situ, in seawater background, at pressures up to 500 bars and temperatures from close to 0°C and, possibly, in some cases, near the maximum temperatures of the venting fluids (about 350°C). Interferences between ions (possibly affecting sensors response) and the possible contamination from the material sensor components must be kept in mind.

It is envisioned that the sensors may be deployed either on fixed, semipermanent moorings (such as anchored platforms, balloons, OBS's etc.) and/or on moving vehicles (free floating, towed, remotely operated, or manned). The limited power supply and maneuverability available will also have to be taken into account.

Sensitive and accurate sensors which operate at high pressures and, in some cases, at high temperature already appear to be available for some in-situ measurements. They include, for example, temperature probes, pressure compensated pH electrodes, salinity probes, high resolution photography, etc. Other sensors appear to be very promising but would need considerable further development to be deployed under in-situ conditions. These potential sensors might include: ion specific electrodes (Pb, Ni, Cu, Cd, Ca NH_4, Br, Cl, F, Cn, I, K, Ag, S, etc.), laser beams (Raman spectroscopy), voltametric cell (for most oxidizable species, inorganic and organic), biological membranes (proteins), liquid and gas chromatography (primarily for gases and organic molecules), classical spectroscopy (UV, IR, MS, NMR; with application for both organic and inorganic chemistry), fiber optic sensors (chemically selective or temperature sensitive). This list is by no means complete, but illustrates some possibilities. Furthermore, other types of sensors may not be commercially available but might nevertheless exist within some specialized research groups.

The participants of this workshop are asked to identify as many of these technologies as possible and to draw some conclusions about their current state of development.

Goals of the Workshop

The main purpose of this workshop is to bring together oceanographers, chemists, biologists, and engineers from academia, industry, and government to discuss the feasibility of in-situ measurement of certain chemical parameters in the deep ocean. The table included is not exhaustive and is meant only to provide an approximation of the sensitivities required. The table does not pretend to be complete and the participants should feel free to suggest other possibilities (for example, measurement of different bond types to carbon within organic species, etc.). Oceanographers and biologists might wish to contribute information on which parameters would be most useful; chemists might wish to address the feasibility of the sensor systems under consideration; and engineers may wish to consider potential methods for deployment of the instrumentation.

Examples of Problems Related to Hydrothermal Vents Which Might be Addressed Through the Use of Diverse Chemical Sensors

The influence of hydrothermal venting on the chemistry of the oceans, and the geochemical cycles of many elements.

Heat and mass balances, and estimation of the magnitude of metal sulfide deposition around active hydrothermal systems.

Amount and nature of temporal variations of hydrothermal activity, and the relationship of the variations to other events - for example, earthquakes.

Relationships between biological activity, chemical composition, and temperature to the understanding of the unique and complex ecosystem surrounding underwater active hydrothermal areas.

Testing of the possibility that some of the molecules needed to form living systems could be, or have been, formed abiogenically around underwater hydrothermal systems.

Dynamics of recharge of hydrothermal systems by seawater.

Propagation, geometry, physics, and temporal variation of water plumes originated by venting of hydrothermal fluids at the sea floor.

Quantification of the chemical input (for example gases) originated directly from the upper mantle and contained in the hydrothermal fluids.

A Comparison Between the Chemistry of Seawater and Selected Hydrothermal Vent Fluids

The following compares the chemistry of seawater and two types of ocean bottom hydrothermal fluids: vent fluids from 21°North (East Pacific Rise), and from the Guaymas Basin (Gulf of California). Both systems have been studied in detail. The Guaymas hydrothermal system is covered with about 500 meters of organic rich sediments; at 21°North, the hydrothermal fluids do not flow through sediments but vent directly out of the basaltic sea floor. The table below is to indicate the approximate magnitude of the signal of chemical inputs from hydrothermal brines into the seawater background.

	(Mult. by)	Seawater	21°N	Guaymas
T(°C)			270-350	100-300
pH		7.8	3.3-4.0	6.0
Alk		2.3	(-.19)-(-.54)	8.1-10.6
H_2				
O_2	(10^{-3})	0.37		
N_2	(10^{-3})	1.1		
CH_4				
CO_2				
CO				
SO_4	(10^{-3})	27.9	0-0.6	0-0.82
NH_3	(10^{-3})	<0.1	<0.1	10.3-15.6
SiO	(10^{-3})	0.16	15.6-19.5	9.3-13.8
H_2S	(10^{-3})	0	6.6-8.4	3.8-6.0
PO_4				
NO_3				
Li	(10^{-3})	0.025	890-1448	630-1070
Na		0.470	0.432-0.510	0.472-0.490
K		0.01	0.023-0.026	0.033-0.049
Rb	(10^{-6})	1.4	27-33	57-86
Be	(10^{-6})	0.00002	13-37	12-91

Mg		0.05	0-0.002	0
Ca		0.01	0.01-0.02	0.026-0.042
Sr	(10^{-3})	0.09	0.06-0.10	0.16-0.23
Ba	(10^{-6})	0.16	7-16	700-5000
V	(10^{-6})	0.05		
Cr	(10^{-6})	0.006		
Mo	(10^{-6})	0.1		
W	(10^{-9})	0.5		
Mn	(10^{-6})	0.004	640-1024	128,000-236,000
Fe	(10^{-6})	0.003	646-2429	17-180
Co	(10^{-9})	0.8	22-230	
Ni	(10^{-6})	0.025		
Cu	(10^{-9})	7.9	20-44	
Ag	(10^{-9})	0.4	0.4	2-230
Au	(10^{-9})	0.02		
Zn	(10^{-6})	12.6	40-106	0.1-40
Cd	(10^{-9})	1.0	17-155	27-46
Hg	(10^{-9})	0.16		
B	(10^{-3})	0.41		
Al	(10^{-6})	0.08	0.004-0.005	
Sn	(10^{-9})	0.1		
Pb	(10^{-9})	0.2	183-359	230-652
N	(10^{-6})	10,000	<1	<1
P	(10^{-6})	2,000	<1	<1
As	(10^{-9})	50.1	30-452	283-1074
Sb	(10^{-9})	2.0		
F	(10^{-3})	0.068		
Cl		0.550	0.472-0.579	0.581-0.637
Br	(10^{-3})	0.8		
I	(10^{-6})	0.5		
He	(10^{-9})	1.58	400-700 *	
Ne	(10^{-9})	6.31	10-15 *	
Ar	(10^{-9})	110	100-200 *	
Xe	(10^{-9})	0.4	0.1-0.3 *	
Th	(10^{-9})	0.002		
U	(10^{-9})	12.6		

Organic species (g/l)

DOC	300-2000		
Volatile fatty acids	5-50		
Non-volatile fatty acids	5-50		
Hydrocarbons	1-50		
Free sugars	20		
Ketones	10		
Aldehydes	5		
Phenols	1-3		
Acetate	70-2,800		1,000's

Formate	30-1,000	1,000's
Glycolate	9-1400	
Lactate	9-130	

All data have to be multiplied by the number in parenthesis (e.g. 10^{-3}: multiply by 0.001) in the second column, concentrations are then in mole/kg, for inorganic species, and g/l for organic species; Alk is in meq/kg. Rare gas data marked with * are extrapolated from other vent areas and are approximate only. Data from: Von Damm, K. L., 1983, Ph.D. Thesis, MIT/WHOI, 241 pp.; Stumm, W. and Morgan, J.J., 1981, Aquatic chemistry, 2nd Edition, John Wiley & Sons, New York, 780 pp.; Broecker, W.S. and Peng, T.-H., 1982, Tracers in the Sea, Columbia Univ. Press, New York, 691 pp.; Thurmann, E.M., 1985, Organic Geochemistry of Natural Waters, Kluwer Acad. Press, 497 pp.; and Campbell et al., in press, and personal communications, etc.

XV. APPENDIX D. List of Participants

Dr. Dennis Bazylinski
Biology Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Albert M. Bradley
Ocean Engineering Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Peter G. Brewer
Chemistry Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Gary Calabrese
Instrumentation Lab
113 Hartwell Avenue
Lexington, MA 02173

Dr. James Callis
Department of Chemistry
University of Washington
Seattle, WA 98195

Dr. Andy Campbell
Dept. of Earth, Atmospheric &
Planetary Sciences
Massachusetts Institute of Technology
Cambridge, MA 02139

Dr. Jim Churchill
Physical Oceanography Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Prof. David Edell
Massachusetts Institute of Technology
Room 20A-127
Cambridge, MA 02139

Dr. Remy Hennet
Postdoctoral Investigator
Chemistry Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Sharon Hibdon
Tufts University
Medford, MA 02155

Dr. Susan Humphris
Chemistry Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. William J. Jenkins
Chemistry Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Kenneth S. Johnson
Moss Landing Marine Labs
P.O. Box 450
Moss Landing, CA 95039

Dr. Charles E. Kolb, President
Aerodyne Research Inc.
45 Manning Road
Research Center at Manning Park
Billerica, MA 01821

Dr. Tom Kulp
Postdoctoral Scientist
Lawrence Livermore National Labs.
Livermore, CA 95440

Mr. Dempsey Lott
Department of Chemistry
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Prof. George Luther
College of Marine Studies
University of Delaware
Lewes, DE 19958

Dr. Chris Munkholm
Tufts University
Medford, MA 02155

Dr. Donald Nuzzio
EG&G
Princeton Applied Research
CN 5206
Princeton, NJ 08543-5206

Dr. Kristin Orians
Massachusetts Institute of Technology
E-34 354
Cambridge, MA 02139

Prof. Frank Sansone
Oceanography Department
University of Hawaii
1000 Pope Road
MSB 307
Honolulu, HI 96822

Prof. Jeffrey Steinfeld
Department of Chemistry
Room 2-221
Massachusetts Institute of Technology
Cambridge, MA 02139

Ms. Martha Tarafa
Research Associate
Chemistry Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Craig Taylor
Biology Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Geoffrey Thompson
Chemistry Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Mr. Andy Trivett
Ocean Engineering Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. John Van Leer
RSMAS
4600 Rickenbacker Causeway
Miami, FL 33149

Dr. Jean K. Whelan
Department of Chemistry
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

Dr. Carl Wirsen
Biology Department
Woods Hole Oceanographic Institution
Woods Hole, MA 02543

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16. Abstract (Limit: 200 words)

Researchers and engineers, from academia, government, and industry met and discussed the feasibility of using state-of-the-art laboratory technology for *in-situ* chemical measurements in the deep ocean, in and around active submarine hydrothermal systems. The concept of an autonomous benthic explorer (SENTRY) was presented to illustrate some of the constraints which must be kept in mind when adapting laboratory analytical tools to the deep ocean. A concensus was reached that some existing technologies either are being, or can be, adapted for *in-situ* measurement, in the near future, at reasonable cost. For many analytical techniques, minimal basic research will be required, and laboratory and *in-situ* testing represent the bulk of the work to be performed. A selection of analytical techniques appear particularly ready to undergo testing and transformations for *in-situ* measurements, including: electroplating, voltametry, potentiometric glass electrodes, and fiber optic technologies. Other techniques, such as *in-situ* Mass Spectrometry, do not appear to meet the criterias of technological readiness for *in-situ* deployment. Some technologies already being utilized or under development for use in the deep ocean include, for example: CO_2, O_2, H_2, H_2S, CH_4 sensors, voltametry for the determination of sulfur chemical speciation, fiber optic sensors for pH and pCO_2 determinations, and automated chemical microlaboratories for a wide variety of applications. These techniques, however require further research for long-term deployment and their ability to perform at high temperature, as encountered around submarine active hydrothermal systems.

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