ADA279035

MarChem 93

The Proceedings

The 1993 Workshop on Marine Chemistry Instrumentation

Sponsored by the Office of
Naval Research and the National
Science Foundation

Accesion For

NTIS CRA&I ☒
DTIC TAB ☐
Unannounced ☐
Justification ________

By ________
Distribution /

Availability Codes

Dist | Avail and/or Special
A-1

STEPHEN J. MARTIN

LOUIS A. CODISPOTI

F. EUGENE DEBONS

DAVID H. JOHNSON

EDWARD J. GREEN

H. LAWRENCE CLARK

DTIC QUALITY INSPECTED 3

Copyright © 1994 Martin Laboratories, Inc. All rights reserved.

For additional copies, please contact:

Stephen J. Martin

Martin Laboratories, Inc.
P.O. Box 58453
Houston, TX 77258

Voice: (713)286-5945

Fax: (713)286-5945

Internet Email: smartin@sccsi.com

Group photograph published with permission from
Russell E. Atha, III, Copyright 1993, Steamboat Hot Shots.

This work relates to Department of Navy Grant N00014-93-1-0448 issued by the Office of Naval Research. The United States Government has a royalty-free license throughout the world in all copyrightable material contained herein.

This material is based upon activities supported by the National Science Foundation under Agreement No. OCE-9305222. Any opinion, findings and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation

CONTENTS

SECTION I

SECTION II. CURRENT RESEARCH, PRESENTATIONS, POSTER ABSTRACTS, AND PAPERS

EXECUTIVE SUMMARY

MarChem 93 focused on bringing scientists from the academic and government communities together with experts from a variety of instrument manufacturers . The meeting followed two years after the successful MarChem 91 workshop, and built on suggestions that arose from that meeting.

Poster sessions, lectures and exhibits showcased innovative developments in chemical instrumentation, key government programs in this area were reviewed, and panel discussions addressed the needs and perspectives of the various communities involved and tried to identify strategies for instrumentation development for the future. However, the excitement engendered by those new technologies that are becoming available was tempered by the (largely justified) perception of instrument manufacturers that the development of chemical instrumentation specifically for oceanographic research was typically not cost effective.

Communications

To continue the progress made during MarChem 93, it is necessary to maintain close contact with a diverse community of technical people working in many different kinds of organizations and located throughout the U.S. The best means to provide effective communications is probably via Internet email.

New Technologies

A series of presentations gave a tantalizing glimpse of a future containing a variety of micro-chemical sensors and new technologies such as biochemically based sensors, fiber optic based sensors, film-based sensors, micro-machined gas-chromatographs, and micro-machined pumps and valves. The benefits of such small-scale devices are clear: smaller instruments, simpler deployment in remote instrumentation, potential cost advantages for large scale deployments.

Needs

An area with clearly developed needs was the broad topic of water sampling and measurement. Here, current global programs have helped us realize that our current approach to making shipboard measurements is archaic. Participants at the workshop felt that significant advances could be made — even with present technologies—in the integration of sampling, automated chemical analysis, and record keeping processes. These advances could be viewed (or even planned) as a series of incremental steps: improved hydrographic bottle sampling, analysis of pumped sea water streams (e.g. on "ships of opportunity"), underway three-dimensional mapping systems, and autonomous measuring systems on platforms such as buoys. However, if such measuring systems are to be exploited fully, a great deal of thought will need to go into achieving the necessary quality assurance.

Perspectives

A recurrent question at this meeting was "How do we encourage the development of widely (commercially?) available chemical oceanographic instrumentation?" The perspective of the industrial representatives was that such development is market driven; however, the marine chemical market is typically small and thus, of itself, unlikely to attract commercial development. Any substantial pressure is thus likely to come either in response to new large programs that need large numbers of instruments or sensors (e.g. the proposed Global Ocean Observing System), or from the use of sensors that are also applicable to broad-based environmental, biomedical, or industrial monitoring and whose development is driven by markets external to marine chemistry.

Strategies and Future Opportunities

Although many innovative ideas are to be found in academic and government laboratories, it was felt that to transform an idea into a marketable product usually required someone from the original laboratory (student, post-doc, scientist) to actively move into the commercial environment. Hesitancy to do this, leaves many potentially valuable tools languishing. Nevertheless, it was also felt essential that marine chemists involve people from outside the field of marine chemistry in the process of instrument development.

One approach—discussed in a report from a National Academy committee (Committee on Oceanic Carbon, Ocean Studies Board (1993) *Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies*. National Academy Press, 85 pp.)— is to solicit the involvement of analytical chemists in the development of tools for oceanographic studies.

Another, complementary, approach is to encourage the use of the Small Business Innovation Research (SBIR) Program as a vehicle for encouraging the participation of small companies in instrument development. (However, success here requires a clear market focus!).

All in all, it was felt that improvement in the future lies in more extensive collaboration between academia, government laboratories, commercial companies and government sponsors. This will allow the field of Marine Chemistry to position itself to influence the development of new technologies and to take advantage of instruments as they become available.

ACKNOWLEDGEMENTS

A special thank you is offered to the workshop sponsors—the Office of Naval Research and the National Science Foundation. The conference would not have been possible without their support.

Many individuals helped make the workshop run smoothly. The conference was arranged with the assistance of Laurie Milne and Peter Hunter. Mrs. Milne answered our many logistical questions and supplied information about the local services. Mr. Hunter was the coordinator for the outstanding meeting facilities. A recording of the meeting was made by Paul Boothe.

Andrew Dickson prepared the *Executive Summary*. Tony Knap, Terry Whitledge, and Bob Pellenbarg are preparing articles to report the results of MarChem 93 in journals and magazines. Russell Atha readily agreed to have his group photograph published in this report.

The contributions of the participants are very much appreciated. The success of the program is due to their substantial volunteer efforts. Members of the group readily volunteered to serve on discussion panels, prepare meeting presentations, papers and news announcements, and serve on the executive committee to plan and execute MarChem 95.

INTRODUCTION

The MarChem 93 workshop on marine chemistry instrumentation was held from August 2 to August 5, 1993. The sponsors were the Office of Naval Research and the National Science Foundation. Forty–four scientists and engineers from government, universities, non–profit organizations, and businesses attended. The theme of the workshop was *Industry, University and Government —A Partnership for Progress.*

The workshop's administrative functions were carried out by Steve Martin. The technical chairman was Lou Codispoti. ONR program managers—Dave Johnson and Ed Green, and NSF program manager—Larry Clark provided technical guidance and funding.

The overall goal of the workshop was to encourage faster transfer of new technology into the fields of marine chemistry and chemical oceanography.

The MarChem 93 workshop had the following specific objectives:

- Identify and bring together leading academic and government scientists in marine chemistry with industry experts in instrument manufacturing
- Review marine chemistry instrument development programs sponsored by the Office of Naval Research, the National Science Foundation, the Department of Energy, and the Environmental Protection Agency
- Review and discuss current status of water sampling and sensor instrumentation
- Present an industry perspective on new product development and marketing, and a government and university perspective on marine chemistry instrument development
- Select water sampling and sensor instrumentation to be recommended to the sponsors for development
- Present posters and exhibits identifying innovative developments in marine chemistry instrumentation
- Encourage academic and government marine chemists to work with instrument manufacturing companies to develop new and improved methods and equipment for marine chemical analyses
- Document the workshop with the publication of presented papers, discussions and recommendations in a report to ONR.

The proceedings of the workshop are reported in two sections. *Section I* contains summaries of the panel discussions and reports the conclusions. The agenda, a list of participants, and information about funding sources such as SBIR programs are also provided in *Section I. Section II* presents the participants' written contributions submitted before, during or after the workshop. The contributions consist of presentation papers, poster abstracts, and written descriptions of current research interests. The reader is invited to contact the author for additional information about his/her work. The addresses and phone numbers for the authors are listed in the section entitled *Participants.*

Section I

PANEL DISCUSSIONS
FUNDING SOURCES
AGENDA
PARTICIPANTS
CONCLUSIONS

PANEL DISCUSSION HIGHLIGHTS

THE FUTURE OF MICROCHEMICAL SENSORS

Panel Chair:	Dave Johnson
Rapporteur:	Charles Neely
Panel:	Gary Yanik Mark Zdeblick Michael Lerner

Recommendations

Newly developed microvalves and micropumps should be investigated for immediate application to oceanographic chemical instrumentation.

Antibody chemistry may provide specific and sensitive assays but response (resetting) time will be slow when dealing with low concentrations of analytes if equilibrium chemistry is used. Methods of increasing response time should be investigated.

Multiple use sensors applicable to marine chemistry, environmental monitoring, medical use, and process monitoring should be investigated because these may have a large enough potential market to justify development costs.

Summary of Panel Discussion

The following presentations preceded the panel discussion:

Micromachined gas chromatography—Paul Holland

Micromachined liquid chromatography—Gary Yanik

Micromachined pumps and valves—Mark Zdeblick

A nose on a chip—Michael Lerner

Langmuir-Blodgett monolayers in selective sensing applications—Charles Neely

The panel discussion then focused on the need for small chemical instruments by the oceanographic community. The following reasons for small instruments were discussed:

- Smaller sensors will allow in situ measurements from a variety of platforms AUVs, CTDs, towed platforms (Sea-Soar).
- Even modest size reductions will be beneficial by reducing bench space requirements on ships.
- In coastal regions, smaller ships will be used for ocean monitoring. Therefore, smaller instruments will be required.
- Reduction in sensor size permits smaller sample volumes.
- Smaller size may provide more rapid response.
- Smaller may mean cheaper. This is especially true for chip type systems such as CHEMFETS. Cost will be especially important when addressing questions that will require many sensors.
- Even small reductions in detector size can have a cascade effect, reducing not only the size of all system components, but also the size of the mounting platforms (ships or moorings).

WATER SAMPLING: PRESENT LIMITATIONS AND FUTURE POSSIBILITIES

Panel Chair:	Vernon Asper
Rapporteur:	Paul Boothe
Panel:	Carlton Hunt Lou Codispoti Andrew Dickson Brad DeRoos

Recommendations

Develop a more integrated systems approach to implementing sampling devices and sensor suites:

- Use a cradle to grave approach emphasizing sample and data integrity (e.g. automated sample tracking, minimal sample handling, integrated supporting parameter determinations like temperature, salinity, nutrients, etc., and data management).
- Include sampling objectives (why are you taking the sample, spatial and temporal resolution needed, etc.) and data management objectives (replication and other QA needs) in design considerations.
- Minimize sample waste.
- Minimize interactions among competing samples that can impact data quality.
- Promote automated, simultaneous determination of multiple paramters from a single water sample (e.g. temperature, salinity, oxygen, nutrients, pH, chlorophyll, light scattering).
- Integrate sample and data tracking (e.g. using LIMS/bar code approach).
- Develop improved water samplers (perhaps follow-on to first WOCE sampler) with the following features:
    1. Chemically inert
    2. Effective flushing, reliable tripping and closure, and volume scalability
    3. Avoidance of sea surface contamination
    4. Minimal buoyancy
    5. Minimal hydrodynamic drag and artifacts
    6. Efficient lowering rate that is decoupled from ship's motion
    7. Good at-sea maintainability.
- Develop improved pumping systems for continuous sampling of chemical species for which *in situ* sensors are not available
- Combine remote sensing (i.e. SeaWiFS Color Scanner 1994 and Japanese Color Scanner 1996) and higher density ground truth sampling to study fine scale oceanic chemical features.
- Develop autonomous sampling and analyses systems to provide low cost, sampling from volunteer ships, buoys and moorings.

Summary of Panel Discussion

This section includes summaries of both Dana Kester's presentation on Water Sampling and the panel discussion which followed his talk.

Question: Are oceanographic water sampling methodologies adequate to meet the future needs of the chemical oceanography research community? If not, how should they be improved?

Sampling bottles (e.g. Nansen, Van Dorn, Niskin, Go-Flo) have been the dominant sampling methodology used by marine chemists for more than a century. Using bottle arrays in increasingly large and flexible rosette samplers has been the primary, evolutionary sampling technology during the past 20 years.

Chemical oceanographers are now being asked to make informed inputs to global change models. To address this situation, we need to characterize and understand meso- and micro-scale chemical features. However, current technologies cannot accommodate the increased sampling rates required for this characterization of second and third order features. Also these technologies often cannot provide sufficiently representative samples (free from sampling artifacts) to adequately study small scale marine processes.

As a result, significant improvements will have to be made in sampling technologies over the next 5 to 10 years. Although the ultimate goal is for *in situ* sensors (obviating the need to bring water samples back to the ship), there will be a need to physically collect water samples for the foreseeable future.

Problem areas in water sampling:

- Inability to collect representative samples of suspended particulates. There is still considerable controversy over artifacts in particle samples from both sediment traps and water bottles (hydrodynamic, induced aggregation, intruder organism effects, incomplete recovery, etc).
- Inability to routinely collect representative near surface and near bottom samples.
- Difficulty in collecting sufficient volumes for deep ocean ultra-trace organic analyses (e.g. PCB's).
- Unresolved poor correlations among data from CTD sensors. There is no convenient way to accurately calibrate CTD sensors using water bottle samples taken concurrently.
- Lack of autonomous chemical analyzers to fully exploit new sampling opportunities or to do increased sampling with static funding (e.g. JGOFS Arabian Sea moorings, Sea Soar, ship of opportunity program, etc.). We are definitely behind the physical oceanography community in developing this capability.
- Marine chemistry community culture:
  1. Conservative and careful, slow to change.
  2. Lack of institutional incentives to develop improved instrumentation such as water samplers.
  3. Lack of incentives among multiple science teams in large programs (e.g. WOCE) to integrate sampling technologies.

SENSORS

Panel Chair:	Stephen Lieberman
Rapporteur:	Alan Shiller
Panel:	Hans Jannasch Richard Thompson Russell Seguin

Recommendations

The funding agencies should develop intern programs to foster interdisciplinary interactions. These programs could provide analytical chemists (i.e., sensor developers) opportunities and incentives to come to oceanographic centers for testing and information exchange. Intern programs could also provide marine chemists with opportunities to visit analytical chemistry, biomedical, and engineering labs to examine new technologies. A similar mechanism could be used to foster academic-business interactions.

Meetings like MarChem 93 are an important means of bringing together relevant players in sensor development. Future meetings could focus on more specific topics, seek out additional representatives of source technology fields, and provide additional background on geochemical problems for the non-marine scientists.

Mechanisms for better interagency cooperation should be developed to avoid overlapping developments (i.e., reinventing the wheel), speed new developments, and enable academic interactions.

An effort should be made to pinpoint sensors which would be useful and reliable for global large-scale monitoring programs, which in and of themselves could be a substantial market for these sensors.

Panel Discussion

Sensors were defined in the initial overview talk as continuous, *in-situ* devices. However, sensing devices can be used in other modes of operation (i.e., periodic or lab-based). The ideal sensor needs to be sensitive and selective, have a stable calibration, consume little power, and be durable over the long-term in a hostile environment. The basic reasons for needing sensors are the desire of marine chemists to increase the spatial and temporal resolution of their measurements. However, some measurement needs may require different types of sensors for the same analyte (e.g., high spatial resolution versus long-term monitoring versus real-time data acquisition).

A fundamental question is how to get sensors out of the lab and into the field, especially in a reasonable timeframe. Encouraging interactions among analytical chemists, marine chemists and engineers is important in this regard. Important "source fields" for analytical developments include analytical chemistry, biomedical sciences, automotive and air pollution engineering, aerospace, and food processing analysis. Possible mechanisms to foster these interactions include meetings such as MarChem, invitations to sensor developers to visit oceanographic centers, and the brokering of interactions by funding agency program managers. In some cases, getting several agencies interested in a development may speed the process.

The grants review process is a potential pitfall in certain academic collaborations because sensor development is sometimes not regarded as fundamental science. Additionally, a collaborative development proposal may need to be reviewed by experts in several different fields. However, it is doubtful (and not really necessary) that the collaborators are at the "cutting edge" of several fields simultaneously.

To get industry involvement in the development and commercialization of marine instrumentation requires an incentive. The marine chemistry market, of itself, is usually not large enough to provide the economic incentive that many companies require to invest in development. An analogy to the development of clinical sensors was made. In that case the medical instrument community knows what the patient (i.e., product) demand will be. For marine chemistry sensors, an obvious tie-in is with environmental monitoring. There is a potential need for sensors to monitor eutrophication problems, metal contamination, etc. These environmental needs may serve to spur industrial development of sensors with oceanographic capability. Also, government interest and new regulations may spur sensor development. The Navy, for example, sees PAH's, PCB's, and metals as primary concerns. However, government regulation can also be an inhibition such as when small businesses are intimidated by the EPA certification process.

Several other important points and issues were raised:

- Response times of sensors are an important consideration. For equilibrium systems, the inherent response time to sub-nanomolar concentrations can be substantial. Organic complexation of metals can be a kinetic limitation.
- Many lab-built marine chemistry instruments are "kluged" together. Getting these from the lab demonstration stage to a reliable, potentially marketable prototype can be a challenge.
- A technology gap appears to exist in the development of sensors capable of detecting low level organic compounds in seawater.
- It can be helpful to the development process to get analytical chemists and their techniques out to sea quickly. Shipboard opportunities abound, but once again, communication of opportunities and incentives to the development are necessary.

NEW PRODUCT DEVELOPMENT AND MARKETING: AN INDUSTRY PERSPECTIVE

Panel Chair: Steve Martin

Rapporteur: Dave Diamond

Panel: Paul Holland
John McDonald
Mary McFarland

Recommendations

The marine chemistry market is generally too small to attract significant interest by instrument developers. This market must combine and coordinate with larger markets like environmental monitoring or biomedical testing.

From the industry point of view, the risk in developing new instruments must be reduced by fee-for-service contracts and joint projects with academia where industry can leverage its development money.

SBIR's, as currently configured, are too small to attract significant sufficient industry interest in new instrument development. Funding agencies should coordinate programs which require new instruments into larger, more sustained programs.

The MarChem committee should work to obtain partial industry sponsorship of the next workshop. This sponsorship would ensure increased industry involvement in the next MarChem meeting.

Summary of Panel Discussion

Industry's first questions regarding new marine instruments are, "What is the market?", and "How can it be addressed?" The marine chemistry market is small, fragmented and worldwide—it cannot easily be measured like the medical testing field (# of people with a given disease) or the environmental monitoring area (# of cars or # of underground gasoline tanks). Mailed advertisements and appearances at trade shows are less effective for new instrument developers than direct interaction with potential customers on research ships.

Marine instrumentation companies based in North America have the potential to expand worldwide, and some attendees reported success in selling instruments abroad. However, companies have difficulty learning about new international opportunities and in taking advantage of those opportunities through their usual networks of dealers, agents and company representatives. One possible international market for marine chemistry instruments is the UNDP (United Nations) oceanography program funded by the World Bank.

Industrial R&D to develop new instruments is difficult to focus. Management skills are needed to ensure the team stays on track and develops a workable instrument. Instrument development teams must include analytical chemists as well as mechanical engineers, electrical engineers, programmers and possibly oceanographers in order to develop a working prototype.

New product development is a high-risk, high-cost activity. There are invariably difficulties in moving from a prototype to large-scale production. Industrial examples shared during the workshop include:

- YSI's enzyme electrode—2 years from idea to prototype and 2 more years to a marketable instrument;

- YSI's multiparameter instrument—a 2 year project to repackage existing instruments into a new instrument;
- Lachat reported a instrument development project which led nowhere as only one instrument was sold. The lesson learned was that instrument development must be driven by market pull, not by scientist and company push. The general rule of thumb for marketing new instruments from the prototype stage is to triple the original estimate of time and money.

In industry, product development money is spread over several new products, not concentrated on single target instruments. This is a way to get the most benefit from the few instrument developers at the company and to reduce the cost of individual instruments.

Effective transfer of an academic chemical or sensor technology to industry requires a direct one-on-one (scientist-to-scientist) relationship. One industrial representative stated that to transfer a new academic idea to a practical marketable product requires someone from academia (student, post-doc, or professor) to "walk with their feet, not with their heads".

Two "major" instrument companies, Perkin Elmer and Hewlett Packard, were involved in MarChem91, but declined to participate this year. In fact, only eleven of the 45 participants at this workshop were from industry. Much discussion centered on how to attract instrument developers to a MarChem workshop given the small market size. Two different ideas were presented concerning the purpose of industrial involvement in the workshop. One view is to transfer ideas for new sensors from academia to oceanographic instrument makers. The second is to have instrument makers unrelated to oceanography inform the marine chemistry community of new technology which may have applicability in oceanography.

Most vendors supplying instruments and technology to marine institutes are small businesses and most of those are concentrated in the Seattle, San Diego and Cape Cod areas of the country.

In response to questions, this panel reviewed the role of EPA in instrument development. The EPA does not directly fund instrument development and does not issue instrument specifications. However, it does define markets by enforcing regulations and can delay the opening of markets until new analytical methods are approved. In contrast, both DOD and DOE issue specifications and develop instruments. One example of the latter is the penetrometer discussed by Dr. Lieberman.

An interesting point of discussion was that the largest demand for new chemical sensors in the future may come from the public. The home sensor market may be larger than either laboratory or field markets, and spinoff technologies may apply to marine chemistry if the methods used are cheap, stable and accurate.

MARINE INSTRUMENT DEVELOPMENT: A GOVERNMENT AND UNIVERSITY PERSPECTIVE

Panel Chair:	Larry Clark
Rapporteur:	Terry Whitledge
Panel:	Bob Pellenbarg Dave Johnson Dan Buttry Marlin Atkinson

Recommendations

The MarChem93 proceedings should contain a summary of the SBIR programs and proposal deadlines.

The SBIR funding agencies represented here should lobby for SBIR listing of marine chemistry instrumentation topics within their own agencies and should coordinate their funding decisions in order to avoid duplication of efforts and to foster development of new instrumentation.

Universities are showing an increased tendency to patent new science and technology as it is developed and published. Continued efforts by academia to seek markets and follow-on development of their technology are in the best interests of the universities themselves and the marine chemistry community and should be encouraged

Technical managers from industry benefit from attending science meetings, and they should be encouraged to continue their efforts to learn current science needs.

Summary of Panel Discussion

The government/university perspective presents a moving target as some agency missions change (DOD) and as government academic funding requires more relevancy to societal needs. The panel discussed new instrument development in terms of three phases:

1. Project or idea initiation,
2. Implementation of the instrument,
3. Development, and acceptance of the new instrument and its measurements by the marine chemistry community.

Initiation

Basic Research—problem driven—involves instrumentation and technology required to make necessary ocean measurements to advance knowledge. Justified on basis of science merit, as determined by peer review.

- May be project-specific initially, having very restricted use.
- May address an oceanographic community need for improved measurement capability.
- No pressure on scientist to identify market or make it manufacturable.

Applied Research—serves mission or regulatory agency needs—requirement driven—needs are identified to fulfill agency requirement; development expertise can be sought out and project directed.

- Initiate via RFP or BAA, etc.
- Might be unique.
- May or may not generate market.

Implementation

Once need has been identified and justified, then a process is needed to make instrument development happen. The developer can:

- Use personal or in-house capabilities; hire expertise.

- Alter personal career track—become technology expert. Use sabbatical time to obtain or supply expertise.
- Collaborate with fellow academics from other departments. This approach is likely to improve instrument's performance and shorten development time.
- Collaborate with private sector.
- Process should be iterative.
- Consider market assessment by other university departments to expand communications and consider capability and design options.

University-private sector collaboration should be facilitated and proactively encouraged by funding agency. Consider having initial designs provide for efficient and cost-effective production.

Adapt existing instruments or technology. To do so requires knowledge of what exists and what capabilities are. Suggests need for good communication of needs and operational experiences including software.

Integration of sensors and instrumentation is important, e.g. the SeaBird CTD has ports for other sensors.

It is beneficial for academic community to tap into industrial knowledge based on materials, miniaturization, packaging, process control, robotics and university-based business development expertise (e.g. Technology Transfer Office).

Acceptance

Prototype testing in field by objective consultants or potential users is important.

Scientific acceptance of data relevancy: published papers, use of data in new research.

Fulfilling mission requirements.

Regulating agency acceptance via scientists, advisors, consultants; or scientific society approval, international intercalibration test.

Legal challenges to data reliability may be a significant concern for certain select, but potentially large environmentally-oriented markets (e.g. public use of radon detectors).

Truth in packaging is important—requires feedback from users on how well instrument operates. A major problem can be marketing an instrument before product is ready.

The broader the use (marketability), the higher the likelihood of rapid community approval and acceptance.

CHEMICAL OCEANOGRAPHIC INSTRUMENTATION OPPORTUNITIES

Panel Chair:	Edward J. Green
Rapporteur:	Gernot Friederich
Panel:	John Downing David Walt Dave Diamond

Recommendations

The panel agreed that water bottle sampling, particularly from depth, will be the mode of collection for many chemical measurements for at least the next 25 years. We strongly recommend that efforts be made to improve the present rosette bottle system in several ways:

- Routine measurements should be integrated into the bottle system (see below), in order to eliminate the "dance" of technicians around the rosette;
- In an ideal integrated bottle package, data reduction should become a transparent and integrated part of instrumentation;
- Better bottle tracking, perhaps with a computer based barcode technique should be implemented to eliminate uncertainty regarding the depth and station of a particular sample;
- Bottles should be collapsible in order to eliminate the head space problem, perhaps using the mylar bag technology proposed for the WOCE sampler;
- Faster bottle sampling is a high priority; we recommend that the WOCE ballistic sampler concept be revisited and consideration be made of a more deliberate engineering design effort. The savings in ship time—particularly for long transects—that could be realized over the years seem to justify a million dollar development effort.

The panel noted that several measurement techniques are ready or nearly ready to meet the requirements for deployment on ships of opportunity. These requirements are continuous or repetitive batch measurement, rugged "gorilla-proof" design, and unattended operation for 2-4 weeks. The surface measurements that appear feasible in the near future are temperature, salinity, nutrients, dissolved oxygen, pH, optical characterization of particulates, chlorophyll fluorescence, surface radiation, underwater optical characterization of the light field, and possibly pCO2 and volatile organic compounds. Our recommendation is that an engineering design initiative be undertaken to package the appropriate sensors in a rugged, physically integrated system with data reporting and assimilation capabilities. Initially a few systems could be deployed on vessels in the research fleet where there would be a greater support level for attendance and calibration. Once the inevitable bugs were ironed out commercial manufacture would be attractive as the market could reach 1,500 units—roughly the number of ships of opportunity.

For chemical instrumentation deployment on moorings, moored and drifting buoys, and fixed (such as oil drilling) platforms, the requirements are similar to ships of opportunity, but with longer deployment times likely, possibly up to 6 months. Additional questions arise with such long durations: stability of reagents, electronics, and resistance to biofouling become very important. The panel could not see an obvious path to overcome these problems and therefore recommends that research elucidating the problems be considered by the agencies. An example of such research would be what are the chemical perturbations introduced by bacterial and fungal mats on intakes.

For 3-dimensional chemical mapping with undulating (Sea-Soar type) systems, long deployments are not the problem, but rather the need for fast response time of the sensors—of the order of 1 second. The panel recognized this type of chemical measurement to be the most difficult of all the operational modes considered. Nevertheless, a few measurements appear to be possible for near-term development; they are mostly optical. Optical particle detection, chlorophyll fluorescence, and in the near future, low dead-volume flow injection methods. Ideally, these should be self calibrating, such as the multi-wavelength ratioing pH method. The panel recommends that such instrumentation development be encouraged.

Summary of Panel Discussion

Because the operational requirements of chemical instrumentation vary widely depending upon the platform and mode of operation, the panel organized its discussion around the operational modalitys. The following were identified:

Underway Operation Mode

Ships of opportunity, including submarines—requirements: continuous or repeating batch measurements; rugged design; unattended operation up to 4 weeks.

Underway surface mapping, hull or outside intake—requirements: not a critical factor; this mode of operation in use at the present time, but advances desirable.

Underway 3-D mapping, pumping systems—requirements: various response time requirements depend ing upon operational details, 1 second to 30 minutes.

Underway 3-D mapping, undulating (Sea-Soar type) systems—requirements: continuous or repeating batch measurements; rugged design; unattended operation for several hours; fast response time of ~1 second.

Autonomous underwater vehicles—requirements: much the same as undulating systems.

Underway 3-D mapping, towed chemical "chain"—requirements: very small sensor size.

Station Keeping Mode

Vertical profiling, bottles—requirements: *improved bottles needed to* eliminate head space, automate bottle tracking, integrate analytical systems, and to speed up collection from depth.

Vertical Profiling, pumping systems—requirements: not a critical factor; this mode of operation in use at the present time, but advances desirable.

Moorings, moored and drifting buoys, fixed platforms—requirements: much the same as ships of opportunity, but with longer deployment times, up to 6 months. Stability of reagents, electronics and resistance to biofouling become problems. Perhaps a Gatling gun approach, a manifold of intakes or full instruments, might be employed.

FUNDING SOURCES

SMALL BUSINESS INNOVATION RESEARCH (SBIR) PROGRAM

SBIR Eligibility

A business concern must be at least 51% owned and controlled by a U.S. citizen(s) or permanent resident aliens, and it must not have more than 500 employees.

SBIR Grant Size

Phase I Research—$100,000 limit mandated by law (Public Law 102–564 of Oct. 28, 1992), with each agency handling the grant details differently. The Navy allocates $70,000 for initial Phase I research with an option for a $30,000 bridging grant to Phase II.

Phase II Research—$750,000 limit mandated by law, with agencies differing on the details of the awards. The Navy allocates $600,000 initially with an option for $150,000 additional.

SBIR Deadlines Relevant to MarChem 93 Participants

Note that closing dates vary somewhat from year to year, and are subject to change by the individual agencies. The larger funding agencies have two program solicitations per year while the smaller agencies have one.

U.S. Department of Defense—July 7

U.S. Department of Energy—June 28

National Science Foundation—June 14

Publications

SBA/SBIR Pre-Solicitation Announcement (PSA) is published by the U.S. Small Business Administration quarterly, in March, June, September and December. The PSA is a master schedule listing the eleven agencies having SBIR grants, the titles of the research topics for the current solicitation period, and the release dates and closing dates for proposals for each agency.

SBIR Program Solicitation is published separately by each major funding agency (like the Department of Defense) two to three months after the PSA. It is a more complete listing of all research topics, with details including category of project, objective, description of the project and of Phases I and II, and potential commercial market. It contains SBIR program descriptions and definitions, instructions for preparing and submitting proposals, selection criteria, contractual information, and descriptions of scientific and technical information assistance available.

Mailing List

The SBA/SBIR Pre-Solicitation Announcement is sent to companies interested in the SBIR program. The address to write for getting on this mailing list follows, and the phone mail system at the listed number allows easy access to the mailing list:

Office of Innovation, Research and
Technology
U.S. Small Business Administration
409 Third Street, Southwest, (8th Floor)
Washington, DC 20416

(202) 205-7777

Program solicitations can be obtained from the individual agencies whose addresses are listed in the PSA.

Departmental SBIR Contacts Relevant to MarChem 93 Participants

(These contacts are for program information, not for supplying program solicitation books.)

U.S. Navy SBIR Programs—Mr. Vincent Schaper, ONR, (703) 696-4286

U.S. Department of Energy—Dr. Samuel J. Barish, DOE, (301) 903-3054

U.S. Environmental Protection Agency—Mr. Donald F. Carey, EPA, (202) 260-7899

U.S. Department of Commerce (NOAA)—Dr. Joseph Bishop, DOC, (301) 763-4240

National Science Foundation—Dr. Roland Tibbetts, NSF, (202) 653-5002

SMALL BUSINESS TECHNOLOGY TRANSFER (STTR) PROGRAM

Definition

The same 1992 law (Public Law 102-564 of October 28, 1992) which renewed the 1982 SBIR program established a new R&D funding program called, "Small Business Technology Transfer Pilot Program", abbreviated as STTR. STTR is a three-year pilot program for the five Federal agencies with R&D expenditures of at least $1 billion. These agencies are: DOD, NASA, DOE, NIH and NSF. The funds allocated to STTR for the three years of the program are at least 0.05%, 0.10% and 0.15% of the extramural R&D budget for the year.

Purpose of STTR

STTR is designed to reserve a small percentage of the R&D budgets of the largest Federal agencies for "cooperative R&D". Cooperative R&D is defined as R&D conducted jointly by a small business and a research (nonprofit) institution in which at least 40% of the work is performed by the small business and at least 30% is performed by the research institution.

Level of Funding

Like the SBIR, STTR provides for two phases of research, a 1-year Phase I award of up to $100K and a 2-year Phase II award of up to $500K. The Navy portion of this money for FY94 is $2.6 million, with a doubling to $5.2 million in FY95.

Literature

Information can be obtained from:

Office of Innovation, Research and Technology
U.S. Small Business Administration
409 Third Street, Southwest, (8th Floor)
Washington, DC 20416

(202) 205-7777

Management

The entire Navy program will be managed by Mr. Vincent Schaper of the Office of Naval Research. He can provide the Navy list of research topics, and he can be reached at (703) 696-4286.

Schedule

The DOD STTR Solicitation was available December 1, 1993 and proposals are due April 1, 1994. The research topics will be from the Military Critical Technology List of October 1992.

Relevance to MarChem 93

STTR is a new attempt by the government to encourage additional high quality, cost effective R&D which leads to technological innovations. The 1992 SBIR program excluded academic institutions, and the new STTR program encourages industry/university collaboration. Federal funding of such collaborative efforts is one of the needs expressed at the MarChem workshop to encourage development of new marine chemistry instrumentation.

AGENDA

Monday
August 2

Morning Session: *Steve Martin*

8:00 Introduction to workshop—*Steve Martin*

Workshop objectives—*Lou Codispoti*

Participants introduction—*Steve Martin*
Participants background and experience, interests and current work, expectations from workshop

Marine chemistry instrument development programs

9:30 ONR programs—*Ed Green, Dave Johnson, Harold Bright*

10:30 NSF programs—*Larry Clark*

11:00 DOE programs—*Creighton Wirick, Brad DeRoos*

11:30 NOAA programs—*Catherine Woody*

Afternoon Session: *Dave Johnson*

Microsensors

2:00 Chemical instrumentation based on silicon micro-fabricated components—*Paul Holland*

2:20 Micromachined liquid chromatography—*Gary Yanik*

2:40 Micromachined actuators—*Mark Zdeblick*

3:00 Langmuir-Blodgett monolayers in selective sensing applications—*Charles Neely*

3:20 A nose on a chip—*Michael Lerner*

4:10 Panel discussion on the future of microchemical devices for oceanography

Panel chair: *Dave Johnson*
Rapporteur: *Charles Neely*
Panel: *Gary Yanik*
Mark Zdeblick
Michael Lerner

Tuesday
August 3

Morning Session: *Ed Green*

8:00 Why we need improved instruments—*Lou Codispoti*

8:15 Water sampling; present limitations and future possibilities—*Dana Kester*

9:00 Panel discussion on water sampling
Panel chair: *Vernon Asper*
Rapporteur: *Paul Boothe*
Panel: *Carlton Hunt*
Lou Codispoti
Andrew Dickson
Brad DeRoos

10:15 Sensors—*David Walt*

11:00 Panel discussion on sensors
Panel chair: *Stephen Lieberman*
Rapporteur: *Alan Shiller*
Panel: *Hans Jannasch*
Richard Thompson
Russell Seguin

Afternoon Session: *Larry Clark*

1:30 DOE programs—*John Downing*

2:00 EPA programs: Field screening instrumentation for hazardous waste sites—Opportunities for technology transfer—*Ed Poziomek*

2:30 Poster/exhibit presentations (about 5 minutes each)

3:30 Posters/exhibits session

Wednesday
August 4

Morning Session: *Lou Codispoti*

8:00 Panel discussion on problems with new product development and marketing, an industry perspective

Panel Chair: *Steve Martin*
Rapporteur: *Dave Diamond*
Panel: *Paul Holland*
John McDonald
Mary McFarland

8:45 Panel discussion on instrument development, a government and university perspective

Panel Chair: *Larry Clark*
Rapporteur: *Terry Whitledge*
Panel: *Bob Pellenbarg*
Dave Johnson
Dan Buttry
Marlin Atkinson

9:15 Panel discussion on selection of instrumentation to be recommended for development

Panel chair: *Ed Green*
Rapporteur: *Gernot Frederich*
Members: *John Downing*
David Walt
Dave Diamond

10:30 NOAA programs—*Bill Busch*

11:00 MarChem 93 report preparation—*Lou Codispoti and Steve Martin*

11:15 Breakout session for discussion panel members to work on report summaries

Afternoon Session: *Lou Codispoti*

2:00 Poster/exhibit presentations (about 5 minutes each)

3:00 Posters/exhibits session

Thursday
August 5

Morning Session: *Steve Martin*

8:00 Panel summaries and recommendations on instrumentation development plans—Panel chairs

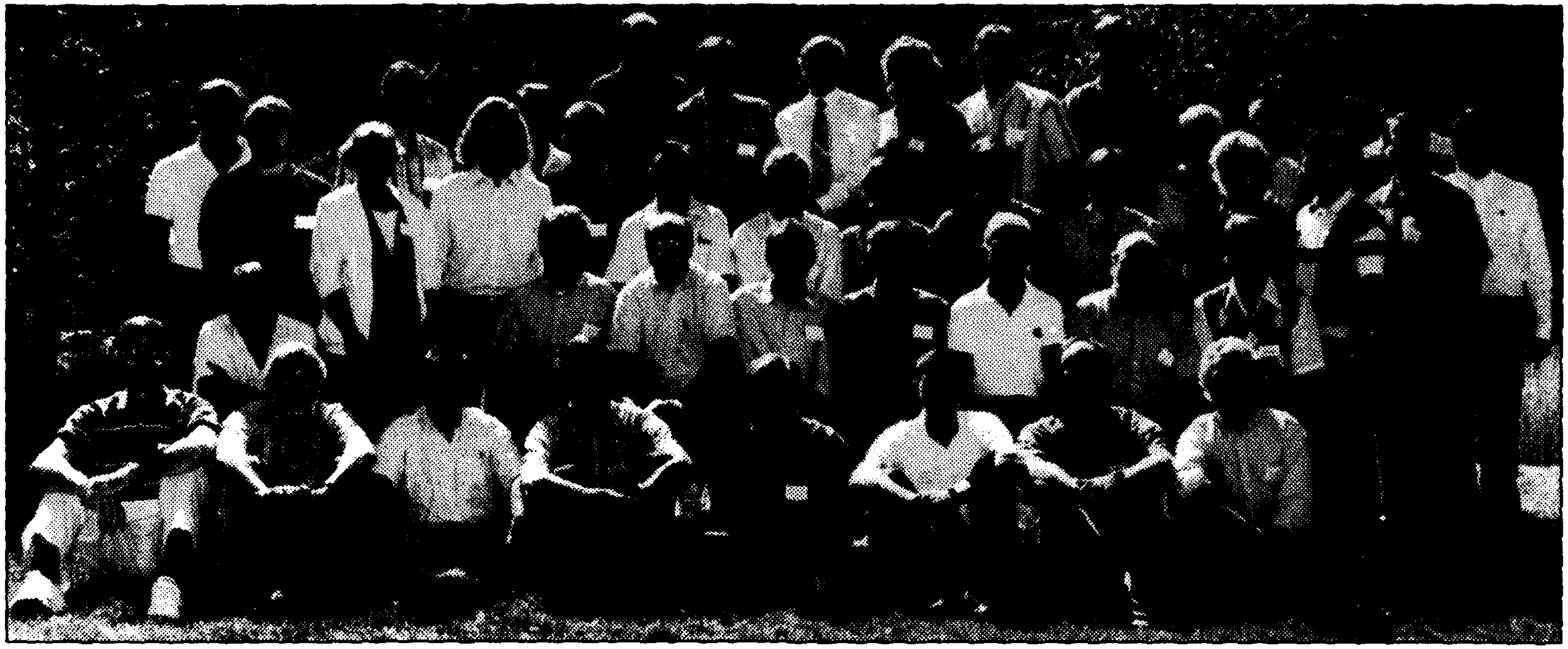
10:30 MarChem 93 report, future goals and objectives, and concluding remarks

12:00 End of MarChem 93 workshop

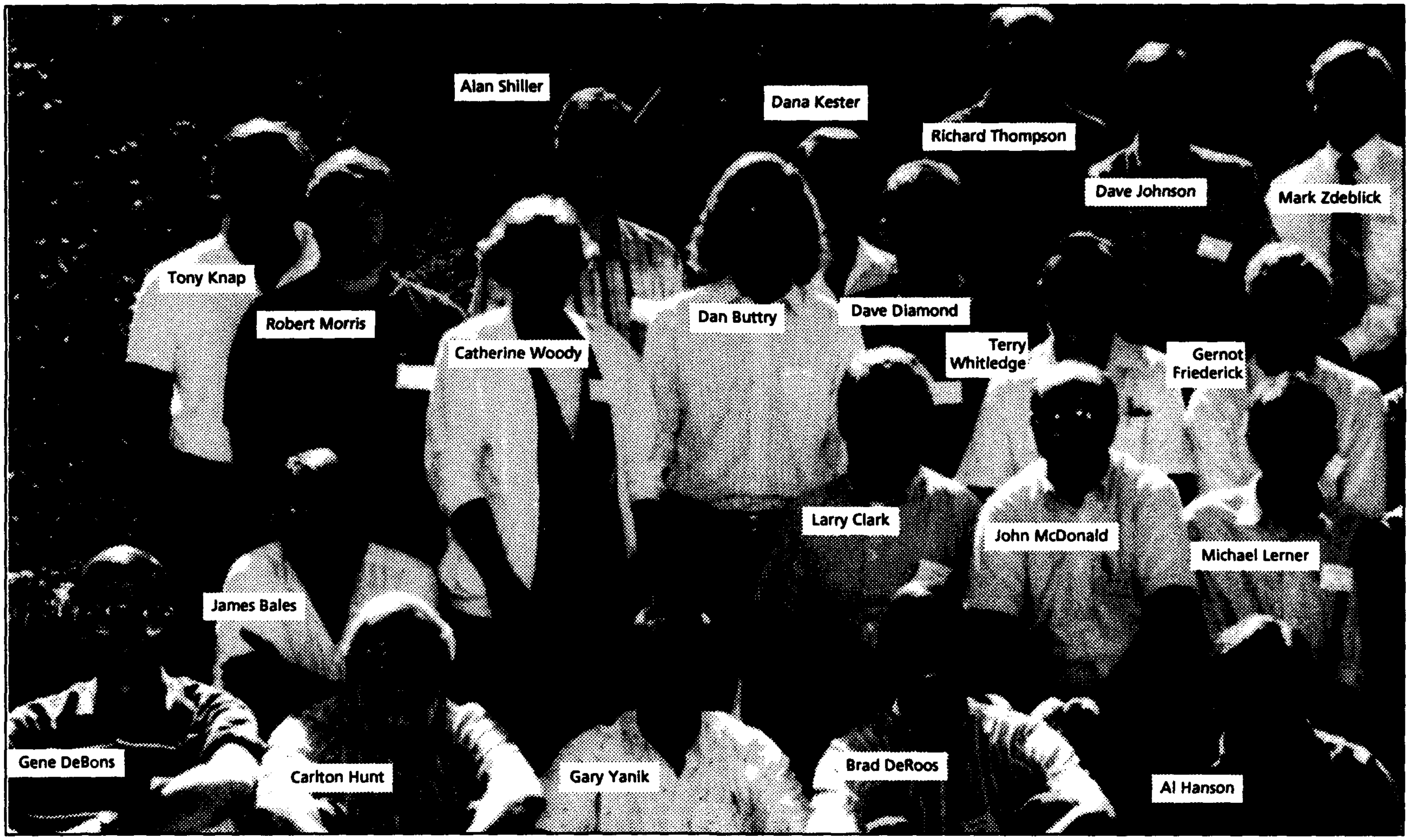
POSTERS & EXHIBITS
presented Tuesday and
Wednesday afternoons

Marlin Atkinson	Potentiostatic Oxygen Sensor for Oceanic CTD's
Dan Buttry	New Strategies for Piezoelectric Metal Sensors
Brad DeRoos	A Sample Container for Oceanographic CO_2 Analysis Use
John Downing	An Expendable Conductivity, Temperature, Depth Instrument with ARGOS Transmission Capability
Gernot Friederich	1. A Moored pCO_2 System 2. Autonomous Seasurface Nitrate Mapping System
Alfred Hanson	An *In Situ* Sampling System for Trace Metal and Transient Species, Preconcentration and Collection in Oceanic Waters
Carlton Hunt	Comparison of Field Measurement and HDDAMS Model Predictions of Dredged Material Plumes at the 6-mile Dump Site
Hans Jannasch	Osmotically Pumped *In Situ* Nitrate Analyzers for Fresh and Seawater Monitoring
John McDonald	YSI Multiparameter Water Quality Monitoring Products
Mary McFarland	ASOM—Automatic Sampler for Organic Micropollutants
Bob Morris and Bob Pellenbarg	An Evaluation of Potentiometric Stripping Analysis for Measuring Trace Metals in Seawater
Ed Poziomek	A Field Screening Method for PCB's in Water
Russell Seguin	Ion Selective Electrodes for Ammonia, Nitrate and Nitrite—Useful as Marine Sensors?
Alan Shiller	Recent Work in our Laboratory on FIA Techniques for Vanadium and Copper
Richard Thompson	Fluorescence Lifetime-Based Fiber Optic Sensors
Catherine Woody	National Data Buoy Center Measurements and Capabilities

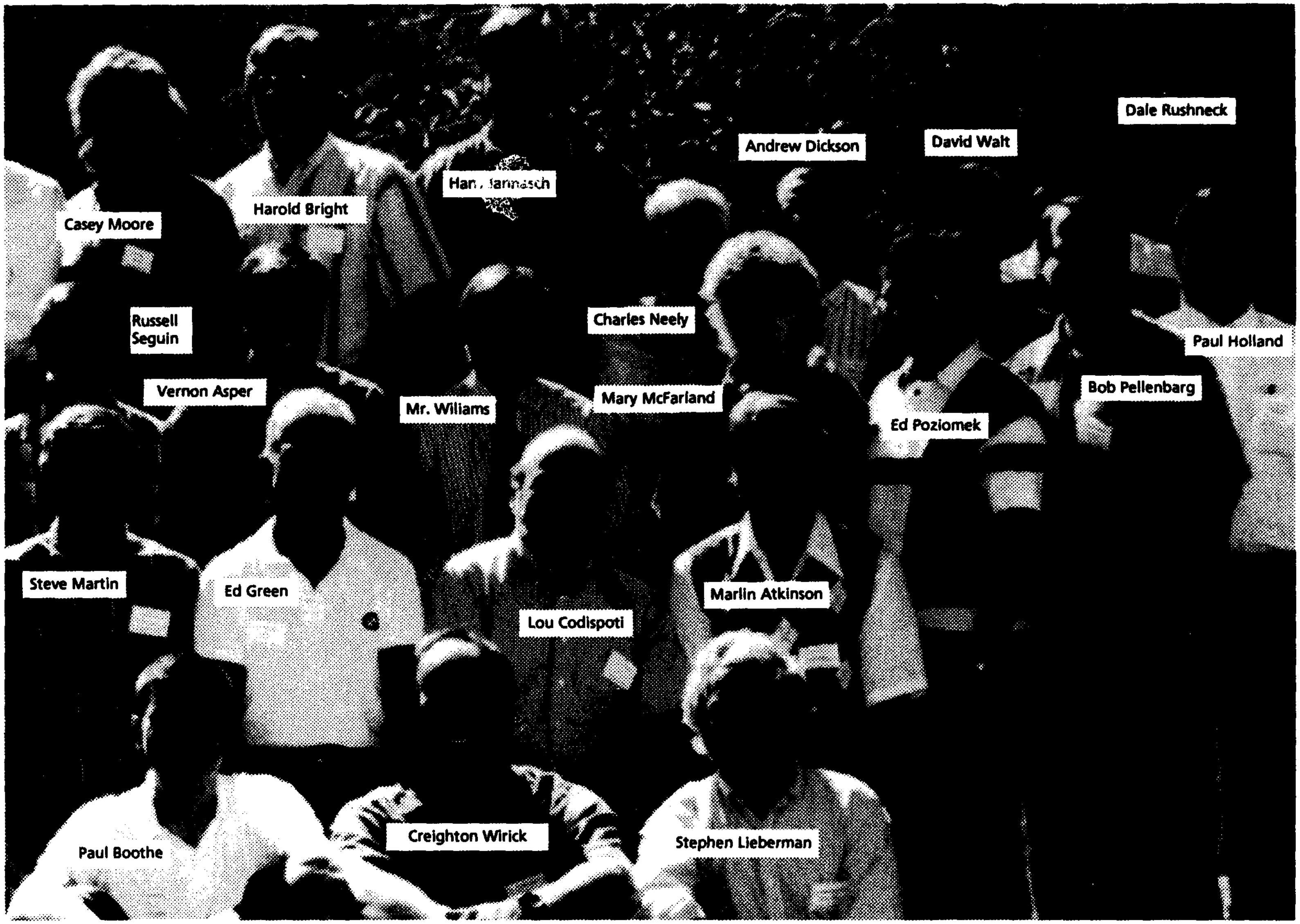
PARTICIPANTS



COURTESY OF RUSSELL E. ATHA, III, STEAMBOAT HOT SHOTS



COURTESY OF RUSSELL E. ATHA, III, STEAMBOAT HOT SHOTS



COURTESY OF RUSSELL E. ATHA, III, STEAMBOAT HOT SHOTS

LIST OF PARTICIPANTS

Vernon L. Asper

University of Southern
Mississippi Center for Marine Science
Center for Marine Science
Stennis Space Center, MS 39529

Voice: (601)688-3178

Fax: (601) 688-1211

Omnet: v.asper

Internet: vasper@whale.st.usm.edu

Marlin J. Atkinson

Hawaii Institute of Marine Biology
P.O. Box 1346
Kaneohe, HI 96744-1346

Voice: (808) 236-7422, 956-8625

Fax: (808)236-7443

Omnet: hawaii.geochem

James W. Bales

MIT, Sea Grant College Program
Underwater Vehicle Laboratory
292 Main St., Room E38-308
Cambridge, MA 02139

Voice: (617)253-9310

Fax: (617)258-5730

Internet: bales@athena.mit.edu

Paul N. Boothe

Department of Oceanography
Texas A&M University
College Station, TX 77843-3146

Voice: (409)845-5137

Fax: (409)845-7191

Harold J. Bright

Office of Naval Research
Code 1141MB
800 North Quincy Street
Arlington, VA 22217-5660

Voice: (703)696-4054

Fax: (703)696-1212

William S. Busch

NOAA
Office of Global Programs
Suite 1225
1100 Wayne Ave.
Silver Springs, MD 20910

Voice: (301)427-2089 Ext 718

Omnet: w.busch.noaa

Daniel A. Buttry

Department of Chemistry
University of Wyoming
Laramie, WY 82071-3838

Voice: (307)766-6677, 766-4363

Fax: (307)766-2807

H. Lawrence Clark

Ocean Sciences Division
National Science Foundation
4201 Wilson Blvd.
Arlington, VA 22203

Voice: (703)306-1580

Omnet: l.clark.nsf

Internet: hclark@nsf.gov

Louis A. Codispoti

Office of Naval Research
Code 324
800 North Quincy Street
Arlington, VA 22217-5000

Voice:(703)696-4204

Fax: (703)696-4884

Omnet: l.codispoti

F. Eugene DeBons

Texaco
E&P Technology Dept.
P.O. Box 770070
Houston, TX 77215

Voice:(713)954-6324

Fax: (713)954-6911

Bradley G. DeRoos

Battelle Marine Sciences Laboratory
1529 W. Sequim Bay Rd.
Sequim, WA 98362

Voice: (206)681-3644
Fax: (206)681-3699
Internet: bg_deroos@pnl.gov

Dave Diamond

LACHAT Instruments
6645 West Mill Rd.
Milwaukee, WI 53218

Voice: (414)358-4200
Fax: (414)358-4206

Andrew G. Dickson

University of California, San Diego
Marine Physical Laboratory—0902
Scripps Institution of Oceanography
9500 Gilman Dr.
La Jolla, CA 92093-0902

Voice: (619)534-2582
Fax: (619)456-9079
Omnet: a.dickson

John P. Downing

Battelle Pacific NW Laboratories
Marine Sciences Laboratories
439 West Sequim Bay Road
Sequim, Washington 98382

Voice: (206)681-3607
Fax: (206)681-3699
Omnet: j.downing

Gernot E. Friederich

MBARI
160 Central Avenue
Pacific Grove, CA 93950

Voice: (408)647-3713
Fax: (408)649-8587
Omnet: g.friederich
Internet: frge@hp850.mbari.org

Edward J. Green

Office of Naval Research
Code 3232
800 North Quincy Street
Arlington, VA 22217-5000

Voice: (703)696-4591
Fax: (703)696-4884
Omnet: e.green.omnet
Internet: green@tomcat.onr.navy.mil

Alfred K. Hanson, Jr.

Graduate School of Oceanography
University of Rhode Island
South Ferry Road
Narragansett, RI 02882

Voice: (401)792-6294, 792-6222 (msg)

Paul M. Holland

SWL/GRC International
P.O. Box 6770
Santa Barbara, CA 93160-6770

Voice: (805)964-7724 Ext. 377
Fax: (805)967-7094

Carlton D. Hunt

Battelle
Ocean Sciences
397 Washington St.
Duxbury, Massachusetts 02332

Voice: (617)934-0571
Fax: (617)934-2124

Hans W. Jannasch

MBARI
160 Central Avenue
Pacific Grove, CA 93950

Voice: (408)647-3717
Fax: (408)649-8587
Omnet: h.jannasch
Internet: jaha@hp850.mbari.org

David H. Johnson

Office of Naval Research
Code 451N
800 North Quincy Street
Arlington, VA 22217-5000

Voice: (703)696-0805
Fax: (703)636-8423

Dana R. Kester

Graduate School of Oceanography
University of Rhode Island
Narragansett Bay Campus
South Ferry Road
Narragansett, RI 02882-1197

Voice: (401)792-6527
Fax: (401)792-6818
Omnet: d.kester
Internet: dkester @ gsosun1.gso.uri.edu

Anthony H. Knap

Bermuda Biological Station for
Research, Inc.
17 Biological Lane
Ferry Reach, GE-01
BERMUDA

Voice: (809)297-1880, -0860
Fax: (809)297-8143
Omnet: a.knap

Stephen H. Lieberman

Navy Command, Control & Ocean
Surveillance Center
Code 521
RDTE Division
San Diego, CA 92152

Voice: (619) 553-2778
Fax: (619)553-6305
Internet: lieberma@nosc.mil

Michael R. Lerner

Yale University School of Medicine
Boyer Center for Molecular Medicine
P.O. Box 9812
New Haven, CT 06536-0812

School: (203)737-4451
Office: (203)737-4482
Secretary: (203)737-4484
Fax: (203)785-3093

Stephen J. Martin

Martin Laboratories, Inc.
P.O. Box 58453
Houston, TX 77258

Voice: (713)286-5945
Fax: (713)286-8856
Internet: smartin@sccsi.com

John W. McDonald

YSI, Inc.
1725 Brannum Lane
P.O. Box 279
Yellow Springs, OH 45387

Voice: (513)767-7241, (800)765-9744
Fax: (513)767-9353

Mary McFarland

Axys Environmental Systems
P.O. Box 2219, 2045 Mills Rd.
Sidney, British Columbia V8L3S8
CANADA

Voice: (604)656-0881
Fax: (604)656-4511

Casey Moore

Wet Labs
P.O. Box 518
Philomath, Oregon 97370

Voice: (503)929-5650
Fax: (503)929-5277

Robert E. Morris

Naval Research Laboratory
Code 6180
Washington, D.C. 20375-5000

Voice: (202)767-3845

Fax: (202)767-1716

W. Charles Neely

Auburn University
Department of Chemistry
179 Chemistry Building
Auburn University, AL 36849-5312

Voice: (205)844-6960, or 5905

Fax: (205)844-6959 (Chem), -5900 (Space Power)

Robert E. Pellenbarg

Naval Research Laboratory
Code 6101A
Washington, DC 20375-5000

Voice: (202)767-2479 or -6206

Fax: (202)404-7139

Edward J. Poziomek

Harry Reid Center for Environmental Studies
University of Nevada–Las Vegas
4505 South Maryland Parkway
Las Vegas, NV 89154-4009

Voice: (702)895-3382, -1442

Fax: (702)895-3094

Dale Rushneck

Interface, Inc.
3194 Worthington Ave.
Ft. Collins, CO 80526

Voice: (303)223-2013

Fax: (303)223-2008

Russell J. Seguin

University of Texas
Marine Science Institute
P.O. Box 1267
Port Aransas, TX 78373

Voice: (512)749-6718

Fax: (512)749-6777

Alan M. Shiller

University of Southern Mississippi
Center for Marine Science
Stennis Space Center, MS 39529

Voice: (601)688-1178

Fax: (601)688-1121

Omnet: a.shiller

Internet: ashiller@whale.st.usm.edu

Richard B. Thompson

Department of Biological Chemistry
University of Maryland School of Medicine
108 North Greene Street
Baltimore, MD 21201

Voice: (410)706-7142 (-7120 msg)

David R. Walt

Department of Chemistry
Tufts University
Medford, MA 02155

Voice: (617)627-3470

Fax: (617)627-3443

Omnet: d.walt

Terry E. Whitledge

University of Texas
Marine Science Institute
P.O. Box 1267
Port Aransas, TX 78373

Voice: (512)749-6769

Fax: (512)749-6777

Omnet: t.whitledge

Creighton D. Wirick

Oceanographic Sciences Division
Brookhaven National Laboratory
Building 318
Upton, NY 11973

Voice: (516)282-3063, -2060

Omnet: c.wirick

Richard Wood

General Oceanics, Inc.
1295 N.W. 163rd St.
Miami, FL 33169

Voice: (305)621-2882

Fax: (305)621-1710

Catherine E. Woody

NOAA
National Data Buoy Center
W/DB 4, Bldg 1100
Stennis Space Center, MS 39529-6000

Voice: (601)688-1021

Gary W. Yanik

PDR Inc.
7289 Garden Road #105
Riviera Beach, FL 33404

Voice: (407)844-7662

Fax: (407)844-7663

Internet: gwyanik@gate.net

Mark Zdeblick

Redwood Microsystems
959 Hamilton Ave.
Menlo Park, CA 94025

Voice: (415)617-1211

Fax: (415)326-1899

CONCLUSIONS

The first MarChem meeting held in 1991 was summarized in a report to the Office of Naval Research (Martin, S.J., L.A. Codispoti, P. Boothe, and D.H. Johnson, 1992. *Proceedings of the MarChem '91 Workshop on Marine Chemistry*. Office of the Chief of Naval Research, Report No. OCNR 12492-10, June 1992, 222 p.). One of the key issues identified in the report was—"How to advance from the current balkanized efforts of oceanographic instrument tinkerers to a system that enables the chemical oceanographic community to take advantage of the best available technology". To solve this problem, one needs to have access to new technology industrial manufacturing. These resources require funding. *Probably the best immediate funding sources are provided by the SBIR and STTR programs.* MarChem participants are encouraged to submit proposals. An SBIR topic on miniaturized chemical instrumentation develop ment has been submitted to ONR. If approved, it will be listed in an upcoming SBIR solicitation.

An effort should be made to communicate on a regular basis via an on-line email network. A bulletin board called MarChem is presently maintained on Omnet. The purpose of the bulletin board is to serve the community interested in improved chemical oceanographic instrumentation. It informs the community about opportunities for cooperative projects with scientists from academia, government and industry, and provides a forum for the exchange of new ideas. This bulletin board will provide information about technical advances, funding opportunities, and meeting announcements, including the proposed MarChem 95 meeting. Not everyone has access to Omnet. Most everyone who has email has access to the Internet. In the near future, the MarChem bulletin board will be moved from Omnet and placed on Internet as a Listserv mailing list. The change will be transparent to Omnet members. Anyone wishing to be placed on the MarChem Listserv should contact Steve Martin at the address listed on page ii. A substantial effort should be made to invite new members to the MarChem "virtual community," especially instrument makers from industry and scientists from environmental fields.

An executive committee has been formed to carry out the organization of the next workshop and to promote instrumentation development through other appropriate means. The members of the committee are:

Larry Clark
Lou Codispoti
Ed Green
Dave Johnson
Steve Martin
John McDonald
Bob Pellenbarg
Alan Shiller

The format of the meetings should be clearly established. In the 1991 report, recommendations were made to have:

- More time available for group discussions
- More unstructured mixing time to allow for valuable informal communications and cross fertilization of ideas
- Group lunches as another way to allow for more informal communications.
- Tutorial lectures on new technologies that can be applied to marine chemistry and on important scientific questions that require new technology
- The formation of sub-groups assigned to work on specific technology areas.

The 1993 conference was organized to carry out these suggestions. One of the sponsors would prefer that the workshop emphasize presentations on new technologies developed in other scientific areas that may have applications to chemical oceanography.

During the meeting, David Walt presented each participant with a copy of a publication on analytical chemistry applied to ocean measurements (Committee of Oceanic Carbon, *Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies*, 1993. National Academy Press, 85p.). The publication addresses many of the technical issues that are being considered by the MarChem participants.

In Chapter 27, Richard Thompson describes a fellowship program to promote the development of marine chemistry methods and instrumentation. Also, he proposes some solutions to the problems with small-scale instrument production.

A substantial effort was made to expose the group to environmental programs sponsored by EPA, NOAA, and DOE. These potentially large markets may provide the economic incentives for some chemical oceanographic instrumentation to be developed.

A major problem that still needs creative thought is how to better integrate the oceanographic instrument market with the larger markets represented by the environmental monitoring and remediation communities. There was general agreement that devices that would autonomously collect time-series chemical data from the ocean would find use in the monitoring and environmental remediation communities, but interaction between the communities appears to be weak. This problem is related to the difficulty that the MarChem 93 organizers had with attracting industry participation. Their issue and the issue of how to gain more financial support for the development of improved instrumentation for marine chemistry and chemical oceanography will be discussed by the Executive Committee in the near future.

Section II

CURRENT RESEARCH, PRESENTATIONS, POSTER ABSTRACTS, AND PAPERS

VERNON L. ASPER

RESEARCH INTERESTS

Most research projects have been oriented toward the development of techniques and equipment for investigating marine particle dynamics. Projects have included sediment traps, camera systems, sediment traps incorporating camera systems, buoy systems, neutrally-buoyant platforms, pumping systems, and a fiber optic based profiling fluorometer. This equipment is applied to investigating the settling characteristics of particles *in situ*, with particular emphasis on large, "marine snow" aggregates. These aggregates are extremely fragile, requiring special handling procedures or non-contact techniques for determining their abundance, size distribution and sinking speeds. Most aggregates appear to settle quite rapidly, but others do not, resulting in their being easily resuspended from the seafloor and transported many hundreds of kilometers from their origins.

Future work will be directed toward developing, expanding and modernizing these techniques and incorporating them into interactive mode platforms. Recent funding will be used to purchase an ROV and a pair of digital cameras for producing stereo pair images of aggregates at depths up to 400m. These images will be analyzed for the three-dimensional distribution of the aggregates, their shape and their volume, all of which have been impossible using previous techniques. Future plans will include developing a sampling system for use on the ROV that will allow collecting aggregates or other objects using the vehicle. Once enclosed in the collection device, aggregates will be observed and their sinking characteristics noted before returning them to the laboratory for analysis. These programs have previously been accomplished in the Panama Basin, Black Sea, Arctic, Lake Baikal, Equatorial Pacific and Antarctica, with plans pending to continue JGOFS work in the Arabian Sea.

MARLIN J. ATKINSON

A POTENTIOSTATIC SOLID-STATE OXYGEN SENSOR FOR OCEANIC CTDs

A non-membrane, potentiostatic oxygen sensor has been developed for oceanic CTDs. The cathode of the sensor is a bundle of 1000, 3 μ-diameter platinum-tipped carbon fibers that are recessed in epoxy. The sensor calibrates directly to oxygen concentration (not partial pressure as do membrane sensors), has a very small pressure effect and relatively fast response. These sensors, however, have two hour-long turn-on transients and long-term decay of output. Neither the turn-on transient nor drift precludes attainment of excellent calibrated oxygen profiles. For HOTS-GOFS casts, the mean error of predicting oxygen concentrations of 19 bottles was not significantly different from the mean error in sampling of Niskin bottles (1.01 μM; mean r^2 of 10 deep casts was 0.9994). This level of error in calibrations can be achieved using only three Winkler determinations on a cast. These types of oxygen sensors offer distinct advantages over membrane oxygen sensors.

JAMES W. BALES

MIT SEA GRANT COLLEGE

The Underwater Vehicles Laboratory at MIT Sea Grant is dedicated to developing the enabling technologies for the creation of a new class of autonomous underwater vehicles (AUVs). These light-weight, low-cost, long-range vehicles will provide a vital complement to existing methods of ocean exploration. The first of these new vehicles, Odyssey, was launched in August 1992 and completed its first round of sea trials off Antarctica in January 1993.

The AUV is designed for operations to 6,000 m depths, although some subsystems on the vehicle are currently limited to 3,000 m. With 50 kg of alkaline batteries, Odyssey has a range of 180 km @ 5 km/hr when equipped with CTD, an optical backscatter sensor, an acoustic modem and an electronic still imaging system (assuming intermittent use of the last two items). Small (2.2 m long) and light-weight (195 kg), Odyssey imposes few operational constraints on an oceanographic research vessel. To the extent possible, Odyssey is constructed from off-the-shelf components to minimize cost (total component cost, excluding mission sensors, of $50,000).

The next generation of tools for studying marine chemistry will be mobile instrument platforms carrying suites of *in-situ* instruments. This will require developing new chemistries in addition to miniaturizing existing instruments and reducing their power consumption. Our intent is to create a multidisciplinary team to address these issues.

MIT MICROSYSTEMS TECHNOLOGY LABORATORIES

Researchers studying microelectromechanical devices at the Microsystems Technology Laboratories are pursuing a wide range of microminiaturized sensors and actuators. Current projects relevant to marine chemistry include:

- *Fluid Flow in Micromachined Devices*: A good understanding of the behavior of fluids in micromachined devices is required to develop microminiaturized instruments for making measurements in the liquid or gas phase. We have developed a test-bed for flow characterization and are studying flow losses in microchannels of different geometries.

- *Microfabricated Flow Chambers for Optical Measurements in Fluids:* A fluid-flow chamber has been fabricated in silicon with three orthogonal functional axes: a flow axis containing a 250-μm diameter channel, an optical waveguide axis intersecting the flow channel at its midpoint, and a viewing axis defined by optical windows above and below the mid-point of the channel. This structure was designed for flow-cell cytometry (where an excitation laser is coupled through the waveguides and fluorescence and scattering are observed through the windows).

However, the components being developed are suited to a wide range of applications.

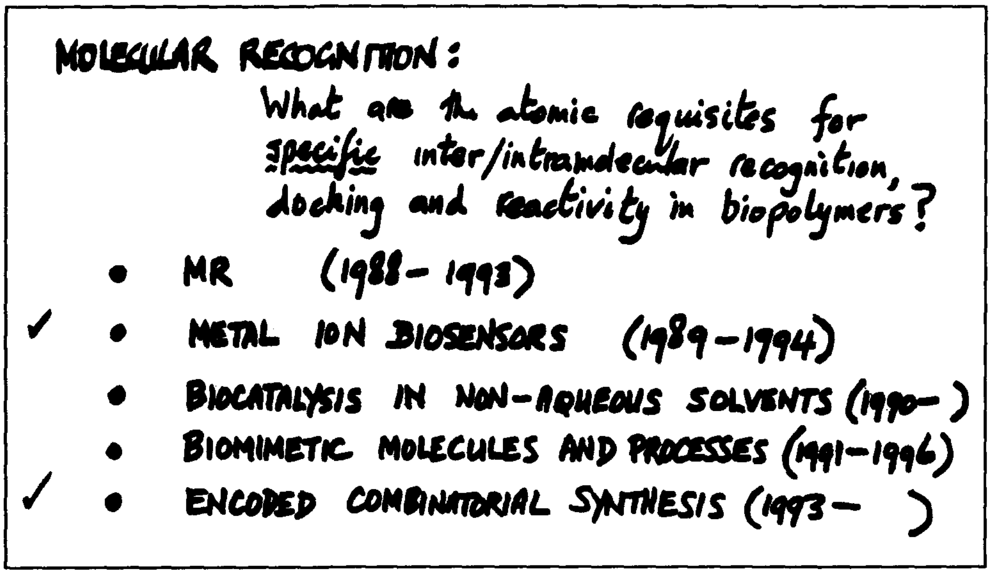
- *Silicon Microvalves:* A silicon microvalve with integrated actuation is being developed that uses a pressure-balance design to allow operation against high-pressure sources. The valve is fabricated from a stack of silicon wafers (and a glass capping layer) and uses electrostatic forces for actuation.

- *Microfabricated Optical Waveguides on Deformable Structures*: The goal of this effort is to develop planar waveguide technologies compatible with microfabricated deformable structures, easing the integration of optical transduction and communication methods into micromachined sensors and actuators.

HAROLD J. BRIGHT

ONR BIOSENSOR PROGRAM

Figure 9-1

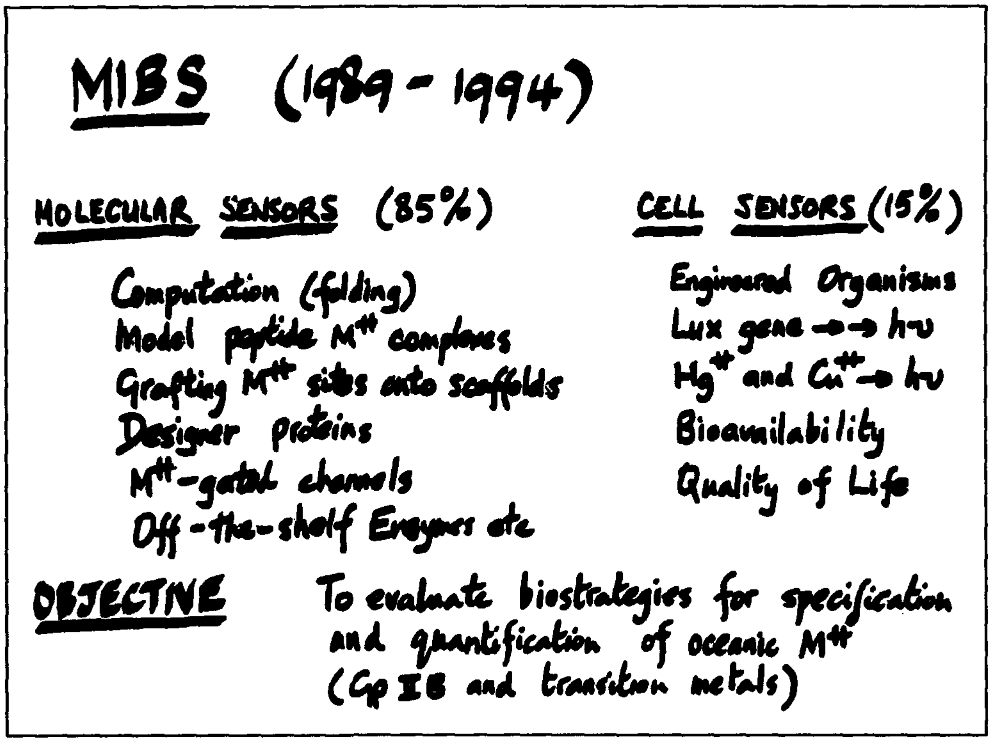


MOLECULAR RECOGNITION:

What are the atomic requisites for specific inter/intramolecular recognition, docking and reactivity in biopolymers?

- MR (1988 - 1993)
- ✓ METAL ION BIOSENSORS (1989 - 1994)
- BIOCATALYSIS IN NON-AQUEOUS SOLVENTS (1990 -)
- BIOMIMETIC MOLECULES AND PROCESSES (1991 - 1996)
- ✓ ENCODED COMBINATORIAL SYNTHESIS (1993 -)

Figure 9-2



MIBS (1989 - 1994)

MOLECULAR SENSORS (85%)	CELL SENSORS (15%)
Computation (folding)	Engineered Organisms
Model peptide M^{++} complexes	Lux gene → $h\nu$
Grafting M^{++} sites onto scaffolds	Hg^{++} and Cu^{++} → $h\nu$
Designer proteins	Bioavailability
M^{++}-gated channels	Quality of Life
Off-the-shelf Enzymes etc	

OBJECTIVE To evaluate biostrategies for specification and quantification of oceanic M^{++} (Gp IIB and transition metals)

Figure 9-3

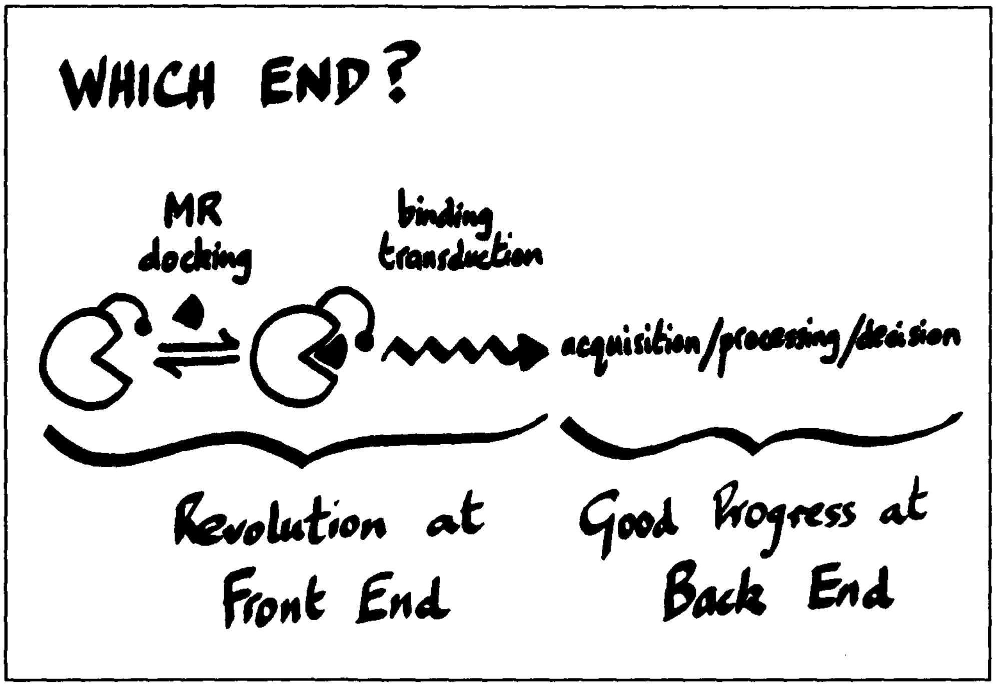


Figure 9-4

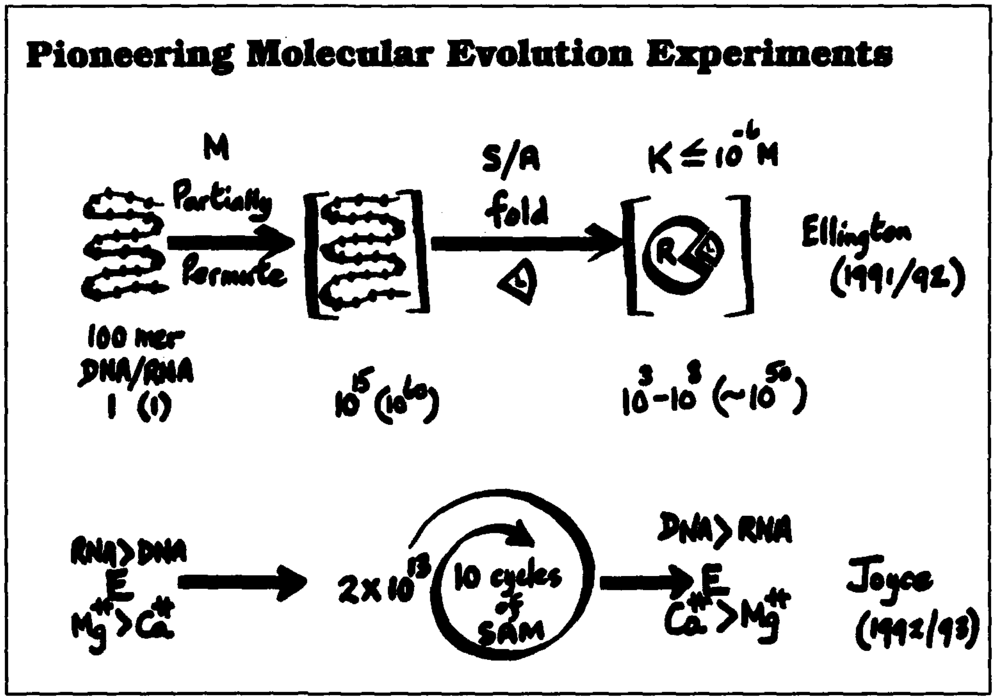

Pioneering Molecular Evolution Experiments

Figure 9-5

How Do You Select for R(K)?

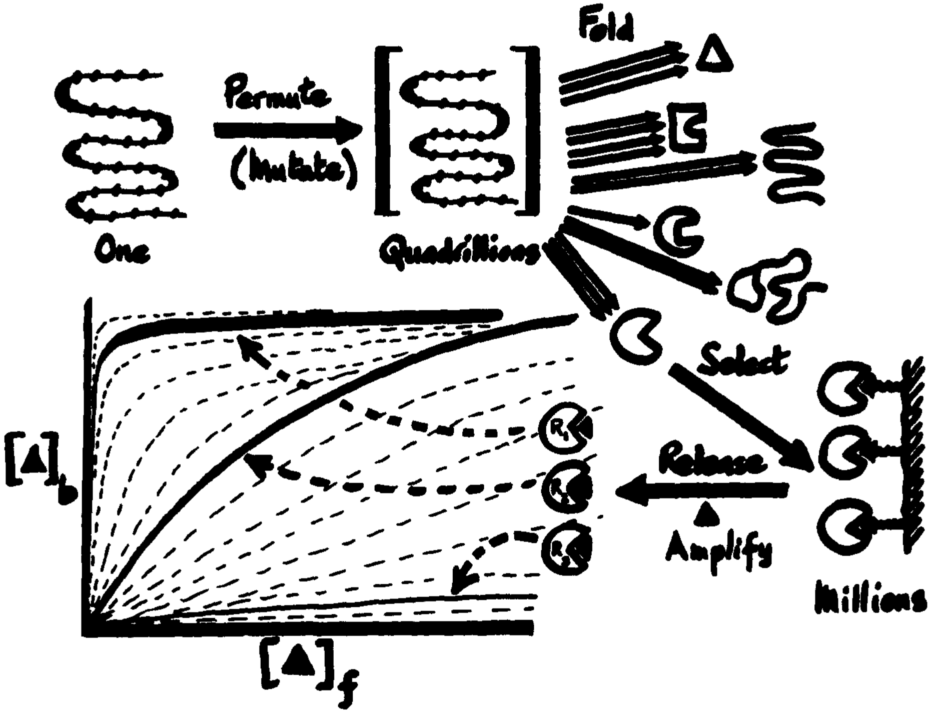


Figure 9-6

The Synthesis Menus, Then and Now

Then
table d'hôte
Instructionist (serial)

Now
à la carte
Selectionist (parallel)

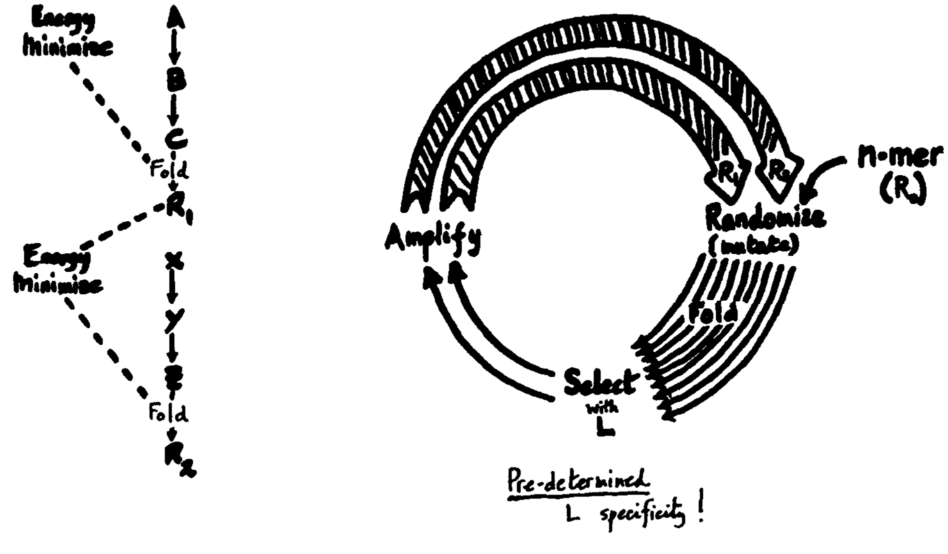


Figure 9-7

Rationale Dictated by Library Size

Since for n–mer heteropolymer with A letters in alphabet

- Complete library $N = A^n$
- 25–mer DNA, $N = 4^{25} = 10^{15}$ } now, or shortly,
- 12–mer polypeptide, $N = 20^{12} = 4 \times 10^{15}$ } feasible on lab scale
- Small biological protein (100–mer), $N = 20^{100} = 10^{130}$!

Therefore the approach must be to use

- Small fractions of randomized space
- Informed searches (eg randomized recognition pocket segments, leaving framework alone)
- Smaller A and n (synthetic heteropolymers, $8^{17} = 2 \times 10^{15}$)
- Encoding schemes
- Chain recombination

WILLIAM S. BUSCH

GOVERNMENT-INDUSTRY ALLIANCE: NEW STRATEGY FOR ENVIRONMENTAL RESEARCH

Issue and Opportunity

The use of offshore oil production platforms provides a unique opportunity for conducting environmental research. The efforts toward implementing this capability are a prime example of industry, government, and scientific communities forming an alliance to solve complex environmental problems.

Traditional platforms, such as ships, buoys, and aircraft, used for gathering data from the upper atmosphere, through the air-sea interface, and down to the seafloor, often lack capabilities needed by researchers. Figure 10-1 compares the major characteristics of these systems. They do not normally allow for long time-series measurements (e.g., 10 to 20 years); they are very dependent on weather conditions; they are of limited use in hazardous and remote environments; and they often allow only minimal experimental flexibility. Spacecraft, while offering broad coverage, are also limited since they can only monitor parameters above and on the surface of the oceans but not beneath it. The use of offshore platforms is a new and potentially valuable concept in conducting oceanic and atmospheric research worldwide.

Ultimately, a network of manned research laboratory units that will be placed on offshore platforms and located throughout the world's oceans is envisioned. Using these, researchers could conduct real-time and in situ experiments as well as establish long time-series monitoring networks. These platforms are unique in that they provide a stable facility that is relatively impervious to hostile weather, fixed at a permanent coastal location, and can provide needed space and support. It is planned that the resulting data would be inputted into a worldwide repository network such as the Global Oceanographic Observations System (GOOS) and actively participate in large-scale programs such as those of the International Committee of Scientific Unions (ICSU).

Importance to Industry

This program provides an unparallel opportunity wherein the private sector, government, and research communities, both domestic and international, can synergistically pool their resources, facilities, and capabilities. It gives the offshore industry direct access to ongoing U.S. government sponsored research programs; its scientists, managers, administrators, policy workers, and decision makers; and interagency coordinating groups that address both policy and scientific issues. This provides industry the ability to influence policy direction and voice opinions, develop channels of communications, and establish links with government counterparts. The credibility gained by both government and industry could then be extrapolated to other areas of partnerships and collaborative activities. In addition, a number of companies have indicated that joint projects of this nature would greatly enhance the public image of the offshore industry regarding environmental issues. Industry already plays a critical role in this area

Figure 10-1

Comparison of sensor platforms for environmental and global change research

Characteristics	Aircraft	Buoys	Offshore Platforms	Satellites	Ships
Data Quality					
Foul weather data available	No, unless special weather mission	Some	Yes, significant advantage over other methods	Some, atmos. profile & sea surface	Very little
Area coverage	Wide	Limited	Limited	Global	Wide
Range from platform	Wide	Minimal	Wide, using accoustic, hard wire, & optical links and Auv's	Wide	Generally limited depending on sensors
Sensor accuracy and resolution	Good	Good	Good	Good	Good
Number of parameters measured	Many	Few	Many	Few	Many
Data processing	Limited	No	Yes	No	Yes
Impact of system's presence on measurements	Limited	Limited	Potentially yes for close-in activities	No	No
Operations					
Onsite instrument maintenance & logistical support	Limited	None	Excellent	None	Limited (depends on mission of ship)
Available working space	Limited	None	Large	None	Limited
Long-term onsite living & working	None	None	Large	None	Limited
Safety concerns, requirements, & personnel procedures	Limited	None	Very stringent	None	Limited
Auxillary support craft/systems	None	None	Potentially many (work boats, dive systems, rov's)	None	Limited
Cost for use of platform	High	Mission dependent	Low	High	Mission dependent
Applications					
Short-term studies	Yes	Yes	Yes	Yes	Yes
Long-term studies (time series)	None	Limited	Very good (possibly 20-30 years, depending on platform)	Yes, huge amount of data, but limited spatially or frequency	Limited (very expensive)
Real-time experimental reconfiguration & change of protocol	None	None	Good	None	Limited
Manned (active scientific participation)	None	None	Good	None	Limited
Insitu measurement capability	Yes (atmosphere) No (ocean)	Yes	Yes	Yes (upper atmosphere)	Yes
Research flexibility	Limited	None	Yes	None	Limited
Climate modelling data	Yes	Yes	Very useful	Yes	Yes
Simultaneous atmosphere, sea surface, pelagic, and benthic measurements	No	Limited	Very good	No	Limited
Biological studies	No	No	Very good	No	Yes (short-term

of environmental concern because of its direct and immediate interface with the public. Its role in providing the goods and services needed to address these issues will be further emphasized in the future.

From another perspective, many large companies and multinational corporations are taking an interactive role with society and are not concerned only with profit margins. They are developing the capability of using resources in a realistic and concerned manner, working synergistically with government. For example, the International Chamber of Commerce has developed a charter that provides 16 guidelines that companies should follow related to environmental sustainable development. This has been accepted and supported by a large number (more than 3,000) of international companies.

Ongoing Efforts

Until recently few, if any, companies have allowed scientists to have limited access to their offshore facilities. Mobil Oil, working with the Flower Garden Ocean Research Project (FGORP), has opened one of their platforms in the Gulf of Mexico to scientific research teams. The Gulf Offshore Satellite Applications Project (GOSAP) is working with seven oil companies in the Gulf of Mexico to obtain "ground truth" data from oil platforms for calibrating satellite sensors.

Through the collaborative efforts of the Private Enterprise and Government Interaction (PRGI) Working Group of the Federal Coordinating Council for Science, Engineering and Technology's (FCCSET) Committee on Earth and Environmental Sciences (CEES), and the American Petroleum Institute (API), federal agencies have been working closely with BP America to establish a well-structured, scientifically credible, and long-range research program. In addition, negotiations to explore the possibilities of working in the North Sea and Arctic regions are ongoing with the National Oceanic and Atmospheric Administration (NOAA), the University of Bergen, Norsk Hydro and the other maritime organizations form Norway, as well as BP International of the United Kingdom. All of those involved are enthusiastic about this program's potential for the science community and their industry.

Research Opportunities

In November 1989 a workshop entitled "Deep Sea Observations" was held in Washington, D.C. to address the new scientific opportunities available by using these platforms. A multidisciplinary approach was taken wherein specialists in oceanographic and climate research and development participated. The findings of this workshop provided a basis for developing a new long-range program to address scientific areas that include:

- Frequency spectra of marine ecosystem variables.
- Biogeochemical processes, the carbon cycle, and new primary production.
- Coupled ocean-atmosphere systems, interactions, and energy transfers.
- Physical oceanographic processes and systems from sea surface to seafloor.
- Meteorological and climate processes and systems.

Specific measurements that researchers would like to make from platforms are outlined in Figure 10-2. Initially, pilot projects using automated systems requiring no operational support from the platform will be conducted for feasibility demonstration. Ideally,

Figure 10-2

Proposed time series measurements that are desirable from offshore platforms

1. **Automatic/Remote (requiring no operational support):**

   A. **High Frequency Observations and Measurements (Daily/continuous)**

   Physics (atmosphere)
   - Outgoing long-wave radiation
   - Wind speed and direction
   - Relative humidity
   - Barometric pressure
   - Surface air temperature
   - Light 0.3 to 3µm

   Physics (ocean)
   - Wave conditions
   - Sea surface temperature
   - Conductivity, temperature, depth (0-1000m)
   - Currents (0-200 m; acoustic profiling of ocean currents, or APOC)
   - Submarine light to less than 0.1% of surface illumination

   Chemistry
   - Dissolved nutrients (NO_3, NO_2, NH_4, UREA, SiO_4, PO_4: 0-500m)

   Biology
   - Chlorophyll profile (plus phaeopigments)
   - Macrozooplankton carbon (euphotic zone plus integrated 0-1000m)
   - Micronekton by acoustics
   - Primary production (to 0.1% light)

2. **Real time Analysis (requiring manned support)**

   A. **High Frequency Suites Observations and Measurements (Daily/continuous)**

   Physics (ocean)
   - Currents (greater than 200 m; moorings)

   Chemistry
   - Total CO_2 alkalinity, $_pCO_2$
   - O_2

   Biology
   - Microbial carbon (in euphotic zone)
   - Phytoplankton carbon (in euphotic zone)
   - Microzooplankton carbon (euphotic zone plus integrated 0-1000 m)
   - Size frequency distributions of living matter (euphotic zone)

   B. **Low Frequency (Weekly-Monthly)**

   Physics (ocean)
   - Lagrangian currents (drifters)
   - Deep conductivity - temperature - depth (CTD) casts (0-2000m)
   - Deep Currents (moorings)

   Chemistry
   - Argon, ^3He particulate organic carbon (POC), nitrogen (PON), phosphorous (POP), and silicon (PSI), (0-2000m)
   - Dissolved organic carbon (DOC), nitrogen (DON), and phosphorous (DOP)
   - Dissolved nutrients (0-2000 m)
   - Deep total CO_2, alkalinity, $_pCO_2$
   - Sinking particles (traps - upper 2000m)

   Biology
   - Depth stratified sampling for all size categories (day/night to 1000m)
   - Replicate water column primary production (three to four per depth per day biweekly)

3. **Additional Measurements**

   Radiation (UV, radiance, downwelling light)
   Depositional
   Rainfall
   Water column currents
   Transmisivity
   Flourometery (measuring flouresense)
   Temp, salinity
   Biomass (acoutically, standing crop & turn-off rates, plankton particle counter)
   Nutrients (nitrate, etc. phosphate, O_2, silicates)
   Photosynthetic rate (primary production)
   Zooplankton biomass
   Acoustic measurements (tomographic techniques and doppler systems)
   Dimethal Sulphide(DMS) (worldwide monitoring system)

calibrated systems could be installed on platforms in areas of the North Sea, the Gulf of Mexico, and the tropical South Pacific to monitor the same parameters at each site for comparative studies.

An important concern is the platform's presence having a possible impact on the measurements. Studies have to be conducted to determine how this potential effect can be minimized and/or accounted for. In addition, data can be taken remotely using instruments placed at distances from the platform with acoustic, optical, and/or hard wire data links back to the platform.

Companies have also suggested that their work boats supporting the platform operations could at times, on a non-interference basis, be used for research activities. In addition, companies have indicated that their terrestrial based sites could also be used by scientists. Many of these are located in areas of high interest to researchers, such as deserts, the arctic and the tropics, and rain forests. Interest has also been shown in placing working labs on weather ships stationed in the North Atlantic.

Each company monitors certain environmental parameters on their platforms regularly and in many instances continuously for operational needs. They are also often required to have extensive environmental surveys of the areas surrounding the platform conducted periodically (i.e., every one to three years). This data, some of which may go back to the early 1970s, can be made available to the science community as needed. The information may be comprehensive for operational needs but not necessarily sufficient for scientific use. It could, however, prove very useful for future planning of environmental activities and installations.

International Aspects

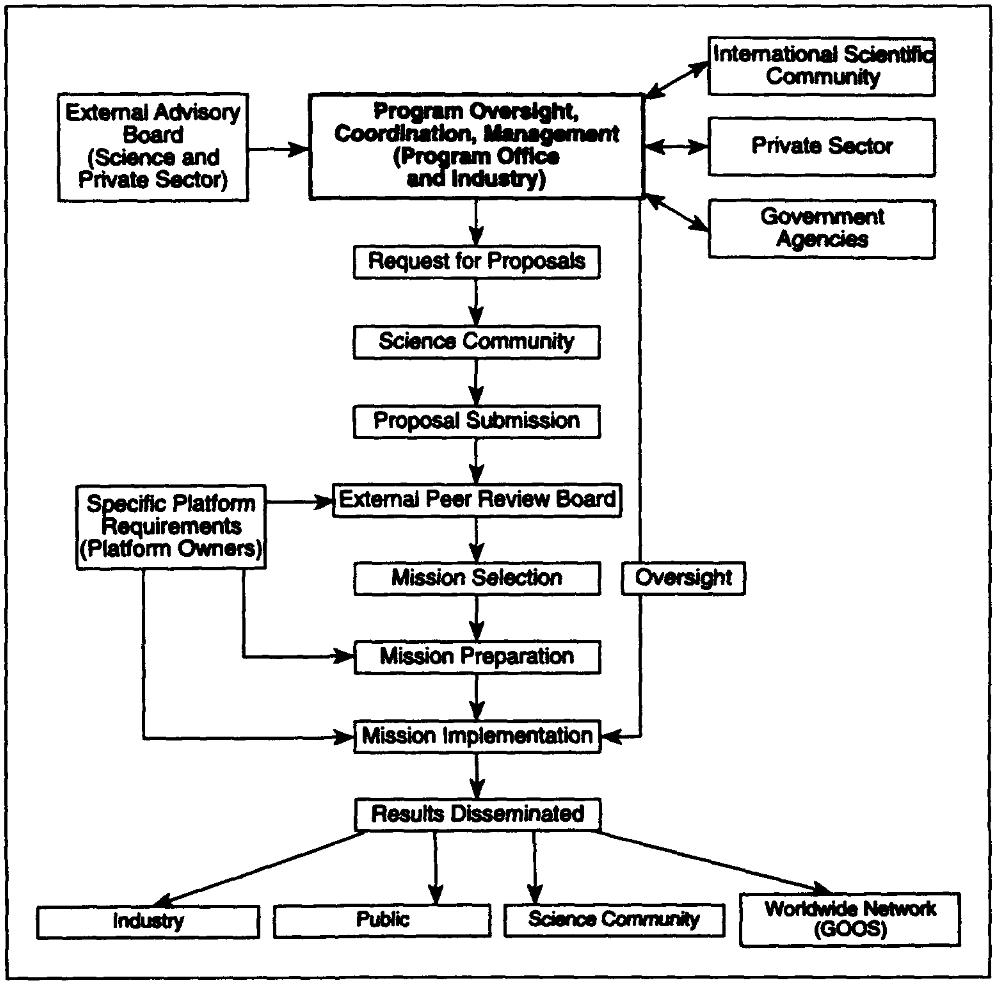
The international importance of this program is exemplified by the enthusiastic support of international and domestic offshore companies and the strong interest shown by researchers involved with large multi-nation scientific organizations, such as ICSU, the International Oceanographic Committee (IOC), and the World Meteorological Organization (WMO) that sponsor programs such as the International Geoscience Biosphere Project (IGBP) and the Joint Global Ocean Flux Study (JGOFS) programs. IGBP's Land Ocean Interaction with the *Coastal Zone* (LOICZ) *program* is studying near shore areas within normal locations of platforms. Note that JGOFS presently operates stations at Hawaii and Bermuda making long-term time series measurements of oceanographic and atmospheric data. Offshore platforms would provide optimal bases from which they could expand the number of JGOFS measurement sites providing better coverage of the oceans. In addition to using GOOS as a network for disseminating data from platforms, the GOOS Health of the Oceans program would directly benefit from access to specific platforms.

Program Structure

Instead of establishing a program on an ad hoc and case-by-case basis, a long-term, well structured, and unbiased research program is envisioned based on meritorious science. While industry and the science community both have specific roles, they also would be full partners involved in all aspects of planning, solicitation, peer review, selection, implementation, and sharing of results as shown in Figure 10-3. Extensive negotiations have already been held with industry. It is agreed that the operations managers of the respective offshore platforms being

Figure 10-3

Framework for a long-term research program using offshore platforms



used, would have the final say and approval of given projects considered for selection based on safety, security, logistics, installation, and any other factors they consider critical. This relationship will be a true partnership based on specific guidelines and criteria agreed to beforehand.

Funding and Support

As always, the practical question of funding is a major concern. The ideal solution, of course, is for a government source of support to be identified. However, in today's climate of fiscal constraint and downsizing, support is not readily available. This does not preclude researchers from submitting proposals that include the use of platforms to traditional funding agencies such as the National Science Foundation, Office of Naval Research, and other groups appropriate to their areas of interest. Private sector groups and industry could also provide support in their areas of focus.

An "Announcement of Opportunity" should be sent to the science community worldwide, describing the program, its opportunities, potential platforms, and oceanic areas. This would allow scientists to consider the advantages of using a platform and submit research proposals to potential funding sources.

In addition, *ongoing and funded programs*, working in coastal areas could consider the unique advantages of using these platforms.

Summary

Although there is intense environmental and scientific interest to work in and obtain long-term data sets from given areas in the Arctic (Barents and Kara Seas), little is being done except for some limited oceanographic ship missions. Russian companies and government organizations are planning to place two platforms in these areas (approximately 73°N) by the year 1997 and 2000, respectively. Now is a golden opportunity for researchers to have a permanent laboratory facility designated into these systems during construction.

Industry has indicated that designs are currently underway for offshore platforms that will work in deep water depths beyond the continental shelf areas. This may provide a good opportunity for the industry and science communities to specify what should be included in the design, such as the *parameters to be monitored*, the special facilities or equipment needed, and in what specific subsea mounting requirements. Looking toward the future, the research community needs an independent semi-submersible type platform that *can operate at any water depths* for long-term observations. This program will provide the basis and experience for developing such systems.

The use of platforms allows long-term monitoring capabilities in specific locations and under hazardous conditions. It also provides a unique opportunity where the research communities and private sectors, both domestic and international, can work synergistically. In addition, this use will allow government institutions, such as the United Nations, to include as appropriate, this data and information in international efforts and decision-making processes, especially those environmentally related and having global implications. These new and "non-traditional" research stations will play significant roles in future marine research, even to the extent of possibly redefining the preferred methods of studying the oceans.

DANIEL A. BUTTRY

CHEMICAL SENSORS FOR THE MARINE ENVIRONMENT

One of the focal points of our research program is the development of chemical sensors for various types of species in liquid environments. We currently are developing metal ion sensors for use in aqueous samples, bacterial sensors for industrial process streams, and are just starting up an effort in sensors for organic compounds in aqueous samples.

The function of any true sensor combines the functions of some sort of chemical selectivity (i.e. the reagent to be sensed interacts with or binds to some selective chemical structure which is part of the sensor) with some method of transduction of the binding event into a measurable signal, such as a voltage change, a mass change, or a change in some spectroscopic quantity of the sensor, such as absorption or fluorescence. Our expertise in thin film chemistry has been valuable to us in designing the chemistry needed for this binding-transduction combination and immobilizing this chemistry onto a surface where it becomes part of the sensing structure. At the moment, we are using two transduction methods, namely fluorescence and piezoelectric mass detection in the sensors described above. The bacterial sensor is based on selective immobilization of the bacterium onto a silica surface (which can be part of a waveguide, such as an optical fiber) followed by tagging the immobilized bacterium with a fluorescent species. Detection is effected via the development of fluorescence intensity. The metal ion and organic sensors rely on use of piezoelectric transducers to detect the mass change at a surface caused by immobilization of the target analyte. In this case, binding of this analyte to the sensor surface is achieved by first immobilizing some type of receptor (e.g. a ligand for the metal or a cyclodextrin for the organic) onto the surface. We have recently developed a new approach to this step which involves attaching the receptor to very high surface area silica particles, then attaching these to the sensor surface. In this way, it is possible to dramatically increase the amount of bound receptor, producing correspondingly increased signals for analyte binding. This immobilization is rugged, and sensors with this configuration are immune to many of the interferences of our "first generation" piezoelectric sensors, which used polymeric receptor binding strategies.

In the context of development of marine chemistry instrumentation, it seems clear that there are several needs associated with development of new chemical sensors. First, strategies for development of chemical selectivity must be further pursued, because the binding discussed above usually must be highly selective. Second, reliable methods of coupling the binding event to some transduction mechanism must also be further elaborated. At the present time, the most attractive one for ultratrace (i.e. $< 10^{-9}$ M) methods is probably fluorescence, while no clear winner seems to have yet emerged for higher concentration species. Third, it is imperative that the issue of fouling be resolved. This is crucial for virtually all of the sensing strategies currently being investigated. Finally, the issues of sensor dynamic range and reversibility when extremely large binding constant receptors are used must be addressed. These fundamental issues relate to the fact that when receptors with very large binding constants for the analyte are used, the analyte will bind from extremely dilute solutions, but, due to the large binding constant, the receptor-analyte complex will not spontaneously dissociate on a reasonable timescale. Thus, the sensor response becomes irreversible and/or the lifetime is dramatically shortened. While there are hints of possible ways to overcome this fundamental limitation, little concerted effort has been expended on this important issue to date.

NEW STRATEGIES FOR PIEZOELECTRIC METAL SENSORS

This poster describes development of a new strategy for metal sensors based on mass measurements at the surface of a mass-sensitive piezoelectric transducer. The approach is to use ligands for the metal of interest immobilized onto very high surface area, porous silica particles which are then immobilized onto the transducer surface. Exposure of the sensor to a solution containing the metal leads to its immobilization onto the transducer surface. The consequent mass change is then detected electronically. The approach has general application to a wide variety of metals to the extent that relatively selective ligands are available for metals of interest. From the standpoint of the marine chemistry community, it should be possible to develop sensors for trace metals such as Cu and Fe.

This new technology has not, to our knowledge, been applied to oceanographic measurements. However, we are in the process of developing the technology for metal quantitation in groundwater samples.

H. LAWRENCE CLARK

OCEANOGRAPHIC INSTRUMENTATION DEVELOPMENT PROGRAM

The Ocean Sciences Division (OCE) supports the Oceanographic Technology and Interdisciplinary Coordination (OTIC) Program. OTIC is within the Ocean Sciences Research Section (OSRS).

The OTIC Program accepts proposals for developing new instrumentation that has broad applicability to ocean science research projects. Instrumentation Development proposals should enhance the observational, experimental, or analytical capabilities of the ocean science research community. Instruments proposed for development must have direct relevance to research activities funded by the OSRS. Instruments may include, but are not limited to, data collecting or observational systems, long-term sensors, and undersea vehicles. Proposals for adapting technology from other fields or for modifying existing instrumentation for ocean science research purposes are eligible, as are workshop proposals to assess current status of technology and instrumentation and to recommend areas for future development.

Normal NSF evaluation criteria for proposals will apply. These criteria include research performance, competence and prior record of the principal investigator, and intrinsic merit of the technology development. Instrumentation development proposals will also be evaluated on the basis of the following equally weighed criteria:

- Scientific merit of research for which the instrumentation will be used.
- Ability of the applicant(s) to undertake instrument development.
- Importance and relevancy of the proposed instrumentation to the successful completion of research for which it is intended.
- Degree to which the instrumentation improves research capabilities for the community and to which it addresses requirements of more than one user group.

Proposals that involve technique development and/or instrumentation directly associated with a specific research project or goal, should be submitted to the appropriate OSRS program as a regular research proposal. Joint funding with the OTIC Program may then be considered on a case-by-case basis.

Target dates for proposal submission are 1 May, and 1 November. Proposals should follow the format of a research proposal and address the evaluation criteria indicated above. Most instrumentation development proposals are mail reviewed only. However, some proposals may also be considered by an OSRS panel to help evaluate the proposed instrument's relevancy to ocean science research topics. Persons intending to submit a proposal may wish to write or call the OTIC Program Director (703-306-1580) prior to developing a formal submission. This may avoid submission of an inappropriate proposal.

This program area is distinct from the Oceanographic Centers and Facilities Section's annual competition for the acquisition of Oceanographic Instrumentation.

Figure 12-1
NSF Ocean Sciences Program

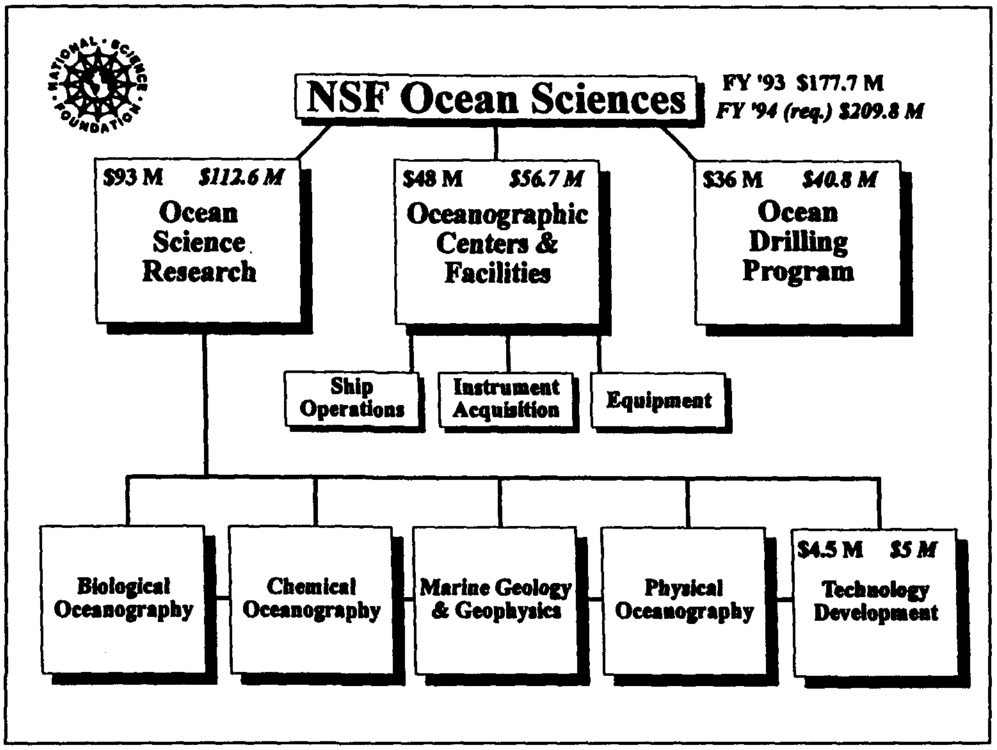
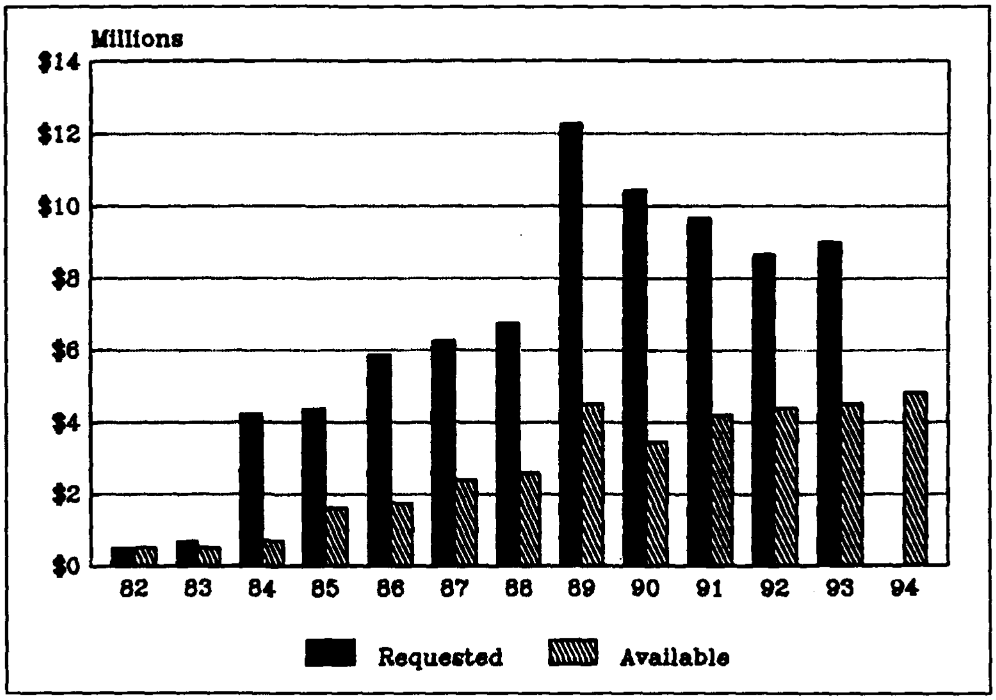


Figure 12-2
NSF Oceanographic Technology Program, instrumentation development for FY '82–'94 (FY '94 is projected.)



LOUIS A. CODISPOTI

RESEARCH INTERESTS

My major research interests include the global nitrogen and carbon cycles and the chemical oceanography of the Arctic Ocean. My interest in improving instrumentation for chemical oceanography stems from the recognition that improved instrumentation is required to enable sampling for nutrients, dissolved oxygen and inorganic carbon on appropriate time and space scales. My role in instrument development has typically been in the overall management of new instrumentation projects and I have been associated with the development of pumping systems, sampling devices, and automated Winkler titration systems.

OPENING REMARKS

Welcome to MarChem 93. Our tasks are:

- To exchange information. This should be easy since we have gathered people from diverse groups who could use improved lines of communications.
- To examine existing modalities for producing improved instrumentation. Do we think that major changes are necessary? If yes, how do we implement the changes?
- To decide whether the MarChem series of workshops is worth continuing. This workshop costs ~\$100,000. Is it worth it? If yes, who will lead the next one? If yes, what changes are necessary? Who will do the hard work of organizing, editing and advocating?

Without comparable equipment, how do we interface with major international, interdisciplinary experiments? For example, we are not doing much *vis a vis* moorings in the Arabian Sea. More importantly, can we affordably measure on appropriate space and time scales without improved instruments?

Physical oceanographers and biological oceanographers appear to be ahead of chemical oceanographers in the development of autonomous instruments!

BRADLEY G. DEROOS

DISPOSABLE CONTAINER FOR SEA WATER SAMPLES

A small container (300 cc), made of a flexible plastic-metal-plastic laminate, is being developed for short-term storage of sea water (10 to 1,000 hours) prior to chemical analysis at sea and ashore. The design goals are to :

- Simplify transfer from rosette samplers to shipboard instrumentation
- Maintain chemical integrity of sea water and dissolved gases
- Minimize the volume of rinse and purge water
- Maximize the number of analyses from each sample draw from a water bottle, and
- Reduce the storage volume and weight of sample containers shipped to, and stowed aboard, research vessels.

The container is easy to rinse and fill; has less than 0.01% initial head space; and can dispense a metered volume of sea water with simple ancillary equipment. Andrew Dickson of Scripps Institution of Oceanography is testing the stability of carbonate parameters in filtered, sterilized sea water stored in prototype trilaminate containers for periods ranging from less than one to more than 240 hours. Dickson is also evaluating the efficacy of filling the containers with sea water and dispensing metered sample volumes to a PC-controlled dissolved inorganic carbon analyzer. This effort is motivated by marine CO_2 chemists who wish to conserve sample water at sea, obtain multiple replicate analyses from a single Niskin draw, and improve logistic efficiency.

ANDREW G. DICKSON

RESEARCH INTERESTS

Overall Research Goal

Increased understanding of the processes controlling the state of the oceanic carbon dioxide system.

Current Research Projects

The production and distribution of reference materials for oceanic carbon dioxide measurements. We have developed a strategy to produce such materials based on sterilized natural sea water and are working in concert with groups in the U.S. and internationally to develop a quality control scheme for sea going carbon dioxide measurements. As part of this work, we have collaborated with Dr. Keeling (UCSD/SIO) to certify these materials for dissolved inorganic carbon, and have developed a certification procedure for the measurement of total alkalinity.

Our work is thus of substantial importance in the execution of a global survey of carbon dioxide in the oceans. It provides a mechanism to ensure that the results obtained by different laboratories, at different times, in different parts of the ocean, are indeed comparable. In addition, we currently play a role advising on a suitable quality control plan for oceanic carbon dioxide measurements. This approach is essential to the interpretation of such results on a global scale.

The measurement of sea water pH using spectrophotometric techniques. Our work has had two directions: a study of the thermodynamic properties of indicator dyes in sea water, and the development of a rugged, automated instrument for sea going measurement based on a commercially available diode array spectrophotometer. This work is now nearing completion, and our prototype instrument is presently at sea on the NOAA R/V Malcolm Baldridge.

The significance of this research lies in the need for reliable, automated, underway instrumentation for the analyses of oceanic carbon dioxide parameters. At present, the best measurements are extremely labor intensive and as a result our ability to sample the ocean appropriately is severely compromised. We believe that our instrument will provide eventually the basis for making CO_2 related measurements on ships of opportunity, and thus open the possibility to a much larger coverage than was previously available.

Future Research Directions

In the near future, I intend us to extend our skills in instrument development to the development of further robust, automated instrumentation for the analysis of the oceanic carbon dioxide system and the related biogeochemical parameters such as oxygen and nutrient concentrations. We shall then deploy such instrumentation in the field.

These instruments will play a significant role as the CO_2 research community transitions its observing approach from having individual investigators on specialized oceanographic research vessels, to a more extended use of ships of opportunity and eventually of autonomous vehicles and buoys as part of a Global Ocean Observing System.

JOHN P. DOWNING

SENSORS AND TECHNOLOGIES FOR MARINE CHEMISTRY MEASUREMENTS: A SEVEN-YEAR PERSPECTIVE FROM THE DOE SBIR PROGRAM

Since 1987, the DOE Environmental Sciences Division, and the Carbon Dioxide Research Division before it, has supported research and development of ocean-measurement technologies in the following areas:

- Physical and chemical parameters (T, pH, C_T, and CO_2)
- Particle flux
- Optical properties
- Water-vapor flux and
- Smart, expendable sensor packages.

In keeping with the scope of MarChem 93, the presentation covers the chemistry-related technologies.

SBIR funding for ocean measurement technologies in the past seven years totaled $3.4 M. Brief descriptions of SBIR projects are published in the annual research summaries for the CO_2 Program available from the Carbon Dioxide Information and Analysis Center at Oak Ridge National Laboratory (615) 654-8765. Research on C_T measurements and expendable sensors was a $0.5 M-part of DOE's Ocean Research Program. Particle-flux technologies are covered because many sea water constituents, pollutants, and biochemically active materials are efficiently scavenged and transported by particles. Calcium carbonate, silica, PAH's, PCB's and thorium are among them. Technologies that will be addressed include:

- pH sensors based on spectrometry and swelling polymers
- CO_2 sensors based on gas filtration correlation, chemical amplification, and specific conductance
- Insect-eye and forward-scatter particle sensors
- Expendable CTDs

Some lessons DOE has learned about SBIR from these topics will conclude the presentation.

Figure 11-1
Technologies for ocean measurements

- DOE/ESD Statistics for 1987 - 1993
  - Phase I Grants: 12
  - Phase II Grants: 6
  - Conversion Rate to Date: 50%
  - Projected Conversion Rate (1994): 66%
  - Total Funding: $3.4 M
  - Level of Effort: 1 man month per year

Figure 11-2
Marine chemistry technologies

- Fiber-optic pH Sensor
- Swelling Polymer pH Sensor
- Gas Filtration CO_2 Sensor
- CO_2 Sensor based on chemical amplification and specific conductance
- Particle Flux Measurement systems based on forward scatter and multi-aperture optics with image processing
- Expendable Smart Packages

Figure 11-3
Lessons learned

- Design commercial potential into topics
- Work as hard at building a cadre of competent reviews as you do at topic design
- Do not look for "Smoking Guns" in Phase I Projects
- Some topic duplication and competition among the Federal agencies is healthy
- Interagency coordination, in our experience, is marginally effective <u>at best</u>
- Recycling of "Innovative Ideas" is a real hazard in SBIR
- Watch the "SBIR Factories" like a hawk
- Shotgun advertising of SBIR topics and mass mailings of letters are not very effective

GERNOT E. FRIEDERICH

CURRENT RESEARCH

I have been employed at the Monterey Bay Aquarium Research Institute (MBARI) since 1987. Some of my recent interests in oceanographic instrumentation have been the design of automated analytical systems to measure some of the standard chemical variables such as oxygen, inorganic nutrients and carbon dioxide. I am also involved in the development of water sampling apparatus such as a profiling pump system and a small volume, high count water sampler.

My interest in improving oceanographic instrumentation has been constant since my first major oceanographic cruise in 1971. Since that time I have been involved in numerous oceanographic programs most of which focused on areas of intense biological activity such as coastal upwelling regions. One of my future interests, aside from instrumentation, will be the combination of the data generated by the autonomous systems on ships and buoys with traditional data sets and remotely sensed data from satellites. This combination of approaches may help in the interpretation of chemical and biological fluxes in complex systems such as those found in the coastal and equatorial upwelling regions.

MOORED CO2, SURFACE MAPPING AND WATER SAMPLING

With C.A. Sakamoto and R.C. Burton

Much of the uncertainty concerning the cycles and budgets of the major bioactive chemicals in the sea arises from drastic undersampling of the system in relation to the actual spatial and temporal variability. During the past year we have addressed this problem with the development of a shipboard sea surface nitrate mapping system that provides navigated, real-time data with minimal operator intervention. We have also developed and deployed a buoy mounted analytical system that determines the difference in partial pressure of carbon dioxide (ΔpCO_2) between the sea surface and the atmosphere. Efforts are underway to develop a small volume water sampler capable of collecting numerous samples and being interfaced with analytical equipment upon retrieval. The test deployments and calibration of these instruments are providing an informative data set in the central California coastal upwelling system.

The nitrate analyzers are based on microprocessor controlled Kloehn syringe modules operating in batch mode. One unit uses two syringe modules and is a high temporal resolution system capable of a two-minute sampling rate. This system integrates shipboard navigation and data from the nitrate analyzer and a flow-through Sea-Tech fluorometer to generate real-time maps of nitrate and fluorescence. This system has been used primarily in Monterey Bay and along the California coast. A simpler and lower temporal resolution system for ocean basin scale mapping has also been developed. This system uses only one syringe module and provides nitrate data every twenty minutes and data logging capability for several other sensors. Incorporation of a GPS system makes this unit independent of the ship's navigation. This system was developed on several equatorial JGOFS cruises during 1992 and is currently on a cruise in the Atlantic.

Early in 1992, the Monterey Bay Aquarium Research Institute (MBARI) launched an investigation of the feasibility of measuring the sea-surface partial pressure of CO_2 (pCO_2) on one of the institute's OASIS moorings. Rather than pursuing a new measurement technology, we decided to adapt to our use a commercially available, nondispersive, infrared analyzer built by LICOR, Inc. The apparatus was designed to measure the difference between sea-surface and atmospheric pCO_2 (ΔpCO_2), using ambient air as the reference gas. This approach would ensure the highest data quality relevant to air-sea exchange of CO_2 and also simplified the first version of this instrumentation. During a mooring turn-around in August 1992, the ΔpCO_2 system was integrated with the OASIS mooring that was re-deployed on August 31, 1992. After several months of testing and some modifications, the system has produced hourly ΔpCO_2 data since the latter part of January 1993.

The water sampler is still in its prototype stage. This sampler will have the capability to collect up to 100 small (~20 ml) samples that will be suitable for routine chemical analysis. Once the samples are collected the sampler is corrected directly to analytical equipment for processing. The sampler could be deployed as part of routine hydrocasts where samples would be collected on the "fly". Mooring and ROV deployments are also being considered.

EDWARD J. GREEN

ONR OCEANIC CHEMISTRY PROGRAM

Figure 18-1

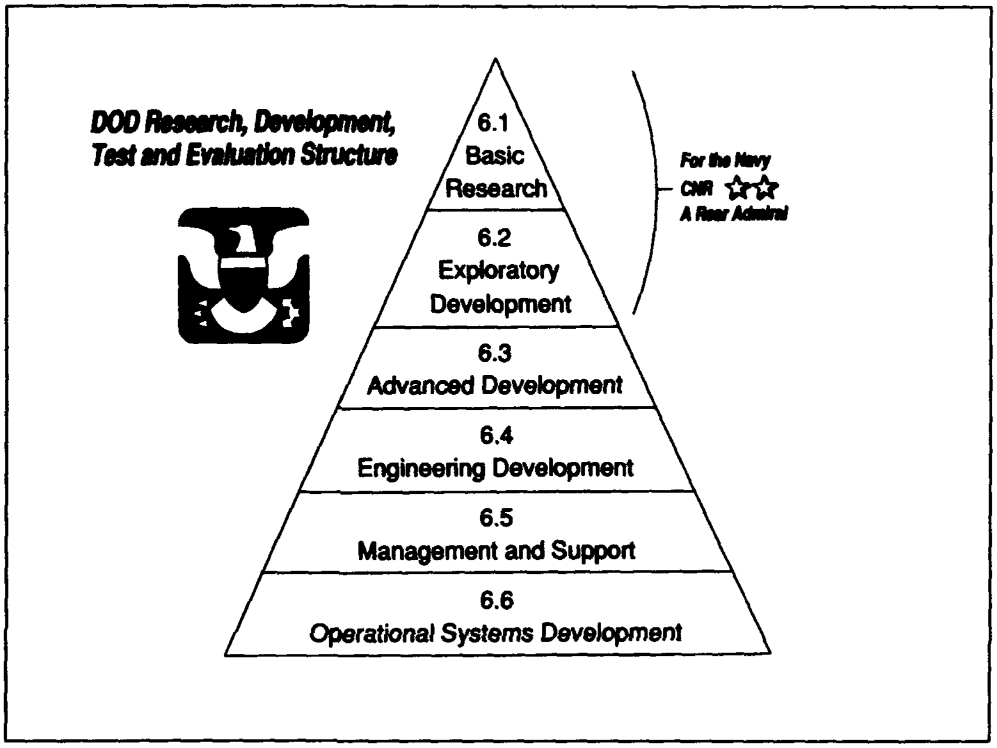


Figure 18-2

Office of Naval Research organization chart

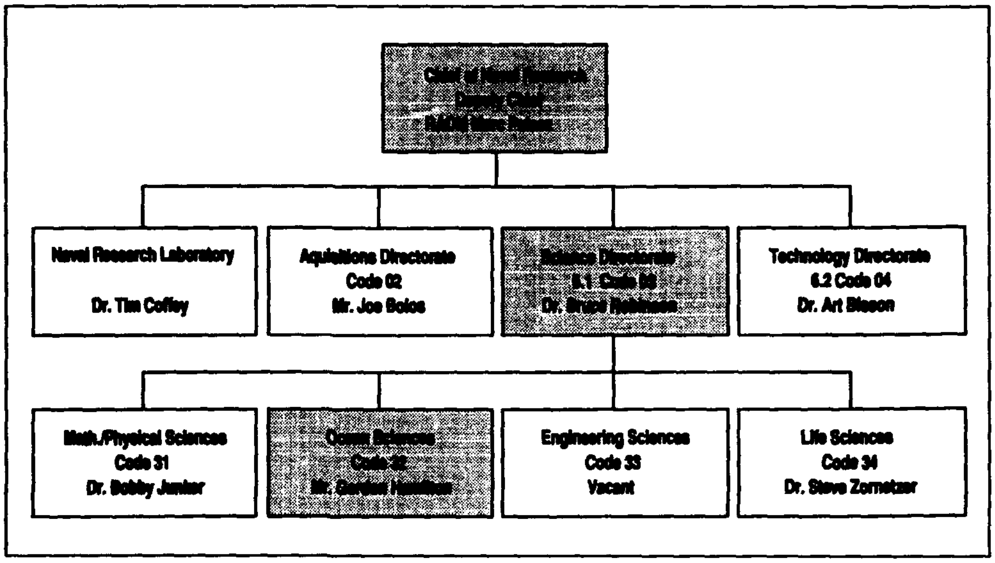


Figure 18-3

Office of Naval Research organizational chart (continued)

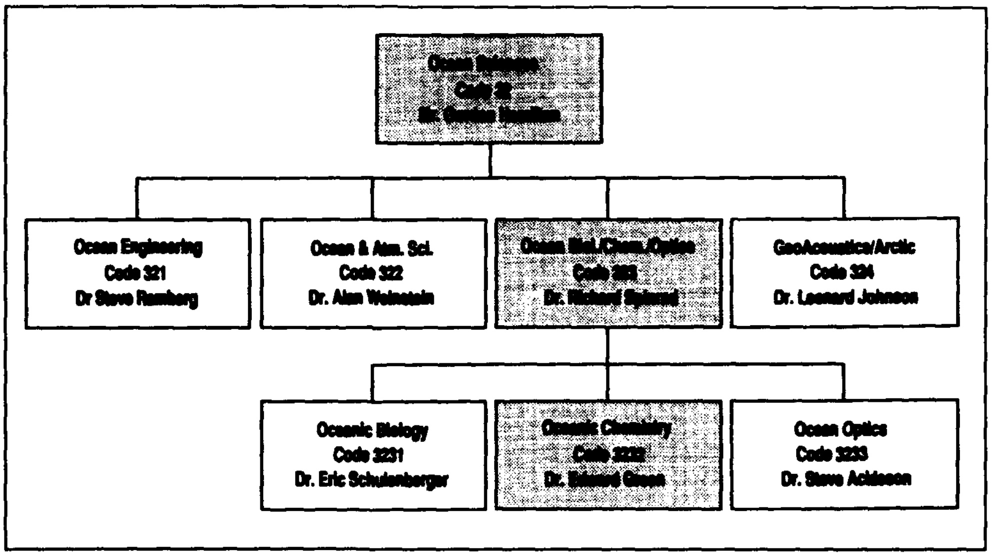


Figure 18-4

Site review institutions

East Coast	**WHOI**	Every year
	LDGO	Odd year
	URI	Odd year
	Miami	Even year
	MIT	Even year
West Coast	**SIO**	Every year
	OSU	Odd year
	UW	Odd year
	Hawaii	Odd year
Gulf Coast	**TAMU**	Even year

Figure 18-5
Non-site review institutions

- UC Santa Cruz
- Moss Landing
- Washington State Univ.
- Univ. Alaska
- Univ. Colorado
- Princeton
- SUNY Stony Brook
- SUNY Syracuse
- Skidaway
- Drexel
- Univ. Illinois
- North Carolina State Univ.

Figure 18-6
Geographical distribution of investigators

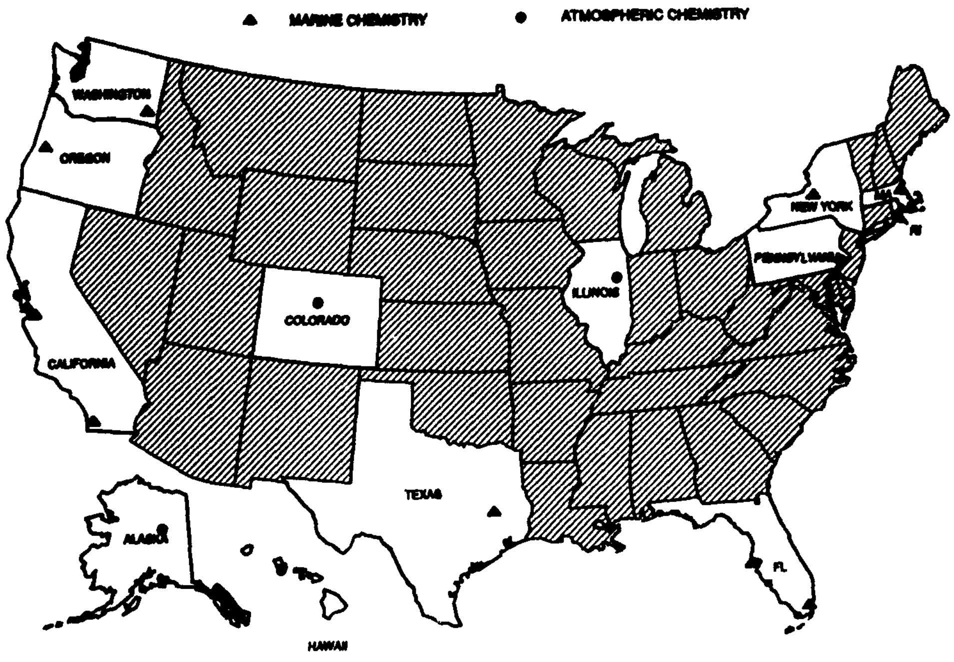


Figure 18-7

Proposals received throughout the year.

But proposals received April-July will usually be deferred to 01 October start.

Figure 18-8
Core program

Current thrust areas:

- **Redox and speciation processes**
- **Photochemical processes**
- **Biogeochemical cycling of trace metals**
- **Air-Sea Fluxes of sulfur species and gases**

Sediment geochemistry usually referred to Marine G&G Program, 1125GG, unless dealing with EQ issues.

Figure 18-9

Accelerated research initiatives

1990-1993	***Biodetection of Trace Metals***	**$200K**
1990-1993	***Subduction and Convection***	**$250K**
1991-1994	***Marine Aggregate Dynamics***	**$300K**
1992-1996	***Marine Aerosols***	**$900K**
1993-1995	***Environmental Quality***	**$1,400K**

Figure 18-10

Fiscal history–1980 to 1993

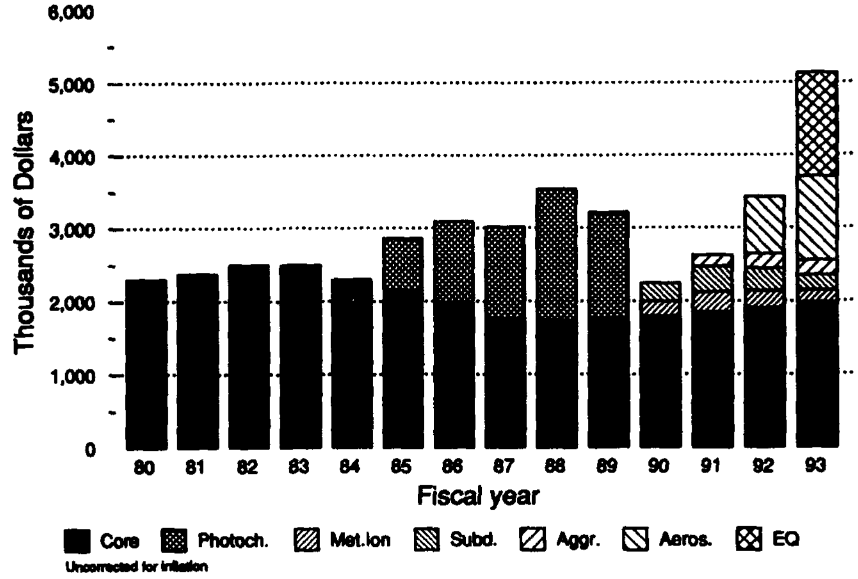


Figure 18-11
Programmatic emphasis

Focus on upper ocean water column
--- short time scale processes
--- short space scale processes

Blue water oriented
--- tends to exclude estuarine, riverine, and nearshore studies except in environmental quality
--- generally does not support aquaculture, mariculture

Figure 18-12
Long-term management goals

- Focus program on the upper water column and marine boundary layer where the Navy "lives".
- Emphasize processes on the short space/time scale commensurate with Navy operations.
- Improve water column, particulate, microlayer sampling technologies for marine chemistry.
  --- Underway water sampling
  --- In-situ sensors
  --- Unattended moored sensors for long-term, synoptic sampling
- Develop theoretical models where applicable (from box to embedded mixing and circulation) linking physical, biological, and chemical processes.

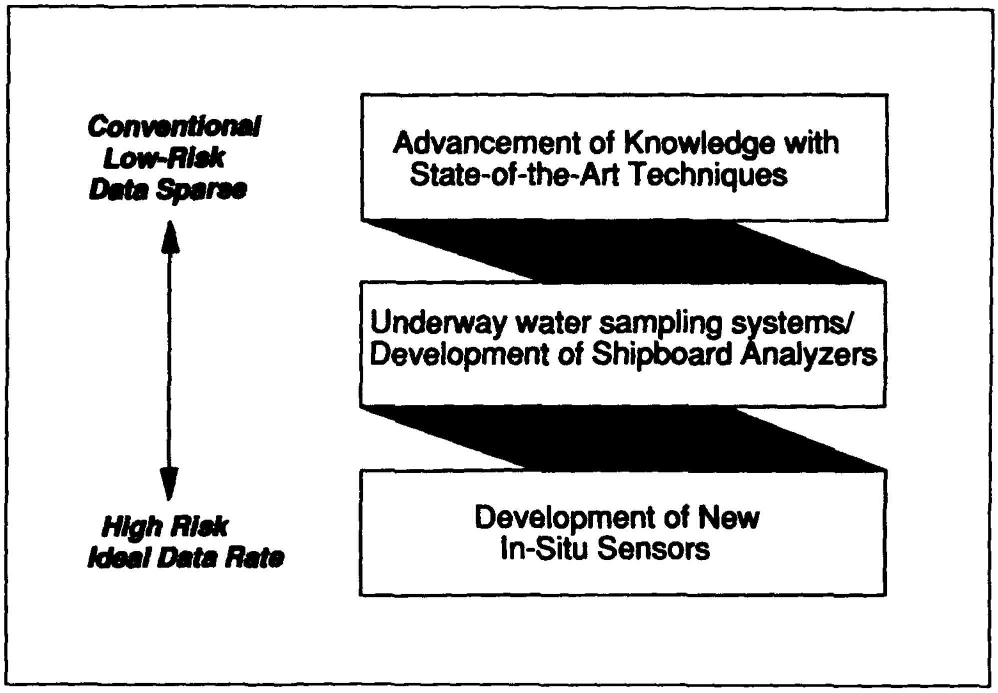


Figure 18-13
Management strategy

ALFRED K. HANSON, JR.

RESEARCH INTERESTS

Oceanography

Marine biogeochemistry and photochemistry, focusing on understanding the influence of chemical, biological, and physical processes on trace chemical distributions in coastal and oceanic waters. Current research involves studies of episodic atmospheric nutrient inputs to the open ocean, biogeochemical cycling in oxygen-depleted estuarine waters, the bioavailability of trace metals, and the effects of ultraviolet radiation on chemical speciation and phytoplankton productivity.

Marine Chemical Instrumentation

Interested in the development and application of submersible chemical sensors for highly-resolved measurements (centimeter depth scale) and continuous monitoring (minutes to months time scales) of various biogeochemical properties in marine waters. Such compact submersible sensors may utilize microscale, continuous-flow chemical reaction and optical detection technologies (absorbance, fluorescence, chemiluminescence) with computer-controlled sensor operation and data acquisition. Applications of interest include sensors for potentially toxic trace metals (Cu^{+2}, Zn^{+2}, etc.), photochemical transients (Fe^{+2}, Cu^{+1}, HOOH, etc.) and selected constituents that serve as indicators of the redox state of marine waters (Mn^{+2}, Fe^{+2}, S^{-2}, etc.).

PAUL M. HOLLAND

CHEMICAL INSTRUMENTATION BASED ON SILICON MICRO-FABRICATED COMPONENTS

Silicon micro-fabricated sensors and components offer significant potential for miniaturization of chemical instrumentation, enhanced ruggedization, and cost reduction. We are currently developing handheld chemical detectors based on this technology for various micro-gas chromatography (μGC) applications. These μGC applications include the detection of treaty prohibited Chemical Weapons materials and precursor chemicals, and the detection of contraband drugs in cargo containers. The compact size of μGC components allows for instrument designs which utilize two or more GC columns operated in parallel. Coupled with enhanced signal processing, correlated column μGC can be used to expand "detection space" and greatly improve chemical selectivity for the automated detection of targeted compounds against complex environmental backgrounds. This offers a promising approach for the development of miniaturized *in situ* gas chromatography instrumentation for the analysis of organic compounds in sea water.

Figure 20-1
Advantages of chemical instrumentation based on silicon micro-fabricated components

Feature	Advantages
Small size and weight	Low power requirements
	Enhanced portability for *in situ* detection
	Potential for faster detection
Small sample sizes	Reduced use of consumables (reagents, carrier gases, etc.)
Robustness	Suitable for "real world" environments
	Low maintenance
Potential low cost	Use as "disposable" sensors

Figure 20-2

Silicon microfabricated thermal conductor detector

Figure 20-3

Miniaturized gas chromatography instrumentation development

DNA program to develop handheld inspection instrument for Chemical Weapons Convention treaty verification

> **Chemicals to be detected have a wide range of chemical and physical properties**

ARPA program to develop handheld instrument for contraband drug detection

> **Contraband chemical signatures must be detected against a wide range of backgrounds in cargo containers**

Potential for developing a miniaturized GC instrument for volatile organics compounds in seawater

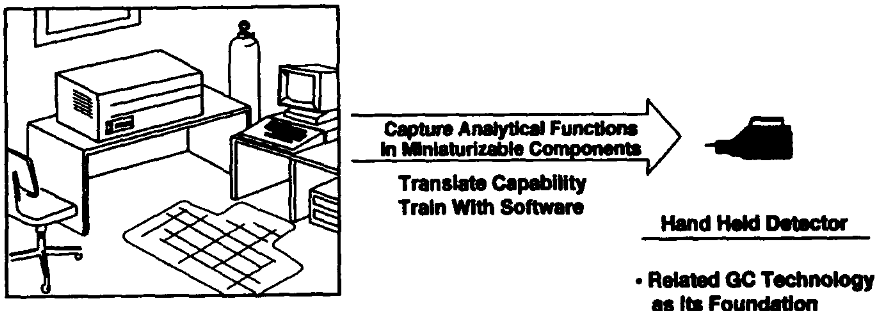
Figure 20-4

General requirements for micro-GC instrumentation

- **Self-contained instrumentation package**
- **Detection sensitivity to meet application needs**
- **Automated operation and signal processing (little or no user intervention required)**
- **Excellent chemical selectivity against background**

Figure 20-5

Program concept



Capture Analytical Functions in Miniaturizable Components

Translate Capability
Train With Software

GC/MS Laboratory Instrument

- **Large**
- **Not Easily Portable**
- **Complex Method & Operation**
- **User Technical Background Required**

Hand Held Detector

- **Related GC Technology as Its Foundation**
- **Fast, On-Site Analysis**
- **Simplified Method & Operation**
- **No Technical Background Required for Users**

Figure 20-6

Chemicals on cwc schedules

SCHEDULE 1	SCHEDULE 2	SCHEDULE 3
1. O-alkyl alkyl phosphonofluoridates	1. Amiton	1. Phosgene
2. O-alkyl N, N-dialkyl phosphoroamidates	2. PFIB	2. Cyanogen chloride
3. O-alkyl S-2-dialkyl aminoethyl alkyl phosphonothiolates	3. BZ	3. Hydrogen cyanide
4. Sulfur mustards	4. Organophosphates having a single methyl, ethyl, or propyl group bonded to the phosphorus atom	4. Chloropicrin
5. Lewisites	5. N, N-dialkyl phosphoramidic dihalides	5. Phosphorus oxychloride
6. Nitrogen mustards	6. Dialkyl N, N-dialkyl phosphoramidates	6. Phosphorus trichloride
7. Saxitoxin	7. Arsenic trichloride	7. Phosphorus pentachloride
8. Ricin	8. 2, 2-Diphenyl-2-hydroxyacetic acid	8. Trimethyl phosphite
9. Alkyl phosphonyldifluorides	9. Quinuclidin-3-ol	9. Triethyl phosphite
10. O-Alkyl O-2-dialkyl aminoethyl alkyl phosphonites and corresponding protonated salts	10. N, N-Dialkyl aminoethyl-2-chlorides and corresponding protonated salts	10. Dimethyl phosphite
11. Chlorosarin	11. N, N-Dialkyl aminoethane-2-ols and corresponding protonated salts	11. Diethyl phosphite
12. Chlorosoman	12. N, N-Dialkyl aminoethane-2-thiols and corresponding protonated salts	12. Sulphur monochloride
	13. Thiodiglycol	13. Sulphur dichloride
	14. Pinacolyl alcohol	14. Thionyl chloride
		15. Ethyldiethanolamine
		16. Methyldiethanolamine
		17. Triethanolamine

Figure 20-7

μGC analysis

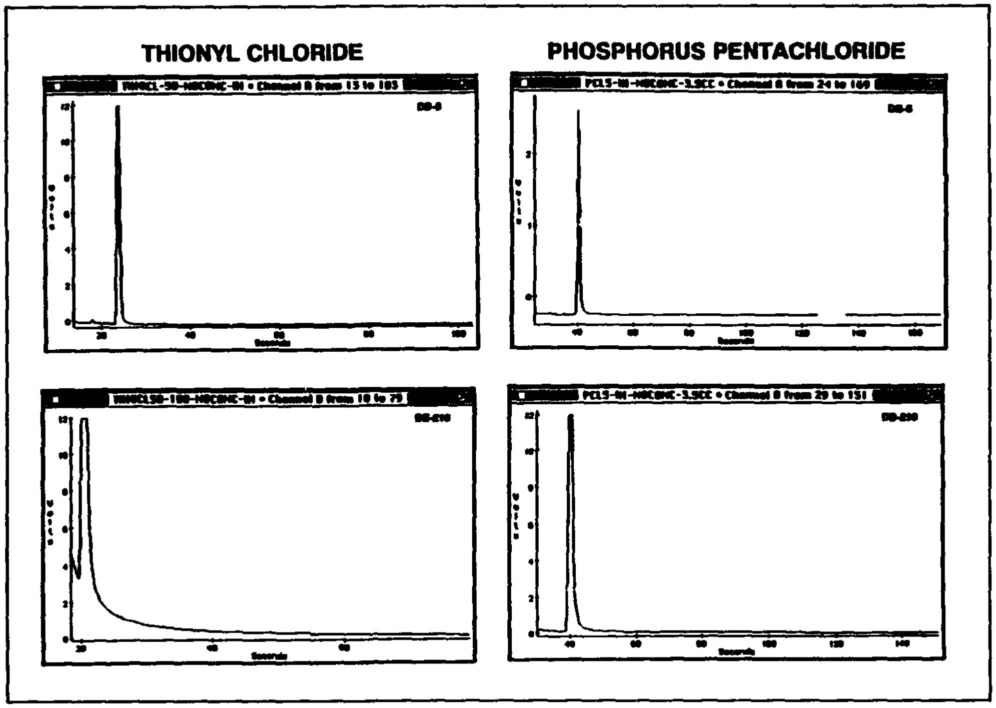


Figure 20-8
Cargo container contents

Coffee
Sea Weed
Passion Fruit
Tiles
Puerto Rico Rice
Earthenware
Lima Beans
Shrimp
Dehydrated Peppers
Facial Soap
Brandy and Cognac
Wearing Apparel

Glycerine
Furniture (2)
Wrapping Paper
Canned Pease
Salad Herbs
Granite
Copper Tubing
Apple Juice
Flax Seeds
Confectionery
Cast Iron Pipe Fittings
MS Glutamate

Crude Iodine
Radiators
Popsicle Sticks
Methyl Salicylate
Cardboard Boxes
Lumber
Cardboard
Dehydrated Celery
Machinery
Wicker and Boxed Goods
Rattan
Basketware

- Difficult to imagine grater diversity in contents as well as packing

Figure 20-9
Correlated chromatography for chemical selectivity

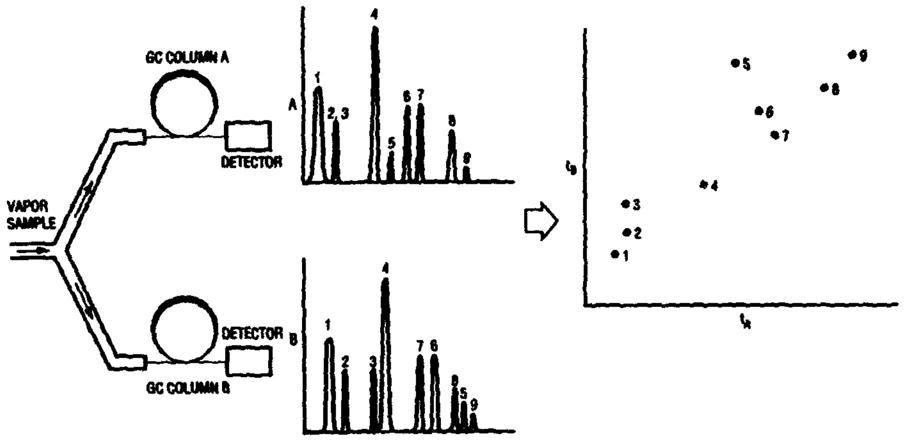


Figure 20-10

Cargo container vapors correlation-composite

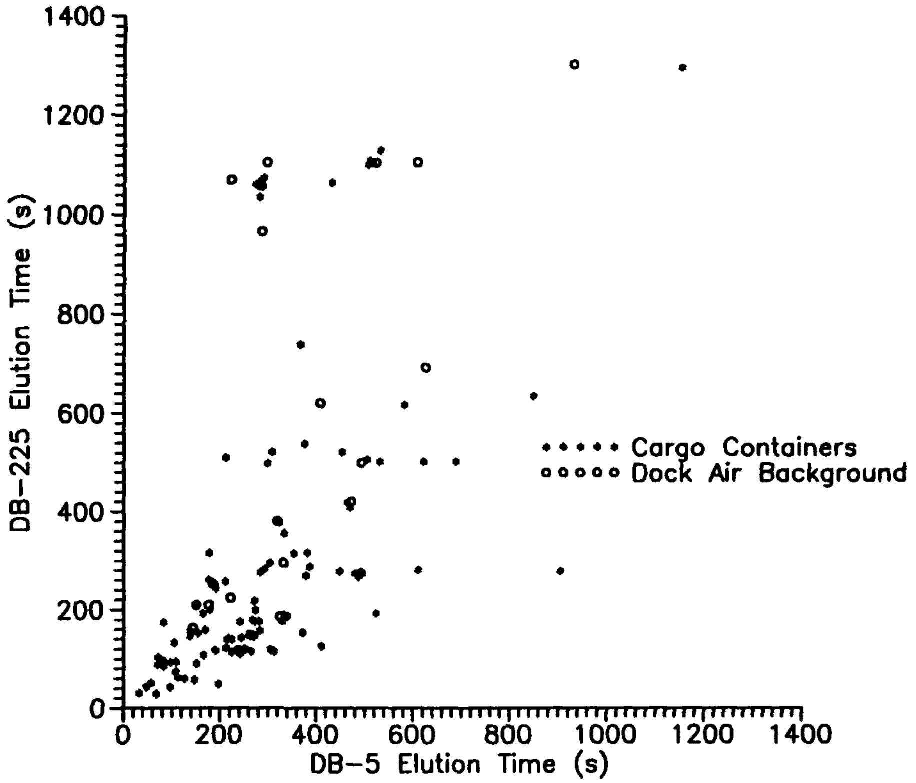
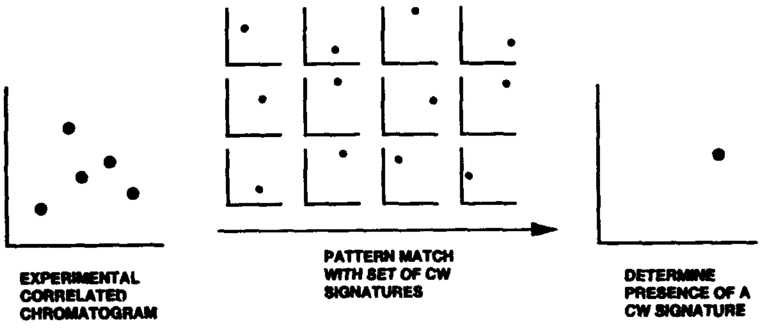


Figure 20-11

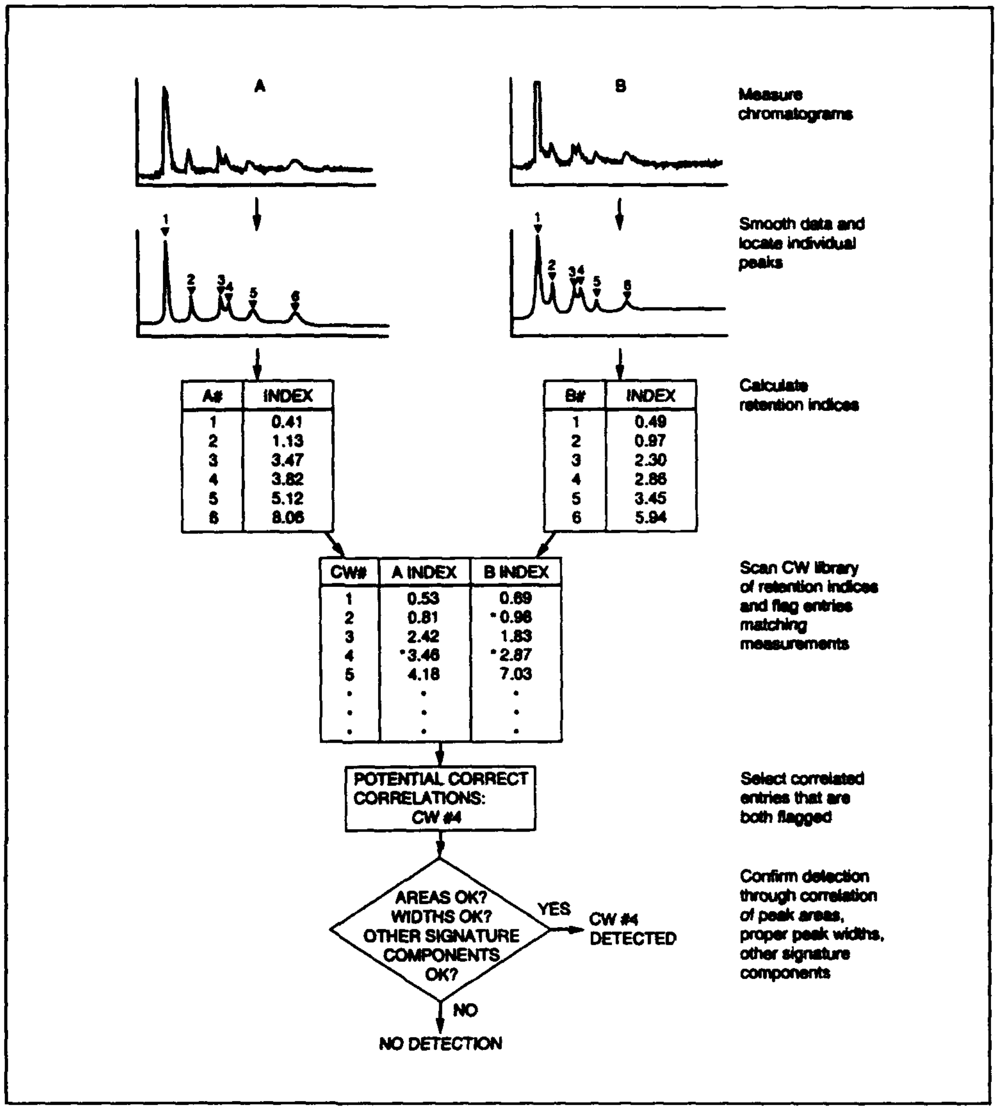
Computation of data overlap with signatures in library



- **Approach can provide accurate analyses of CWC chemicals *without* revealing identity of proprietary or military R&D materials**

Figure 20-12

Overview of signal processing approach



A#	INDEX
1	0.41
2	1.13
3	3.47
4	3.82
5	5.12
6	6.06

B#	INDEX
1	0.49
2	0.97
3	2.30
4	2.86
5	3.45
6	5.94

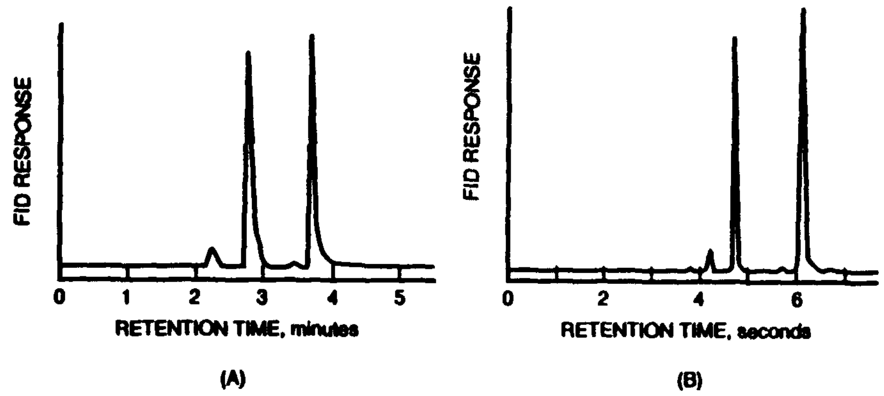
CW#	A INDEX	B INDEX
1	0.53	0.69
2	0.81	*0.96
3	2.42	1.83
4	*3.46	*2.87
5	4.18	7.03
.	.	.
.	.	.
.	.	.

Figure 20-13

Purge and trap technique in seawater

- **Rapid extractions of volatile organics without sample pre-processing**
- **Avoids chemical background "noise" from solvent**
- **Large pre-concentration factors possible**
- **Sub part-per-trillion detection limits possible**
- **Limited to purgeable organics**

Figure 20-14
Fast GC



Comparison of a conventional chromatogram (A) and a fast chromatogram (B) for a mixture of benzene, toluene, and xylene run under similar conditions

Figure 20-15
Diagram of potential μGC based system

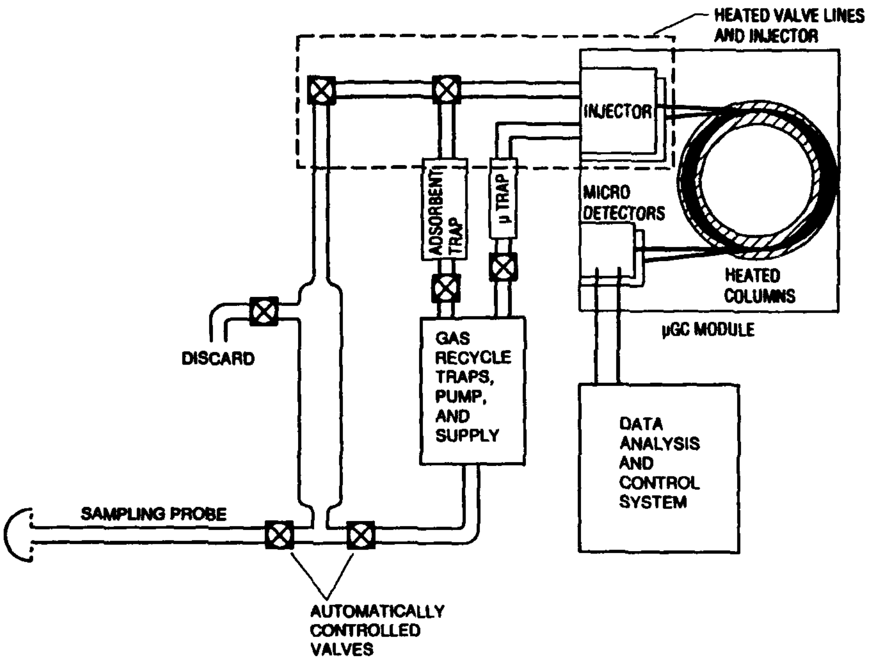


Figure 20-16
Marine instrumentation for μGC

Demonstrated to date:

- **Ultratrace detection in seawater using purge and trap technique**
- **Rapid analysis using fast GC techniques**
- **Good chemical selectivity using correlated column GC**
- **Automated signal processing for chemical analysis**
- **Compact μGC instrumentation**

Other R&D issues remain, such as:

- **Sampling "front end"**
- **Pressure housing**

HANS W. JANNASCH

THE MBARI CHEMICAL INSTRUMENTATION PROGRAM

With Carole Sakamoto, Gernot Friederich, and Kenneth S. Johnson

One of the main objectives of the MBARI Chemical Instrumentation Program is to develop a series of automated chemical analyzers which will radically simplify and expand our ability to collect chemical data from the marine environment, and to use these to study marine biogeochemical cycles. The need for these types of instruments has been brought into focus by the necessity to study the chemical variability within the ocean. Current chemical methods, i.e., bottle sampling followed by laboratory analyses, simply cannot obtain enough data at a reasonable expense. As a result, the advancement of our knowledge of biogeochemical cycles in the ocean is, in many cases, dependent on new instrumentation capable of autonomously detecting chemical concentrations at sea.

MBARI is therefore developing a series of self-contained chemical analyzers which can operate aboard ships, on moorings and in situ. These include

- Long-term *in situ* analyzers for nutrients and trace metals which use simple osmotic pumps to propel both the sample and reagents through a miniature flow injection style manifold,
- Colorimetric batch analyzers which are capable of in situ near-real time data collection (e.g. from an ROV, AUV or submersible),
- Surface nutrient mapping systems, which can continuously monitor, log and plot surface nutrient concentrations on cruise tracks, and
- A moored surface ΔpCO_2 analyzer capable of measuring the disequilibrium of CO_2 across the air/water interface.

All analyzers are designed to operate for extended periods of time without a trained chemist, standardize themselves at necessary intervals, and use as little power as possible. Advances in this area have many significant advantages over the traditional methods, including higher data densities, reduced contamination, near-real time data feedback and a significant reduction in expensive sample handling and ship-time.

OSMOTICALLY PUMPED NITRATE ANALYZERS FOR LONG-TERM MONITORING OF FRESH AND SEAWATER ENVIRONMENTS

With Carole M. Sakamoto and Kenneth S. Johnson

Temporal variations of chemical species in the fresh and seawater environments must be continuously determinable to further our understanding of non-steady state biogeochemical cycling in such aquatic environments. Our current knowledge of major oceanographic processes, including production, hydrothermal venting and global warming, as well as chemical variabilities in freshwater systems, is limited due to the lack of continuous long-term time series of chemical data.

To solve this dilemma, scientists are in need of new technologies for measuring concentrations of a wide variety of dissolved chemical species *in situ* for extended periods of time. So far, only a limited number of in situ chemical sensors and analyzers have been used in oceanography, but they are rarely relied on for long-term use because of problems with calibration and stability.

We are therefore developing a mechanically simple, self-standardizing chemical analyzer for long-term *in situ* analyses of dissolved nutrients and trace metals in aqueous environments (Jannasch and Johnson, 1992). This system is based on chemically powered osmotic pumps which are used to propel both the sample and reagents through a miniature flow injection style manifold. Shown here are the analyzers and some of their initial data.

DANA R. KESTER

CURRENT RESEARCH

My research during the past several years has been concerned with the redox cycling of iron in surface ocean waters, with interactions among physical, chemical, and biological processes in marine environments, and the applications of ocean color remote sensing to marine chemical studies. Some of the chemical systems in addition to iron that we have been investigating include oxygen, carbon dioxide, the major plant nutrient elements (N, P, and Si), and hydrogen peroxide. Our approach has been to combine field, experimental, and chemical modeling methods to understand the processes that result in spatial and temporal variability of these constituents and their various chemical forms. These studies involved field work at 140°W near the equator in 1990 and 1992, work in Rhode Island coastal waters, and laboratory and mesocosm experiments.

It has been evident for a number of years that many marine chemical studies undersample the spatial and temporal variability of the oceans. Technologies are becoming available that will enable us to obtain a variety of chemical measurements from marine environments with *in situ* sensors and analytical systems which transmit their data ashore on a daily basis. There is also a considerable network of Volunteer Observing Ships, drifting buoys, and moored arrays presently providing data on the physical properties of the oceanic environment, that could be adapted for obtaining chemical data with appropriate analytical systems.

In addition to building on the present capabilities to make *in situ* chemical measurements, we should develop more reliable and automated sampling devices for collecting water samples from research ships.

WATER SAMPLING: PRESENT LIMITATIONS AND FUTURE OPPORTUNITIES

Introduction

Sampling is one of the critical technologies for marine chemical studies. For this discussion I will adopt a general perspective of what constitutes "sampling" to include the collection of seawater, the acquisition of chemical data, and the degree to which these data reflect the chemical conditions of the marine environment.

In this morning's discussion I would like to consider the following issues:

- Performance specifications of chemical oceanographic water samples
- Suitability of existing samplers
- Automated chemical documentation of water samples
- Sampling required to resolve the spatial and temporal chemical variations in the ocean.

Before going into these considerations, I wonder to what extent those of us at this workshop have had similar or different experiences with oceanic water sampling. During the discussion session people might want to relate some of their experiences. I have assumed that people at this workshop will have had fairly recent experience collecting seawater samples at sea. Is this correct? If you have been involved in oceanic water sampling during the past five years raise your hand. How many of you used rosette samplers? How many of you hung bottles on a hydro line? How many of you think our water sampling technology could be improved with a new generation water sampler?

Sampling Bottles

The first oceanographic sampler that I used was a Nansen bottle. I have been told that Fritjof Nansen designed this sampler while drifting in the Arctic Ice onboard the Fram during 1893-1896. The Nansen bottle served oceanographers for about six decades. In the early 1960s when I was a student at the University of Washington, the Oceanography Department machine shop was developing and building a new type of sampler based on a design by Van Dorn. The Van Dorn bottle was made with a PVC tube and rubber plumber's helpers drawn together with rubber tubing for closures. Based on my experiences the three most successful commercially available ocean water samples have been the Nansen Bottle, the Niskin Bottle, and the GoFlo Bottle.

A number of specialized samplers have been developed by various investigators. Sterile expandable bags are available for microbiological sampling. Bill Broenkow developed a syringe sampler. During the past couple of years in my laboratory we developed an *in situ* extraction sampler which Al Hanson will show in a poster presentation. Woods Hole Oceanographic Institution and Battelle New England developed the WOCE "Almost" Sampler with NSF support.

If one were to design a next generation water sampler, there are a number of performance criteria that should be considered:

- Avoid chemical contamination or sample alteration—non-corrosive materials, non-metallic, no organic leachates (plasticizers), non-reactive to gases (H_2, H_2S, O_2, etc.)
- Reliable closure--no leakers
- Reliable tripping—no pre- or post-trippers
- Effective flushing—minimal soaking time
- Avoid contamination while passing through the air-sea interface—close-open-close
- Volume scalability—for example 5, 10, 30 Liter capacities
- Avoid rosette buoyancy
- Minimal hydrodynamic drag
- Avoid disruption of water column stratification
- Permit efficient lowering rate (for example, 60 m/min)
- Decouple from the ship's motion
- Good maintainability at sea and during storage—repairable

A list such as this may well contain incompatible requirements, in which case compromises must be made or samplers must be optimized for certain types of applications.

One of the questions we should address in the workshop discussion is whether we are satisfied with the samplers available today, or whether we think improvements can be made, and if so what should they be.

Automated Sample Documentation

A water bottle will provide a sample of ocean water for a wide range of experimental and research purposes, but we often require a substantial level of documentation for that sample to be useful. I raised this issue on the Omnet Marchem '93 Bulletin Board last October hoping to prompt some discussion prior to this workshop. While several people responded with polite statements of agreement, there was no real discussion about the need or feasibility of better and automated sample documentation. About the only result of my Omnet posting seems to have been the request to present a talk here today. Maybe people regard this as a non-problem, but I will outline it anyway.

Let's assume that you are a marine chemist who wants to study some particular chemical substance in seawater, perhaps a trace element, a radionuclide, or an organic constituent. This substance might be in dissolved or particulate forms. You get on a research ship, go to a place in the ocean where this substance may have some interesting chemistry, biology, or geochemistry and you lower a water bottle to bring up some seawater for processing and analysis.

At the present time you will undoubtedly "document" your sample with at least the following information:

- Latitude, longitude, and depth of sample collection
- Date and time of collection
- Whatever ancillary chemical and physical properties of the seawater you and your associates can manage.

The place where we could make substantial improvements in data return, in sample integrity, and in operational efficiency is through the automation of the ancillary measurements.

I would guess that a high percentage of our marine chemical sampling is now done with a rosette sampler and CTD system whenever possible. Using a CTD system possibly with sensors for dissolved oxygen, chlorophyll fluorescence, and light transmission or scattering can be very helpful in characterizing the water column and in selecting sampling depths for almost all chemical studies. In cases where the CTD-rosette system might compromise the sample being collected, suitable water bottles are hung on a hydro line and a CTD profile might be taken in a separate cast.

The ancillary data that we usually obtain with water sampling include salinity with a benchtop salinometer, Winkler oxygen, and nutrients (phosphate, nitrate, and silicate). I would guess that reversing thermometers are being used less and less, because a well-calibrated CTD can measure ocean temperatures and pressures (sample depth) more reliably than the mercury-in-glass reversing thermometers. To perform just the three basic ancillary chemical measurements (salinity, oxygen, and nutrients) in a typical chemical oceanographic sampling program requires about 2-3 well-trained analysts. In addition to these three basic measurements it would be useful to extend the chemical documentation of virtually all oceanic water samples to include pH, chlorophyll fluorescence in the upper ocean, and particle light scattering. In place of the plastic tube now placed onto the stopcock of a sampling bottle to draw samples today, we might envision a "smart tube" that would include a manifold with a few sensors and flow-through analyzers to automatically document the properties of each sample and to log the results into a database containing the cast data.

I think we have the basic technology today that is needed to automatically acquire the following variables while drawing samples from a sampling bottle:

- *Temperature*
- Salinity
- Oxygen
- Phosphate, nitrate and silicate
- Chlorophyll fluorescence
- pH
- Light scattering

These data would serve several functions. They would provide the investigator with ancillary measurements to complement the main objective of the sampling. They would provide systematic verification of the reliability of the sampling procedure by comparing the in situ sensor data with the data obtained while drawing samples. When transmitted to oceanographic data centers they would increase the overall oceanic chemistry database by acquiring these data systematically and routinely. While this approach seems to be technically achievable, the main question we would have to consider is how much would it cost to develop and deploy such a sample logging system, and would the costs be justifiable? The answer to these questions depends on how many people need such a capability. It is not worthwhile for any one of us, or for even a small subset of marine chemists, to use such a system. But if there are 100-500 marine chemists worldwide who would benefit from such a system, it may be worthwhile developing.

Sampling the Spatial and Temporal Scales of Variability

Another factor that must be considered in the context of water sampling is the degree to which the sampling methods, and the sampling design, capture the spatial and temporal scales of oceanic variability. Twenty to thirty years ago chemical oceanographers could make useful oceanic measurements within the context of the "Steady-State Assumption". That is, a set of samples, a profile, or an oceanic basin transect obtained one year was representative of almost any year. Sure, people realized that mixed layer and euphotic zone properties changed with diel and seasonal cycles, but they thought that below a couple of hundred meters chemical oceanographic properties changed only very slowly if at all (probably on glacial cycle time scales, and possibly on global oceanic circulation time scales of 10^3 years).

We used to think that the horizontal and vertical chemical gradients in the ocean could be resolved with discrete samples having vertical resolution ranging from 10-20 meters in the upper 200 m to about 200-500 meters in deep waters, and with station spacing of perhaps 500 km across an ocean basin (about every 5 degrees of latitude or longitude).

With the advent of the CTD, with the *in situ* oxygen sensors, with the increased vertical resolution of the GEOSECS program, with the studies of oceanic rings and eddies, with the WOCE intensive hydrographic surveys, and with increased attention to time-series data to reveal interannual and decadal variability, we now realize that most conventional sampling methods undersample the time and space scales of ocean chemical variations. About ten years ago I became increasingly concerned that studies I was conducting on oceanic processes were biased by undersampling. We made use of CTD-O_2 systems to obtain improved information on vertical gradients. We began taking virtually all of our analytical methods to sea in a custom-built clean portable laboratory, so that samples could be analyzed rapidly and while on station. This was possible even for atomic absorption analyses of trace elements. We also experimented with a variety of vertical pumping systems to get better resolution in the upper 124 meters.

These approaches helped to improve the spatial resolution in systems such as Gulf Stream rings, and upwelling systems such as off the coast of Peru, but we are still severely limited by the temporal sparsity of oceanic sampling. If we can mount field campaigns of 30-60 days per year we are doing pretty good (and we are using quite a large amount of high-cost ship time).

Coupling *In Situ* and Satellite Remote Sensing Data

Within the past year Mimi Fox and I have been examining the possibilities of combining *in situ* chemical measurements with ocean color satellite remote sensing data. In anticipation of the next generation of ocean color that should be available a year from now with the launch of the SeaWiFS sensor, we have been examining the historical Coastal Zone Color Scanner (CZCS) data that were obtained from late 1978 through mid-1986. Our first such analysis was done on CZCS data from the South China Sea. More recently we have been examining the CZCS data for the waters off the northeastern U.S. with 4 km regional data and some 1 km local data. Satellite imagery provides good spatial resolution (about 1 km) of near-surface ocean properties virtually anywhere in the world with temporal scales of 1-2 days, except for periods when the ocean is obscured by cloud cover. The global average oceanic cloud cover is about 60%. In northeastern U.S. offshore waters we find fairly good temporal coverage from CZCS, but cloud cover is often persistent for the months of December through February.

Our experience shows that satellite remote sensing can be a useful tool in defining the spatial and temporal scales of near-surface ocean variations, but it must be augmented by in situ measurements for several reasons. If you are concerned with chemical variables that are influenced by oceanic primary production processes, you will want to know not only the chlorophyll variations in the first optical depth of the water column (which are sensed by a satellite), but also the variations at the chlorophyll maximum layer, which in many areas may be at depths of 50-100 m. To get the best quantitative data from ocean color data requires some "sea truth" observations. These are needed to separate the effects of chlorophyll, suspended sediments, and blue-absorbing organic substances from the "ocean color" signal, and they may also be useful in applying atmospheric attenuation corrections for such effects as aerosols.

We believe that to make full use of satellite remote sensing for marine chemical studies we will need a network of autonomous in situ sensors to complement the satellite data. With existing technology these sensors could be expected to measure temperature, salinity, chlorophyll, oxygen, pH, and light scattering by particles. These sensors and flow-through analyzers could be deployed on ships of opportunity, including merchant ships, and they could be deployed on moored or drifting buoys, at fixed depths or with a profiling capability. Much of the technology needed for such deployments already exists.

Summary

We can summarize the following areas for improvement of marine chemistry water sampling:

Improve the water bottle design used in marine sampling for—
- better maintainability at sea more reliable protection against leakage
- improved hydrodynamics
- reduced buoyancy associated with closed-opened-closed cycle

Develop automated chemical documentation of samples at the time of transfer from the water bottle in order to—
- reduce presently labor intensive tasks
- improve the yield of ancillary data associated with marine chemical sampling
- provide verification of sample integrity
- obtain a common set of parameters—latitude, longitude, depth, date, time, temperature, salinity, oxygen, nutrients, pH, chlorophyll fluorescence, and light scattering

Improve the spatial and temporal resolution of upper ocean marine chemical observations by—
- integration with remote sensing data
- deployment of sensors and chemical analyzers on ships of opportunity
- deployment of sensors and analyzers on moored, drifting, and profiling platforms

MICHAEL R. LERNER

A BIOSENSOR UTILIZING G-PROTEIN COUPLED RECEPTORS

Abstract: Work is in progress to construct a biosensor that recognizes small organic molecules such as diesel fuel and organic waste. Throughout the animal kingdom, nature relies on G-protein coupled receptors (GRs) to detect a vast range of agents. Examples of factors for which GRs exhibit high sensitivity and selectivity include odorants, lipids, peptides, ions, sugars and photons. To adapt these powerful recognition devices for biosensor applications, we have harnessed to the process by which animals change color. Many species including fish and amphibians use cells called melanophores to rapidly effect this transformation (In human beings the equivalent cell is the melanocyte which is responsible for skin and hair color). Activation of GRs on the surfaces of melanophores causes them to translocate intracellular pigment granules in either a centrifugal or centripetal manner (depending on the specific receptor) which causes darkening or lightening respectively. Immortalized melanophores expressing cDNA clones coding for GRs have been shown to faithfully detect the chemicals which are their normal ligands. GR mediated changes in the appearance of melanophores are observable in as little as 12 seconds with standard equipment (microplate reader) and the result is apparent to the naked eye in minutes.

Specific Aim: Our goal is to develop a biosensor capable of rapidly and specifically detecting small quantities of organic molecules. The sensor is based on two critical components: G-protein coupled receptors (GPCRs) and frog melanophores.

GPCRs are Nature's primary detectors for small chemicals. To get a feeling for the potential detection range of these receptors, some examples are listed in Figure 23-1. In particular, the list includes the

Figure 23-1

G-protein Coupled Receptors

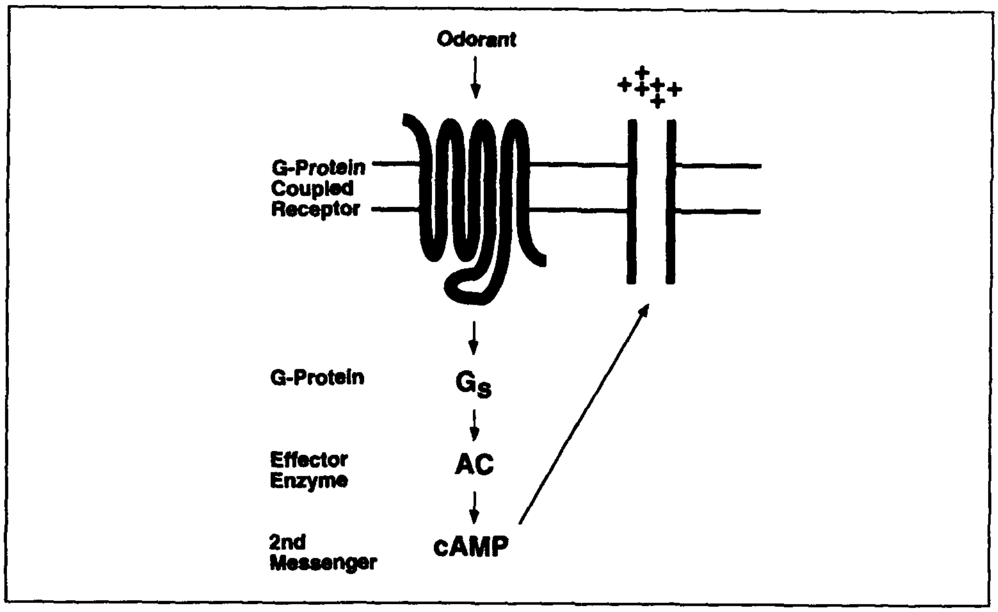
Acetylcholine muscarinic
Adenosine
ACTH
Adrenergic
Anaphylotoxin/C5a
Angiotensin
Bombesin/GRP
Bradykinin
Calcitonin
CGRP
Cannabinoid
Chemokine
Cholescystokinin
C5a
Cytomegalovirus
Dopamine
Endothelin
fmet-lue-phe
GABA(b)
Galanin
Glucagon
GLP
Glutamate-metabotropic
GHRH
Histamine
Interleukin 8
Leucotriene
LH
LHRH
MSH
Melatonin
Neuromedin
Neuropeptide Y
Neurotensin
Olfactory
Opiate
Oxytocin
PTH
PTH like hormone
PACAP
PAF
Prostaglandin
Secretin
Serotonin
Somatostatin
Sperm chemotractant
Substance K
Substance P
Tachykinin
Thromboxane
TRH
TSH
Thrombin
VIP
Vasopressin

olfactory receptors which animals use to recognize chemicals in their environment.

GPCRs signal ligand recognition via interrelated intracellular pathways.

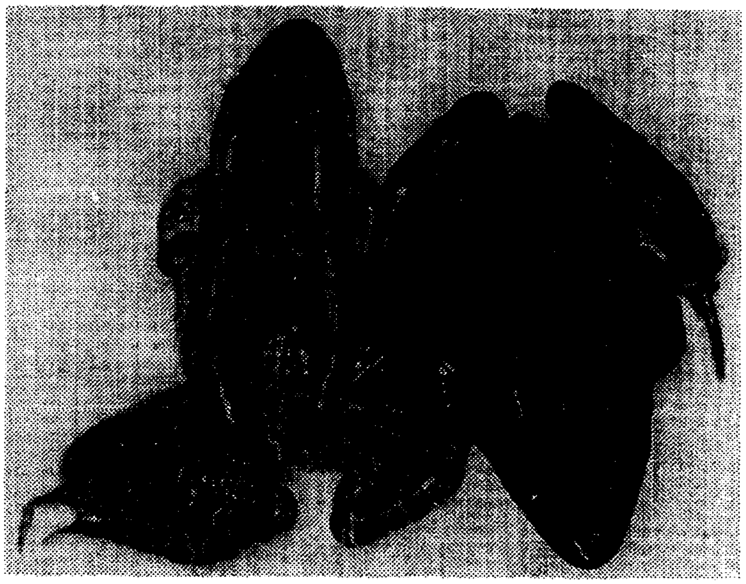
Figure 23-2 provides a schematic example of the predominant signaling pathway used by olfactory receptors which centers on generating the second messenger cAMP.

Figure 23-2



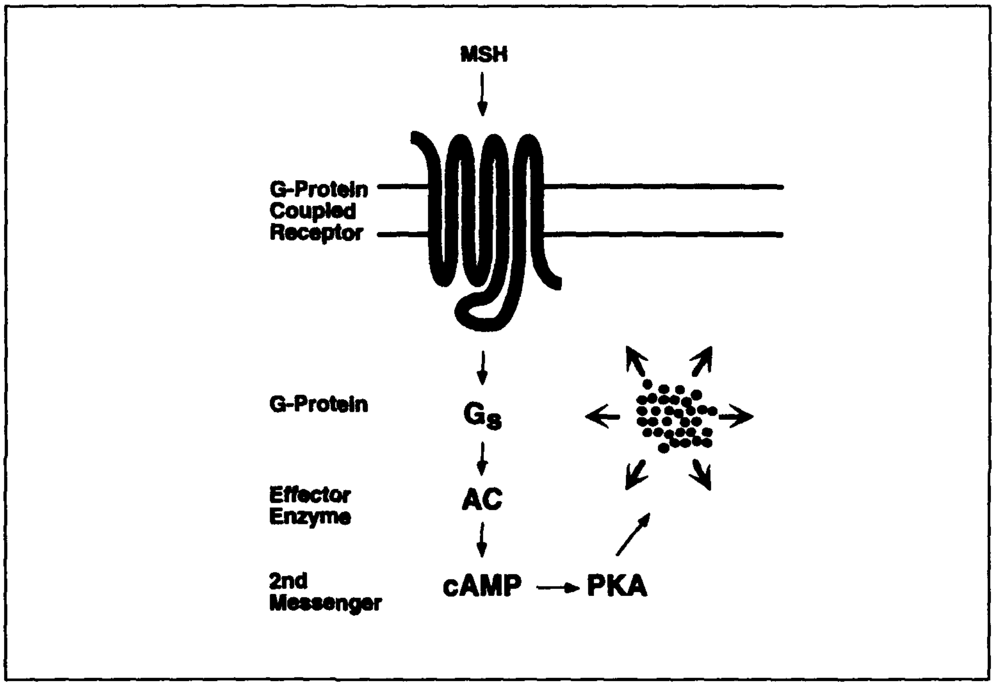
Many animals have spectacular abilities to control and rapidly alter their coloration. In vertebrates, rapid color changes are mediated by the action of GPCRs. An example of this ability is shown in Figure 23-3. The frog on the left has been treated with melatonin while the one on the right has been given melanocyte stimulating hormone (MSH).

Figure 23-3



The hormones melatonin and MSH stimulate receptors that lower or raise second messenger levels within skin cells called melanophores. Cell color depends on these levels because they influence the distribution of intracellular pigmented organelles called melanosomes. The melanin containing granules ride an internal "railway" system of microtubules. When second messenger levels fall, the melanosomes are collected in a single central location making the cell appear light in color. When levels rise, the melanosomes disperse throughout the cell causing it to darken. Figure 23-4 shows a schematic of how MSH acts. Importantly, the central aspects of the MSH receptor controlled pigment dispersion signaling pathway are the same as the one used by olfactory receptors to register odorant detection.

Figure 23-4



To construct a general purpose small molecule sensor, one direction that we are taking is outlined in Figure 23-5. The schematic describes the idea that if odorant receptors functioned like ones for MSH, melanophores would change color upon encountering appropriate odorants.

To begin construction of the biosensor, the first step was to create an immortalized melanophore cell line which retained its in vivo ability to lighten and darken in response to GRCR activation. This has been accomplished as shown in Figure 23-6. Here, the same field of cells in culture are shown before and after treatment with MSH to induce pigment dispersion.

Once the melanophore line had been established, the next step in constructing a biosensor was to develop a reliable means of expressing an exogenous receptor in the cells such that it would duplicate the function of the endogenous MSH receptor. At least three criteria had to be met. These were that (a) cDNA coding for a receptor of interest could be efficiently introduced into the pigment cells, (b) in the presence of a new receptor, melatonin could still preset the cells at the lightly colored state and (c) specific agonists produced pigment dispersion. To solve these problems we turned to cDNA coding for the human ß2 adrenergic receptor which is a well characterized receptor that is known to stimulate cAMP production. Figure 23-7 illustrates the expected result.

Figure 23-5

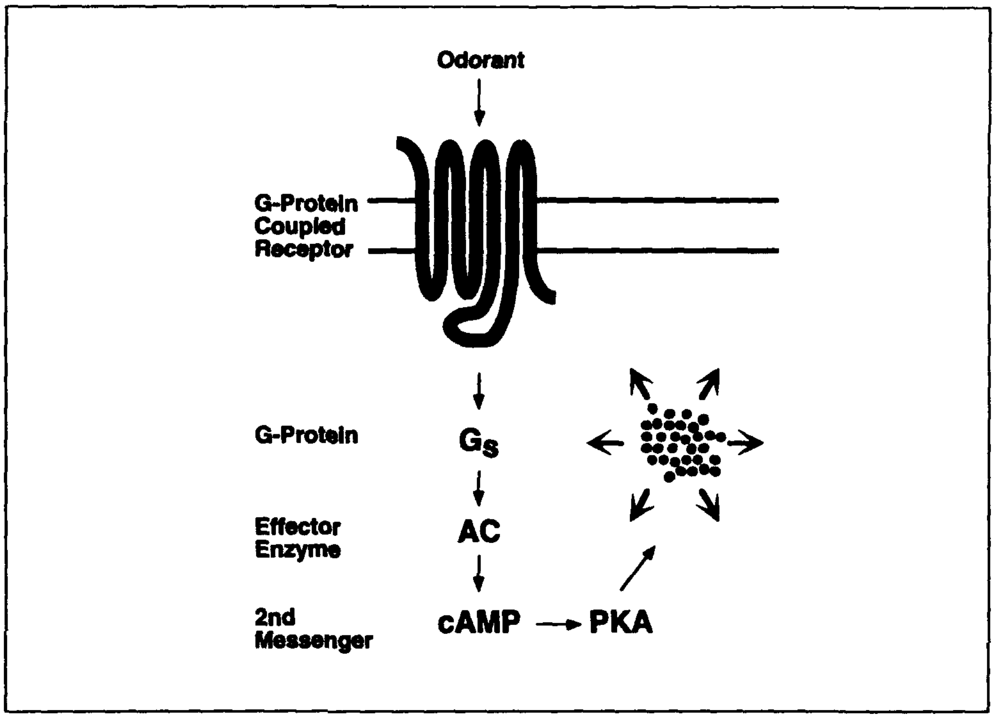


Figure 23-6

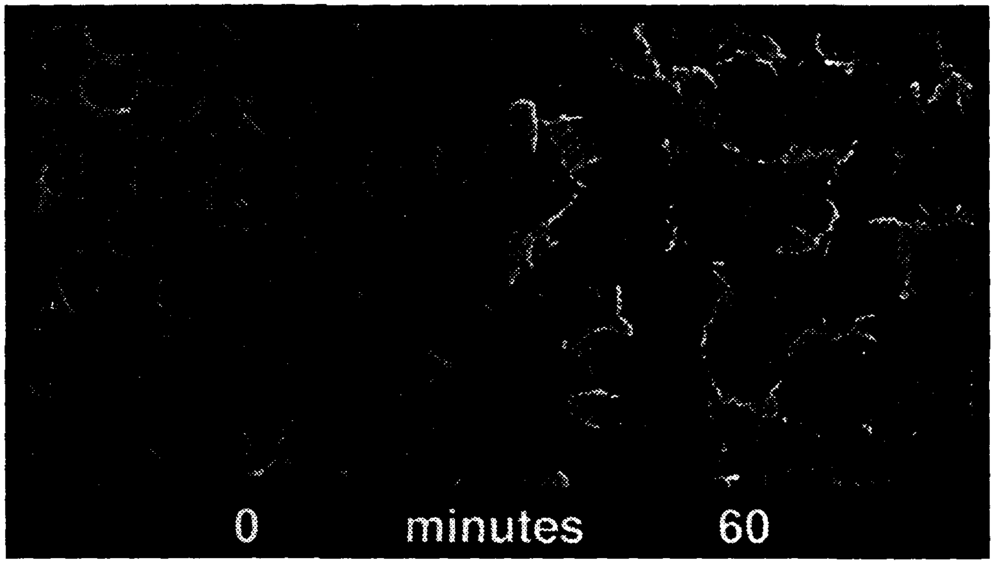
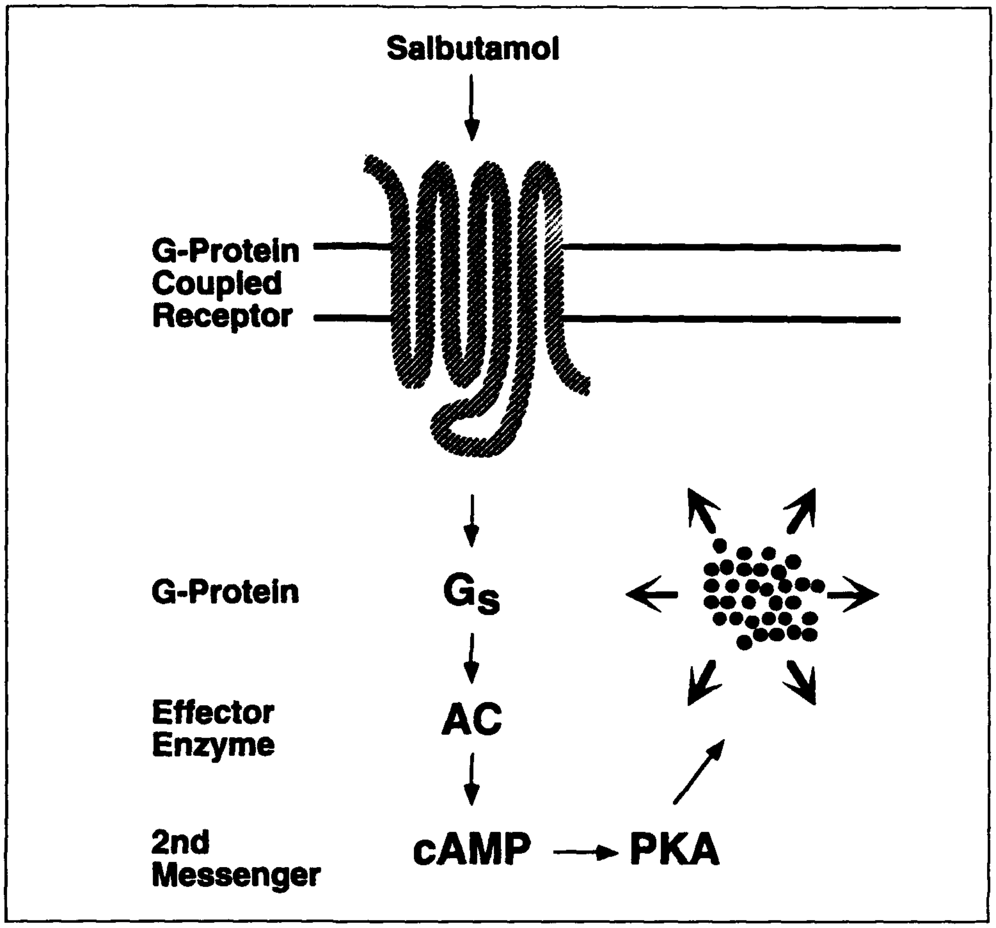
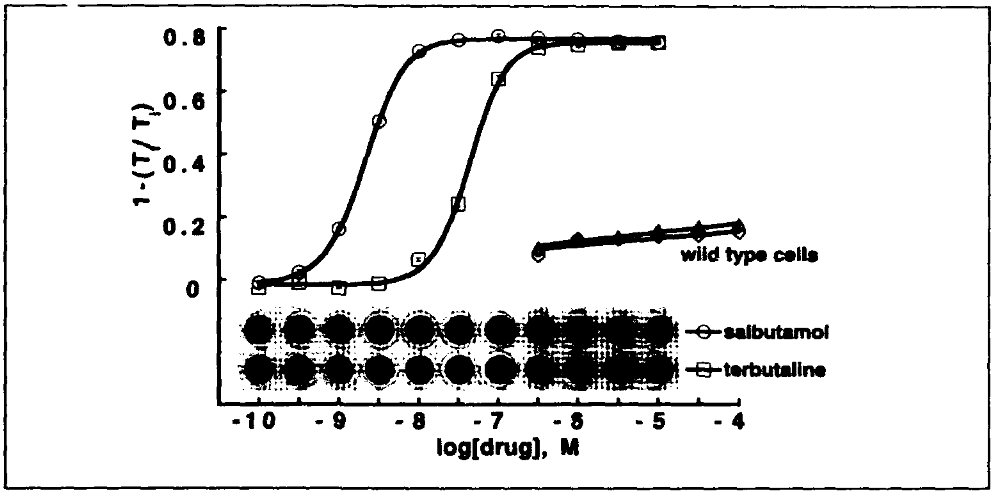


Figure 23-7



The human ß$_2$ adrenergic receptor functions appropriately in the pigment cells shown in Figure 23-8. Here the effect of ß$_2$ adrenegic agonists on melanophores which stably express the receptor is displayed. The inset shows two rows of wells from a microplate whose wells contain equal numbers of confluent recombinant pigment cells. After lightening the cells with melatonin, from left to right the wells received increasing concentrations of salbutamol or terbutaline. The graph quantitates agonist induced darkening at 60 minutes in the receptor expressing cells but not in the wild type controls. The curves were obtained from four equivalent sets of wells, one of which is shown. That the receptor function is highly reproducible is reflected by the errors bars which are almost hidden within the data points. In addition, the EC50 values for the two agonists agree with the established ones.

Figure 23-8



To demonstrate that melanophores functionally express not just the ß$_2$ adrenergic receptor but GPCRs in general, the 15 different GPCRs shown in Figure 23-9 have been expressed. To date, there have been no failures.

Figure 23-9

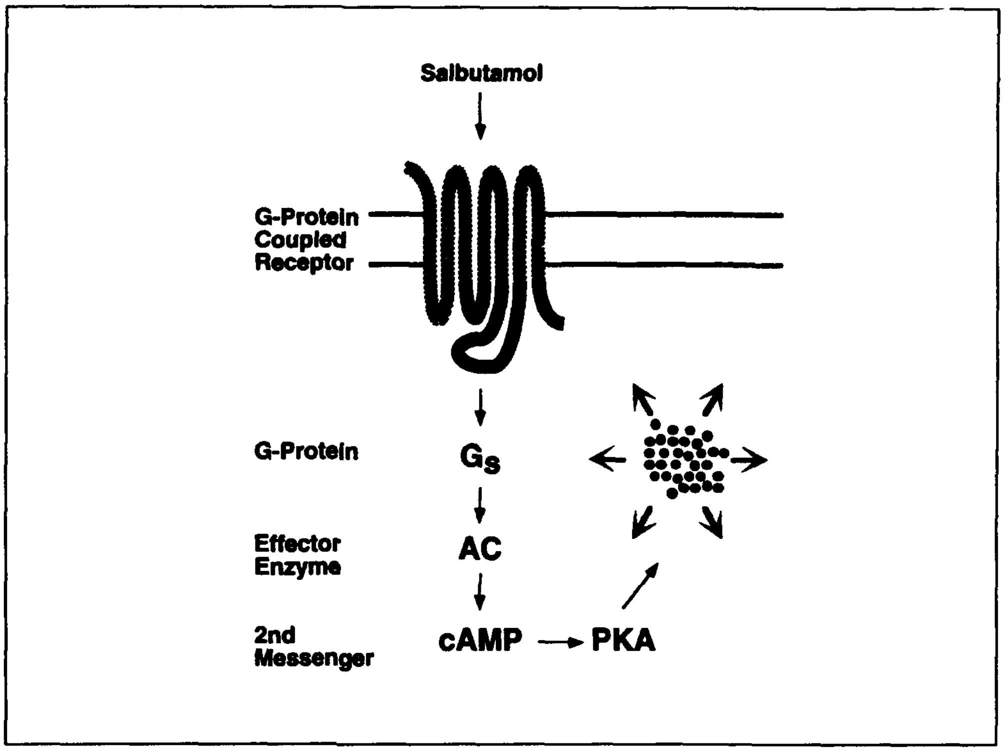
- ○ α2 Adrenergic receptor
- ● β2 Adrenergic receptor
- ● Angiotensin II receptor
- ● Bombesin/GRP receptor
- ● Dopamine 1 receptor
- ○ Dopamine 2 receptor
- ○ Dopamine 3 receptor
- ○ Dopamine 4 receptor
- ○ Muscarinic 4 (chick) receptor
- ● Muscarinic (fly) receptor
- ● Platelet activating factor receptor
- ● Substance K receptor
- ● Substance P receptor
- ● Thromboxane A$_2$ receptor
- ● Thyrotropin releasing hormone receptor

● = agonist induces cell darkening
○ = agonist induces cell lightening

Unless noted, receptors are mammalian

At the present time we are working on expressing olfactory receptors in melanophores. Because little is known about what odors each of the many hundreds or even thousands of olfactory receptors in any animal respond to, we decided to break the problem up into 2 pieces. These sub problems are (a) to show that the signal transduction parts of olfactory receptors couple efficiently to the pigment dispersion pathway in melanophores and (b) to demonstrate specific olfactory responses. Figure 23-10 describes the accomplishment of step (a). A chimera consisting of a ß$_2$ adrenergic receptor in terms of ligand recognition and an olfactory receptor in terms of G-protein coupling has been made via recombinant cDNA methods. Melanophores expressing the chimera disperse their pigment and darken on exposure to specific agonists such as salbutamol. We are now working on step (b).

Figure 23-10



In conclusion, I believe that we are well on our way to constructing a general purpose, small molecule biosensor. Because it is based on naturally occurring olfactory receptors, it has the potential to detect any chemical that can be smelled by an aquatic or terrestrial animal.

STEPHEN J. MARTIN

R & D INTERESTS

My primary interest is the commercialization of technology derived from research in analytical chemistry. My goal is to develop instrumentation and methods that improve current analyses and solve specific problems. Most of my efforts are directed to field methods for real-time, *in situ* chemical analyses . Some of the projects I am currently working on are:

- The MarChem program as a means to encourage the development of advanced chemical oceanographic instrumentation for *in-situ* measurements.
- Establishing MarChem as a virtual community on the Internet.
- A monitor to measure organic compounds in water. The device can be operated aboard a small boat to quantitatively analyze low concentrations of organic pollutants. Eventually, the device will be packaged to operate in an AUV or disposable buoy.
- A low-cost monitor to measure oceanic solar radiation using the Volunteer Observing Ships (VOS) network.
- An *in situ* technique to measure subsurface organic pollutants.

JOHN W. McDONALD

CURRENT RESEARCH

I am presently involved in the development, evaluation, and production of sensors for water quality assessment, and in the field testing of the multiparameter systems which utilize these sensors. I am particularly interested in technology which reduces the flow dependence of dissolved oxygen measurements and in utilization of ion selective electrodes for *in situ* field measurements. I also have some practical experience with temperature, conductivity, pH, and depth sensors.

I have a great deal of field experience with the two YSI multiparameter water quality instruments which have been released in the recent past. The YSI 6000 is a totally self-contained, deployable sonde which is presently oriented toward longer term monitoring applications (either remote or attached to a data collection platform), and utilizes the recently patented Rapid Pulse dissolved oxygen system which minimizes flow dependence. The Grant/YSI 3800 Water Quality Logger is a two-piece instrument which is oriented primarily toward spot sampling applications and was developed as part of a program with the National Rivers Authority in Great Britain.

My hands-on experience with these instruments has been confined almost exclusively to freshwater applications, and therefore I am particularly looking forward to obtaining input about their potential worth in marine environments at the MarChem 93 Conference. More importantly, via participation in the workshop, I hope to become better educated with regard to the new sensor technology which is being developed through industrial-university- government partnership. This information will aid YSI in determining whether we might be able to make a contribution in this area.

MARY MCFARLAND

AUTOMATIC SAMPLER FOR ORGANIC MICROPOLLUTANTS (ASOM): RECENT DEVELOPMENTS

Two years ago, at MarChem91, Dr. Rod Badger of Seastar Instruments introduced INFILTREX II, an *in situ* sampler for trace contaminants, based on solid phase extraction (SPE) technology. Since that time, Seastar has become Axys Environmental Systems, a member of the Axys Group of companies, and INFILTREX technology has been applied to the design of a large volume, multi-sample instrument for monitoring trace organic contaminants.

Development of ASOM, the Automatic Sampler for Organic Micropollutants, was initiated in 1990 by a European consortium studying contaminant transport between rivers, estuaries and coastal waters. Lack of information on transport processes prevented regulators from effectively enforcing emission controls and prompted the development of MERMAID (Marine Environmental Remote-controlled Measuring And Integrated Detection systems). One of a host of EUREKA projects, MERMAID is a joint undertaking between partners in Germany, Norway, France and Canada to develop a remote-controlled automated measuring and sampling system for substances influencing the oxygen balance in major waterways (heavy metals, organic micropollutants, chlorophyll, and degradable organic matter).

MERMAID is a monitoring station which can be installed on a buoy or fixed platform. It incorporates meteorological, chemical and biochemical sensors, linked by a platform management system (PMS). The station has been designed for maximum flexibility and modularity, and accommodates event-triggered monitoring. The first system is now being installed on a large discus buoy to be deployed in Elbe estuary, and a network of MERMAID stations extending into the North Sea will soon be established by the German Hydrographic Service (BSH).

While many chemical parameters can now be measured directly by automated analyzers, at present there is no technology which will allow in situ analysis of water for trace organic contaminants. ASOM provides an ultra-clean system for concentrating organic contaminants onto resin columns which can then be transported to the laboratory for analysis. Sampling can either be preprogrammed (for time integrated monitoring), manually triggered, or event controlled. At present, a predetermined turbidity level can automatically be used to trigger sampling. ASOM incorporates six separate resin columns and six particulate filters, with the necessary mechanical control devices to facilitate collection of six sample sets. Flow rates through the columns can be selected from a range of 10 to 40 L/hr while flow through the filters can be up to 10 times the column rates to allow for capture of large amounts of suspended particulates. Following the collection of each sample, a preservative can be passed through the column and filter to inhibit bacterial growth.

ASOM and the other sampling modules of MERMAID, are controlled by the platform management system which is remotely operated via a radio link to a shore station and a modem link to the central control site at BSH. More remote installations will be linked by satellite in the future. Two way communications allow queries to be made as to the current status of ASOM and the history of the current sampling regime. Simple diagnostics also provide some remote troubleshooting capabilities. Error messages are relayed immediately to central control and describe such problems as low flow due to filter clogging.

Future developments in field SPE sampling technology will likely be along the lines of further automation and lower detection limits. Axys has made a conscious decision to move from oceanographic applications of this technology to estuarine and limnological applications. Indeed, the most recent demand we have encountered is for drinking water monitoring. This transition has taken us from the need for a substantial pressure housing to "INFILTREX in a box", a simple pump/flow meter system with accompanying extraction column and pre-filter. It has also forced us to look at new and more effective extraction resins, and to study the complex interactions between contaminants and the ever-present humic substances found in fresh waters.

The market for sampling instrumentation capable of detecting ultra trace levels of contaminants in water is rapidly increasing. In the short term, financial considerations will likely govern the type of instruments developed and the market for this technology. In the long term, however, more stringent sampling regulations and more sophisticated analytical instrumentation will influence further developments in an ever expanding market.

ROBERT E. MORRIS & ROBERT E. PELLENBARG

AN EVALUATION OF POTENTIOMETRIC STRIPPING ANALYSIS (PSA) FOR MEASURING TRACE METALS IN SEAWATER

There has been long, and continuing, interest in developing the ability to rapidly assay seawater for trace metal content. Indeed, it is desirable to directly assay the seawater so that the analyst can minimize handling and avoid contamination of the sample, and thus further reduce analysis time. With these general goals in mind, we have preliminarily evaluated a newly available commercial analytical system based on potentiometric stripping analysis (PSA).

PSA is essentially an electrochemical analysis technique in which analytes of interest are concentrated onto a thin mercury film supported on a glassy carbon electrode. Then, the analytes of interest are stripped out of the film; monitored currents and voltages are indicative of the analytes of interest. The PSA system used in our laboratory is supplied by Radiometer America, and offers a unique combination of well engineered hardware supported by a dedicated personal computer controlled by proprietary software.

We have examined the utility of the Radiometer system for field measurements of copper and zinc in seawater, and will discuss the "ocean truth" obtained by our work. The PSA technique appears to offer a useful combination of sensitivity, speed, ease of operation, and durability which should be of interest, and use, to the oceanographic community. However, our research has identified several concerns which are commonly associated with new technology and its initial applications. We will discuss these issues, also.

Mention of manufacturer's names in this abstract, and in the formal presentation, in no way constitutes any endorsement of specific equipment or manufacturer.

Analysis Requirements

- Proven method for analysis of sub-PPM levels of metals in seawater
- Adaptable to field use, rugged enough for transport
- An "off the shelf" solution to the problem
- Requires a minimum of adaptation and verification
- Short analysis times with a minimum of sample preparation

Figure 27-1
Methodology

EQUIPMENT

- **Radiometer Tracelab potentiometric stripping analyzer**
    - ▸potentiometric stripping unit
    - ▸sample container with electrode fixture
    - ▸autoburettes (3)
    - ▸personal computer / printer for control and data analysis
    - ▸basic methods and operating software supplied with instrument

MODIFICATIONS

- instructions to utilize autoburettes for std and oxidant addition
- automatic storage of raw data and results on disk
- removal of metal contaminated components
- method modifications for lower analyte levels
    - ▸burette rinse and purge routines
    - ▸longer stripping times
    - ▸decreased amounts of standard addition volumes

Figure 27-2
PSA instrumentation

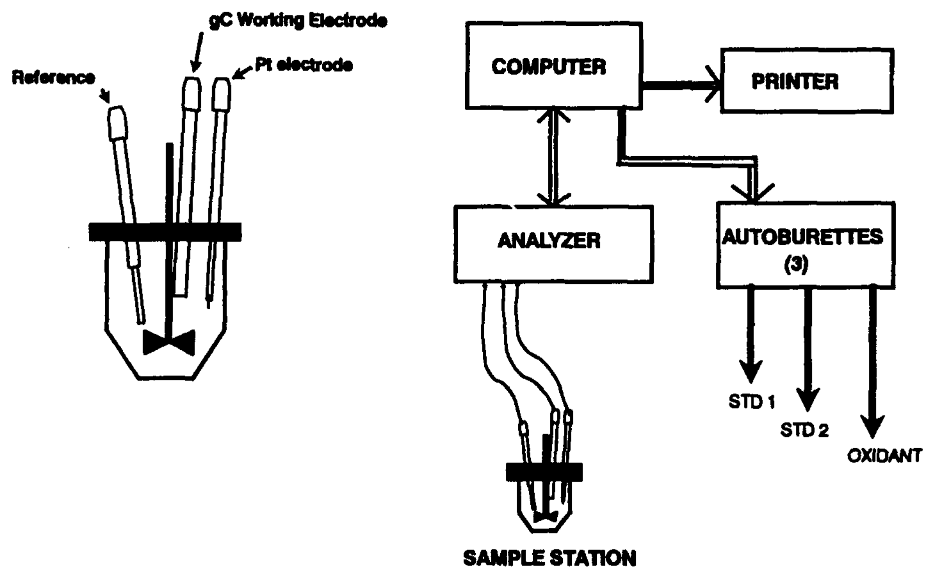


Figure 27-3

Potentiometric Stripping Analysis (PSA)

ELECTROLYSIS

- plate analyte into Hg film on working electrode

$$M^{n+} + ne^- \longrightarrow M(Hg)$$

- 100 - 1000X concentration of metal
- amount of metal amalgamated is proportional to electrolysis time

STRIPPING

- potential removed from working electrode
- metal reoxidized back into solution from Hg film as potential drops more (+)

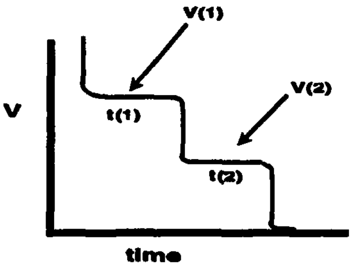
$$M(Hg) + \tfrac{n}{4}O_2 + nH^+ \longrightarrow M^{n+} + \tfrac{n}{2}H_2O$$

$$M(Hg) + \tfrac{n}{2}Hg^{2+} \longrightarrow M^{n+} + \tfrac{n}{2}Hg$$

- sequential stripping of metals with respect to redox potentials (qualitative)
- stripping time proportional to concentration in amalgam (quantitative)

Figure 27-4

PSA measurement method (continued)



Element	Optimum pH Range	Optimum Electrolysis Potential, E vs SCE, V	Redox Potential E(1/2) vs SCE, V
Cu	0 - 3	-0.7 to -0.95	-0.25
Pb	0 - 3	-0.8 to -1.2	-0.50
Cd	0 - 3	-1.0 to -1.2	-0.65
Zn	2 - 6	-1.3 to -1.4	-1.05

Jagner, D. *Analy. Chem*, 50, (1978) 1924-29.

Figure 27-5

PSA measurement method (continued)

CALCULATION OF RESULTS:

$$[M] = \frac{t_s}{t_{s+a} - t_s}$$

t_s = sample stripping time
t_{s+a} = time after standard addition

DETECTION LIMIT:*

- Dependent on stripping time
- Reported for metals of interest in sea water < 0.1 ppb (75 min / sample)
- Has been shown to agree well with AA analysis of sea water (0.1M HCl)

*(Jagner, D and Aren, K. *Analy. Chim. Acta* 107 (1979) 29-35)

Figure 27-6

Instrument operation sequence

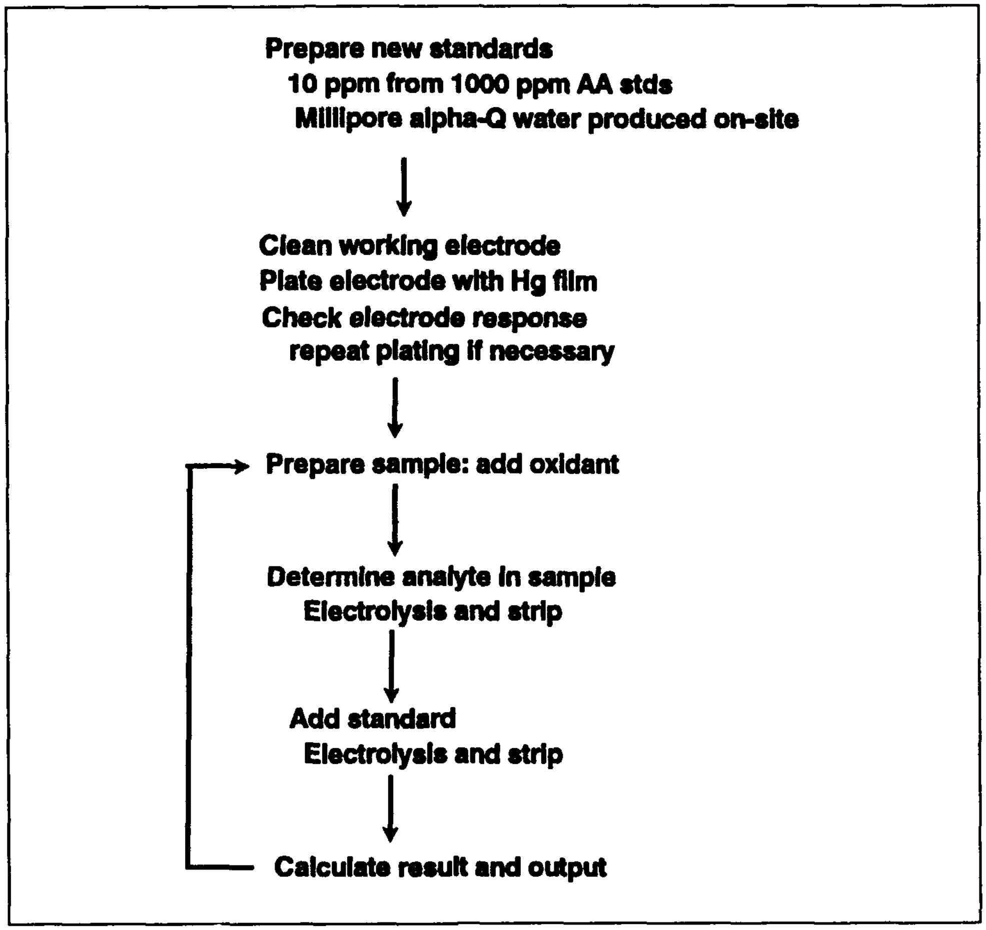


Figure 27-7

PSA method: operating parameters

Method	Electrolysis Potential, mV	Electrolysis Time, min	Standard Addition, ppb	Sample Analysis Time, min.
Cu (routine)	-900	4	250	10
Cu (high sensitivity)	-900	16	100	35
Zn	-1400	1.5	250, 50	5

Figure 27-8

PSA: evaluation

	ppb Cu	
Synthetic Seawater	8	
Synthetic Seawater + Cu	63 , 69 , 62	($\bar{x} = 64$)
Millipore Water + Cu	56 , 56 , 64	($\bar{x} = 59$)

EFFECT OF pH ON ANALYSIS OF ADDED Cu IN SYNTHETIC SEAWATER

pH	ppb Cu
6.3	66
4.5	56
2.6	56
1.9	63

pH	ppb Zn
6.3	44
1.9	54

Figure 27-9

Zinc in acidified seawater: interferences

- **Intermetallic compound formation prevented simultaneous determinations of Cu and Zn**
    - **Ga added to complex Cu**
- ***Variations in sample pH prevented accurate adjustment on routine basis***
- **Below pH 2.0 - 2.5, H^+ constitutes primary oxidant**
- **Metal contamination found in apparatus: components eliminated**
    - **neoprene electrode sleeves**
- **Trace contamination in ACS reagent grade NaOAc buffer**
    - **reagent recrystallized**

Figure 27-10

Advantages/disadvantages

<u>ADVANTAGES</u>

- **provided same-day analysis during field exercise**
- **easily transported, modular**
- **methods can be modified and tested in field**
- ***data are exportable to ASCII format***

<u>DISADVANTAGES</u>

- **analysis times can be > 30 min for [M] < 10 ppb**
- **no current limiting to prevent destruction of gC electrode**
- **software "key" required, fixed installations limited**
    - **▸inhibited establishment of backup system with key installed**
- **no access to real-time measurements evaluate validity of analysis**

Figure 27-11

Recommendations

- <u>INCREASE ANALYSIS TIMES:</u>

  Increase lower detection limit

  Raise detected analyte levels above background

- <u>CONTINUE METHOD OPTIMIZATION</u>

  Using field samples and AA results:

  - ▸ **Isolate source of high Zn background levels**
  - ▸ **determine optimum analysis time for adequate sensitivity**
  - ▸ **determine electrolysis time limits**
  - ▸ **investigate elimination of Hg oxidant to reduce background**
  - ▸ **determine optimum permissible pH range**

W. CHARLES NEELY

USE OF LANGMUIR-BLODGETT MONOLAYERS IN SELECTIVE SENSING APPLICATIONS

With S. Patharana, T.A. Roppel and V. Vodyanoy

The Langmuir-Blodgett (LB) technique can not only simply produce mono layers which are essentially two-dimensional crystals, but can also provide important information on the basic nature of their interactions with other molecules. This information can be used to develop sensor applications for specific substances.

This report considers the behavior of such monolayers in two different applications:

- The elucidation of the optimum mole ratios of stearic acid and the ionophore, valinomycin, in mixed monolayers, which are required for production of maximally ordered systems. These well-ordered systems are shown to act as sensing elements for the strongly selective detection of potassium ion in the presence of other ions including sodium ion. The application of these films to fabrication of a CHEMFET in which such a potassium ion binding LB monolayer is deposited on the gate of a MOSFET, is discussed.
- The differing interactions of two isomeric odorants, (+) and (-) carvone, in monolayers of stearic acid can be used to distinguish between these two molecules which have very similar physical properties by greatly differing odorant characteristics.

EDWARD J. POZIOMEK

FIELD SCREENING INSTRUMENTS FOR HAZARDOUS WASTE SITES—OPPORTUNITIES FOR TECHNOLOGY TRANSFER

Immunoassay technology has matured considerably, and immunoassay kits are being used more extensively in the field. GC remains the most popular field screening technology for organic compounds. Improvements in GC use, especially in conjunction with various sampling methods, continue to be made. Mass spectrometry (MS) in combination with GC has drawn the attention of commercial developers toward potential environmental applications. Many more examples are appearing on the use of transportable GC/MS units in the field. Man-portable GC/MS devices are being projected for the future. Fiber optic sensors, biosensors, and ion mobility spectrometry (IMS) also continue to draw the attention of the developer and user communities relative to prospects for the future. Integration of monitoring and measurement technologies with a core penetrometer system has progressed rapidly in the last two years to the point that various field demonstrations have been held and more are being planned. New developments in sampling and sample handling continue to be made, thus enhancing the utility of various existing field screening methods. X-ray fluorescence spectrometry remains the field screening technique of choice for inorganic materials. More attention is being paid toward improving data handling in field screening generally.

It was clear that the Environmental Protection Agency is taking steps to encourage the use of field analytical techniques including a regional customer focus, methods standardization throughout EPA, the adoption of existing procedures within and outside EPA, and the use of performance-based methods. Considerable progress has been made in the past two years by both the Department of Energy (DOE) and the Department of Defense (DOD) in demonstrating and evaluating field monitoring and measurement technologies. Resources are being applied to expedite technology transfer to the user. The DOE is funding applied research and development in a number of areas including contaminant identification, data analysis, nondestructive assay of container contents, and waste stream and airborne contaminant monitors.

Opportunities for technology transfer to marine chemistry instrumentation development include in situ, stand-off, and smart chemical sensors; portable instruments; immunoassay and chemical kits; and sampling and sample handling techniques.

A summary of Dr. Poziomek's overhead transparencies follows:

Presentation Outline

- Field screening definition and needs
- State-of-the-technology of field screening instruments and devices
- Examples of emerging technologies
- Technology integration
- Opportunities for technology transfer to marine chemistry instrumentation development

Overall Objectives

- Minimize the number of field samples sent back to the laboratory for analysis
- Save time and resources

Levels of Analytical Support

- Level 1—Field screening or analyses using portable instruments
- Level II—Field analyses using more sophisticated field portable analytical instruments
- Level III—Laboratory analysis using methods other than CLP-RAS (Contract Laboratory Program-Routine Analytical Services)
- Level IV—CLP-RAS
- Level V—Non-standard methods

Field Screening Equipment

Categories

- Disposable
- Portable
- Fieldable
- Mobile

Critical Technology Needs

- *In-situ*, stand-off, and smart chemical sensors
- *In-situ* and field portable analytical methods for the analysis of contaminants in all types of environmental media
- Nonintrusive characterization instruments
- Data-handling and expert systems
- Sampling devices for soil-gas, soil and ground water

Field Screening Needs

A major challenge

Air, water, terrestrial, and sub-surface
- Organic
- Inorganic
- Biomarker
- Radionuclide
- Mixed

Chemical Classes of 200 Priority Hazardous Substances

VOCs	26.5 %
Organophosphates/carbamates	2.0 %
Phthalates	3.0 %
Benzidines/aromatic amines	4.0 %
Miscellaneous	6.0 %
Reactive intermediates:	6.0 %
Nitrosoamines/ethers/alcohols	7.5 %
Halogenated pesticides/related compounds	8.5 %
PAHs	8.5 %
Phenols/phenoxy acids	10.5 %
Inorganic elements/radionuclides	17.5 %

International Symposium on Field Screening Methods—February 1993

Emerging technologies
- Chemical sensors
- Fiber optic sensors
- Advances in mass spectrometry
- Transportable GC/MS
- Biosensors
- Ion mobility spectrometry
- Fluorescence spectrometry
- Data handling and systems integration

Technology Utilization
- Advances in gas chromatography
- Case studies: gas chromatograph
- Developments in sampling and sample handling
- Field experiences: French Limited superfund site
- Case studies: integrated technologies
- Cases studies: immunoassays
- Case studies: field instruments
- Laboratory support

Field Screening Instruments and Devices

Most mature

- Gas chromatographs
- X-ray fluorescence spectrometers
- Photoionization devices
- Flame ionization devices
- Ccatalytic surface oxidation devices
- Detector tubes
- Kits based on immunoassays
- Kits based on chemical reactions

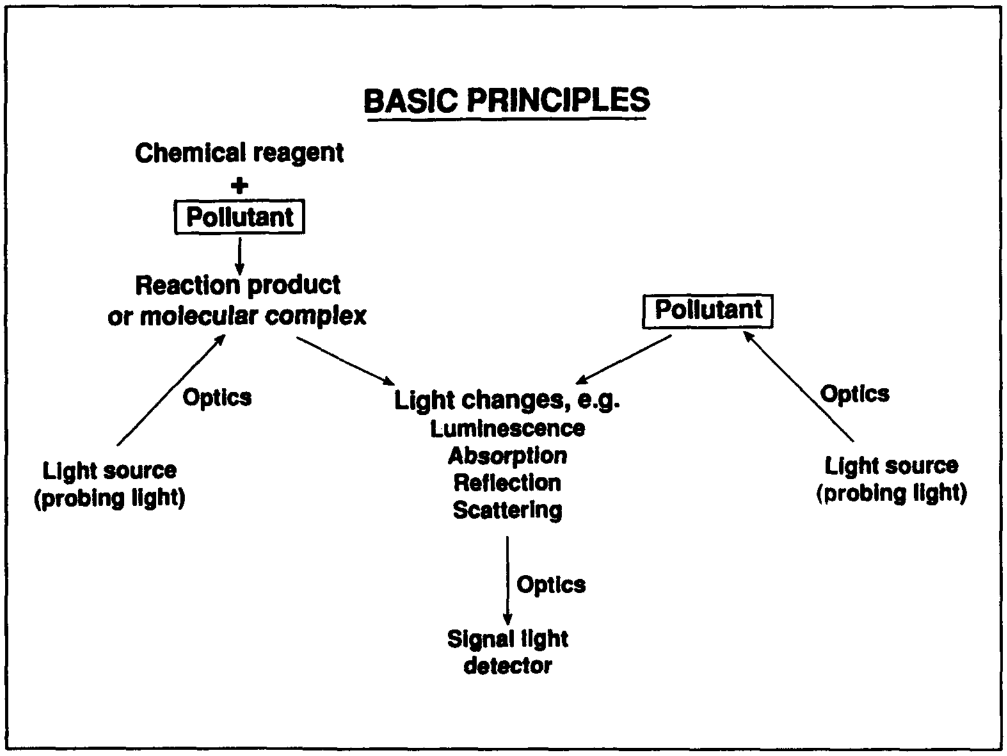
Being improved

- Mass spectrometers
- Gas chromatographs/mass spectrometers
- Infrared systems
- Wet chemistry items

Emerging

- Mass sensors
- Fiber optic sensors
- Electrochemical sensors
- Biosensors
- Ion mobility spectrometers
- Various spectroscopic instruments
  e.g., Ultraviolet
  Luminescence
  Surface enhanced Raman

Figure 29-1
Fiber optic chemical sensors



Fiber Optic Sensors

Challenges

- Selective indicating levels
- Suitable electro-optical devices for long-term unattended operation
- Implementation of field studies and sensor placement protocols

Electrochemical Analysis for Metals in Water

Improvements

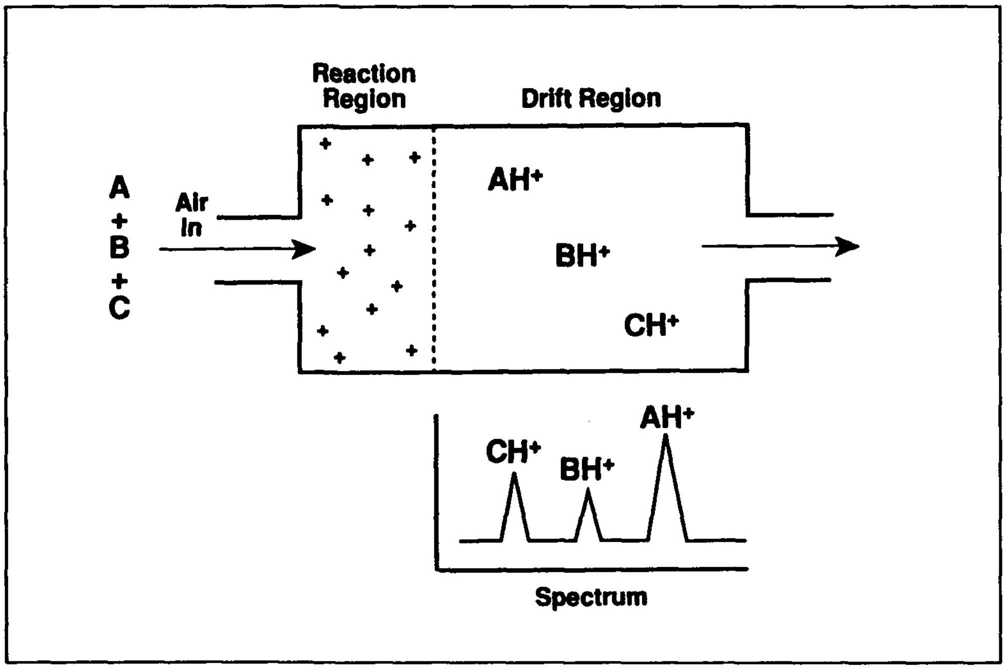
- Tailored electrode surfaces
- Ultramicroelectrodes
- Disposable electrode strips
- Alternative to X-ray fluorescence

Biosensors

Challenges

- Biomaterials for compounds of environmental concern
- Improved stability and shelf life of biomaterials
- Improved immobilization techniques
- Biomaterials that can be used in the gas phase
- Integration of sampling technologies

Figure 29-2
Ion mobility spectrometer schematic



Ion Mobility Spectrometry

Challenges

- Ionization chemistry configuration
- Complications of ambient air gas phase reactions
- Delineation of limitations—non-radioactive ionization sources
- Smaller analyzers
- Sampling

Figure 29-3
In situ IMS monitor design

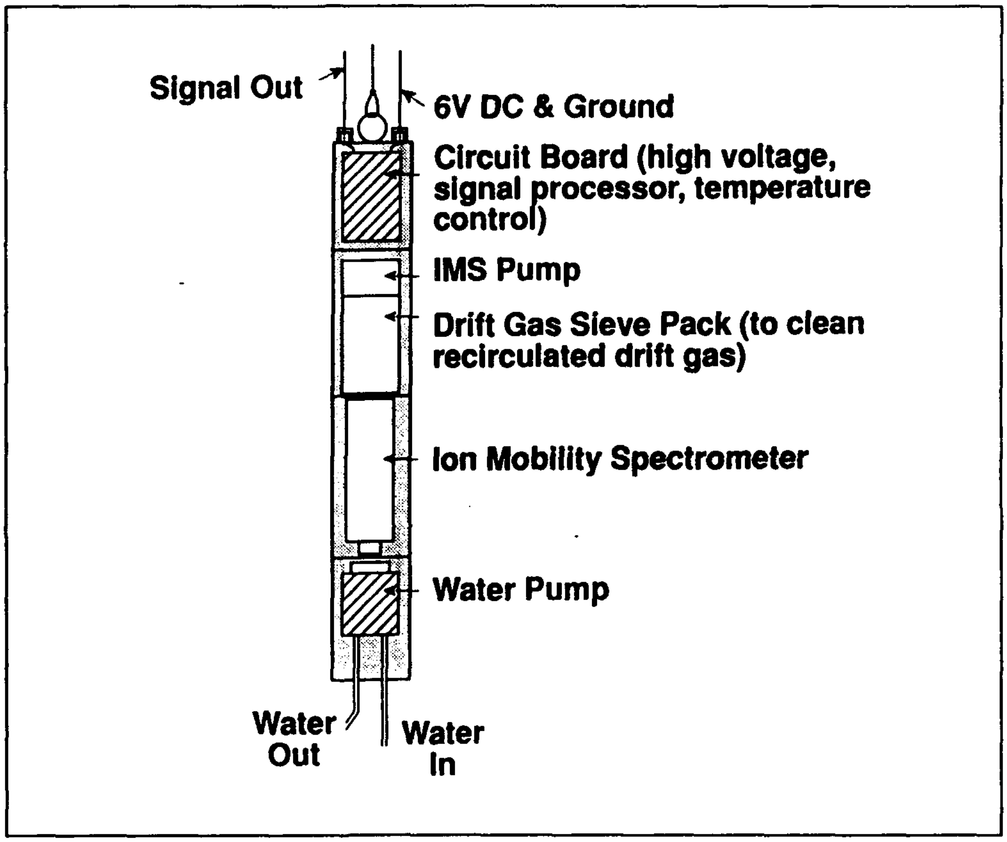
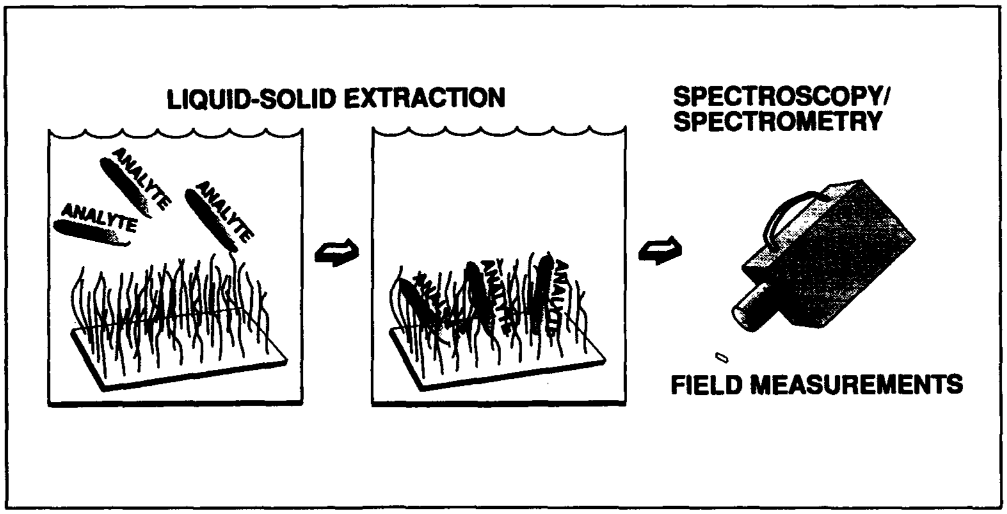


Figure 29-4
Technology integration



Chemical Sensors for Field Screening with a Cone Penetrometer

An integrated system

- Explosives
- Solvents
- Metals
- Groundwater modeling
- Radionuclides
- Geophysical parameter
- Specific classes
  - Chemical and biological
- Site monitoring

Recent Reports on Use of Field Screening Instruments/Kits

- Immunoassay field kits
  2,4-D, gasoline, diesel, m-xylene, PCBs, PCP, PAHs
- Portable x-ray fluorescence analyzers
  Metals
- Chemical kits
  Dinoset, PCBs, Cl-organic, Cr.
- Microbiological kits
  Coliforms, E. Coli
- Handheld microprocessor based photometer
  Analytes/reaction products, 400-700 nm
- Portable gas chromatographs
  VOCs

EPA 9th Annual Waste Testing & Quality Assurance Symposium,
Arlington, VA, July 1993

Opportunities for Technology Transfer to Marine Chemistry Instrumentation Development

- *In-situ*, stand-off, and smart chemical monitors
- Portable instruments
- Immunoassay and chemical kits
- Sampling and sample handling techniques

Although the information in this presentation has been funded in part by the U.S. Environmental Protection Agency under Cooperative Agreement No. 818353 with the University of Nevada–Las Vegas, it has not been subjected to Agency review and, therefore, does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Russell J. Seguin

CURRENT RESEARCH

Traditionally, ion selective electrodes (ISEs) have been plagued with host of problems, including interferences, drift, temperature dependencies and aging. Manufacturers of such probes usually recommend their use in the lab at constant temperature, after the solutions have been adjusted to constant ionic strength. Still, the simplicity of a pH-type probe is appealing for field monitoring: ISEs can also be used in turbid waters without filtration, provide rapid response without heating the solution, and usually require fewer (if any), more stable reagents than colorimetric methods.

Theoretical compensations, changes in the preparation and calibration of the electrode, and performing 2-point *in situ* calibrations can significantly improve the performance of an ISE in the field. Selective membranes can also be used to both concentrate the analyte and reduce the amount of interferences encountered. I am focusing my current research on adapting ammonia gas electrodes (pH based), ammonium ion selective electrodes and nitrite/nitrate electrodes for use in the field.

I have found that the detection limits of a nitrite or ammonium ISE are limited to 50-100 micromolar (μM) in sea water, due to the interference of other ions. These probes, however, can be used with reasonable accuracy in fresh water when corrections are make for variations in pH, temperature and ionic strength. A new, recently developed nitrite selective membrane has greater selectivity than the traditional nitrate membrane; nitrate is easily converted to nitrite with a cadmium reduction column in a flow injection instrument.

In sea water, a flow-through version of the traditional ammonia gas electrode can detect down to 1 μM ammonia; problems include a non-linear calibration curve below 10 μM, and the need to prevent the precipitation of calcium and magnesium oxides with a complexing agent when the pH is raised to liberate the ammonia gas. The use of a cationic exchange membrane to concentrate the ammonium ions from low-pH sea water into the linear portion of the calibration curve was investigated, but ammonium ion transport was too slow below 100 μM. The ionic interferences of the ammonium ISE can be eliminated by concentrating ammonia gas as ammonium ions across a microporous membrane via dialysis into a low-pH solution containing no interfering ions. We are currently optimizing the sensitivity and precision of this approach.

ION SELECTIVE ELECTRODES FOR INORGANIC NITROGEN SPECIES:

We are developing a field instrument to measure inorganic nitrogen species in natural waters that will be suitable both for site measurements and long-term deployment. The ideal instrument will be submersible, self calibrating and capable of long-term deployment. Ion Selective Electrodes (ISEs) offer the potential convenience of a pH electrode, and on the surface, appear ideally suited for field measurements. We have investigated the behavior of several types of ISEs in the lab with fresh and sea water samples, and are currently working on methods to enhance their performance using perm-selective membranes.

Sensors

The simple design, freedom from turbidity and stirring effects, and use of stable reagents (or in some cases no reagents) make ISEs an appealing choice as probes for monitoring natural waters. Unfortunately, ISEs require a knowledgeable user and conditions of controlled ionic strength and temperature for best performance. In addition, ion selective membrane eventually "age" and slowly loose their response, or can become fouled. Reference electrodes can also drift and experience junction errors, as experienced users of pH electrodes well know.

There are two basic types of ISEs used for measuring ammonia, nitrite and nitrate ions. Ion selective membranes can be made for all three species, and can be used to construct ISEs analogous to a pH electrode (with the membrane taking the place of the hydrogen ion selective glass). These ISEs exhibit interferences from other ions with similar size and charge density, although a newly developed nitrite ionophore has impressive selectivity.

The second type of ISE is actually a gas-sensing electrode, and is commercially available for nitrite and ammonia. A pH electrode is mounted in a concentrated solution of the desired ion and pressed against the surface of a microporous, gas permeable membrane whose opposite face is in contact with the sample solution. When the pH of the sample is adjusted with concentrated acid (for nitrite) or base (for ammonia), the ions in the sample are converted into gaseous nitrogen oxides or ammonia gas, transported across the membrane, are partially converted back into the original ions, and thus change the pH of the internal electrode. The change in pH (mV) is logarithmically related to the acidity of the ion in the sample solution. These types of sensors are relatively free from ionic interferences, but are affected by other volatile acids or bases.

Conclusions

Nitrate ISEs suffer from a severe chloride interference, with a threshold for nitrate detection above 200 µM; the performance of the ammonium ISE is only slightly better, due to sodium ion interference. The new nitrite ISE is much more selective, and can detect 2–3 µM nitrite, even in sea water (although the calibration curve is no longer linear at these low concentrations, and may shift with changes in temperature). We found that the ammonia gas-sensing electrode can detect 1–2 µM NH_3 in sea water (again, with non-linear calibration curves below 10 µM); similar results can be expected for nitrite with a commercial NO_x gas sensor. We plan to use the nitrite ISE coupled with a copperized cadmium reduction column to measure nitrate. It is also likely that using selective membranes will increase the sensitivity and selectivity of these ISEs.

ALAN M. SHILLER

CURRENT RESEARCH

Our laboratory studies the geochemistry of trace elements in natural waters. Current research includes studies of trace elements in the Mississippi River and its outflow region in the northern Gulf of Mexico; the behavior of reactive trace elements (aluminum, gallium, iron, manganese) in the Atlantic Ocean; and studies of the Kuroshio Current near Japan. Additionally, we are involved in the development of new flow injection techniques for the analysis of trace elements. Most of this work focuses on development of colorimetric techniques in which the analyte catalyzes a color-producing reaction.

In speaking of trace elements, one is generally (though not exclusively) talking about transition elements and metalloids. Typically, these elements are found dissolved in natural waters at parts-per-billion levels and lower. Determination of the physical-chemical speciation of trace elements is also important; however, most techniques only provide information about total dissolved concentrations.

Trace elements are important in part because some can be toxic at very low concentrations while others may serve as trace nutrients. However, most of the interest in these elements stems from their wide variety of geochemical behaviors which allows them to be used as tracers for various environmental processes. For example, some trace elements are indicators of dust input to the ocean, others indicate oxygen-depleted environments, and others have distributions profoundly affected by biological processes.

From a sampling and analysis standpoint, there are five concerns in trace element work. 1) Contamination (e.g., from sampling gear and reagents) is a constant problem. 2) Interferences (primarily the sea salt matrix but also organics and other trace elements) can present a formidable obstacle in technique development. 3) The most common analytical techniques involve extraction of the trace element followed by graphite furnace atomic absorption determination. These techniques are time consuming and require well-trained personnel. 4) Many of the most sensitive analytical methods (graphite furnace AA, ICP-MS) require specialized and expensive analytical instrumentation. 5) Some promising analytical techniques from the literature require chemicals which are either extremely hazardous or not commonly available.

RECENT WORK IN OUR LABORATORY ON FIA TECHNIQUES FOR VANADIUM AND COPPER

Why Vanadium?

The biogeochemistry of vanadium has received attention for a variety of reasons, including the enrichment of this element in bituminous materials, its association with certain types of uranium deposits, its redox chemistry, its enrichment in some tunicates, and its role in nitrogen fixation.

In rivers, vanadium concentrations range from <0.5 nM to 50 nM with a mean of about 15 nM. In seawater, concentrations are around 35 nM with a slight depletion in surface ocean concentrations. There is some controversy about the extent of inter-ocean changes in vanadium concentrations. In interstitial waters, concentrations above 100 nM are possible. Limited evidence argues for the most oxidized form of vanadium (vanadate, V(V)) being the predominant form in oxidizing natural waters.

Vanadium Analysis

Most low level vanadium analyses are performed using a preconcentration technique followed by graphite furnace atomic absorption. ICP-MS has also been used. There is a well-known catalytic-photometric technique (Fishman and Skougstad method) which has been used and several other catalytic-photometric techniques which are either cumbersome or interference-prone.

Recently, Sugiyama and Hori (Analyt. Chim. Acta 261 (1992) 189) described a continuous flow analysis method for vanadium based on the catalysis of the oxidation of Bindschedler's green leuco base (BGL). They report a detection limit of 21 pM. We are investigating and adapting this technique for our purposes.

Chemical Concerns

The basis of this method is the catalytic effect of trace vanadium on the oxidation of BGL by bromate. The reaction mixture is adjusted to pH 3.5-3.9. The end product is detected at 720 nm.

Our first problem was that we have been unable to find a commercial source of BGL. However, the oxidized dye (Bindschedler's green—BG) was obtained from Pfaltz & Bauer. We prepare a solution of BG and reduce it with sodium diothionate using a 1:2 molar ratio (BG:NaD). Excess dithionate will interfere with the oxidation reaction which is central to this technique and too little dithionate results in a high baseline (since BG is the detected end product).

We were unable to obtain anything close to the previously reported sensitivity. However, we found that both Tiron and sulfosalicylic acid act as activators for the reaction. We have been working mainly with Tiron because we felt that it might help limit iron interferences.

The Flow System

Figure 1 shows a schematic of our flow system. The 400 cm heating coil consists of Teflon tubing wrapped around a cartridge heater. A transformer provides the heater with 12.6 VAC which results in a surface temperature around 50°C.

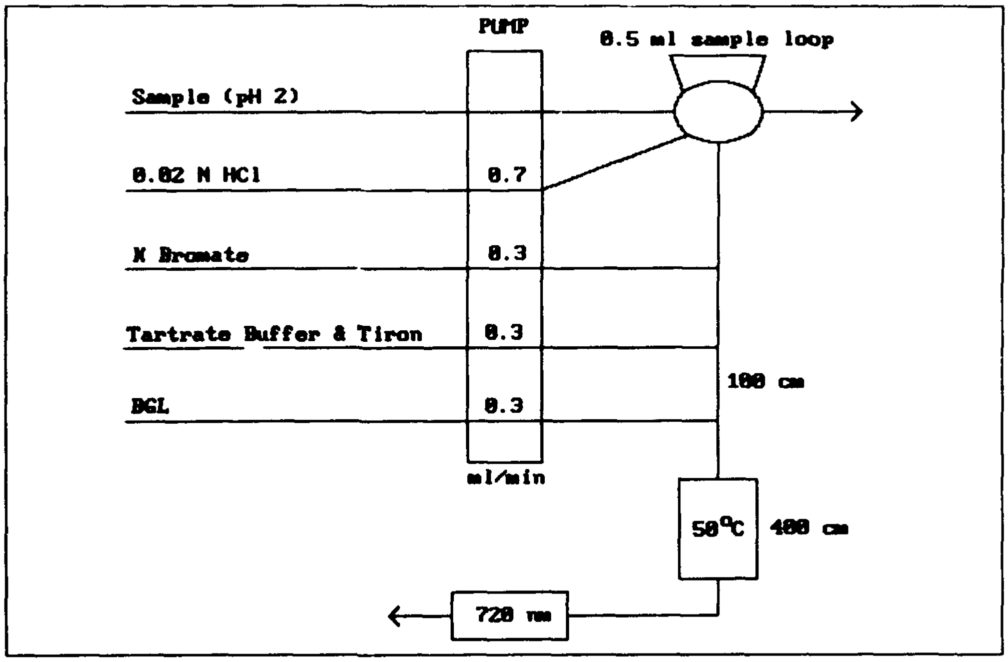


Figure 31-1
Vanadium system

Most of our work has been done using a commercial spectrophotometer with a 10 mm, 80 µl flow cell as the detector. We have also tested the system with a Betteridge-type LED-phototransistor detector. Our detector places a red LED and a phototransistor on opposite sides of a commercial 10 mm flow cell with 19 µl illuminated volume. The detector circuit consists of two op amps: the first converts the phototransistor current to a voltage and the second inverts and scales the output voltage.

Results

Our system (using the commercial spectrophotometer) provides an absorbance of ~0.16 for the injection of 500 µl of 10 nM vanadium. Baseline noise is such that the technique has a detection limit less than 0.5 nM. (Note, this is without any sort of preconcentration.) Use of Tiron as an activator seems to eliminate any iron interference (at least up to 5 µM Fe). Our tests on acidified river samples yield results within 10% of pre-concentration/AAS results.

Injecting seawater samples into the 0.02 M HCl carrier stream seems to result in a blank equivalent to about 5 nM--we are not yet sure if this is a simple salt effect or a more serious major ion interference. However, the response to vanadium additions is the same in acidified seawater as in the 0.02 M HCl. Note that Sugiyama and Hori's method has a potentially large (>50%) salt effect.

What's next?

We need to continue looking into interferences and salt effects. We have not yet added automated valves and data collection to the system.

Why Copper?

Low levels of free dissolved copper have been shown to have deleterious effects on rates of primary production. Thus, many biological oceanographers would be interested in an easy copper technique. Since it is uncomplexed copper which is bio-active, there is also interest in methods which can distinguish free and total dissolved copper.

In rivers, dissolved copper is typically about 20 nM. In the open ocean, dissolved copper ranges from ~0.5 nM in surface waters to ~3 nM in the deep Atlantic to ~8 nM in the deep Pacific. In surface ocean water (as well as rivers) most copper is probably complexed with natural organics. There is also some evidence of small amounts of reduced Cu(I) in surface waters and it would not be surprising to find Cu(I) in reducing waters.

Copper Analysis

Most analyses of dissolved copper in natural waters involve pre-concentration followed by graphite furnace atomic absorption spectrophotometry. Catalytic-colorimetric methods are available, though these are generally not sensitive enough to be used without pre-concentration. Recent work in Johnson's lab (Coale et al., *Analyt. Chim. Acta* 266 (1992) 345) has described a sensitive chemiluminescent FIA technique also involving a pre-concentration step.

The goal of our work has been to see if we can develop an FIA technique for dissolved copper, sensitive at the 0.5 nM level which does not require pre-concentration. This would simplify the flow system and make the technique more generally available. To this end we have been investigating the flavin mononucleotide (FMN) chemiluminescent method of Yamada et al. (*Bull. Chem. Soc. Jpn* 58 (1985) 1137). They reported a detection limit of about 1 nM.

Chemical Concerns

The oxidation of FMN by hydrogen peroxide produces light. Addition of trace copper enhances this reaction. Because Cu and FMN are oppositely charged, the addition of ionic surfactants inhibits the reaction while non-ionic surfactants seem to have little or no effect. The reaction is optimized at pH 5.8.

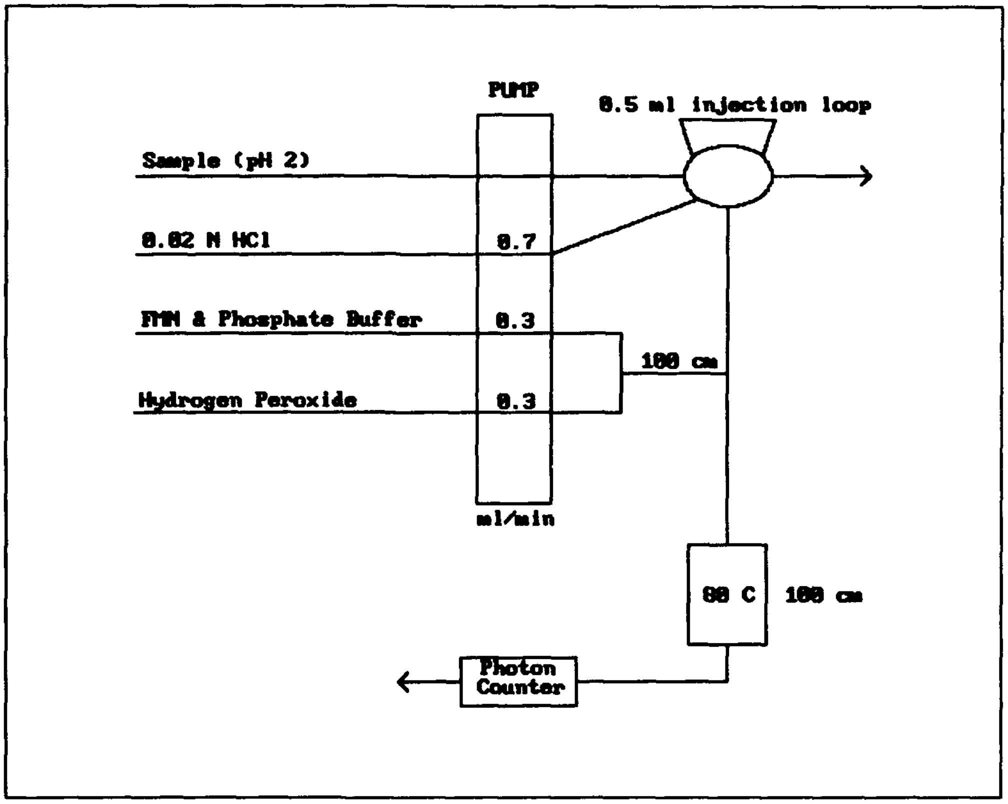
The major chemical problem with this system is finding an appropriate buffer. Yamada et al. found that a phosphate buffer was most appropriate because other buffers suitable for the necessary pH range seemed to inhibit the signal. However, the buffer capacity of phosphate is at a minimum in this range. Having a high buffer capacity is important for us since we want to be able to inject acidified samples into the flow system. To date we have not resolved this problem.

The Flow System

Figure 2 shows a schematic of our flow system. The 100 cm heating coil consists of Teflon tubing wrapped around a cartridge heater. A transformer provides the heater with 24 VAC which results in a surface temperature around 80°C.

The heart of our photon counting system is a Hamamatsu HC124 compact PMT complete with high voltage supply and signal processing. The HC124 costs only ~$500 and provides a dark count rate of ~100 counts per second (cps) at room temperature. We use a lead-acid battery to power the system. The 70 nsec TTL output pulses from the HC124 are fed into a home-built logic-selected divider circuit which scales the pulses to about 1 μsec. This output is then fed to an Onset Tattletale IVa which we will eventually use to automate system valves.

Figure 31-2
Copper system



Results

At present we're using a 500 μl injection and get a peak response of ~2200 cps/nM. The baseline is about 40,000 cps; experiments with a copper chelator indicate that the baseline is due to uncatalyzed reaction rather than copper contamination. Baseline noise (using degassed reagents) is about 330 cps, yielding a detection limit of 0.5 nM.

Although the system response to injections of spiked seawater is about the same as to injections of dilute acid standards, seawater seems to give a double peak. As yet we do not understand the origin of this.

What's next?

We need to do more experiments with different buffers. Also, the origin of the double peak when injecting seawater needs to be explained.

RICHARD B. THOMPSON

WORKSHOP COMMENTS

Fellowship Program

Several attendees proposed that the development of marine chemistry methods and instruments might be facilitated by scholarly interchange between analytical chemists and ocean scientists. Similarly, some attendees emphasized that the closest possible cooperation should exist between industrial developers and public sector (university or government) originators of ocean instrumentation. Both of these needs might be met by an interchange program for doctoral and more senior people that would provide salary, benefits and travel for periods of three months to one year. This relatively small program would encourage analytical chemists and others to go to sea in cooperation with ocean scientists, or ocean scientists to visit academic or government facilities such as the Center for Fluorescence Spectroscopy here at Maryland to learn new techniques. In the same way, industrial scientists could be supported while visiting academic or government labs to facilitate transfer and development of measurement technologies. The fellowship would be focused on cross-disciplinary awards, not simply to support ocean scientists. Such fellowships, probably few in number, will still be very effective in promoting cross-fertilization of analytical chemistry and ocean science, and the technology transfer and production of ocean instruments.

Small-Scale Instrument Production

Instruments used in ocean science seem to fall into three categories. The first are those instruments which are so widely used and required in such numbers that they can be profitably produced by private firms. Examples include CTD's, sampling bottles and current meters. A second category are those instruments which are so specialized in application or complex that only a few can (or should) be built. Examples might include instruments built for specialized environments such as in the vicinity of hydrothermal vents. However, there is a third category of instrument of which perhaps dozens are needed, but far too few to be profitably produced by a private firm. Instruments such as the fast pulse fluorometer (Wirick) or Sea-Soars are examples which might be required in up to a few dozen units, but for which the sunk cost of design, testing, production and support might be insufficiently covered at a reasonable price unless many more units were produced. Thus for these instruments, the market is too small to support a company making a business manufacturing such instruments. Moreover, some instruments are difficult to "commercialize"; i.e., to produce in a reliable, "idiot-proof", user-friendly form with well-tested software, which can deter product development even if the market exists and the technology is in hand. Yet for use by researchers, instruments and software need be considerably less refined. At present, the only expedient is to custom-build individual units or have modest production runs in oceanographic institute machine and electronic shops. Yet few institutes can maintain machinist and electronics shops even comparable to a small company's, because the volume of work is usually not great enough to justify the investment; as a result, producing fifty copies of a relatively sophisticated instrument might be beyond their capacity.

One approach to this shortfall might be to designate particular facilities at oceanographic institutes or Navy labs as oceanographic instrumentation meso-production facilities, and supplement their capabilities in personnel, CAD-CAM capability, CNC machine tools, electronic engineering, software engineering, and testing facilities. Perhaps one could be established on each coast. The mission of these facilities would be to construct custom oceanographic instrumentation at cost for users, and provide the wherewithal for low-rate production of instruments for the oceanographic community. These facilities would provide a focus of expertise and resources not only in all facets of marine instrumentation construction, but also for low rate production. Note that instruments developed at such a facility could be more readily produced in small quantities, and it would be a goal of the facility to transfer the technology of instruments which are likely to be produced commercially in quantity. Thus a nutrient sensor developed at an academic institution could be produced in small numbers for installation on UNOLS oceanographic ships, and subsequently engineered for production and installation on crafts of opportunity. Moreover, instruments developed with the aid of the instrument facility could be readily copied by the facility for other users, at present, to get a copy of an instrument, the developer must build it for other users or provide plans, neither of which may be convenient or affordable.

FLUORESCENCE LIFETIME-BASED FIBER OPTIC SENSORS

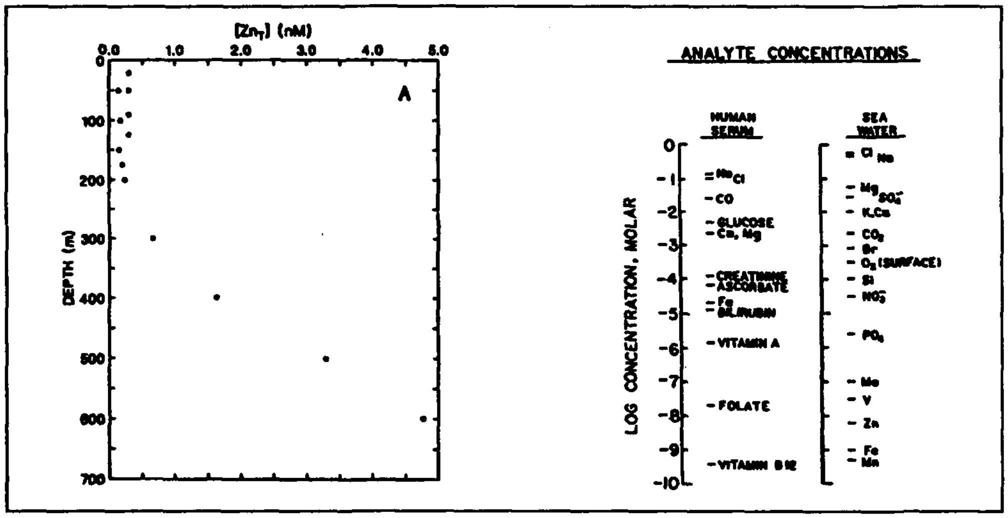
Background

Oceanic Zinc: levels, distribution

Marine Chemistry:

- Sampling (costly, slow)
- Contamination
- Complex medium

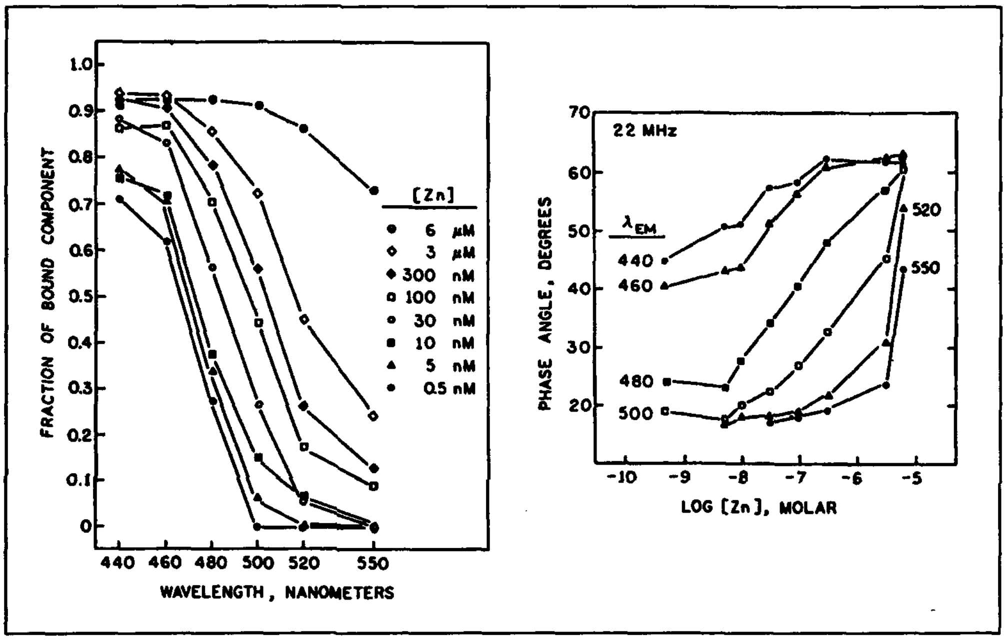
Figure 32-1



Objectives

Sensitivity: detection limit < 10^{-10} M
Selectivity: > -60 dB re [Mg]
Dynamic range: > 3 log unit
Response, reset time: seconds
Compatible with shipboard use
Usable at kilometer depths
Flexible approach for other applications
Prefer *in situ*, nonconsuming sensor

Figure 32-2



Approach

Carbonic anhydrase/dansylamide indicator system
Ratiometric transduction
Incorporation into fiber optic sensor

Figure 32-3
Zinc biosensor scheme

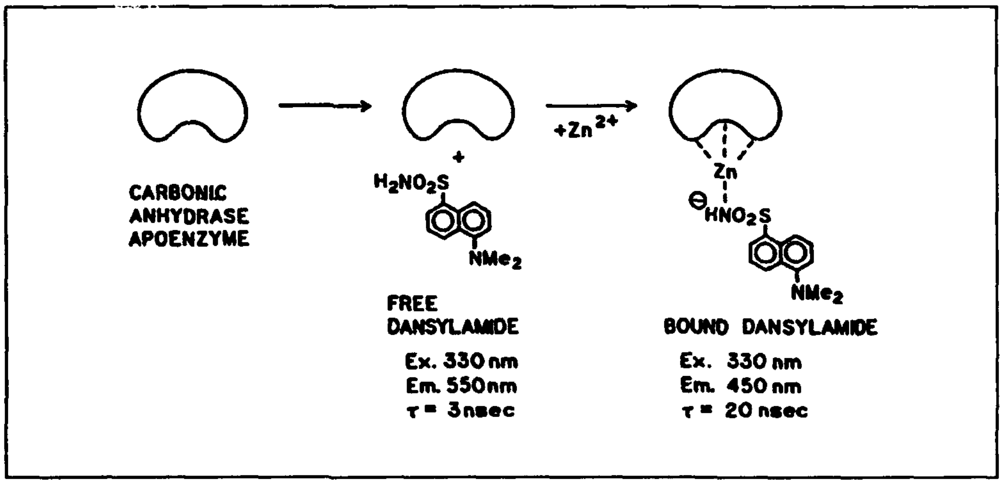
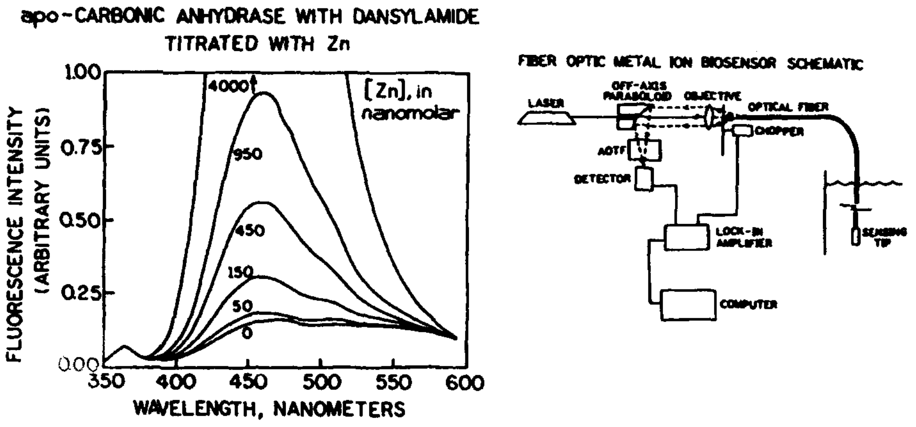


Figure 32-4



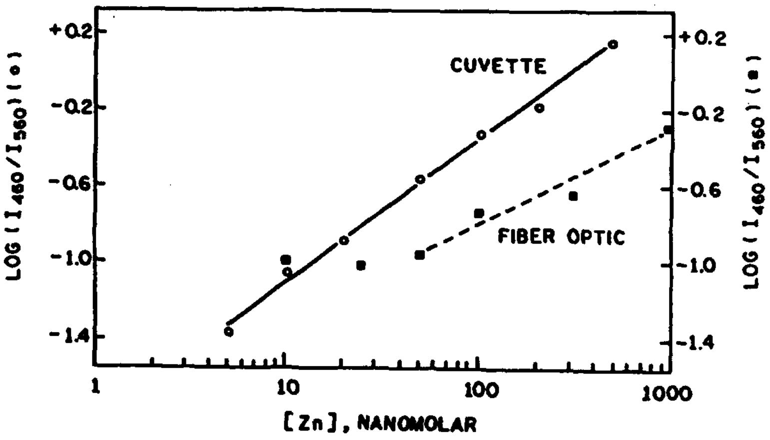
Results

Ratiometric results

Lifetime-based sensing: advantages

Lifetime-based sensing of Zinc

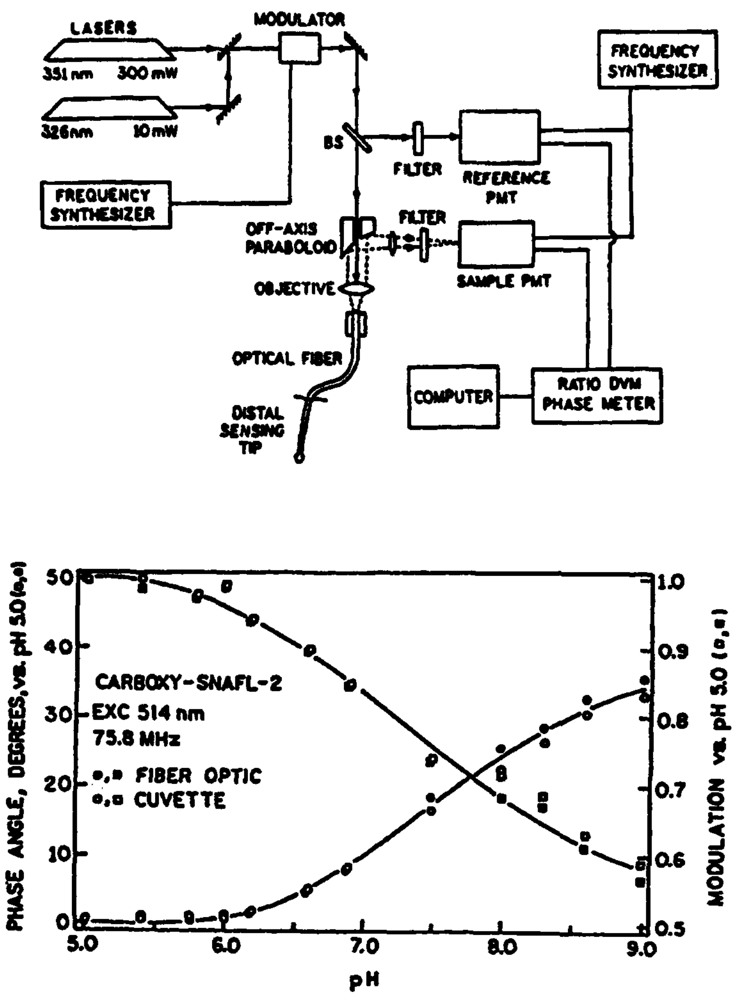
Figure 32-5



Advantages

Insensitive to source variation, inner filter effects
Insensitive to indicator level, photobleaching
Potentially large dynamic range: 55dB
Can suppress background photoluminescence
Robust, facile calibration

Figure 32-6



DAVID R. WALT

SENSORS

Sensors are self-contained analytical devices that reside in a sample and continuously measure the concentration of chemical species or physical parameters. These devices are beginning to find their way into a variety of venues in which continuous monitoring is essential including clinical, environmental, fermentation, and chemical process control. Although conventional sensors have been around for decades (e.g., pH electrodes) there have been tremendous strides made in recent years to enhance their applicability to a variety of measurement needs. A great deal of credit must go to major developments in electronic and optical components as well as computer-aided signal processing.

Sensors are based on four distinct transduction mechanisms: electrical, optical, mass, and thermal. The critical aspect of sensor fabrication is to couple selective recognition chemistry to one of these transducers. Such coupling imparts appropriate selectivity, sensitivity, and specificity to the analyte of interest. A wide range of recognition chemistries can be employed such as selective polymers, ion-binding materials, enzymes, antibodies, dyes and electron transfer reagents.

Several recent trends have revolutionized the way in which sensors can be fabricated and used. Sensor dimensions have been reduced to the submicron range for intracellular measurements. Sensor arrays have been prepared to provide spatial resolution of samples such as tissue preparations. Pattern recognition techniques such as neural networks have been employed to deconvolute complex signals coming back from a variety of semi-selective sensors. These recent innovations bode well for the ultimate goal of allowing sensors to achieve the type of sensitivity and complex recognition capabilities of the olfactory system in higher organisms.

The marine environment poses a particularly challenging venue for sensors. Instrumentation must be designed to resist corrosion and use minimal power while sensors must be extremely sensitive, resist fouling and be essentially self-calibrating. These design criteria have limited the implementation of sensors to a small number of marine analytes.

TERRY E. WHITLEDGE

CURRENT RESEARCH

My research interests continue to focus on the collection of nutrient data that can be used to assess the dynamic processes occurring on the continental shelves and estuarine areas of our coastline. The inability to maintain a ship program of measurements that can attain a time series of measurements for weeks or months has driven me to develop unattended *in situ* chemical analyzers which can collect data at relatively short time intervals of a few minutes for at least a month's duration. My approach has been to utilize the existing chemical methods with flow injection analysis techniques that are constructed with small micropumps and valves. The chemical analyzers are powered with a sealed lead-acid battery and controlled with a Tattle Tale programmable microprocessor which also acts as the data storage device. The analysis for nitrate using the cadmium reduction technique has been the measurement most thoroughly investigated, however dissolved silicon and colloidal carbon measurements have also been tested.

The prototype instruments have been deployed as a part of the NOAA Nutrient Enhanced Coastal Ocean Productivity (NECOP) program which is investigating the effects of nutrient efflux from the Mississippi and Atchafalaya Rivers on the Gulf of Mexico shelf. The *in situ* nitrate analyzers were placed on nearsurface Lagrangian drifters in the river plume and deployed at time series sites for periods of 1 to 2 days. Deployments of the in situ nitrate analyzer were also made in Copano Bay, Texas during a brown tide bloom of a small Chrysophyte. The mooring was deployed for intervals of about a week over a 2 month period.

The instrument development and testing to date have been successful to the degree that relatively precise pumping of the reagents can be maintained. Nearly all types of microgear and peristalic pumps have been tested for precise flow rates over relatively long periods of time. Although power consumption was an initial concern, the precision of pumping rate has been the most important aspect of obtaining reliable results. The best configuration at this point in time is a combination of microgear and peristalic pumps. It was found that the degradation of chemical reagents in the warm Gulf of Mexico waters also becomes an important factor for deployment periods longer than a few days.

CREIGHTON D. WIRICK

DOE OCEAN MARGIN PROGRAM

Description

The Department of Energy has traditionally supported long-term interdisciplinary studies of coastal ocean systems as part of its concern for the dispersal and fate of energy-related materials in the environment. The approach has been to conduct regional studies along the U.S. continental shelves, utilizing instrument moorings and ship tracks to measure water mass movements, currents, and upwelling dynamics; spatial and temporal concentrations of chemical species and particles; biological productivity, ecological dynamics, and consumption within lower-level food chains; and biogeochemical fluxes of organic particles, nutrients, and mineral phases in the water-column and sediments. During FY 1992, the DOE restructured its regional coastal-ocean programs into a new Ocean Margins Program (OMP). The primary objectives of the OMP are to: (1) quantify the ecological and biogeochemical processes and mechanisms that affect the cycling, flux, and storage of carbon and other biogenic elements at the land/ocean interface; (2) define ocean-margin sources and sinks in global biogeochemical cycles; and (3) determine whether continental shelves are quantitatively significant in removing carbon dioxide from the atmosphere and isolating it via burial in sediments or export to the interior ocean.

To meet these objectives, research is being supported to: (1) understand the physical, biogeochemical, plant, animal, and microbial mechanisms, processes, and interactions that affect the input, assimilation, and transformation of carbon in coastal waters and sediments; and (2) develop and apply new instrumentation and molecular biological techniques to obtain high frequency in situ measurements of the environmental and biological factors affecting carbon fluxes in the ocean. Future plans involve melding this research into a field program to assess the exchange of carbon and other biogenic elements between estuarine systems, the shelf, and the interior ocean near Cape Hatteras, NC, where burial and cross-shelf exchange is expected to be maximum.

Rationale

Coastal ocean margins play an important role in the exchange of materials between the land and the sea and in the biogeochemical cycling of carbon. The input of nutrients to coastal areas from both land-based sources (via rivers) and interior-ocean sources (via coastal upwelling and frontal exchange) cause as much as 50% of the primary production of the global ocean to occur along the ocean margins. The extent to which this biologically assimilated carbon is exported to the deep ocean or buried in coastal sediments in still uncertain, and needs to be answered in order to develop accurate budgets for the global flux of carbon and the buildup of greenhouse gases in the atmosphere. In addition, this research is necessary to: (1) predict the dispersal and biogeochemical fate of carbon, nutrients, and other biogenic elements in coastal water; (2) quantify primary productivity and ecological dynamics in ocean-margin systems; and (3) examine the impacts of nutrient loading from anthropogenic sources.

DOE Instrumentation

Development opportunities

- Small Business Innovation Research (SBIR)
- Instrumentation programs
- Science programs

DOE SBIR—March 93

Instrumentation for ocean measurements:

- RITS partial pressures at the ocean surface (CO_2, DMS, NO_X)
- Autonomous water vapor flux at surface
- Near surface & near bottom phenomena (air-sea exchanges, boundary layers)
- Methods & reagents for nutrients (not a call for an instrument)

OMP Program

Program managers:

George Saunders and Curtis Olsen
Environmental Science Division
Office of Health and Environmental Research
Office of Energy Research
Department of Energy

OMP Goal

To determine whether continental shelves:

- Remove significant atmospheric CO_2
- Isolate CO_2 from the atmosphere
    - Burying it in sediments
    - Exporting it to the interior

OMP Focus

Phase I

- New process research
- New biotechnological methods
- New instruments

Phase II

- Cape Hatteras field program (1993-1996)

OMP Analytical Instrumentation

- Somma-coulometer to measure 0_2 and CO_2 (BNL)
- High-temp catalytic oxidation DOC method (MBL)

OMP Profiling Instrumentation

- ROV aggregate measurement video system (MBARI, Texas A&M)
- Large-volume cross-flow filtration system (WHOI, Texas A&M)

OMP Moored Instrumentation

- Moored multisensor fiber optic fluorometer (SSC)
- Moored submersible incubation device (WHOI)
- Moored fiber-optic chemical sensor for pCO_2 (WHOI)
- Moored fast repetition rate fluorometer (BNL)

Figure 35-1
BNL moored fluorometer

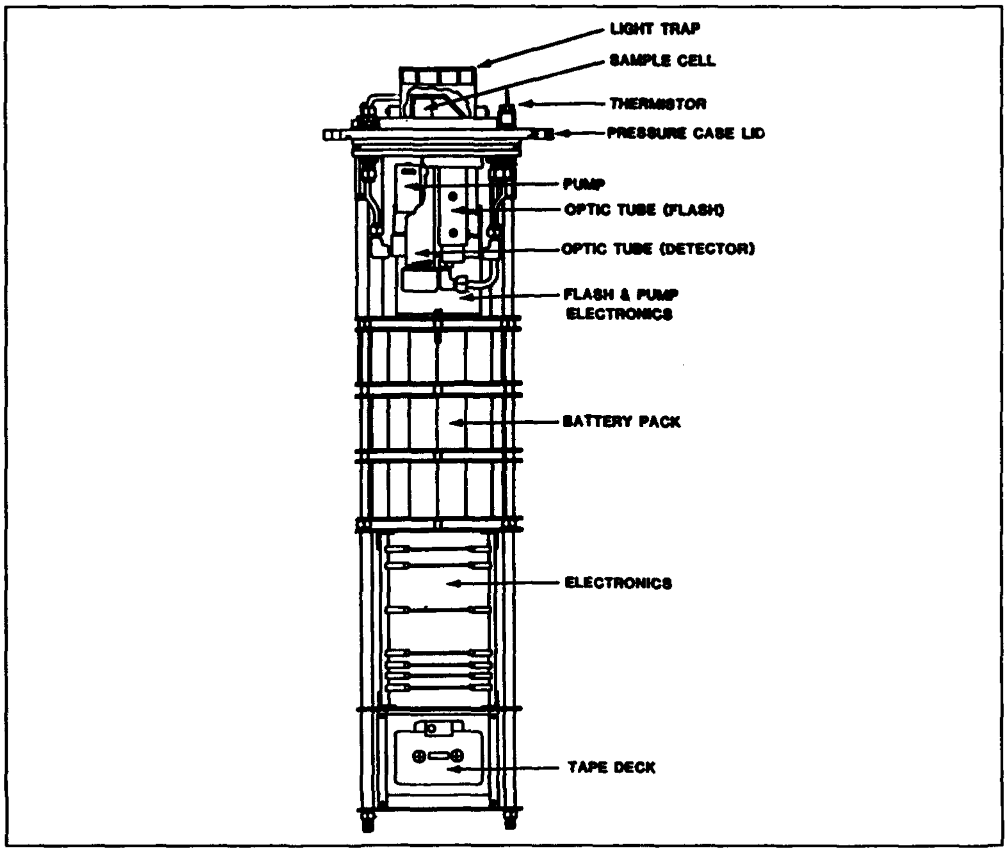


Figure 35-2

DOE fast repetition rate fluorometer

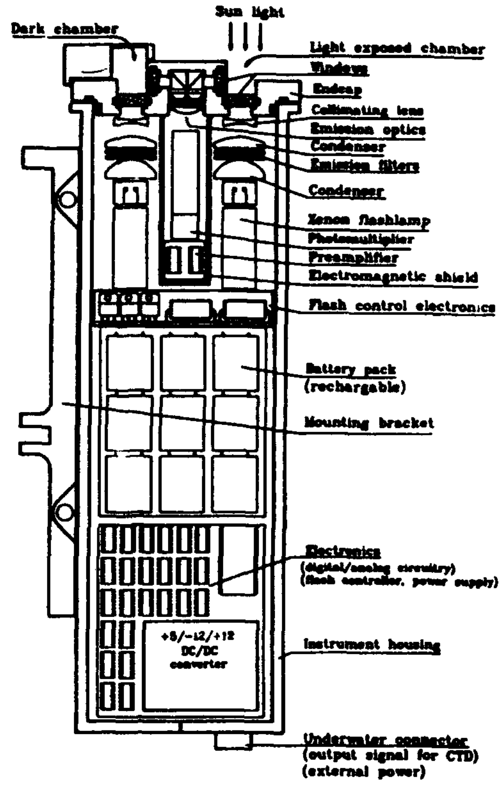
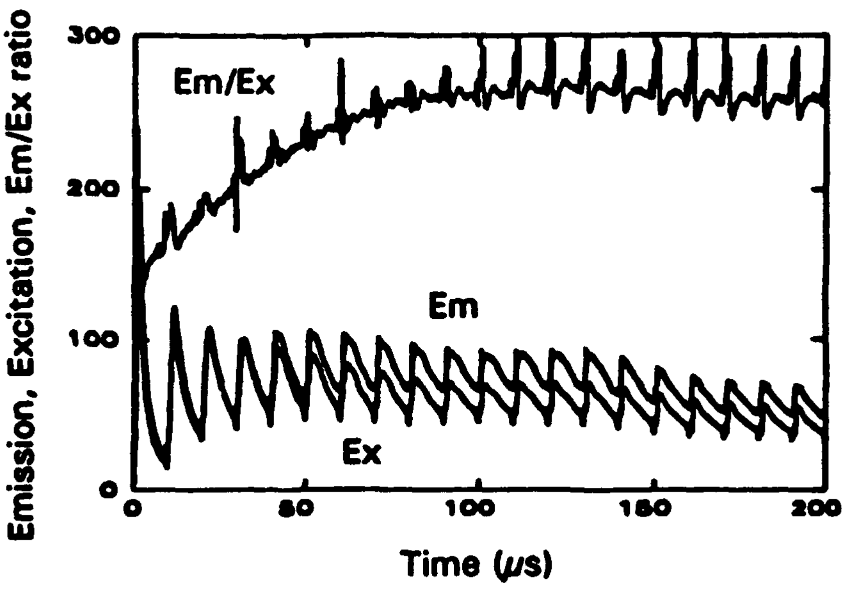


Figure 30-3

Moored FRR



Summary

DOE supports instrumentation

- SBIR program
- Science programs

DOE Ocean Margin Program projects (8)

DOE instrumentation efforts succeed

- Programmatic needs
- Adequate level of support
- Long-term support (5 years)
- Instrumentation used in programs

CATHERINE E. WOODY

NATIONAL DATA BUOY CENTER: NEW PROGRAMS

The National Data Buoy Center (NDBC) wants to establish a cooperative working group consisting of those Federal and state governments, private industry including fisheries and offshore oil production, and academia interested in developing a long-term, fixed-station oceanographic monitoring network using NOAA's moored buoys and Coastal Marine Automated Network (C-MAN) sites. The oceanographic data collected will supplement ship data; provide continuous long-term oceanographic data; and provide subsurface ocean data, surface calibration data, and algorithm development for satellite imagery.

NDBC is expanding its capability to install oceanographic sensors on their existing platforms to collect long-term oceanographic data in support of those agencies, private and public, concerned with environmental conditions and long-term changes in estuaries, coastal zones and deep ocean environments. We are interested in the development of reliable, low maintenance sensors that can withstand long deployments without sacrificing data integrity. NOAA has achieved this for collection of marine atmospheric data, ocean temperature, and wave spectra; the buoy systems are capable of collecting these data for periods of up to two years and are serviced about once a year. The data acquisition and processing electronics suitable for *in-situ* use are already in place. The data are monitored in real time, and problems that arise are known within 24 to 48 hours and frequently repaired within six weeks or less. NDBC has the capability to adapt the system to include oceanographic sensors.

NDBC maintains several types of platforms suitable for oceanographic data collection. The first is the moored buoys. These range in size from 12 to 3 meters. The largest are the 12- and 10-meter discus buoys. These are used to operate primarily in deep water where high waves are possible. Because they are expensive to build, NDBC uses a 6-meter "Nomad" in deep water. The hull is boat shaped and is very stable in rough water. The 3-meter buoy is discus shaped and was designed to operate in nearshore/shelf regions. However, they have been successfully deployed in deeper water (2500 m). They are small, relatively low cost, and are perfect for coastal and estuarine monitoring.

A second group of platforms are the C-MAN sites. These are fixed stations along our coasts and are a combination of light houses located on beaches and rocks, piers, and offshore light towers. Being located in the coastal zone, these stations provide invaluable data in environmentally critical areas. They are relatively easy to access. Oceanographic sensors can be mounted on the light towers, or they can be deployed on a buoy with a line-of-site data transmission to the land-based stations.

NDBC also maintains drifting buoys in the Southern Hemisphere for the TOGA experiment. These buoys continuously transmit data for 18 to 24 months until their power supply is depleted. The buoys are expendable. They would be excellent vehicles to gather basic oceanographic data from remote areas of our world's oceans.

Figure 36-1
No-GOFS scenario

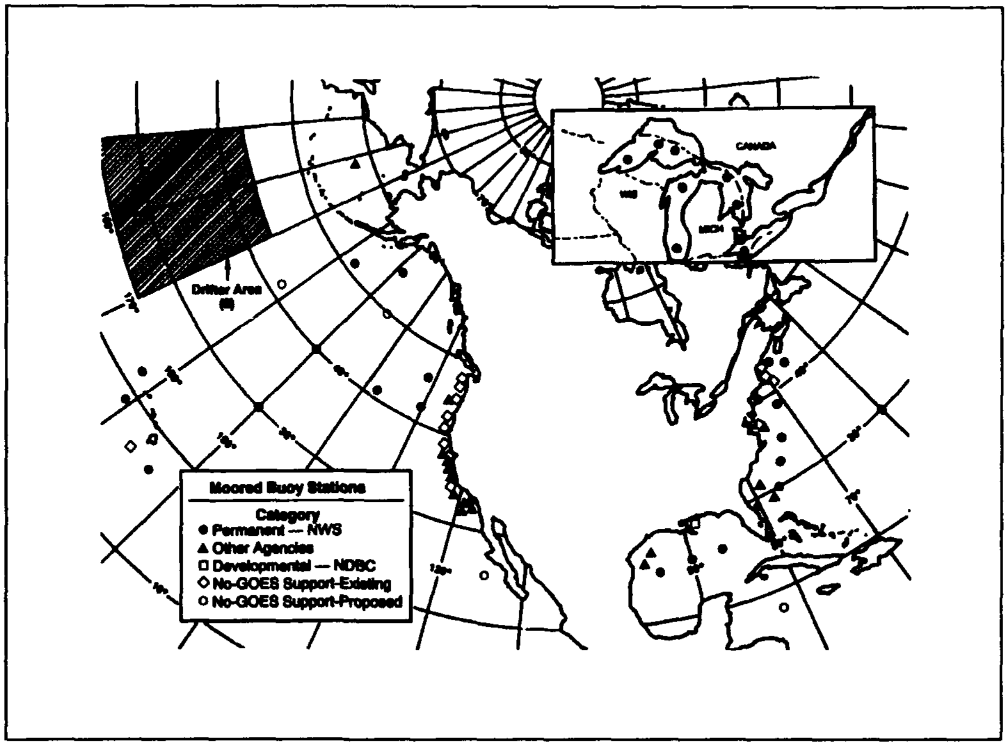


Figure 36-2
NDBC buoy locations

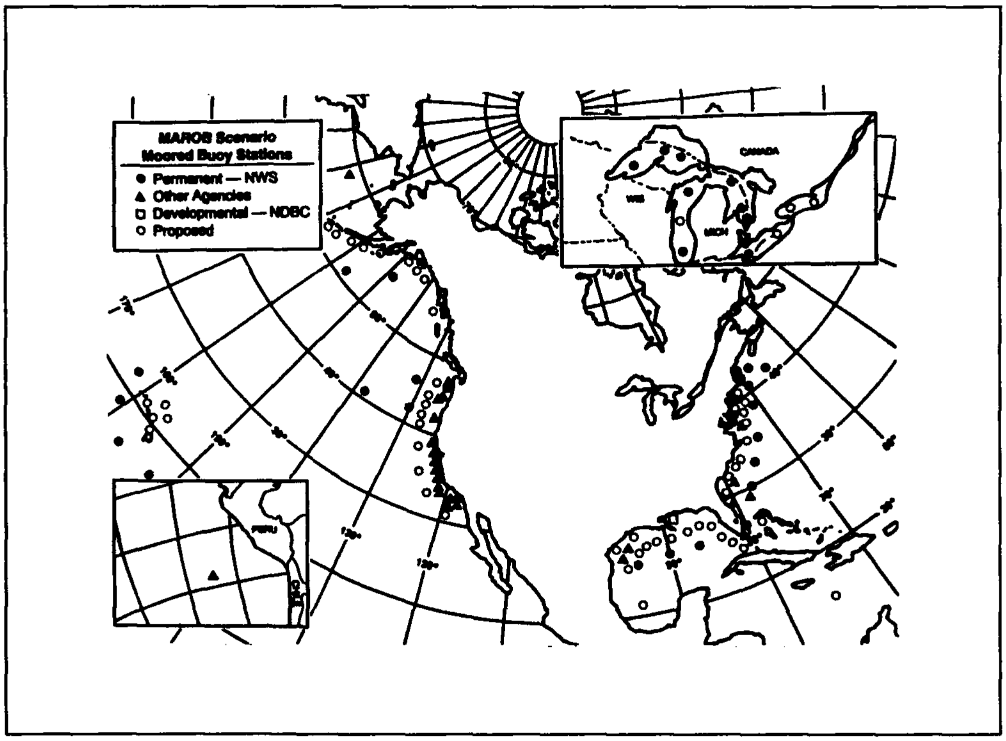


Figure 36-3

Moored buoy hull characteristics

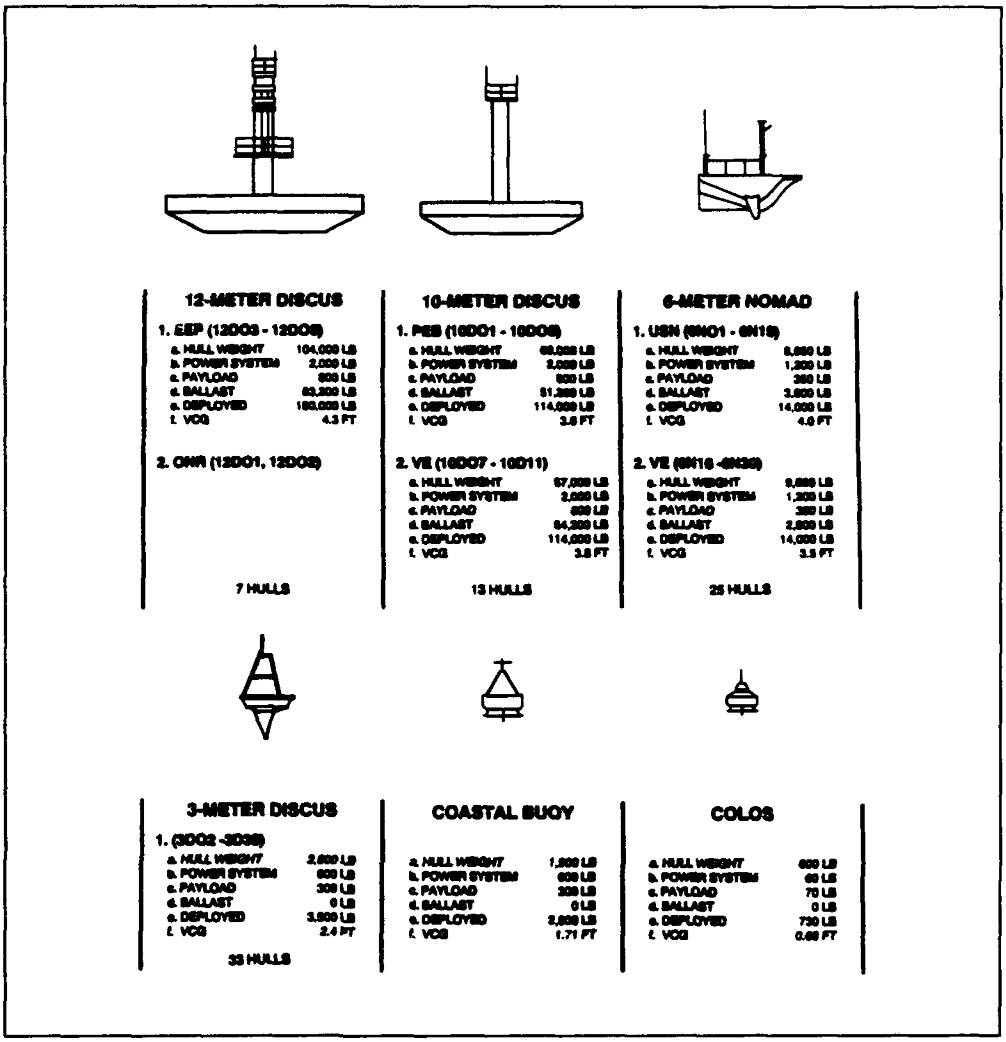


Figure 36-4

Ndbc standard mooring systems

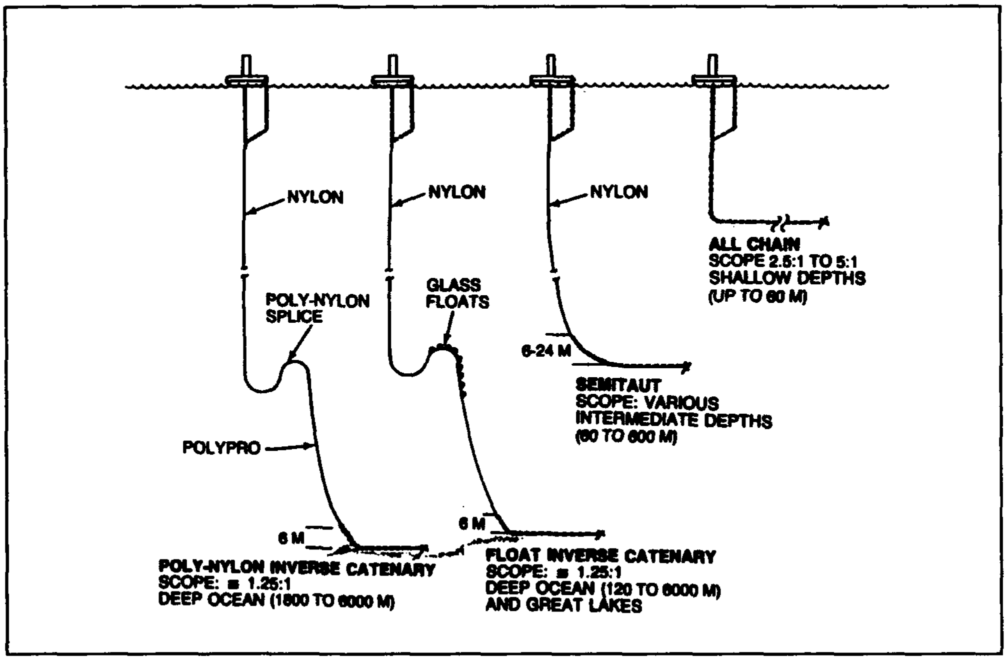


Fig ure 36-5

C-MAN sites

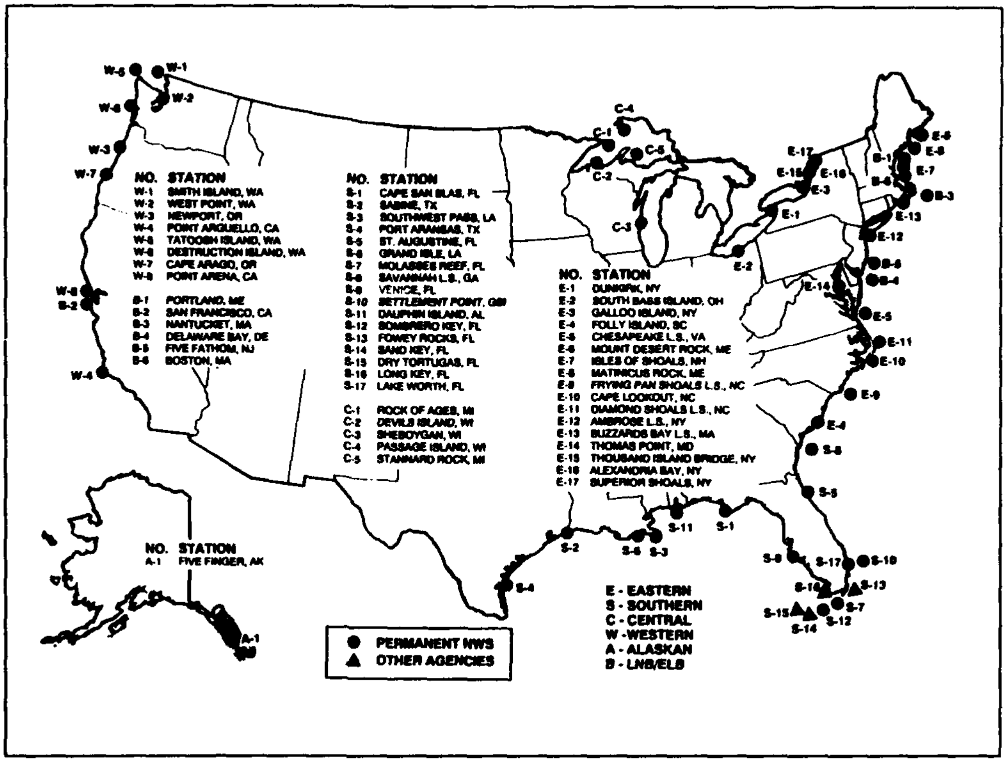


Figure 31-6

TOGA drifting buoy locations June 1, 1992

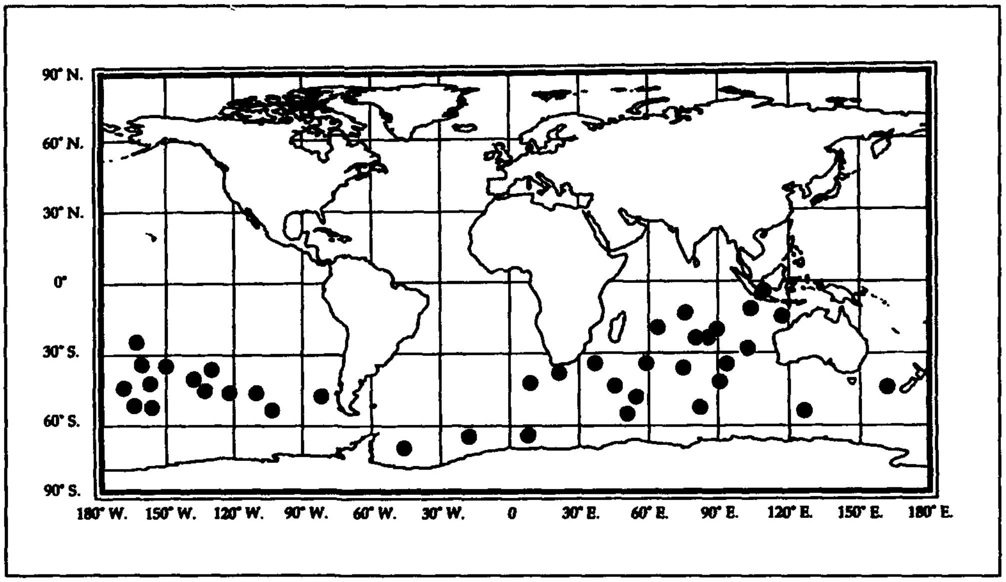
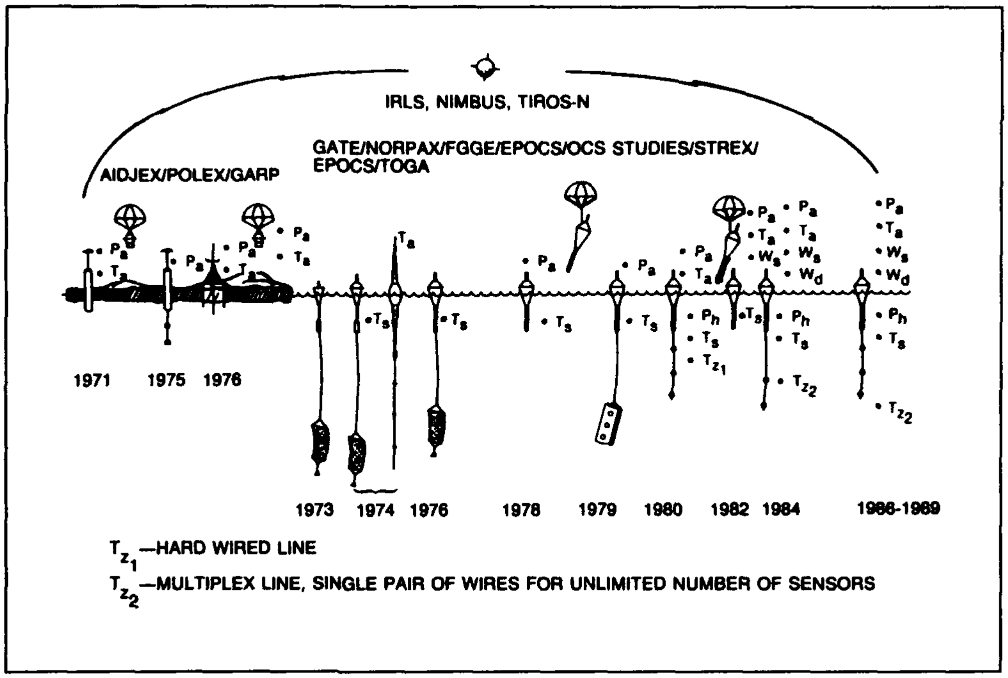


Figure 36-7

Drifting buoy technology development



GARY W. YANIK

MICRO LIQUID CHROMATOGRAPHY

A typical HPLC system consists of: solvent reservoir, high pressure pump, autosampler or other injection device, column, one or more detectors, data collection/analysis component, and waste receptacle.

Presently these systems are quite massive and operate at flow rates too high for available microbore columns. Systems designed for low microliter per minute flows are entering the market while research is proceeding on capillary chromatography. Although capable of low flow rates these systems are still massive and not capable of battery operation.

A goal would be to miniaturize the system to a large-scale integrated circuit that would contain not only the electronic components but the wet components such as the column and flow cell for the detector.

To achieve miniaturization, one could:

Utilize the silicon foundry (integrated circuit) process to fabricate the column as a "ditch" in the silicon substrate. The interior of the "ditch" would be derivitized with different reagents depending on the intended LC application (e.g. reverse phase, ion exchange, chelate). Experience with capillary chromatography has demonstrated the efficacy of internally coated columns. Such systems could be derivitized specifically for the intended use following manufacture of the chip. Specific derivitization of the column with an agent specific for a single compound or class of compounds would make specific detection possible.

Utilize integrated opto-electronics techniques to fabricate an optical source and detector on the same silicon substrate. Laser diode induced fluorescence is a good candidate for high sensitivity detection. Additionally, standard UV/vis or electrochemical detection either separately or in combination could be employed for the detection of a wide variety of compounds.

Technical challenges include:

Pumping at nanoliter per minute (estimate) rates will be a challenge. A piezoelectric, fluistor or other micromachined actuator may be applicable. These pumps would be incorporated into the chip at the head of the column. Two pumps with different inlet solvents could be used to generate gradients or simply flush the column following an analysis.

Column fouling and contamination will be challenging. Filtering and backflushing would extend column life. Possibly a column could be so small and inexpensive that "extras" could be included and switched in as needed. Because most of the contamination would come from the sample, a method of sample preparation that eliminates particulates would have to be devised. A sample preparation system external to the system chip providing for electro osmosis of the sample would also serve as the "injector" which would suck the sample in by the pumps in the micro LC system chip.

MARK ZDEBLICK

MICROFABRICATED VALVES AND INTEGRATED ELECTROFLUIDIC CIRCUITS

Figure 38-1
The opportunity

- **The Instrumentation industry is undergoing changes similar to those that have taken place in the computer industry.**
- **The trend is to improve performance while substantially reducing size and cost.**
- **Today's instruments use large, heavy and expensive mechanical and electro-mechanical components.**
- **Redwood's solid state technology provides the size, cost and performance benefits that will enable a revolution in instrumentation.**
- **Redwood's microvalves replace electromechanical solenoids.**
- **Redwood's Electro-Fluidic modules replace mechanical manifolds and pressure regulators.**

Figure 38-2
TECHNOLOGY
Integration progression

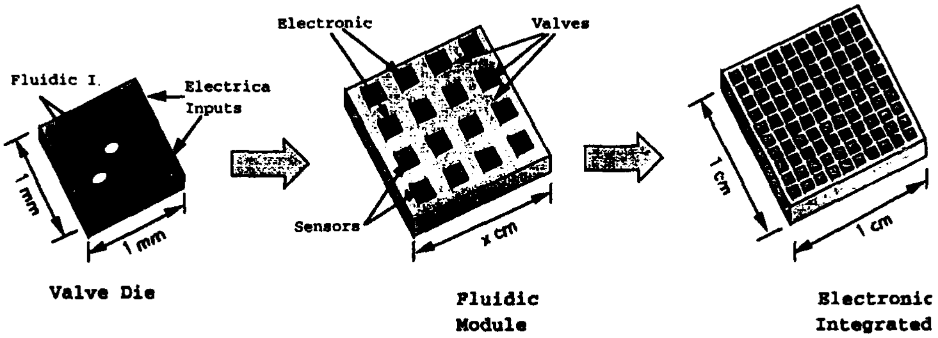


Figure 38-3
CORE TECHNOLOGY
The Fluistor™ microvalve

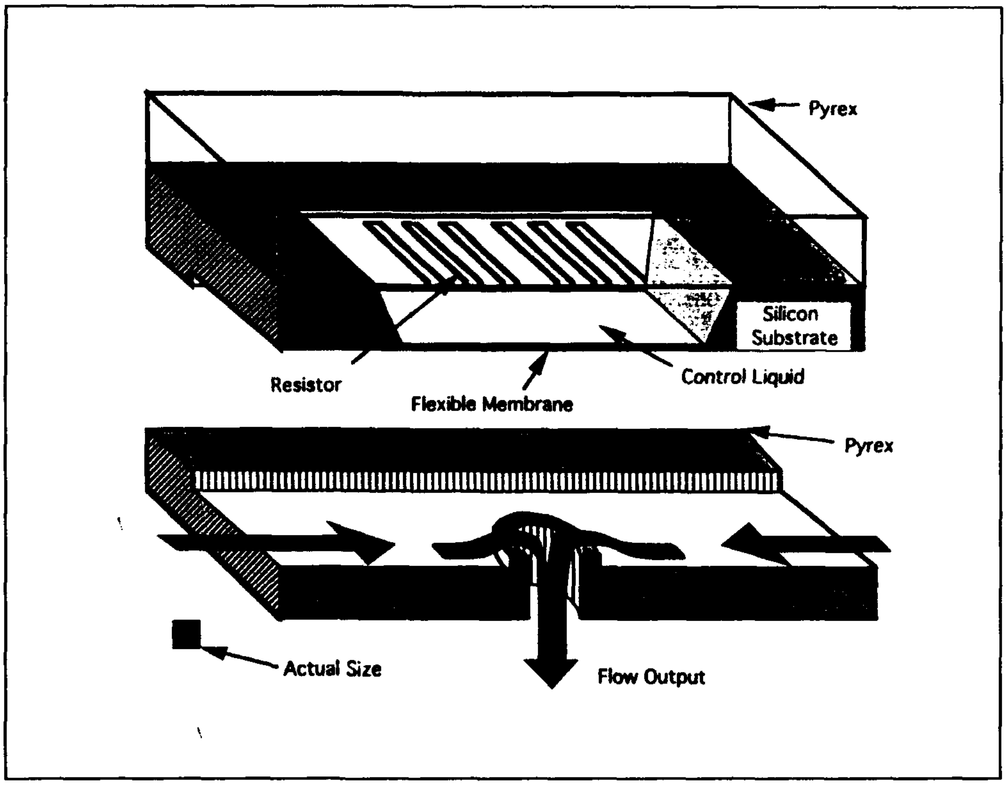


Figure 38-4
TECHNOLOGY
Component progression

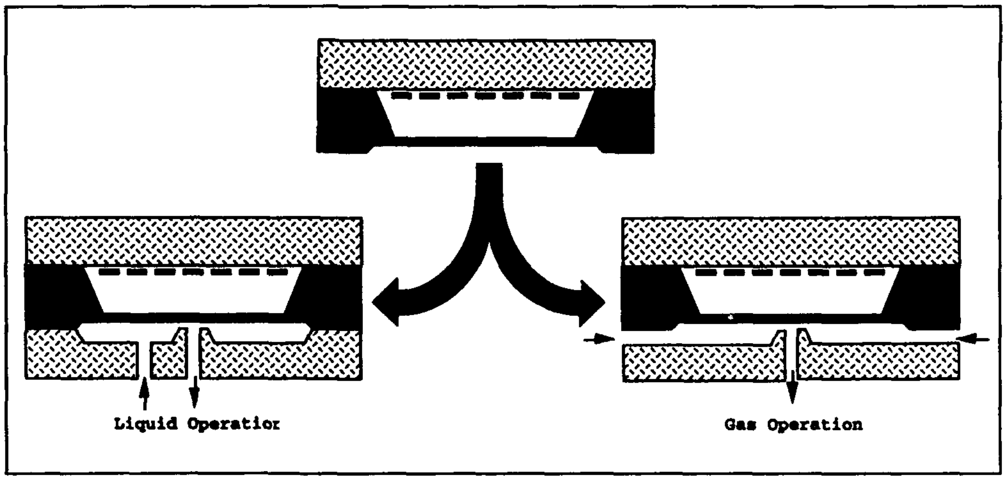


Figure 38-5
TECHNOLOGY
Component progression

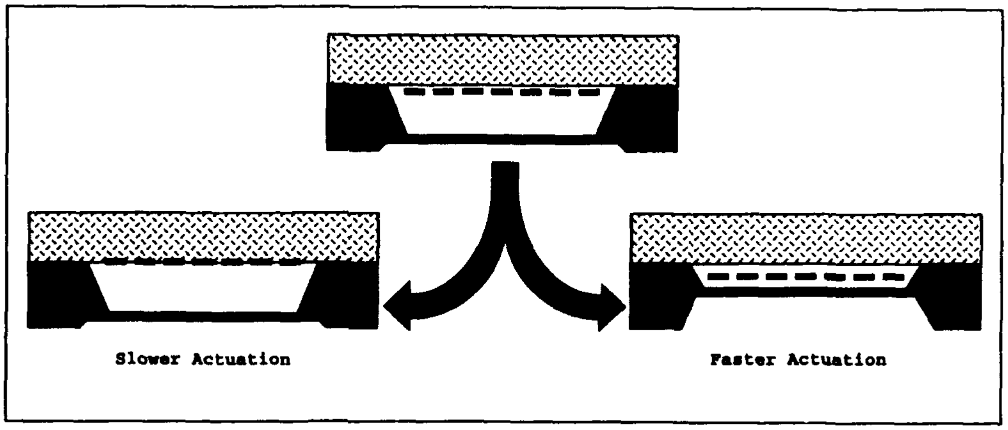


Figure 38-6
TECHNOLOGY
Multi-chip module today

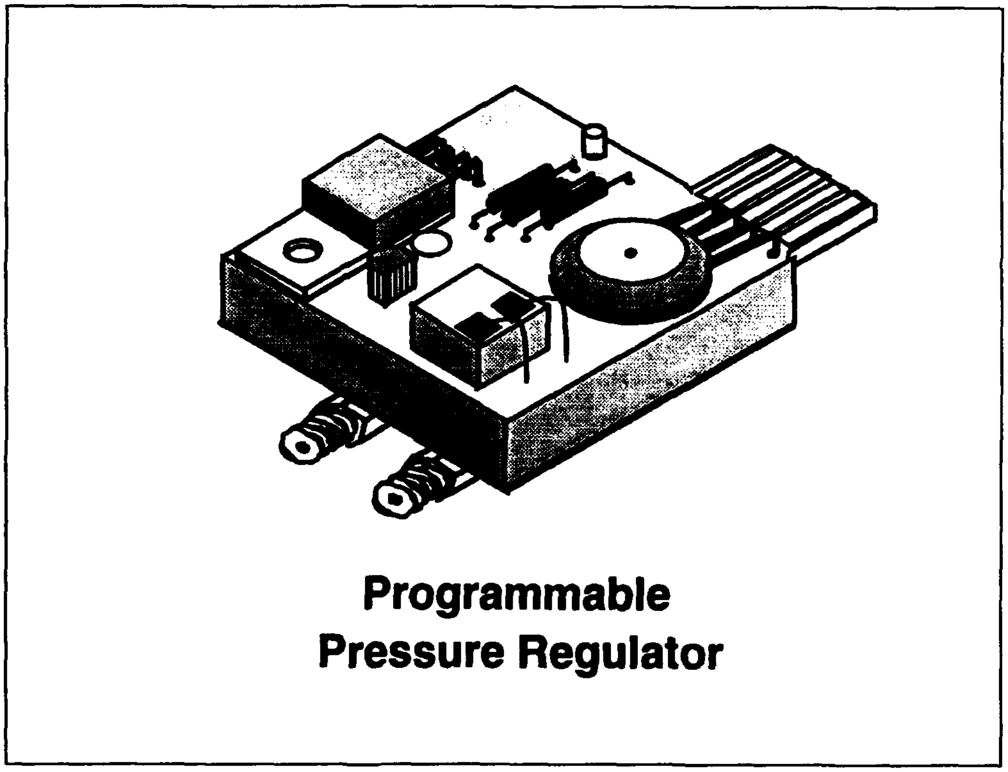


Figure 38-7

APPLICATIONS

Analytical instrumentation: gas chromatography

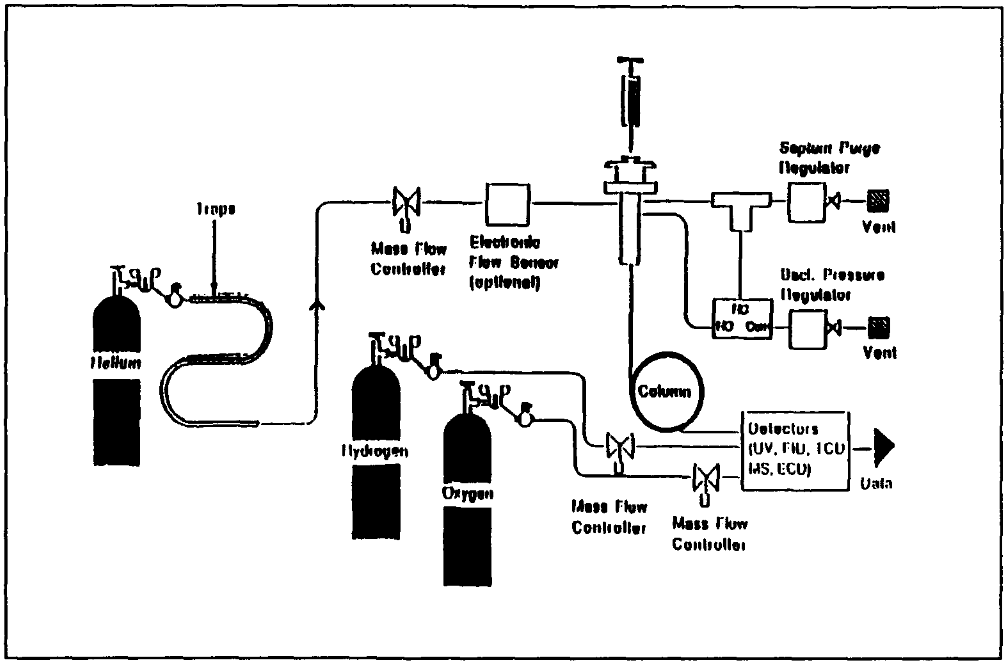


Figure 38-8

APPLICATIONS

Medical instrumentation: fluidic multi-chip module

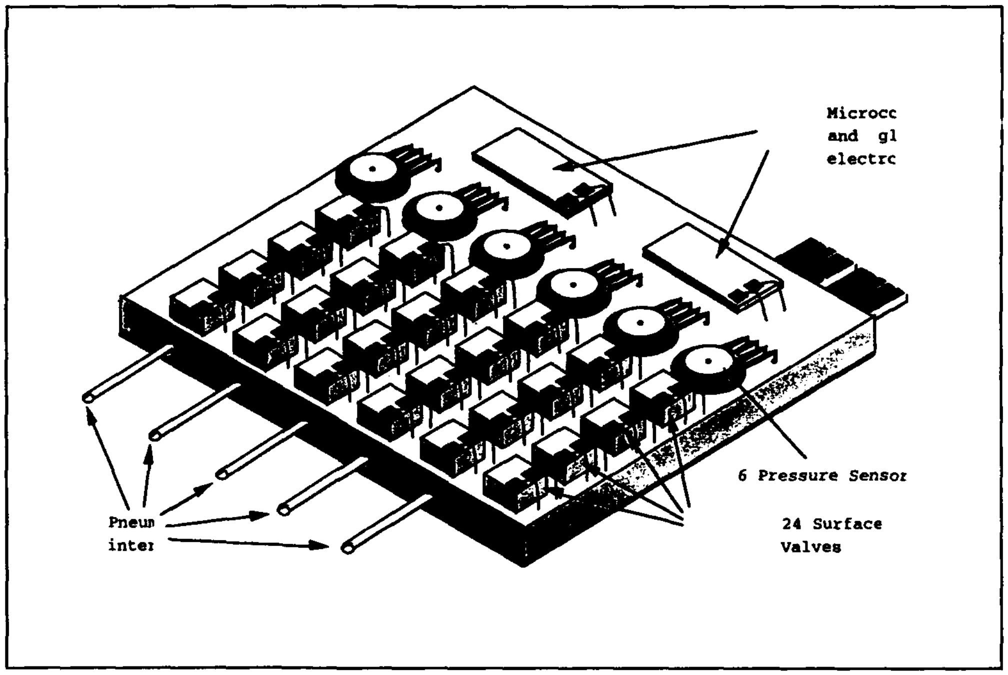


Figure 39-9
APPLICATIONS
Biotechnology

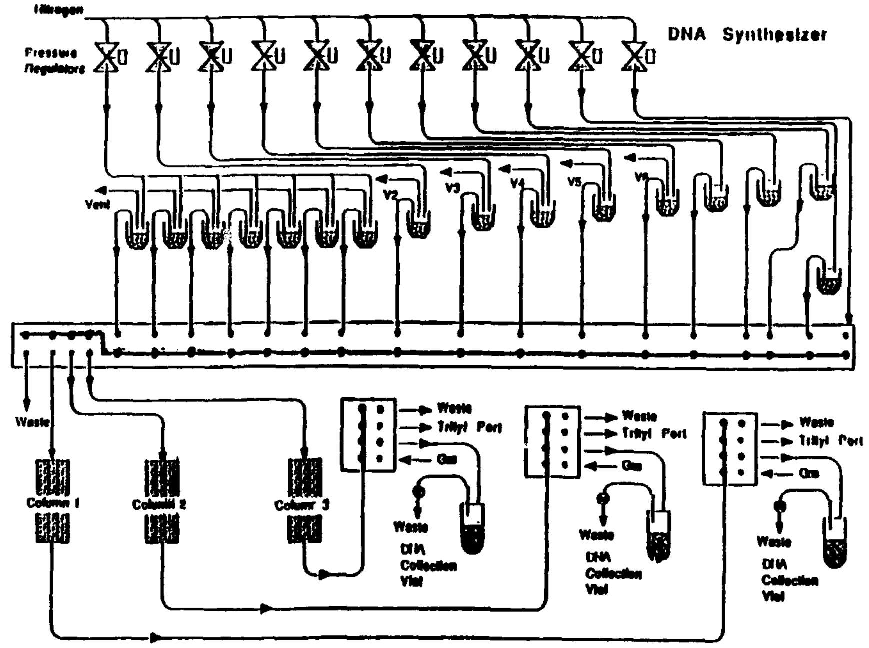
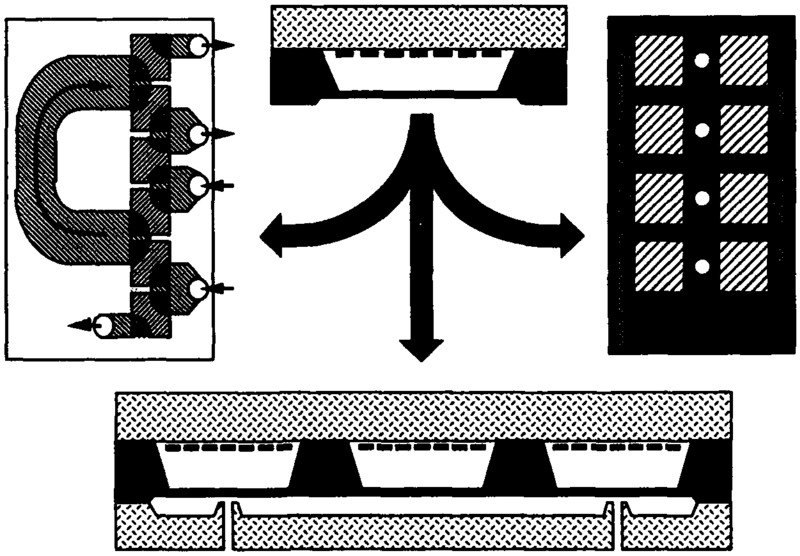


Figure 38-10
TECHNOLOGY
Integrated circuit progression



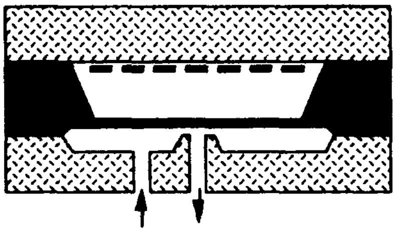


Figure 38-11
TECHNOLOGY
Performance envelope v. product

	Demonstrated	Product
Pressure Range:	vacuum to 3000 psi	0 to 200 psia
Max Flow Rate:	15 slpm @ 80 psi	6 slpm @ 80 psi
Leak Rate:	< 1 µl/min @ 80 psi	20 µl/min @ 20 psi
Operation:	Normally Open & Closed	Normally Open
Fluid:	Gas & Liquid	Gas

Figure 38-12
Advantages over solenoid valves

- Smaller Size
- Lighter Weight
- Zero Dead Volume
- Lower Manufacturing Cost
- Proportional Response
- Lower Power Consumption
- Wider Dynamic Range (100 times improvement)
- Multi Chip Module Compatibility
- Integration Capabilities

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
1994

3. REPORT TYPE AND DATES COVERED
Final

4. TITLE AND SUBTITLE
MarChem93, The Proceedings, The 1993 Workshop on Marine Chemistry Instrumentation

5. FUNDING NUMBERS
N00014-93-1-0448

6. AUTHOR(S)
Stephen J. Martin, Louis A. Codispoti, F. Eugene DeBons, David H. Johnson, Edward J. Green, and H. Lawrence Clark

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Stephen J. Martin (713-286-5945)
Martin Laboratories, Inc.
P.O. Box 58453
Houston, TX 77258

8. PERFORMING ORGANIZATION REPORT NUMBER
ML10448

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Co-sponsored by the National Science Foundation

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release;
Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The MarChem93 workshop was held August 2-4, 1993. The purpose of the workshop was to bring together scientists from industry, universities, and government organizations and encourage them to improve ocean chemical instrumentation (OCI).

The development of OCI is not progressing rapidly because: 1. Funding is limited to SBIR and STTR programs, 2. Market size is small and commercial applications are limited, and 3. Instrument developers are not organized to communicate effectively on a continuous basis.

Recommendations are: 1. Establish MarChem as a virtual community on the Internet, 2. Continue to hold the MarChem workshop every two years, 3. Exploit large markets with applications for OCI such as environmental chemistry, and 4. The Executive Committee should have regular meetings to identify new members, new technology, and funding opportunities.

The Executive Committee should identify research efforts in the field of chemical oceanographic instrumentation and recommend these opportunities to the appropriate funding agencies as suitable topics for Announcements of Opportunity, Broad Agency Announcements, or Request for Proposals.

14. SUBJECT TERMS

marine chemistry	chemical sensors
chemical oceanography	chemical instrumentation
oceanic chemistry	chemical analyses

15. NUMBER OF PAGES
144

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
Unclassified	Unclassified	Unclassified	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102