http://www.nap.edu/catalog/2202.html

We ship printed books within 1 business day; personal PDFs are available immediately.

Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies

Committee on Oceanic Carbon, Ocean Studies Board, National Research Council

ISBN: 0-309-59832-X, 96 pages, 6 x 9, (1993)

This PDF is available from the National Academies Press at: http://www.nap.edu/catalog/2202.html

Visit the National Academies Press online, the authoritative source for all books from the National Academy of Sciences, the National Academy of Engineering, the Institute of Medicine, and the National Research Council:

- Download hundreds of free books in PDF
- Read thousands of books online for free
- Explore our innovative research tools – try the "Research Dashboard" now!
- Sign up to be notified when new books are published
- Purchase printed books and selected PDF files

Thank you for downloading this PDF. If you have comments, questions or just want more information about the books published by the National Academies Press, you may contact our customer service department toll-free at 888-624-8373, visit us online, or send an email to feedback@nap.edu.

This book plus thousands more are available at http://www.nap.edu.

THE NATIONAL ACADEMIES
Advisers to the Nation on Science, Engineering, and Medicine

Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies

Committee on Oceanic Carbon
Ocean Studies Board
Commission on Geosciences, Environment, and Resources
National Research Council

COMMITTEE ON OCEANIC CARBON

TARO TAKAHASHI, Lamont-Doherty Earth Observatory, *Chair*
ROBERT BERNER, Yale University
PETER BREWER, Monterey Bay Aquarium Research Institute
ELLEN DRUFFEL, Woods Hole Oceanographic Institution
HUGH DUCKLOW, University of Maryland
CHARLES D. KEELING, Scripps Institution of Oceanography
JORGE SARMIENTO, Princeton University
SHARON SMITH, Brookhaven National Laboratory, Department of Energy
ERIC SUNDQUIST, U.S. Geological Survey, Woods Hole
PIETER TANS, National Oceanic and Atmospheric Administration
DAVID WALT, Tufts University
RAY F. WEISS, Scripps Institution of Oceanography
JAMES YODER, University of Rhode Island

Additional Contributors

KENNETH S. JOHNSON, Moss Landing Marine Laboratory
PETER JURS, Pennsylvania State University
MARK E. MEYERHOFF, University of Michigan
GEORGE H. MORRISON, Cornell University
JANET G. OSTERYOUNG, North Carolina State University
RICHARD THOMPSON, University of Maryland
EDWARD S. YEUNG, Iowa State University
ALBERTO ZIRINO, Naval Ocean Systems Center

Staff

EDWARD R. URBAN, JR., *Staff Officer*

OCEAN STUDIES BOARD

COMMISSION ON GEOSCIENCES, ENVIRONMENT, AND RESOURCES

Acknowledgments

The committee was aided in preparation of this report by a group of expert contributors—analytical chemists and oceanographers—listed on the committee page of this report. These individuals contributed the technical information about the measurement technologies described in this report and provided recommendations for actions necessary to bring closer interactions between the fields of chemical oceanography and analytical chemistry. This report would have been impossible without their efforts.

Contents

CONTENTS

Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies

Summary

Understanding the chemical composition and processes of the ocean is of great importance because of a major role played by the ocean in regulating changes in the global environment. The ocean interacts with the atmosphere and land masses through complex cycles of biogeochemical and hydrological processes. To understand oceanic processes a range of measurements are required, from the poles to the equator as well as from the ocean surface to deep-ocean sediments. New techniques that allow precise measurements rapidly over extensive global areas and over a long term are needed to acquire information relevant to global change studies. Ocean scientists tend to rely on well-established techniques when making measurements, in order to maintain the compatibility of new data with data collected in the past.

Measurement science is one of the most active fields of chemistry today. Advances in microelectronics, computers, and sensing devices have accelerated the development of measurement instruments and techniques. Many of these innovations could be used for ocean measurements, although some of the new methods are not well known to ocean scientists. The use of new techniques of analytical chemistry for ocean science applications is impeded by limited interactions between ocean scientists and analytical chemists. Significant technical innovations will be required to make many of the new techniques amenable to the ocean environment, however.

A group of analytical chemists and ocean scientists was brought together by the Committee on Oceanic Carbon of the National Research Council (NRC) Ocean Studies Board to identify techniques of analytical chemistry

that could be used in ocean science. This report highlights the state of the art of measurement technologies offering new promise for ocean measurements. In particular, the group focused on new techniques for measuring seawater analytes that are important for understanding key aspects of the ocean's role in the global carbon cycle. The committee also noted other seawater analytes whose improved measurement would contribute to a better understanding of ocean processes. The report does not encompass all areas of chemical oceanography; instead, it highlights a subset of the possible measurements that could be useful for obtaining improved understanding of the global carbon cycle. The report focuses on *in situ* measurements of dissolved analytes in seawater that might not be feasible in the near future but could play an important role in global ocean observations of the future. The committee believes that the most difficult problem is in designing sensors of the desired selectivity, stability, and sensitivity for dissolved analytes in the open ocean.

The committee acknowledges that the particulate flux of carbon out of the euphotic zone, the transformation of particles, and sedimentation and diagenesis on the seafloor are important processes that need to be understood for a full characterization of the ocean carbon system. However, the focus on dissolved analytes was selected because one objective of this report is to interest analytical chemists in applying their techniques to ocean studies. Furthermore, some of the sensor techniques discussed in this report may be modified and engineered for *in situ* measurements of dissolved species in pore waters of sediments.

This report identifies technical hurdles and opportunities and discusses the role that government and academia can play in overcoming the nontechnical barriers to successful research, development, and transfer of these technologies to the ocean science community. Major conclusions and recommendations, discussed in detail at the end of this report, fall into two major categories, the role of the federal government and the role of academic scientists. Achievement of the recommendations will require cooperative activities between the federal government, industry, and academia (NRC, 1992).

SUMMARY OF RECOMMENDATIONS

Among the variety of techniques that could be developed for ocean measurements in the future, research and development in several areas seems to hold promise to improve capabilities for ocean measurements, including long-term remote, profiling, and shipboard sensors. The report specifies the priority analytes that must be measured to improve our understanding of the ocean's role in the global carbon system. **The committee recommends that resources be made available to attract specialists in synthetic or**

ganic chemistry and polymer materials to develop systems that rely on selective reactions (recognition chemistry) for ocean measurements. Biosensors are becoming available for a variety of analytes and could contribute to ocean measurement techniques. Other research areas that will undoubtedly improve measurement capabilities include electrode and sensor design and mathematical techniques for experimental optimization. New measurement techniques are now available because of advances in microcomputer control and analysis. **Development of microcomputer-based *in situ* instruments is another area of great potential for control of sampling, analysis, and communication by remote instruments.** The report describes the attributes of an ideal *in situ* sensor. Research will be required to improve these characteristics for sensors that will be deployed on long-term remote moorings or autonomous vehicles. The constraints listed are less applicable for profilers, for which speed of the measurement, selectivity, and reversibility are more important. New techniques must be compared extensively with existing methods, so that the continuity of time-series observations and their quality will be assured. Development and long-term maintenance of relevant standards and calibrants are needed to assure data continuity and are an integral part of the long-range global observations that represent the backbone of global change studies.

The Federal Government's Role

The federal government must take the lead in supporting the research and development effort for ocean instrumentation because the government, through its agencies, is the beneficiary and ultimate consumer of most ocean measurements. Regardless of the approaches taken, it is clear that a considerable investment of time and resources will be required to develop the arsenal of chemically selective and stable host compounds that will be required to measure all the key oceanic species via *in situ* chemical sensor technology.

Relevant standards and calibrants are vital to the ability of chemical oceanographers to make analytical measurements of quality high enough to be useful for studies of global change. **The committee recommends that agencies supporting new ocean measurement technology, such as the Department of Energy, the National Science Foundation, the National Oceanic and Atmospheric Administration, the National Institute of Standards and Technology, and the Office of Naval Research, devote a portion of their budgets to support development and maintenance of standards and calibrants.**

Finally, the federal government could ensure that resources are available for instrument development. A major premise of this report is that improved ocean instrumentation will be necessary to acquire the data neces

sary to evaluate global change. **The committee recommends that the federal government take steps to expedite instrument development.** There are a range of approaches that might be taken, some of which could be accomplished by reprogramming existing funding rather than allocation of new fiscal resources. One possible step would be to establish research buoys and vessels that would serve primarily as test platforms for instrumentation. The time frame for instrument development often exceeds the duration of research grants. Therefore, another step to improve the instrument development process would be for federal agencies to devote some of their instrument development funds to long-term (7 to 10 years) grants and to maintain instrument engineering groups.

The Role of Academic Scientists

The committee chose to categorize analytes into groups with different levels of priority for measurement in the mid-term future; priorities are based on the committee's charge "to recommend new technologies for the measurement of carbon dioxide and other biologically important elements and compounds." **In order to promote interdisciplinary activities between oceanographers and analytical chemists, the committee recommends that oceanographers identify a limited number of analytes on which analytical chemists can focus.** This report lists analytes that are most important for studies of the ocean carbon cycle; development of techniques and instrumentation for these analytes is a priority for such studies. As new techniques become commonplace and new information is gathered, it is possible that a reprioritization of the analytes will be necessary, with a concentration of resources to solve the most important remaining measurement problems.

The committee recognizes that successful implementation of a development effort for ocean instrumentation requires extensive ongoing transfer of information and opportunities between the ocean science and analytical chemistry communities. **The committee recommends a multipronged approach to disseminating information to the chemistry community in general and the analytical chemistry community in particular. In addition, the committee believes that an effort should be undertaken to apprise both the public and undergraduate and graduate students of the opportunities in this field.** A number of potential vehicles for accomplishing these goals are discussed in the recommendations section.

Introduction

The flow of chemicals through the ocean system has a fundamental impact on global processes, including the Earth's energy balance. For example, the ocean holds approximately 60 times as much dissolved carbon dioxide species (TCO_2) as are present in atmospheric carbon dioxide. Perturbations in the flow of carbon dioxide through the ocean-atmosphere system are closely linked to climate change during glacial periods (Lorius et al., 1990). Human perturbation of the carbon cycle, which has resulted in a 30% increase in atmospheric carbon dioxide since 1850, has the potential to produce even greater climate changes than were experienced over the last glacial cycle (Ramanathan, 1988).

Chemical distributions in the ocean are also strongly influenced by human activities on local scales, particularly in the coastal ocean. Nutrient enrichment in the New York Bight and Chesapeake Bay has led to anoxia in the water column and significant impacts on marine resources (Officer et al., 1984; Falkowski et al., 1980). New measurement technologies will be required to achieve an adequate understanding of the cycling of carbon and other biologically important chemicals in the coastal ocean. Coastal areas present special difficulties in understanding because of the complexity of coastal processes and their greater variability in both space and time.

In many cases, the impact of human disturbances cannot be predicted because a fundamental understanding of natural chemical cycles is lacking, due to insufficient information on the distributions of chemical components in the ocean. For example, we do not yet understand in adequate detail what processes control primary production (photosynthetic production of

biomass) in many areas of the ocean. Such knowledge is critical because primary production in the ocean acts as a "biological pump" to move carbon dioxide from the ocean surface layer, where it exchanges with the atmosphere, to the deep ocean. Future scenarios for greenhouse warming are impossible to evaluate until we understand how this "biological pump" operates. The oceanic absorption of fossil fuel CO_2 is difficult to observe and understand due to the large and variable background of the natural carbon cycle (Tans et al., 1990), which is itself subject to climatic perturbation.

Primary production in the ocean is controlled by major nutrients, such as nitrate and phosphate, but also by certain trace metals. Dissolved iron was hypothesized (over 50 years ago) to be a key nutrient limiting primary production rates in the sea. However, credible data for the concentration of dissolved iron in seawater have only become available in the last 8 years. Iron is present in surface seawater at concentrations less than 0.5 nanomole per kilogram. These low concentrations of dissolved iron suggest that it is, in fact, a nutrient that can limit primary production in the ocean (Martin et al., 1989). The role of iron in limiting productivity of the ocean can be resolved only when measurements of dissolved iron at concentrations below 1 nanomole per kilogram become routine. There is evidence that other trace metals could also control phytoplankton growth.

Chemical analyses of seawater present unique difficulties. These problems are not limited to iron. In fact, with the exception of the major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) found in seawater, most other elements are present at trace concentrations (Figure 1). The biologically limiting compounds are almost exclusively present at concentrations less than a few micromoles per kilogram seawater, posing significant challenges to their measurement. Their concentrations must be determined in the presence of more than 1 million-fold excess of major ions. Trace metal measurements typically require the sample to be concentrated greatly before analysis by even the most sensitive techniques. Contamination from ships and sample containers is a ubiquitous problem, and extreme care must be taken to protect sample integrity. Determination of the chemical speciation of elements at these concentrations is even more difficult. For example, copper, which is present in surface seawater at concentrations of less than 1 nanomole per kilogram, is bound by an unidentified ligand with a high specificity for the metal (Coale and Bruland, 1988). This ligand is present at concentrations on the order of 1 nanomole per kilogram and appears to regulate the free copper activity.

The interest in coordinated international studies of the global environment has increased since it has become apparent that humankind is affecting the composition of the atmosphere and ocean on a global scale. One proposal that has been accepted by the International Oceanographic Commission is for a global ocean observing system (GOOS). GOOS, as presently
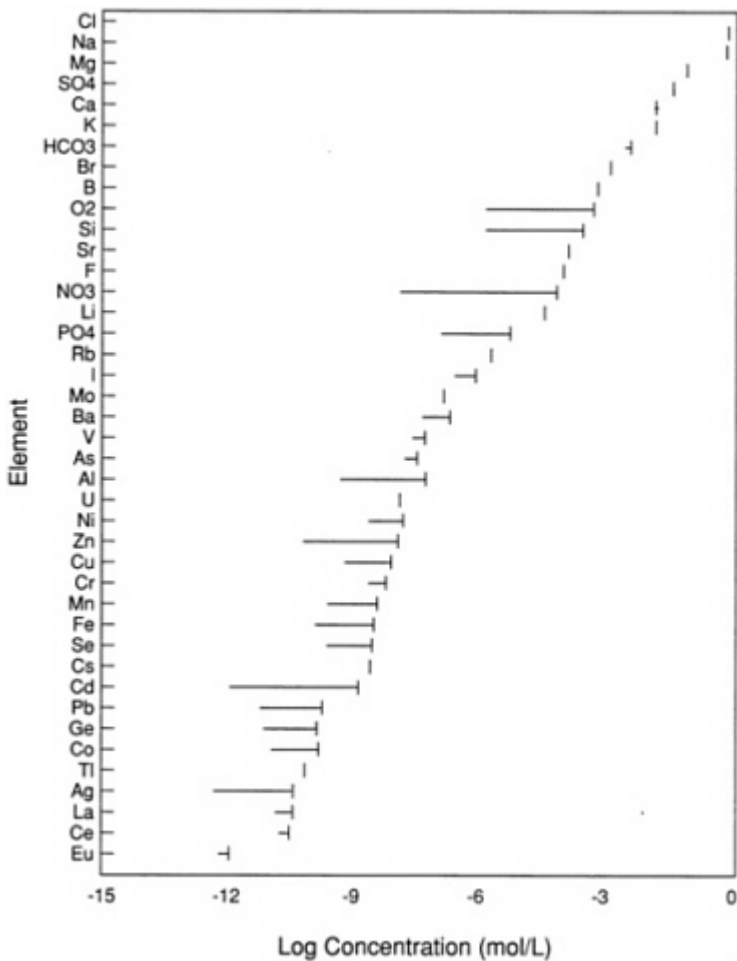
Figure 1
The range of concentrations for a variety of elements in seawater. Data are from Bruland (1983). Reprinted with permission of Academic Press.

envisioned, consists of components for climate monitoring, assessment, and prediction; monitoring and assessment of marine living resources; coastal zone management and development; assessment and prediction of the health of the ocean; and marine meteorological and oceanographic services. The successful implementation of several of these components will depend on development and deployment of chemical sensors that are not yet available for long-term use in the ocean.

Collection of data over long periods of time often is required to resolve chemical changes in the ocean because there is a great deal of natural variability in chemical concentrations over time. The natural cycles of biologically active chemicals in the surface layer of the ocean are characterized by large seasonal changes in concentration. Variability in concentration can also occur on a daily cycle because of the respiration, photosynthesis, and nutrient uptake of plants in response to light and dark. Interannual changes in chemical distributions also result from processes such as El Niño that occur only a few times each decade. These temporal variations of different frequencies are often superimposed on slow concentration changes due to human activity. For example, lead concentrations in the surface waters of the Atlantic Ocean appear to have decreased about twofold from 1979 to 1984 to values near 100 picomoles per kilogram, as a result of the phasing out of leaded gasoline in North America (Boyle et al., 1986). The decrease in lead concentrations is obscured, however, by the large variability in the Atlantic Ocean produced by movement of the Gulf Stream and the water masses it sheds. This trend could only be identified by comparing concurrent measurements of the isotope ^{210}Pb, which is a natural radioactive decay product of uranium, and stable lead (primarily ^{207}Pb), which has an anthropogenic source.

World ocean circulation can be pictured as flow along the "oceanic conveyor" from its source in the North Atlantic through the ocean depths to the North Pacific via the Antarctic Circumpolar Current, where it returns along the surface, through the Indian Ocean to its source in the North Atlantic (Broecker, 1991). About 1000 to 1500 years are required for sea-water to complete this cycle. During this time, chemicals that are released from sinking organic matter through decomposition by microorganisms accumulate in the water, while those that are scavenged onto sinking particles are depleted. Concentrations must often be measured with high precision to detect the chemical changes that occur with time in the ocean. The concentration of total carbon dioxide, $TCO_2 = [CO_2] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$, increases by about 20% from an initial value near 2 millimolar as seawater follows this path from the surface to the deep ocean and back to the surface, due primarily to respiration. If TCO_2 and oxygen are measured with a precision and accuracy of better than 0.1% and 1%, respectively, it is possible to detect the change in TCO_2 due to the increase of carbon dioxide

in the atmosphere since the Industrial Revolution. Such measurements have been used to reconstruct the past composition of the atmosphere (Brewer, 1978). Measurements of tracer chemicals such as chlorofluorocarbons, tritium, and ^{14}C, largely introduced to the ocean by human activities, are used to determine the rates at which reactions occur as seawater completes the global circulation pattern.

There are large gaps in our fundamental knowledge of organic compounds dissolved in seawater, and the concentrations of dissolved organic carbon and nitrogen are still matters of debate. The molecular identity of little of the pool of organic carbon dissolved in the ocean is known with any certainty. There is almost no knowledge of the temporal variability of individual organic compounds, their spatial distributions, or their role in sequestering atmospheric carbon or other chemical species. This information is essential if the role of the oceans in global processes is to be understood. Many organic compounds are directly measurable at natural concentrations found in the ocean by using techniques such as derivitization of amino acids and by measuring reducing sugars by pulsed amperometric detection. Identification of other specific components of the oceanic carbon pool will be possible with improved measurement capabilities, leading to a better understanding of chemical and biological processes in the ocean.

NEED FOR NEW APPLICATIONS OF ANALYTICAL CHEMISTRY TO OCEANOGRAPHY

The objective of this report is to review the potential application of methods of analytical chemistry to study the ocean carbon cycle and processes—physical, chemical, and biological—that affect carbon fluxes. The committee sought to identify state-of-the-art measurement technologies that could produce significant progress in our understanding of oceanic bio-geochemical cycles. These promising analytical technologies are reviewed briefly. The report focuses on analytical methods that could operate continuously on mid-ocean moorings, drifting buoys, or commercial ships making regular ocean passages. Continuous measurements are critical to understand the spatial and temporal variability of processes that are fast and discontinuous, such as gas exchange, primary production, and bacterial uptake of dissolved material, as well as the processes that control the variability. Laboratory-based measurements of discrete samples are also considered for cases in which chemical measurement technologies have not advanced to the stage of continuous *in situ* or shipboard use.

The status of measurement technologies for ocean chemicals is being reviewed for several reasons. First, presently employed technologies for chemical measurements are inadequate for global system science. Many of the ocean's physical and biological parameters, such as surface temperature,

light transmission, up-and down-welling irradiance, and chlorophyll fluorescence, can be measured frequently from satellites or open-ocean moorings over long periods of time. These measurements have led to rapid advances in our understanding of the oceanographic processes that control these variables. However, remote sensing of chemical parameters is limited. In most cases, chemists can study dissolved chemical distributions only when research vessels are present on station to collect water samples. For instance, at a typical sampling site, one might determine the vertical distribution of an analyte in the water column by acquiring a dozen or more samples in Niskin bottles from the surface to depths of kilometers. Even using a sophisticated water collecting device called a rosette, collecting the samples at one site can take hours. In other cases, one can immerse a pump at a preset depth to bring water to the surface for analysis, but this method cannot be used for sampling water from great depths. Dependence on ship-based sampling leads to severe undersampling in both time and space.

Undersampling is a particularly strong limitation on large-scale studies of globally significant processes, such as the air-sea transfer of carbon dioxide and the factors regulating oceanic primary production. The seasonal variability in parameters such as the partial pressure of carbon dioxide (pCO_2) in surface seawater is often an order of magnitude greater than the changes that might be expected due to a doubling of atmospheric carbon dioxide. Solving the undersampling problem is essential to our ability to predict the impact of increasing carbon dioxide on future climate.

Second, chemical measurements over global scales represent highly challenging problems that can be addressed effectively by analytical chemists and oceanographers. Rapid advances in microelectronics, detection techniques, and data collection and analysis have solved many of the problems associated with chemical analysis and have opened the frontier on new methods of chemical sensing. New types of selective chemical reactions are available through advances in biotechnology. The materials sciences have provided new technologies for the production of microelectrodes, micropumps, fiber optics, and novel polymers, all key components for sensing chemicals dissolved in the ocean. Developments in these areas are being prompted by the growing requirements of clinical chemistry, environmental monitoring, and industrial process control.

The need for a new generation of chemical observing systems for the ocean is widely recognized. Global science initiatives including the Joint Global Ocean Flux Study (GOFS, 1984) and the Ridge Inter-Disciplinary Global Experiments (RIDGE, 1989) have identified developments in chemical sensing that are required to meet their scientific objectives. At least five recent program announcements from federal agencies—the National Science Foundation, the Office of Naval Research, the Department of Energy,

and the National Oceanic and Atmospheric Administration—have called for the development of new sensor technology.

New chemical technologies are needed for measurements on a local scale as well. Each year $133,000,000 is spent for ocean monitoring programs required to protect the marine environment (NRC, 1989), so that improvement in techniques could have a substantial impact on the cost of measurements that contribute to this monitoring cost. Monitoring results must be incorporated into the environmental management process in a timely manner. However, this is not possible if there are long time delays between sampling and availability of data or there are insufficient numbers of measurements to interpret the processes that are occurring. There are not enough ships, scientists, technicians, or funds to support the ship-based measurements that would be required to collect these data. Consequently, alternative methods must be sought.

The shortcomings of existing methods will be surmounted only by using new approaches. This report discusses and identifies new and emerging measurement technologies from the field of analytical chemistry that could be applied to chemical and biological oceanography, ranging from those that must be confined to land-based laboratories to methods that can be used in shipboard laboratories, ship-tethered profilers, and long-term *in situ* sensors. The ultimate implementation of new measurement technologies will be in the form of *in situ* measurements. The ocean is constantly changing; consequently, measurements of rates are essential to understanding ocean processes. Techniques that provide continuous monitoring capability are to be preferred to those that require discrete samples.

The committee attempted to project the availability of new technologies up to 15 years into the future. This longer-range view is consistent with the 10-year development cycle needed for introducing new instrumentation into the ocean measurement field as described by Wunsch (1989). The slow pace of introducing new techniques is due primarily to the extreme requirements of the ocean system. There are other nonenvironmental limiting factors, such as the lack of testing facilities, that could be changed to speed instrument development. Of course, it is likely that, within 15 years, unforeseen scientific developments and technical breakthroughs will make new measurement opportunities available.

A final objective of this report is to highlight the exciting opportunities afforded by this interdisciplinary endeavor and to encourage greater cooperation between analytical chemists and ocean scientists. Several past efforts have been aimed at bringing together practitioners of the diverging fields of marine chemistry and analytical chemistry (Goldberg, 1975, 1988). Graedel et al. (1988) noted that developments are needed in two types of analytical capabilities —real-time data acquisition and instruments for labo

ratory use—for studying the air-sea interface. They listed a number of analytes for which surface ocean time series measurements would be useful: pCO_2, pH, O_2, argon, a fluorescence proxy for chlorophyll, dimethyl sulfide, methyl halides, and isotopes of major nutrient elements. Martin et al. (1988) described a number of analytical techniques that could be applied to studies of the seawater-sediment interface and chemical processes at the ocean bottom. These included electrochemical and fluorescent techniques, combined with new specific chemistries. Potential new methods of concentration and fractionation of dissolved organic material were also described. The development of chemical measurement technologies for ocean sciences requires cooperative efforts by scientists from these two fields and communication between them. The ocean chemistry community is a small one, whereas the analytical chemistry community represents one of the largest subdisciplines of chemistry. Organization of departments, professional societies, and scientific journals have the tendency to impede interactions among fields as different as ocean science and analytical chemistry. Thus, scientific culture slows progress at the interface between these fields. Progress will continue to be slow until appropriate mechanisms and incentives can be instituted to encourage interactions between scientists in these two disciplines, and to accommodate interdisciplinary work. If analytical chemists are made aware of the exciting opportunities available in the field of ocean science, they are more likely to choose an ocean measurement problem and adapt their analytical techniques to it. By fostering interdisciplinary research efforts, the development of ocean measurement technology should progress more rapidly.

Oceanographic Measurements

PRIORITY ANALYTES

To focus the activities of the analytical chemists and oceanographers that participated in this study, the committee developed a list of priority analytes for sensor development (Table 1). The list of priority analytes focuses on carbon system components and related biologically important analytes, topics of critical importance to oceanographers, Earth scientists in general, and society at large. The list of analytes was divided into four categories, with emphasis being placed on the relative importance to understanding the oceanic carbon cycle:

Priority 1 — Quantifying the Anthropogenic Carbon Input

Priority 2a — Understanding the Biological Pump

Priority 2b — Tracing Water Masses

Priority 3 — Other Analytes of Interest

Priority 3 analytes were suggested by chemical oceanographers who responded to a questionnaire. These parameters are of interest to many oceanographers and could benefit from attention by the analytical chemistry community, even though they are not necessarily related to the carbon cycle directly. The position of analytes within a priority group is not significant. The committee recognizes that virtually any chemical sensor that can operate in seawater could be used to produce scientifically valuable data. For example, the list does not include any of the major ions found in seawater (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}) because the concentration of each of these

TABLE 1 Priority Analytes for Studying the Ocean's Role in the Global Carbon Cycle

Analyte	Concentration (or delta value) in Seawater[a]	Present Precision	Desirable Measurement Frequency for In Situ Sensor	Present Measurement Technologies[b]
Priority 1 — Quantifying the Anthropogenic Carbon Input				
Total carbon dioxide (TCO$_2$)	1800-2450 μmol/kg[3]	1 μmol/kg	1/h	Coulometric titration of extracted CO$_2$
pCO$_2$	100-1500 μatm	0.3-1.5 μatm	1/h	Gas chromatography or infrared analysis
pH	7.4-8.9 pH	0.005 pH - potentiometry 0.001 pH - for high-quality spectrophotometry	1/s to 1/h	Potentiometric; colorimetric and fluorometric indicators
Alkalinity	1900-2500 μmol/kg	2 μmol/kg	1/h	Acidimetric titration
Carbon-13 (δ^{13}C)	-2 to +2‰ (TCO$_2$) -19 to -22‰ (DOC) -18 to -31‰ (POC)	0.02 to 0.07‰ 0.05 to 0.1‰ 0.05 to 0.1‰	1/h mooring (save for on-land measurement)	Isotope ratio mass spectrometry (IRMS)
Carbon-14 (Δ^{14}C)	+150 to -250‰ (DIC) -150 to -540‰ (DOC) +150 to -100‰ (POC)	2 to 10‰	1/d mooring (save for on-land measurement)	Accelerator mass spectrometry (small samples, low precision) or counting (large samples, high precision)
Priority 2a — Understanding the Biological Pump				
Dissolved organic carbon	35-200 μmol/kg	5-20%	1/s profiling 1/h mooring	High-temperature combustion or UV oxidation followed by IR spectrophotometry
Particulate organic carbon	7-100 μg C/L	5%	1/d mooring (save for on-land measurement)	Discrete samples (closed tube combustion)

Parameter	Range	Precision	Sampling	Method
Nitrate	0–45 µmol/kg	0.05 µmol/kg	1/s profiling 1/h mooring	Continuous flow analysis (CFA) with colorimetry; chemiluminescence; direct UV spectroscopy
Phosphate	0–3.5 µmol/kg	0.05 µmol/kg	1/s profiling 1/h mooring	CFA with colorimetry; chemiluminescence; direct UV spectroscopy
Silicate	0–190 µmol/kg	0.05 µmol/kg	1/s profiling 1/h mooring	CFA with colorimetry
Ammonium	0–10 µmol/kg	2–10 nmol/kg	1/s profiling 1/h mooring	Coulometric titration; CFA with colorimetry; fluorometry
Iron	<0.05–2.5 nmol/kg	5%	1/h	Graphite furnace atomic absorption spectrometry (GFAAS); chemiluminescence; cathodic stripping voltammetry
Nitrogen-15 ($\delta^{15}N$)	+3 to +7‰ (DIN) NO_3^- none available (DON) ~2 to +10‰ (PON)	0.1‰ 0.1‰	1/h mooring (save for on-land measurement)	IRMS
Algal pigments	0–10 mg/m^3	0.1 ng/L	1/s profiling 1/h mooring	HPLC
Oxygen	0–350 µmol/kg	0.5%	1/s profiling 1/h mooring	Amperometric electrode; fluorescence
Oxygen-18 of dissolved oxygen ($\delta^{18}O$)	+22 to +40‰	0.1‰	Measure ashore	IRMS

Analyte	Concentration (or delta value) in Seawater[a]	Present Precision	Desirable Measurement Frequency for In Situ Sensor	Present Measurement Technologies[b]
Priority 2b — Tracing Water Masses				
Chlorofluorocarbons	0-5 pmol/kg	1%	1/s profiling 1/h mooring	Electron capture gas chromatography
Argon-39	0.03-0.1 dpm/L (STP) of argon	10%	1/yr	Decay counting
Tritium	0-10 tritium units	0.01 tritium units	Measure ashore	Helium-3 ingrowth and mass spectrometry
Helium-3/helium-4 ratio (δ³He)	−15 to +500‰	1‰	Measure ashore	IRMS
Priority 3 — Other Analytes of Interest				
Minor nutrient compounds				
Zinc	0.05-10 nmol/kg	0.05 nmol/kg	1/d	Stripping voltammetry, GFAAS IDMS, fluorescence
Copper	0.5-6 nmol/kg	0.1 nmol/kg	1/d	Stripping voltammetry, GFAAS, IDMS, chemiluminescence
Tracers of air-sea interaction				
Aluminum	0.4-40 nmol/kg	0.2 nmol/kg	1/d	Fluorometry, GFAAS, GC
Lead	5-175 pmol/kg	1 pmol/kg	1/month	Stripping voltammetry, GFAAS, IDMS, chemiluminescence
Dimethyl sulfide	0.03-10 nmol/kg	0.02 nmol/kg	1/d	GC
Radon-222	4-7 dpm/100 L	0.5 dpm/100 L	1/d	Decay counting

Tracers of hydrothermal input				
Manganese	0.1-4 nM	?	1/h	GFAAS; stripping voltammetry; chemiluminescence; kinetic colorimetry
Helium-3	$\geq 7.7 \times 10^{-14}$ cc STP/g	1%	1/h	Mass spectrometry
Tracers of interactions with particles				
Thorium-234	200-2400 dpm/1000 kg	100 dpm	1/d	α spectrometry, or β, gamma counting, mass spectrometry
Thorium-230	0.05-2 dpm/1000 kg	0.05 dpm		α spectrometry, or β, gamma counting, mass spectrometry
Lead-210	0.5-25 dpm/100L	3-5%		α spectrometry, or β, gamma counting, mass spectrometry

[a] Isotope values given in delta values, not concentrations.

[b] Measurement frequencies are not necessarily met by these technologies. These are presently used technologies.

[c] kg = kilogram of seawater, L = liter of seawater.

can usually be calculated more accurately from conductivity measurements than it can be measured directly. However, in some environments, such as those existing in the deep ocean, around deep-sea hydrothermal vents, in evaporite basins, and in river plumes, the concentrations of these elements can be altered significantly. For example, the concentration of calcium changes as a result of dissolution of calcium carbonate shells in the deep ocean, by as much as 75 micromoles per kilogram seawater, or 0.75%. Hence, calcium is not conservative in deep ocean environments. In evaporative environments, the ratios of many major ions change as a result of successive precipitation of calcium sulfate, sodium chloride, potassium chloride, and other evaporite compounds. Sensors of major ion concentrations could be extremely valuable for tracing the sources and sinks of these ions. Table 2 summarizes the technologies considered in this report and how they relate to the priority analytes.

Sensors or analyzers exist for some of the priority analytes, such as O_2, pH, and NO_3^-. The challenge in these cases is to improve sensor stability, response rates, or lifetime. However, for most of the priority analytes, there is no existing sensor or analyzer system that will operate for long time periods without operator intervention. The development of sensors for most of these analytes, such as chlorofluorocarbons or dissolved iron, must circumvent the difficulties posed by low analyte concentrations or interference from other dissolved material. Development of specific sensing chemistry is the ultimate means of circumventing these problems.

Priority 1 — Quantifying the Anthropogenic Carbon Input

The carbon dioxide reservoir in seawater is presumably increasing in size in response to the burning of fossil fuels at a rate of approximately 1 micromole per kilogram per year in surface waters; increases are less in the deep ocean. The magnitude of this change could be estimated by measurements of the carbon dioxide flux into the ocean or measurements of the concentration of carbon dioxide. Measurements of the partial pressure of carbon dioxide (pCO_2) allow us to define the flux of carbon across the air-sea interface, whereas measurements of total carbon dioxide dissolved in seawater (TCO_2), the sum of CO_2 species present in seawater, allow us to assess the size and rate of change of the TCO_2 pool due to all processes. Because of the large size of the carbon reservoir and relatively small rate of increase, however, these measurements must be made with high precision and accuracy. If 50% of the fossil fuel CO_2 emission is taken up by the ocean, the globally averaged air-sea pCO_2 difference required to drive the present oceanic uptake of fossil fuel carbon dioxide should be approximately 8 microatmospheres (µatm). pCO_2 should be measured to a precision significantly better than this, for example 1 µatm, to produce useful

Table 2 Technologies for Chemical Measurements

Techniques	Analytes That Could Be Measured
Mass spectrometry	$\delta^{13}C$, $\Delta^{14}C$, iron, $\delta^{15}N$, argon-39, $^3He/^3H$, zinc, copper, aluminum, lead, manganese, ^3He, Th isotopes
Electrochemical techniques	
Potentiometry	pCO_2, pH, ammonium
Constant potential techniques at steady state	pCO_2, O_2
Pulse voltammetry	Iron, O_2, zinc, copper, aluminum, lead, DMS, manganese
Stripping voltammetry	Iron, zinc, copper, aluminum, lead, DMS, manganese
Coulometry	TCO_2, DOC, POC, ammonium
Spectrophotometry	
Absorbance	pCO_2, pH, nitrate, phosphate, iron, ammonium, zinc, copper, aluminum, lead, LMW compounds
Luminescence	pCO_2, pH, DOC, nitrate, iron, ammonium, O_2, zinc, copper, aluminum, lead, manganese
Raman	CFCs, LMW compounds
Fiber optics	DOC, nitrate, phosphate, silicate, iron, ammonium, algal pigments, O_2, zinc, copper, aluminum, lead, DMS, LMW compounds, manganese
Refractive index	Alkalinity
Piezoelectric mass sensors	DOC
New chemistry	pCO_2, pH, DOC, nitrate, phosphate, silicate, iron, ammonium, algal pigments, O_2, zinc, copper, aluminum, lead, DMS, LMW compounds, manganese, algal toxins
Chromatography and electrophoresis	DOC, nitrate, phosphate, CFCs, DMS, LMW compounds
Flow injection analysis and continuous flow analysis	pCO_2, pH, nitrate, phosphate, silicate, iron, ammonium, zinc, copper, aluminum, LMW compounds, manganese

DOC = Dissolved organic carbon
POC = Particulate organic carbon
CFCs = Chlorofluorocarbons
DMS = Dimethyl sulfide
LMW = Low molecular weight
Th isotopes = Thorium isotopes (^{234}Th and ^{230}Th)

data. pCO_2 can be estimated from pH measurements in combination with TCO_2 measurements, requiring an accuracy of 0.001 pH unit to match a PCO_2 precision of about 1 µatm. Sensors for pCO_2 and pH would be useful for long-term (>1 month) deployments to provide data about temporal variability. Stability would be of prime importance, but sampling could be less frequent (one per hour) than for profiling sensors, requiring a slower response time. If both the CO_2 difference across the air-sea interface and the gas transfer rate (which may be inferred from wind speed) were measured simultaneously, the net CO_2 flux across the sea surface could be determined. To determine a valid parameterization of the air-sea gas transfer constant, the actual rate of gas transfer should be measured simultaneously with relevant parameters, such as ΔpCO_2, wind speed, temperature difference between water and air, sea surface roughness, and possibly other factors. Measurements of TCO_2 require a precision and accuracy of better than 1 micromole per kilogram per year to be useful in detecting, within a few years, the signal of anthropogenic carbon input to the ocean from combustion of fossil fuels.

In seawater, the cationic charges of strong electrolyte species (such as Na^+, Mg^{2+}, and Ca^{2+}) always exceed the anionic charges (such as Cl^- and SO_4^{2-}) . The total ionic balance in seawater is maintained by the anions [OH^-, HCO_3^-, CO_3^{2-}, and $B(OH)_4^-$] generated by dissociation of weak acids. Alkalinity is a measure of the ionic charge imbalance of the strong electrolyte species, and hence is independent of temperature and pressure. It is changed by dilution and biological processes such as dissolution or precipitation of calcium carbonate and by utilization or respiration of NO_3^-. Its value ranges from 2200 to 2350 micromoles per kilogram in the surface ocean and ranges from 2400 to 2450 micromoles per kilogram in the deep ocean. Because the pCO_2 in surface waters and hence the air-sea partition of CO_2 is sensitive to alkalinity changes, it is one of the important quantities that needs to be monitored in global seawater.

The stable carbon isotopes, ^{12}C and ^{13}C, are fractionated in various natural processes. $\delta^{13}C$ is a measure of the per mil deviation of the $^{13}C/^{12}C$ ratio from that of a Pee Dee Belemnite (PDB) limestone standard. The photosynthetic pathways (C-3 and C-4) fix the lighter carbon isotope (^{12}C) preferentially, so that $\delta^{13}C$ values of plant samples are 6 to 23% less than those of the original CO_2 Pools, $^{12}CO_2$ preferentially passes across the air-sea interface into the atmosphere, so that TCO_2 in the surface ocean has $\delta13C$ values about +1 to 2%. Because of the release into the atmosphere of fossil fuel CO_2 (ancient plant material) with a $d^{13}C$ of about-27%, $d^{13}C$ values for atmospheric CO_2 decreased from-7.5% in 1978 to-7.8% in 1988. Likewise, average $d^{13}C$ values for CO_2 dissolved in surface ocean waters decreased from about +2% to +1.6% during the past 20 years. This information has been used to put limits on global CO_2 budget calculations

by Quay et al. (1992). To be useful to estimates of the anthropogenic CO_2 uptake by the ocean, the ^{13}C measurements must be extremely carefully standardized. The isotope ratio is measured using isotope ratio mass spectrometry with a precision of about 0.04% in the $\delta^{13}C$ unit. Control of isotopic standards must be better than 0.05%.

Measurement of the levels of naturally produced [14]C (half-life of 5730 years) in both dissolved CO_2 and organic carbon allows the estimation of long-term turnover in the ocean. [14]C produced through atmospheric testing of nuclear weapons nearly doubled the existing natural levels of ^{14}C in the atmosphere in the late 1950s and early 1960s. Bomb-produced ^{14}C provided a spike tracer to observe short-term turnover of carbon within the CO_2 and organic pools. At present, ^{14}C in DOC is measured on carbon dioxide produced by oxidation of seawater DOC using ultraviolet radiation or high-temperature catalytic oxidation. [14]C in POC is measured on carbon dioxide produced from closed-tube combustion techniques. The [14]CO_2 evolved from these small samples is measured using accelerator mass spectrometric techniques with a precision of 0.4 to 2%. Better precision is needed, especially for deep-ocean samples in which the bomb ^{14}C signal is smaller.

Priority 2a — Understanding the Biological Pump

The combined activity of planktonic organisms in the ocean (phytoplankton, protozoans, zooplankton, viruses, and bacteria) results in the fixation of dissolved carbon dioxide and nutrients into organic matter in the ocean surface layer and the export of some fraction of the fixed carbon downward. This process, the biological pump, is responsible for maintaining the gradient of increasing TCO_2 with depth in the oceanic water column. It is necessary to improve our capability for measuring the spatial and temporal distributions of a variety of chemical compounds, to gain a better understanding of how the biological pump operates, and to be able to predict future changes in the ocean carbon cycle.

Biological activity in the upper and deep ocean results in the formation and breakdown of particulate and dissolved organic carbon and nitrogen (POC, PON, DOC and DON). Particulate organic carbon levels in surface waters of the open sea range from about 0.5 to 50 micrograms carbon per kilogram seawater. The degree of cycling of organic material in the surface ocean and the downward flux is still only poorly known. There is a slow fallout of material to the bottom year-round, with seasonal pulses in areas underlying surface zones of high primary productivity. Presently, organic material can be measured only in discrete samples. New approaches for measuring these compounds at greater frequencies are needed.

Concentrations of dissolved organic carbon in open ocean waters are low (35 to 200 micromoles carbon per kilogram seawater). Despite the low

concentration, the mass of DOC in the ocean is about half as large as the pool of carbon in terrestrial biomass and comparable in size to all the carbon dioxide in the atmosphere. Transformations in the size and composition of this DOC pool have the potential to alter the balance of the global carbon cycle. However, we do not yet have an accurate estimate of the mass of DOC or a detailed understanding of what controls its rate of turnover, much less its composition or function in microbial food webs. There is not yet a generally accepted analytical method to characterize DOC, although there is much interest in improving high-temperature combustion methods using discrete samples. For precise determination of the oceanic carbon pool, DOC sensors and analyzers must be capable of producing data of high accuracy and precision (1%) in the oceanic concentration range. Moored sensors capable of operating for periods of weeks to months are desirable because DOC concentrations may change dramatically during algal blooms, for example. Identification and measurement of specific components of DOC are as important as measuring total DOC. This approach will require basic research into DOC composition, which may also be aided by new measurement technologies.

There is also a great need to measure DON with accuracy. DON is the primary form of nitrogen in much of the surface ocean and may limit phytoplankton production in many areas. The difficulty in measuring DON is largely analytical, and accurate values for deep water will only be obtained after new direct DON methods are developed. Measurement of certain forms of DON is probably more important for understanding the global carbon cycle than is knowledge of concentrations for most trace metals.

The major plant nutrients (nitrate, phosphate, silicate, and ammonium) that support primary production should be measured from once to several times daily over periods of months to a year, or continuously from ships, at a precision of 0.01 micromole per kilogram. The use of these nutrients varies by phytoplankton species. Nutrients can be supplied by mixing and flow from underlying water masses and by regeneration of nutrients through the action of bacteria and herbivores. The ability to predict the timing and strength of phytoplankton blooms depends on an understanding of the effects of nutrient supply and physical factors (such as water density gradients and turbulence) on primary production.

Iron, an important plant micronutrient, is adsorbed rapidly onto particles and becomes unavailable for uptake by phytoplankton. The major source of iron to the ocean is in the form of atmospheric dust. Relatively little is known about the temporal variability of total iron in surface waters, but available data suggest that measurements with a precision of 20 picomoles per kilogram or better might be required. Almost nothing is known about iron speciation [Fe(II), Fe(III)], although the hydrolyzed product of Fe(III) is the stable form. Because algal productivity varies daily, season

ally, and annually, understanding primary production requires that measurements be made with appropriate frequency to describe the variability at each of these time scales.

The fractionation of nitrogen-15 versus nitrogen-14, as designated by d^{15}N, can provide information about biological processes involving nitrogenous compounds because such processes fractionate these two stable forms of nitrogen. Techniques for measuring δ^{15}N natural abundance in nitrate, ammonium, and particulate matter with a precision of 0.1 δ unit are needed.

Phytoplankton contain a wide array of pigments in addition to chlorophyll, and pigment concentrations, types, and ratios are often specific to certain taxonomic groups. Thus, sensitive detection of individual pigment types with a precision of at least 0.1 nanogram per liter can provide information on phytoplankton community composition. More accurate, widespread, and frequent measurements of phytoplankton pigments are also needed to validate satellite estimates of plant biomass. In recent years, flow cytometry has been adapted from medical use to sort and count phytoplankton cells containing different pigment types, increasing the level of information about phytoplankton communities. Knowledge of pigment concentrations is necessary to study the coupling of primary productivity with higher levels of the oceanic food web, such as the productivity of marine fisheries.

Oxygen accumulation in the sunlit upper water column is a reflection of net primary production. Oxygen is produced as part of the photosynthetic process and consumed by respiring organisms. To be a useful indicator of primary production and respiration, oxygen must be measured with a precision of 0.5% or better against a background concentration of 350 micromoles per kilogram in surface waters, at a frequency of about 10 times per day.

Priority 2b — Tracing Water Masses

Chlorofluorocarbon (CFC) compounds (Freons®) are important tracers of ocean circulation. Since CFC-11 and CFC-12 were released at different rates, their concentrations as well as their ratios can be used to determine when a water mass left contact with the sea surface over the 50 years since Freons® were released into the atmosphere and taken up by the ocean. CFC-113 and carbon tetrachloride are being investigated as additional tracers. Picomole levels of CFCs dissolved in seawater are determined using a gas chromatograph equipped with an electron capture detector. The World Ocean Circulation Experiment (WOCE) Hydrographic Program calls for measurements with a precision and accuracy of 1% and a detection limit of 0.005 picomole per kilogram (Sarmiento, 1988).

Argon-39 is a cosmogenic isotope that is chemically inert and has a radioactive decay half-life of 269 years. Because it is excluded from bio

logical cycles and its decay half-life is roughly comparable to the time scale for global ocean circulation, it is suited for studies of ocean circulation rates. However, because of its low concentrations in seawater (0.03 to 0.1 dpm per liter of argon gas at standard temperature and pressure), a seawater sample of about 1000 liters is needed to provide enough argon for a determination with a 10% precision, counted over several months. Thus, only a few measurements are made per year. A more rapid analytical method is needed.

Helium-3 is a decay product of radioactive tritium (^3H, half-life = 12.44 years) that has been produced by nuclear bombs as well as naturally by cosmic rays in the upper atmosphere. Because virtually all ^3He atoms escape from the surface ocean to the atmosphere, the ^3He/tritium ratio in subsurface seawater samples indicates the time since the water's last exposure to the atmosphere. Both ^3He and tritium are measured by gas mass spectrometry. Alternatively, tritium may be measured by gas counting with a detection limit of 0.05 to 0.08 tritium unit, where 1 tritium unit represents a $^3H/H$ ratio of 1×10^{-18}. A degassed water sample is sealed and stored for several months to allow the decay product ^3He to accumulate in the container. The amount of ^3He is then measured by mass spectrometry, yielding a detection limit of 0.001 to 0.003 tritium unit when 400-gram water samples are used. With this technique, the time since a water mass left the surface can be determined within a range from several months to 30 years.

Priority 3 — Other Analytes of Interest

Analytes in this category are not necessarily related to the carbon cycle, but are of interest to chemical oceanographers. Improvement in technologies to measure these analytes could advance the ability of chemical oceanographers to study how Earth systems function.

Several elements, particularly zinc and copper, could play a role as trace nutrients for phytoplankton. They are known to be important for growth of terrestrial plants, but neither the requirement for these nutrients nor the elemental distributions in seawater are well known. The biological availability of both zinc and copper is controlled by their complexation with organic material. Analytical methods that have the distinction of being able to discriminate chemical forms of the metal are needed. These measurements reflect the chemical reactivity and biological availability or toxicity of the metal more accurately.

The transfer of particles and gases between the ocean and the atmosphere is an active area of research. Information from studies of air-sea transfers is crucial for putting boundaries on models of global cycles of carbon and other biologically important elements. Aluminum and lead are delivered to the surface ocean, primarily on windborne particles, so that

concentrations of these elements can be a measure of windborne particle transport. Dimethyl sulfide is produced in the surface ocean and released into the atmosphere. In order to investigate the circulation rate of oceans and air-sea gas transfer rates in localized areas, inert compounds (such as SF_6) that can be detected in minute quantities have been injected into surface as well as deep oceans. SF_6 is an ideal tracer because of its low solubility in water (hence it does not alter the density of seawater significantly), lack of a natural source, and high detection limit (10^{-12} mole by gas chromatograph equipped with an electron capture detector). SF_6 has been injected into water masses of a desired density to investigate their lateral and vertical mixing rates. Use of tracers purposely injected into the ocean will become more common in the future. Because noble gases present in seawater (helium, neon, and argon) are excluded from biological cycles, they often serve as useful tools in oceanography for tracing physical mechanisms and processes. The difference in the ratios of these gases, as well as nitrogen, in air and in surface ocean water has been used to study air-sea gas transfer mechanisms, such as air injection via gas bubbles. Other noble gases, such as radon-222 (having a half-life of 3.8 days) produced in water or in sediments from the uranium decay series have been used to estimate the material transfer rate across the air-sea or sediment-water interfaces. Helium has been injected into surface waters with SF_6 in order to investigate the gas transfer rate in open oceans. Krypton-85, having a half-life of 10.67 years, is released into the atmosphere from nuclear fuel refineries and nuclear weapons factories. It has been used as a tracer of large-scale atmospheric circulation, as well as ocean water circulation.

Tracers of photochemical reactions include low-molecular-weight compounds, such as formaldehyde, pyruvate, and acetylaldehyde. The rates of these photochemical reactions are important to measure so that natural degradation of DOM can be quantified. Also, their variability due to increased ultraviolet radiation (from decreases in tropospheric ozone levels) should be studied. The ChemRawn IV conference had a major focus on photochemical reactions (Goldberg, 1988).

Since the discovery of widespread hydrothermal activity on the seafloor and plumes of altered water in the water column, it has become obvious that circulation of seawater through both high-temperature and low-temperature rocks can add or remove elements, potentially affecting global balances of some elements. For example, dissolved manganese concentrations in open-ocean seawater are as low as 0.2 nanomole per kilogram, but concentrations can be as high as 10 millimoles per kilogram in hydrothermal environments. ^{3}He is enriched in hydrothermal plumes and can be used as a tracer of the volume of hydrothermal fluids and their dispersion away from their source. Sensors with high response rates (>10 measurements per minute) would be useful for determining the spatial distribution of manganese.

Many trace metals are removed from the oceanic water column through adsorption to particle surfaces or incorporation in biological particles. Adsorbed radioisotopes allow oceanographers to study particle transport phenomena. The naturally occurring isotopes of thorium, as well as lead-210, are particularly useful for these studies.

PRESENT STATUS OF MEASUREMENTS

Most analyses consist of four operations—sampling, pretreatment, calibration, and detection. These operations are combined in chemical sensors. For *in situ* measurements, the transducing device or sensor is brought to the sample, rather than a sample being transported to the sensor. In general, most chemical analyses benefit from minimal sample manipulation, making *in situ* measurements preferable to ship-based measurements, which in turn are usually better than those in which the sample is brought back to a land-based laboratory. Conversely, the difficulties of performing chemical analyses multiply as the analytical method and instrumentation are brought from land-based laboratories to ships, and perhaps ultimately incorporated into an immersible device. In performing chemical analysis of seawater, several factors determine the desirability and feasibility of performing the analysis *in situ*, on board ship, in land-based laboratories, or remotely from a satellite or aircraft. These issues are summarized below.

Of course, all chemical analyses may be performed in a land-based laboratory, but there are several reasons for not taking this approach. Ships can only collect a limited number of samples because of time, expense, sea state, and space limitations. Samples from field sites are necessarily brought back in some form that may be altered (e.g., adsorb to or desorb from walls of container). Microorganisms present in samples may, by their metabolism, affect the concentration of the analyte of interest for long periods after the sample is collected, unless metabolic processes can be stopped by sterilization or poisoning of the samples. The sterilization procedure must not affect the analyte of interest. In addition, the composition of a seawater sample can be changed by photochemistry if it is exposed to light. As water samples collected from great depths are depressurized, the equilibria of dissolved gases and speciation of ions change. Procedures have been developed to minimize these negative effects. A possible alternative for some analytes is to deploy a sample collector, rather than a sensor, remotely. If samples could be stabilized, the sampling platforms could be deployed for months, perhaps, and recovered later for sample processing. In addition to these purely chemical issues, it is nearly always useful to achieve rapid analyses of samples to guide further sampling. If samples are not analyzed until later, flaws or bias in the sampling technique will not be evident until

it is too late to resample or to alter the sampling technique for the remaining samples.

Despite these caveats, many analyses are done on land either because the sample can be stored without changing the concentrations of the analytes it contains or because the apparatus required for the analysis cannot be operated on board a ship. For instance, some radionuclides are measured on land for both reasons. Samples analyzed on land can be spiked immediately with another (artificial) isotope of the same element to fill the adsorption sites on container walls and to serve as an internal standard. The mass spectrometers required for isotope ratio analyses are often too sensitive to vibration and motion for shipboard use. Analytes present at greater than trace levels, or which can be stabilized with some pretreatment, may also be analyzed successfully on shore.

The barriers to introducing some analytical techniques for shipboard use can be daunting, particularly those requiring complicated equipment; even simple tasks like weighing chemicals on a balance or reading a buret can be challenging when the seas are rough. Presently, most shipboard chemical analyses are carried out with instruments not designed for shipboard use. Instruments designed for use on ships must endure a humid, corrosive atmosphere; withstand shock and violent motions of the ship; survive greater extremes of temperature than in the usual laboratory; and function with limited and poor quality power and water supplies. Approaches to develop new instruments will need to include not only chemistry but also physical engineering and design to make the shipboard environment less daunting for chemical instrumentation. Better ships and power systems are needed. These problems affect not only the instrument itself but also any computers that control the instrument or collect the data it generates. This is increasingly important, as many oceanographers take part in research cruises that originate in ports distant from their home institutions and may have to take their own specialized equipment with them. At times, it is most convenient to package an entire laboratory in a standard shipping container, which may be transported to the ship and carried as deck cargo. Some common "utilities" found in chemical laboratories, such as fume hoods and gas lines, are not routinely used on ships. In addition, it should be noted that shipboard conditions are often suboptimal for the human operators of the instrumentation as well; seasickness affects the efficiency of many scientists at sea.

The above information demonstrates why some analytical techniques are seldom or never used at sea. For instance, the large gas lasers typically used in ultrafast and Raman spectroscopy are fragile, require 500-volt three-phase power, and must be cooled by a significant flow of fresh water. Yet despite these limitations, nearly all types of analytical techniques have been used at sea in some form, including electrochemical techniques, absorption

and emission spectroscopies, optical and electron microscopies, as well as classical titrations and manometry. In fact, most types of analytical chemical determinations on seawater samples have been performed on board ships. However, the majority of shipboard analyses are "routine" analyses, such as measuring oxygen by Winkler titration and nutrients by colorimetry. Almost all metal, isotope, and organic carbon analyses are carried out on land. Shipboard techniques are compromises between the need to process many samples rapidly and the cost and difficulty of performing analyses at sea, as compared with land-based laboratory measurements.

For many of the same reasons that measuring analytes at sea is preferable to returning samples to land, it is desirable to measure analytes *in situ*. An additional benefit of using *in situ* sensors is the potential savings in labor cost per sample. In general, adapting chemical analyses for use in the ocean is much harder than adapting methods and instrumentation for shipboard use. Even simple devices must be completely redesigned. Power and data transfer are often problems when the apparatus is at the end of miles of cable. High-density data storage makes real-time data transfer technically unnecessary, although transfer may be required for scientific purposes, as for real-time modeling and prediction. Adequate power remains a problem, however. Pressure-proof housings are available, and electrodes and windows can be engineered, but other limitations exist. In particular, even the simplest mechanical manipulations of solutions, such as dispensing, mixing, and titration, are difficult to automate. Various approaches have been used to circumvent these problems. Laboratory robots have been used in land-based laboratories for multistep analytical procedures, but adaptation for shipboard, and especially *in situ*, applications will not be possible in the near future.

Perhaps the most important new approach to chemical measurements has been the use of sensors for oceanic chemistry. Sensors comprise a transducer and its supporting electronic instrumentation. The key feature of sensors is their ability to monitor the concentration of a particular analyte continuously, so that the dimension of time can be added to the traditional three dimensions of spatial measurements. An example of a sensor is a pH electrode, coupled with a high-impedance voltmeter and a means of standardization and temperature compensation *in situ*. In principle, such a sensor can monitor pH continuously for days at a time while transferring the data to a recorder or memory device. One can contemplate towing an array of sensors at various depths simultaneously, obtaining three-dimensional continuous data sets, improving on the two-dimensional data available from vertical profiles. Most sensors must be calibrated regularly.

For *in situ* measurement, the foregoing discussion has implied the use of profiling devices lowered from stationary surface vessels or towed behind moving vessels. Yet the problems created by currents, weather, and

high-sea states in deploying instruments from surface vessels (and successfully retrieving them) has prompted development of other platforms. In particular, the mechanical problems in deploying a device 1 kilometer deep in the ocean are caused more by the drag of the 1000-meter cable than by the weight of the instrument itself. Thus, other strategies have been used to bring the analysis to the sample, including unmanned underwater vehicles, buoys, and manned submersibles. At present, for unmanned submersible vehicles, the problems of autonomous operation, navigation, small size, power requirements, and reliability overshadow the advantages of cable-free operation, but solution of these problems will eventually make wider use of these devices likely. There have been significant advances over the past decade in the development of optics and electronics for underwater vehicles, including remotely operated vehicles (ROVs). These systems provide the opportunity for optical observations, as well as acoustical and chemical measurements by appropriate instruments attached to the ROV.

Buoys, on the other hand, are already widely used for many sorts of physical oceanographic measurements, and the development of new sensors would allow buoys to be important platforms for chemical and biological oceanographic measurements as well. Their capabilities for long-term unattended operation, even in environments as hostile as the Arctic, are well demonstrated. Issues in the use of buoys are the availability and reliability of sensors, and electrical power sources. However, modest sampling frequencies (e.g., 1 to 10 samples per day) would enable them to operate from solar energy and batteries. Newly developed methods for data storage and on-board processing will allow greater data storage before retrieval. Data transmission from sensors to satellites is still a limiting factor, however.

Aircraft and Satellites

Although not well suited for chemical oceanography per se, satellite-and aircraft-based remote sensing is a growing adjunct to direct chemical measurements. Despite their limited sensor suites, satellites offer unsurpassed volumes of data covering vast areas of the ocean, virtually in real time. Moreover, the nature of orbits is such that the same measurement may be repeated over the same section of ocean for years at a time, which is very useful for evaluating long-term variability. Satellites primarily conduct passive sensing of electromagnetic radiation in the visible, near-infrared, and microwave frequencies. In addition, specialized satellite radars actively measure mean surface height and sea state. Sea surface temperature may be determined very precisely from satellites, providing additional physical oceanographic information. Physical oceanographic information is an important adjunct to chemical and biological measurements because temperature affects chemical reaction rates, gas solubilities, and organism growth.

Sea state affects gas transfer by changing the sea surface area due to waves and entrained bubbles.

Passive satellite measurements of reflected intensity at visible wavelengths allow mapping of ocean color. Ocean color is dominated by the amount of chlorophyll and phaeopigments present, which in turn can be related to primary productivity. Ocean color is also an important indicator of the presence or absence of nutrients and various physical oceanographic phenomena.

The major constraint to using satellite remote sensing is the relative opacity of the ocean and clouds to electromagnetic radiation. Thus, satellite measurements are limited to the very top layer of the ocean and usually provide little evidence about processes occurring below the ocean surface.

Their high cost has limited the number of satellites launched for ocean observations. Among them have been the U.S. Navy's Seasat and Geosat. In addition, the Landsat series, the Earth Resources Satellite-1, TOPEX/Poseidon, INMARSAT maritime communications satellites, various weather satellites, the Global Positioning System satellites, and the Argos transponder have all greatly aided ocean science in general, if not chemical oceanography in particular. A number of other satellites will be launched in the next 5 years to monitor physical and biological oceanographic conditions. Despite this limited variety of sensors, satellites are an indispensable tool for oceanography.

Aircraft can perform almost all the measurements that satellites can, but on a more limited spatial scale. Some additional measurements can be made from aircraft that cannot be made from satellites. For example, several aircraft have been used as platforms for remote laser-based spectroscopies (lidar), using wavelengths that are strongly attenuated by the atmosphere (e.g., ultraviolet) and therefore not practical for satellites. Also, an aircraft can determine whether ships are in the way before turning on a potentially hazardous laser beam. Although, in principle, aircraft can scan very wide areas of the ocean (e.g., 80,000 square miles per hour in an SR-71 aircraft flying at greater than 70,000 feet altitude), in practice for optical studies they often operate at lower altitudes to minimize attenuation and scattering, and consequently have a much reduced "footprint." In comparison with ships, however, their enhanced capabilities are substantial. One shortfall in existing aircraft is their relatively limited range and the limited time available to make measurements. Aircraft built for maritime surveillance, such as the NASA P-3 aircraft, can spend only a few hours over mid-ocean areas; even large jet transports have less than 15 hours endurance. As a result, aircraft are widely used primarily for coastal monitoring rather than for the open ocean. A notable exception was the use of aircraft passes concurrent with ship-based sampling in the 1989 Joint Global Ocean Flux Study North Atlantic Bloom Experiment. Whereas a research vessel might cost $10,000

to \$20,000 per day to operate, aircraft costs approach \$48,000 per day for a modest-sized jet transport.

As noted above, aircraft can perform active optical spectroscopic measurements remotely. Potential spectroscopic techniques include fluorescence, Raman, and Rayleigh scattering measurements. Pulsed lasers can, in principle, provide depth resolution in the same manner as the range gate in a monopulse radar. Adequate power and cooling can be provided on board aircraft, but alignment and stability of optical devices remain problems. The cost and difficulty of developing instrumentation for airborne use is thus at least equal to that of developing shipboard devices, because airborne systems are also constrained by weight and size limits. Moreover, the available optical techniques remain limited in the chemical analytes that may be sensed because they are remote methods.

THE IDEAL IN SITU SENSOR

Sensors can be based on a variety of transduction mechanisms, including electrochemical, optical, mass, and thermal. Different types of sensors, along with their transduction mechanisms, will be discussed later in this report. All sensors possess a transduction element connected to supporting instrumentation. Selectivity is achieved via the transducer. The qualities of an ideal sensor obviously depend on the application, with different qualities necessary for sensors used in shipboard laboratories, towed sensors, or sensors deployed on long-term remote moorings. Depending upon the specific application, sensors should possess the following qualities.

- Manufacturable in large quantities. Handcrafted, one-of-a-kind sensors cannot hope to gain the acceptance necessary for routine implementation by ocean scientists. Sensors must be reasonably consistent in their performance characteristics. Moderate-to large-scale manufacturing processes applied to sensor fabrication will assure this type of consistency.
- Cost effective. Many instruments are expensive, yet the scope of the ocean measurement problem ideally is addressed by making many continuous measurements with a large number of instruments. The likelihood of deploying many instruments increases with decreasing cost.
- Fully automated. In order to be deployed for unattended operation, sensors must be fully automated. This automation pertains principally to the supporting instrumentation necessary for operation of the sensor and for signal processing. Power requirements, on-board data handling, and data storage must all be configured appropriately for the particular application. It is desirable, but not required, that sensors and supporting instrumentation be able to transmit data via telemetry to receivers on satellites, ships, or land.

- Stable and long lasting. Most sensors will depend upon a chemically selective layer attached to an appropriate transducer element. The system of chemical reactions contained within the selective layer must be stable or reversible or, if irreversible, be based on a renewed or continuously delivered reagent that maintains the ability of the sensor to detect the desired analyte.
- Calibrated. In order for sensors to gain acceptance as deployable measurement tools, they must remain calibrated for extended periods of time (weeks to months) or must be self-calibrating.
- Resistant to environmental conditions. After deployment, sensors must be resistant to mechanical shocks from waves and be insensitive to, or compensate for, changes in temperature, pressure, salinity, and biofouling that they will invariably encounter in the ocean environment. Biofouling and corrosion are major problems for instruments that are deployed for long periods of time. Appropriate sensor and instrument design, as well as selection of appropriate materials compatible with such a harsh environment, must be taken into account.
- Selective. Sensors should have minimum interference from nonanalyte parameters such as temperature, ionic strength, pressure, and other chemical species not being measured. One route to successful sensor design will rely on the identification of appropriate and selective recognition chemistry.

Technologies for Chemical Measurements

As part of its deliberations, the committee estimated the ease of implementing the chemical technologies described below for *in situ* applications (Table 3).

MASS SPECTROMETRY (FENN ET AL., 1990)

Mass spectrometry (MS) is useful for a variety of purposes in environmental monitoring and research, including characterization of proteins, distinguishing among sources of compounds by the ratios of various isotopes (e.g., $^{13}C/^{12}C$), and measurement of heavy metals. MS is critical for reconstructing the pathways of carbon flow in marine systems. Construction of carbon budgets, recognition of controls on the carbon cycle, and calibration of a CO_2 paleobarometer are also important in studies of Earth history. Success in all these studies depends critically on the development and wide availability of adequate MS instrumentation. Due to natural fractionations of stable isotopes, compounds produced in various groups of organisms have slightly different isotopic compositions. Individual compounds are "isotopically labeled" at their source. These natural labels can be followed through the marine carbon cycle, and effects of secondary processes can be dissected in detail. In the past, all those intercompound differences were invisible because the available methods required samples so large that preparative isolation of individual compounds for isotopic analysis was impractical. Recently, however, isotope ratio monitoring techniques have been developed. For analysis of individual organic compounds, the effluent of a

high-resolution gas chromatograph is routed to a microscale combustion furnace. In turn, the products of combustion (principally CO_2, but also N_2) are led to the ion source of an isotope mass spectrometer. As the bursts of gas from the combustion of individual chromatographic peaks pass through the ion source, the relative abundance of ^{13}C or ^{15}N can be measured with a precision of about 2 parts in 10,000, good enough to observe natural variations. The entire system operates under conditions of continuous flow, so hundreds of measurements can be made within a single chromatographic run. Determining the sources and fates of individual organic compounds will be a major theme in marine organic geochemical research in the future, and its dependence on MS instrumentation is extreme. Marine laboratories in other countries are quickly entering this area, but laboratories in the United States are experiencing difficulty in finding funding to purchase the necessary instrumentation.

TABLE 3   Analytical Technology Applied to *In Situ* Measurements

Chemical Sensing		Sample Processing		Data Analysis, Interpretation	
D	Mass spectrometry	S	Chromatography/electro- phoresis separations	E	Chemometrics
E	Electrochemistry			E	Communications
E-S	Fluorometry	E	Flow injection analysis/ continuous flow analysis	E	Data storage/handling
E	Absorption spectroscopy				
D	Raman spectroscopy	D	Robotics		
D	Fourier transform infrared spectroscopy				
S	Refractive index				
D	Satellite				
D	Piezoelectric mass sensing				
E-S	Immunochemistry/bio- chemistry				
S	Polymers/new materials				
D	Recognition chemistry				

D = Difficult—Unlikely to see widespread application to *in situ* measurements in the next 15 years.
S = Straightforward—With some investment, could see application in 5 to 15 years.
E = Easy—No major technical barriers to application between now and 5 years hence.

A mass spectrometer is a device in which a sample is ionized and the ions are sorted and counted on the basis of their mass-to-charge ratios. Ions can be formed by several methods. A recently developed method, in which an ion beam sputters a nebulized liquid vapor, leaves molecules with multiple negative or positive charges. This permits the identification of very large molecules. Also, solid samples of molecules with masses of up to 300,000 daltons can be vaporized from surfaces using lasers with wave

lengths matched to the absorption wavelengths of the molecules. Mass analysis can be performed on the resulting ions using a variety of techniques, including: electrostatic, magnetic, double focusing, quadrupole lens, ion trap, time of flight, and Fourier transform ion cyclotron resonance. These methods have potential relevance for marine chemistry, but must circumvent the extreme difficulties of measuring materials dissolved in seawater.

MS can be used for characterizing dissolved organic material (DOM) in seawater and in surface films and particulate organic material (POM) and dissolved material associated with sediments. As organic matter can serve as binding sites for trace metals, DOM identity and concentrations must be known to understand trace metal kinetics in seawater. Characterization of oceanic DOM is also important for a better understanding of biological processes. At present, most of the dissolved organic compounds found in seawater are unidentified. Carbohydrates and proteins, measured as total (free plus combined) hydrolyzable amino acids and sugars, constitute 5 to 20% of the DOM. Other components, such as lipids and low molecular weight organic compounds (e.g., formaldehyde and pyruvate), occur at much lower concentrations. Another identifiable organic constituent of seawater is DMSP [dimethylsulfonio-propionate, a precursor of dimethyl sulfide (DMS)]. DMSP is an important source of DMS to the atmosphere, having a role in formation of cloud condensation nuclei. With the MS systems available now, several thousand different molecules could be identified in seawater in land-based laboratories. A remaining problem is to isolate these compounds, which are present at concentrations many orders of magnitude more dilute than the major dissolved constituents of seawater. Emphasis should be placed on solution of basic problems of collection and purification of substances dissolved in seawater.

Many investigators are using MS to characterize the structures of organic compounds obtained from marine particulate organic matter from sediment traps and from suspended particulates. The origins and alteration of this material are of great interest, and the molecules within it are generally susceptible to structural analysis. There is a great need for advanced instrumentation in this area, particularly for MS-MS systems. American laboratories are generally falling behind those in other countries in equipping for these techniques.

Combinations of chromatography and MS are useful for oceanography. Gas chromatography combined with MS is a mature technique for analyses of complex mixtures and isotopic analysis. Liquid chromatography can be combined with MS to examine polar, labile substances without chemical derivatization, and is already applied in a variety of marine laboratories. This technique is sensitive enough to detect analytes in the picomolar range. Another application of MS is in combination with capillary zone electro

phoresis. Efficient chromatographic separation can be achieved with this combination.

These methods are ready to use now for land-based applications, but are expensive. Oceanographers are aware of many MS methods, but because of the cost, such methods are not readily available. This problem could be solved by a time-sharing arrangement or the development of national facilities. Mass spectrometers are in general too bulky and require too much stability and power to be used on board ocean-going vessels. Quadrupole mass spectrometers are sometimes taken to sea, however, for various biological experiments, such as studies of respiratory gas exchange by marine organisms. With further advances in ion traps, more MS devices may be used on board ships. Unfortunately, the only way to determine analytes quantitatively is to calibrate the equipment with identical, isotopically labeled molecules. New developments, particularly using internal standards in chromatographic combinations, may alleviate this problem.

Accelerator mass spectrometry (AMS) is now being applied to measure the age of carbon in seawater. AMS is revolutionizing the measurement of light isotopes such as ^{14}C in dissolved CO_2 as well as DOC in seawater, requiring as little as a few hundred milliliters of sample. The older beta decay counting methods required 150-liter samples that were difficult and expensive to obtain. An AMS facility began operating at the Woods Hole Oceanographic Institution in 1991 at a cost of several millions of dollars. Seawater samples collected by the WOCE program will be analyzed in this facility. This AMS facility may also eventually be used for measuring ^{10}Be for marine geology research.

Inductively coupled plasma-mass spectrometry (ICP-MS) is revolutionizing the measurements of refractory metals, such as titanium, and can provide a wealth of isotopic information that could only be obtained previously with great difficulty. ICP-MS has been used as a fast and sensitive technique for measuring ^{230}Th in marine sediments (Shaw and Francis, 1991) and barium in seawater (Klinkhammer and Chan, 1990). For the future, advances in the capabilities of mass spectrometers can be expected (Table 4), developed by interdisciplinary groups of academic, government, and industry scientists. It is unlikely, though not impossible, that MS techniques will be appropriate for buoy development.

ELECTROCHEMICAL TECHNIQUES

This section focuses on techniques designed to probe the interaction of an electrode with a seawater sample, especially those that derive a signal from oxidation-reduction reactions. From the point of view of measurements important to chemical oceanography and ocean science, the following electrochemical techniques have the most likelihood of application in the

near future: potentiometry, constant-potential techniques at steady state, pulse voltammetry, stripping voltammetry, and coulometric titrations (see Whitfield and Jagner, 1981, for review).

Table 4 Expected Advances in the Field of Mass Spectrometry

	1991	1996	2006
Overall sensitivity of detection	1–100 picomoles	1–100 femtomoles	Attomole
Molecular Weight			
Laser matrix time of flight	300,000 daltons	10^6 daltons	
Electrostatic quadrupole	130,000 daltons	10^6 daltons	
Time of flight	<500 daltons	10,000 daltons	
Electrostatic-sector	>3000 daltons	>10,000 daltons	
LC-MS			
Flow probe	5–50 picomoles		
Sector	<1200 daltons		
	~5000 daltons		
Flow electrostatic quadrupole	<1 picomole	Femtomole	
Electrostatic-ion trap	~3000 daltons		

Of these, potentiometry employs the simplest instrumentation, in that it requires only an electrometer for measurement of the potential difference between the sensing electrode and a reference electrode. The other techniques additionally require a current source and control circuitry, usually packaged together as a potentiostat. Coulometric techniques also require a means to determine charge, which is often done by incorporating an electronic integrator into a potentiostat. The technology of modern electronics provides for these purposes robust and inexpensive instruments, many of which include microprocessors suitable for controlling the experiment and manipulating the resulting data.

Potentiometry (Buck, 1984)

The potential of an electrode is related directly to the activities, and thus indirectly to the concentrations, of the chemical species involved in the equilibria that establish the potential. The main virtues of potentiometry are simplicity, very low power requirements, and the possibly small size of the sensors. The main drawback is that an unwanted reaction may enter into determination of the potential and sensitivity may be poor. Potentiometric sensing, as a transducing technique, can be coupled with an infinite variety of novel chemical reactions to solve specific analytical problems, as described below in the section on new chemistry. A wide variety of potentiometric ion-selective electrodes (ISEs) already have been developed (see

Table 5), and several are now being used, or are potentially useful, for measuring key ocean elements. The most common use of direct potentiometry (as compared with potentiometric titrations) is for measurement of pH (Culberson, 1981). Most other cation electrodes are subject to some degree of interference from other major ions. Electrodes for sodium, potassium, calcium, and magnesium have been used successfully. Copper, cadmium, and lead electrodes in seawater have been tested, with variable success. Anion-selective electrodes for chloride, bromide, fluoride, sulfate, sulfide, and silver ions have also been tested but have not yet found wide application.

Table 5 Potentiometric Ion-Selective Electrodes

Glass
H^+, Na^+
Solid State
Silver sulfide-based pressed pellet type—Ag^+, S^{2-}, Cd^{2+}, Cu^{2+}, Pb^{2+}, I^-, Br^-, Cl
Single crystal-F^-(LaF_3)
Organic Membrane (Liquid or Polymer)
Ion exchanger or charged carrier—NO_3^-, Cl^-, Ca^{2+}
Neutral carrier—K^+, Ca^{2+}, Li^+, Na^+, Mg^{2+}, H^+, CO_3^2

New polymer membrane-based ISEs for nitrate and carbonate exhibit detection limits and selectivities that may be applicable for ocean measurements. In addition, a number of these ISEs can be used as internal transducers for the design of useful potentiometric gas sensors. For example, dissolved CO_2 can be detected potentiometrically by using either a glass membrane electrode or a polymer-based carbonate ISE, in conjunction with an appropriate reference electrode, behind an outer gas permeable membrane. Novel differential pCO_2 sensors based on two polymer membrane-type pH sensors have also been developed recently.

Constant Potential Techniques at Steady State

Electrochemical detection under convective conditions has been applied widely in freshwater measurements. In addition, seawater measurements have been combined with flow injection analysis (FIA) and high pressure liquid chromatography (HPLC) (D.C. Johnson et al., 1986). Well-developed commercial product lines exist, and detection limits are typically in the range of femtomoles. For *in situ*, shipboard, and land-based measurements employing HPLC or FIA, electrochemical detection could provide increased capabilities with respect to compound-specific detection and improved detection limits. The limitations of this approach are determined completely by the requirements of FIA or HPLC.

The use of microelectrodes for steady-state measurements is less well developed but has special promise for sensors and monitors in cases where power and size are important constraints (Montenegro et al., 1991). The size and shape of microelectrodes can be tailored specifically to the analytical problem. The nature of the electrode response depends on the time scale of the experiment. Electrode arrays can be fabricated with thousands of small elements. Lithographic procedures raise the possibility of very low per-item cost of manufacturing identical arrays.

Pulse Voltammetry (Osteryoung, 1988; Osteryoung and O'Dea, 1986)

Modern pulse voltammetry employs stepwise changes in potential, the sequence of which is controlled by software. Thus, the exact choice and timing of potential steps can be tailored to the specific analytical problem. Standard pulse sequences routinely employed in electroanalytical investigations include those of square wave, normal pulse, and other voltammetries.

The current resulting from a chemical reduction is directly proportional to concentration and typically can be measured with a relative precision of 0.2% and an absolute accuracy of better than 1%. For typical conditions and electrodes of conventional size, the change in current per change in concentration is on the order of 70 nanoamperes per micromolar. Detection limits in the worst case are about 1 micromolar and are typically 0.1 micromolar; in favorable cases, nanomolar concentration detection limits can be achieved. The linear range, over which signal is proportional to concentration, is typically a factor of 10^4 to 10^6, for example 10 nanomolar to 1 micromolar.

The response, though of low resolution, is specific to the reacting species. It is possible, therefore, to determine metals in a specific oxidation state [e.g., As (III)] or as a specific complexed ion. Particulate material does not affect the response of the electrodes to dissolved material. The electrochemical behavior of organic compounds tends to be similar for different compounds in which the same functional group is reacting. Thus, voltammetric measurements can be used to give semiempirical quantification of classes of compounds without going through the expense and difficulty of determining the identity of individual compounds present. Measurements can be carried out at characteristic times of 10 microseconds to 10 seconds, thus providing considerable scope for optimization.

Stripping Voltammetry (Zirino, 1981; Shuman and Martin-Goldberg, 1984; Van der Berg, 1989)

Voltammetry can also be employed in the stripping mode; that is, the material of interest is accumulated in or on the electrode, and once concen

trated is voltammetrically "stripped" from the electrode. Concentration factors of 10^5 can be achieved routinely, and thus detection limits in the range 10^{-11} to 10^{-12} molar can be achieved. At these levels of concentration, fidelity of the sample becomes the factor that controls the quality of the result. This technique has been used widely in oceanographic science, especially for the determination of metals such as lead, copper, cadmium, and zinc. Stripping voltammetry at mercury electrodes yields detection limits in aqueous solution of 30 picomolar for copper and 0.3 nanomolar for zinc (Stoeppler, 1991). Problems of interferences by other elements in either aqueous or amalgam solution have been studied exhaustively, and well-documented procedures exist for eliminating these interferences.

Stripping voltammetry has been used to study the distribution of Zn(II) between labile and inert complexes in seawater with total zinc concentration of 50 nM (Muller and Kester, 1990). Formation constants of Zn(II) with various inorganic complexing agents (e.g., Cl^- and NO_3^-) have been measured by anodic stripping voltammetry at total zinc concentrations of 10 nM (Komorsky-Lovríc and Branica, 1987).

Distributions between labile and inert complexes have been determined in samples with 15 nM Cu(II) and Zn(II) by anodic stripping at a micromercury electrode (Daniele et al., 1989). The technique of absorptive stripping voltammetry holds great promise for the determination of electroactive substances that can be adsorbed at an electrode. New developments in the use of microelectrodes for stripping voltammetry provide the possibility of extending the extensive body of laboratory procedures now employed to *in situ* measurements. Ligand competition voltammetry is also being carried out on seawater samples.

Coulometry (Bard and Faulkner, 1980)

Coulometry comprises a set of techniques in which the total charge required (not the current, as in potentiometry) to oxidize or reduce the chemical species of interest is measured. The prime virtue of coulometric techniques is that they link the quantity of substance determined directly to the quantity of electrical charge, and thus expensive and often difficult procedures for standardization or calibration can be minimized or eliminated.

Coulometric procedures are robust theoretically in that $Q = nFN$, where Q is quantity of charge, n is the number of electrons in the reaction, F is the Faraday constant, and N is the number of moles of reactant. This simple relationship is little affected by environmental variations (e.g., temperature or ionic strength). Coulometric procedures are also robust technically, in that the charge is just the integral with respect to time of the current. Coulometry is also easy to automate and operate under remote control. The accuracy of coulometric determinations is typically as good as 0.1%. Preci

sion of 0.01% can be achieved, and it may be possible to achieve accuracies this good in special cases.

The coulometric principle can be applied in many different ways to determine specific substances. The most obvious and direct way is to electrolyze a sample of known volume at constant potential. However, coulometry can also be applied in titrations at constant current, employing a reagent that is oxidized or reduced in the process. Coulometry may also be employed in titrations by coulometric generation of reagent. Examples include the determination of CO_2 by reaction with ethanolamine, with subsequent titration with coulometrically generated base. Another coulometric reagent generation is for determination of SO_2 by coulometrically generated iodine. Coulometric titration is now the method of choice for determination of TCO_2 in seawater (Johnson et al., 1987). Finally, it can be used for the generation of standards, particularly for substances that are difficult to prepare and store, and for *in situ* calibration. Coulometry may also be used for detection in liquid chromatography and flow injection analysis.

New electrochemical techniques can be applied directly to presently employed amperometric methods to optimize the potential-time waveform and current sampling scheme. For example, steady-state amperometric measurements at constant potential may be converted to pulsed operation with synchronous sampling of current in a way that improves performance but is transparent to the user. Optimal sampling schemes for individual methods can be developed through laboratory research. This type of development is exemplified by the Endeco® pulsed oxygen sensor. For remote operation, as from buoys, improvement in performance of computers should make it possible to convert amperometric techniques to voltammetric techniques. Determining the voltammetric response (which might consist of 150 data points per concentration measurement) provides better statistical definition of the current-concentration relationship. Knowledge of the voltammetric response could also provide the ability to compensate directly for changes in the properties of the reaction being used to determine concentration. This approach is presently practical in a laboratory research setting and, assuming further improvements in technology of computers, should be possible in oceanographic applications in the near future. Again, this type of development could be made transparent to the user.

The size, shape, and material of the electrode can be tailored to the application. Problems of response time, for example, often can be solved by using a smaller electrode. The use of new electrode materials, including possibilities for modification of the electrode surfaces, could lead to new measurement capabilities. This emphasizes the importance of the development of polymers, new materials, and recognition chemistry, as discussed in the section on new chemistry. Size, shape, and choice of material all present new technical opportunities that can be applied now, but also present many

possibilities for longer-term development. Routine practice in laboratories lags significantly behind present technical capabilities. Modern instrumentation is qualitatively superior to that of even the mid-1980s.

Major commercial efforts have gone into the development of sensors based on microelectrodes fabricated by means of lithography. Commercial products have not resulted because markets have not been identified that would support the volume required for economical production. Deterioration of response with time for *in situ* measurements might be decreased by employing multiple electrodes and using each only once. For example, present lithographic technology can allow production of line electrodes 20 micrometers wide, individually addressable, with 80-micrometer spacing. A 10-centimeter-long strip would contain 1000 electrodes.

The electrode material also may be manipulated to achieve more specific or more reliably controlled performance. Specific catalysts for desired reactions may be incorporated into the electrode material or bound to the surface of the electrode. A present example is the coating of a carbon or other inert electrode with a polymer film impregnated with a mercuric salt. The resulting electrode is catalytic for reduction of metals, such as Pb^{2+}, that are soluble in mercury. This is an area of research that could pay off through qualitative improvements in accuracy, precision, and response time.

Developments in electroanalytical chemistry are driven by technical advances in electronics, computers, and materials. Present scientific capabilities available in a research laboratory will be applicable for field measurements with the advent of smaller, less expensive, more powerful computers. Miniaturization of electrochemical cells, which can improve performance, especially response time, can be implemented most effectively in the context of miniaturization of control circuitry. Concomitant low cost could make disposable systems a practical reality. Sophisticated data analysis and data handling techniques can, with better facilities for computation, be handled in real time.

SPECTROPHOTOMETRY

Absorbance

Spectrophotometry encompasses a broad family of techniques, but fundamentally is very simple: the analyte in a sample (perhaps with a reagent added) absorbs some fraction of light at some selected wavelength, which may be correlated with the analyte's concentration by Beer's Law. The essence of the method is to compare the amount of light absorbed by a sample in the presence and absence of a specific analyte. The instrumentation necessary for spectrophotometry has been available for nearly half a century; however, diode array detectors have changed the performance of

single-wavelength instruments radically. The various forms of spectrophotometer differ primarily in details of light sources, dispersive element, and detector. The classical Beckman and Cary spectrophotometers can measure absorbance in the ultraviolet (UV) to near-infrared (near-IR) (250 to 1500 nanometers). Classical IR spectrophotometers use different sources and bolometric detectors to cover the range from about 2500 to more than 10,000 nanometers. Fourier transform IR (FT-IR) spectrophotometers use a more complex technique to cover the same wavelength range, with significant advantages (see section on infrared below). Atomic absorption spectrophotometers make use of lamps producing line spectra of particular elements to detect volatilized atoms of those elements by their characteristic absorbance lines. Photoacoustic and thermal lensing spectrophotometries make use of the conversion of absorbed light into heat to detect absorbance indirectly by measuring sound evolved and deflection by changes in refractive index, respectively.

For the purposes of chemical oceanography, spectrophotometry is limited to wavelengths from the UV to near-IR (250 to 1500 nanometers). The various forms of spectrophotometer differ primarily in combinations of light sources, dispersive elements, and detectors.

The principle of spectrophotometric measurement involves the comparison of two similar light levels, leading to an inherent weakness in the technique. In particular, as the concentration of absorbing analyte decreases, the two light levels become more and more similar until they cannot be distinguished. Thus, the sensitivity and accuracy of the method are very dependent upon the stability of the light source, the precision of the detectors, and the reproducibility of the sensor matrix. As a rule of thumb, with non-solid state sources and detectors, absorbance differences of 0.0001 unit are difficult to measure. The maximum extinction coefficient for a molecule in the visible or near-IR region (determined by the oscillator strength) is about 2×10^5 liter mole^{-1} cm^{-1}. Thus, the detection limit for classical spectrophotometry is perhaps a few nanomoles per liter of "solvent." More commonly, detection limits are set by the presence of interfering contaminants in the sample; this is especially true for complex media like seawater.

Some spectrophotometric techniques work to enhance sensitivity or utility in other ways. The advent of semiconductor diode array detectors permits entire spectra to be acquired simultaneously instead of one wavelength band at a time. Also, automated spectrophotometric analyzers originally developed for clinical use have been adapted for use at sea when many samples must be analyzed over a period of time. Computational techniques for signal averaging, smoothing, integration, and data analysis have been widely implemented in modern instruments. From the standpoint of chemical oceanography, spectrophotometry is a mature technology that is widely used and accepted.

Spectrophotometry can also be employed after reaction of the analyte with a reagent or indicator to enhance or enable an analysis to be made. Many analytes of interest, such as metal ions, are determined indirectly as complexes with organic molecules. Thus, cupric ion [Cu(I)] has a modest absorbance by itself, but has a 1000-fold greater absorbance when complexed with bathocuproine. Moreover, some such complexes are insoluble in water and may be extracted from aqueous solutions as a preconcentration step before spectrophotometry. Preconcentration has been widely used in trace analysis by spectrophotometry.

Ideally, the indicating chemistry is reversible, allowing continuous long-term measurement. If nonreversible chemistry is used to form a color, provision must be made for continuous delivery of the reagent indicator, especially if it consumed in the analysis. In general, this is more difficult than the spectrophotometric measurement itself. Various clever methods have been suggested for continuous reagent delivery, while true long-term, unattended operation is not yet demonstrated. On board ships, however, "field" spectrophotometric instruments have proven rugged and reliable, and are very widely used, particularly for enzyme-based analyses. The sampling rate can be rather high, with continuous operation possible when the spectrophotometer is used with an immersible pump and connecting pipe to the depth of interest.

Developments in traditional forms of spectrophotometry, as well as new methods, could find greater use in ocean measurements. Spectroscopy based on absorption of visible light may have reached a limit in its traditional form, however. Spectrophotometry will remain in wide use due to its ease, low cost, and great versatility. In many ways it remains the first choice for analysis, but its low sensitivity makes it useful for a rather limited spectrum of analytes.

Many analytes listed in Table 1 have been measured spectrophotometrically in seawater for some time, including many metal ions and some gases, although spectrophotometry is the preferred method for only a minority. Some analytes, like alkanes, are spectrophotometrically "silent," or do not form colored complexes with other reagents. Similarly, individual nuclides cannot be distinguished by classical spectrophotometry, and many of the other analytes, such as halogenated pesticides and metal alkyls, are more easily determined by other methods, such as gas chromatography with electron capture detection, or emission spectroscopy. Indeed, many of the analytes, such as zinc or copper, are present at trace levels and are not measurable by spectrophotometry.

Infrared

Infrared spectroscopy is a well-established technique for determining molecular structure. It is essentially an absorption spectrophotometric tech

nique using a different wavelength. Because spectral bands are much sharper than those in the UV-visible region, highly selective determinations can be made. Information is particularly rich in the mid-IR region of 3 to 15 micrometers. More recently, some very useful results have been obtained using wavelengths of 0.7 to 3 micrometers. IR spectroscopy is not a highly sensitive technique, since absorption coefficients are low, particularly for dissolved samples.

Very promising is the use of FT-IR spectroscopy as a detector for gas or liquid chromatography. With proper extraction and preconcentration steps, FT-IR can be a useful technique for studying organic compounds in the ocean. This approach will be limited to land-based instruments for now, but shipboard instruments are conceivable. As for remote mapping, FT-IR combined with chemometrics shows promise for classifying materials in the surface layer of the ocean (Bronstein and McGrath, 1989; Kolber et al., 1990).

FT-IR is a relatively new method of performing IR adsorption measurements. In classical IR spectrophotometry, the absorbance of a sample is measured as the wavelength (or frequency) is varied. In FT-IR, an entire spectrum is acquired simultaneously as an "interferogram," in which the absorbance data are encoded; the spectral data are obtained by calculating the Fourier transform of the interferogram. The advantages of this approach are its efficiency, in that it effectively scans the entire spectrum at once rather than serially in small increments; its generally higher resolution; and the capability for digital signal averaging and other manipulations that are otherwise difficult. The main disadvantage is the relative cost and complexity of the instruments; instrument costs are decreasing, however.

Instrumentation for IR spectroscopy has gone through a major change since the availability of FT-IR. Improved noise levels and spectral resolution have resulted. Complete systems can be purchased for under $30,000, with little need for user intervention. These systems are not quite rugged enough for oceangoing applications, but future developments in making them more rugged are forthcoming. It is useful to note that entire FT-IR instruments have been sent to explore the atmosphere of Mars, so size, weight, and power requirements are readily met.

Luminescence

Luminescence (emission) spectroscopy encompasses photoluminescence-based techniques such as fluorescence and phosphorescence, plasma-excited luminescence, and chemi-and bioluminescence. Although these techniques differ in their means for raising the sample to an excited electronic state, all are based on measuring the light subsequently emitted when the excited atom or molecule returns to its ground state. These techniques are more

sensitive than the absorption spectrophotometric techniques described above. In absorption spectrophotometry, the instrument must distinguish the difference between two similar light levels, whereas in emission spectrometry (ideally) the blank or background produces no signal at all. The fact that the exciting light in photoluminescence methods is a different color than the emitted light permits the former to be filtered out. In the case of chemi-and bioluminescence there is no exciting light per se, no light filtering is necessary, and detection limits below attomolar (10^{-18} mole) quantities are achieved with simple instruments.

Fluorescence and phosphorescence techniques are powerful, versatile, and widely used in chemical analysis. While few of the analytes listed in Table 1 are intrinsically fluorescent as solutes in seawater, some can be determined directly or indirectly using added indicator molecules. For example, aluminum ion can be determined by the fluorescence of the 8-hydroxyquinoline complex ion. Hundreds of organic chelators exhibiting this behavior are known. Specificity can be a problem, however, because some compounds will bind up to 25 different ions. Some indicating schemes rely on fluorescence upon binding a chelator to the metal ion, a less useful method because of the higher baseline signals. Luminescence methods are less applicable with nonmetals and anions, because fewer photoluminescent complexes are known. The most widely used emission spectroscopic technique in ocean science is fluorescence, primarily because it permits sensitive determination of chlorophyll. *In situ* fluorometers designed to measure chlorophyll are now commercially available, an index of the broad interest in this analyte. The sophisticated "double pulse" fluorometer provides a measure of the fraction of chlorophyll actually engaged in photosynthesis, and thus the fraction of photosynthesizing biomass that is functional (Kolber et al., 1990). Chemical reactions designed to attach fluorescent markers to amino acids allow measurement at natural concentrations by high-performance liquid chromatography. This is a model for techniques that might be developed for other types of organic compounds. Fluorescence has also been used to provide semiquantitative measurements of oil (NRC, 1985).

Phosphorescence is growing in importance for condensed phase determinations as techniques become available for reducing the quenching effects of solutes such as oxygen; at present it is practical mainly for solid samples. Today's instruments, with powerful dye lasers for excitation, offer detection limits in the micromolar range; sample preconcentration further increases sensitivity while at the same time minimizing the deleterious effects of high salt concentrations on background levels.

An important adjunct to photoluminescence methods is the use of time resolution. Following excitation, photoluminescent species spend a brief time in the excited state before subsequent re-emission of the photon. For classical fluorescence, this lifetime is in the nanosecond range, whereas for

phosphorescence, the emission commonly takes micro-or milliseconds to appear. Different molecules exhibit lifetimes ranging from 10^{-3} to 10^{-11} seconds due to many different phenomena. Thus, by mechanically, electronically, or optically "gating" the detector, photoluminescence emission from interfering species may be temporally filtered out, enhancing the signal-to-noise ratio. The success of this approach may be inferred from published determinations of lanthanides at the 10^{-13} molar level (Diamandis and Christopoulos, 1990).

Chemiluminescence and bioluminescence offer the most sensitive of all the luminescence-based measurements (equaling radioisotope methods), while requiring only modest instrumentation. These methods are based on light emission from chemically generated excited state molecules. Thus, there is no need for excitation light. For instance, adenosine triphosphate may be detected at attomolar concentrations by hand-held instrumentation in seconds using firefly luciferase. Relatively few analytes of interest participate directly in chemiluminescent reactions, however, so methods must be designed to relate the chemi/bioluminescent intensity to the analyte level using some coupled reaction, which limits this method to a small number of analytes. It might be possible to alter microorganisms genetically to yield the desired analyte-chemiluminescent reaction. Using integrating detectors such as charge-coupled devices or fast photographic film, as little as a few enzyme molecules become detectable (Bronstein and McGrath, 1989). Some recent research has shown that chemiluminescent methods may be adapted for *in situ* determinations of some metal ions (see the section on flow injection analysis). Nitrate, iron, manganese, copper, and cobalt are all detected with chemiluminescent techniques.

While chemiluminescence is easy, inexpensive, sensitive, and often selective, it remains little used because of the difficulty in coupling recognition chemistry to chemiluminescent reagents. The instrumentation is simpler than for fluorescence and thus can be constructed for *in situ* use; luminometers for monitoring bioluminescent organisms are commercially available. However, the technique requires consumable reagents, which are somewhat more difficult to incorporate into an immersible sensor for continuous monitoring, although Johnson and his colleagues (see the section on flow injection analysis) have reported progress in this area. Luminol chemiluminescence has been used from time to time for some analytes such as transition metals, but the method is nonspecific and requires use of strongly basic compounds for the reactions. Peroxyoxalate chemiluminescence has been reported as useful for determining certain fluorescent molecules in liquid chromatography, but remains seldom used. A recent advance of substantial interest is the development of *bis*-adamantanyldioxetane derivatives as chemiluminogenic enzyme substrates (Schaap, 1988). These molecules are extremely stable until hydrolyzed by enzymes such as alkaline phosphatase, whereupon they emit

light. At present, chemiluminescence is not the method of choice for any of the analytes listed in Table 1.

Atomic emission spectroscopy can be employed, generally with an inductively coupled plasma for thermal excitation. The sample is introduced into the plasma as a mist of ultrafine droplets, and the monochromator and detector are set to measure the intensity of an atomic emission line characteristic of the element. This technique is powerful, general, sensitive, linear, and able to measure over 70 elements, and, as a result, is widely used. Response is typically linear over four orders of magnitude in concentration with relative standard deviations of 1 to 3%. In low-salt aqueous solutions, detection limits range from 10 to 1000 nanomolar without preconcentration. Significant problems with saline samples remain, but use of Babington nebulizers alleviates these problems somewhat.

All of these emission techniques have been used to analyze seawater, but their suitability for use at sea or *in situ* varies. Inductively coupled plasma emission spectroscopy permits determination of 60 elements sequentially or simultaneously with good sensitivity and precision; however, it is not sensitive enough for some of the rare earth elements and trace metals without preconcentration, and is obviously unsuited for molecules. While inductively coupled plasma techniques are unsuited for *in situ* use, they have been integrated into flow injection and chromatographic systems. Incorporation of extraction and preconcentration into a continuously operating system appears difficult. Probable future developments in this technology include improvements in sample introduction to the plasma, particularly with techniques such as capillary electrophoresis and supercritical fluid chromatography; optical improvements such as multichannel high-sensitivity detectors and acousto-optic tunable filters; Fourier transform-based instrumentation; and improved chemical methods for extraction and preconcentration.

Optical and laser technologies also offer the prospect for improvements in fluorescence and phosphorescence determinations. An important development is the use of fluorescence and phosphorescence with optical fiber sensors.

Raman

Raman spectroscopy is based upon the Raman effect, in which a fraction of light incident on a sample will scatter at wavelengths differing from that of the original wavelength. The change in frequency is determined by the composition of molecules in the sample. Thus, a sample of water excited with light having a wavelength of 400 nanometers will emit scattered light not only at 400 nanometers but also at a trio of longer wavelengths (near 463 nanometers), whose frequency difference from the excitation cor

responds to the stretching frequency of-OH bonds in water. The Raman spectrum thus detects the same phenomena as does infrared spectroscopy, but the relative intensities of bands measured by the two techniques differ.

Raman scattering is a weak phenomenon; before lasers offered powerful, monochromatic light, Raman was an effect observed rather than exploited. Until very recently, spectra often required hours to acquire, even using lasers with several watts of power. A substantial limitation arises from interference by photoluminescent impurities in the sample, generally constraining Raman spectroscopy to longer wavelength lasers, even though the strength of the scattering declines as the fourth power of the frequency of the incident light.

At present, Raman spectroscopy for ocean measurements is limited by the weakness of the phenomenon and the type of equipment required. Seawater exhibits background fluorescence due to dissolved organic solutes, and thus sensitivity is further compromised. An especially important interferant is chlorophyll, which fluoresces upon excitation with argon lasers.

Two variations of Raman spectroscopy offer substantial signal enhancement. The first is resonance Raman spectroscopy, in which the intensity of scattering is enhanced up to 10^6-fold, increasing the speed and selectivity of this method. In some cases, the wavelength of excitation may be chosen to maximize the enhancement of a particular component in a solution. A second important Raman spectroscopic technique is surface-enhanced Raman spectroscopy (Garrell, 1989). The strength of the signal is greatly enhanced when the solute of interest becomes adsorbed to a metal surface such as etched platinum. This technique has been combined with electrochemical methods so that the adsorption of a solute, such as amino acids, proteins, and other organic molecules, to the surface of an electrode is modulated by electrical potential or redox reactions. This method can be exploited with optical fibers and metal colloids and may ultimately offer the potential for *in situ* applications. Other important new developments in Raman methods include ultraviolet excitation and Fourier transform Raman spectroscopy. For examination of particles, molecular orbital laser excitation, coupling laser-Raman with scanning electron microscopy, was developed.

Finally, the introduction of new detectors, such as diode arrays and charge-coupled devices (CCDs), has been a boon for Raman spectroscopy. CCDs permit the accumulation of light in the manner of photographic film; additionally, their noise level is lower than that of the photomultiplier tube. In addition, by combining CCDs or diode arrays with optical dispersive elements, entire spectra may be collected in fractions of a second.

Recent work by Angel and Myrick (1990) suggests that certain contaminants might be monitored by Raman spectroscopy *in situ* through optical fibers, but the above caveats still remain. The depths accessible would be limited mainly by optical loss in the fiber. The use of the fiber permits

the expensive, fragile components to remain aboard ship; even so, it would not be trivial to construct a seagoing Raman spectrometer for shipboard use. A relatively high sampling rate (one per millisecond, for instance) might be achieved. Adequate power and cooling water, and a stable platform must be available. Raman signals can emanate from the fiber itself. Power consumption by the lasers typically used (a few kilowatts) is too great to deploy a Raman spectrometer on an autonomous buoy.

Fiber Optics (Wolfbeis, 1991; Angel, 1987; Seitz, 1988)

Fiber optics can be used to deliver light over long distances. Fiber optic sensors provide a means to measure properties of seawater continuously using changes in the characteristics of a transmitted light beam. To make measurements, light is sent down an optical fiber to excite the sample (Figure 2). The sample in its natural state (for example, chlorophyll) or as reacted with a dye modulates the light by absorbance or it emits fluorescent light, which is carried back to a detector via the same, or a second, fiber. The concentration of the material to be measured can be determined by the degree of absorbance, by the amount of emitted light, or by the excited state lifetime. Optical fibers consist of a "cladding" of one type of glass or plastic surrounding a core of another type, so that light is trapped in the core and can be transmitted over long distances. The attenuation of the signal depends on the color of the light and the fiber material. If a larger fiber is used, the signal increases, but so does the noise.

Many analytes do not absorb or emit light. In these cases, indicators must be employed. Optical sensors are made by attaching a selective indicator layer to the distal tip of an optical fiber. Optical sensors employ well-known spectroscopic principles; the innovation is in making sensors for measuring specific substances dissolved in seawater using indicators, biological molecules, or various reagent systems. Some of the advantages of optical sensors are that they are small (50 to 250 micrometers), are free from electromagnetic interference, and allow continuous monitoring. The research challenge is to develop suitable indicators that provide stable measurement. Another advantage is that no direct electrical connections are required. In addition, fiber sensors can be multiplexed; that is, a single instrument can support multiple sensors, for samples at different depths or for different analytes. Optical fibers are useful for applications where it is difficult to transfer power to a remote device because of their low attenuation. Calibration and stability can be improved, in some cases, by employing ratio measurements using indicators having multiple absorption or emission peaks. By ratioing the peaks, calibration curves can be derived that are independent of the absolute dye concentration (at various analyte concentrations), light intensity, and other effects.

Generalized Fiber Optic Sensor

Model of CO₂ Fiber Optic Sensor

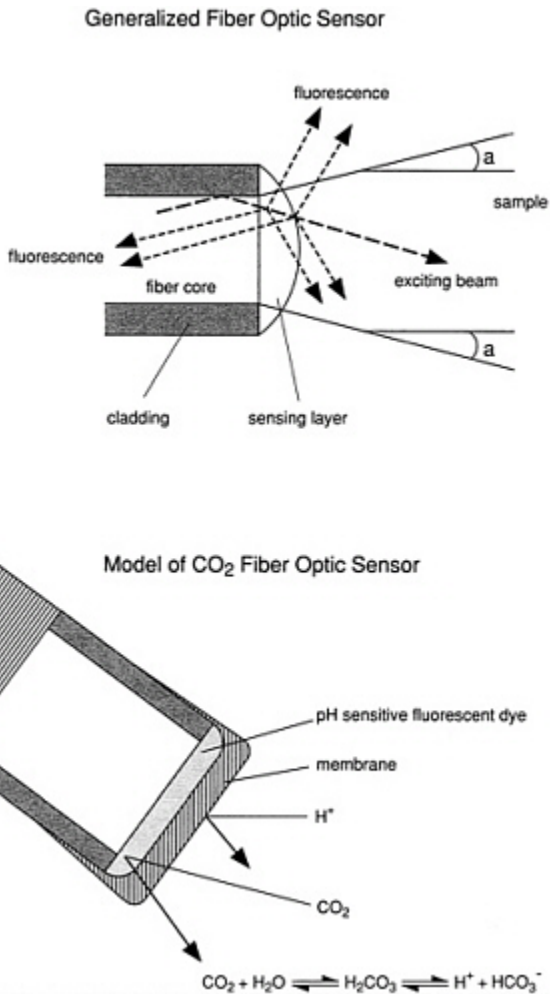$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Figure 2
Fiber optic sensing. The top figure shows the characteristics of a generalized fiber optic sensor. The bottom figure shows a fiber optic sensor for carbondioxide.

One application for fiber optic sensors is for measuring CO_2 in seawater. Sensors are being developed with solution-filled tips behind a membrane permeable to CO_2. Recent collaborative work has resulted in a CO_2 sensor with resolution equivalent to 7 µatm pCO_2 (Goyet et al., 1992). For CO_2 sensors, reversible indicators are used. In systems where irreversible chemistry may be useful, reagent delivery systems may be employed to replenish reagents continuously (Luo and Walt, 1989).

Sampling with fiber optic sensors can be continuous if needed; otherwise they can be operated discontinuously, with a lower duty cycle. These sensors could be used for laboratory-based or *in situ* applications. The cost of instrumentation for fiber optic systems should be $25,000 to $50,000. Sensors would need to be replaced periodically (several weeks to many months), depending upon their design. Sensors using fiber optic probes will be available within 5 years for some applications and within 10 years for some others. Sensors for pH, CO_2, and O_2 are in development now; new sensors should be capable of measuring from high concentrations down to 1 part per million for ions and organic materials. Basic research is still required for specific applications.

Refractive Index (Eisenberg, 1965; Yeung, 1986)

Salinity measurements are most often used in oceanography to determine seawater density. The conventional measure used by oceanographers for determining salinity is conductivity. This is feasible because the salt content of seawater is well defined, as is the temperature-related compressibility. As an alternative, the refractive index of water is a good descriptor of density when temperature is known or can be measured. Refractive index provides a high-precision method for determining the density of pure water. As various salts are added, the refractive index is a less exact predictor of density, although relative measurements can still be useful.

Commercial refractive index instruments are available, with a light beam and two photodiodes. If there is no difference in refractive index, and thus density, between sample and reference cells (such as a quartz crystal), light hits both photodiodes equally. If the reference cell and sample cell differ in density, diffraction pushes the beam to one side. This device does not depend on the absolute intensity of the light beam. The response time is on the order of 0.1 second. The precision of the bench top model is to the sixth or seventh decimal place. The position sensor has a high dynamic range, and the device has no moving parts. This technology is ready for evaluation for oceanographic measurements with very little additional developmental work. A coil of optical fiber with a refractive index close to that of seawater, combining clad and unclad fibers, could possibly provide a more sensitive device, although intensity depends on fiber coil geometry. Calibration will be difficult for these sensors. The effect of biofouling could be

reduced by using relative measurements (since the intensity is not crucial) and by various chemical, optical, and mechanical means. The cost of these devices is $5,000.

PIEZOELECTRIC MASS SENSORS (ALDER AND MCCALLUM, 1983; CAREY AND KOWALSKI, 1986; THOMPSON ET AL., 1986; WARD AND BUTTRY, 1990)

A piezoelectric mass sensor is a device that measures the amount of material adsorbed on its surface by the effect of the adsorbed material on the propagation of acoustic waves. Piezoelectric devices work by converting electrical energy to mechanical energy. There are a number of different piezoelectric mass sensors. Thickness shear mode sensors measure the resonant frequency of a quartz crystal. Surface acoustic wave mode sensors measure the amplitude or time delay. Flexure mode devices measure the resonant frequency of a thin Si_3N_4 membrane. In shear horizontal acoustic plate mode sensors, the resonant frequency of a quartz crystal is measured.

These piezoelectric crystal oscillators are very accurate mass sensors because their resonant frequencies can be measured precisely with relatively simple electronic circuitry. For certain quartz crystals, the resonant frequency is inversely related to the crystal thickness. A crystal resonating at 5 megahertz is typically 300 micrometers thick. If material is coated or adsorbed on the crystal surface, the resonant frequency will change (decrease) in proportion to the amount of material added. The effect of adsorbed mass on the oscillator frequency varies according to the operational mode of the device. In any case, interpretation of mass via changes in frequency or amplitude assumes that the coated films are rigidly elastic and infinitesimally thin (that is, an extension of the crystal).

Piezoelectric mass sensors have been used for gas phase sensing (for example, SO_2, H_2S, and HCl) using crystals coated with chemisorbent films (including polymers) that interact specifically with these gases. Even immobilized enzymes have been employed as selective coating materials (for example, formaldehyde sensing using immobilized formaldehyde dehydrogenase; Guilbault, 1984). Indeed, the nature and selectivity of the coating material used to achieve chemical recognition of the target species is the key to fabricating useful analytical sensors based on piezoelectric devices.

The use of piezoelectric mass sensors for solution phase measurements is still under development. Whereas considerable success has been achieved with these devices for detecting the mass of electrodeposited analytes in solution (on thin films of conducting metal electrodes deposited on the quartz crystals), detecting mass changes due to selective chemical interactions at the surface (for example, antibody-antigen reactions) has been less successful. Changes in frequencies do occur, but the direction and magnitude of change are not always predictable. The main reason for this is that

piezoelectric mass sensors respond to the viscosity of the sample in the microenvironment at the crystal-solution interface. This surface viscosity can change (even when bulk phase viscosity does not) as a result of such surface chemical interactions, and also in response to temperature. In fact, piezoelectric devices are very good viscometers. This can be corrected for to some extent by using a reference crystal (in a differential measurement mode) that does not possess the chemically selective reagent on its surface, or a reference crystal with a nonactive form of the same chemically selective coating. Similar differential designs are also required to minimize effects of nonspecific adsorption. In practice, it may be difficult to match the nonspecific binding properties of the reference and analytical crystals. This problem can limit the accuracy of analytical data obtained with these mass-sensitive devices in the presence of multiple analytes. Adsorption onto the surface of the selective chemical coating is generally reversible when the free energy of adsorption is less negative than about-16 kilo-joules per mole.

The rate of sampling with piezoelectric sensors is limited by their physical characteristics and present technology to the millisecond range for applications in the liquid phase. The technique is versatile in that it can be used in a variety of locations. The solid state electronics necessary to operate the piezoelectric sensor are easily miniaturized, and data can be recorded continuously or periodically. A small computer with a reasonable memory could easily record data over long times. There may be some problems in deep-sea locations, simply because of the complications in packaging the sensor for high-pressure environments. although this problem may be surmountable.

The main advantage of piezoelectric devices is that, in principle, any process that results in a mass change at an interface can be measured. However, this very nonselective transduction process is also a major disadvantage in that it mandates the use of even more selective surface chemistries than are required for other types of chemical transducer systems. This will make the implementation of piezoelectric chemical sensing devices for ocean measurements rather difficult, but by no means impossible. Indeed, the coupling of pattern recognition techniques with an array of marginally selective piezoelectric transducers may, in the future, make these devices more useful for quantitative ocean measurements.

NEW CHEMISTRY

Immunochemistry

Immunoassays can be carried out by creating antibodies that bind with molecules of interest (antigens). Antibodies are created by injecting the

antigen into rabbits (or other animals, such as chickens) and then extracting the resulting antibodies. Assays can be made sensitive by labeling a given amount of antigen with fluorescent or radioactive compounds, or enzymes, thus creating a labeled analyte reagent. The difficulty in making antibodies to low-molecular-weight analytes depends on the molecules; it can take 6 months and several animals to produce a useful polyclonal antibody reagent. Monoclonal antibodies are more selective for particular compounds, but are more costly to develop. Antibodies have a shelf life of more than I year, with refrigeration.

An example of an immunoassay is the enzyme-linked immunosorbent assay (ELISA), which uses 96-well plates with antibodies bound on the sides of the wells. The characteristic of interest is the binding constant for the immunoreaction, which is defined as the association constant between antibody and antigen. It is important to generate a good antibody with strong binding.

Of the two classes of immunoassays, heterogeneous and homogeneous, homogeneous assays are generally much faster and easier to automate, although the detection limits are not as low as for heterogeneous assays. Homogeneous assays for small analyte molecules are based on competitive binding, and can be direct or indirect.

A practical factor limiting the routine use of immunochemistry for environmental monitoring is that many U.S. Environmental Protection Agency-approved methods require analyses by gas chromatography and mass spectrometry (GC-MS) for measuring pollutants. This is a case in which state-of-the-art techniques cannot be applied because government regulations mandate use of techniques that were well developed when the regulations were formed. Immunochemistry techniques could be faster and cheaper than GC-MS, although they may not be as sensitive in some cases. Analysis of certain samples may require some extraction steps. For example, many organic compounds bind to particulates and must be extracted before analysis. Whether immunoassays can be implemented with these organic extracts remains to be seen.

It requires about 2 hours to carry out an immunoassay, in either land-based or shipboard laboratories, using a single 96-well microtiter plate and associated plate reader. Simultaneous use of multiple plates can further increase sample throughput. New reagents must be developed for each analyte. It is expensive to make appropriate reagents and develop the chemical procedures, but the subsequent cost per sample is very low. These techniques are available now; what remains is to develop methods, that is, to make antibodies toward the desired analytes.

Making antibodies to some small molecules and ions, particularly if they are insoluble, reactive, volatile, or toxic, can be difficult. Few antibodies to the analytes listed in Table 1 have been developed. A variety of

dissolved organic carbon molecules could be measured by immunoassay. Various chloro-and fluorocarbons may be among those few that can be detected, although the issues of solubility and compound immunogenicity could be important factors, depending on the specific compounds to be sensed. One class of analytes of great importance for sensor development are the toxins released by toxic algae under bloom conditions. Present techniques of detection are to monitor toxin concentrations accumulated by suspension-feeding organisms. In addition, it should be possible to develop reliable and selective immunoassays to detect free metal ion levels (e.g., manganese and iron) using antibodies raised toward specific organic ligand chelates of these metal species. For example, a heterogeneous immunoassay method was recently reported for the detection of Hg(II) with high selectivity over all other heavy metals (Wylie et al., 1991).

Polymers and New Materials

An area that offers tremendous potential for advancing the state of the art of measurement technologies is that of polymer and materials science. This field has been identified as one of the critical technologies essential to maintaining U.S. industrial competitiveness. In recent years, high-temperature superconductors, thin diamond films, and lightweight ultrastrong polymeric materials have been developed. These materials and others should have a major impact on the ultimate successful implementation of ocean instrumentation. These developments will contribute to a variety of disparate areas of sensor and instrument design.

Materials with selective binding or transport properties will have a major impact on sensor design and fabrication. Selectivity in either binding or transport can be exploited for a variety of measurement needs. This selectivity can be either intrinsic, that is, built into the chemical properties of the material, or coupled with selective carriers that allow a non-selective material to be converted into a selective one (see the section on recognition chemistry). An example of the latter is the use of valinomycin as a selective carrier in a polyvinyl chloride membrane to form a potentiometric potassium ion sensor. Advances in the fields of gas separation materials for air purification and membrane development for desalinization are contemporary examples illustrating the importance of selective materials. As these materials are identified, they can be exploited for the design of selective measurement schemes.

A second area in which new materials will have an impact on oceanographic measurements is that of corrosion resistance. Many materials, particularly metals, are incompatible with the ocean environment. Consequently, alternative materials or suitable protection measures must be developed. New corrosion-resistant materials are essential. For example, organic con

ducting polymers could presumably replace certain metallic conductors. Films of diamond or other materials may be employed to encapsulate materials sensitive to corrosion.

Biofouling is another problem with deployable ocean instrumentation that could be reduced by using new materials. Presently, toxic antifoulants must be released continuously to prevent adhesion and growth of organisms on virtually all submerged materials. This poses a particular problem for analytical instrumentation, as both the antifoulant and biological layers can perturb or interfere with the measurements being made. Ideally, more passive methods to prevent biofouling should be utilized. Advances in understanding microbial adhesion will assist in the design and preparation of suitable new materials. Similar advances in developing new materials for tissue and organ transplants compatible with blood and the responses of the human defense system may be transferable directly to reducing the biofouling on ocean instruments.

Finally, many new materials will affect the development of ocean instrumentation and sensors. These include new optical components, such as lenses, filters, light-emitting diodes and laser diodes, conducting ceramics or organic polymers that can be used in the preparation of new electrodes, piezoelectric devices, and new materials for energy storage. These areas undoubtedly will significantly affect the ability of analytical chemists to design new sensors, develop new transduction schemes, and construct new instruments.

RECOGNITION CHEMISTRY (DOBLER, 1981; LEHN, 1985; IZATT AND CHRISTENSEN, 1987)

Successful development and implementation of various chemical sensors for ocean measurements (based on optical, electrochemical, or mass transducers) requires concomitant advances in the design or discovery of organic or inorganic molecules that interact selectively with the important ocean analytes. These developments are particularly important for *in situ* sensors where no separation of ocean components or addition of external reagents occurs before or during the measurement step.

The importance of recognition chemistry has been highlighted in several of the previous sections. Developments in recognition chemistry are important for the design of *in situ* sensors and are a high-priority research area. In practice, the surfaces or membranes of any *in situ* sensing device will contain chemical species that interact selectively and reversibly with the analyte to yield a detectable signal. For example, in the glass membrane pH electrode, already used widely in the ocean for *in situ* pH measurements, negatively charged silicon oxide (Si-O$^-$) sites of the glass interact with protons. Increased proton activity reduces the amount of negative

charge on the surface of the glass, thereby altering the phase boundary potential between the surface of the glass membrane and the solution. The activities of other cations (for example, Na^+ and K^+) required to yield the same phase boundary potential are much greater (sometimes as high as 10^{11} times, depending on the exact composition of the glass material), because these species exhibit much weaker interactions with the $Si-O^-$ sites. This is perhaps the simplest, yet most impressive, example of analytically useful chemical recognition and selectivity. The challenge is to achieve this level of selectivity (while maintaining reversibility) within other electrochemical devices, as well as newer optical and piezoelectric devices.

Synthetic organic chemistry is critical to progress in this area. Indeed, the design of metal ion binding ligands for use in sensors, as well as for preparative separation processes in metallurgy and related areas, is currently an active area of research. A wide range of crown ethers, cryptands, hemispherands, and acyclic molecules containing electronegative oxygen atoms or mixed oxygen and nitrogen electron donor atoms in appropriate geometric positions within these ionophore structures have been synthesized, and some of these compounds have been used for the development of relatively selective optical and electrochemical sensors for Na^+, Ca^{2+}, Li^+, K^+, and most recently Mg^{2+} (Figure 3). Naturally occurring antibiotics with macrocyclic structures, such as valinomycin (for K^+) and monensin (for Na^+), may also be used for the fabrication of ion sensors. Other molecules possessing various combinations of oxygen and sulfur atoms (as ether links) or all-sulfur-based thiacrown structures exhibit selective recognition of certain transition metals (Ag^+, Cu^{2+}, Zn^{2+}, and others). In all cases, cation selectivity is dictated by the size and shape of the binding site formed by the three-dimensional configuration of electronegative oxygen, nitrogen, and sulfur atoms.

The design and synthesis of molecules that interact with specific anionic species has received far less attention. In contrast with cationic recognition, there is no known generic arrangement of electrophilic atoms that provides the basis for recognizing and distinguishing anions. While the synthesis of the macrocyclic structures with multiple positively charged nitrogen sites, in the form of guanidinium or polyamines, has been successful (in terms of binding various anionic species), the resulting structures do not exhibit analytically relevant anionic selectivities. Moreover, the presence of positive charges on these structures, required for anion interaction, is highly pH dependent, and this limits the potential *in situ* application of such chemical recognition reagents. Indeed, such sensors can only function effectively when the sample solution is buffered or a buffered region exists at the surface of the sensor. An alternative strategy involves the synthesis of organic molecules possessing electrophilic carbon atoms that can react reversibly with certain nucleophilic anions (particularly CO_3^{2-}) to form an
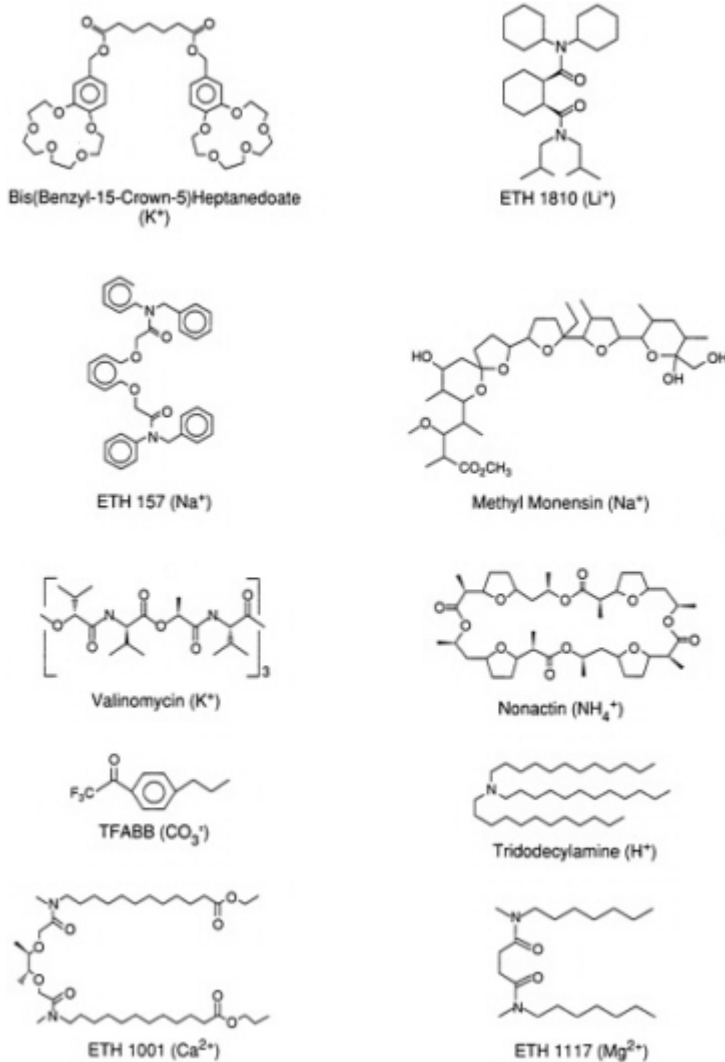
Figure 3

Structures of some natural and synthetic ionophores to fabricate electrochemical and optical ion-selective sensors.

ionic adducts. Generally, trifluoroacetophenone-type derivatives have proven useful for such purposes, and optical as well as electrochemical carbonate sensors based on this novel recognition chemistry have been developed.

The use of metal ion-ligand complexes as well as organometallic species to achieve guest-host-type recognition has also received considerable attention for the selective binding of both anions and neutral species, including gases. For example, there is evidence suggesting that dibasic phosphate interacts selectively with certain dibenzyltin dichloride structures, and nitrite can bind specifically as an axial ligand to the central Co(III) ion of vitamin B_{12} structures. These interactions have been used to devise sensors for these anions, although the exact chemistry involved is not yet fully understood. In preliminary studies, metalloporphyrins and metallophthallocyanines with varying metal ion centers [e.g., Mn(III), In(III), Co(II/III), and Sn(IV)] and peripheral structures have also proven useful for achieving some chemical recognition of anions and gases. Here, the nature of the metal center and the exact three-dimensional structure of the surrounding porphine or phthallocyanine ligand can control the degree of binding of anions and gases (for example, O_2) as axial ligand to the metal. So-called picket fence-type porphyrins are structures in which the nearly planar metalporphine ring is at the bottom of a pocket formed by large organic molecules attached in one direction from this planar base structure. While certain Co(II) and Fe(II) picket fence porphyrins can bind oxygen gas reversibly, possibilities also exist for incorporating hydrogen binding sites within the appended picket fence chains so that the binding of larger neutral and anionic species can be stabilized within the pockets of these structures.

The use of large organic structures containing three-dimensional chemical recognition pockets is not limited to porphyrin-type molecules. Indeed, various cyclodextrins exist in which the orientation of the repeating carbohydrate structure forms a hydrophobic inner core that can interact selectively with hydrophobic chemical analytes of appropriate size (benzene, pyrene, phenols, and others). Similar principles of recognition by size exclusion or inclusion can be achieved with certain polymeric structures, particularly when target chemical species are present during the polymerization process (for example, polypyrrole). In such cases, called molecular imprinting, the target ionic or neutral species can act as a template to dictate the final three-dimensional structure of the resultant polymeric film, thereby creating a polymeric material with a preferential interaction or permeability toward the target species.

The committee recognizes that the design and synthesis of molecules or structures that exhibit useful chemical recognition properties is extremely difficult, with a high risk of failure. Advanced molecular modeling methods are beginning to be applied to this area, but preliminary results are

mixed. In many cases minimum-energy structures that are predicted to have ideal conformations for selective interactions with target species do not bind the target species with adequate selectivity. Mimicking the inherently high selectivity of biological molecules, such as enzymes and antibodies, may be the most rational approach to achieving selective chemical recognition through classical organic and inorganic chemistry. Indeed, with powerful advances being made in elucidating protein structures (via two-dimensional nuclear magnetic resonance spectroscopy, x-ray crystallography, and other means), it may now be possible to synthesize much smaller molecules with binding sites (for anions, cations, gases, and neutral organics) that are similar to those of proteins that are known to exhibit selective interactions with these target species. Regardless of the approaches taken, it is clear that a considerable investment of time and resources will be required to develop the arsenal of chemically selective and stable host compounds that will be required to measure all the key oceanic species via *in situ* chemical sensor technology. The committee believes that such an investment would be worthwhile, given the great potential of selective chemical reactions for *in situ* use in the ocean.

Chromatography and Electrophoresis (Ewing et al., 1989; Pimental and Coonrod, 1987)

Chromatography and electrophoresis are used to separate dissolved constituents in seawater. Chromatography is based on partition of the individual components between gas or liquid passed through a column and the liquid or solid stationary phase. This partition is based on solubilities of dissolved material in the different phases and specific chemical interactions with column components. Electrophoresis separates materials on the basis of electrical charge and size as solvents flow through the plate.

Gas chromatography and liquid chromatography are mature separation techniques that are used for many ocean measurements. They have proven to be invaluable in the analysis of samples for organic compounds, by separating components that have different chemical or physical properties. Instruments are attached to the end of the columns to detect, quantify, and identify the components. Many different types of detectors have been used in conjunction with chromatography. Most notable is the combination of chromatography with mass spectrometry, whereby much information can be obtained from a single sample. Chromatographic techniques can also be used simply as an extraction or preconcentration step before subsequent chemical measurements. Chromatography takes advantage of a number of the properties of molecules and ions in solution and at surfaces. Their behavior in seawater is often vastly different than in fresh water, given the higher ionic strength of seawater, so that greater study of the behavior of

ions and molecules in seawater will be needed to advance the field of analysis of materials dissolved in seawater.

Advances in chromatography in the past 20 years have been achieved both in the chromatographic columns and in detectors that measure concentrations of chemicals in the outflow from the column. Improvements in column chemistry and in flow and solvent characteristics have increased speed, selectivity, and resolution of chromatographic sewparations. Many of the spectroscopic techniques described in this report, including mass spectroscopy, are used at the effluent end of gas chromatographic or high-performance liquid chromatography columns to measure concentrations by a range of so-called "hyphenated" techniques such as GC-MS, GC-FTIR, HPLC-UV-fluorescence diode array detectors, and others. Recent developments in computer control of flow regimens and mixtures of carrier phase solvents show promise for improving chromatographic techniques. Capillary chromatography with supercritical liquids and field-flow fractionation also show promise (Pimental and Coonrod, 1987). The latter technique allows separation of larger macromolecules and particles by application of temperature differences or electric fields across a flow.

Chromatographic systems are inexpensive, and are generally rugged enough to be operated on a research vessel or could be modified relatively easily for this purpose. It is possible to pass large volumes of water through an adsorbent in a device that is the size of an double-A battery, for preconcentration and separation.

Ion chromatography is very promising for ocean measurements. Anions and cations with concentrations below parts per billion can be separated and detected. The chromatographic retention time provides information on the chemical form of the ion, its oxidation state, and whether it is complexed with another material.

Future developments that may facilitate ocean measurements from vessels or buoys include miniaturization of chromatographic equipment (so less solvent is needed per analysis), new solvent transport systems, such as electrokinetic transport, to reduce power requirements on the pumps, and more sensitive detectors for liquid chromatography. Certain combinations of very short columns and flow injection analysis are also promising for real-time studies.

Electrophoresis has been used for decades to separate organic molecules on the basis of molecular charge. Capillary zone electrophoresis combines high voltage with electrophoretic mobility to measure ionic compounds. By adjusting the pH, many organic compounds can be made ionic. If one uses fused silica capillaries, there is bulk (electro-osmotic) flow of solution. The combination of electrophoretic and electro-osmotic flows brings improved separation. Detectors are placed at the end of the flow, as in chromatography. This method can be used to determine the major ions in

seawater. Detection with on-column preconcentration is possible for concentrations down to 1 part per billion. There are hybrid methods that allow separation of neutral solutes by interactions similar to liquid chromatography. The power requirements for capillary zone electrophoresis are low, so it could be used to drive flow injection analysis. The minimum cost of these devices is $15,000 for commercial systems.

Flow Injection Analysis and Continuous Flow Analysis

Flow injection analysis (FIA) is a robust method for automating complex chemical analyses (Ruzicka and Hansen, 1988). It is relatively simple and can be adapted for use with a variety of detectors, including spectrophotometers, fluorometers, mass spectrometers, and electrochemical analyzers. It has been used on board ships to determine dissolved nutrients (Johnson et al., 1985) and trace metals (Sakamoto-Arnold and Johnson, 1987; Elrod et al., 1991). Unsegmented continuous flow analysis (CFA) systems based on the principles of FIA can operate *in situ* over the entire range of depths found in the ocean (Johnson et al., 1986a, 1989).

An FIA system consists of a pump, injection valve, manifold of capillary tubing and a flow-through detector (Figure 4). The injection valve is omitted from CFA systems. Chemical reagents are mixed continuously by pumping them together with a carrier solution. The seawater sample is periodically introduced into the carrier stream by the injection valve in FIA or introduced continuously in CFA. The mixture then flows through the detector. Typical analysis times range from 1 to 8 minutes for chemical determinations in seawater. A variety of manipulations can be performed with FIA systems. These include concentration with resin columns, solvent extraction, dialysis, separation with membranes, and derivatization. FIA systems are commercially available and are also easily constructed.

Flow injection analysis with chemiluminescence detection (FIA-CL) can be used to determine a variety of metals in seawater, including cobalt, copper, manganese, and iron, with detection limits in the picomolar concentration range. These reactions typically involve the formation of a metal complex with an organic ligand and oxidation of the complex. Reaction products in the excited state decay by emitting a photon of light which can be used to quantify the metal concentration. FIA-CL systems are capable of achieving precision and accuracy similar to those obtained by graphite furnace atomic absorption spectrophotometry systems.

A second advantage of FIA and CFA is their ability to operate underwater for extended periods of time (Johnson et al., 1986b). It is often desirable to obtain high resolution profiles of dissolved chemicals to examine their spatial and temporal variability. CFA systems have been used to measure spatial variability in nutrient distributions in the upper ocean (Johnson

Figure 4
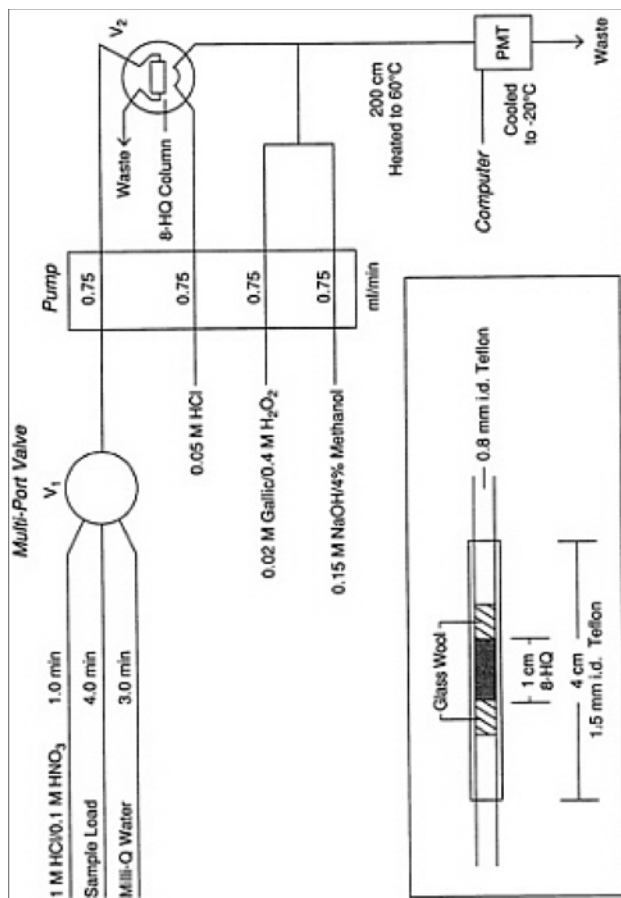Schematic of the FIA system used to determine cobalt in seawater. This system incorporates two valves, which allows cobalt to be concentrated on a column of immobilized 8-hydroxyquinoline (8-HQ) and magnesium ions in the seawater matrix to be removed by washing the column with water at pH 5.6. Reprinted with permission from Sakamoto-Arnold and Johnson (1987). Copyright 1987 American Chemical Society.

et al., 1989) and in redox reactive chemical concentrations around hydrothermal vents (Johnson et al., 1986a). These systems have used conventional peristaltic pumps to propel the sample and reagents through the system.

Good spatial and temporal resolution can be obtained with systems based on peristaltic pumps because they produce high flow rates. However, systems based on peristaltic pumps are limited to deployment times of no longer than a few days because of the lifetime of the tubing used in the pump. The feasibility of using osmotic pumps to propel the sample and reagents for longer deployments is now being explored. Osmotic pumps are widely used for *in vivo* drug delivery systems. They can run for extended periods of time and do not require an external power source, as they operate on the difference in the osmotic pressure between the external seawater and an internal filling solution (Theeuwes and Yum, 1976). Typical flow rates with osmotic pumps are 1 to 10 microliters per hour. A reagent pump would consume a reagent volume of about 10 milliliters per year, and a sample pump would accumulate a sample volume of about 100 milliliters per year. The response time of an osmotically pumped system would be limited by the time required to flush the flow cell of the detector. At these low flow rates, at least 12 minutes would be required to flush a 1-centimeter-path-length photometer cell. However, for long-term deployments of up to 1 year, sampling rates of once per hour would be sufficient. Osmotically pumped CFA systems are now operating in the laboratory, and ocean deployments are expected to begin in the near future.

A CFA system based on osmotic pumps would be extremely simple, and quite inexpensive to build. Instruments based on this design begin to fall within the realm of chemical sensors. A sensor system is usually considered to be much less complex than the typical FIA system. However, the mechanical simplicity of an osmotically pumped CFA system would certainly fall within the framework of a chemical sensor (Ruzicka and Marshall, 1990).

The primary constraints on development of FIA for oceanographic research do not now appear to be the mechanical and electrical systems needed to operate them on board ship or *in situ*. Long-term stability of reagents will be a problem for deployments with osmotically pumped systems. These reagents must be stable for year-long time periods. The stability problem might be solved by using the time release strategy employed in drug delivery.

Robotics (Hurst and Mortimer, 1987)

Two hundred and fifty million chemical analyses are performed each day in the United States for quality assurance, environmental monitoring, medical diagnostics, toxicology, forensics, commerce, research and development, and other purposes. This large number of analyses is due in part to

a rapid increase in the number of laws mandating chemical testing. The increase in testing has surpassed the increase in the training of analytical chemists, which creates the need for faster, high-quality automated analyses. The need for analyzing an increasing number of samples with a diminishing supply of trained analysts may be addressed by the development of automated chemical instrumentation. To promote the development and use of laboratory automation, the National Institute of Standards and Technology formed the Consortium on Automated Analytical Laboratory Systems in 1990, with members from industry and the federal government.

Different analysis regimens, defined by operational complexity and the number of samples that must be run each day, require different types of automation (Figure 5). Dedicated automation includes processes that are highly automated for repetition of a single task. Although Technicon Autoanalyzers® have been taken to sea for 20 years, these fall into the dedicated automation category and are not good examples of the potential of flexible automation, which allows automation of numerous sequential steps. Flexible automation includes more sophisticated laboratory robots, with a spectrum of operational complexities and a moderate number of samples. These robots are called flexible because they can be reprogrammed for different tasks and for a series of tasks that comprise a laboratory procedure. In actual practice, however, once a robot system is built for a specific analysis, it is rarely reconfigured for another method. The use of robots does not always decrease expense. Software development often accounts for a large percentage of development costs. Setting up automated systems requires expertise in computers and mechanical engineering. Usually it takes so much time to remove system errors that robots are not very flexible. Automated processes should not necessarily be designed with the same steps as those used by human technicians, because of the different sensor sets.

Robots have been used in laboratories for a number of applications, including ELISA, transfer of bacterial plaques from agar plates to liquid media, analysis of cranberry juice, and microwave dissolution of environmental samples. How does the performance of laboratory robots compare with that of technicians? Robots are usually slower than technicians because their sensor sets are inferior to those of humans and thus more testing is required to ascertain completion of actions. Robots do not get interrupted, and their performance does not degrade over long periods of time. Sampling rates by robots depend on the procedure being automated. Technicians usually do better than robots on accuracy and precision in the short run, but robots perform better over the long run. Robotic precision has been improved by switching from volumetric to gravimetric measurements. For example, in making chromatographic calibration standards, better than 1% precision can be achieved, using mixtures robotically prepared by gravimetry.
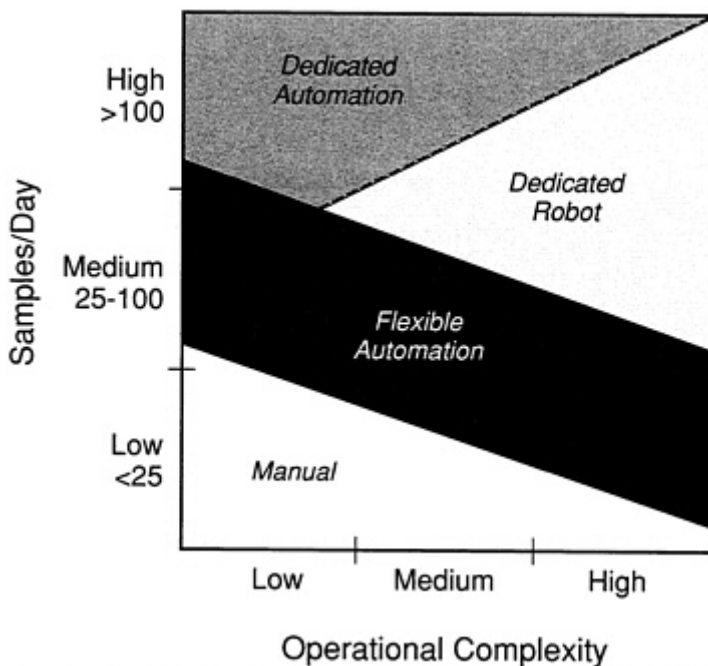
Figure 5
Decision matrix for choosing whether or not to automate a laboratory method, and if so, what kind of automation to use. Courtesy of Zymark Corporation, Hopkinton, Massachusetts, USA.

Robotic errors tend to be major, so that errors can be spotted more easily. In fact, robot-based laboratory procedures can provide a record of all steps for quality control purposes.

Because of vibrations, power stability, and particularly corrosion, commercial laboratory robotic systems available today would have problems on ships. This problem provides an opportunity for research engineers to develop means to modify some sections of the ship to improve power and platform stability. Environmental constraints of a sea-based system were never factored into the design of today's laboratory robots, but the systems could be modified somewhat to reduce these problems. For now, robots would be most feasible for land-based measurements. In the future, however, robots could be important for at-sea measurements, because continuous or repeated measurements are often made over the course of many days.

The base cost for a robot is about $25,000. The average complete cost for an analysis system that actually does a routine analytical task is two to five times this amount. This includes the costs of set-up, creating custom devices, custom software, and training. Land-based systems are available now, and sea-based systems are a distinct future possibility. Time, talent, and money will be needed to develop them. Robots can be set up to carry

out virtually any kind of analysis. Sea-based robotic systems must be designed to handle the power problems, the vibration and stability problems, and the corrosion problems presented by a shipboard environment.

Chemometrics

Analytical chemistry deals with quantitative, numerical concepts and with data. Chemists use statistics routinely to analyze their data and to present it, but usually at an elementary level. A relatively new subfield within chemistry is *chemometrics*. Chemometrics involves the application of multivariate statistics, mathematics, and computational methods to chemical measurements. It exists at the interfaces among the larger fields of chemistry, mathematics and statistics, and computer science. The goals pursued are varied and include designing and selecting optimal measurement procedures and experiments, gathering the best-quality analytical data, and gleaning the maximum amount of useful chemical information from the data. Specific areas of focus include statistics, sampling, experimental design, optimization, signal processing, factor analysis, resolution, calibration, modeling and parameter estimation, structure-property relations, pattern recognition, library searching, and artificial intelligence. Statistical thinking and methodology pervade this list, although the emphasis varies among items. Martin et al. (1988) suggested that application of chemometric methods to data obtained from marine samples could help classify organic components in samples, detect patterns in the data that merit further study, and serve as a noise filter.

The progress of the field of chemometrics can be traced with the aid of a series of six review articles published at 2-year intervals in *Analytical Chemistry* (for example, Brown, 1990) which cover noteworthy advances. A series of recent textbooks also cover the field (for example, Massart et al., 1988). Recent topical reviews on subjects related to multivariate analysis of analytical data have appeared (for example, Jurs, 1990). Relatively few formal courses in chemometrics exist at either the undergraduate or graduate level. Chemometrics education is largely *ad hoc,* via short courses, symposia, textbooks, and tutorials. A compilation of tutorials taken from *Chemometrics and Intelligent Laboratory Systems* is available (Massart et al., 1990). Topics included are experimental design and optimization, signal processing, multivariate calibrations, and model building. This brief discussion of chemometrics is meant to provide sources of details about chemometrics methods rather than giving the basic information itself. The books and review articles cited provide a thorough introduction to the major topics covered here that could be important for ocean measurements.

Experimental design, response surfaces, and optimization of experiments are all important components of chemometrics. Many trade-offs exist among

the number of experiments performed, the number of variables that can be tested for effect, and the efficiency of approach to the optimum experiment with the fewest number of replications. The simplex method (Walters et al., 1991) has been employed widely for optimization, especially in chromatography. For simplex optimization, the number of experiments needed to reach an optimum set of conditions is less than all possible combinations. This method is evolutionary in that it directs the experiment toward the optimum, the computations are simple, and it is amenable to automation. Self-optimizing analytical systems based on simplex optimization have been described in the literature. The use of self-optimizing analytical instruments would be of great value for unattended instrumentation in ocean measurements. The application of standard experimental design methods to oceanic measurements should be a routine part of designing all experiments, particularly those that are expensive to perform and difficult to repeat.

Calibration and mixture analysis addresses the methods for performing standard experiments with known samples and then using that information optimally to measure unknowns later. Classical least squares, iterative least squares, principal components analysis, and partial least squares have been compared for these tasks, and the trade-offs have been discussed (Haaland, 1992). These methods allow a superior spectroscopic experiment to be performed because they allow the calibration of the method to depend in an optimal way on the experimentation done. These calibration methods ensure that the best measurements are done. They are especially useful for noisy data with substantial interferences, such as those found in many types of ocean science measurements.

Multivariate model building allows the construction of models to connect independent variables and observations. Multiple linear regression analysis, principal components regression, partial least squares, and many other advanced statistical techniques have been used. The goal of such investigations may be estimation of the parameters in a mathematical model to assess the relative importance of the independent variables on the dependent variable, or it may be to generate the ability to predict unknown observations. Validation of the models constructed using either internal validation (such as jackknifing or duplexing) or external prediction (true prediction of unknowns) is an important component of such studies. Another important component of such studies is the determination of how to choose the best set of independent variables from among those available. Principal components analysis, factor analysis, and partial least squares have been used successfully in this area, especially for spectral data.

Classification and clustering methods allow the analysis of data when the observations to be explained are not quantitatively known. Discriminants can classify patterns of data into categories. Clustering methods can

seek common characteristics among subsets of data taken from a larger data set. These classes of analysis can be used fruitfully with very large data sets to search for patterns among the data. Certain chemometric methods have been applied to ocean science for some time, primarily for data analysis. Optimization and some other newer chemometric techniques are just beginning to find their way into marine chemistry. Often, it is desirable to put the data into categories or classes, and these pattern recognition methods are well suited to such tasks.

Some of the software to support chemometric methods is available in commercial form. Other software can be located by searching the literature or compilations such as the *Scientific Computing and Automation Resource Directory*. However, many methods of chemometrics are available only from the developers or through reports in the scientific literature rather than as software. It is likely that software well suited to ocean science would have to be produced by combining commercially available software with custom-written software to gain the specificity needed.

Communications

One of the primary benefits of chemical sensors is the ability to obtain chemical data in real time. Real-time data can be used to adjust and optimize experimental protocols and sampling design as data are obtained. Communication of these data is not now a problem for chemical sensors that are operated on board ship, or which are tethered to the ship by a hydrographic cable. Electromechanical cables with two or four conductors are almost universally available on research ships. These cables have a bandwidth great enough to transmit data at 4800 baud over 10,000 m. This should be sufficient for most ship-based chemical sensor applications. Far greater bandwidths can be obtained with fiber optic cables. These are not now in general use for oceanography, as there is limited demand for them, but submarine fiber optic cable and repeaters are available.

Data communications is a much greater problem for remotely operated systems, such as those deployed on moorings in mid-ocean. A limited commercial capability for transmitting data via satellite is provided by Service Argos, Inc. The Argos system is flown aboard the NOAA Advanced TIROS-N satellites in a low earth orbit. As a result, Argos transmitters require little power, and complete units weigh as little as 165 grams. An Argos transmitter aboard an oceanographic buoy can send only 32 bytes of data to a satellite on each orbit, however. The mean number of satellite passes per day ranges from 7 at the equator to 28 at the North and South Poles. There is no capability for two-way communication, which would allow instructions to be transmitted to the sensor.

Several other alternatives to the Argos system exist, but all have prob

lems. The NASA GOES satellites, in geostationary orbits, now have the capability for continuous data transmission at 100 baud. This data rate will become 1200 baud in the near future. The transmitters require 30 watts of power, which is difficult to provide on a continuous basis for year-long time periods, but is feasible for intermittent use. This system can accommodate a limited number of users. Commercial communications satellites can also be used, but the transmitters again require large amounts of power and a large antenna.

Communications will be a problem for retrieving data from remotely operated sensors as they become available. The benefits of near-real-time transmission of data from remote sites are clear. The data can be incorporated into oceanographic models to improve model predictions. Transmission of the data also eliminates the risk of losing the complete data set if the buoy is lost. For telemetered data, processing close to the sensor should be emphasized, to reduce the size of the data stream. For example, computed concentrations, rather than raw data, should be telemetered. Chemometric procedures programmed into the instruments can be used to help in this data reduction process. A new generation of satellites that provide the equivalent of a global cellular communications network will be necessary to take full advantage of chemical sensor systems.

Recommendations and Implementation

Ocean sensors have the potential to measure a variety of analytes dissolved in seawater, particularly with the combination of a variety of transduction mechanisms. The ultimate instrument package could combine sensors based on electrochemical, mass, optical, and piezoelectric mechanisms, all employed for measuring different parameters. No single technology will be useful for solving all measurement problems. Nonsensory types of instrument packages, such as gas chromatographs, capillary zone electrophoresis, and mass spectrometers, will continue to be of some value in addressing ocean measurement needs in the future. Extensive *in situ* measurements are vital for calibration of measurements made remotely from aircraft and satellites. It is impractical to make frequent and detailed measurements from ships, due to lack of both physical and human resources to undertake such an immense task. Sensors will provide the capability to discover many previously unobserved chemical processes and to achieve a better understanding of the ocean system.

THE FEDERAL GOVERNMENT'S ROLE

As discussed in the introduction, there are compelling reasons to study the ocean. The role that the ocean plays in the world's climate, pollution, and food resources can be understood fully only with appropriate measurement capabilities. The development of chemical measurement technologies is critical to understanding both the large-and small-scale processes of the ocean. The U.S. government must take the lead in supporting the research

and development effort for ocean instrumentation because the government, through its agencies, is the beneficiary and ultimate consumer of most ocean measurements. Consequently, it must facilitate the advances and implementation of new measurement methods, through funding agency, commercial, and academic research and development. The committee concluded that the market for ocean instrumentation is too small to stimulate significant commercial interest, so that government support (both financial and administrative) is also required to encourage companies to produce new instruments. The uniformity, documentation, and engineering support afforded by commercial development is critical to widespread acceptance of new technology. One funding vehicle that already exists and has been used to some extent is the Small Business Innovation Research (SBIR) programs. Agencies that sponsor or carry out ocean science measurements should include instruments as examples in their list of desired research for SBIR programs. SBIR programs are too limited in time and total funding, however, to sustain the development of some instruments.

An instrument development program has a 10-year development cycle, as discussed earlier in this report. The nature of ocean measurement instrumentation requires interdisciplinary programs that tend to require longer-term commitments than do single-discipline efforts. These programs require a long time to test and prove the suitability of the instrumentation to the particular measurement need. Many iterations may be required, including extensive ship time to allow researchers to develop confidence in a new measurement technology. The ability to communicate remote data via satellite and other means must also be improved for maximum advantage from chemical, as well as other types, of sensors. Acoustic telemetry adds some promise for underwater data transmission, although it is limited by the variability of the acoustic medium at the long wavelengths that must be used.

Ocean measurements have global impact. Consequently, federal involvement must occur at an international level as well. The International Oceanographic Commission is promoting the idea of a global ocean observing system, which would eventually require new chemical and biological sensors. Various agencies must be involved in coordinating this international effort, including the Department of State, as ocean measurement needs are international in scope. Finally, the Fulbright Program, as well as NATO fellowships, should be used to disseminate new measurement technologies and research expertise throughout the world community.

Research and Development Needed

Regardless of the approaches taken, it is clear that a considerable investment of time and resources will be required to develop the arsenal of chemically selective and stable host compounds that will be required to

measure all the key oceanic species via *in situ* chemical sensor technology. The committee recommends that resources be made available to attract specialists in synthetic organic chemistry and polymer materials to the field of selective recognition chemistry for ocean measurements. For telemetered data, processing close to the sensor should be emphasized, to reduce the size of the data stream.

Standards and Calibration

The ability to make analytical measurements depends intimately on the availability of well-defined standards and calibrants. Many measurements of analytes in seawater (such as DOC and DON) cannot be compared among laboratories because of the lack of appropriate reference materials and blanks for instrument calibration and testing. Intercomparison exercises are critical (Williams, 1992). Seawater is a highly complex medium that makes development of standards particularly difficult. The committee recommends that agencies supporting new ocean measurement technology, such as the Department of Energy (DOE), the National Science Foundation (NSF), the National Oceanic and Atmospheric Administration (NOAA), the National Institute of Standards and Technology, and the Office of Naval Research (ONR), devote a portion of their budgets to support development and maintenance of standards and calibrants. Without standards it will be impossible to develop, let alone deploy, new measurement techniques. Quality control for oceanographic data is crucial as the number of laboratories scattered around the world, both shipboard and land based, measure analytes in seawater. It is unfortunate that funding for production of standards and for calibration is often the first to suffer when agency budgets are cut.

Resources for Instrument Development

Perhaps the major thrust of this report is that improved ocean instrumentation will be necessary to acquire the data necessary to evaluate global change. As noted by Wunsch (1989), the present process and resources for developing ocean instrumentation are inadequate. Present funding for ocean research is ill suited for instrument development because the funding process provides support for a period of 3 to 5 years. Yet ocean instrumentation takes longer to develop than typical laboratory instrumentation, because it must be made to work reliably in a hostile ocean environment *after* being demonstrated on the laboratory bench. For instance, constructing a specialized instrument for use on land might take 2 to 4 years before publishable results are obtained. For an *in situ* device, an additional 3 to 5 years might be required. Thus, few results will be obtained before funding lapses. Moreover, there is overt technical risk in developing new instru

mentation, where both sponsor and scientist may have nothing to show for the effort. Contrast this with studies employing existing methods that provide results immediately and continuously for both sponsor and scientist. Clearly, the time scale and goals of existing programs are antithetical to instrument development. To achieve efficiency in instrument development, sustained involvement of instrument engineers should be pursued. The most common approach now is to employ engineers for the duration of a project. A longer-term approach, as used in the past by NOAA and NSF, should be renewed.

The emphasis of most sponsored research is for new knowledge, which limits the availability of ship resources for instrument development. The importance of ruggedness and reliability for *in situ*, moored, and autonomous instruments translates into a great need for repeated testing in their development. Ocean instruments are analogous to spacecraft in their need for reliability in a hostile environment. For instrument development, testing is an iterative process, with many trials of different components, configurations, and designs typically performed before adequate performance is achieved. Thus, testing ideally is carried out frequently; under reproducible, well-understood conditions; and often on short notice. For ocean instrumentation, the most important part of development is testing the device at sea. The rate limiting step is availability of ship time. Whereas most instrument development has been carried out on large ships, this is not the most efficient means of instrument development. Unfortunately, ship time (precious at $20,000 a day for transoceanic vessels) is mainly allocated for the acquisition of new knowledge during extended cruises. Such extended cruises are far from ideal for testing, since conditions vary with the different places ships go; the extended cruise does not permit quick return to the laboratory for modifications; the operational aspects of the cruise (course, speed, use of other equipment such as depth sounders) may be ill suited to testing a particular device; and the expeditionary nature of cruises requires months of preparation. Oceanographic cruises are often planned at least a year in advance. Despite these drawbacks, much instrument testing is done on cruises simply because no other option is available.

The problem of access to ship time is more difficult for commercial enterprises than for academic ocean scientists, the latter having some fraction of institutional ship time earmarked for their use. For specialized ocean instrumentation, which usually has a small market, the cost of development is prohibitive if ship time is paid for directly. As is the situation for development of instruments by academics, a large portion of the ship time for commercial instrument development is obtained on craft of opportunity or piggybacked with academic research. The difficulty of doing this varies with the sponsoring institution. A few larger companies able to operate their own ships can spread operating costs of the ships over several devel

opment programs. It is crucial to note that a large fraction of the high cost of development is attributable to the duration of the development process. For instance, a 5-year development program accomplished in 3 years would save 2 years of salary and benefits of the participants. Clearly, improving access to ship time for instrument developers would enhance availability of ocean instrumentation.

There are a range of approaches which might be taken to expedite instrument development. One would be to establish research vessels or moored buoys whose primary mission would be to serve as test platforms for instrumentation. Instead of embarking on extended cruises to scattered destinations, these ships would operate in a few areas for which oceanographic data are available in abundance. These ships would be operated on a short-notice basis, with maximum flexibility for handling different sorts of equipment. Repeated visits to the same areas, probably in near coastal areas, would enable moored devices or buoys to be repaired, recalibrated, or returned to shore easily. These ships could be made available for use by academics, government personnel, or commercial ventures in instrument development; this broad use would leverage the resource greatly. Ship scheduling would be controlled by some central authority, such as the University-National Oceanographic Laboratory System (UNOLS) that is presently used to schedule regular oceanographic cruises. If instrument development were viewed as a national priority such that sufficient resources were made available, specifying ships for this purpose should be considered.

The use of buoys for instrument testing also shows great promise. Buoys that are part of the Joint Global Ocean Flux Study are located in the Atlantic and Pacific oceans for the purpose of regular measurements over long time periods. These buoys are visited by ships on a regular basis and are being used for long-term testing of instruments.

Even without additional resources, much can be done to expedite instrument development. Ship time requests for the purpose of instrument development might be coordinated by UNOLS to make more efficient use of the available vessels. Government-funded vessels might be utilized by commercial ventures as well as by academics, if some equitable prioritization and cost sharing system were developed. Other means for expediting testing might be sought, including making more vessels of opportunity available when these are suitable. Navy and Coast Guard ships might be used when this does not conflict with their primary missions. Cooperation for instrument testing already exists informally; what is required is a mechanism whereby the respective bureaucracies can be encouraged to cooperate. Similarly, the realization that development takes longer and has goals and milestones different from those of ocean science should encourage sponsors of ocean science to restructure their support. In particular, the funding periods must be extended and greater provision made for testing.

The research enterprise is better served by identical, well-documented devices throughout the world than by sporadic availability of unique, poorly documented devices; consider the impact on optics research if scientists were obliged to build their own lasers, or on physical oceanography if each scientist built profilers for conductivity, temperature, and depth rather than buy standard models from commercial vendors. While it will still be justifiable to develop instrumentation for a single use, those seeking support for developing widely useful instrumentation should demonstrate that developed instruments have the potential to move beyond proof of principle.

THE ROLE OF ACADEMIC SCIENTISTS

Priority Setting by the Oceanographic Community

The committee chose to categorize a number of analytes in terms of their importance for measurement in the ocean in the coming decade. The selections reflect the needs of the major oceanographic research programs, particularly for understanding the ocean's role in the global carbon cycle, and include some other analytes associated with other issues of great scientific interest. In order to make an interdisciplinary effort between oceanographers and analytical chemists work, oceanographers must be willing to identify a limited number of analytes on which analytical chemists can begin to focus. This report focused on understanding the global carbon cycle, but the committee does not suggest exclusion of other areas from research support.

Education and Training

The committee recognizes that successful implementation of an ocean instrumentation development effort requires extensive ongoing transfer of information and opportunities between the ocean science and analytical chemistry communities. The committee recommends a multipronged approach to accomplish this information transfer. In addition, the committee believes that an effort should be undertaken to educate both the public and promising students about the opportunities in this exciting field. Potential vehicles for accomplishing these goals include the following.

1. Organize miniconferences (for example, a ChemRawn conference; e.g., Goldberg, 1988) or 1/2-to 1-day symposia at major analytical chemistry and ocean science conferences (for example, the Pittsburgh Conference, Gordon Conference, and American Geophysical Union) devoted exclusively to discussing the recent advances and challenges in developing ocean measurement technologies.

2. Explore the establishment of a true organizational "home" for analytical oceanography, preferably as a new subdivision within an already existing American Chemical Society Division (for example, Analytical Division, Environmental Chemistry, and Geochemistry).

3. Important measurement issues must be communicated *from* the ocean science community and new analytical advances *to* the ocean science community. The effort should involve articles in professional and trade journals and conference presentations for both communities. These mechanisms could improve transfer of information between ocean scientists and analytical chemists.

a. The need and opportunities for analytical research relating to ocean measurements could be publicized through articles in key journals or magazines (*Analytical Chemistry:* e.g., Johnson et al., 1992, *C & E News, Journal of Chemical Education*, and others).

b. Information about new measurement technologies could be publicized to oceanographers through *EOS, Oceanography, Sea Technology*, and other publications.

c. Videos and brochures describing the kinds of measurement tools and techniques required to study and understand ocean chemistry could be prepared by agencies and societies that would benefit from the development of new ocean measurement technologies.

d. Undergraduate chemistry curricula can be developed that expose students to concepts of environmental chemistry as they relate to current global oceanography issues (for example, global warming and coastal pollution).

4. Interactions between practitioners of ocean science and analytical chemistry can be encouraged by establishing new funding initiatives at government agencies (for example, NSF, ONR, NOAA, and DOE) to foster interdisciplinary research between oceanographers and analytical chemists on timely ocean measurement problems. The academic reward structure for analytical chemists depends on contributions to chemistry, not marine science. Likewise, marine scientists are rewarded for contributing to marine sciences, not analytical chemistry. The availability of appropriate reward structures will affect whether or not the hoped-for results of publicity, education, and training are achieved. These might include

a. New research initiatives in auxiliar areas of fundamental importance to the future of ocean measurement instrumentation (for example, anticorrosion, antifoulants, and recognition chemistry).

b. Opportunities for academic analytical chemists to attend summer workshops at oceanographic institutions for the purpose of learning more about today's ocean measurement technologies. Based

on this first-hand exposure, these scientists could incorporate more examples of oceanographic measurement techniques into their undergraduate and graduate analytical curricula. In addition, such an experience might stimulate more research initiatives by these faculty in ocean measurement technologies.

References

Alder, J.F., and J. L. McCallum. 1983. Piezoelectric crystals for mass and chemical measurements. A review. *Analyst* 108:1169.

Angel, S.M. 1987. Optrodes: Chemically selective fiber-optic sensors. *Spectroscopy* 2(4):38–48.

Angel, S.M., and M.L. Myrick. 1990. Wavelength selection for fiber optic Raman spectroscopy. *Applied Optics* 29:1350–1352.

Bard, A.J. (editor). 1973. *Encyclopedia of Electrochemistry of the Elements*, Marcel Dekker Inc., New York, 495 pp.

Bard, A.J., and L.R. Faulkner. 1980. Bulk electrolysis methods, *in: Electrochemical Methods: Fundamentals and Applications*, A.J. Bard and L.R. Faulkner (eds.), John Wiley & Sons, Inc., New York, pp. 370–428.

Boyle, E.A., S.D. Chapnick, and G.T. Shen. 1986. Temporal variability of lead in the western North Atlantic. *J. Geophys. Res.* 91:8573–8593.

Brewer, P.G. 1978. Direct observation of the oceanic CO_2 increase. *Geophy. Res. Lett.* 5:997–1000.

Broecker, W.S. 1991. The great ocean conveyor. *Oceanography* 4:79–89.

Bronstein, I., and P. McGrath. 1989. Chemiluminescence lights up. *Nature* 338:599–600.

Brown, S.D. 1990. Chemometrics. *Anal. Chem.* 62:84R–101R.

Bruland, K.W. 1983. Trace elements in sea-water, *in: Chemical Oceanography,* J.P. Riley and R. Chester (eds.), Academic Press, Inc., New York, pp. 157–220.

Buck, R.P. 1984. Electrochemical methods: Ion selective electrodes, *in: Water Analysis*, R.A. Minear and L.H. Keith, (eds.), Academic Press, Inc., Orlando, Vol. II, Part 2, pp. 249–321.

Burlingame, A.L., D.S. Millington, D.L. Norwood, and D.H. Russell. 1990. Mass spectrometry. *Anal. Chem.* 62:268R–303R.

Carey, W.P., and B.R. Kowalski. 1986. Chemical piezoelectric sensor and sensor array characterization. *Anal. Chem.* 58:3077–3084.

Coale, K.H., and K.W. Bruland. 1988. Copper complexation in the Northeast Pacific. *Limnol. Oceanogr.* 33:1084–1101.

Culberson, C.H. 1981. Direct potentiometry, *in: Marine Electrochemistry: A Practical Introduction*, M. Whitfield and D. Jagner (eds.)., John Wiley & Sons, New York, pp. 187–261.

Daniele, S., B. Salvatore, M.A. Baldo, P. Ugo, and G. Mazzocchin. 1989. Determination of heavy metals in real samples by anodic stripping voltammetry with mercury microelectrodes. Part 2. Application to rain and sea waters. *Anal. Chim. Acta* 219:19–26.

Diamandis, E.P., and T.K. Christopoulos. 1990. European chelate labels in time-resolved fluorescence immunoassays and DNA hybridization assays. *Anal. Chem.* 62:1149A–1157A.

Dobler, M. 1981. *Ionophores and Their Structures*, John Wiley, New York, 379 pp.

Eisenberg, H. 1965. Equation for the refractive index of water. *J. Chem. Phys.* 43:3887–3892.

Elrod, V., K.S. Johnson, and K.H. Coale. 1991. Determination of subnanomolar levels of iron(II) and total dissolved iron in seawater by flow injection analysis with chemiluminescence detection. *Anal. Chem.* 63:893–898.

Ewing, A.E., R.A. Wallingford, and T.M. Olefirowicz. 1989. Capillary electrophoresis. *Anal. Chem.* 61:292A–303A.

Falkowski, P.G., T.S. Hopkins, and J.J. Walsh. 1980. An analysis of factors affecting oxygen depletion in the New York Bight. *J. Mar. Res.* 38:479–506.

Fenn, J.B., M. Mann, C.K. Meng, S.F. Wong, and C.M. Whitehouse. 1990. Electrospray ionization principles and practice. *Mass Spectrom. Rev.* 9:37.

Garrell, R.L. 1989. Surface-enhanced raman spectroscopy. *Anal. Chem.* 61:401A–411A.

GOFS. 1984. *Global Ocean Flux Study*. National Academy Press, Washington, D.C., 360 pp.

Goldberg, E.D. (editor). 1975. *The Nature of Seawater: Proceedings of the Dahlem Workshop on the Nature of Seawater*. Dahlem Workshop on the Nature of Seawater, Berlin, 1975, 719 pp.

Goldberg, E.D. (editor). 1988. ChemRawn: Modern chemistry and chemical technology applied to the ocean and its resources. *Appl. Geochem.* 3:1–135.

Goyet, C., D.R. Walt, and P.G. Brewer. 1992. Development of a fiber optic sensor for measurement of pCO_2 in sea water: design criteria and sea trials. *Deep-Sea Res., Part A*, 39:1015–1026

Graedel, T.E., P.G. Brewer, and F.S. Rowland. 1998. Panel 4: Chemistry at the air-sea interface. *Appl. Geochem.* 3:37–48.

Guilbault, G.C. 1984. Determination of formaldehyde with an enzyme piezoelectric crystal detector. *Anal. Chem.* 55:1682–1684.

Haaland, D.M. 1992. Multivariate calibration methods applied to the quantitative analysis of infrared spectra, *in: Computer-Enhanced Analytical Spectroscopy*, P.C. Jurs (ed.), Plenum Press, New York, pp. 1–30.

Hurst, W.J., and J.W. Mortimer. 1987. *Laboratory Robotics: A Guide to Planning, Programming, and Applications*, VCH Publishers, New York, 129 pp.

Izatt, R.M., and J.J. Christensen (editors). 1987. *Synthesis of Macrocycles: The Design of Selective Complexing Reagents*, John Wiley, New York. 480 pp.

Johnson, D.C., S.G. Weber, A.M. Bond, R.M. Wightman, R.E. Shoup, and I.S. Krull. 1986. Electroanalytical voltammetry in flowing solutions. *Anal. Chim. Acta* 180:187–250.

Johnson, K.M., J. McN. Sieburth, P.J. le B. Williams, and L. Brandstrom. 1987. Coulometric total carbon dioxide analysis for marine studies: Automation and calibration. *Mar. Chem.* 21:117–133.

Johnson, K.S., C.L. Beehler, C.M. Sakamoto-Arnold, and J.J. Childress. 1986a. *In situ* measurements of chemical distributions in a deep-sea hydrothermal vent field. *Science* 231:1139–1141.

Johnson, K.S., C.L. Beehler, and C.M. Sakamoto-Arnold. 1986b. A submersible flow analysis system. *Anal. Chim. Acta* 179:245–257.

Johnson, K.S., K.H. Coale, and H.W. Jannasch. 1992. Analytical chemistry in oceanography. *Anal. Chem.* 64:1065A–1075A.

Johnson, K.S., R.L. Petty, and J. Thomsen. 1985. Flow-injection analysis for seawater micronutrients. *Adv. Chem. Ser.* 209:7–30.

Johnson, K.S., C.M. Sakamoto-Arnold, and C.L. Beehler. 1989. Continuous determination of nitrate concentrations *in situ. Deep-Sea Res.* 36:1407–1413.

Jurs, P.C. 1990. Chemometrics and multivariate analysis in analytical chemistry, *in: Reviews in Computational Chemistry*, K.B. Lipkowitz and D.B. Boyd (eds.), VCH Publishers, Inc., New York, pp. 169–212.

Klinkhammer, G.P., and L.H. Chan. 1990. Determination of barium in marine waters by isotope dilution inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* 232:323–329.

Kolber, Z., K.D. Wyman, and P.G. Falkowski. 1990. Natural variability in photosynthetic energy efficiency: A field study in the Gulf of Mexico. *Limnol. Oceanogr.* 35:72–79.

Komorsky-Lovríc, S., and M. Branica. 1987. Trace metal speciation by anodic stripping voltammetry. Part VII. Interaction of zinc with chloride, nitrate, sulfate, iodide and hydroxide. *J. Electroanal. Chem.* 226:253–261.

Lehn, J.M. 1985. Supramolecular chemistry: Receptors, catalysts, and carriers. *Science* 227:849–856.

Lorius, C., J. Jouzel, D. Raynaud, J. Hansen, and H. Le Treut. 1990. The ice-core record: Climate sensitivity and future greenhouse warming. *Nature* 347:139–145.

Luo, S., and D.R. Walt. 1989. Fiber optic sensors based on reagent delivery with controlled-release polymers. *Anal. Chem.* 61:174–177.

Martin, J.J., R.M. Gordon, S. Fitzwater, and W.W. Broenkow. 1989. VERTEX: Phytoplankton/iron studies in the Gulf of Alaska. *Deep-Sea Res.* 36:649–680.

Martin, W.R., S.R. Emerson, and C. Lochmuller. 1988. Panel 5: Chemical processes at the ocean bottom. *Appl. Geochem.* 3:49–55.

Massart, D.L., B.G.M. Vandeginste, S.N. Deming, Y. Michotte, and L. Kaufman. 1988. *Chemometrics: A Textbook*. Elsevier, Amsterdam, 488 pp.

Massart, D.L., R.G. Brereton, R.E. Dessy, P.K. Hopke, C.H. Spiegelman, and W. Wegscheider (editors). 1990. *Chemometrics Tutorials: Collected from Chemometrics and Intelligent Laboratory Systems an International Journal*, Vol. 1–5. Elsevier, Amsterdam, 427 pp.

Montenegro, I., M.A. Queiros, and J.L. Daschbach (editors). 1991. *Microelectrodes: Theory and Experiment*. NATO ASI Series E, Kluwer Academic, Dordrecht, Netherlands, 497 pp.

Muller, F.L.L., and D.R. Kester. 1990. Kinetic approach to trace metal complexation in seawater: Application to zinc and cadmium. *Environ. Sci. Technol.* 24:234–242.

NRC. 1985. *Oil in the Sea: Inputs, Fates and Effects*. National Academy Press, Washington, D.C., 601 pp.

NRC. 1989. *Managing Troubled Waters: The Role of Marine Environmental Monitoring*. National Academy Press, Washington, D.C., 125 pp.

NRC. 1992. *Oceanography in the Next Decade: Building New Partnerships* . National Academy Press, Washington, D.C., 202 pp.

Officer, C.B., R.B. Biggs, J.L. Taft, L.E. Cronin, M.A. Tyler, and W.R. Boynton. 1984. Chesapeake Bay anoxia: origin, development and significance. *Science* 223:22–27.

Osteryoung, J. G. 1988. Electrochemical methods of analysis. *Methods Enzymol.* 158:243–267.

Osteryoung, J G., and J.J O'Dea. 1986. Square-wave voltammetry, *in: Electroanal. Chem., Methods of Enzymology*, A.J. Bard (ed.), Marcel Dekker, New York

Pimental, G.C., and J.A. Coonrod. 1987. *Opportunities in Chemistry: Today and Tomorrow*. National Academy Press, Washington, D.C., 244 pp.

Quay, P.D., B. Tilbrook, and C.S. Wong. 1992. Oceanic uptake of fossil fuel CO_2: Carbon-13 evidence. *Science* 256:74–79.

Ramanathan, V. 1988. The greenhouse theory of climate change: A test by an inadvertent global experiment. *Science* 240:293–299.

RIDGE. 1989. *Ridge Inter-Disciplinary Global Experiments: Initial Science Plan*. RIDGE Office, University of Washington, Seattle, 90 pp.

Ruzicka, J., and E.H. Hansen. 1988. *Flow Injection Analysis*, 2nd ed., Wiley-Interscience, New York, 498 pp.

Ruzicka, J., and G.D. Marshall. 1990. Sequential injection: A new concept for chemical sensors, process analysis and laboratory assays. *Anal. Chim. Acta* 237:329–343.

Sakamoto-Arnold, C.M., and K.S. Johnson. 1987. Determination of picomolar levels of cobalt in seawater by flow injection analysis with chemiluminescence detection. *Anal. Chem.* 59:1789–1794.

Sarmiento, J. 1988. A chemical tracer study for WOCE: Report of a workshop held in Seattle, Washington, January 22 and 23, 1987, U.S. WOCE Planning Report 10, U.S. Planning Office for WOCE, College Station, Texas, 181 pp.

Schaap, A.P. 1988. Chemical and enzymatic triggering of 1, 2-dioxetanes. *Photochem. Photobiol.* 47 (supp.):50s.

Seitz, W.R. 1988. Chemical sensors based on immobilized indicators and fiber optics. *Rev. Anal. Chem.* 19:135–173.

Shaw, T.J., and R. Francis. 1991. A fast and sensitive ICP-MS assay for determination of ^{230}Th in marine sediments. *Geochem. Cosmochim. Acta* 55:2075–2078.

Shuman, M.S., and M. Martin-Goldberg. 1984. Electrochemical methods: anodic stripping, *in: Water Analysis*, R.A. Minear and L.H. Keith (eds.). Academic Press, Orlando, Vol. 2, Part 2, pp. 346–388.

Stoeppler, M. 1991. Analytical chemistry of metals and metal compounds, *in: Metals and their Compounds in the Environment*, E. Merian (ed.), VCH, New York, Chap. I.4a., pp. 105–120.

Tans, P.P., I.Y. Fung, and T. Takahashi. 1990. Observational constraints on the global atmospheric CO_2 budget. *Science* 247:1431–1438.

Theeuwes, F., and S.I. Yum. 1976. Principles of the design and operation of generic osmotic pumps for the delivery of semisolid or liquid drug formulations. *Ann. Biomed. Eng.* 4:343–353.

Thompson, M., C.L. Arthur, and G.K. Dhaliwal. 1986. Liquid-phase piezoelectric and acoustic transmission studies of interfacial immunochemistry. *Anal. Chem.* 58:1206–1209.

Van der Berg, C.M.G. 1989. Electroanalytical chemistry of seawater, *in: Chemical Oceanography*, Vol. 9, J.P. Riley (ed.), Academic Press, New York, pp. 198–245.

Walters, F.H., L.R. Parker, Jr., S.L. Morgan, and S.N. Deming. 1991. *Sequential Simplex Optimization*. CRC Press, Inc., Boca Raton, Florida, 325 pp.

Ward, M.D., and D.A. Buttry. 1990. *In situ* interfacial mass detection with piezoelectric transducers. *Science* 249:1000–1007.

Whitfield, M., and D. Jagner (editors). 1981. *Marine Electrochemistry: A Practical Introduction*. John Wiley & Sons, New York, 529 pp.

Williams, P.M. 1992. Measurement of dissolved organic carbon and nitrogen in natural waters. *Oceanography* 5:107–116.

Wolfbeis, O.S. (editor). 1991. *Fiber Optic Chemical Sensors and Biosensors*. CRC Press, Boca Raton, Florida, Vol. 1, 413 pp., and Vol. 2, 358 pp.

Wunsch, C.I. 1989. Comments on oceanographic instrument development. *Oceanography* 2(2):26.

Wylie, D.E., L.D. Carlson, R. Carlson, F.W. Wagner, and S.M. Schuster. 1991. Detection of mercuric ions in water by ELISA with a mercury-specific antibody. *Anal. Biochem.* 194:381.

Yeung, E.S. 1986. Refractive index detector, *in: Detectors for Liquid Chromatography*, E.S. Yeung (ed.), John Wiley & Sons, Inc., New York, pp. 1–28.

Zirino, A. 1981. Voltammetry of natural sea water, *in: Marine Electrochemistry: A Practical Introduction*, M. Whitfield and D. Jagner (eds.), John Wiley & Sons, New York, pp. 421–503.