New Sensor Technology for In Situ Measurements of Ocean Chemistry

By David R. Walt and Edward R. Urban, Jr.

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Chemical processes in the ocean and at its interfaces with the atmosphere and the seafloor play a major role in regulating global biogeochemical cycles. Predicting the impact of human disturbances on these cycles requires a fundamental understanding of how they operate over a range of time and space scales. Unfortunately, the chemical properties of the ocean have not been sampled adequately at proper scales, or in some cases with adequate calibration standards, to create comprehensive global data sets for such understanding to be developed. Remote sensing of chemical parameters from aircraft and satellites is limited to few analytes and to the top layer of the ocean. Ship-based sampling has accomplished relatively few sampling tracks spread over time and over the ocean surface. The resulting lack of data limits our understanding of such processes as the air-sea flux of carbon dioxide (for understanding global warming) and the factors regulating oceanic primary production on a global scale.

Member nations of the International Oceanographic Commission are designing a global ocean observing system (GOOS) to implement routine monitoring of key oceanic parameters for eventual monitoring and prediction of global climate, ocean health, and other factors important to society. The implementation of many GOOS components will depend on the development and deployment of new chemical sensors for long-term (months to years), continuous use in the ocean.

A group of analytical chemists and ocean scientists was brought together by the Committee on Oceanic Carbon of the National Research Council's (NRC) Ocean Studies Board to identify techniques of analytical chemistry that could be used in ocean science. The result of the committee's deliberations is an NRC report, Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies (NRC, 1993). The report, summarized below, focuses on seawater analytes that are important for understanding key aspects of the ocean's role in the global carbon cycle and on *in situ* measurements of these analytes.

The following is an ideal *in situ* sensor: manufacturable in large quantities, cost effective, fully automated, long lasting, stable in its calibration or self-calibrating, resistant to environmental conditions, and selective. Increased research and development activity will be required to design sensors with these attributes for deployment on long-term remote moorings, autonomous vehicles, and profilers. State-of-the-art measurement technologies (not necessarily sensors) that are most promising for *in situ* use include electrochemistry, spectrophotometry, and flow injection and continuous flow-analyses. The most difficult problem in designing sensors may be to achieve the desired selectivity, stability, and sensitivity for measuring dissolved analytes in the open ocean, where analyte concentrations are low and sensors must operate unattended for weeks or months at a time. Once sensors capable of measurements under these conditions have been developed, adapting them for use in coastal areas, sediments, and other environments in which analytes are found at higher (although more variable) concentrations should require only design modifications.

New biosensors based on selective immunochemical and other reactions are being developed. The development of such sensors will require the cooperation of specialists in synthetic organic chemistry, polymer chemistry, oceanography, electrical and mechanical engineering, and sensor design. Chemometric techniques carried out by microcomputer-based *in situ* instruments could enable optimized sampling and chemical analysis, remote data analysis, and more efficient communication of data to ships and satellites.

Cooperative activities among the federal government, industry, nonprofit research laboratories, and academia will be required to overcome the barriers to successful research, development, and transfer of new measurement techniques and systems to ocean science. The federal government

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must lead the research and development effort for ocean instrumentation because government agencies are the beneficiary, and ultimate consumer, of most ocean measurements. A number of approaches could be taken to expedite instrument development. One approach would be to establish buoys and vessels dedicated as test platforms for instrument research and development. Another approach would be for federal agencies to devote some of their instrument development funds to long-term (7 to 10 y) grants (Wunsch, 1989) and to maintain instrument design and engineering groups.

Successful implementation of a development effort for ocean instrumentation will require extensive transfer of information and opportunities between the ocean science and analytical chemistry communities. Measurement science is one of the most active fields of chemistry today and could provide new sensors and techniques for ocean science. Analytical chemists and instrument specialists welcome the opportunity to apply new techniques to novel measurement needs, but need to know which analytes oceanographers (and their agency sponsors) are most interested in measuring. The Committee on Oceanic Carbon divided into three levels the priority analytes that must be measured to improve our understanding of the ocean's role in the global carbon system:

Priority 1—Quantifying the Anthropogenic Carbon Input—TCO_2, pCO_2, pH, alkalinity, and $\delta^{13}C$ and $\Delta^{14}C$ of inorganic and organic carbon species

Priority 2a—Understanding the Biological Pump—dissolved and particulate organic carbon, nitrate, phosphate, silicate, ammonium, iron, $\delta^{15}N$, algal pigments, dissolved oxygen, and $\delta^{18}O$

Priority 2b—Tracing Water Masses—chlorofluorocarbons, ^{39}Ar, tritium, and $\delta^{3}He$.

Priority 3—Other Analytes of Interest—minor nutrient elements (zinc and copper), tracers of air-sea interaction (aluminum, lead, dimethyl sulfide, and ^{222}Rn), tracers of hydrothermal input (manganese and ^{3}He), and tracers of interactions with particles (^{234}Th, ^{230}Th, and ^{210}Pb).

A multifaceted approach should be used to disseminate information to chemists, particularly to analytical chemists, and to improve communication between the communities. Potential vehicles for accomplishing this goal include the ChemRawn (Goldberg, 1988) and MarChem workshops, articles in a variety of journals that seek to bridge the gap between the fields (e.g., Johnson *et al.*, 1992; Sarmiento, 1993), and cross-disciplinary sessions at oceanography and chemistry society meetings.

There are many exciting research opportunities available to analytical chemists and measurement scientists in the area of ocean-based chemical measurements. Likewise, ocean scientists have much to gain from collaborations with analytical chemists. Cooperation and communication between oceanographers and analytical chemists could be encouraged by funds designated for joint research from agencies with interests in ocean research and/or instrumentation (e.g., National Science Foundation, Office of Naval Research, National Oceanic and Atmospheric Administration, Department of Energy, and the National Institute for Standards and Technology).

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References

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

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

National Research Council, 1993: Applications of Analytical Chemistry to Oceanic Carbon Cycle Studies. National Academy Press, Washington, D.C.

Sarmiento, J., 1993: Ocean carbon cycle. *Chemical and Engineering News* (May 31), 30–43.

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