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SPECTROSCOPY IN OCEANOGRAPHY

by

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"Truly a rare and marvellous affair. A philosopher not in his study but on the high seas, far away from all scientists and among sailors, not in quiet and solitude, but amidst savage shoutings, not in peace but in danger of life!"*

THE layman may regard the oceans as uniform masses of water, as invariant as they are timeless, their composition stirred into one homogeneous body of water by the relentless waves. Were this so, a single authoritative determination of each of the constituents would be sufficient. Marine chemistry would lack a "raison d'être."

In actuality, the composition of the oceans varies considerably. A large volume of fresh water is daily added by rivers, melting ice and rainfall, while a similarly huge volume is removed by vaporization and freezing. These processes thus dilute or concentrate the total salt content of the waters in different climatic regions. The temperature and composition of different water masses affect their mixing. Cold, but less saline water, sinks from the sea surface in high latitudes and flows equatorward at depth then rises again in middle and low latitudes. The ocean is in constant motion, not just in waves and tides that characterize its surface, but in great currents that may flow between continents. These currents can be likened to enormous "rivers" carrying not only great quantities of heat from one part of the world to another, but huge volumes of water. The Gulf Stream carries 25-30 million cubic meters of water *per second* through the Florida Straits, reaching 80-100 million cu m/sec off Chesapeake Bay. These numbers can be better appreciated when one considers that the combined discharge of all the world rivers into the oceans is just over 1 million cu m/sec or that the total water consumption for New York City over a ten year period was 50 cu m/sec!

Similar currents exist in other parts of the world. The West coast of South America is caressed by the cold Humboldt Current. This current is noted for exceptionally high concentrations of carbon, silicon, phosphorus and nitrogen, elements vital for supporting marine life. Thus the Humboldt teems with life, fosters the largest commercial fishing in the world,

[However] "if a person suffer much from sea-sickness, let him weigh it heavily in the balance. I speak from experience: it is no trifling evil, cured in a week."†

and is the home of the mightiest game fish on record, the black marlin. Occasionally, however, disaster strikes in the form of El Nino. Every few years the Humboldt disappears and a flow of warm surface water, depleted in nutrient elements, takes its place. This is El Nino. Fish and birds die by the million, the commercial fisheries are closed and torrential rains wreak havoc on the coast. El Nino is a classic example of the way compositional variations in ocean waters can control marine life and man's dependence on the sea.

Until recently, the oceans with their vast area and volume have seemed a safe site for disposal of waste. Suddenly we realize that this may not be so. Man's wastes, particularly off the shores of the highly developed nations, are not dispersed uniformly throughout the ocean but may be concentrated by chemical and biological mechanisms. Typically the level of mercury in the ocean is about 0.1 part per *billion*. In contrast, the values found in tuna are in the neighborhood of 0.5 parts per *million*. Combustion products of chemical fuels, radioactive material from nuclear fission, and the organic poisons from pesticides may equally be concentrated by various marine organisms and thus enter the food chain leading back eventually, and disastrously, to man.

The composition of the sea bed often reflects the chemistry of the overlying waters. Only as recently as 1965 anomalous bodies of water were discovered in the Red Sea (1). These hot brines (56°C, 133°F) contain ten times as much salt as do normal sea-water, with metals such as Zn, Cu, Pb, Fe and Mn 1,000-50,000 times more concentrated. The sea floor beneath contains deposits estimated at 24 million tons of Fe, 2.9 million tons Zn, 1.1 million tons Cu as well as smaller quantities of Pb, Ag and Au. Total value is put at 2.5 billion dollars. The deep waters of the Black Sea have no oxygen; the sediments beneath are rich in organic matter and contain appreciable quantities of hydrogen sulphide.

*Translation of part of the preface by H. Boerhaave to his Dutch edition of the works of Count L.F. Marsilli (1786), who was one of the early pioneers in chemical oceanography.

†From Charles Darwin (1845), The Voyage of the Beagle, in retrospect of the advantages and disadvantages of the scientist going to sea. Also heartily endorsed by this author (G.T.).

All of these factors, resulting from the interaction of the sea with its boundaries (continents, sea-floor and atmosphere), with its constituents (marine plants and animals), and more recently from man's direct intervention, cause compositional changes, the understanding and measuring of which give us marine chemists our jobs.

The development of chemical oceanography closely parallels that of suitable experimental techniques and adequate sampling equipment. Although speculations regarding the saltiness of the sea were made by the ancient Greeks, systematic chemical measurements did not begin until the 18th and 19th Centuries. Robert Boyle (1670) and Lavoisier (1776) were among the early pioneers in identifying the various salts present in the sea. Dittmar (1884) reported on the quantitative aspects of sea-water analysis using gravimetric and volumetric techniques. He noted that, although the total salt content may be variable, the *ratios* of the *major* constituents remain *almost* constant. Only in the last 50 years have we begun to probe the mysteries of the oceans in more detail as scientists with modern instruments have applied the analytical techniques of their various disciplines. The most recent analyses have confirmed those of Dittmar.

In 1882 Manet predicted that *all* elements would be found in sea-water. K, Na, Ca, Mg, S and Cl had been identified in sea-water by 1819, Br in 1826, B in 1853, Sr and F in 1865. The development of the optical emission spectrograph by Bunsen and Kirchoff in 1860 paved the way to the identification of other elements. However, it was not by direct analysis of sea-water but by inference: the analysis of ashes of marine organisms, the elemental composition of which is determined by uptake from sea-water. Iodine was first recognized in marine algae; later Ba, Co, Cu, Pb, Ni, Ag and Zn were noted in marine organisms before their discovery in sea-water. Recently, from many different analytical techniques mostly involving some kind of spectroscopy, chemists have confirmed the presence of 73 elements in sea-water.

Measurements made in marine chemistry are not uniquely oceanographic; only the origin and nature of the samples are unusual. Because of the wide range of the subject I will concentrate principally on inorganic analytical aspects rather than physical or organic chemistry. I should stress, however, that marine organic chemistry is a vital field of great importance in studies of the food chain, the origin of petroleum, communication and sensing in organisms, pollution and the future possibility of drugs from the sea. Naturally, all analytical techniques such as gas chromatography, mass spectrometry, Raman, NMR, UV and IR spectroscopy are an integral part of this branch of marine chemistry.

Here I wish to consider three oceanographic analytical problems: sea-water, marine organisms and marine sediments, as well as the role of spectroscopy in each. First, however, I should point out that much of marine chemistry, though by no means all, is done in shore-based laboratories and not at sea. Analysis at sea is beset by many difficulties, particularly the rolling and pitching of the ship and vibration from engines and generators. The old adage "one hand for the ship and one for yourself" still holds. High frequency motions and vertical accelerations make accurate weighing nearly impossible. Wide temperature variations, high humidity, and often poor voltage and frequency control in the power supply would terrorize

any instrument manufacturer. Combine these sorts of vicissitudes with those of logistics in transporting equipment and personnel to and from ships (large ocean-going research vessels are out at sea for periods of 6 to 12 months with frequent changes of scientific party and equipment at foreign ports), and with the more personal problems of "mal de mer," boredom and family separations, and it becomes evident that obtaining good, precise measurements at sea is not easy. This does not mean, however, that the marine chemist does not go to sea. A few analytical techniques, including spectrophotometry, titrimetry and potentiometry are nonetheless feasible and routinely carried out on board ship. Problems in sample collection, possible contamination, treatment of special samples before storage are such that many research chemists have to spend one to two months per year at sea collecting and preparing their samples for subsequent analysis back in the laboratory. Some of these aspects are treated in the following discussions.

SEA-WATER contains about 3.5% dissolved solids, but of these only 12 elements are present in amounts greater than 1 ppm. Table 1 shows the average composition of sea-water including trace elements ranging in concentration from 0.5 ppm (nitrogen) to 4 parts per trillion (gold). These salts are mainly derived from the continents where the rocks are continually being broken down, small quantities being dissolved and carried to the oceans via the rivers.

Table 1.
Average Composition of Sea-water

Major Elements: (>1 ppm)		Trace Elements: (<1 ppm)	
Cl	19,000	N	0.5
Na	10,500	Li	0.17
Mg	1,350	Rb	0.12
S	885	P	0.07
Ca	400	I	0.06
K	380	Ba	0.03
Br	65	Al, Fe, Mo, Zn	0.01
C	28	As, Cu, U	0.003
Sr	8	Mn, Ni, V	0.002
B	4.6	Ti	0.001
Si	3.0	Sn	0.0008
F	1.3	Se	0.0004
		Co	0.0001
		Cr	0.00005
		Ag	0.00004
		Hg, Pb	0.00003
		Bi	0.00002
		Au	0.000004

The effects of changes in temperature, pressure and concentration of dissolved salts on the physical properties of sea-water, and thus its mixing, are parameters of interest to the physical oceanographer. Determination of the total salt content (salinity) rather than individual major elements is usual since the ratios of the major elements (with the exception of Si) do not vary greatly geographically or temporally, although, of course, the total salt content may vary appreciably. Analysis is generally done by measurement of the electrical conductivity or determination of the chloride content (salinity=0.03+1.805 Cl). Dissolved oxygen and silica are additional measurements commonly made to help characterize a given water mass. These are all measurements that

Table 2.
World Production from Ocean Water, 1968*
 (Annual value = \$400,000,000)

Material	Tons/year	% of Total World Production
NaCl	35,000,000	29
Br	102,000	70
Mg (metal)	1,06,000	61
Mg (compounds)	690,000	6
Fresh water	142,000,000	59

*From Reference 14

need to be, and are routinely done, at sea. The major elements present in sea-water have some direct commercial value as well as importance in controlling basic physical and biological processes. The world production figures for recovery of major constituents from sea-water are shown in Table 2; total value was \$400,000,000. Future demands for fresh water will have to be met by desalination of sea-water.

Trace elements in sea-water are the constituents that vary most and cause the major analytical problems. They play an important role in the life systems, for example Zn in enzymes, Fe in the respiratory pigment haemoglobin in higher animals and Cu in haemocyanin, the oxygen-carrying molecule of mollusks and arthropods, and Si and Ca in skeleton formation of marine plants and animals. The biologist's concern is for those elements of nutrient value for studies of the fertility and productivity of the oceans: C, N, P and Si. Dissolved trace elements in sea-water are also part of the world's mineral reserves. The oceans can be likened to a vast ore body (reserves of 50 quadrillion tons), the physical properties of which are itemized in Table 3. It is a unique ore body in that it is continuously being replenished; 40 billion tons of solids are added per year by the rivers, 6 billion tons in solution. Commercial possibilities have traditionally excited many businessmen: a ¼ cubic mile per year of sea-water could provide American needs for Si, Mg, Cl, Na and Br; 1½ cu mi could supply the K and S; 5 cu mi B and I; 50 cu mi Th and F; greater than 100 cu miles would be required to supply sufficient quantities of other metals. Recovery is the catch. To "mine" 1 cu mi per year would require 2,100,000 gallons of sea-water to be processed every minute and with 100% efficiency would provide \$940,000 worth of 17 critical metals: Sb, Bi, Cd, Cr, Co, Au, Pb, Mn, Hg, Mo, Ni, Ag, Sn, Ti, U, and Zn—an ore value of only \$0.02/hundred tons. At present recoveries are neither economically nor technically feasible, but future depletions of the world continental reserves may leave us with no choice.

Variations in concentrations of trace elements reflect biological and boundary interactions of the seas. The direct analysis of sea-water for these components demands techniques with sensitivities in element determination from 10^{-6} to 10^{-11} g. The low levels of trace elements in sea-water also present problems in collection and storage of samples. For many element determinations large volumes of sea-water are required to provide sufficient measurable quantity of an element (Fig. 1). Collecting containers have to be made of inert materials to avoid contamination. Storage of sea-water may lead to adsorption of elements on the walls of the containers or leaching of elements from the walls.

Many spectroscopic techniques are not sufficiently sensitive for direct analysis of sea-water and analysts are forced to resort to preconcentration techniques. The choice of technique is obviously influenced by such factors as equipment availability, cost, precision and accuracy required, sensitivity, number of samples, speed of analysis etc. We mention some of the more common techniques but a fuller discussion can be found in reference (2) and its bibliography.

- (1) Neutron activation—this is one of the few techniques with sufficient sensitivity and precision for direct analysis of sea-water. It also has the added advantage that after irradiation it is independent of contamination by inert materials, and separations can thus be done more easily. Elements determined by this method and γ -spectroscopy include As, Ba, Sr, Au, Rb, Cs, Cu, Mn, Zn, Sb, Cr, Co, Se, Ag and U.
- (2) Isotope dilution and mass spectroscopy—this method is also feasible for direct analysis of sea-water since it has sensitivity limits of 10^{-7} to 10^{-9} g. Elements commonly determined include Li, Ba, U and Sr.

Table 3.
Physical Properties of the Ocean Ore Body

Average Depth:	2.36 miles
Surface area:	140×10^6 sq miles
Volume:	330×10^6 cu miles
Mineral content:	165×10^6 tons/cu mile
Total reserves:	50×10^{15} tons

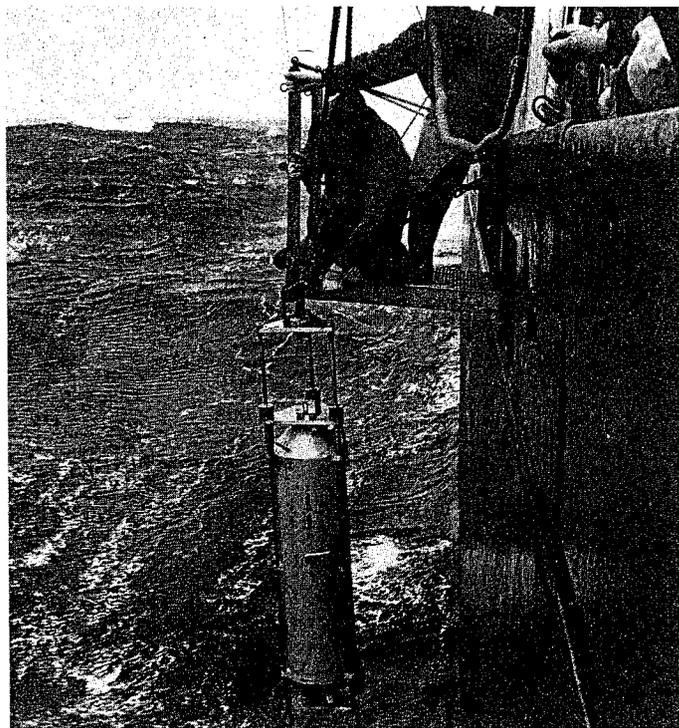


Figure 1. A large-volume (35 gal, 130 liter) water collecting bottle being lowered over the ship's side. The bottle is made of aluminum and is Teflon-lined. Spring activated neoprene-lined stoppers close "on command" by a heavy weight sliding down the wire and releasing a catch. This bottle was originally designed at the Woods Hole Oceanographic Institution for collecting sufficient volumes of sea-water to measure radioactive nuclides introduced into the oceans as "fallout" from atmosphere-exploded nuclear devices. These nuclides are used as tracers for studying ocean mixing processes as well as being monitored to ensure their levels in the water and in organisms do not reach hazardous levels.

- (3) Emission spectroscopy—Requiring concentration, except for the major elements, this technique had been selected before the advent of gamma or atomic absorption spectroscopy. Procedures included co-precipitation with mercury or copper sulphide, with ferric hydroxide or 8-hydroxyquinoline. An ion-exchange concentration has also been tried for elements such as Au, Bi and Cd. Marine chemists are closely following the developments of plasma jet excitation sources as a possible sensitive tool with the emission spectrometer.
- (4) Flame photometry—is commonly applied to the direct determination of Ca and Sr in sea-water. It is also satisfactory for determining Ba, Li, Rb and Cs after ion-exchange concentration. Recent advances in instrument design and flame stabilization show promise for its further application to sea-water analysis.
- (5) Atomic absorption spectroscopy—is being increasingly adopted for sea-water analysis in conjunction with concentration procedures. Good determinations of Co, Cu, Zn, Pb, Fe, Ni and Mn have been reported with ammonium pyrrolidine dithiocarbamate (APDC) as the concentrating, chelating agent, and methyl isobutyl ketone (MIBK) as the extracting solvent. Rb and Li have been determined by direct aspiration of untreated sea-water.
- (6) Spectrophotometry—is commonly adopted for measurements of the nutrient elements, for example, nitrite (strychnidine or diazonium color), P and Si (molybdate color). It is also a common technique for analysis of some trace metals such as Cu (diquinolyl color), Cd (dithizonate color) and B (carminic acid color). It is one of the few techniques that can be routinely used at sea.
- (7) Fluorometry—has better sensitivity than spectrophotometry but is less common because of interference effects. It has found some support for Al (pontochrome blue-black R), Be (morin), Ga (8-hydroxyquinoline) and U (sodium fluoride).
- (8) X-ray fluorescence—has detection limits above emission spectroscopy yet is very little used. Determinations of Cr, Cu, Co, Mn, Fe, Ni, V and Zn, after preconcentration, have been reported.
- (9) Polarography—is becoming more popular whether as cathode ray, anodic stripping or square-wave polarography. Elements very nicely determined by these techniques, particularly anodic stripping voltammetry, include Cu, Pb, Cd, Zn, Mn, Al and U. Some details of the element speciation in sea-water are also possible with this method.

PLANTS and animals in the sea are responsible for some of the most dramatic changes in sea-water composition. Many elements, particularly nutrient and trace metals, are taken up and concentrated by the organisms that inhabit the surface waters of the oceans. The "fixing" of these elements depletes the surface waters and inhibits further productivity. After the death of the organisms, their remains sink into the deep waters where they are oxidized and the elements returned to circulation. The return of these nutrients to the surface governs the organic productivity and hence the fisheries in the various regions of the sea.

The study of the elemental composition of marine organisms is thus important in terms of productivity, in the movement and transfer of ions from surface to deep waters, and in the concentration of elements from sea-water. This latter aspect provides a remarkable and interesting phenomenon. Concentration by the organism, compared to the abundance of the element in sea-water, can be as high as a millionfold. Moreover, organisms can be very specific for which element they concentrate. For example, Carlisle (3) has shown that some tunicates concentrate V, some Nb, some neither element, but none concentrates both elements. Ti may be concentrated by some ascidians over one million times (4). Nicholls *et al* (5), employing emission spectrographic techniques for analysis of plankton (small, often microscopic plants and animals that live at or near the sea surface and which are the primary link in the food chain), predicted from their early results that "for any given chemical element there will be at least one planktonic species capable of spectacularly concentrating it." Here at Woods Hole, in conjunction with Nicholls and coworkers, I am continuing this work using direct-reading emission spectrometry. We have not yet found it necessary to refute that original prediction.

Table 4.
Concentration Factors for Some Metals
in Commonly Eaten Shellfish*

Element	Scallop	Oyster	Mussel
Ag	2,300	18,700	330
Cd	2,260,000	318,000	100,000
Cr	200,000	60,000	320,000
Cu	3,000	13,700	3,000
Fe	291,500	68,200	196,000
Mn	55,500	4,000	13,500
Mo	90	30	60
Ni	12,000	4,000	14,000
Pb	5,300	3,300	4,000
V	4,500	1,500	2,500
Zn	28,000	110,300	9,100

*Element concentration in the organism/element concentration in sea-water (15)

The possibility of "farming" certain marine species and "mining" them for their metal concentrates is not so futuristic as it sounds (6) and in at least one instance is fact, e.g. iodine from seaweed. From another point of view, concentration of certain toxic metals in species eaten by man is not at all welcome as indicated by the concentration factors for elements found in common shellfish (Table 4). Mercury poisoning, through concentration of that metal by shellfish, has already resulted in 52 deaths and 168 serious illnesses to the residents of Minimata, Japan (7). Even now, Hg level in some swordfish and tuna, and shellfish in certain regions is close to our own levels of tolerance. Indiscriminate discharges from industrial plants, particularly from the electrolytic production of chlorine and caustic soda, from incineration of discarded electrical equipment, from antifouling paints and from crop applications and seed treatments put mercury into the air, soil and water. The surprising evidence of biological concentrations emphasizes how little we know of the natural cycle of mercury in the environment and how the difference between tolerable natural background levels and levels harmful

to man and animals may be very small. This may well be true for other heavy metals. Let's worry when we read that New York is currently putting 5×10^7 g Ag, 2×10^9 g Cr, 9×10^8 g Sn and 5×10^9 g Pb per year into the Atlantic in dredge and sewage sludge (8).

Analysis of marine organisms, as with continental biological materials, involves drying and ashing. Low-temperature ashing with oxygen plasma, or refluxing with acid-peroxide mixtures prevents loss of volatile elements. With many species, the body tissues and fluids are composed almost entirely of the combustible elements C, H, O and N and only a few milligrams of ash may remain from a large volume of original sample.

In selecting an analytical technique the marine chemist is bound by constraints: (a) a large number of elements need to be quantitatively analyzed (samples are hard to come by and we have little knowledge concerning most element distributions); (b) there are often only small amounts of sample available (<1-100mg); (c) the matrices in which the elements are present are complex and variable both with respect to major and trace element composition; (d) the heterogeneous nature of the material requires careful sampling and preparation to ensure that the analyzed sample is representative and free from contamination; (e) many of the elements are present in vanishingly low concentrations (<1ppb-100ppm).

These considerations favor spectroscopic instrumental analysis and in the chemistry department at Woods Hole we combine several methods. For extremely small samples (<10mg) we prefer neutron activation with γ - spectrometry; a limited number of elements, those requiring high precision and accuracy, are better suited to atomic absorption and/or spectrophotometry. For the majority of samples and elements we rely on direct-reading emission spectrometry.

The emission technique we have developed is for powdered ash samples and dc arc excitation (9). For homogenization and final reduction to powder, the Spex 5100 Mixer/Mill with methacrylate or agate grinding vials does a good job and reduces contamination (10). Because of the large number of elements we determine, and the wide range of volatilities in the dc arc, we chose a split-burn technique with buffered samples. The elements currently determined on our direct reader (1.5m, Paschen-Runge grating mount) are: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, In, K, La, Li, Mg, Mn, Mo, Na, P, Pb, Pd, Rb, Sb, Si, Sn, Sr, Te, Ti, V, Y, Zn and Zr. For standardization we prepare artificial mixes as close to the composition of the natural samples as possible. This means we need a wide range of standards, both in composition and elemental concentrations (Table 5). The speed of analysis with the direct reader, the speed of data processing—we have developed our own computer program for this (11)—plus the improved accuracy from using standards similar to the samples, offset the disadvantages of working with multiple standards.

THE third aspect of spectroscopy in oceanography that I shall consider here concerns marine sediments mainly composed of inorganic alumino-silicate minerals brought into

Table 5.
Standardization Matrices for Emission
Spectrometric Analysis of Marine Organisms

Organism	Matrix Composition (wt %)*
Calcareous (Foraminifera-type)	CaCO ₃ 100%
Siliceous (Radiolaria-type)	SiO ₂ 100%
Ctenophore (Mnemiopsis-type)	NaCl 90.66% MgO 6.90% KCl 2.44%
Cephalopod (Loligo-type)	NaCl 39.70% KCl 36.35% Ca ₃ (PO ₄) ₂ 23.95%
Composite Plankton	CaCO ₃ 60.0% Al ₂ O ₃ 10.0% KCl 3.0% Na ₂ CO ₃ 20.0% SiO ₂ 5.0% MgO 2.0%

*Spex G standards (49 elements in graphite) or Spex Ca standards (calcium carbonate) are mixed with our matrices to provide a range of concentrations from 0.1% to 0.0001%.

the sea by rivers, glaciers, winds and volcanic eruptions. Also present are those particles made up of the biogenous skeletons and shells (mainly calcium carbonate and silica) that reach the bottom when organisms die. In addition new minerals may be formed on the sea-floor from certain metal salts precipitating from sea-water. The most abundant sediments and the range and complexity of their major element composition are indicated in Table 6. Any given sample may consist of a mixture of these three principal types and the proportions may vary greatly with distribution and depth of the deposit.

Table 6.
Chemical Composition of the
Three Principal Types of Deep Sea Sediments
(wt %)*

Composition	Red Clay	Calcareous ooze	Siliceous ooze
SiO ₂	53.93	24.23	67.36
TiO ₂	0.96	0.25	0.59
Al ₂ O ₃	17.46	6.60	11.33
Fe ₂ O ₃	8.53	2.43	3.40
FeO	0.45	0.64	1.42
MnO	0.78	0.31	0.19
Ca	1.34	0.20	0.89
MgO	4.35	1.07	1.71
Na ₂ O	1.27	0.75	1.64
K ₂ O	3.65	1.40	2.15
P ₂ O ₅	0.09	0.10	0.10
H ₂ O	6.30	3.31	6.33
CaCO ₃	0.39	56.73	1.52
MgCO ₃	0.44	1.78	1.21
C	0.13	0.30	0.26
N	0.016	0.017	-

*From reference 16

Analytical studies of marine sediments contribute to the understanding of pathways and residence times of elements in the oceans, the formation and distribution of various sediments, and the possibility of discovering and mapping economic mineral deposits. In shallow water on the continental shelves, for example, are exploitable deposits of sand and gravel, calcareous shell deposits of value in cement and chemical industries, and deposits of phosphates ($\text{Ca}_3\text{F}(\text{PO}_4)_3$) for fertilizer and chemical industries. Recently discovered off the coast of California are over 6,000 square miles of phosphate beds estimated at 1.5 billion tons (14,000-420,000 tons/sq mile).

Other fascinating and, if recovery techniques are perfected, commercially viable deposits that occur on the sea-floor are the so-called "manganese nodules." These ores are actually composed of hydrated oxides of iron and manganese precipitated from sea-water; they often contain variable but economically worthwhile amounts of metals such as Co, Ni, Cu, Mo, Zn and Pb. Deposits occur as earthy, black, round to ovoid nodules from pea to cannonball size, as coatings up to several cm thick on other rocks, or as large slabs or pavements over a meter in length. The Blake Plateau off the eastern USA has 3,000 square miles of ferromanganese covered floor; the Pacific Ocean has 1.5 trillion tons of nodules in surface deposits (Fig. 2).

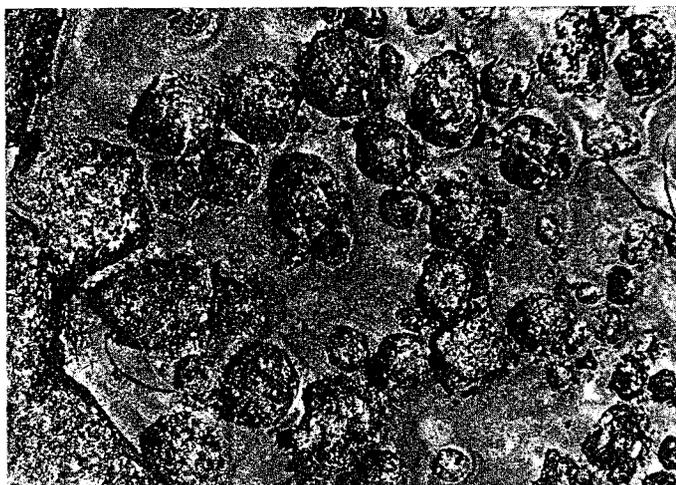


Figure 2. A deep-sea camera reveals manganese nodules littering the sea-floor. It is estimated that on the bottom of the Pacific Ocean there are 1.5 trillion tons of nodules, and they are forming at an annual rate of 10 million tons.

The composition of nodules in the Pacific (Table 7) may vary with geography and depth; Co-rich nodules are found in the mid-Pacific; Co-poor, Mn-rich ones are found near shore; Atlantic ocean deposits close to the continent are relatively impoverished in Ni, Cu and Co. The reasons for the different compositions and the modes of formation of nodules are questions that keep people like me awake at night. A single mechanism involving simple precipitation of dissolved iron and manganese and other metals from sea-water is not satisfactory since the compositional variations in nodules are greater than those in sea-water. Some of us believe that nodules marginal to continents are enriched in Mn because reduced Mn^{2+} migrates rapidly upward through the interstitial waters of the sediments and is oxidized and precipitated at the sediment surface. The other metals are not as mobile and migrate slower than the sediment is being deposited thus never reach the surface. In the open ocean this is not so because sediment deposition rates

are much slower. In addition, some scientists believe that volcanic eruptions on the deep sea floor may inject solutions rich in Fe and Mn into the waters. Whatever the ultimate source of iron and manganese, oxidation of Fe^{2+} and Mn^{2+} in sea-water results in the precipitation of colloidal hydrated oxides. These precipitates have a large surface area and very efficiently adsorb other trace metals. Growth of the nodules continues at a slow enough rate to ensure that a continuous supply of metal-containing water moves over the nodule surface. Unfortunately, those nodules richest in needed metals like Cu and Ni are the ones in deepest water and whose recovery presents the greatest difficulty and cost. Mining companies are now attempting various recovery procedures to ascertain the commercial possibilities.

Collection (Fig. 3) and analyses of the different marine sediments, with their complex and variable compositions, is no easy or routine task. Although the best major element analyses are still done by classical gravimetric and volumetric techniques in conjunction with spectrophotometry, these are neither rapid nor suited for large numbers of samples. The heterogeneity of the samples and the need to plot their distributions both spatially and in time, often necessarily involve numerous samples and favor rapid instrumental analysis.

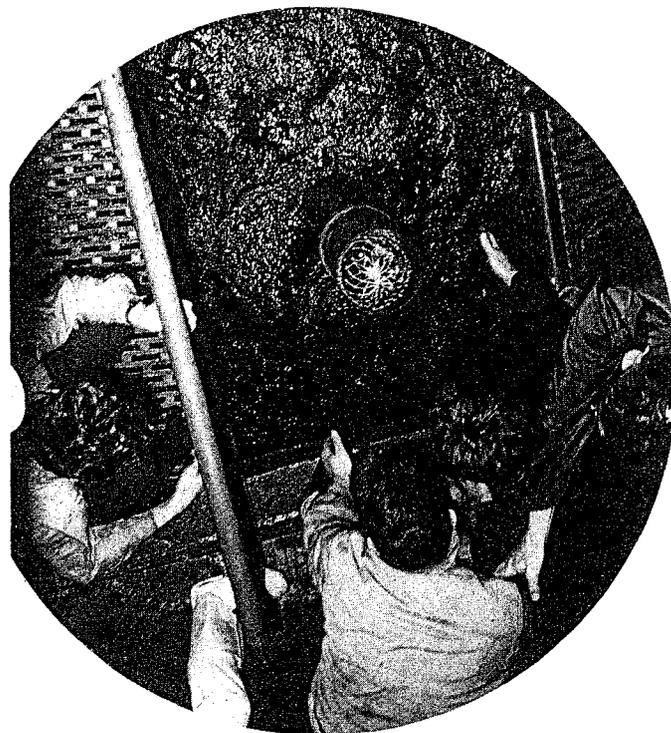


Figure 3. A sediment-collecting device, the free-fall core or "boomerang" corer (developed jointly by Woods Hole Oceanographic Institution and Benthos Co.) can be dropped from a moving ship and requires no wire lowering. When it penetrates the sediment a trip-lever releases the large glass spherical floats which lift the liner containing the core to the surface, leaving the iron weight stand and barrel behind. The glass spheres contain a signalling device so they can be located at the surface and recovered with the core.

X-ray fluorescence is nicely suited for major elements. Being non-destructive, it allows trace element determinations to be made on the same aliquot by the same or other techniques. As this method becomes more common we are beginning to cope with interference effects, even in these multi-element silicate samples, and are able to apply theoretical or empirical corrections.

Table 7.
Average Composition of Manganese Nodules
from the Pacific Ocean (% Wt)*

Element	Min.	Max	Mean
Fe	2.4	26.6	14.0
Mn	8.2	52.2	24.2
Ba	0.08	0.64	0.18
Co	0.014	2.3	0.35
Cu	0.028	1.6	0.53
Pb	0.02	0.36	0.09
Mo	0.01	0.15	0.05
Ni	0.16	2.0	0.99
Ti	0.11	1.7	0.67
V	0.021	0.11	0.09
Zn	0.04	0.08	0.05

*From reference 17

Emission spectrometry is also widely favored. For major elements we prefer spark excitation since we require precision and accuracy better than $\pm 5\%$. For reasons of homogenization, reduction of matrix effects and more precise standardization, we have developed a lithium borate fusion process followed by dissolution of the fusion mix in dilute nitric acid appropriately spiked with internal standards. These solutions are sparked in a vacuum-cup electrode and can be aspirated after further dilution into the atomic absorption spectrometer for determination of Na, K Ca, Mg and Sr.

Marine sediments generally contain anywhere from 20-70 elements in the range 1-1000 ppm. The concentration of these trace elements will vary greatly depending on the type of sediment and the environment of deposition (Table 8). X-ray fluorescence, neutron activation and atomic absorption spectroscopy are commonly called on. For certain selected elements, flame emission and absorption spectrophotometry may be chosen, although interference effects and difficulties in putting the samples into solution inhibit their general practicality.

Table 8.
Average Trace Element Content of Sediments
from Different Marine Environments (ppm)*

Element	Near Shore	Deep Sea	Manganese Nodule
Ba	750	2237	3100
Co	13	116	3400
Cr	100	77	10
Cu	48	570	3300
Ga	19	20	17
Ni	55	293	5700
Pb	20	162	1500
Sn	21	20	300
Sr	250	587	1000
V	130	330	590
Zr	160	145	340

*From reference 18

We have chosen dc arc excitation and direct reading emission spectrometry as our main workhorse, with a similar method to that outlined for the analysis of marine organisms. We obtain precision and accuracy of the order $\pm 10\%$ for most elements and retain sensitivity down to 1 ppm or less. Standardization is from artificial mixes or, preferably, from natural silicate or carbonate reference samples of which there are now a wide variety (12). To offset the disadvantages of the direct reader with its necessarily limited number of elements and wavelengths, we have set up a 3 meter Littrow-type spectrograph so that light from a single excitation can be read by both instruments simultaneously. The spectrograph provides a permanent record, and we can identify or measure wavelengths and elements not available on the spectrometer.

THE wide variety, heterogeneity and complexity of samples the marine chemist may be asked to analyze present a continuing challenge to his analytical abilities. To meet the challenge, spectroscopy has proved to be the most valuable and widely adopted tool. The key to successful analysis in marine chemistry is to be flexible and adaptable in methods of sample collection, handling and preparation, and in choice of analytical technique. Every sample being unique, there is no place for fixed mode, routine procedures.

The aim of marine chemistry is to describe the oceans in terms of concentration, chemical state, pathways and time constants for the elements and compounds therein. The ocean, its contents and its boundaries form a complex, multi-dimensional system. Its study is approached through various scientific disciplines that span the range of observable phenomena. Thus the marine chemist's work must mesh with that of many scientists from other disciplines. This is not to say that the marine chemist should be pictured in the role of concubine or mistress, ever present and only offering required services. Rather, he should be seen on a more moral plane, as an active partner in a successful marriage of natural sciences.

More and more we recognize that it is on the ocean we will depend for many of our future resources. As we do we should realize that, although bountiful, it is not limitless and, moreover, it is no longer a virgin frontier. By our own neglect we are seriously polluting the oceans in many respects, thus not only sacrificing part of the potential of its resources, but increasing the cost of effectively harvesting them.

The only way to ensure wise exploitation of the ocean is through the acquisition of knowledge about all phases of marine life and ocean processes. The Marine Science Commission has summarized this very succinctly in a recent report to the President (13): "There is much to be learned about this planet Earth, and many keys to learning are in and under the sea. The total body of oceanic knowledge is advanced best by the pursuit of fundamental understanding of the biological, physical, geological and chemical characteristics of the oceans. Continuing and substantial support of basic marine science is a national investment which will provide an underpinning for all future activities in the sea."

See p. 8 for References

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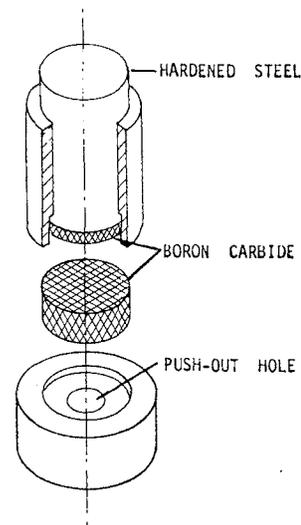
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3/16	necked crater, 3/16" dp.	4001	L-3903	101-L	S-13	24.20
1/4	crater, 3/16" dp.	4002	L-3900	103	S-8	22.00
1/4	angular platform, center post	4003	L-3948	104-L	P-2	30.80
3/16	necked crater, 3/32" dp.	4004	L-3906	105-S		20.90
3/16	necked crater, 3/16" dp.	4005	L-3909	105-D	S-14	20.90
1/4	flat necked upper	4007	L-3960	101-U	C-8	22.00
1/4	undercut, center post upper	4008	L-3963	104-U	C-7	24.20
3/16	double-ended, 1/16" r., 2" l.	4009	L3955	5712		26.40
1/4	pointed upper, 120°	4010	L-3966	108	C-2	22.00
1/2	solution disc, 1/8" thick	4011	L-4075	106	D-1	15.40
1/2	platrode, extruded	4012	L-4078	1907	D-3	19.80
1/4	porous cup, .025" floor, 1-1/2" l.	4014	L-3927	203		26.40
1/4	porous cup, chamfered floor, 7/8" l.	4015	L-3933	204	PC-1	25.30
1/4	crater, 1/16" dp.	4016	L-3982	4196	S-5	23.10
1/8	pedestal, 1-1/1" l.	4017	L-3919	1964	S-1	17.60
1/4	anode cap, 9/32" dp., thin wall	4018	L-3918	1998	S-3	17.60
1/8	pointed upper	4019	L-4036	1992	C-1	17.60
1/8	crater, 1/4" dp.	4020	L-3979	5440		17.60
1/4	necked crater, 1/16" dp.	4021	L-4012	1988	S-4	24.20
1/4	boiler cap	4022	L-3915	300		28.60
3/16	boiler cap	4023	L-3916	301		28.60
1/4	flat rod	4024	L-3921	107	C-3	19.80
1/4	mandrel for rotating electrode, 2" l.	4026	L-3970	2022		24.20
1/2	solution disc., .200" thick	4027	L-4072	861	D-2	17.60
1/2	platrode, molded	4028	L-4081	1909		19.80
3/16	necked crater, 3/16" dp.	4029	L-4000	5915		20.90
3/16	necked crater, 3/32" dp.	4030	L-4006	7250		20.90
1/4	mandrel for Combination Analyzer	4032	SP-1003	2025		24.20
1/8	necked crater, 1/8" dp.	4033	L-3905	781		20.90
1/8	crater, .059" dp.	4034	L-3975	2509		17.60
1/8	crater, 3/16" dp.	4035	L-3977	5000		17.60
1/4	porous cup, .025" floor	4037	L-4928	5680		26.40
1/4	anode cap, 9/32" dp.	4038	L-4024	1990	S-2	17.60
3/16	rounded upper, 1/16" r.	4039	L-3951	105-U		18.70
3/16	rounded upper, 1/16" r., 2" l.	4040	L-3954	5710		19.80
1/4	rounded upper, 1/16" r.	4041	L-3957	100-U	C-5	22.00
1/4	necked crater, 3/16" dp.	4042	L-4018	1989		24.20
1/8	pedestal, 1" l.	4043	L-4042	1993		13.20
1/4	anode cap, 1/32" dp.	4044	L-4030	1991		17.60
1/4	center post crater, 1/4" dp.	4046	L-4054	1995		23.10
1/4	curved platform, center post	4049	L-3945	1335		26.40
1/4	anode cap, 1/16" dp.	4070	L-4031	5630		17.60
1/8	flat rod	4071	L-3922	1509	C-6	15.40
3/16	flat rod	4072	L-3923	2615	C-9	15.95
1/8	rounded upper, 1/32" r.	4073	L-4037	5001		18.70
1/4	vacuum cup, 3/8" post, 2" l.	4074		6010		38.50
3/4	O.D. Teflon Cup for 4074 or 4075	4074A		6010A		12.00/10
1/4	vacuum cup, 5/8" post, 2" l.	4075		6011		38.50
1/4	tapered mandrel, 1-1/8" l.	4078	L-3969	2021	D-4	19.80
1/4	.054" micro-cup, .062" cp.	4079	L-4257	115		24.20
1/4	.096" micro-cup, .075" dp.	4080	L-4259	117		24.20

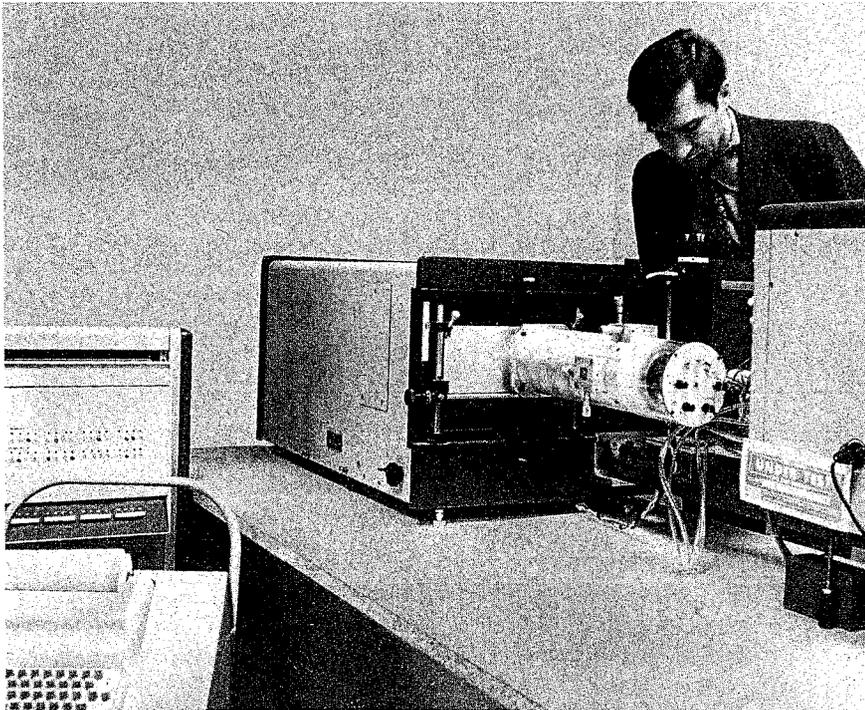
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We even have a man who talks to this machine so if you have mountains of ores, rocks, minerals, slags, corrosion deposits, organic ashes, pollutant particulates or just dust to analyze by the hour, day and week send us a portion or two to feed to our voracious, beneficent, electronic monster. If you prefer to talk to a mere human first, call Lou Casper.

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without Recorder	2400.
without Recorder or PM power supply	2000.

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Type	Programmable; voltage automatically drops when photomultiplier anode current exceeds a certain limit.
Voltage range	200-2200V, negative polarity..
Voltage adjustment	200 and 20V steps with vernier over 25V
Stability	0.01%
Output connector	MHV, coaxial

Amplification

Photon Counting

Type	Ratemeter
Range	30 to 3,000,000 cps full scale in 11 steps
Zero Suppress	Covers entire dynamic range
Period (RC x 4.8)	0.5 to 100 sec in 7 steps; uppermost value may be increased to any value through addition of external capacitance
Input	Through a remotely located discriminator-preamp. to BNC connector on rear
Outputs	Integrated signal for the recorder, adjustable. Integrated signal, to control the HV power supply. Non-integrated standardized pulses.

Direct Current

Range	3×10^{-8} to 10^{-5} amperes in 6 steps
Zero Suppress	Covers entire dynamic range
Input	BNC connector on rear

Recorder

Type	10" wide potentiometric, stripchart
Responsivity	10 mV full scale
Chart Drive Speeds	0.25, 0.5, 1, 2.5, 5.0 and 10 cm/min through push-button switching
Cross-chart Speed	0.5 sec
Zero Adjust	Over full scale
Chart Paper	Z-fold
Event Marker	Second pen on right side actuated by 6VDC pulse
Ink supply	Externally fillable; blow-out unclogging device.
Pen lifter	Manual, for both the main pen and the marker
Accuracy	$\pm 0.25\%$ of full scale
Deadband	$\pm 0.1\%$ of full scale
Reference Voltage	Temperature compensated zener diode

Cabinet

Type	19" rack panel, 18" high, 16" deep
Weight	Approx. 100 lb.

Power Required

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