A STUDY OF CERTAIN TRACE METALS IN SEA WATER USING ANODIC STRIPPING VOLTAMMETRY

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ABSTRACT

Anodic stripping voltammetry utilizing a thin film mercury composite graphite electrode has been evaluated and applied for the direct analysis of the metals, Zn, Cu, Pb, and Cd in sea water. The electrode was observed to follow theoretical behavior for thin film electrodes and the technique was found not to be adversely affected by dissolved organic material in sea water. Good precision (ca., 5%) was obtained in both coastal and open ocean waters at the in situ concentrations of Zn, Cu, Pb, and Cd. It was shown that this method is at present most suitable for measurements of Cu, Pb, and Cd in sea water. Evidence is given suggesting that Ni may interfere with the determination of Zn through formation of an intermetallic compound, and further studies are indicated to understand this phenomenon. The anodic stripping apparatus was adapted and used conveniently on shipboard. It was demonstrated that stripping analysis could be combined with a method for the destruction of dissolved organic matter (photo-oxidation with ultra-violet radiation), and with an acidification procedure to obtain measurements of trace metal speciation in sea water.

An argument for the existence of Cu-aspartic acid chelates in sea water has been described theoretically and demonstrated empirically; suggesting that a significant fraction of Cu and other trace metals may be expected to be organically sequestered in sea water. A study of coastal waters employing the total method (anodic stripping-photo-oxidation-acidification) indicated the presence of a significant group of organic ligands that complex Cu (ca., 60%). It was also shown that the waters subject to gross pollution contain about 30% of the total Cu in very stable organic complexes that release Cu only when the dissolved organic matter is destroyed, and not when the pH of this sea water is adjusted to 3.

An open ocean trace metal study of a thermal-front zone in the western Sargasso Sea gave data for Cu, Zn, Pb, and Cd that compared favorably with other relevant investigations. Higher free metal concentrations were observed south of the front than to the north, providing further evidence that these fronts may mark a change between southern and northern conditions in the Sargasso Sea. Data obtained from shipboard analyses using the total analytical method indicates the presence of weak organic complexes with Cu and Pb in open ocean waters.

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CHAPTER ONE

INTRODUCTION

1.1 Marine Cycle of Trace Metals.

Unlike the major constituents present in sea water, several trace metals exhibit non-conservative behavior (Høgdahl, 1963). Schutz and Turekian (1965) have suggested a number of mechanisms that possibly can control trace element concentrations in sea water. The main sources are from rivers and the atmosphere, and the supply varies with geographical location and season. The removal routes such as organic activity, hydrolysis and precipitation, or adsorption on particulate matter, are also variable in space and time. Thus, the trace element concentrations will depend not only on the mixing and transport properties of the ocean, but also on biological and geochemical processes occurring in sea water. Variations in trace element concentration can be expected that are quite independent of observed salinity differences. Consequently, we must make many measurements of the minute quantities of trace metals present, in order to develop a comprehensive picture of the trace element distribution in the oceans.

1.1.1 Biological Role

The importance of trace metals in stimulating growth of phytoplankton in cultures is well known and has been comprehensively documented by Provasoli (1963). It appears that the growth of algae in the ocean is greatly dependent on the availability of trace metals and on the complexing or chelating power of the dissolved organic matter present.

For example, Johnston (1964) has demonstrated that either no growth, or only poor growth, can be obtained with diatoms (also dinoflagellates that were part of the natural inoculum) when chelated trace metals are not included in the culturing medium. As a result of a large number of culturing experiments, with varying water types collected during different seasons, Johnston concludes that "the supply of chelating substances is frequently the most crucial aspect of phytoplankton nutrition in sea water."

Moreover, Barber and Ryther (1969) have recently shown that the addition of a strong chelator or an undefined zooplankton extract (includes trace metals, chelators?) could improve the growth of phytoplankton in nutrient-rich, newly-upwelled water from the Cromwell Current. They suggest that organisms actually condition the surrounding sea water for optimum growth by release of natural organic chelators. Phytoplankton cultures in non-enriched but "aged" upwelled sea water (had been at the surface for some time) grew at a rate comparable to the chelator or zooplankton extract enriched freshly-upwelled water. However, even this "aged" water could be improved by the addition of chelator (Na_2EDTA*) or zooplankton extract.

Goldberg (1965) has made an interesting observation that provides further evidence of the importance of trace metal chelates for marine organisms. The transition metals follow a certain order (Irving - Williams) of stability for analogous complexes with many ligands that contain nitrogen as the donor atom (i.e., $Mn^{++} < Fe^{++} < Co^{++} < Ni^{++} < Cu^{++} > Zn^{++}$, Cotton and Wilkinson, 1962). A certain parallel with this order can be found for the metals concentrated by some organisms,

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* Disodium ethylenediamine tetra-acetate

where enrichment factors relative to the metal concentration in sea water are sometimes very large (e.g., 10^5). This suggests that either chelation is used by the organisms to incorporate trace metals, or there is preferential uptake of chelated species.

The mechanisms through which the chelation of trace metal, or chelated trace metal species, promote or inhibit phytoplankton productivity in the oceans are not known. The actual pathways are probably quite complicated.

For example, does the chelate-metal equilibrium provide a buffering system to keep the amount of ionic metal species at an acceptable level for uptake? Are metal-organic molecules preferentially incorporated by the organisms, and if so, does this uptake depend on the molecular size of the chelated metal species? The strength of the metal-ligand bonding may be important. Barber (personal communication, 1969) has some evidence indicating that the growth rate of phytoplankton can be stimulated or inhibited by the choice of sequestering agent added to the medium. It is clear that the interactions between trace metal species and algae can be extremely complex.

In summary, this brief survey indicates that trace metal species play an essential but little understood role in primary production in the oceans. The distribution of trace metals in the oceans will be affected by the biota, their excretory products and the dissolved organic matter present. Valuable insight into this problem can be gained by measurements of trace metal speciation in the natural medium-raw sea water. The most valuable data are those accompanied by standard biological measurements such as nutrient concentrations and estimates of primary production.

1.1.2 Geochemical Role

In order to formulate a comprehensive model describing the distribution of trace metals in the ocean, it is necessary to study the mechanisms through which these metals are eventually deposited on the ocean floor. The oceanic distribution of trace metals depends primarily on the rate at which the various deposition processes occur, that is, on whether the mechanism that eventually places a metal in the sediment is faster or slower than the mixing times of the oceans. A very slow sedimentation process would allow a metal to be distributed equally throughout the ocean (*e.g.*, Li). Rapid sedimentation would deposit the trace metal locally, giving highly variable concentrations in the ocean.

The processes operating to take a metal out of the water column are not difficult to visualize. They are: precipitation as a distinct phase; coprecipitation with other phases: incorporation within minerals (*e.g.*, clays); incorporation by biota, which upon death eventually sink to the bottom; and adsorption on detritus (inorganic or organic). However, the problem is to evaluate which mechanisms are most important and where in the oceans these processes are significant.

Some insight into this problem can be obtained from a consideration of a theoretical and experimental study (Krauskopf, 1956) which attempted to evaluate the factors that might be controlling the geochemistry of thirteen trace metals in sea water.

Krauskopf empirically considered and rejected deposition of trace metals through the formation of insoluble phases. Solutions of metal ions were added to sea water until precipitation occurred (pH maintained between 7.8-8.2). The amount of metal ion in solution was monitored until a constant value was obtained. In addition, some of the precipitate was added to fresh sea water and the amount of soluble metal determined as before. The equilibrium solubility value for the dissolved metal was assumed to lie between these two determinations.

The experimental data were compared with the predicted amounts based on the solubility product (approximately corrected to sea water ionic strength) for the insoluble phase assumed to have formed. The agreement was usually within an order of magnitude. However, no correlation could be made when these experimental data were compared to the known sea water concentrations of the various trace metals.

Although, there can be objections to his experiments, for example, the effect of trace metal complex formation (inorganic and organic) was not considered, nor were the insoluble phases actually characterized, his conclusion appears valid. Of the elements tested (Zn, Cu, Pb, Bi, Cd, Ni, Co, Hg, Ag, Cr, Mo, W, V) the oceanic distribution of none were found to be controlled by solubility equilibria.

The possibility that precipitation by sulphide might be a controlling factor (assuming rapid ocean circulation) was also ruled out by Krauskopf. In addition, it seems unreasonable that restricted areas of high sulphide content could influence the trace element distribution for the entire ocean. These regions have a high sulphide content because they are not exposed or renewed by large quantities of oxygenated water from the general ocean circulation. The Black Sea, Cariaco Trench, and certain fjords are examples of these areas. However, there can be no doubt that sulphide precipitation affects some trace metal distribution on a local scale.

Finally, Krauskopf experimentally tested adsorption as a possible mechanism for deposition of trace metals. The adsorbents used were hydrated Fe_2O_3, hydrated MnO_2, apatite, clay (montmorillonite), plankton, and peat moss. These were chosen as representative of the principal adsorbing materials in sea water (the peat moss simulates terrestrial organic matter). He found that, "adsorption is a possible control for all metals except V, Co, Ni, W, Cr." It was assumed that V, W, Ni, and Co would be controlled primarily by organic reactions (biological interactions), whereas, Cr deposition might result from local reduction and precipitation of the hydroxide.

The ratios of adsorbate to adsorbent used in these experiments were of the order expected in sea water, but the absolute concentrations were approximately three orders of magnitude greater. Whether these laboratory observations apply to natural processes occurring in the oceans must be considered questionable.

Recently, Kharkar et. al. (1968) studied the stream supply of dissolved trace metals (Ag, Mo, Sb, Se, Cr, Co, Ru, and Cs) from ten major rivers in the United States and also from the Rhône (France) and the Amazon (Brazil). In the course of this investigation, they conducted experiments, using radioactive tracers, to examine the adsorption and desorption properties of some common absorbents for selected trace metals both in distilled water and in sea water. These absorbents were clays (montmorillonite, illite, and kaolinite), reagent ferric oxide and manganese dioxide, freshly precipitated ferric hydroxide, and peat. The absorbates were the elements Co, Ag, Se, Cr, and Mo.

Their results were in general agreement with Krauskopf's findings with regard to the adsorption of trace elements from sea water by particulate matter. However, adsorption of trace metals was usually less efficient in the sea water medium. Their field analyses also revealed that some fraction of the Co, and to a lesser extent Ag, and Se, adsorbed on particulate material in streams is always released on contact with sea water.

Schutz and Turekian (1965) undertook an extensive investigation, using neutron activation analysis, into the oceanic distribution of several trace elements. Their data corroborates Krauskopf's conclusions regarding Co and Ni. They concluded that Co and Ni (also Ag) are removed near shore, either by incomplete degradation of organisms which had previously incorporated these metals or the metals were adsorbed on particulate organic debris. In the open ocean, they suggested that Co and Ni are probably deposited by co-precipitation with MnO_2.

It would appear from these studies that adsorptive deposition mechanisms, supplemented in some cases (near shore) by sedimentation resulting from biological processes, may be the controlling agent for the distribution of trace metals in the oceans and in marine sediments.

1.1.3 Combined Biological and Geochemical Role

The biological and geochemical processes which influence the oceanic distribution of trace metals cannot be considered as separate entities. It would be unrealistic to assume that trace metal species remain unchanged during incorporation and subsequent concentration by biota. The metal species are returned to the water column or perhaps the sediments as part of excretory and degradation products. The production of metal-chelates from interactions with organisms can be expected.

Moreover, the sequestered metals may take completely different pathways in sea water not available, for example, to hydrated metal ions.

In addition, previous interactions of metals with terrestrial organic material may introduce trace metal species with an independent residence time. That is, salting out of organically complexed trace metals at the river - salt water interface may occur. Trace metals incorporated in clay minerals could be the inorganic counterpart. Conversely, a dissolved metal organic complex entering the ocean may remain intact for a very long time if it is nonbiodegradable and geochemically very nonreactive.

In summary, the presence or formation of organo-metallo compounds in sea water can have a profound effect on the interactions between trace metals and organisms. Further, the deposition of trace metals by adsorption on various particulate material will be influenced or possibly controlled by the sequestered metal ions in solution. For example, the adsorption efficiency of charged inorganic colloids (i.e., Fe_2O_3, MnO_2) will be affected by metal-chelates, many of which have no charge.

At present, most of the trace elements have been detected in sea water, but still very little is known about the variations in their concentrations with depth and position. This is also true for seasonal variations in the surface waters. Even less is known about the types of chemical species present. Studies are needed to investigate the fundamental processes that are involved in the interactions of trace elements in biological and geological cycles, and to determine the effect of ocean mixing and currents on their distribution.

1.2 Purpose of this Investigation

Our goal in the chemistry of trace metals in marine environment has been aptly stated by Høgdahl. It is, "to determine, not only the total concentrations of the trace elements in the oceans, but also the concentration of the various forms in which elements can exist in the seas, as a function of time, location, and depth and to correlate the results with biological activity, geochemistry and the physical chemistry of the elements, and the hydrodynamical picture of the ocean." This is obviously a formidable task.

The purpose of this investigation is the evaluation and application of anodic stripping analysis for the measurement of trace metals in sea water. A method developed by Matson (1968) using a thin film mercury composite graphite electrode appears to be an extremely valuable analytical tool. It permits the examination of trace quantities (10^{-9}M) of metals present in natural waters with a precision of 5%.

Of considerable importance is the fact that it appears possible to resolve a part of the complex spectrum of chemical speciation in sea water, because this electrochemical technique senses free or reactive metal ions (see Section 2.1 for definition). This method can be combined with a photo-oxidation procedure for the destruction of dissolved organic matter in sea water. Direct analysis by anodic stripping voltammetry of raw sea water and organic-free sea water should provide a measure of the free and the organically combined trace metal in sea water.

The extent of trace metal speciation is not known in the oceans. Therefore, the open ocean shipboard measurements using the method outlined were conducted with the dynamics of the oceans in mind. It is most important in trace metal studies to have measurements of salinity and temperature. No complete description for the marine distribution of trace elements can be developed unless the hydrodynamical parameters are understood or can be assessed.

CHAPTER TWO

ANODIC STRIPPING ANALYSIS IN SEA WATER EMPLOYING A THIN FILM MERCURY COMPOSITE GRAPHITE ELECTRODE

2.1 Methods for Analysis of Trace Metals in the Oceans

For some time, workers have been gathering data in an attempt to understand the mechanisms governing the oceanic distribution of certain elements. However, accurate measurements of $1/10^9$-$1/10^{12}$ amounts of a trace constituent are very difficult. Most measurements have been beset with the analytical hazards inherent in preconcentration and extraction procedures. It is extremely difficult to avoid contamination when a number of chemical manipulations and reagents are necessary to attain a suitable detection level. Most reagent grade chemicals have higher levels of trace metal impurity than does ocean water.

Recently, techniques have been employed that avoid much of the analytical procedure associated with earlier measurements. Specifically, the more extensive use of neutron activation (Schutz and Turekian, 1965), isotope dilution (Chow and Patterson, 1966), and atomic absorption (Spencer and Brewer, 1969) methods have eliminated many of the previous sources of contamination. Nevertheless, prior concentration is still usually necessary in order to obtain sufficient sensitivity for many elements.

These technically advanced methods must also reckon with sample storage. Rarely have trace metal analyses taken place aboard ship. Concentrations may change with time. For example, adsorption on the walls and leaching of ions from the container can be serious sources of error (Orren, 1967; Robertson, 1968). Also slow reactions with other constituents may result in loss or unavailability of trace constituents (Orren).

It is becoming increasingly evident (see Chapters 1 and 4) that some and possibly many of the trace metallic elements in the oceans are present not as free ions but as complexes, even mixtures of complexes with varying degrees of stability, reactivity, and quite possibly differing chemical behavior. It is necessary, therefore, to consider not only the problem of accurate measurement of total metal concentration but to ask how can we differentiate between the various chemical species of an element which are involved in the interactions between the biosphere, hydrosphere, and lithosphere.

The reported concentration data with few exceptions (see Section 4.2.1) do not distinguish among the chemical forms of the metal that may be present. These newer techniques, although extremely sensitive, have not discriminated between the free ionic form of the metal and the metal ion sequestered with an organic ligand.

Moreover, the term "free" metal has been rather loosely used by various workers. Often it is meant to imply the ordinary simple ionic form. Operationally, what is usually involved is the sum of any and all forms of the metal which are reactive and are detected by the particular analytical method used. In the present dissertation, it will be used to denote the fraction of the total metal that is readily reactive (reducible) at a thin film mercury electrode during anodic stripping analysis of raw sea water. This fraction includes hydrated metal ion, and the readily reactive metal ion sequestered in organic and inorganic solute species. The latter group will be called labile.

2.2 Choice of Method for the Investigation of Trace Metal Speciation in the Oceans

2.2.1 Requirements: Limited Sample Storage

The study of trace metal speciation in the oceans places rather rigorous requirements on the selection of an analytical method. No or limited sample storage is a prerequisite. Therefore, the analyses must be done aboard ship; otherwise, changes in sample composition (i.e., speciation) between the time of sampling and subsequent shore analysis are probable.

For example, large volume ($>$10 1.) high density linear polyethylene jerry cans, previously seasoned with sea water, appear to be an excellent container for storage of trace metal samples. Negligible uptake or release of trace metals, by this container, has been observed over a several month period (Spencer and Brewer, 1969). However, it was found, in this present investigation, that the dissolved organic carbon content of sea water stored in this container can increase by fivefold over a comparable period (e.g., from 0.5 mg/l to 2.5 mg/l). This release of plasticizer, evident even by smell, can supply organic material that could upset the natural balance of trace metal species originally present.

Storage in Pyrex or Vycor must contend with probable contamination from such elements as Pb and Cu that can be leached from the container walls by sea water. Quartz would provide an acceptable storage vessel, but large volume quartzware is prohibitedly expensive. Hence, shipboard analysis of trace element speciation in sea water is highly desirable in order to avoid the complications and expense of sample storage.

2.2.2 Requirements: Direct Analysis

Analysis of trace metal speciation in sea water must also be direct. Preconcentration or extraction procedures tend to destroy the naturally occurring complexes. For example, preconcentration by evaporation or freeze-drying produces either changes in the ionic strength or a phase change, which can precipitate, condense, or decompose the natural organic complexes, and, therefore, rules out any meaningful measurement of the trace metal species originally present.

Solvent extraction with an added chelator is a commonly employed and essential procedure in the chemical analyses of many trace elements in the oceans. This technique allows a suitable detection level to be obtained for subsequent analysis by, for example, colorimetry or atomic absorption spectrometry. This method will be considered in detail, not only because it is widely used, but also because previous trace metal speciation studies in sea water (see Section 4.2.1) have employed this technique. The following discussion will also apply to those cases (i.e., some colorimetric analyses) where the sequestering reagent need not be extracted.

2.2.2.1 Extraction with an Added Sequestering Agent

Solvent extraction of an added chelator must contend with the competition of the naturally occurring complexing agents. Some of the latter may form more stable complexes than the reagent. Moreover, other complications are possible if complete equilibrium is not obtained between the trace metal ions, the natural ligands, and the added sequestering agent. For example, the release of metal ion from naturally occurring complexes or the uptake by the added chelator may be sterically hindered. Consequently, the rate of equilibration would be slow.

Therefore, the chelating-agent-extraction experiment provides information about labile trace metal species displaying fast kinetics. The non-measurable fraction includes not only metal ions so strongly complexed by natural ligands that they are essentially unavailable to the reagent, but also species having a slow kinetic step which prevents the attainment of equilibrium with the reagent during the time of the experiment.

Moreover, the optimum conditions for a chelate-extraction experiment are the worst for a study of trace metal speciation. For example, it is essential that a sequestering reagent be selected which forms very stable complexes with the trace metals of interest. However, the amount of readily reactive metal ion in raw sea water (pH unchanged) will be overestimated for, even metal ions strongly bound in some naturally occurring complexes may be reactive toward such a good chelating reagent.

In theory, it should be possible using a chelation-extraction procedure to differentiate some trace metal species (e.g., readily reactive from strongly bound). A series of sequestering reagents which form chelates of varying stability (i.e., weak to strong) with a particular metal could be employed. If there are no serious problems with either variations in the extraction efficiencies or the attainment of equilibrium conditions, an estimate of the stability range for the natural metal chelates present will be obtained. In practice, this type of experiment appears too qualitative to give results of significant value and too time consuming for routine analysis.

2.2.2.2 Extraction with an Immiscible Solvent

Extraction procedures employing an immiscible solvent or a series of solvents would also permit naturally occurring metal-chelates to be approximately classified (*i.e.*, polarity) and the quantities estimated. For example, ether extraction would remove nonpolar complexes, whereas butanol would extract polar molecules. There is overlap, however, and thus this technique appears most useful as a method for obtaining a larger quantity of sample for the identification of trace organics or metal-organics present in sea water. It is not as suitable as a routine quantitative method for trace metal speciation studies because extraction efficiencies must be rigorously known and controlled. This is best accomplished in a land-based laboratory.

2.2.3 Limitations of Available Methods

The analytical methods currently used for studies of trace elements in natural waters appear unsuitable for measurements of trace metal speciation in sea water. None of the techniques surveyed fulfilled the requirements, which are analysis aboard ship (limited sample storage) with no preconcentration necessary (direct analysis) and the ability to differentiate trace metal species (not primarily a total concentration method).

For example, neutron activation is an excellent direct method for total analysis of many rare elements. However, it is expensive (i.e., reactor facilities needed), requires sample storage, and only gives information about the total concentration of an element.

Atomic absorption spectrometry is another good direct method for total analysis of many elements in natural waters. However, the measurement of trace metals in sea water by this technique requires a preconcentration step (e.g., solvent extraction with an added chelator). Moreover, atomic absorption is primarily a total concentration method that may require sample storage. It is possible to put an atomic absorption apparatus aboard ship (Fabricand et. al., 1962).

Other methods that require preconcentration and sample storage are emission spectroscopy and mass spectroscopy. Colorimetry and polarography require preconcentration but not necessarily sample storage. These latter analyses could be done aboard ship.

Finally, for methods employing isotope dilution, the experimental conditions are adjusted (e.g., made acid) to optimize equilibration of the isotopic spike. Therefore, if equilibration is complete, these methods should not be adversely affected by sample storage or by the subsequent preconcentration that may be required for analysis. However, this technique also yields total metal concentration.

Thus, all of the more important experimental methods were briefly considered and rejected as unsuitable for trace metal speciation studies in sea water. Although, modifications of some of the existing techniques are possible (see Sections 2.2.2.1 and 2.2.2.2), these procedures give only limited qualitative information on speciation and the ultimate method appears too complex for routine shipboard analysis. Therefore, a new approach was necessary for the investigation of trace metal speciation in the oceans.

2.2.4 Choice of Method

A new method has been applied to the study of trace metal speciation in sea water. The method is anodic stripping voltammetry employing a thin film mercury composite graphite electrode. This electrode was developed and defined by Matson *et. al.* (1965). Moreover, Matson (1968) suggested some techniques for obtaining trace metal data using anodic stripping analysis in natural waters and with aerosols. His research, primarily of an exploratory nature, was concerned with changes in the concentration and in the chemical forms of trace metals, particularly Pb, that result from industrialization in urban regions. He obtained results indicative of natural Pb-chelate species in lake and river waters, and suggested a theoretical approach which might not only demonstrate trace metal speciation but also yield information on equilibrium and rate constants of trace level chelating reactions.

Thin film anodic stripping analysis is a sensitive new tool. The detection limits, for some trace elements of 10^{-10}M or better, obviate the need for preconcentration steps. Good precision (*i.e.*, 5%) has been obtained by direct analysis of aqueous solutions containing trace metals at the 10^{-6} to 10^{-9}M level, and in the present work it has been shown that the analysis can be performed on shipboard. The method is also economical (the electronic monitoring equipment is inexpensive) thereby allowing its extensive use by investigators with small budgets. But, most importantly, thin film anodic stripping voltammetry looks directly at free metal ion.

Therefore, this analytical technique appears not only suitable, but actually ideal, for the study of trace metal speciation in sea water.

Anodic stripping has been applied to sea water only to a limited extent. Macchi (1965) using a slow period dropping mercury electrode made 42 determinations of zinc in a sample of sea water and found a coefficient of variation of 4.5%. Matson measured Cd, Cu, and Pb in several sea water samples from Boston Harbor. Healy (personal communication) is presently measuring Zn, Cu, Pb, and Cd in the Pacific Ocean by a differential technique that uses two hanging mercury drop electrodes. Also, the rather high concentrations of Zn (39μ g/l) and Cd (4μ g/l) in Dead Sea brine were determined by anodic stripping voltammetry with a hanging mercury drop electrode (Ariel and Eisner, 1964). Recently, Whitnack and Sasselli (1969) also employing a hanging mercury drop electrode, measured the concentrations of Zn, Cu, Pb, and Cd in a surface sea water sample from the Pacific Ocean.

However, since there have been only a few analyses for trace metals in sea water by anodic stripping techniques in general, and the Matson system in particular, it was necessary to establish the characteristics of the thin film mercury composite graphite electrode for anodic stripping analysis of sea water. Recent work by Carter (personal communication) using the Matson electrode revealed some artifacts that further warranted a thorough examination of the entire analytical system and the interpretation of its results.

2.3 Analytical Investigation

2.3.1 Introduction

Although, anodic stripping analysis is not a new method, it has only recently been employed for trace metal determinations (see reviews by Shain, 1963; Barendrecht, 1967). The technique achieves extraordinary sensitivity in a relatively simple and rapid manner. The material sought is reduced at an electrode (*e.g.*, mercury) of small volume by electrolysis for some predetermined time (plating time) which may be minutes or perhaps, in special cases, hours. After this step, the material is reoxidized, using a linearly varying potential, in a short time, which may be milliseconds or seconds depending on the scan rate. The current is monitored during the metal oxidation, and the peak current response, in microamperes, can correspond to quantities of material as small as 10^{-12} moles. The integrating effect of the long plating and short stripping time makes it possible to increase the sensitivity to several orders of magnitude beyond that of ordinary polarography.

In this section, the results will be given of an extensive investigation in which the thin film anodic stripping method was evaluated and an analytical procedure developed for trace metal analysis in sea water. The topics that will be considered and discussed include: 1) choice of experimental variables, 2) sea water as a medium for electrochemistry (*i.e.*, voltammograms from sea water), 3) determination of free metal concentration, 4) precision, 5) artifacts (*e.g.*, double peaks), and 6) interferences.

2.3.2 Analytical Parameters

2.3.2.1 Cell Geometry

A cell and electrode system similar to that described by Matson was used in this present investigation; however, larger cell volumes were employed. Sea water samples of about 100 ml were necessary to ensure that a sufficient quantity of Pb and Cd could be plated. These elements were expected to approach limiting values of 0.04 μg/l (Chow and Patterson, 1966) and 0.03 μg/l (Mullin and Riley, 1954, 1956), respectively, in sea water.

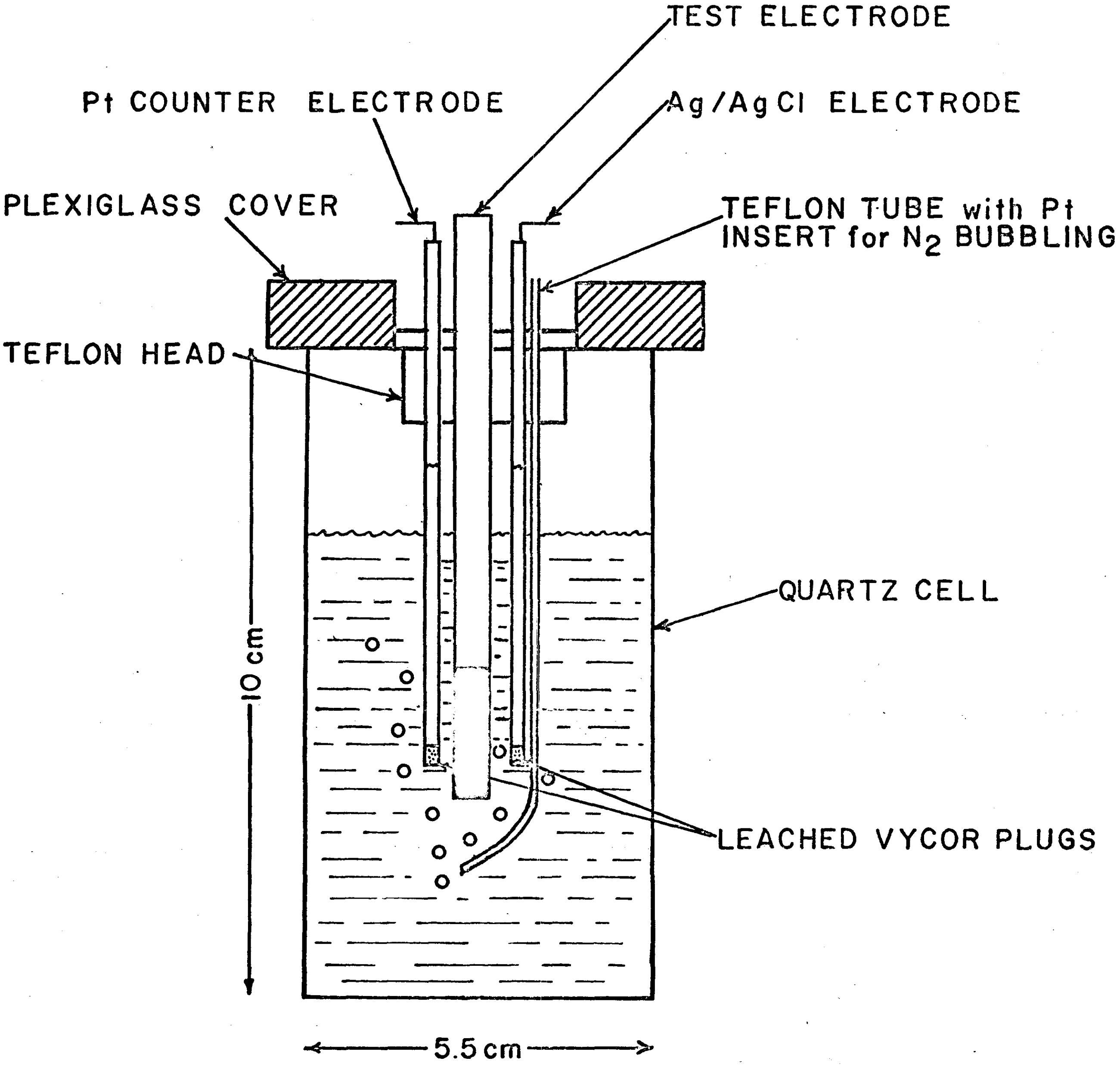
a. Electrodes

A diagram of the stripping cell and electrodes appears in Figure 2-1. Details of the design and preparation of these electrodes have been given by Matson. Briefly, a 4.0 cm^2 thin film mercury composite graphite test electrode was used. The thin film of Hg, equivalent to 2×10^{-7} moles/cm^2, was prepared by total plating 8×10^{-7} moles of Hg from 10 ml of sea water onto the 4.0 cm^2 polished graphite surface. The Hg was added to the sea water as the chloride (80 μl of 10^{-2}M $HgCl_2$). The electroplating conducted at -0.10 v versus the Ag/AgCl electrode in sea water for a plating period of 45-60 minutes (5-6 cell half-times).

The Ag/AgCl reference electrode was prepared by slow anodization of a 0.04 inch diameter silver wire in 0.1N NaCl, and subsequently placed in sea water. A 0.02 inch diameter platinum wire served as the counter electrode. The reference and counter electrodes (4 inches in length) were isolated from the solution by 4-7 mm Vycor plugs (4 mm diameter) joined by Teflon tubing to 4 mm diameter glass tubing

FIGURE 2-1

Diagram of Cell Used in Anodic Stripping
Voltammetric Studies with the Thin Film
Mercury Composite Graphite Test Electrode



STRIPPING CELL and ELECTRODES

which contained a reservoir of sea water.

The electrodes were contained in a machined Teflon head (Figure 2-1). This head was designed to sit in a machined Plexiglass cover for the large quartz cells (50-150 ml sample volumes). In addition, this head could be used directly with smaller quartz vials (10-25 ml sample volumes).

b. Stirring

Stirring of the solutions was accomplished by water-saturated nitrogen bubbling at 170-200 ml/minute. The bubbler, Teflon tubing (inside diameter 0.02 inch) stiffened with a platinum wire was placed just below the test electrode. The bubbles hit the electrode. An average half-time for plating Cu in a 100 ml sea water solution with this type of stirring was 3 hours.

2.3.2.2 Electronics

A chopper-stabilized Heath polarographic module (Model EUA-19-2) used in conjunction with a switching manifold allowed four samples to be plated simultaneously. Any of the four test electrodes could be individually stripped with the polarographic module by a simple switching operation. The stripping response (output from the polarographic module) was plotted on 18 x 25 cm graph paper using an x-y recorder (Mosley 135M). A photograph of the experimental set-up appears in Figure 2-2; a diagram in Figure 2-3.

2.3.2.3 Plating Potential

The optimum plating voltage is the potential at which the current is only limited by the rate of mass transport to the electrode (stirring). Although there is no

FIGURE 2-2

Photograph of Experimental Apparatus

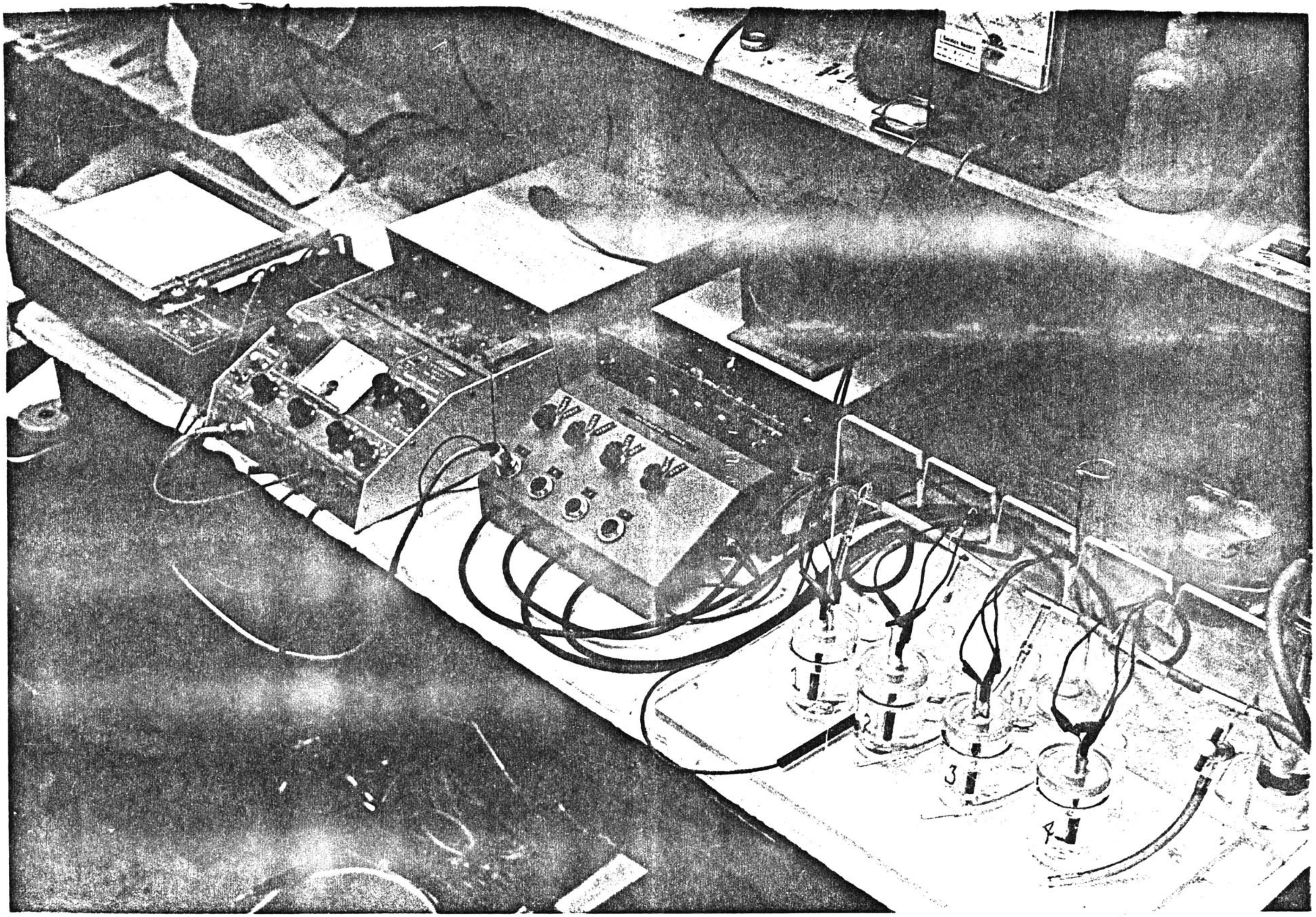

1
2
3
4

FIGURE 2-3

Diagram of Experimental Apparatus

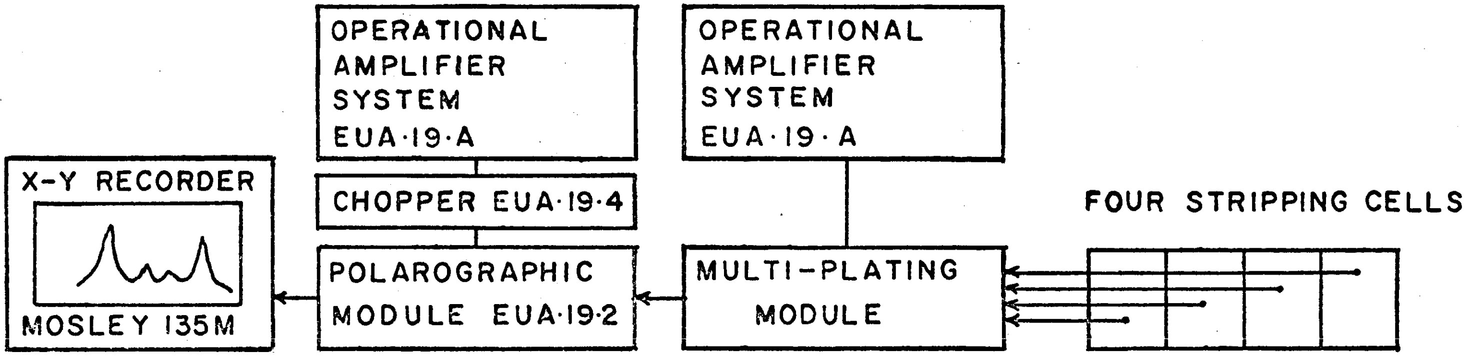


DIAGRAM OF ANODIC STRIPPING APPARATUS

equation predicting this electrodeposition potential for a metal, it will be more negative than respective polarographic half-wave potential. The latter resulting because, in stripping analysis, the concentration of metal in the amalgam will be of the order of 10^5 times the concentration of the ion in solution.

The selection of the proper plating potential can be determined by a plot of stripping response versus plating voltage. This will indicate the potential at which a steady state anodic current occurs for a particular metal. The optimum electrodeposition potential is generally about 400 millivolts below the stripping peak potential. However, with a complex ligand background involving reducible metal-organic species, the selection of a steady state plating potential is more complicated (see Section 5.1.3). In this case, which will apply to many natural waters, the determination of free metal must carry a clear statement of the electrodeposition potential employed.

2.3.2.4 Plating Time

The electrodeposition interval can be established by trial analysis with a particular set of natural water samples (*i.e.*, sea water). A response versus plating time experiment (only a few points are necessary) will enable the proper plating period to be selected. Also, a single preliminary scan can show the individual components present and permit their concentration to be estimated. In practice, this allows the final experimental parameters to be selected, including not only the plating time, but the instrument sensitivity and plating potential range.

2.3.2.5 Current Sensitivity and Scan Rate

The maximum current sensitivity, that can be utilized to monitor the stripping response, is determined by the scan (sweep) rate. As the scan rate is increased, the peak current (i_p) also increases because the time (t) base is lowered $(Q = i_p t)$. However, the base line also increases with scan rate. The base line represents the current associated with the charging or discharging of the electrical double layer due to the redistribution of ions about the electrodes when the potential varies. Therefore, a sweep rate must be selected that enables the stripping signal to be monitored with a current setting that produces maximum sensitivity without loss of precision.

The optimum balances attained for stripping analysis in sea water for this research were:

Plating Potential	Scan Rate	Current Sensitivity
-0.40 to -1.10v*	16.7 mv/sec	0.5 - 1 μamp/cm
-1.10 to -1.35 v#	16.7 mv/sec	1 - 2 μamp/cm

---

* versus the Ag/AgCl electrode in sea water.

\# At potentials more negative than -1.10 v, larger quantities of hydrogen ion are being reduced. Therefore, a less sensitive current setting may be required when the background current ramp due to hydrogen production is large.

2.3.2.6 Voltage Range

The accuracy of a potential setting is 0.5% with the Heath Company polarographic module, EUA-19-2. Sweep rates were individually calibrated from the time change for a 1000 mv scan. Therefore, a voltage range was selected that allowed the sweep rate to be determined to 0.5%. A voltage sensitivity setting equivalent to 50 mv/cm fulfills this requirement. Moreover, it provides a very convenient read out from the Mosley x-y recorder (135 M) using 18 x 25 cm graph paper. The 25 cm abscissa represents a 1250 mv range.

2.3.3 Sea Water: Medium for Anodic Stripping

Sea water is a very attractive medium for physiochemical studies. The world oceans present an electrolyte solution of almost constant composition (Riley and Tongudai, 1967; Culkin and Cox, 1966). The ionic strength varies from about 0.6 to 0.7 while the pH generally changes only from 7.8 - 8.3 (Skirrow, 1965). Sillén (1967) has suggested that a model sea water containing 1 kg solution, 0.478 mole Na, 0.064 mole Mg, 0.550 mole Cl^- and 0.028 mole $SO_4^=$ would be an ideal ionic medium for studying the equilibrium of the minor components.

Although, this research was not directly concerned with equilibrium problems, sea water turned out to be an excellent medium in which to do anodic stripping voltammetry. The reliable behavior of the electrode system over long periods can be directly attributed to sea water as a good working medium. The relatively high concentration of Cl^- appears to improve the reversibility of many electroreductions. Carter (personal communication, 1968), for example, found the thin film mercury composite graphite electrode in dilute NaCl, KCl, and $NaNO_3$ to be much more subject to the effects of contamination by organic matter, which, in some cases, can lead to unpredictable non-ideal response.

2.3.4 Voltammograms from Sea Water

A voltammogram is a plot of the stripping response (current) versus voltage (time). In this investigation, a current-voltage curve is generated from the oxidation, during a linearly varying potential (anodic direction), of metals amalgamated in the thin film mercury composite graphite electrode. An actual voltammogram from sea water showing various stripping peaks appears in Figure 2-4.

2.3.4.1 Peak Potential

According to theory, the stripping peak potential for a particular metal obeys the following equation (Roe and Toni, 1965):

$$E_p = E'^{o} + \frac{2.3}{\phi} \log \frac{\delta 1 \nu \phi}{D_o} \qquad (2{:}1)$$

The symbols are defined as follows:

E_p = The peak potential.
E'^{o} = The formal potential.
$\phi = \frac{nF}{RT} = 0.039\, n\, mv^{-1}$ (n = the number of electrons involved in the charge transfer).
ν = The sweep rate in mv/sec.
1 = The thickness of the mercury film.
δ = The thickness in cm of the unstirred layer of solution adjacent to the electrode. The diffusion gradient in δ is assumed to be linear.
D_o = The diffusion coefficient of the species being reduced.

Satisfactory agreement was found between the peak potentials observed in sea water and those calculated by Matson for 1M NaCl. The comparison of these data is presented in Table 2-1.

FIGURE 2-4

Voltammogram from Open Ocean Water

60 minute plating step at −1.35 v

vs. the Ag/AgCl electrode in sea water

16.7 mv/sec sweep rate

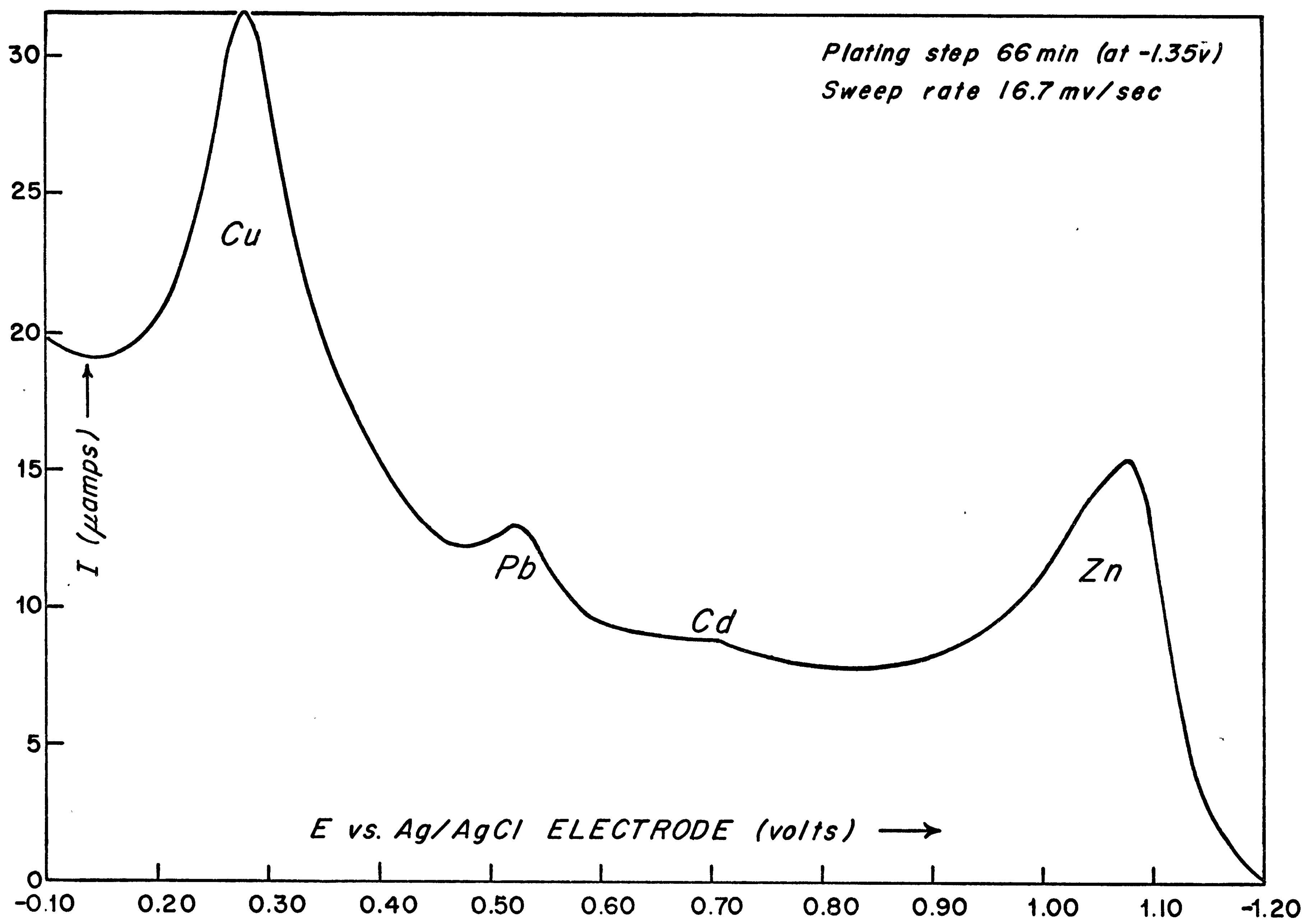

Plating step 66 min (at -1.35v)
Sweep rate 16.7 mv/sec
Cu
Pb
Cd
Zn
I (μamps) →
E vs. Ag/AgCl ELECTRODE (volts) →
30
25
20
15
10
5
0
-0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
-1.20

TABLE 2-1

OBSERVED POTENTIALS IN RAW SEA WATER VS. CALCULATED POTENTIALS FOR 1M NaCl

Metal	E_p* Calculated *vs*. SCE	E_p Observed *vs*. SCE#
Zn	- 1.083 v	- 1.08 to - 1.09 v
Cd	- 0.720	- 0.69 to - 0.72
Pb	- 0.583	- 0.51 to - 0.53
Cu	Variable with Cu concentration in amalgam	

* E_p calculated for 20 mv/sec, $\delta = 10\mu$, and $1 = 0.15\mu$.

Corrected from Ag/AgCl electrode.

2.3.4.2 Peak Current

The peak current should obey the following equation also derived by Roe and Toni:

$$i_p = n\,FA1C_R{}^{o}\,\nu\phi/e \qquad (2:2)$$

where,

F = the faraday; e = 2.718;

A = the area of the electrode;

$C_R{}^{o}$ = the concentration of reduced metal in the electrode at the beginning of the stripping step.

The proportionality of i_p to $C_R{}^{o}$ has been repeatedly verified over the range of trace metal concentration (i.e., 10^{-7} - 10^{-10}M) expected in sea water for Cu, Pb, and Cd. However, there was a larger deviation associated with Zn than the ca. 3% which might be expected from the theoretical equation. An average variation of 12% was observed. This can be attributed to the asymmetry of the zinc peak and therefore the peak area must be measured rather than the simple peak height (current) (see Section 2.3.7.1).

The direct relationship between i_p and ν was checked for a number of sweep rates that would be used for anodic stripping analysis in sea water. The predicted proportionality was found for the scan rates tested (10-30 mv/sec).

Therefore, within the limits of this experimental test, the thin film mercury composite graphite electrode in sea water follows the predictions of the Roe-Toni equations for theoretical behavior of a thin film electrode.

2.3.5 Determination of Free Metal Concentration

Anodic stripping analysis with a thin film mercury composite graphite electrode is governed by the following equations (Matson). The concentration of reducible material at any time in the plating step is given by the expression:

$$C_o(t) = C_o^o e^{-k_c t} \qquad (2:3)$$

and the coulombs used in plating by

$$Q = NC_o^o (1 - e^{-k_c t}). \qquad (2:4)$$

For partial plating without significant bulk concentration changes, the exponential decay of solution concentration can be ignored and this becomes

$$Q = Nk_c C_o^o t. \qquad (2:5)$$

In these expressions

$C_o(t)$ = the concentration in solution of the species being reduced at any time;

C_o^o = the initial concentration of the species being reduced;

Q = the total amount of reduced species in the electrode measured in microcoulombs;

N = a constant equal to nFV, where : n = the number of electrons in the reduction;

F = the Faraday (96,491 coulombs);

V = sample volume,

and k_c = the cell constant, equal to $D_o A/\delta V_{cell}$.

One method of determining the concentration of free metal in solution is, simply, a peak height or area measurement of the stripping response from a single scan in a calibrated cell. Hovespian and Shain (1967) have used this procedure very successfully. However, this technique requires rigid control of experimental conditions such as stirring, temperature, and cell volume. This method was considered unsuitable for stripping analyses aboard ship because experiments must be performed in a rather unpredictable environment.

2.3.5.1 Method of Standard Additions

It was decided to calibrate each cell by the method of addition of spikes of each metal in every analysis. This procedure is time consuming, but more exact and allows a great degree of experimental flexibility. For example, subtle changes in the area of the test electrode during sample changes are no problem. In addition, variations in stirring rate from run to run are accountable. Deviations resulting from temperature fluctuations are minimized. Sample handling is reduced; therefore, the possible introduction of contaminants lessened, because the volume need only be approximated prior to analysis (i.e., no pipetting is necessary) and later determined.

The sea water analyses by anodic stripping voltammetry were generally conducted under conditions where a relatively small fraction of the metal was plated out. According to equation (2:5), a linear response is expected for Q versus spike addition. This has been repeatedly observed for all the metals studied (Zn, Cu, Pb, and Cd) in coastal and open ocean waters.

The concentration of free metal is generally determined by adding two spikes and repeating the analysis after each addition. The response (Q), when plotted against spike addition (μg/l) gives a straight line which is extrapolated to the zero value for Q. The interception point on the abscissa is equal to the concentration (μg/l) of the free metal as defined in Section 2. 1 originally present in solution. The cell constant does enter the calculation but it can be obtained from the slope which is equal to $k_c t$.

2.3.6 Actual Stripping Parameters

A typical voltammogram is presented in Figure 2-5 for an anodic stripping analysis of an open ocean (Sargasso Sea) sample. The concentration of free metal for this raw unfiltered water was determined by two spike additions (larger peaks). The initial peaks were obtained using a 60 minute plating time; current sensitivity of 2 μamp/cm; sweep rate of 16.7 mv/sec, and a plating potential of - 1.35 v versus the Ag/AgCl electrode in a cell volume of 117 ml. This stripping scan represents 2.5 μg/l Zn, 0.029 μg/l Cd, 0.38 μg/l Pb, and 0.46 μg/l Cu.

In the present research the defining analytical parameters employed for anodic stripping voltammetry in sea water using a thin film mercury composite graphite electrode are:

Cell volume	60 - 120 ml
Plating potential......	- 0.80 to - 1.35 v vs. Ag/AgCl electrode
Plating time	30 - 60 minutes
Scan rate	16.7 mv/sec
Current sensitivity	0.5 - 2 μamp/cm
Voltage sensitivity	50 mv/cm

2.3.7 Precision Limits

2.3.7.1 Correlation of Peak Height with Peak Area

FIGURE 2-5

Typical Voltammogram from the Anodic Stripping Analysis

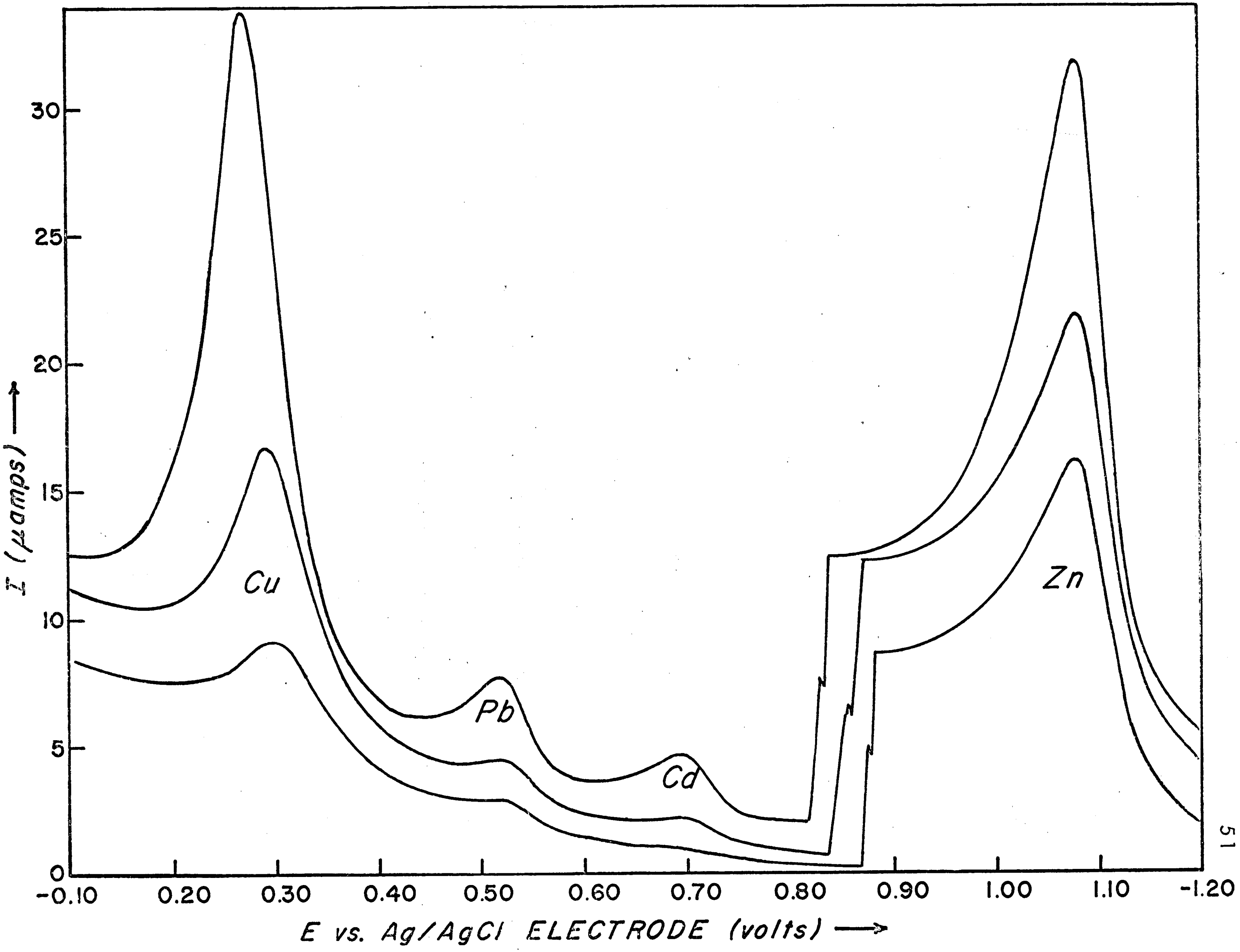
of a Sea Water Sample from the Open Ocean

(Sargasso Sea)

60 minute plating step at −1.35 v

vs. the Ag/AgCl electrode in sea water

16.7 mv/sec sweep rate



30
25
20
15
10
5
0
I (μamps) ⟶
Cu
Pb
Cd
Zn
-0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
-1.20
E vs. Ag/AgCl ELECTRODE (volts) ⟶

In Figure 2-6, the base line (determined from a 5 minute plating step) has been subtracted from the voltammogram. This presents the response peaks in a more normal perspective. The Cd, Pb, and Cu waves are reasonably symmetrical, but Zn is distinctly asymmetrical.

Figures 2-7 to 2-10 are plots of the trace metal concentration obtained from peak heights versus the amounts found from peak areas. The method of standard additions (using two spikes) was employed. The peak areas were measured to 0.001 inch by planimetry. It is obvious that peak height instead of peak area can be used satisfactorily for Cu, Cd, and Pb. Much of the scatter is caused by the interpolation necessary in obtaining the total area of the peak. Since the Pb and Cu waves do not separate completely, it is necessary to draw in the missing segments before a planimeter can be used. There is no difficulty obtaining a precise peak height, because the base line can be fitted quite well.

For Zn, the peak height and peak area do not correlate as well. This is expected for an asymmetrical peak. However, the points showing the poorest agreement result from those cases where the Zn peak has assumed a bell-like shape. Peak area, therefore, must generally be used to determine the concentration present. Since the Zn stripping peak occurs on the current ramp for the production of hydrogen, there may be some loss of precision associated with the proper fitting of the base line under the Zn wave.

2.3.7.2 Coefficient of Variation

A plot of the coefficient of variation versus the concentration of metal in some

FIGURE 2-6

Voltammogram from Figure 2-5 with the Base Line Removed

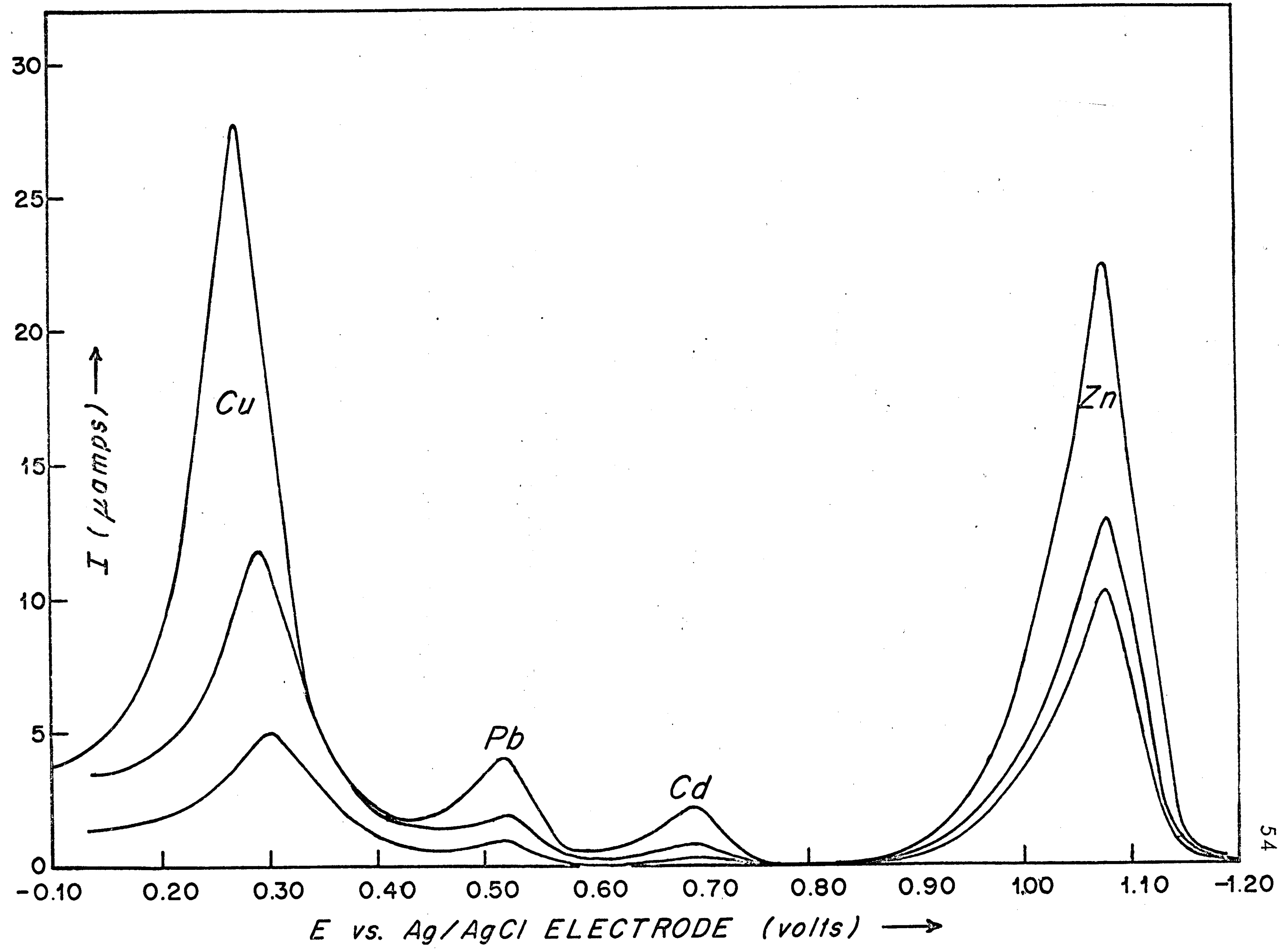

30
25
20
15
10
5
0
I (μamps) ⟶
Cu
Pb
Cd
Zn
-0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
-1.20
E vs. Ag/AgCl ELECTRODE (volts) ⟶

FIGURE 2-7

Determination of Cu Concentration in Sea Water: Peak Height Versus Peak Area

FIGURE 2-8

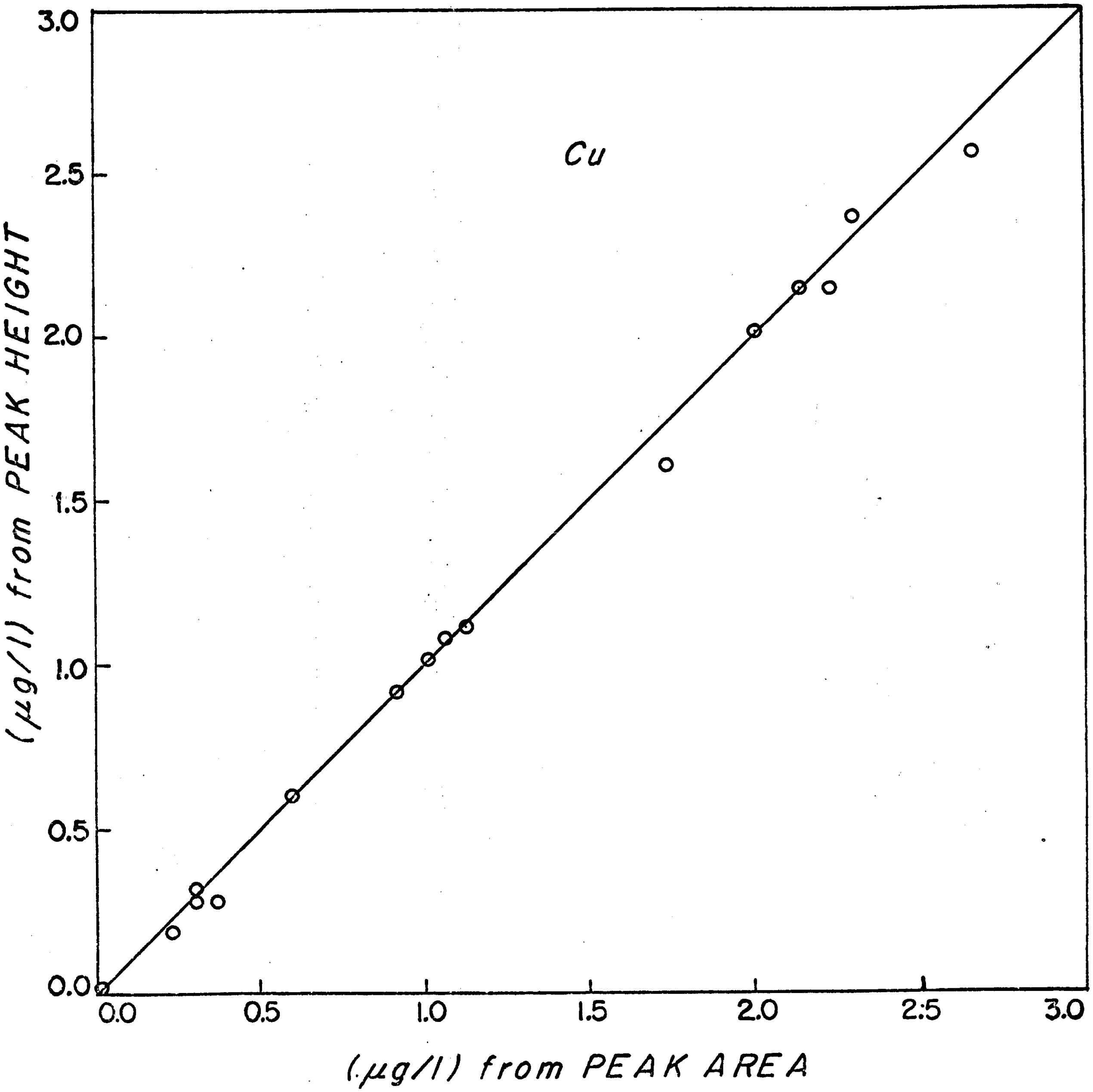
Determination of Pb Concentration in Sea Water: Peak Height Versus Peak Area

FIGURE 2-9

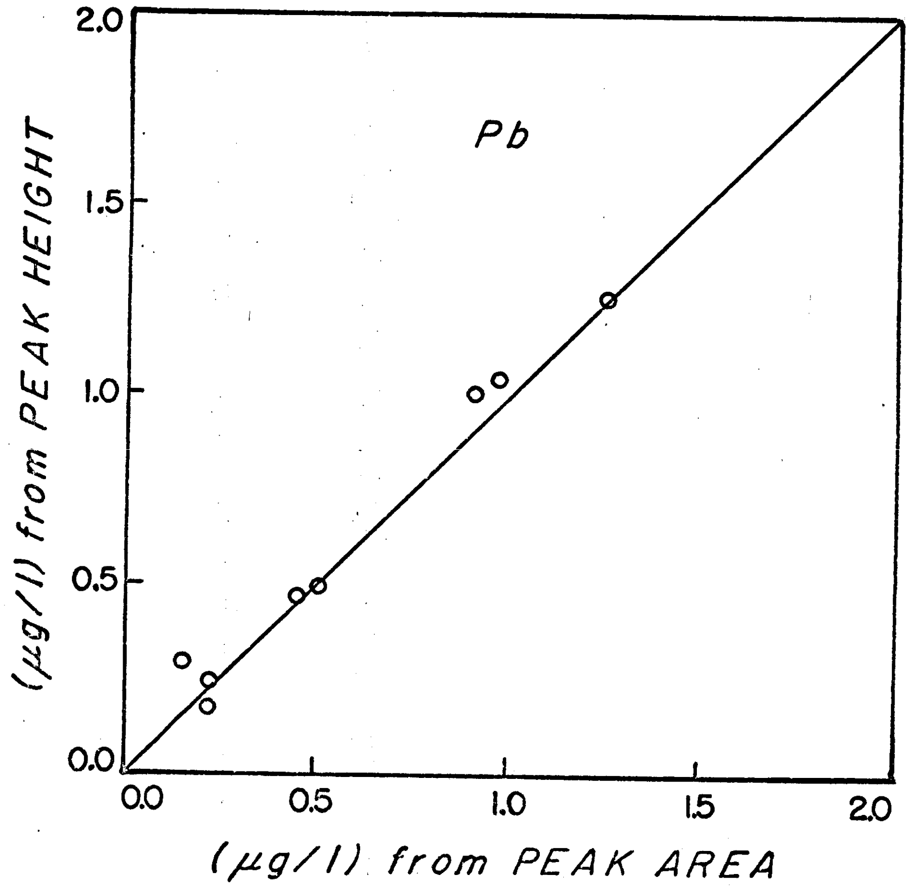
Determination of Cd Concentration in Sea Water: Peak Height Versus Peak Area

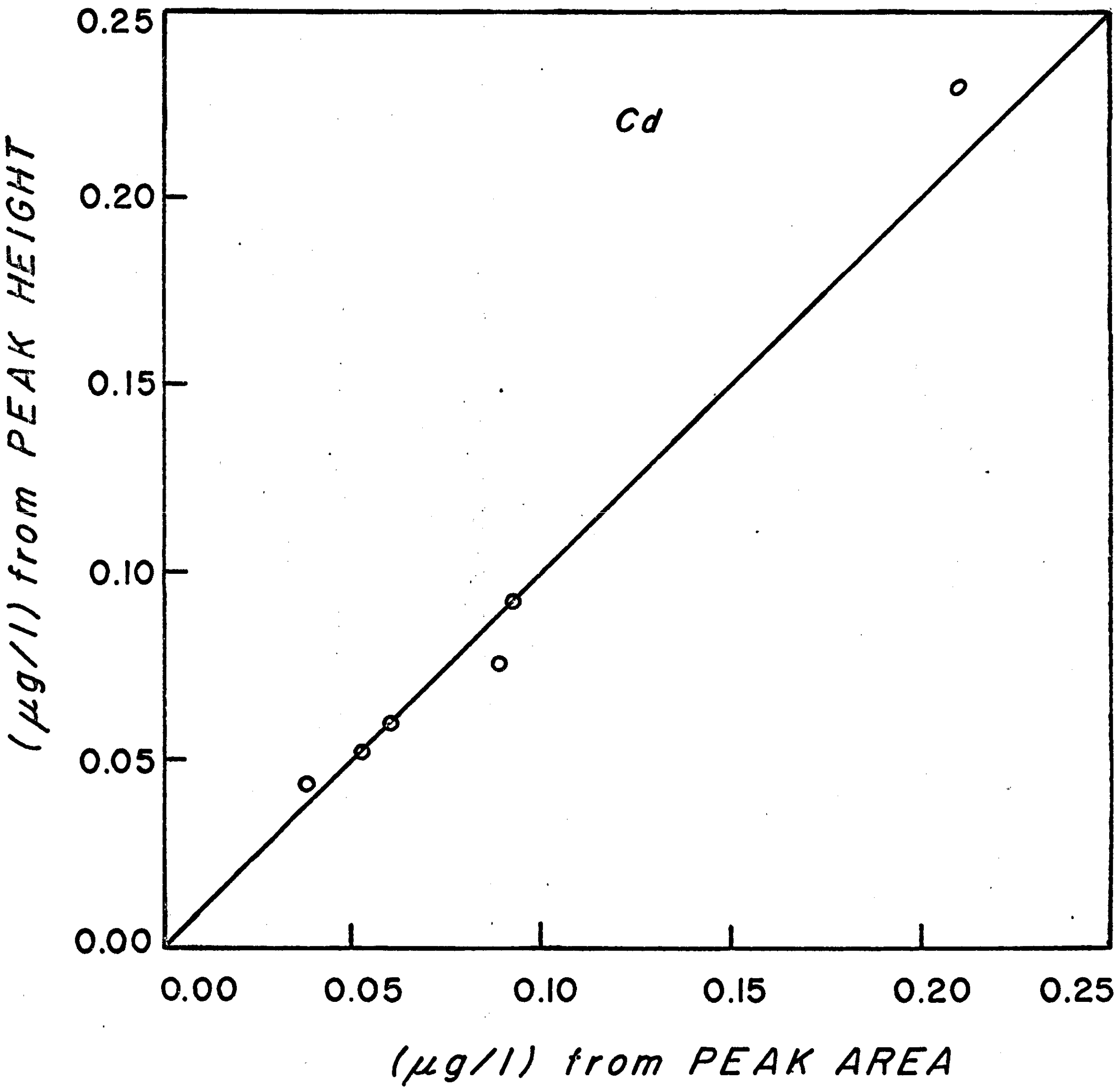
FIGURE 2-10

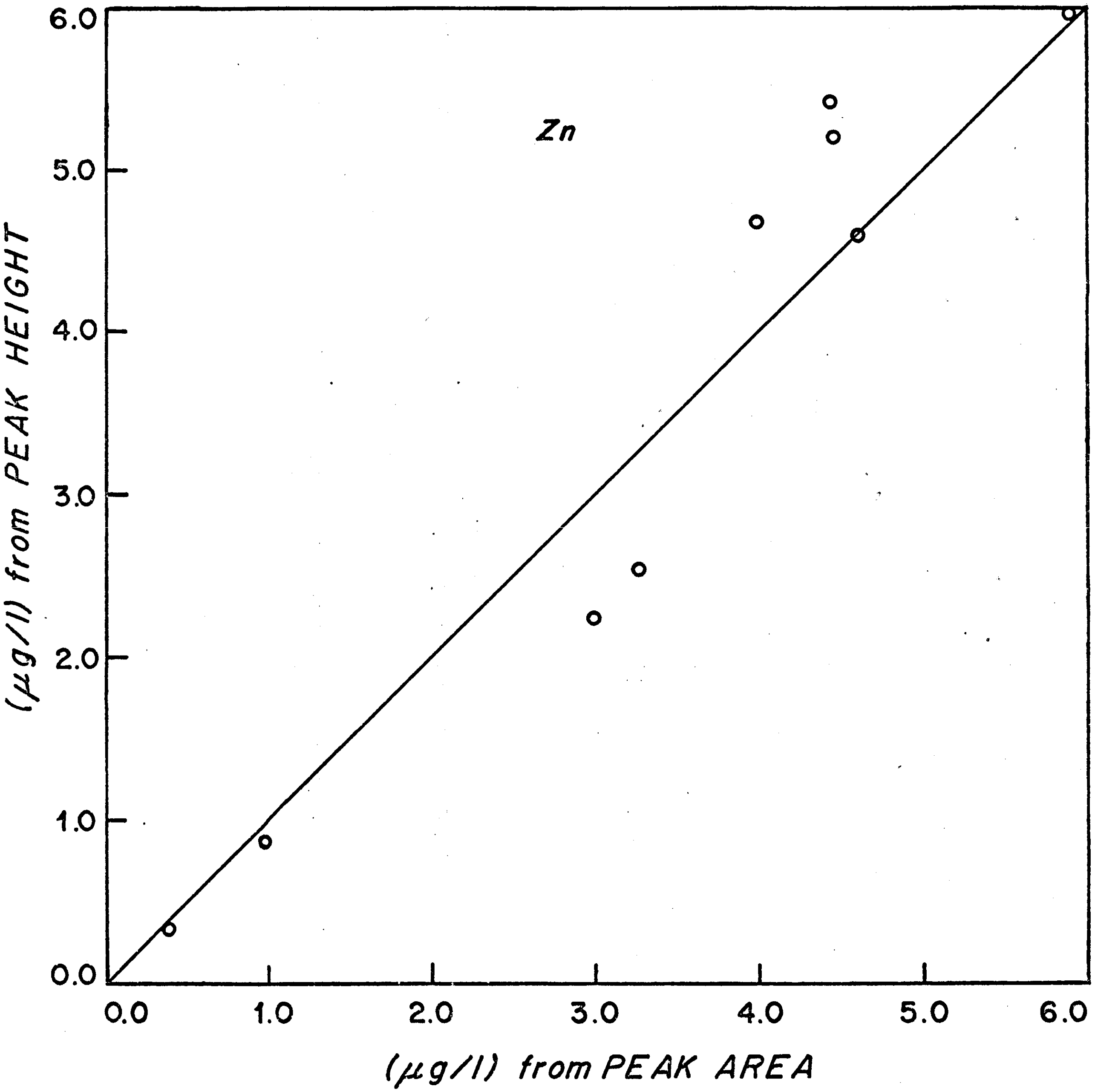
Determination of Zn Concentration in Sea Water: Peak Height Versus Peak Area



Cu
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.0
0.5
1.0
1.5
2.0
2:5
3.0
(μg/l) from PEAK HEIGHT
(.μg/l) from PEAK AREA


Pb
2.0
1.5
1.0
0.5
0.0
(μg/l) from PEAK HEIGHT
0.0
0.5
1.0
1.5
2.0
(μg/l) from PEAK AREA


Cd
0.25
0.20
0.15
0.10
0.05
0.00
(µg/l) from PEAK HEIGHT
0.00
0.05
0.10
0.15
0.20
0.25
(µg/l) from PEAK AREA


Zn
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(μg/l) from PEAK HEIGHT
0.0
1.0
2.0
3.0
4.0
5.0
6.0
(μg/l) from PEAK AREA

sea water samples is depicted in Figure 2-11. The coefficient is generally less than 10% and the average values are: Zn, 4%; Cu, 4%; Pb, 6%, and Cd, 5%. There is also no trend associated with the concentration of metal -- the precision for small amounts is comparable to that for larger concentrations.

These data of precision were obtained from duplicate samples run in separate cells, and the quantities of free metal were determined by the method of standard additions using two spikes. The use of separate cell analysis avoids systematic errors associated with any one cell. The concentrations of trace metal are measured in cells displaying a significant degree of individuality. For example, the cell constants may differ by 20% and the base lines including the hydrogen ramp have unique characteristics. Analyses in separate cells are comparable to the determination of the hydrogen ion concentration in aliquots using two pH meters. Cell anomalies can be easily recognized.

2.3.8 Artifacts

2.3.8.1 Double Peaks or Doublets

Matson, occasionally observing double peaks or peaks with shoulders in the stripping curves of trace metals, attributed these to partial complexing of the redissolved metal by a strong ligand or ligands. The validity of the theoretical arguments supporting this interpretation has been questioned by Carter,* who found that double peaks could be produced in solutions free of complexing agents. When the thin film mercury composite graphite electrode was manufactured by plating mercury out at -0.1 v, a double peak for lead resulted. No double peak was

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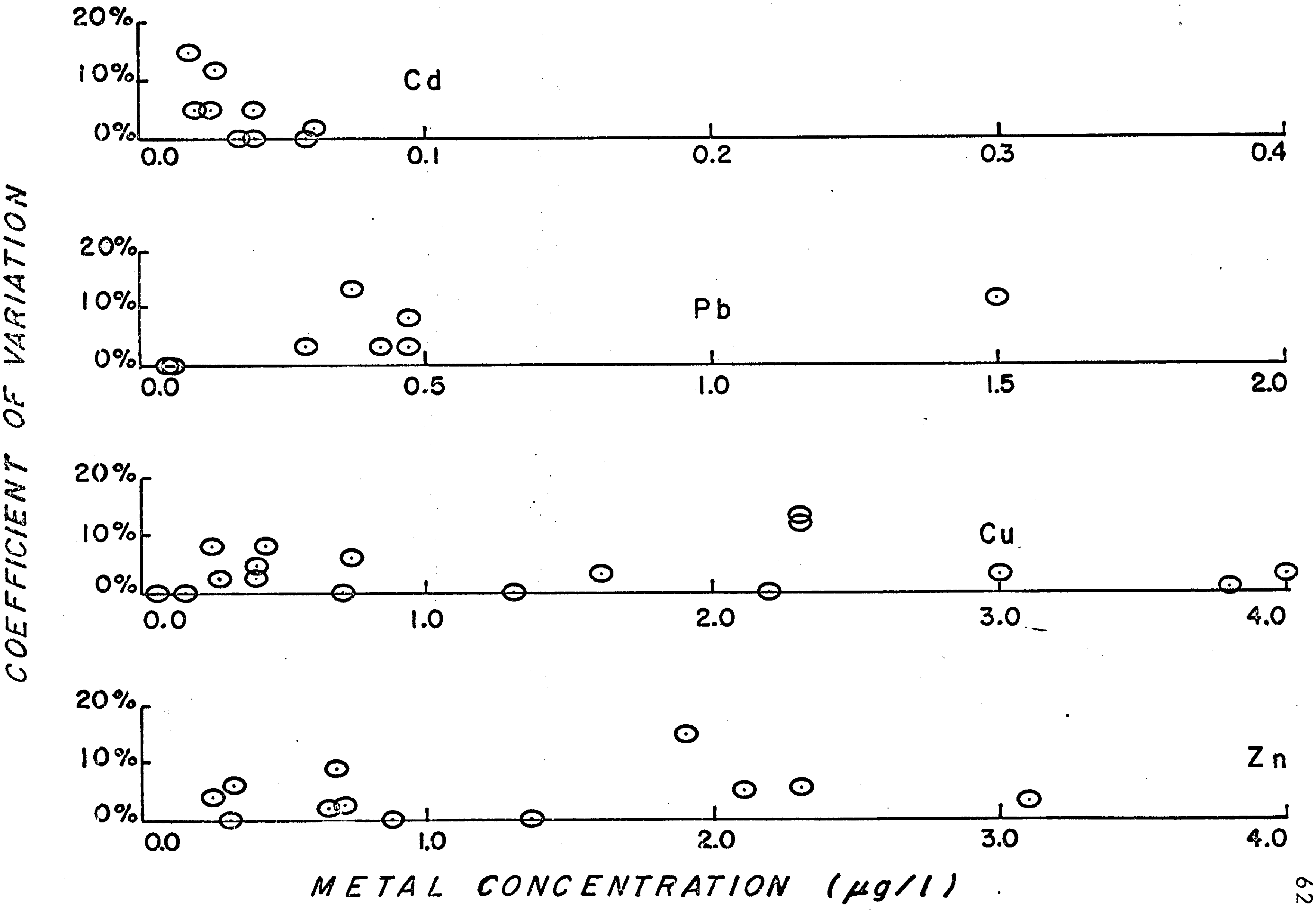
* Personal communication, 1968.

FIGURE 2-11

Coefficient of Variation Versus Concentration

for Cu, Zn, Cd, and Pb


COEFFICIENT OF VARIATION
20%
10%
0%
Cd
0.0
0.1
0.2
0.3
0.4
Pb
0.0
0.5
1.0
1.5
2.0
Cu
0.0
1.0
2.0
3.0
4.0
Zn
0.0
1.0
2.0
3.0
4.0
METAL CONCENTRATION (µg/l)

observed when the mercury plating was carried out at - 1.0 v.* Plating at intermediate potentials produced lead peaks with shoulders.

Inhomogenities on the final electrode surface has been suggested as a tentative explanation. If the mercury does not completely cover the graphite surface, plating will occur both on mercury and graphite sites. For some metals, e.g., Pb, the stripping potentials are significantly different from mercury and from graphite, and a double peak results.

The sea water samples analyzed during CHAIN cruise 85 and subsequent experiments rarely show double peaks. In the occasional instances when two peaks occurred -- only with Cu -- it was attributable to a faulty manufactured electrode or an electrode that had deteriorated.

2.3.8.2 Adsorption

Recent studies (e.g., Menzel, 1967; Menzel and Ryther, 1968) indicate that the quantity of organic carbon dissolved in sea water is remarkably constant over a wide range of depths and throughout the major portion of the world oceans. Menzel reports an average dissolved organic content of about 0.6 mg C/l for sea water below the euphotic zone. This amount of carbon reflects a rather dilute organic solution of 5×10^{-5} M C in sea water. Nevertheless, adsorption of organic material on the active mercury surface of the test electrode must be considered as possible source of error in trace metal determinations using the anodic stripping voltammetric method. That is, non-theoretical electrode behavior may be observed if the ad-

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* vs. Ag/AgCl electrode

sorbed organic molecules seriously interfere with either the mass transfer of electroactive species or the electron transfer to these species at the electrode surface.

The average variation (ca., 5%) found for the precision of analysis using stripping voltammetry in sea water (Figure 2-11) suggests that any adsorption phenomena must be acting in a predictable and reproducible manner. Either the electrode area decrease that might occur from the adsorption of organic molecules does not vary during analysis, or the adsorption is slight and no significant interference occurs during the reduction and subsequent oxidation of metal species.

Since the cell constant (Section 2.3.5) is directly proportional to the electrode area, it was possible to establish from cell constant measurements in both raw filtered sea water and in organic-free sea water whether significant adsorption of organics was actually occurring. The cell constant based on the copper response was determined in two different samples of raw filtered coastal water (Falmouth, Massachusetts) and also in four samples of these waters in which the organic matter had been destroyed by ultra-violet irradiation (see Chapter 3). These data are presented in Table 2-2.

This experimental evidence shows that adsorption is not a serious problem even in the presence of the higher dissolved organic background in coastal water (ca., 2 mg/l). The variations noted are no greater than those normally observed between runs on separate portions of the same sample. The slightly higher cell constant in the organic-free sea water can be attributed to changes in cell geometry. The irradiated samples volumes (60 ml) were approximately half the quantity used for the raw filtered sea water analyses, and consequently, these will be more

TABLE 2-2

CELL CONSTANT MEASUREMENTS BASED ON THE COPPER RESPONSE IN RAW FILTERED COASTAL SEA WATER AND IN ORGANIC-FREE COASTAL SEA WATER

	Cell Constant*
Raw Filtered Coastal Sea Water	$1.1 \pm 0.1 \times 10^{-4}$ liter^{-1} min^{-1} (2 samples)
Organic-Free Coastal Sea Water#	1.3 ± 0.2 (4 samples)

---

* These data have been normalized by not including the sample volume in the calculation.

Dissolved organic material destroyed by ultra-violet irradiation (Chapter 3).

efficiently mixed (nitrogen bubbling) but somewhat more variable.

Thus, under normal experimental conditions, adsorption of natural organic material in sea water is of negligible effect. It does not seriously affect the precision or inhibit the efficiency of anodic stripping analysis in sea water.

2.3.9 Interferences

2.3.9.1 Introduction

There have been reports suggesting that intermetallic compound formation may occur between the various metals deposited on an Hg electrode (e.g., Kemula et. al., 1958; Hovsepian and Shain, 1967). These phenomena have been observed during analyses employing a hanging mercury drop electrode in solutions containing metal ions at concentrations greater than 10^{-5}M (Barendrecht, 1967). Generally, the effect resulting from the formation of an intermetallic complex with another metal is a reduction in the magnitude of the signal for the metal sought and, in some cases, the production of a separate peak for the oxidation of the complex. An example of an intermetallic compound pertinent to this present investigation is Zn-Ni.

The metal amalgams formed during stripping voltammetry with a thin film mercury composite graphite electrode are more concentrated than those produced with a hanging mercury drop electrode. Consequently, interference from intermetallic complexes can appear at much lower metal concentrations. Matson (1968) has shown the increase in the stripping response for Cu (5×10^{-8}M) from the presence of 3×10^{-7}M Ni. According to Matson, no effect was noticeable when the Ni concentration was at or below 10^{-8}M. Unfortunately, this is not correct. It was found in the present research, that although the Ni concentration in sea water is ca., 10^{-8}M, both the Cu and Zn signals can be affected by its presence. Thus, this effect depends on the quantity of free Ni (reducible) and not on the total Ni concentration in the aqueous solution.

The possibility of Ni interference arises when the analysis is extended to include Zn. This requires using an electrodeposition potential near - 1.35 v vs. the Ag/AgCl electrode in sea water.* In open ocean water Ni is the major offender. But, it is conceivable that in areas of upwelling where the Co concentration may be high (10^{-8}M), some interference could occur at potentials > -1.25 v, through the possible formation of Zn-Co complexes.

The chemistry of intermetallic compound formation is complicated (see for example, Hovsepian and Shain) and warrants independent research. Thus, the physicochemical investigation which these phenomena deserve was beyond the scope of the present dissertation. However, many open ocean samples were analyzed (Chapter 6) in which complexing between Zn and Ni was apparently occurring. Therefore, exploratory experiments were conducted which attempted to characterize the effects and to estimate the possible errors introduced.

This preliminary study revealed that, although definite interference was introduced from production of Zn-Ni intermetallic compounds, the anomaly was systematic in its effect. However, until the intermetallic complex formation is better understood, it is suggested that investigators wishing to use anodic stripping

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* All voltages will be referred to the Ag/AgCl electrode in sea water in these sections.

analysis, with the thin film mercury composite graphite electrode, in sea water as an analytical tool, confine their measurements to the determination of Cu, Pb, and Cd. No anomalies occur at plating potentials of < -1.15 v, and these three elements are therefore free from interferences.

In the following sections, the experimental evidence for the presence of intermetallic complexes of Zn-Ni will be given. Additional data will be presented suggesting that Zn-Ni introduces a systematic error in the amount of free Cu and Zn determined in open ocean samples at -1.35 v. Further, an evaluation of the open ocean data (see Chapter 6) indicates that the contribution from free Ni was only minor for sea water of the northwestern Sargasso Sea.

2.3.9.2 Intermetallic Zn-Ni Complexes

The Ni interference resulting from intermetallic compound formation in the thin film of mercury during anodic analysis can be characterized as follows: when Ni spikes (yielding 10^{-8} M increases in solution) are added to sea water containing Cu and Zn (at 10^{-8} M), significant increase ($> 5\%$) in the Cu stripping response can be observed at plating potentials more negative than the electrodeposition voltage for Ni (-1.15 v). This increase in the Cu peak is accompanied by a simultaneous decrease in the Zn wave. Therefore, the effect is tentatively ascribed to the formation of a Ni-Zn intermetallic complex, the reoxidation of which is coincidental with the Cu stripping peak.

This effect can also be demonstrated for the in situ levels of Ni and Zn in sea water. In raw sea water, the Cu response free from interference can be obtained by plating at < -1.15 v. If this step is followed by analysis at -1.35 v (holding all other analytical parameters constant), an increase in the Cu response will be observed. This effect can be directly attributed to a Zn-Ni complex and not to Cu for the following reason: the stripping peak potential for Cu varies sensitively with the Cu concentration in the amalgam (see Section 2.3.4.1), i.e., as the Cu amalgam concentration increases, the stripping peak for Cu shifts anodically. No change in the Cu peak potential occurs in the experiment outlined, although the peak response increases. Therefore, the Cu in the amalgam behaves normally; the increase results from the oxidation of the Ni-Zn complex formed at the in situ concentration of these metals in sea water.

2.3.9.3 Systematic Nature of Zn-Ni Intermetallic Complexes

Hovsepian and Shain (1967) have shown using stripping analysis to study intermetallic complex formation between Co and Zn in hanging mercury drop electrodes, that intermetallic compounds can be described thermodynamically and an equilibrium constant determined experimentally. The Zn-Ni complex formed in the stripping analysis of sea water with the thin film mercury composite graphite electrode also displays systematic behavior. Specific examples of this character observed for sea water analyses conducted at a plating potential of -1.35 v are as follows:

(1) The precision of analysis does not change when Ni interference is present.

(2) Both the Cu and Zn response show $< 5\%$ variation for replication in a single cell.

(3) The response of Cu and Zn is linear with plating time over a period of 5 to 60 minutes.

(4) The response of Cu and Zn is linear with spike additions amounting to 5 µg/l Cu and 14 µg/l Zn.

These data indicate that the Ni interference affected the open ocean water analyses in a constant manner, and that the magnitude of the effect depends on the quantity of free Ni available in any one sample. Thus, because the plating time is held constant, the original Cu response and the additional response resulting from spikes are high by a constant amount. This yields an apparent free Cu concentration which is higher than the quantity actually present. Conversely, the Zn response, original and spikes, is lower by a constant factor. This gives, by the method of standard additions, a value for free Zn which is lower than the true quantity.

Although, the concentration of free Ni present in the open ocean water analyses is not known, an estimate of the total Ni in the northwestern Sargasso Sea (36°-38°N, 65°-67°W) can be obtained from the recent data of Spencer and Brewer (1969).* The amount of Ni in the surface layer (0 to 200 meters) is _ca._, 1 µg/l with some seasonal variation. An increase is observed below these depths to _ca._, 2 µg/l at 1500 meters. These investigators also have unpublished results (personal communication) for the Puerto Rico Trench suggesting that higher concentrations of Ni (1.5 to 2 µg/l) are present in the southwestern Sargasso Sea. The possible errors introduced by the presence of free Ni will be discussed in detail when the open ocean study is considered in Chapter 6. Briefly, it was concluded

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* The analytical procedure is noted in Section 6.

that only the photo-oxidized (organic-free) samples were seriously affected by intermetallic complex formation.

In summary, the complete evaluation of Zn-Ni intermetallic complex formation within the thin film of mercury and its effects on sea water analyses using anodic stripping at plating potentials where this interference prevails requires a thorough study. The systematic characteristics noted for this intermetallic compound would suggest that a suitable correction could be devised from which the actual free concentration of Zn and possibly Ni could be determined. This is certainly worthy of future research.

2. 3. 10 Conclusions

As a result of this analytical investigation which examined anodic stripping voltammetry in sea water using the thin film mercury composite graphite electrode in sea water, the following conclusions were drawn:

(1) Sea water is an excellent medium for anodic stripping voltammetry.

(2) In sea water, the thin film mercury composite graphite electrode does follow theoretical behavior for thin film electrodes.

(3) Cu, Cd, Pb, and Zn can be measured directly in sea water without preconcentration.

(4) Very good precision (ca., 5%) is attainable for analyses of Cu, Pb, Cd, and Zn, and the precision appears to be independent of concentration.

(5) Adsorption of naturally occurring organic material onto the test electrode is of negligible effect. That is, it does not inhibit the response nor seriously affect the precision of anodic stripping analysis with the thin film electrode in sea water.

(6) Ni may interfere with the measurement of Cu and Zn at plating potentials > -1.15 v <u>vs</u>. the Ag/AgCl electrode in sea water. Therefore, it was suggested that routine analyses in sea water be confined to Cu, Cd, and Pb. However, a study of this interference (Ni-Zn intermetallic compound) should be pursued not only because of its purely physicochemical interest, but also because it appears possible to obtain data for the concentration of Ni in sea water. Thus, extending the usefulness of anodic stripping analysis with the thin film mercury composite graphite electrode in sea water.

(7) The technique is quite suitable for shipboard analysis and the monitoring equipment is inexpensive.

(8) Free metal is measured by anodic stripping analysis and a method to examine trace metal speciation in sea water can be developed. The analytical system designed and tested for shipboard investigation of trace metal speciation in the oceans will be discussed in the following chapters.

CHAPTER THREE

METHODS FOR DETERMINING TRACE METAL SEQUESTERED ORGANICALLY IN SEA WATER

3.1 Degradation of Organic Matter

The anodic stripping voltammetric technique using the thin film mercury composite graphite electrode provides a means of measuring free metal in natural waters. However, much valuable information could be obtained from an additional measurement of the total metal present. A suitable oxidation method for the degradation of dissolved organic matter would enable the total amount of metal (free plus organically sequestered) to be determined by anodic stripping analysis. Therefore, routine analyses of free metal and organically complexed metal would be possible in natural waters. It was decided to investigate several methods for the oxidation of organic matter in sea water to determine which would be most suitable to complement the anodic stripping voltammetric measurements.

3.1.1 Wet Oxidation

There are a number of wet oxidation procedures currently in use for the oxidation of dissolved organic material in sea water. Digestion of the sample with a strongly oxidizing acid such as hot concentrated perchloric (Corcoran and Alexander, 1964) or persulfuric (Slowey and Hood, 1966) has been used. However, the strongly acid sample resulting from this treatment would be unsuitable for subsequent anodic stripping voltammetry because of the hydrogen evolution. Moreover, the problem of obtaining and keeping trace metal free acids is severe, and significant sample contamination is often introduced by these reagents.

Menzel and Vaccaro (1964) have advocated the use of potassium persulfate as an oxidant after prior treatment of the sample with phosphoric acid to remove inorganic carbon. This method is very effective and is receiving wide popularity for the destruction of dissolved organic carbon in sea water. However, the procedure requires the addition of 100 mg of potassium persulfate and 0.2 ml of 3% phosphoric acid to 5 ml of sea water. Therefore, it is unsuitable as a means of destruction of organic matter before use of the sample for anodic stripping voltammetry, for much the same reasons as the strong acid digestion. The sample is acidic, has a high concentration of foreign reagent, thus altering the background electrolyte solution, and is probably trace metal contaminated.

3.1.2 Ultra-violet Oxidation

It has been known for a considerable time that ultra-violet irradiation can promote many chemical reactions, particularly photo-oxidation; however, only recently has this technique been applied to sea water.

Armstrong et. al. (1966), in a most significant paper, showed that ultra-violet irradiation can oxidize completely many organic compounds in sea water at its natural pH. The following compounds were tested and found to be completely oxidized by exposure to a radiation intensity of 0.020-0.025 W/cm^2 over a period of one hour: pyridine, 2,2-bipyridine, adenine, ethyl alcohol, methyl alcohol, glucose, glucosamine, acetic acid, oxalic acid, formic acid, palmitic acid, dimethylamine, casein, glycerol, phenylalanine, and "humic acid."

The apparatus used by Armstrong et. al. consisted of a 1200 W mercury arc tube mounted vertically allowing 12 samples in quartz vials of ca. 110 ml volume placed concentrically around the lamp to be irradiated. The incident radiation was measured by actinometry and the absorbed radiation estimated to be between 0.020-0.025 W/ cm^2 at the sample surface. The lamp was a relatively inefficient source, most of the emitted energy being heat, thus necessitating cooling of the sample tubes. This was accomplished by blowing a stream of air over the apparatus from a fan mounted underneath the tubes. In spite of these precautions, the samples became quite hot, and the temperature measured at the top of the sample container varied from 60°-80°C.

The method appears to be well suited for treatment of samples prior to anodic stripping voltammetry. No addition of reagents or other manipulations of the sample is required, and the sample is contained in a high purity quartz vessel throughout the experiment.

3.1.3 Choice of Method

Williams (1969) has compared the persulfate oxidation method and the ultraviolet irradiation technique. His data are reproduced in Table 3-1. The results clearly demonstrate that little difference in efficiency can be detected between the two methods, and either is a means of complete destruction of dissolved organic matter (carbon) in sea water.

Because of its simplicity, seeming effectiveness, and freedom from ionic strength changes and from the possibility of contamination by adding reagents, the

TABLE 3-1

Wet Oxidation (A) compared with Ultra-violet Oxidation (B) on the same samples, after Williams, 1969.

Depth of sample (m)	Organic carbon (mg C/liter)		
	A	B	B - A
Surface	0.71	0.78	0.07
Surface	0.76	0.93	0.17
Surface	0.84	0.90	0.06
Surface	0.82	0.87	0.05
5	0.76	0.93	0.17
98	0.55	0.64	0.09
280	0.62	0.57	-0.05
435	0.49	0.52	0.03
750	0.56	0.49	-0.07
970	0.49	0.49	0.00
70	0.87	0.85	-0.02
240	0.77	0.66	-0.11
420	0.49	0.61	0.12
650	0.42	0.51	0.09
750	0.43	0.61	0.18
1,090	0.46	0.55	0.09
10	0.60	0.79	0.19
100	0.57	0.66	0.09
475	0.77	0.75	-0.02
970	0.50	0.48	-0.02
1,370	1.03	1.20	0.17
1,980	0.35	0.45	0.10
2,940	0.54	0.63	0.09
Amazon River	1.03	1.22	0.16
Mean	0.64	0.71	0.07

photo-oxidation technique was examined for its applicability to samples for anodic stripping voltammetric analysis. In order to avoid unnecessary heating, which might result in volatility losses, an apparatus utilizing a small, low power but highly efficient immersion lamp was devised. The apparatus is shown in Figure 3-1.

The lamp is manufactured by Ultra-violet Products, Inc., San Gabriel, California (Model No. PCQ9G-1). It was used <u>in situ</u> by immersion in a small Pyrex reaction vessel (70 ml). A 24/40 Ŧ ground glass joint seals the vessel from the atmosphere.

This high efficiency lamp emits between 80-90% of its radiation at 2537Å. An order of magnitude calculation indicated, however, that the energy absorbed would be about 10 times smaller than the absorption obtained with the Armstrong <u>et. al</u>. system. Thus, a much longer irradiation period is necessary to procure comparable degradation. Even with prolonged irradiation, however, the temperature of the reaction medium does not go above 50°C.

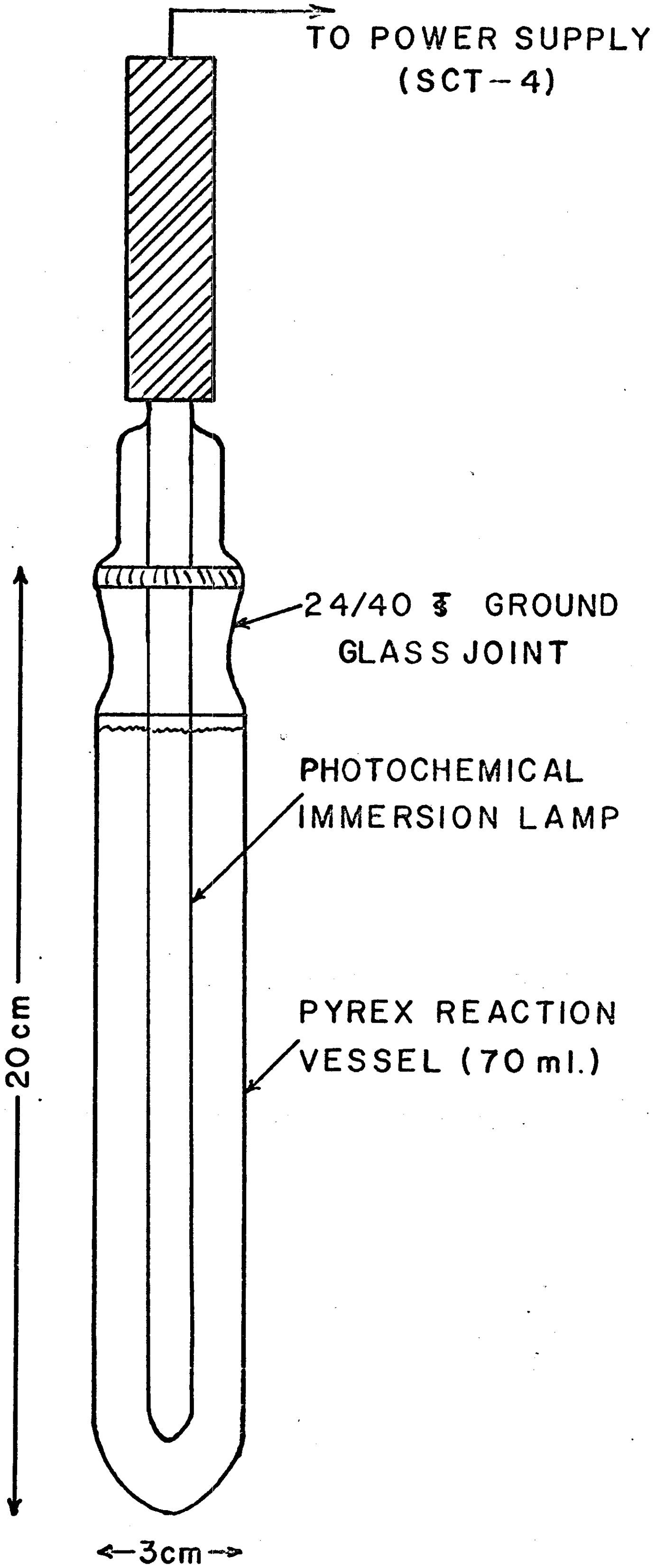
3.1.4 Experimental Test

The modified ultra-violet oxidation apparatus was tested for effectiveness. Filtered Woods Hole harbor water, containing 2.0 ± 0.2 mg/l dissolved organic carbon, was irradiated for various times. The dissolved organic carbon was then determined using the Menzel and Vaccaro persulfate oxidation procedure. The results are presented in Table 3-2.

The oxidation of dissolved organic carbon, within the limits of error, follows first order kinetics. The rate constant is 7.4×10^{-3} min^{-1} and the half time for

FIGURE 3-1

Ultra-violet Irradiation Apparatus



ULTRA-VIOLET IRRADIATION APPARATUS

TABLE 3-2

Time Study of Degradation of Dissolved Organic Material (Carbon) by Photo-oxidation with Ultra-violet Radiation

Dissolved Organic Carbon (mg/l)	Time Sea Water Irradiated (Minutes)
2.0 ± 0.2	0
1.5 ± 0.2	60
1.3 ± 0.2	95
0.8 ± 0.1	160
0.4 ± 0.1	245

degradation is 94 minutes. The plot from which these data were calculated appears in Figure 3-2. Armstrong et. al. also found first order kinetics with a rate constant of 5 x 10^{-2} min^{-1}, although in a later paper, Armstrong and Tibbits (1968) using a medium power mercury arc lamp (380 W) reported that the destruction of dissolved organic carbon in sea water from the English Channel did not follow first order kinetics.

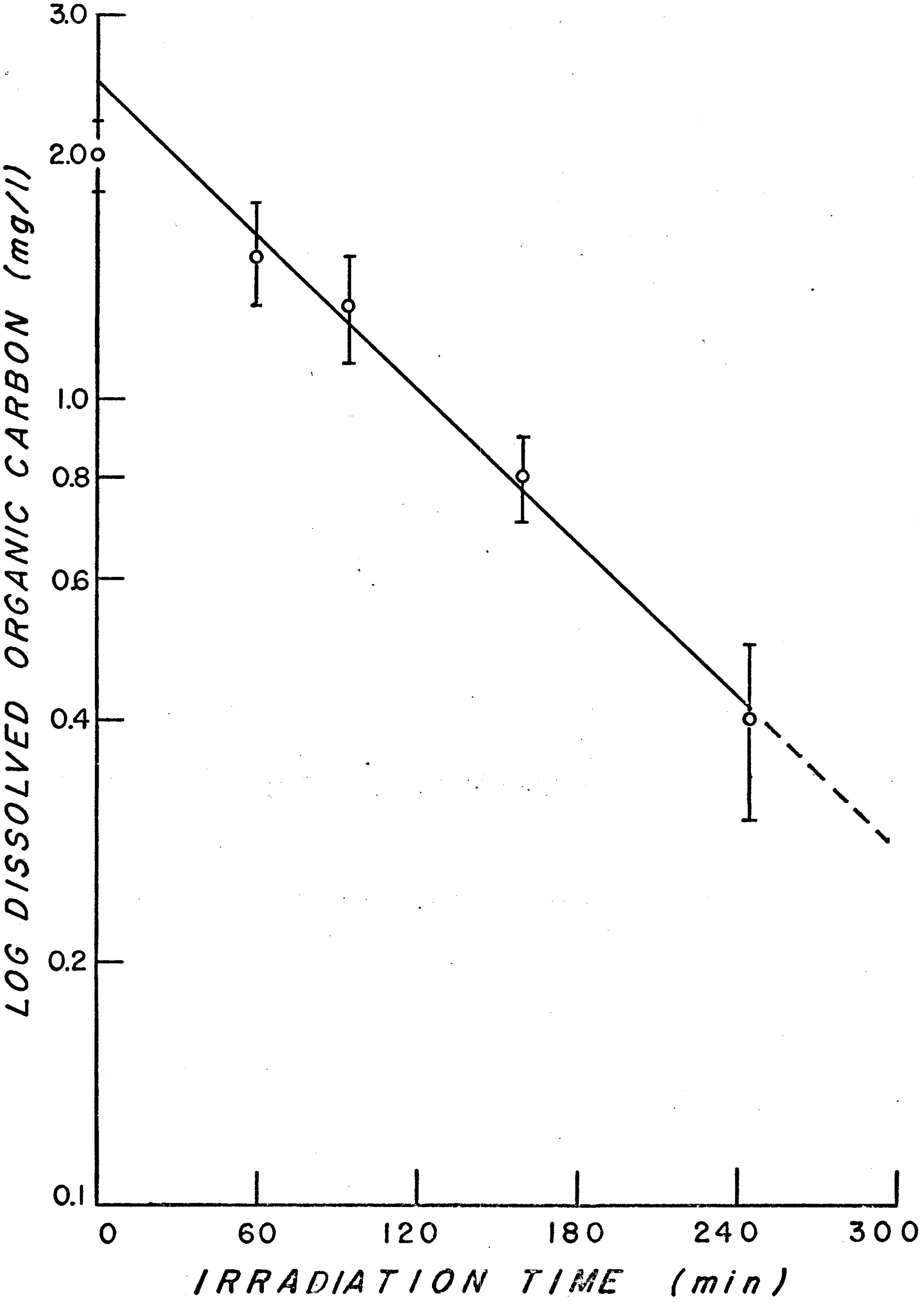
In the latter investigation, the decomposition of dissolved organic matter was determined by the amount of oxygen consumed during irradiation. This should be a better measure of the total amount of material degraded, than the Menzel and Vaccaro method which determines only the dissolved organic carbon. However, the kinetics cannot be evaluated because the actual numbers and precision limits are not stated. Whereas, the precision of the persulfate technique indicates that only 90% degradation can be established.

In summary, the modified ultra-violet oxidation method used in this research is effective in destroying dissolved organic matter (determined as organic carbon). It is not as efficient as the apparatus used by Armstrong et. al. (1966). However, the addition of O_2 or H_2O_2 is not required to ensure oxidation. Also, the temperature of the irradiated sample does not rise above 50°C. Finally, and more importantly, this apparatus can be conveniently used for shipboard analysis.

Direct analysis for the amount of free metal and for the major fraction of the organically bound metal is now possible for four of the trace metals present in sea water: Zn, Cd, Pb, and Cu. The procedure consists simply of analysis by stripping voltammetry with the thin film mercury composite graphite electrode of an untreated

FIGURE 3-2

Plot of Log Concentration Dissolved Organic Carbon Versus Irradiation Time


3.0
2.0
1.0
0.8
0.6
0.4
0.2
0.1
LOG DISSOLVED ORGANIC CARBON (mg/l)
0
60
120
180
240
300
IRRADIATION TIME (min)

sea water sample. This yields the concentration of free metal. An aliquot is irradiated for a sufficient time to ensure complete degradation of the dissolved organic matter (carbon) and reanalyzed. This gives the total amount of metal present. The total metal minus free metal equals the metal sequestered organically.

3.2 Acidification of Sea Water

3.2.1 Effect of Acidification

When the pH of sea water is lowered by the addition of acid, weakly acidic complexing agents will release sequestered metal ions. Under acid conditions, the ionization of a weakly acidic chelator is repressed, and metal ions must compete with a larger concentration of hydrogen ions for chelating sites. Only a very stable metal-ligand compound can complex a significant amount of metal at, for example, pH 3.

This phenomenon can be illustrated by considering the competition between Cu and H for sites on the aspartic acid molecule. By letting aspartic acid be H_2L and using the equilibrium and concentration data presented in Section 4.2.3.3, the following relationships can be calculated:

$\frac{H_2L}{CuL}$	$\frac{HL}{CuL}$	pH
0.00013	1.3	8
0.0013	13	7
0.013	130	6
0.13	1300	5
1.3	13000	4
13.0	130000	3

In order to complex the same amount of Cu at pH 3 as at pH 8, the aspartic acid concentration would have to be increased by five orders of magnitude. A ligand, however, having the same characteristics as aspartic acid with all equilibria except Cu, where its stability constant is assumed to be $10^{13.6}$ rather than $10^{8.6}$, would still complex some Cu at pH 3. In general, significant sequesteration of trace metals will occur at pH 3 only if the ratio of the association constant for the trace metal - free ligand reaction is at least four orders of magnitude greater than the association constant for the competing hydrogen ion - free ligand reaction (*i.e.*, $K_{CuL}/K_{HL} \geqq 10^4$). This assumes a trace metal concentration in sea water of 10^{-7} M (*e.g.*, Cu, Zn, and Ni) and only considers one to one complexes.

3.2.2 Empirical Demonstration of the Effect of Acidification on a Metallo-organo Complex

Filtered Woods Hole dock water was spiked to contain 4×10^{-8} M Pb. This quantity of Pb was then complexed by additions of disodium ethylenediaminetetra-acetate amounting to 8×10^{-7} M. No Pb peak was visible at a pH of 7.65, when analyzed by anodic stripping voltammetry. The pertinent analytical variables were:

Cell volume	100 ml
Plating potential	-0.80 v *vs.* Ag/AgCl electrode
Plating time	10 minutes
Voltage sensitivity	50 mv/cm
Current sensitivity	2 μ amp/cm
Sweep rate	16.7 mv/sec

The pH of this solution was lowered by microliter additions of 6 N HCl and the stripping response of Pb recorded at selected intervals. The results of this study are depicted in Figure 3-3. The competition from hydrogen ions becomes significant at a pH between 4 and 3, with Pb being released from the Pb-EDTA complex. The Pb continues to increase as the pH decreases. The release was not followed to completion because increased hydrogen evolution begins to distort the Pb peak (see Section 3.2.3).

3.2.3 Limitations of Acidification

There are limitations to analyzing acidified sea water samples using anodic stripping voltammetry with the thin film mercury composite graphite electrode. When the pH is lowered, the potential at which hydrogen generates is raised. At a pH of 3, for example, only Cu and Pb can be determined, and no data for Cd and Zn can be obtained.

Lowering the pH to 2 or 1 would give information on more stable metal complexes. However, this procedure requires the addition of a large amount of acid which increases the danger of contamination. In addition, the ability to determine Pb, and possibly Cu, would be lost due to the presence of larger quantities of reducible hydrogen ion.

3.2.4 Example of Acidification of Sea Water

An unfiltered 50 m sea water sample from the North West Atlantic (31°N, 63°W) was acidified by 20 µl additions of 6 N HCl. The Cu response as a function of pH is illustrated in Figure 3-4. The analytical variables used to monitor Cu by anodic stripping were:

FIGURE 3-3

Effect of Acidification on a Pb-EDTA

Complex in Sea Water

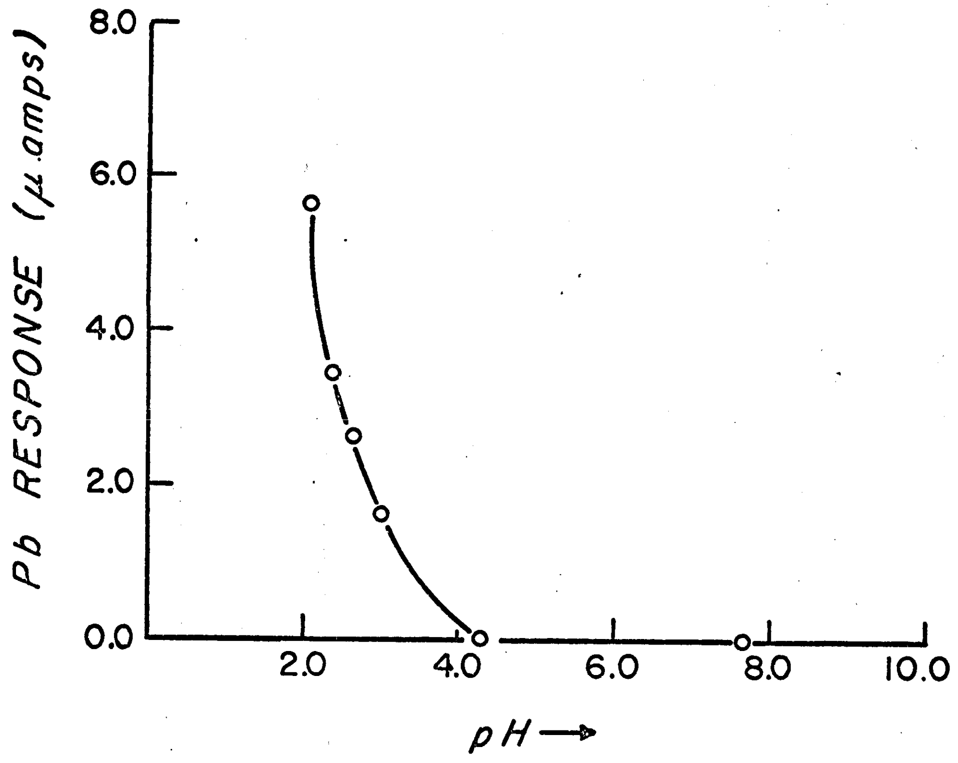
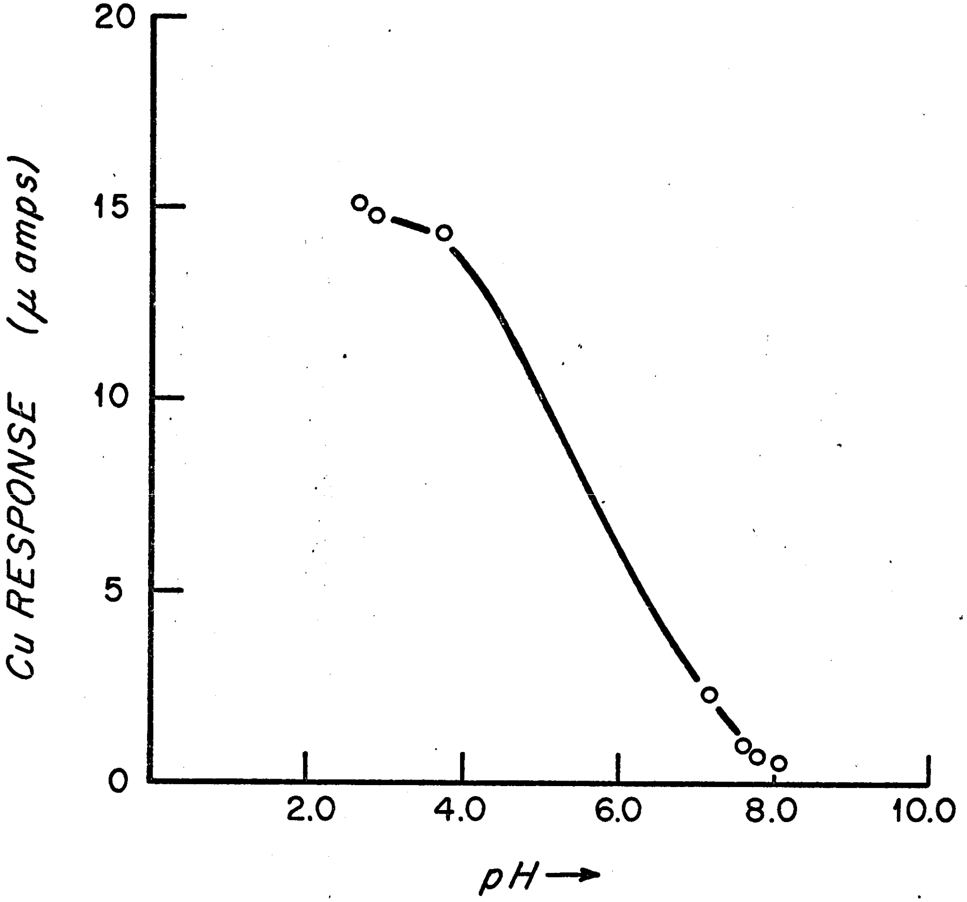

Pb RESPONSE (μ.amps)
8.0
6.0
4.0
2.0
0.0
2.0
4.0
6.0
8.0
10.0
pH →

FIGURE 3-4

The Cu Response as a Function of pH in
a Sea Water Sample from the North West Atlantic


20
15
10
5
0
Cu RESPONSE (μ amps)
2.0
4.0
6.0
8.0
10.0
pH →

Cell volume	100 ml
Plating potential	-0.90 v vs. Ag/AgCl electrode
Plating time	8 minutes
Voltage sensitivity	50 mv/cm
Current sensitivity	4 μ amp/cm
Sweep rate	16.7 mv/sec

An increase in the Cu response begins as soon as the pH is lowered from its initial value of 8.1. There is a marked increase in the amount of Cu released below pH 7.5, which is similar to the behavior observed with Pb-EDTA (3.2.2) below pH 3.5. In this case, however, the Cu response reaches a nearly stable value at a pH of 3.5. Moreover, this is not a typical behavior for Cu, but it has been observed and verified for a number of ocean samples (see Chapter 6). It strongly suggests that a number of ligands of moderate and varying stability (i.e., ≤ Pb-EDTA) with Cu must exist in sea water.

Further evidence linking the increase in metal concentration observed during acidification in sea water with release of metals from an organically sequestered state will be presented in Chapter 5. When organic free sea water (irradiated) is acidified, no observable change in the metal concentration occurs.

In summary, acidification of sea water will provide evidence for the amounts of Cu and Pb sequestered by moderately stable weakly acidic ligands. This will give important information to an area in need of serious study: trace metal speciation.

CHAPTER FOUR

TRACE METAL SPECIATION IN SEA WATER

4.1 Introduction

In Chapter 1, the significance of trace metal speciation in sea water was discussed. The possible role of trace metals, in various chemical forms, in governing productivity in the oceans was stressed. In addition, the geochemical consequences of trace metal speciation in affecting trace metal deposition (*e.g.*, residence time) were emphasized. It was concluded that any attempt to understand the mechanisms controlling the marine distribution of a trace metal will require a quantitative knowledge of the amounts of the various species present, and ultimately, the chemical identification of these forms.

Although, chelation of trace metals is often postulated to explain geochemical and biological phenomena, our present knowledge concerning this problem is extremely meager. In this chapter, an argument for the existence of trace metal organic complexes in sea water will be derived theoretically and demonstrated empirically.

4.2 Theory

4.2.1 Indirect Evidence for Organically Complexed Trace Metal in Sea Water

Precise measurement of a trace metal present at the 10^{-7}-10^{-8} M concentration level in sea water is an extremely exacting task. Only recently have sensitive techniques such as isotope dilution, atomic absorption and neutron activation made reliable analysis at the trace level possible. Therefore, most of the data involving speciation in sea water is relatively new.

Torii and Murata (1966) investigated the distribution of Cu and Zn in the Indian and the Southern Ocean waters. The concentration of these elements was determined spectrophotometrically using sodium diethyldithiocarbamate for Cu and dithizone for Zn. The concentration data for both Zn and Cu were slightly less than the averages for the previous observations in the world oceans (i.e., 3 μg/l Cu, and 10 μg/l Zn, after Goldberg, 1963). They concluded that the possible presence of unextractable forms (i.e., nonreactive) of these metals would result in lower values (see Section 2.2.2.1).

Fonselius and Koroleff (1963) reported the distribution of Cu and Zn in the Ligurian Sea. The amounts of these metals were obtained spectrophotometrically using the dithizone method. In addition to emphasizing how little is known about the chemical forms of trace metals in sea water, he suggested that only the ionic form of these metals would be measurable by extraction of dithizone complexes. This interpretation is not completely correct (see Section 2.2.2.1).

Using an extraction procedure (diethyldithiocarbamate and chloroform), and subsequent analysis by neutron activation, Hood and Slowey (1964) found some fractions of Mn, Cu, Zn to be nondialyzable from sea water taken in the Gulf of Mexico.* Moreover, the amounts extracted by a chelating agent (diethyldithiocarbamate) gave lower values for Cu and Zn in untreated sea water than in sea

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* This confirms an earlier study (Rona et. al., 1962) which indicated that non-dialyzable and non-extractable forms of Mn and Zn may exist in sea water.

water in which the organic matter was destroyed by persulfuric acid digestion. This suggests that organic complexes of Cu and Zn were present. However, only the data for the total metal concentrations were presented in this report.

Slowey, Jeffrey, and Hood (1967) reported the presence in sea water (Gulf of Mexico) of Cu that was extractable with a non-polar solvent (chloroform). The amount of Cu in the chloroform extract was determined by neutron activation. The maximum amount of extractable Cu found was 56% (0. 18 μg/l from 0.32 μg/l); however, a high procedural blank is worrisome. For example, taking a probably optimistic estimate of 10% for the overall precision of the method, the uncertainty in the percentage extracted almost includes zero, i.e., 56 ± 35%. These are not very impressive data for the presence of organically complexed Cu in sea water.

Alexander and Corcoran (1967) determined Cu by spectrophotometry in sea water from the Florida Straits. Neocuproine was used as the colorimetric agent for "ionic" Cu* in untreated sea water and for the total soluble Cu in organic free (perchloric acid oxidized) sea water. They always found the concentration of "ionic" Cu to be below 2 μg/l, while the total Cu varied from (4 to 13 μg/l). The reported precision of analysis for 4 samples of pier sea water indicates that the differences are real and significant. This is rather good evidence for the presence of complexed Cu in sea water.

Williams (1969) reported organically associated Cu between 11 to 26% of the total Cu in sea water at the San Diego Trench (0-500 meters). The Cu was

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* Their use of ionic copper to designate the species readily reactive with neocuproine is incorrect; see Section 2.2.2.1.

determined spectrophotometrically following the carbon tetrachloride extraction of the Cu chelate formed by the addition of sodium diethyldithiocarbamate. The total Cu was obtained by analyzing the sea water samples after the dissolved organic matter had been destroyed through photo-oxidation with ultra-violet radiation.

The reported precision at the 5 μg/l Cu concentration level was ± 0.05 μg/l (one sigma). This quantity is about one order of magnitude greater than the average amount of Cu found in the non-irradiated sea water (ca., 0.6 μg/l). Thus, the data would be more impressive if the precision limits had been reported for the more appropriate lower level. In addition, the incorrect or incomplete interpretation about what is being measured with a chelate-extraction technique continues to be reported in the oceanographic literature. Williams calls the measurable Cu, inorganic, in raw sea water, yet states that the unmeasurable Cu in this water must exist organically associated and have a stability constant greater than Cu-EDTA! It is obvious that the fraction of organically associated Cu is probably higher than reported (see Section 2.2.2.1).

Finally, the organically associated Cu includes both soluble organocopper complexes and the Cu adsorbed or occluded by organic colloids. Unfortunately, it is beyond the scope of this investigation to separate these soluble and insoluble metal species. This distinction will remain semantic. Therefore, all metal, other than the readily reducible species (inorganic and organic) in raw sea water, will be reported as existing complexed by soluble organic chelates. Nevertheless, some fraction of these metals are probably associated with organic molecules that are not in true solution.

4.2.2 Theoretical Postulation of Metal Chelates

The above papers provide the major body of evidence for the existence of naturally occurring metal-chelates in sea water. Although, these data would seem to suggest the presence of organometallo complexes in the oceans, the amounts and significance of these has not been clearly established. Moreover, their existence is not completely accepted. Duursma and Sevenhuysen (1966) state that:

> "It is often assumed in current literature that certain rare-metal ions essential for life in the sea, may be partly bound to organic compounds. These metals are supposed to be linked by a chelate or complex bond to the appropriate organic molecules, so that their concentration in sea water may be higher than would be the case if their occurrence in ionic form only were involved. So far there is no direct proof of this assumption and, to our present knowledge no chelating compounds have as yet been isolated from sea water. Neither does the list of known dissolved organic compounds (Duursma, 1965) give any clear indication that large numbers of chelating organic substances do occur."

In addition, they conducted solubility experiments designed to measure possible organo-trace metal complexing in sea water. The concentration of the following metals, Fe^{3+}, Zn, Ni, Co, and Cu in equilibrium with insoluble phases was determined with and without the presence of natural and synthetic organic material. An increase in the amount of metal in solution in the presence of the organic material would be considered evidence of complexing. They concluded that the occurrence of chelated trace metals in sea water had not been demonstrated by these experiments.

Free amino acids have been isolated from sea water. Siegel and Degens (1966) found an average of 60 µg/l of total free amino acids in Buzzards Bay, Massachusetts.

Amino acids form stable metal chelates (Sillén and Martell, 1964), and therefore, there is evidence for the presence of sequestering agents in sea water. Nevertheless, the question of whether metal-organic complexes can be significant in the oceans must be answered. In this section, a theoretical argument in support of the existence of amino acid-metal compounds will be given.

4.2.2.1 Presence of Free Amino Acids in Sea Water

The specific amino acids found by Siegel and Degens showed some percentage variation from sample to sample. An average based on 8 samples from different locations in Buzzards Bay revealed that the predominant species were glycine (21%), serine (13%), aspartic acid (10%), glutamic acid (10%), and ornithine (8%).

Amino acids, in general, will complex trace metals, but they can also complex Mg ion (Sillén and Martell). Although, Mg-amino acid complexes are of low stability, Mg is present at a relatively high concentration in sea water. The concentration of Mg is 6 x 10^{-2} M, whereas many trace metals are present at the 10^{-7}-10^{-8} M level. Because of this concentration difference between Mg and trace metals, the stability constant of a trace metal chelate must be about 6 orders of magnitude greater than that of the sequestered Mg ion. This fact was illustrated by Johnston (1964).

4.2.2.2 Competition between Cu and Mg for Amino Acids

The following relationship can be set up for 1-1 complexes between Cu^{++} - amino acid and Mg^{++} - amino acid:

$$Mg + L = MgL \qquad (4:1)$$

$$Cu + L = CuL \qquad (4:2)$$

where the charges have been neglected, and L is the concentration of free ionized amino acid. Using concentrations rather than activities,* then

$$\frac{(MgL)}{(Mg)\ (L)} = K_1 \tag{4:3}$$

$$\frac{(CuL)}{(Cu)\ (L)} = K_2 \tag{4:4}$$

and K equals the stability constant.

The ratio of the amount of copper complexed to magnesium complexed is:

$$\frac{(CuL)}{(MgL)} = \frac{(Cu)}{(Mg)} \times \frac{K_2}{K_1} \tag{4:5}$$

By putting in the appropriate concentrations for Mg and Cu ions in sea water, the ratio becomes:

$$\frac{(CuL)}{(MgL)} = (6 \times 10^{-5} - 6 \times 10^{-6}) \frac{K_2}{K_1} \tag{4:6}$$

where (Cu) is 10^{-7} - 10^{-8} M, and (Mg) is 6×10^{-2} M.

Although, no data are available for the stability constants of amino acids and cations in sea water, Sillén and Martell give information for certain amino acids in other electrolyte solutions. Using these data for three of the amino acids found in quantity by Siegel and Degens, the following values are obtained for the above ratio:

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* This is a valid assumption because the stability constants determined in other electrolyte solutions for the metal-aspartic acid complexes are only approximate when used for sea water. If the true thermodynamic stability constants were known in sea water, the ratio (eq. 4:5) would differ by the factor (activity coefficient Cu)/(activity coefficient Mg) which should be close to unity because the ions have about the same ionic size and charge. The ratio of the activity coefficients for the uncharged metal complexes would also be near one.

Amino Acid	$\frac{K_2}{K_1}$	$\frac{(CuL)}{(MgL)}$
Glycine	$10^5 - 10^6$	0.6 - 60
Aspartic Acid	10^6	6 - 60
Glutamic Acid	10^6	6 - 60

The ratio clearly indicates, that in sea water, Cu will successfully compete with Mg for amino acids ligands. Whether the reduction in free Cu would be significant and observable depends on other equilibria.

The competition from other trace metals ions must be considered. The (CuL)/(MgL) ratio was derived assuming that Cu was the only trace metal present. In sea water, the complexing of Cu by, for example, aspartic acid, would be mitigated through equilibria between the amino acid and Mg, Ca, H, and trace metals. The most important of the latter would be Ni and Zn. The ligand has to satisfy all equilibrium requirements.

4.2.2.3 Cu-Aspartic Acid Chelates in Sea Water

An order of magnitude calculation can be made for the amount of Cu-aspartic acid chelate formed in the presence of competing ions. As noted previously for sea water, the major contestants for this amino acid ligand are Mg, Ca, Ni, Zn, and H. Letting H_2L represent aspartic acid, the following equilibria are probable:

$$(H_2L)/(H^+)(HL^-) = K_a \qquad (HL^-)/(H^+)(L^=) = K_a'$$

$$(MgL)/(Mg^{++})(L^=) = K_1 \qquad (CaL)/(Ca^{++})(L^=) = K_2$$

$$(NiL)/(Ni^{++})(L^{=}) = K_3 \qquad (NiL_2^{=})/(NiL)(L^{=}) = K_4$$

$$(ZnL)/(Zn^{++})(L^{=}) = K_5 \qquad (ZnL_2^{=})/(ZnL)(L^{=}) = K_6$$

$$(CuL)/(Cu^{++})(L^{=}) = K_7 \qquad (CuL_2^{=})/(CuL)(L^{=}) = K_8$$

However, for the purposes of this calculation, the complexes represented by K_4, K_6, and K_8 can be neglected since they are second order effects. Therefore,

$$\text{Total ligand} = (L^{=}) + (H_2L) + (HL^{-}) + (MgL) + (CaL) + (NiL) + (ZnL) + (CuL) \qquad (4:7)$$

By using the following data for the various equilibria, equation (4:7) can be rewritten in terms of $(L^{=})$.

Cation	Concentration in Sea Water	Stability Constant#
(H)	10^{-8} M	$K_a = 10^4$; $K_a' = 10^{10}$
(Mg)	6×10^{-2}	$K_1 = 10^{2.4}$
(Ca)	10^{-2}	$K_2 = 10^{1.6}$
(Ni)	10^{-7}*	$K_3 = 10^{7.1}$
(Zn)	10^{-7}*	$K_5 = 10^{5.8}$
(Cu)	10^{-8} to 10^{-7}	$K_7 = 10^{8.6}$

[#] Stability constants for aspartic acid and cations taken from Sillén and Martell.

* Estimated.

After substitution, equation (4:7) is

$$\text{Total ligand} = (L^{=}) + 10^{-2}(L^{=}) + 10^{2}(L^{=}) + 16(L^{=}) + 0.4\,(L^{=}) +$$

$$(L^{=}) + 0.06\,(L^{=}) + (4 \text{ to } 40)\,L^{=} \qquad (4:8)$$

Thus the only cations seriously competing for the aspartic ligand are H, Mg, and Cu. Equation (4:8) can be simplified to read:

$$(L^{=}) = \text{Total ligand}/(122 \text{ to } 158) \qquad (4:9)$$

or $$(L^{=}) = (8 \times 10^{-3}) \text{ to } (6 \times 10^{-3}) \text{ Total ligand} \qquad (4:10)$$

The concentration of aspartic acid in coastal sea water was 4×10^{-8}M (Siegel and Degens). Therefore, to a first approximation, the free ligand would be 2.4×10^{-10}M at 10^{-7}M Cu, and 3.2×10^{-10}M at 10^{-8}M Cu. According to the equilibrium governed by K_7, these free ligand concentrations would yield, respectively, a CuL concentration of 1.0×10^{-8}M and 0.12×10^{-8}M.* Thus, a significant amount of Cu could be complexed.

4.3 Experimental

4.3.1 Experimental Test for Complexing of Cu by Aspartic Acid

In order to test the theoretical prediction of a decrease in the free Cu concentration by the presence of aspartic acid ligand, sea water from Buzzards Bay was photo-oxidized to destroy the dissolved organic matter (see Chapter 3). This procedure sought to prevent the presence of natural chelators from obscuring changes in the Cu concentration due to additions of aspartic acid. Also, the final amount of Cu in this sea water was 1.8×10^{-7}M, which is equal to the original concentration plus the Cu spikes added to establish the initial quantity of Cu present.

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* Since there are several approximations in this calculation, the numbers should not be taken too literally.

Aspartic acid* was added at the 10^{-8} M level to 100 ml of this organic free sea water. The Cu response was monitored in the usual way by anodic stripping. In addition to the cell volume, the pertinent experimental parameters were:

Plating potential	0.90 v *vs*. Ag/AgCl electrode
Plating time	5 minutes
Current sensitivity	1 µamp/cm
Voltage sensitivity	50 mv/cm
Sweep rate	16.7 mv/sec

The results of this experiment are depicted in Figure 4-1. The largest uptake of Cu occurred with the initial addition of aspartic acid. The decrease in the free Cu concentration was less marked with succeeding additions. At an aspartic acid concentration of 4×10^{-7} M, there is a 20% reduction in free Cu. Moreover, for the interpolated aspartic acid concentration of 4×10^{-8} M, there is evidence for the formation of sequestered Cu. This agrees favorably with the theory which predicted uptake of Cu by aspartic acid at this low level.

Adsorption of naturally occurring organic material onto the thin film mercury graphite electrode was found not to be significant during anodic stripping analysis in sea water (see Section 2.3.8.2). However, it was possible to further demonstrate that actual chelation is taking place by conducting another experiment at a lower concentration of Cu (7×10^{-8} M). If adsorption were occurring, the decrease in free Cu will depend only on the amount of aspartic acid; that is, at a known quantity of aspartic acid the percentage change in the Cu response will be independent of

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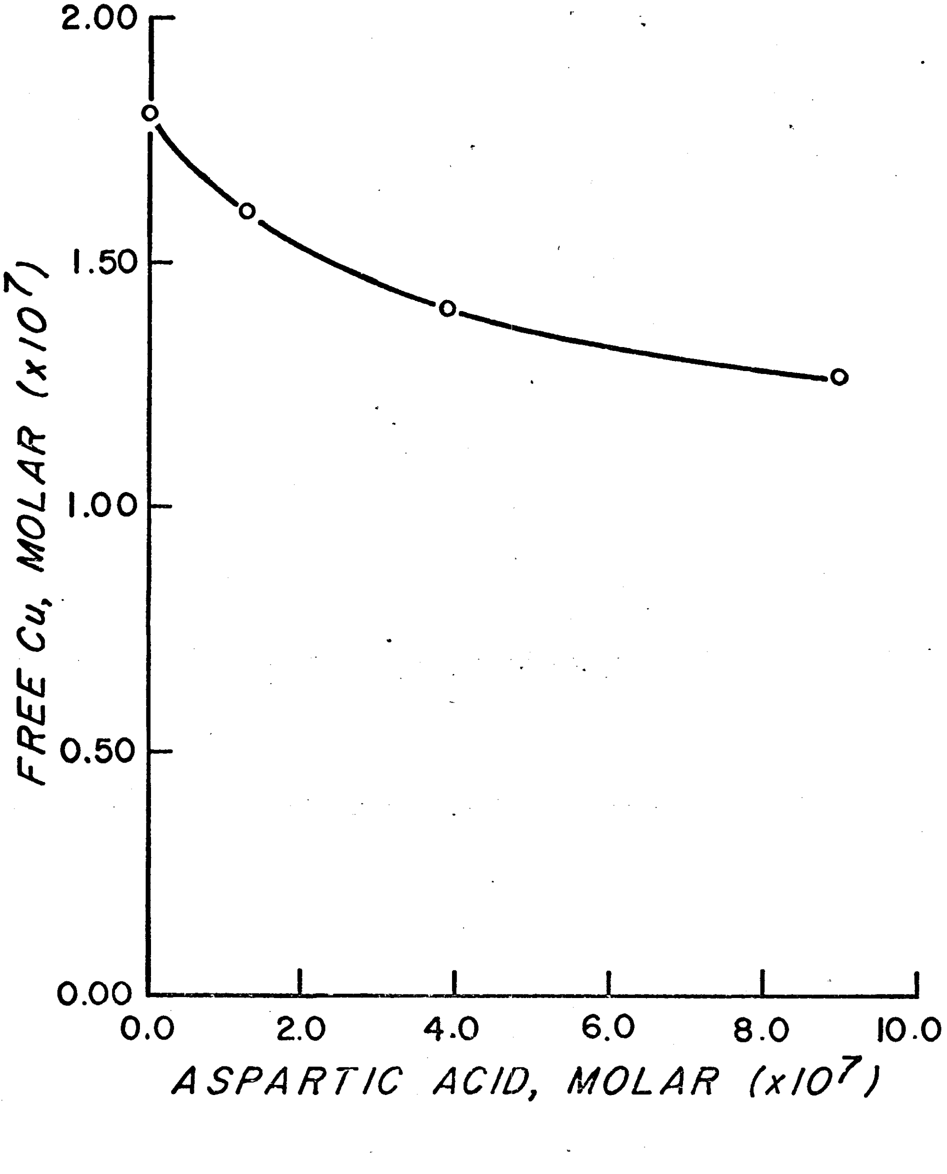
* Aspartic acid added as the acid and the pH of the sea water remained unchanged.

FIGURE 4-1

Cu Response Versus Additions of Aspartic
Acid in Organic Free Sea Water from
Buzzards Bay, Massachusetts


2.00
1.50
1.00
0.50
0.00
0.0
2.0
4.0
6.0
8.0
10.0
FREE Cu, MOLAR (x10^7)
ASPARTIC ACID, MOLAR (x10^7)

Cu concentration. Whereas, genuine complex formation will depend not only on the quantity of amino acid, but also on the amount of free Cu.

At an aspartic acid concentration of 5×10^{-7} M, 4×10^{-8} M of CuL (Figure 4-1) is formed in the solution originally at 1.8×10^{-7} M Cu, while 0.8×10^{-8} M Cu was sequestered in the less concentrated Cu sea water solution (7×10^{-8} M). Thus, the fraction of complexed Cu is greater by a factor of two for the larger concentration of free Cu. This is consistent with theory, and, therefore, actual complexing of Cu by aspartic acid does take place.

4.4 Conclusions

It was shown that an organic ligand known to occur in sea water and at its in situ concentration can and will complex Cu. Moreover, the carbon associated with 4×10^{-8} M aspartic acid amounts to 2 μg/l. Whereas, a reasonable estimate of the dissolved organic carbon in ocean water is 500 μg/l. Therefore, aspartic acid representing only 0.4% of the organic carbon in sea water will complex Cu.

Thus, the indirect evidence for trace metal speciation presented at the beginning of this chapter would seem to be real. In addition, these data suggest that many of the ligands present in sea water are better complexing agents than aspartic acid. Since the competition between metal ions and hydrogen ion becomes less important as the stability constants increase, most of the total ligand will be bound with metal ions rather than unionized. Thus, a significant fraction of Cu and other trace metals may be expected to be organically sequestered in the oceans.

Duursma (1968) recently calculated the amount of trace metal complexing in sea water for a compound that might be structurally related to a humic acid. Using quinoline-2-carboxylic acid at concentrations equivalent to 0.2 mg and 2.0 mg carbon/l, he concluded that chelation of trace metals can be important even though the main fraction of this particular ligand is bound to Ca and Mg. Contrary to an earlier opinion (see Section 4.2.2), he suggests a major effort to understand the problem of chelation of metals in sea water.

CHAPTER FIVE

APPLICATION OF TOTAL ANALYTICAL METHOD (ANODIC STRIPPING-PHOTO-OXIDATION-ACIDIFICATION) IN COASTAL SEA WATER STUDY: DIRECT EVIDENCE FOR TRACE METAL SPECIATION

In the following, the use of anodic stripping voltammetry with the thin film composite graphite electrode, itself, and the combined use with either the photo-oxidation method for dissolved organic carbon or the acidification procedure is demonstrated. Direct evidence is given for the presence, in coastal sea water, of a significant group of organic ligands that complex copper. The presence of sequestered copper is further supported by a butanol extraction of chelated copper from sea water. The presence of copper in the butanol extract was confirmed by atomic absorption analysis.

5.1 Pseudopolarographic Evidence

5.1.1 Polarography

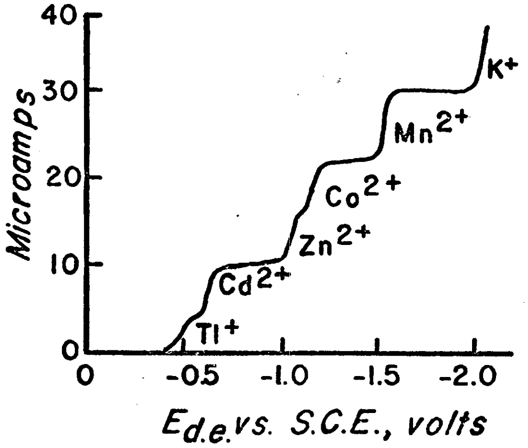
In normal polarography, the potential at the dropping mercury electrode is varied slowly and linearly in the cathodic direction. The current is monitored during this voltage sweep (polarogram). When the decomposition potential (voltage where the ion is reduced at the mercury drop) for a particular metal is reached, a marked increase in current is observed. The magnitude of this diffusion current is proportional to the concentration of the metal in solution. A polarogram (Kolthoff and Lingane, 1941) for a number of metals at 0.001 M in 0.1 N KCl is reproduced in Figure 5-1.

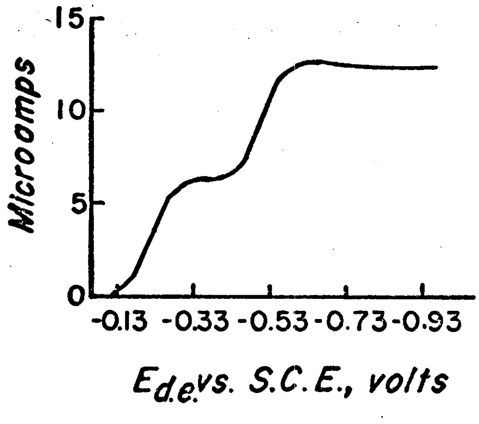
FIGURE 5-1

Polarogram of a Solution Containing Several Metal Ions Each at a Concentration of Approximately 0.001 M in 0.1 N KCl Containing 0.01% Gelatin, after Kolthoff and Lingane, 1941

FIGURE 5-2

Polarogram of a Solution Consisting of 0.002 M Cu $(NH_3)_4^{++}$, 0.2 N Ammonium Perchlorate, and 1 N Ammonia, with 0.01% Gelatin as a Maximum Suppressor, after Kolthoff and Lingane, 1941


40
30
20
10
0
Microamps
0
-0.5
-1.0
-1.5
-2.0
$E_{d.e.}$ vs. S.C.E., volts
Tl+
Cd2+
Zn2+
Co2+
Mn2+
K+


15
10
5
0
Microamps
-0.13
-0.33
-0.53
-0.73
-0.93
$E_{d.e.}$ vs. S.C.E., volts

The resulting waves on the current vs. voltage scan represent reduction steps. Each reducible species has a characteristic wave, which is indicative not only of the species but also of the medium. If there is more than one oxidation state possible for the species being reduced, and if the free energies of the respective oxidation states are sufficiently different, there may be more than one wave. For example, a hydrated species such as Cr^{+++} can display stepwise reduction. Another example of stepwise reduction appears in Figure 5-2. This was also taken from Kolthoff and Lingane who state:

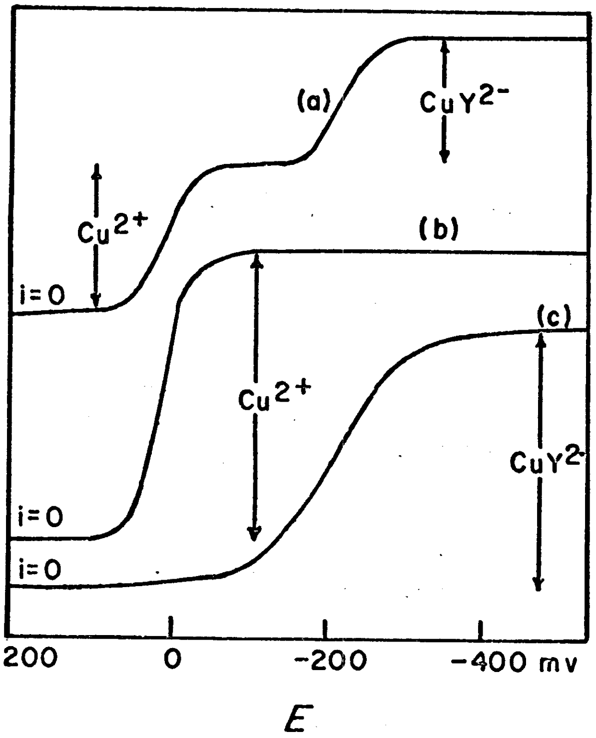
> "The first wave corresponds to $Cu(NH_3)_4^{++} + e^- = Cu(NH_3)_2^+ + 2\ NH_3$ and the second to $Cu(NH_3)_2^+ + e^- = Cu(Hg) + 2\ NH_3$."

In rare cases separate waves may be observed for two forms of the same metal. This can occur when there is slow equilibration between "free" and complexed ions, where both are present in the same solution. These complexes may be inorganic or organic, and the wave of the complex is displaced (usually negatively) from that of the simple ion. An example of this phenomenon is shown in Figure 5-3 (after Schwarzenbach and Sandera, 1953).

Polarography does not possess sufficient sensitivity for direct analysis in sea water. Even by assuming a lower detection limit, a clear indication of stepwise reduction would be doubtful. Many trace metal complexes, both inorganic (i.e., Cl^- and OH^-) and organic (see Chapter 4) probably exist in sea water. Therefore, a number of overlapping waves of many different species would be superimposed and the current-voltage curves difficult to interpret. The resulting hypothetical polarogram would indicate whether complexing of trace metals was significant in

FIGURE 5-3

Polarograms of (a) Mixture of 0.5 m M in Cu^{++} and 0.5 m M in $CuY^{=}$ (Y = ethylenediamine tetra-acetate), (b) 1 m M in Cu^{++} and (c) 1 m M in $CuY^{=}$. The background electrolyte is 0.1 M KNO_3, after Schwarzenbach and Sandera, 1953


(a)
CuY^{2-}
Cu^{2+}
i=0
(b)
Cu^{2+}
i=0
(c)
CuY^{2-}
i=0
200
0
-200
-400 mv
E

sea water. It is doubtful that more quantitative information could be resolved.

5.1.2 Pseudopolarography

Pseudopolarography is an interesting variation on normal anodic stripping voltammetric technique. A pseudopolarogram is a record of the stripping current produced by the readily reactive species of a particular metal versus the potential at which the plating was carried out. It is obtained by initially plating, for a fixed time, at a potential slightly above the decomposition voltage for a particular metal. With the plating time held constant, the potential is lowered in successive increments (100 mv) and the stripping response (oxidation current) recorded at each stage. A current-voltage curve similar to a polarogram is obtained.

A distinct wave will be observed for the hydrated metal ion. However, stepwise reduction, even in a well defined system (*e.g.*, known inorganic or organic complex species) would be difficult to resolve because the voltage increment employed can include several oxidation states. The resolving power could be extended by using smaller voltage intervals, but the analysis time is greatly increased. Moreover, subtle changes in the stripping peak potential, indicative of different decomposition voltages, are obscured by the general predominance of the hydrated species. Therefore, stepwise reduction is difficult to observe.

Direct pseudopolarographic analysis of sea water is possible, but it shares in the same criticism voiced toward normal polarography (hypothetical case). Pseudopolarography is valuable, because this technique can directly indicate whether complexing of trace metals is significant in sea water.

5.1.3 Woods Hole Dock Water: Pseudopolarographic Study

The Cu present in filtered Woods Hole dock water was analyzed by pseudopolarography. The stripping response was recorded at 100 mv steps from -0.3 to -1.10 v *vs.* the Ag/AgCl electrode using a 10 minute plating period. The results are presented in Figure 5-4.

It is immediately evident that a distinct wave for Cu is observed, but it is not a normal steeply rising one. Rather, the Cu response is a drawn-out function of electrodeposition potential. There are three possible explanations for this behavior:

1) Sorption of Organics

Absorption or adsorption of organic molecules on the electrode surface. Desorption of these organics, as the potential of the mercury electrode is lowered, would increase the electrode area, and therefore, the efficiency of the cell. The Cu response would, therefore, increase as the plating potential decreased.

2) Inorganic Complexes

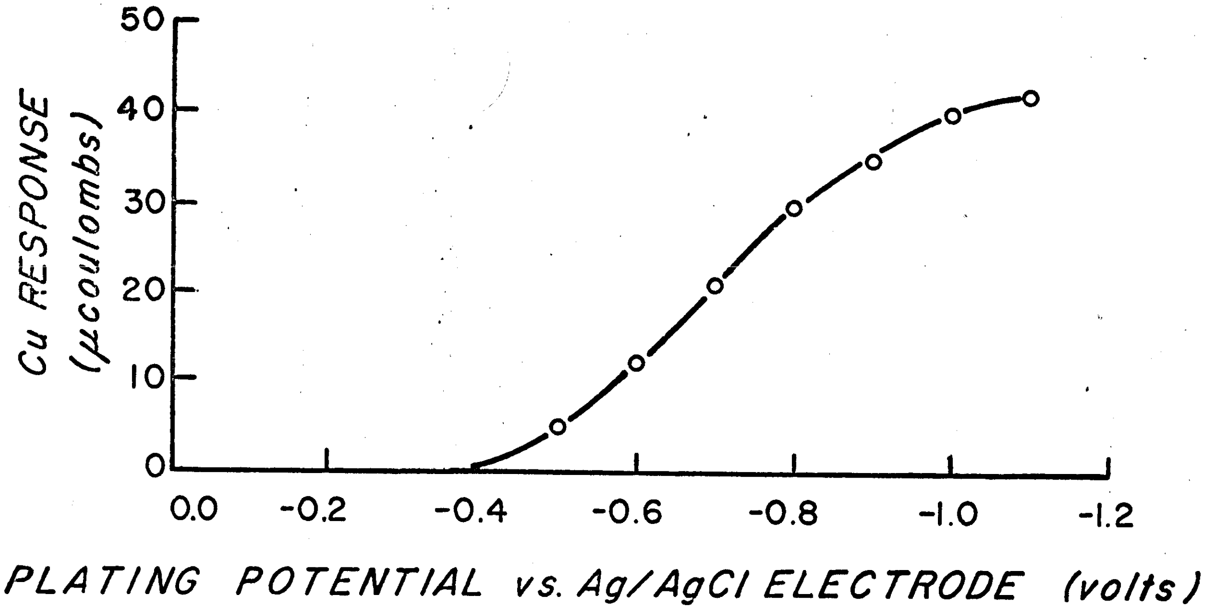
It has been mentioned that stepwise reduction of complexes would not be observed. Therefore, the presence of an irreversibly-reduced inorganic complex of copper or of a mixture of inorganic complexes with overlapping waves could also produce a pseudopolarograph of this shape.

3) Organic Complexes

Organically complexed copper could also produce this type of behavior. Because of the high dissolved organic carbon (*ca.* 2.0 mg/l) in Woods Hole dock water, and the wide variety of organic compounds present, it is

FIGURE 5-4

Pseudopolarogram of Raw Filtered Woods Hole Dock Sea Water


Cu RESPONSE (μcoulombs)
0
10
20
30
40
50
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
PLATING POTENTIAL vs. Ag/AgCl ELECTRODE (volts)

therefore likely, that a number of reducible species are involved.

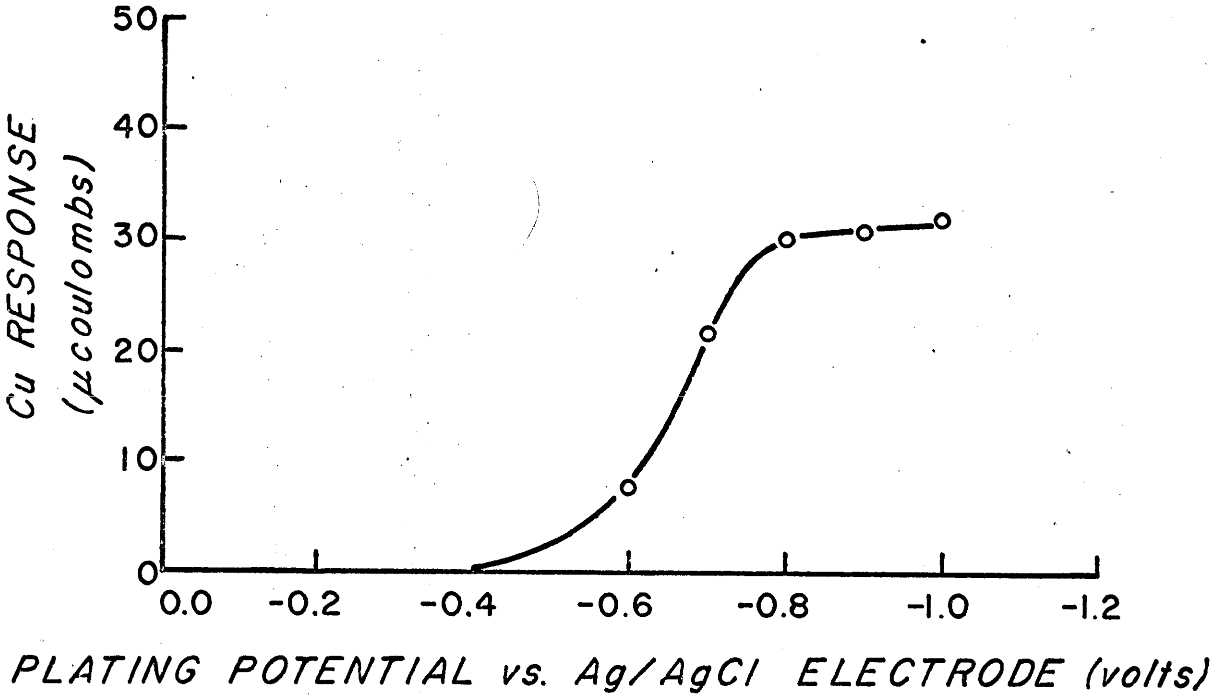
A pseudopolarogram of irradiated filtered Woods Hole dock water (Figure 5-5) ruled out inorganic copper complexes. There was a marked difference in the copper behavior as a function of plating potential when the dissolved organic matter was destroyed. The pseudopolarogram assumed a normal shape, and below -0.80 v, copper was no longer affected by lowering the electrodeposition voltage. This type of pseudopolarographic behavior (normal) for copper is also observed in 0.7 N NaCl solution prepared with water (organic free) previously distilled from a potassium permanganate solution.

Even with the high organic background present in Woods Hole dock sea water, absorption and/or adsorption of organic molecules on the electrode surface was found not to be serious. The cell constant, based on additions of known amounts of copper standard to the sea water followed by immediate plating and stripping cycles, was the same within 3% when the plating was done at -0.80 v and at -1.00 v. The observed copper response of the raw water, however, increased by 34% when the plating was changed from -0.80 v to -1.00 v. If this difference were due to inhibition of mass transfer or electron transfer at the electrode surface because of adsorbed organic material, the cell constant would have changed correspondingly. It was therefore concluded, that the effects observed must be the result of complexation of copper by organic ligands present in sea water.

The apparent concentration of free Cu was determined at -0.80 v and -1.00 v. At -0.80 v, 1.6 μg/l Cu was present, whereas 2.1 μg/l Cu was indicated at -1.00 v.

FIGURE 5-5

Pseudopolarogram of Irradiated Filtered Woods Hole Sea Water


Cu RESPONSE
(μcoulombs)
50
40
30
20
10
0
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
PLATING POTENTIAL vs. Ag/AgCl ELECTRODE (volts)

Thus, there is a significant amount of organically complexed Cu reduced between -0.80 v and -1.00 v.

In summary, the pseudopolarographic character of Cu reflects the presence of reducible Cu sequestered by organic ligands. The increase in the stripping peak between -0.80 v and -1.00 v is directly proportional to the amount of reducible copper and not to desorption of organic molecules from the mercury surface. This is direct evidence for the presence of organically complexed trace metal in sea water.

5.2 Quantitative Analysis of the Organically Complexed Copper Present in Coastal Waters

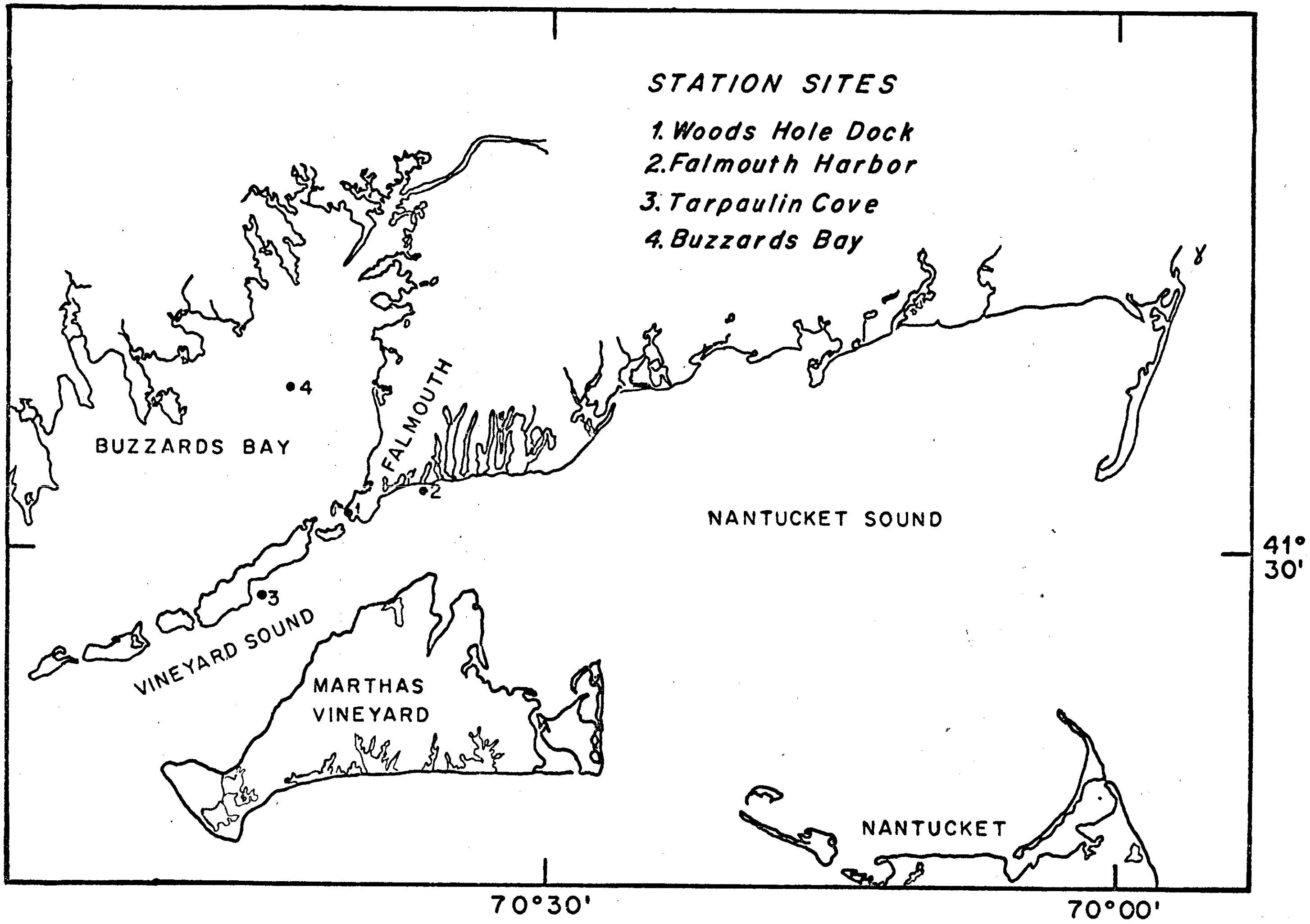
A study was initiated to establish the amounts of various Cu species in surface waters near Falmouth, Massachusetts. The concentration of free Cu present in raw filtered sea water, in acidified filtered sea water, and in irradiated sea water (organic free) was determined by anodic stripping voltammetry with the thin film mercury composite graphite electrode. This analysis yields, respectively, the amount of Cu in the free state at the in situ pH of sea water; the amount of Cu released by weakly acidic ligands when the pH of the sea water is adjusted to approximately 3; and the amount of Cu associated with all organic ligands.

5.2.1 Station Sites

Surface sea water was collected with a glass sampler from the R.V. ASTERIAS on June 13, 1969. The station locations are shown in Figure 5-6. These sites were chosen in an attempt to obtain sea water from differing water masses.

FIGURE 5-6

Station Sites for Coastal Sea Water Study


STATION SITES
1. Woods Hole Dock
2. Falmouth Harbor
3. Tarpaulin Cove
4. Buzzards Bay
4
BUZZARDS BAY
FALMOUTH
2
NANTUCKET SOUND
41° 30'
3
VINEYARD SOUND
MARTHAS VINEYARD
NANTUCKET
70°30'
70°00'

5.2.1.1 Tarpaulin Cove

This sample was taken when the incoming tide had reached peak velocity. Therefore, it should be indicative of waters on the continental shelf. Trace metal speciation would probably be different than the inshore water, which is closer to terrestrial inputs of organics and trace metals.

5.2.1.2 Buzzards Bay

Buzzards Bay does not flush very efficiently. The water has a significant residence time, and may reflect the effects of aging. It would be interesting if the trace metal species were also distinctive.

5.2.1.3 Falmouth Harbor and Woods Hole Dock

These samples are gratuitously classified as sea water, since they are more a reflection of Falmouth, Massachusetts, than ocean water. In addition to normal inputs, aeolian and runoff, a significant amount of pollutants can be expected. These waters contaminated by powerboat exhausts, automobile exhausts, plumbing wastes, etc., should reflect this dubious distinction in terms of trace metal species.

5.2.2 Sample Treatment

With the exception of the Woods Hole dock water, these samples (10 1) were filtered with a pressure filtration unit (Spencer, personal communication) through combusted glass fiber filters. The Woods Hole dock sea water (4 1) was filtered under suction, with a 0.45μ membrane filter (Millipore HA). The filtered samples were stored undisturbed in 10 1 high density, linear polyethylene jerry cans until analyzed. The analysis was completed eleven days after collection.

5.2.3 Sample Analysis

5.2.3.1 Filtered Sea Water

Aliquots of raw filtered sea water were analyzed in separate cells, by anodic stripping voltammetry with the thin film mercury composite graphite electrode. The pertinent analytical parameters were as follows:

Sample volume	120 - 130 ml
Plating potential	-0.90 v *vs.* Ag/AgCl electrode
Plating time	10 - 40 min
Voltage sensitivity	50 mv/cm
Current sensitivity	1 μ amp/cm
Sweep rate	16.7 mv/cm

5.2.3.2 Acidified Sea Water

Duplicate samples were acidified by the addition of 70 μl of 6 N HCl. The pH of the solution was determined after analysis. This treatment yields a pH of approximately 3. With the exception of a current sensitivity of 2 μ amp/cm and a plating time of 7-16 minutes, the analytical variables were exactly the same as the raw filtered sea water.

5.2.3.3 Irradiated Sea Water

The samples were irradiated for a period of 20 - 24 hours in the apparatus previously described (Sections 3.1.3 and 3.1.4). Duplicates were run on Falmouth Harbor sea water. The cell volumes were between 60 - 65 ml and the other parameters identical to the acidified sea water analysis.

5.2.4 Results

5.2.4.1 Precision of Analysis

The data for this analysis of organically complexed copper in coastal waters are presented in Table 5-1. The precision obtained for duplicates was better than 5% with the exception of Tarpaulin Cove where the acidified aliquots gave a 13% variation. A 3% deviation was observed when the entire irradiation and analysis were replicated with Falmouth Harbor water. Therefore, the Cu variations are real and significant.

5.2.4.2 Copper Speciation

In Table 5-1, the total copper is the amount present in the irradiated (organic free) sea water. The free Cu represents the concentration found in the raw filtered sample. Therefore, the total complexed Cu is the difference between these two values.

The weakly complexed Cu is defined as the amount released by low stability ligands when the pH of the sea water was adjusted to about 3. The strongly complexed copper is the metal not observable by acidification, but released when all the organic matter was destroyed. Therefore, the strongly complexed Cu equals the total metal minus the amount present in the acidified sample (free plus weakly complexed).

Except for the Woods Hole dock sea water, acid (6 N HCl) was added to the organic free sample after the total concentration of Cu was determined. The concentration of Cu was redetermined in the acidified organic free sea water.

Table 5-1

COPPER SPECIATION IN COASTAL WATERS

Location	Total Cu	Free Cu	Total Complexed Cu	Weakly Complexed Cu	Strongly Complexed Cu
Woods Hole Dock	4.4 μ g/l	1.6	2.8	1.5 (2.6)*	1.3
Falmouth Harbor	4.0 (4.0)#	1.3	2.7	1.7 (3.0)	1.0
Buzzards Bay	4.5 (4.5)	2.2	2.3	1.6 (2.9)	0.7
Tarpaulin Cove	2.3 (2.3)	0.7	1.6	1.6 (2.9)	---

After the destruction of organic complexes and the addition of acid.

* pH of sea water sample.

As anticipated there was no observable difference between the value for the latter, and the concentration of copper in the organic free sea water. This procedure serves as an internal check on the completeness of the ultra-violet oxidation and the purity of the acid reagent.

It is evident that the major fraction of the dissolved Cu exists in an organically combined form. In addition, most of these chelating agents are weakly acidic ligands of low stability. An average for these stations reveals that 63% of the total Cu in coastal surface water is organically sequestered. This figure compares quite favorably with data obtained by other investigators. For example, Alexander and Corcoran (1967) reported that Cu exists primarily as a soluble complex in the Straits of Florida. An average of the surface water for eight of their stations indicates that 80% of the total Cu to be complexed (see Section 4.2.1). Williams (1969) found 25% of the total Cu associated with organic material in the surface water at the San Diego Trench. This percentage is probably low (see Section 4.2.1).

Thus, the purpose of this study has been satisfied. Direct quantitative evidence has been presented which documents the existence of organically complexed copper in sea water. However, some of the by-products are of equal interest and demand comment.

5.2.5 Discussion: The Existence of Very Stable Metal-Chelates

The waters subject to gross pollution (Woods Hole dock and Falmouth Harbor) contain a significant amount of organic ligands that do not release Cu at pH 3.

This group contains an average of 28% of the total Cu. In Buzzards Bay, the fraction is 15%. At Tarpaulin Cove, 13% could exist by considering the analytical error limits.

These complexing agents may be characteristic of near shore pollution. However, they may also be associated with normal runoff and will be present in relatively unpolluted coastal regions. Moreover, they could be manufactured <u>in situ</u> by plants or perhaps animals and released as excretory products. Although, this investigation cannot resolve which of these input sources is most responsible, the results suggest that many of these metallo-organo complexes must be rapidly salted out or degraded. If this phenomenon were not occurring, the Buzzards Bay and Tarpaulin Cove waters would show a larger fraction.

These ligands are probably weakly acidic but form relatively stable complexes with Cu. A much larger concentration of hydrogen ions is needed to compete satisfactorily with the Cu ions for chelating sites. Their stability constant with Cu must approach a value close to or greater than a Pb - ethylenediamine tetra-acetate (EDTA) complex. In sea water, the latter did not release a significant amount of Pb until the hydrogen ion concentration was greater than 10^{-3}M (Figure 3-3). The association constant for the Pb-EDTA molecule is 10^{18} in 0.1 N KCl (Sillén and Martell, 1964).

Thus, a very stable group of Cu chelates exists near shore, and their concentration decreases seaward. There is also a corresponding decrease in total dissolved Cu. If salting out of these Cu containing molecules is a significant mechanism, swift deposition of a large amount of the entering Cu occurs near shore. The latter statement is speculative and not completely supported by the data. However, this phenomenon is geochemical interest and warrants further investigation.

5.2.6 Discussion: The Existence of Low Stability Metal-Chelates

When these samples were acidified to about pH 3, an average of 1.6 μ g/l Cu was freed. The amount of Cu released represented 34% (Woods Hole Dock), 42% (Falmouth Harbor), 36% (Buzzards Bay) and 70% (Tarpaulin Cove) of the total Cu present at these respective locations. Thus, the highest fraction of weakly complexed Cu was at Tarpaulin Cove where the sea water was most indicative of the open ocean (continental shelf). Moreover, the amount of Cu free (0.7 μ g/l) and the total Cu (2.3 μ g/l) present are much lower than the other stations.

Therefore, the sea water associated with the incoming tide contains relatively low amounts of total Cu, of which, the major fraction is weakly chelated. These properties may allow the offshore waters to be readily distinguished from the inshore water. In the latter, both the free and the total Cu concentrations are higher, but the percentage of weakly complexed Cu is lower.

Spencer and Brewer (1969) observed the same variation for total Cu in the Gulf of Maine. The Cu was analyzed by atomic absorption spectrometry, after the methyl isobutyl ketone extraction of an added sequestering agent (ammonium pyrollidine dithiocarbamate) to acidified sea water (pH 2.5). Surface samples taken during September, 1966 had a mean total Cu concentration of 4.0 μ g/kg inshore (<30 miles from coast) and 2.3 μ g/kg offshore (>30 miles from coast).

These values compare extremely well with the amounts of total Cu observed "inshore and offshore" by this present investigation.

5.2.7 Discussion: Ligand Excess

In this study, the total complexing fraction (low and high stability chelates) was not a function of the total Cu present. An average of 63 ± 6% was observed for the copper complexed, whereas the total Cu gave a mean variation of 3.8 ± 1.0 μ g/l. These data indicated, that at least to a concentration of 4.5 μ g/l Cu (Buzzards Bay), the amount of complexing was not limited by ligands. In addition, this evidence suggests that an excess of ligands to trace metals is probable in sea water because of the rather high dissolved organic background.

5.3 Independent Confirmation for the Presence of Chelated Cu in Coastal Waters

5.3.1 Introduction

In Falmouth Harbor surface water, a considerable quantity of Cu (2.7 μ g/l) was complexed by organic molecules. Therefore, this sample was selected in an attempt to extract some of these chelated species into an organic solvent. The evidence for the presence of weakly acidic chelating groups suggested that many of these ligands would be polar. Hence, butanol was employed because of its polar character and slight solubility in water.

5.3.2 Butanol Extraction

A 150 ml sample from Falmouth Harbor was extracted with 50 ml of butanol.

The concentration of Cu remaining in the extracted sea water and in a butanol saturated blank (also Falmouth Harbor water) was determined by anodic stripping. These samples were acidified prior to analysis, but the experimental variables were the same as those used for raw filtered sea water (5.2.3.1).

5.3.2.1 Extractable Copper

The results from the extraction experiment were as follows:

Sample	Volume	pH	Cu Present
Blank	130 ml	3.1	2.9 μ g/l
Extracted Falmouth Harbor Water	127	3.4	1.9

This analysis revealed that the Cu concentration in acidified Falmouth Harbor surface water was reduced by 1.0 μ g/l through extraction. This amount corresponds to 0.15 μ g of Cu in the 50 ml of butanol. Even if the free copper (1.3 μ g/l) present in Falmouth Harbor water had the same solubility in butanol as in sea water, only 0.05 μ g could be removed. Therefore, a significant amount of organically complexed Cu can be extracted with butanol.

5.3.2.2 Atomic Absorption Analysis of the Butanol Extract

The presence of Cu in the butanol extract was confirmed by atomic absorption analysis. Fifty milliliters of the butanol was evaporated to dryness and the residue taken up in 5 ml of redistilled water. The analysis by anodic stripping indicated that 0.15 μ g Cu or 30 ppb should be present in the aqueous solution. The Cu found by atomic absorption was 44 ppb.

The agreement between the two analyses was extremely encouraging. Moreover, the Cu found by atomic absorption should be higher. The anodic stripping determination gave data only for the extraction of ligands that release metal on acidification. Some of the very stable complexes are also extracted, and according to atomic absorption analysis, the Cu they contain amounts to 14 ppb. This value corresponds to 0.5μ g/l in the original sea water. The Falmouth Harbor water contained 1.0μ g/l Cu in very stable chelated species.

5.3.2.3 Conclusions

The combined analyses indicated that 37% (1μ g/l from 2.7μ g/l) of the Cu in weak chelates, and 50% (0.5μ g/l from 1μ g/l) of the strongly sequestered Cu were extracted from Falmouth Harbor surface water. However, the unknown solubility of free Cu in butanol exaggerates the amount of weak complexes extracted. In addition, any difference in precision between anodic stripping and atomic absorption analysis is inherent in the value for the extraction of very stable complexes. Therefore, rather than the absolute numbers, the confirming evidence that organically complexed Cu exists in sea water was the most significant result of the extraction experiment.

Nevertheless, it was reassuring to find such good agreement between two independent analytical techniques. The existence of trace metal organic complexes in coastal sea water has been established beyond a reasonable doubt. Moreover, the total method (anodic stripping - photo-oxidation - acidification) used to provide quantitative information about trace metal speciation has been completely supported and justified. This convincing testimony should provide an additional stimulant toward the isolation and identification of extractable organic species.

CHAPTER SIX

SHIPBOARD TRACE METAL ANALYSIS IN OPEN OCEAN WATERS USING THIN FILM ANODIC STRIPPING VOLTAMMETRY

6.1 Introduction

Samples were collected during Cruise 85 of the R.V. CHAIN in the oceanic region near latitude 30°N. This was of particular interest because this so-called "thermal-front" zone apparently acts as an oceanic barrier or boundary for the distribution of certain mesopelagic fish (Backus et. al., 1969).

Thermal fronts are characterized by rapid changes in surface water temperature over distances of 10 km or less (i.e., 1°C/10 km; Voorhis and Hersey, 1964). They are major oceanic features that can extend for hundreds of miles in an east-west direction (Katz, 1969; Voorhis, 1969). The front is limited to about the upper hundred meters, but its influence is apparent further down the water column. For example, Katz found a small disturbance in the density surface (σ_t) at the bottom of the thermocline, 1250 meters below a surface region containing a frontal zone.

Voorhis and Hersey feel that these fronts have a significant role in the determination of the surface circulation and temperature of the Sargasso Sea. Backus et. al. have suggested that the fronts are the best evidence for the existence of the so-called "Atlantic subtropical convergence." According to Katz, the available data on thermal fronts (or the fronts as presently understood) can be explained as resulting from the confluence of surface water due to the net Ekman transport arising from the distribution of the northeast trades and the prevailing

Westerlies. However, only limited data are available from the few studies (e.g., Voorhis and Hersey, 1964; Katz, 1969; Voorhis, 1969) that have attempted to investigate and understand the mechanisms governing the dynamics of these frontal phenomena.

The biological significance of these frontal regions is also reflected in primary production variations in a meridional direction. In the longtitude of Bermuda, Ryther and Menzel (1960) found an average production for five stations north of 30°N (i.e., to 35°N) of about 0.7 g $C/m^2/day$. However, a five station average south of 30°N (i.e., to 25°N) indicated a production of only 0.1 g $C/m^2/day$. In addition, this alteration in productivity near 30°N coincided with a marked change in the temperature of the mixed layer. This could be interpreted as a thermal frontal system reflecting a transition from northern to southern conditions in the Sargasso Sea.

This cruise offered an excellent opportunity to study the distribution of trace metals in a significant ocean area. The thermal fronts would be extensively mapped through the salinity and temperature characteristics, and the trace metal sampling stations chosen to allow measurements on either side of these apparent convergences. It was of interest to observe how the trace metal species might reflect the presence of thermal fronts, and/or the possible variations in the biological realm.

6.2 Hydrography

In the week prior to CHAIN 85, an airborne infrarometer survey (Naval Hydrographic Office) of the area south of Bermuda between 62°W and 72°W indicated only weak temperature discontinuities. According to Katz* (personal communication), two lines of discontinuities (barely 1°C) could be traced from 62°W to their apparent convergence at 67°30'W. On this basis, the meridian of 67°30'W was selected as the transit for studies during this multi-discipline thermal-front cruise.

A record of the surface temperature (at 5 meters) which is also characteristic of the temperature of the mixed layer appears in Figure 6-1. The depth of this layer and the temperature structure of the subsurface layers are depicted in Figure 6-2. The apparent frontal steps (Figure 6-1) are enumerated and their reproducible nature (over time) is also shown. On the basis of the hydrographic data (particularly σ_t, Figure 6-1), however, only the group of thermal discontinuities, labeled C, at about 26°N can be considered as a frontal band. The σ_t variation at B is best described as "an anomaly of warm saline surface water possibly without zonal extent as suggested by its being unrecorded by widely spaced tracks of the areal survey" (Katz, personal communication). A is not significant.

6.3 Station Sites

Using the information from the hydrographic survey, stations were selected that allowed the waters north and south of the frontal zone C to be sampled. The station sites appear in Figure 6-3, with the frontal region indicated by wavy lines. Station 858 was at the southern edge (25°17'N, 67°37.5'W) and various depths to ca., 3000 meters were sampled. The upper 1000 meters at the northern edge

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* The hydrographic data and the preliminary interpretation of these results, have been provided by Dr. Eli J. Katz.

FIGURE 6-1

Temperature, Salinity, and Density (σ_T) of the Surface
Mixed Layer in the SW Sargasso Sea

At the top is the temperature as a function of latitude during the north-south transit; below it is the return. Data was recorded along the meridian 67°30'W ± 10'. The sensor was hull-mounted five meters below the surface. The stages of the step-like increase in temperature are labeled A, B and C_1 - C_3. The two lower plots of salinity and density are from eighteen hydrostations made during the return transit, after Katz (personal communication).

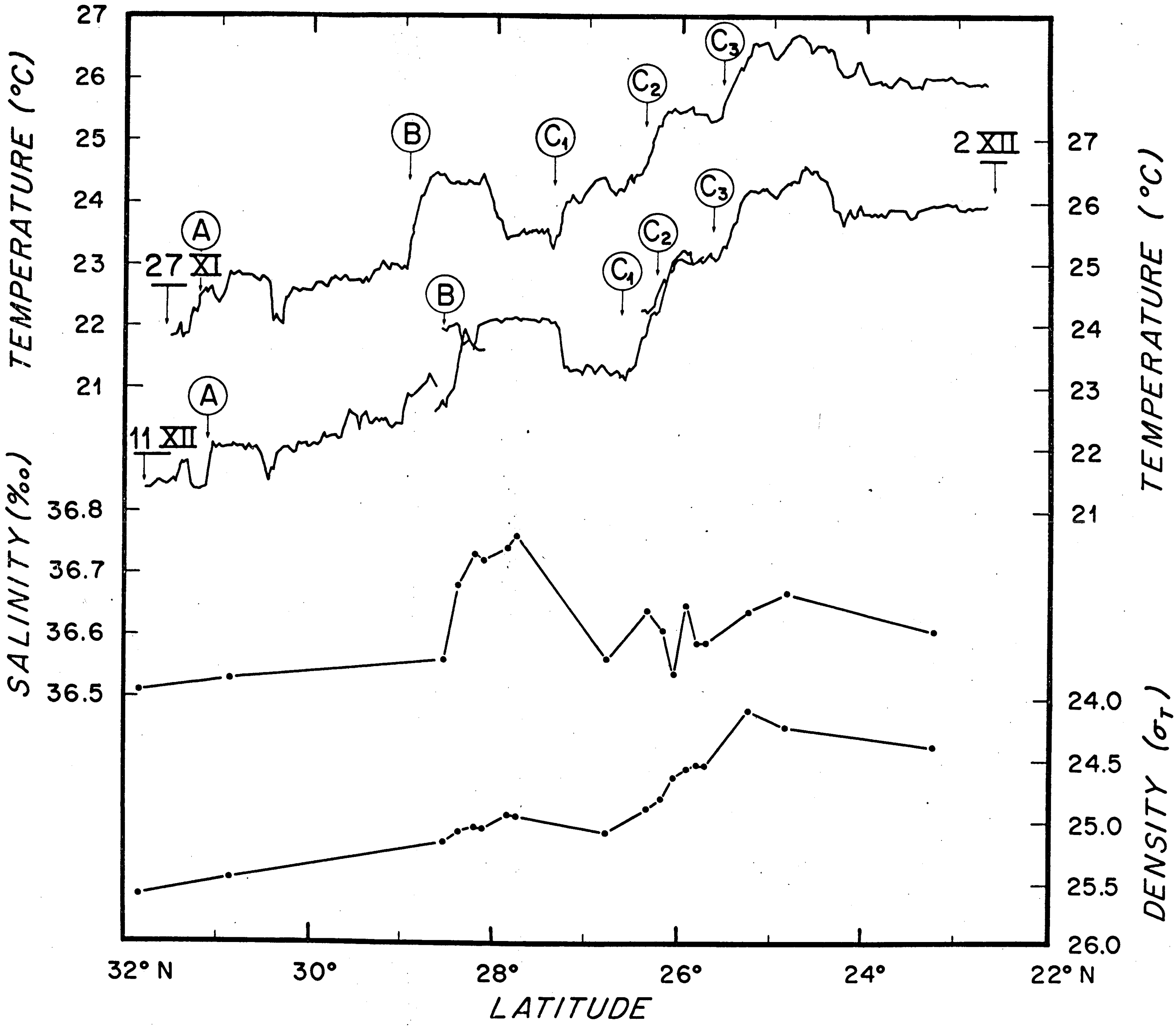
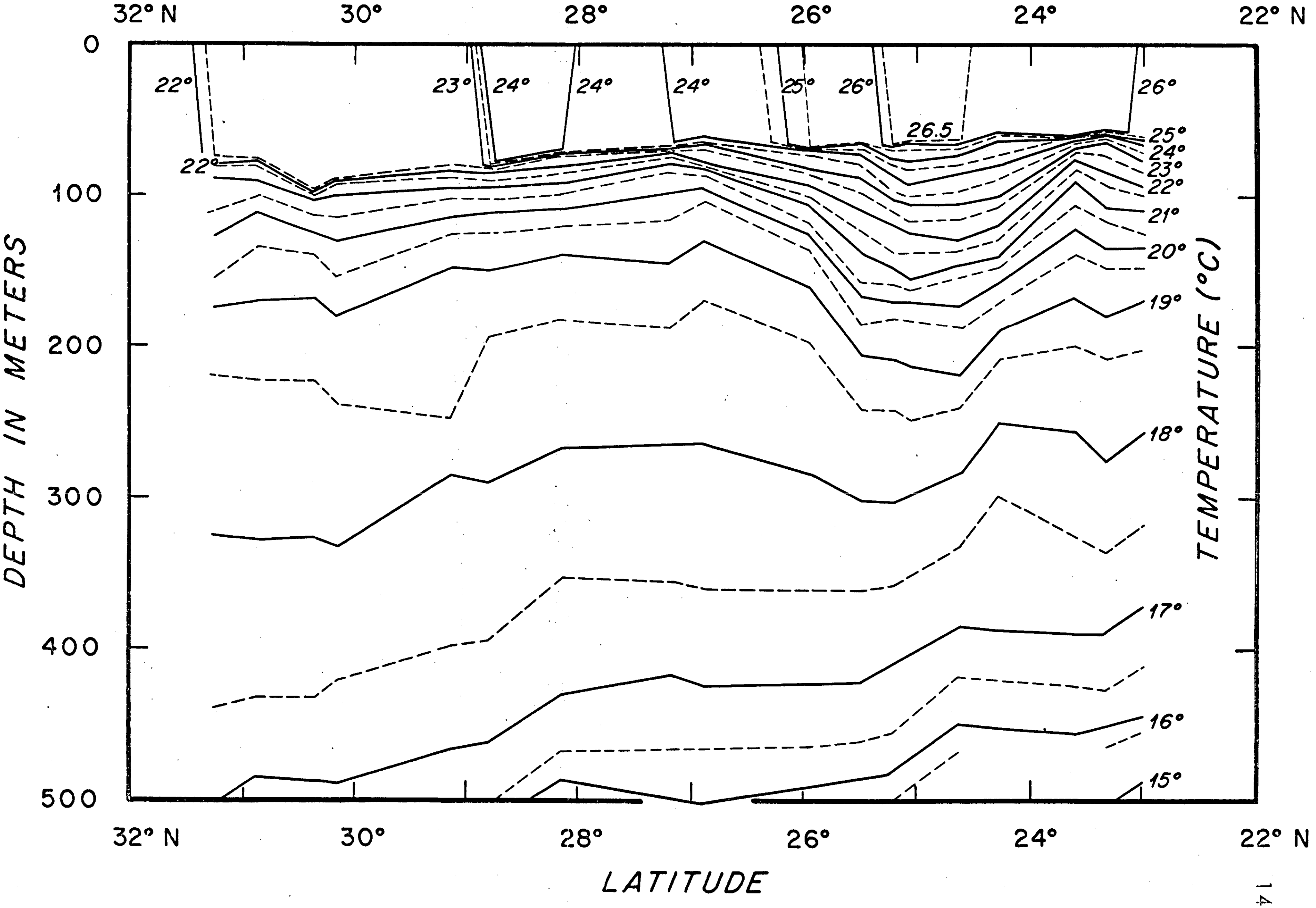

TEMPERATURE (°C)
27
26
25
24
23
22
21
27 XI
11 XII
2 XII
A
B
C1
C2
C3
TEMPERATURE (°C)
27
26
25
24
23
22
21
SALINITY (‰)
36.8
36.7
36.6
36.5
DENSITY (σT)
24.0
24.5
25.0
25.5
26.0
32° N
30°
28°
26°
24°
22° N
LATITUDE

FIGURE 6-2

Temperature Section

The section is based on expendable bathythermographs launched during the north-south transit. Intersections of the isotherms with the surface are derived from the hull temperature record. The slope of these isotherms through the mixed layer is schematic. All the large scale structures were reproduced on the return section, after Katz (personal communication).

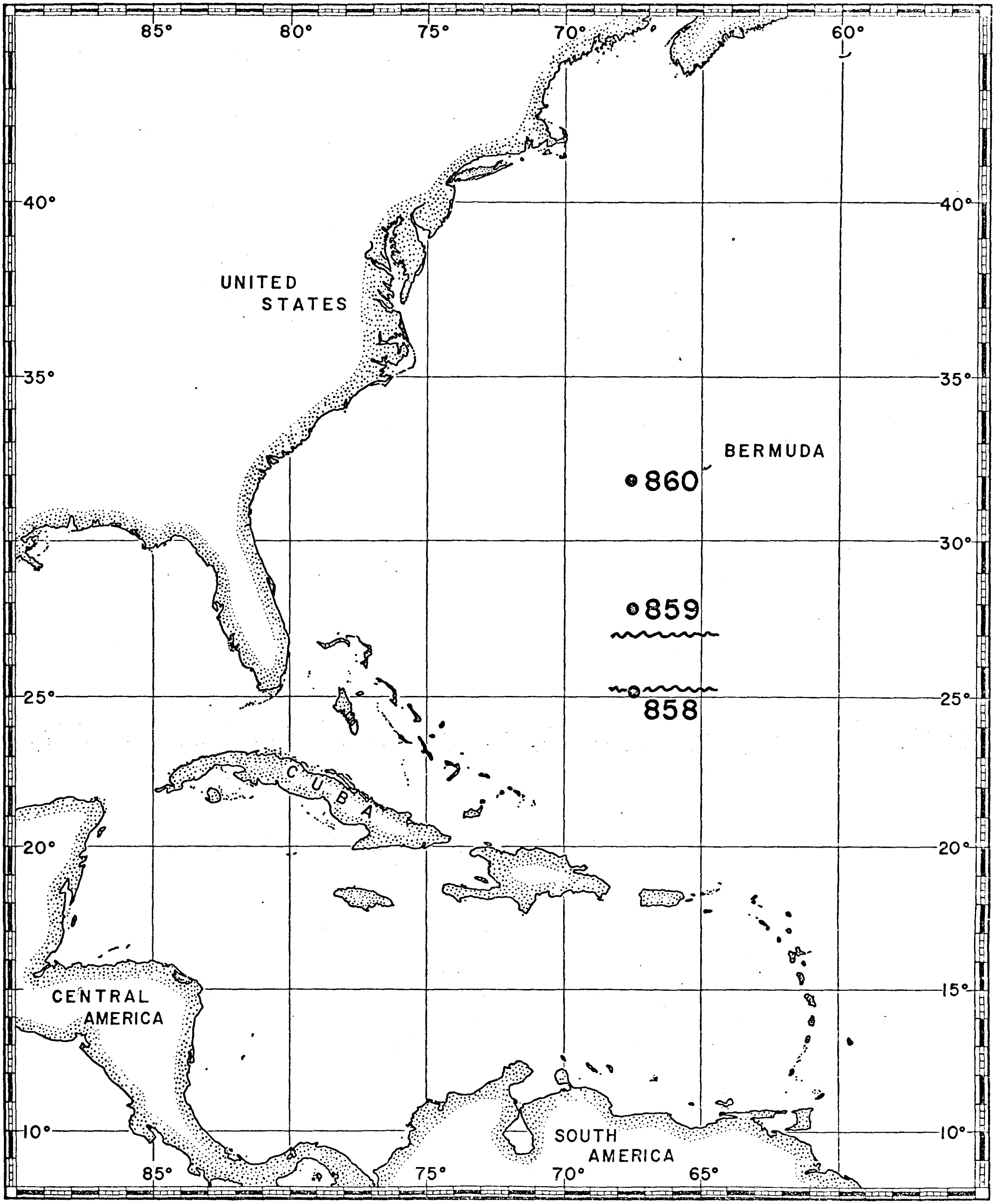


32° N
30°
28°
26°
24°
22° N
0
100
200
300
400
500
DEPTH IN METERS
LATITUDE
TEMPERATURE (°C)
22°
23°
24°
24°
24°
25°
26°
26°
26.5
22°
25°
24°
23°
22°
21°
20°
19°
18°
17°
16°
15°

FIGURE 6-3

Large Volume Sampling Station Sites.

Thermal front region indicated by wavy lines.


85°
80°
75°
70°
65°
60°
40°
35°
30°
25°
20°
15°
10°
UNITED STATES
BERMUDA
860
859
858
CUBA
CENTRAL AMERICA
SOUTH AMERICA

was sampled at Station 859 (27°49'N, 67°35'W). Station 860 (31°49'N, 67°33.5'W) provided an additional look at the water north (about 200 miles) of the frontal zone. This station would serve as a possible control, and would also provide several additional samples from depths below 1000 meters.

6.4 Sampling Technique

The sea water samples were obtained with a large volume (140 liter) sampler (Bodman *et. al.*, 1961). This sampler was designed for multipurpose use and has been employed extensively for radioisotope studies in the oceans (*e.g.*, Bowen and Sugihara, 1965). It has also seen service in a study of the vertical distribution of Pb in sea water near Bermuda (Chow and Patterson, 1966).

The actual depths sampled were determined in the standard manner from the temperatures of the protected and unprotected reversing thermometers on a Nansen bottle placed 5 meters above the sampler. Any sampler malfunction (*e.g.*, "pretripping") will be evident from a comparison of the salinity of the sea water in the Nansen bottle with that in the large volume sampler. The sampling depths were also confirmed from the salinity and temperature data available from the regular hydrographic station.

6.4.1 Sample Handling

The sea water samples for anodic stripping analysis were obtained immediately after the sampler was secured on the ship. They were taken directly from the Polyethylene spigot, which had been flushed for several minutes. Stoppered 500 ml sea water seasoned Pyrex bottles were used to transport the samples from the deck into the main laboratory. The samples were then transferred to the doubly-distilled water washed quartz cells and sealed with a cover of Parafilm "M" to await analysis.* In a few cases the samples remained, undisturbed, in the Pyrex bottle for a few hours before transfer to the quartz cells.

6.5 Experimental Procedure

Four sea water samples were plated simultaneously and individually analyzed through use of the multiplating manifold (Section 2.3.2.2). Duplicates were usually run on raw sea water and on the acidified samples (70 µl 6N HCl added to give ca., pH 3). Aliquots (60-70 ml) were placed in the u.v.-irradiation apparatus (Figure 3-1) and photo-oxidized for a period of four hours. These were analyzed singly.

The metal concentrations were determined by the method of standard additions (Section 2.3.5.1). Combined spikes of: Cu and Zn (10^{-9} moles), and Pb and Cd (10^{-10} moles) were added separately as their chlorides. Two spike additions were normally made since no appreciable increase in precision was observed with three or four spikes. An attempt was made to double the response with each spike addition.

In most analyses, a five minute plating step and scan was initially run. This procedure is sufficient to give the proper base line necessary for the correct peak height interpretation. It also allows the optimum plating time to be estimated.

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* It was observed that significant and unpredictable trace metal contamination was introduced by filtering relatively small volumes ($<$1000 ml), under suction, in a Pyrex glass filtering apparatus using 0.45 µ (47 mm diameter) filters (Millipore HA or Ag (Flotronics)).

The experimental parameters employed for the various samples are tabulated in Table 6-1.

6.6 Open Ocean Station Data

The concentrations of trace metal (Zn, Cu, Pb, and Cd) observed in raw, acidified (ca., pH 3), and irradiated sea water by anodic stripping analysis using the thin film graphite electrode are tabulated in Tables 6-2 to 6-4 for Stations 858* to 860, respectively. The concentration profiles from raw sea water analyses at the three stations appear in Figure 6-4, and the quantities of Cu and Pb measured in acidified samples at Stations 859 and 860 are illustrated in Figure 6-5.

6.7 Possible Sources of Error

Filtering small volumes of sea water (<1 liter) introduced trace metal contamination into the open ocean samples (see Section 6.4.1). Therefore, only unfiltered samples were analyzed. Thus, the possible contribution of trace metals incorporated in particulate matter must be considered for the acidified sea water analyses, where the hydrogen ions can compete with these metals for binding sites.

According to Jacobs and Ewing (1969), the range of particulate matter in the North Atlantic is 0.5 - 250 μg/l with a mean (88 determinations) of 50 μg/l. The largest concentration of this insoluble material generally occurs in the surface layer. Spencer and Sachs (1969) found with the exception of Al and Fe, very

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* Only raw sea water measurements at Station 858.

TABLE 6-1

ANALYTICAL PARAMETERS EMPLOYED FOR SHIPBOARD ANALYSIS OF OPEN OCEAN SEA WATER USING ANODIC STRIPPING VOLTAMMETRY WITH A THIN FILM MERCURY COMPOSITE GRAPHITE ELECTRODE.[#]

	Raw Sea Water	Acidified Sea Water*	Irradiated Sea Water ǂ
Cell Volume	100-130	100-130	60-70
Plating Potential (v)ϕ	-1.35	-0.90	-1.35
Plating Time (min)	30-60	10-30	10-30
Scan Rate (mv/sec)	16.7	16.7	16.7
Current Sensitivity (μamp/cm)	2	2	2
Voltage Sensitivity (mv/cm)	50	50	50

[#] Metal concentrations determined by method of standard additions.

* pH adjusted to ca., 3 by addition of 70 μl 6N HCl.

ǂ Irradiation period of ca., 4 hours.

ϕ Versus the Ag/AgCl electrode in sea water.

TABLE 6-2

TRACE METAL CONCENTRATION IN SEA WATER OF THE NORTHWEST ATLANTIC OCEAN

at 25° 19'N, 67°37.5'W (Station 858).

			Trace Metal Concentration (μg/l)							
			Raw Sea Water				Acidified Sea Water		Irradiated Sea Water	
Depth (meters)	Salinity (‰)	Temperature (°C)	Zn	Cu	Pb	Cd	Cu	Pb	Pb	Cd
0	36.693	26.59	1.3	0.9	0.4	0.04				
60	36.780	26.41	0.8	0.5	1.1	0.06				
265	36.538	18.20	4.2	2.3	0.81	0.066				
408	36.152	17.20	0.5	0.7	0.56	0.041				
675	35.652	12.00	2.3	0.8	0.6	0.03				
1000	35.068	6.20	4.5	1.1	0.5	0.04				
1592	35.008	4.22	2.9	1.0	0.50	0.03				
3000	34.963	2.76	2.4	1.1	0.4	0.05				

TABLE 6-3

TRACE METAL CONCENTRATIONS IN SEA WATER OF THE NORTHWEST ATLANTIC OCEAN at 27°47'N, 67°35'W (Station 859).

Depth (meters)	Salinity (‰)	Temperature (°C)	Trace Metal Concentration (µg/l) Raw Sea Water				Acidified Sea Water		Irradiated Sea Water	
			Zn	Cu	Pb	Cd	Cu	Pb	Pb	Cd
0	36.793	24.19	0.7	0.3	0.37	0.017	0.9	1.0	1.6	0.02
48	36.751	24.02	1.9	0.5	0.5	0.04	0.46	0.47	0.9	0.04
94	36.688	21.19	2.3	0.2	0.18	0.023	3.1	1.0	0.8	0.04
288	36.493	17.75	0.2	0.4	0.45	0.025	1.62	0.6		
479	36.374	16.20	0.7	0.2	0.4	0.02	1.94	0.73	0.5	0.02
663	35.576	12.19	1.6	0.4	0.42	0.061	0.93	0.42		
935	35.086	7.10	3.0	0.7	0.47	0.062	1.8	0.72	0.8	0.08

TABLE 6-4

TRACE METAL CONCENTRATIONS IN SEA WATER OF THE NORTHWEST ATLANTIC OCEAN

at 31°49'N, 67°33.5'W (Station 860).

			Trace Metal Concentration (μg/l)							
			Raw Sea Water				Acidified Sea Water		Irradiated Sea Water	
Depth (meters)	Salinity (‰)	Temperature (°C)	Zn	Cu	Pb	Cd	Cu	Pb	Pb	Cd
0	36.495	21.20	0.3	0.1	0.29	0.026	0.4	0.35	0.2	0.05
50	36.496	21.26					0.46	0.31	0.2	0.06
104	36.617	21.18	0.9	0.1	0.045	0.02	0.9	0.9	0.7	0.03
300	36.542	18.24	2.5	0.5	0.4	0.03	1.7	1.2		
454	36.396	17.19	0.7	0.2	0.2	0.02	1.7	0.8		
700	35.840	14.11	0.6	0.2	0.2	0.04	0.8		0.7	0.1
969	35.057	6.80	0.1	0.1	0.059	0.034	0.87	0.34		
1483	35.010	4.23	1.4	0.4	0.47	0.040	0.5	0.5		0.05
1948	35.007	3.74	0.3	0.4	0.12	0.042	1.03	0.28		
4113	34.915	2.32	0.4	0.1	0.050	0.038	0.32	0.23	0.4	0.05

FIGURE 6-4

CONCENTRATION OF Zn, Cu, Pb, AND Cd

IN RAW SEA WATER VERSUS DEPTH

AT STATIONS 858, 859 AND 860

STATION 858 = -.-.-

STATION 859 = -+-+-

STATION 860 = -o-o-

FIGURE 6-5

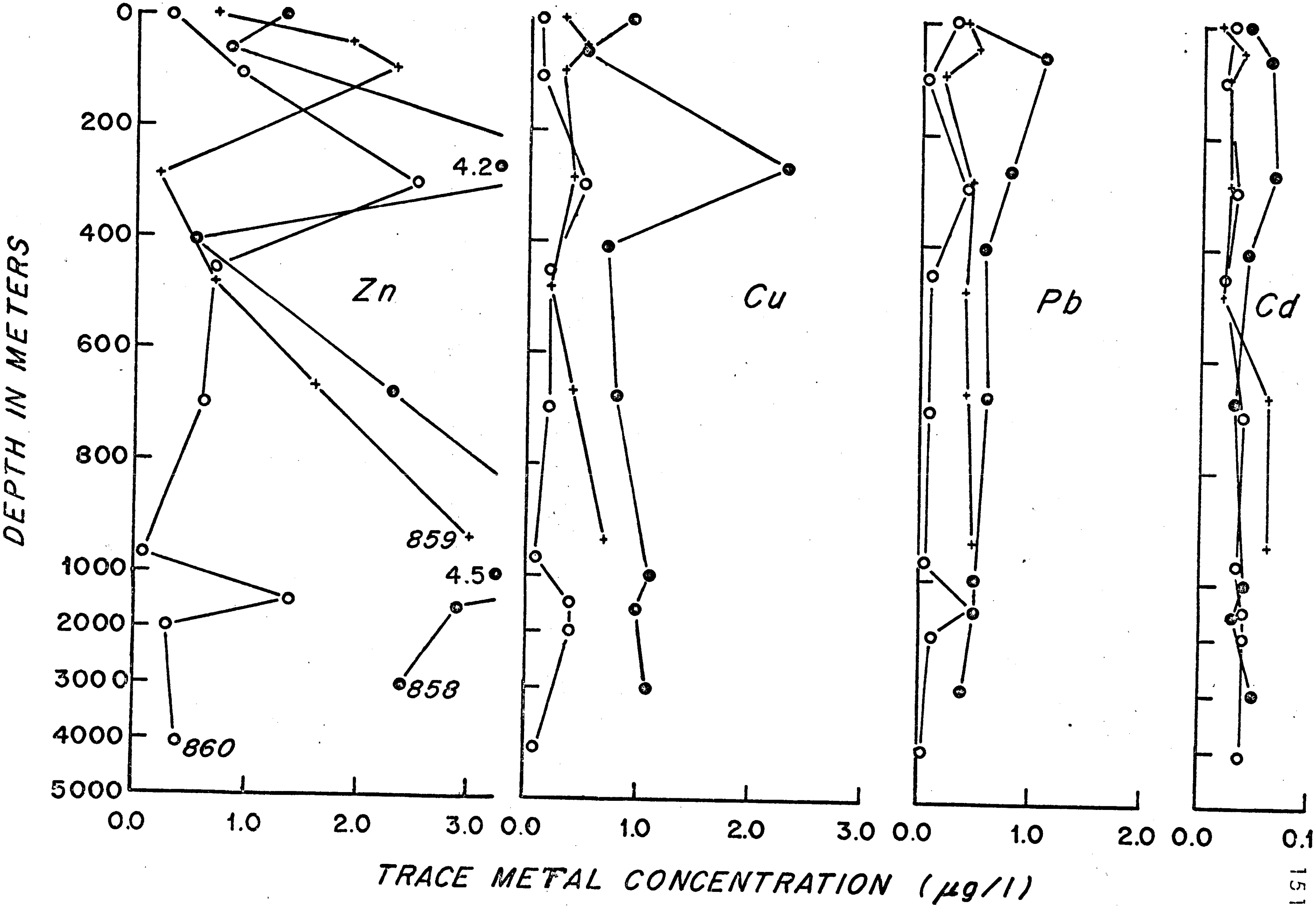
CONCENTRATION OF Cu AND Pb IN ACIDIFIED

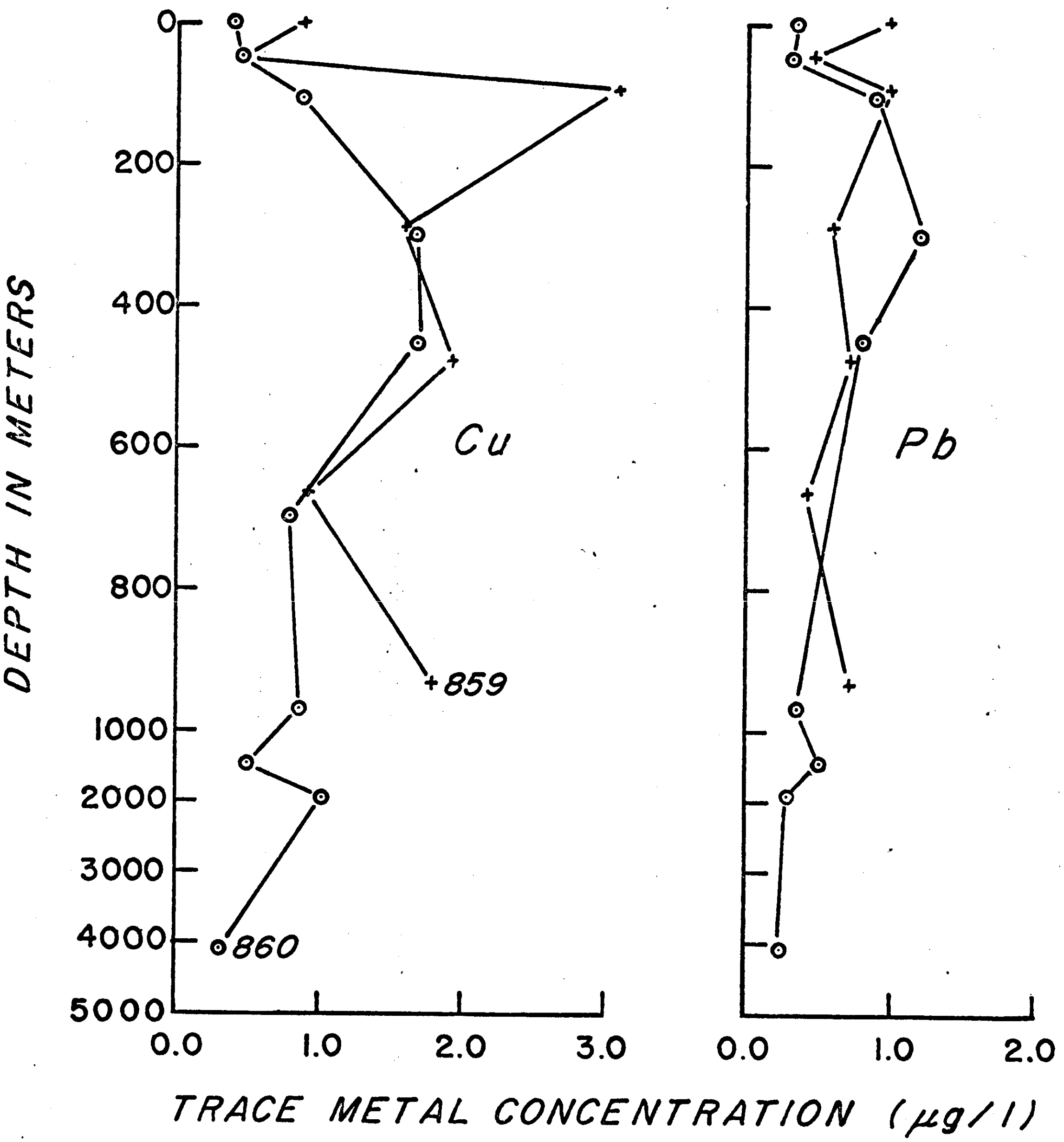
SEA WATER VERSUS DEPTH AT STATIONS

859 AND 860

STATION 859 = -+-+-

STATION 860 = -o-o-


DEPTH IN METERS
0
200
400
600
800
1000
2000
3000
4000
5000
Zn
4.2
4.5
859
858
860
Cu
Pb
Cd
0.0
1.0
2.0
3.0
0.0
1.0
2.0
3.0
0.0
1.0
2.0
0.0
0.1
TRACE METAL CONCENTRATION (μg/l)


DEPTH IN METERS
0
200
400
600
800
1000
2000
3000
4000
5000
0.0
1.0
2.0
3.0
0.0
1.0
2.0
Cu
Pb
859
860
TRACE METAL CONCENTRATION (µg/l)

small quantities of trace metals to be incorporated in particulate matter from the Gulf of Maine. The following average percentages were calculated from their data: Fe (4%), Al (6%), Cu (0.02%), Zn (0.024%), and Ni (0.04%). Thus, in open ocean water, the contribution of trace metals other than Al and Fe from particulate matter can be considered negligible. For example, only about 0.05 µg/l total Cu could be released in the sea water sample reported by Jacobs and Ewing to contain the largest quantity of particulate matter (250 µg/l) in the northwest Atlantic Ocean. Thus, no serious errors are introduced by the practice of not filtering.

6.7.1 Nickel-Zinc Interference

The possibility of a systematic error resulting from intermetallic complex formation between Ni and Zn has been discussed in Chapter 2. This interference can be introduced when analyses are conducted at plating potentials > -1.15 v *vs.* the Ag/AgCl electrode in sea water. Therefore, anomalies may be present in the analyses of raw sea water and in the irradiated samples, both of which were examined using a plating potential of -1.35 v. Although, it was impossible to reanalyze the samples, it was possible to evaluate the data and estimate where the contribution from possible intermetallic complex formation between Ni and Zn was significant.

At Stations 859 and 860 (Tables 6-3 and 6-4), the amounts of free Cu found in raw sea water are relatively low. The average for seventeen depths at these stations is 0.25 µg/l Cu. It is doubtful that this small amount of Cu could be seriously overestimated. Therefore, the Ni interference is apparently not significant at these stations. All measurements of Cu, Zn, Pb, and Cd can be considered valid.

Larger concentrations of free Cu were observed for the depths sampled at Station 858 (Table 6-2). The average amount of Cu was 0.97 μg/l, and this is much greater than the mean (0.25 μg/l) noted for the other stations. The Pb data also displays the same variability. That is, the average free Pb found at this location is 0.7 μg/l, whereas the average amount at Stations 859 and 860 is 0.3 μg/l. Indeed, there is a parallel trend for both Cu and Pb -- the highest free concentrations for these metals are at Station 858 and the lowest at 860. This suggests that the higher free Cu values at this station are real. Therefore, the Cu and Zn data will be considered reliable, and the contribution from Ni-Zn anomalies only minor.

These statements are supported by the probabilities associated with a null hypothesis based on the <u>Student's t Test</u> for the mean values of Zn, Cu, and Pb (raw sea water) in the upper 1000 meters at the three stations. The means are listed in Table 6-5 and the probabilities in Table 6-6.

Although the probability data will not support a difference for the average concentrations of Zn at the three stations, they do indicate that the mean values of Cu and Pb are probably different between Station 858 and 859 (or 860). Therefore, the argument for minimal Ni interference based on the low concentration of Cu at Stations 859 and 860 would suggest only a minor contribution from Ni at Station 858.

TABLE 6-5

AVERAGE FREE METAL CONCENTRATION IN RAW SEA WATER OF THE UPPER 1000 METERS AT THREE SITES ALONG A MERIDIAN (67°30'W) IN THE WESTERN SARGASSO SEA

Station Number	Location	Average Free Metal Concentration (μg/l)			
		Zn	Cu	Pb	Cd
858	25°19'N, 67°37.5'W	2.2	1.1	0.7	0.04
859	27°47'N, 67°35'W	1.5	0.4	0.4	0.04
860	31°49'N, 67°33.5'W	0.9	0.2	0.2	0.03

TABLE 6-6

PROBABILITIES OF NULL HYPOTHESES AMONG THE SAMPLING STATIONS FOR THE RAW SEA WATER MEAN VALUES OF Zn, Cu, AND Pb IN THE UPPER 1000 METERS

Null Hypothesis No difference between	Probability* Zn	 Cu	 Pb
Station 858/859	> 0.10	< 0.05	< 0.01
Station 858/860	> 0.10	< 0.02	< 0.001
Station 859/860	> 0.10	> 0.10	> 0.10

* Derived using Student's _t_ Test.

The irradiated sample data are considerably more difficult to assess. The quantities of free Cu, Zn, and possibly Ni vary when the organic matter is destroyed and, therefore, the degree of Zn-Ni interference can be more severe as a result of these speciation changes. It was not possible to evaluate this error. Thus, the Cu and Zn concentrations in the photo-oxidized samples have not been reported. Further studies in these ocean areas may allow these results to be reinterpreted.

6.7.2 Precision

Over the whole range of trace metal concentrations in this study, the mean average error observed for analyses of duplicates (measured in separate cells) of raw and acidified sea water were:

	Mean Average Error	Range	Number of Duplicates
Zn	7%	0.1 - 4.5 μg/l	14
Cu	6	0.1 - 3.1	25
Pb	7	0.045 - 1.2	22
Cd	8	0.017 - 0.066	12

The average error is independent of concentration because the plating time and sensitivity are adjusted such that the stripping response (peak height or peak area) is about the same in every analyses.

In Tables 6-2 to 6-4, the Zn and Cu data for raw sea water have been rounded off to the nearest 0.1 μg/l because of possible Ni interference. In addition, only one significant figure to the right of the decimal is reported when the measurement of metal concentration is based on a single determination (e.g., irradiated sea water analyses).

6.8 Trace Metal Data: Comparison with Other Relevant Studies

6.8.1 Copper and Zinc

Recently, Spencer and Brewer (1969) have published the results from a study of the distribution of Cu, Zn, and Ni in the Sargasso Sea. Although, their stations were several hundred miles north of Station 860 in this investigation, a meaningful comparison can be made. In addition, they have unpublished data for the distribution of these metals in the Puerto Rico Trench (ca., 20°N), which are based on samples that were collected and analyzed employing the same techniques and personnel as the above work. Thus, an estimate of the quantities of metal associated with more tropical conditions in the Northwest Atlantic Ocean is available. This provides a good and internally consistent set of data with which the most southern station (858) in the present research can be compared.

The details of the experimental procedure employed by these workers has been published by Brewer et. al. (1969). Briefly, the trace metals were analyzed by atomic absorption spectrometry, after methyl isobutyl ketone extraction of acidified sea water (pH 2.5), after added chelating agent (ammonium pyrollidine dithiocarbamate). Therefore, it is possible directly to compare their results for Cu with the amounts found in acidified samples (ca., pH 3) by this present study. It is also possible to contrast the free metal concentrations of Cu and Zn in raw sea water with respect to their measurements.

6.8.1.1 Copper

In the northwestern Sargasso Sea, Spencer and Brewer have data for several shallow (ca., 200 meters) stations in the vicinity of 37°N, 65°W, but the most relevant station is at 36°50.0'N, 65°10.0'W where various depths to 1500 meters were sampled. At this site the average Cu concentration, over 7 depths from 5 to 1500 meters, was 0.5 μg/kg with a standard deviation of 0.3 μg/kg. The Cu concentrations in acidified sea water measured at 8 comparable depths for the most proximate station (860, at 31°49'N, 67°33.5'W) in the present study, was 0.9 μg/l with a standard deviation of 0.5 μg/l (Table 6-7). This agreement is quite good and provides an independent check on both techniques.

According to Spencer and Brewer (personal communication), the dissolved Cu concentration in the Puerto Rico Trench is higher and somewhat more variable than at their northern station in the Sargasso Sea. The average surface concentration was 2.7 ± 2.4* μg Cu/kg. The upper 1000 meters was not sampled, but a mean value of 1.8 ± 1.1* μg Cu/kg was observed between 1000 and 2000 meters. Thus, 2 μg Cu/kg can be taken as a reasonable average to which the data at Station 858 (25°19'N, 67°37.5'W) might be compared.

At Station 858, the mean amount of free Cu in raw sea water for 7 depths (surface to 1592 meters) was 1.1 ± 0.6* μg/l (Table 6-7). As might be expected (cf. Station 860), the free Cu in raw sea water is lower than the amount found at pH 2.5 for sea water in the Puerto Rico Trench. It is unfortunate that the acidified sea water analyses were not conducted. Nevertheless, the agreement is reasonably

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* Standard deviation.

TABLE 6-7

COMPARISON OF TRACE METAL DATA FROM CHAIN CRUISE 85 (NORTHWEST ATLANTIC OCEAN) WITH OTHER RELEVANT STUDIES

Location	Average Trace Metal Concentration			
	Cu	Zn	Pb	Cd
Station 858 (25°19'N, 67°37.5'W)				
Raw Sea Water (0-1592 meters)	1.0 ± 0.6 µg/l	2.4 ± 1.6 µg/l	0.6 ± 0.2 µg/l	0.04 ± 0.02 µg/l
Station 859 (27°47'N, 67°35'W)				
Raw Sea Water (0-935 meters)	0.4 ± 0.2	1.5 ± 1.0	0.4 ± 0.1	0.04 ± 0.02
Acidified Sea Water	1.5 ± 0.7		0.7 ± 0.2	
Irradiated Sea Water			0.9 ± 0.5	0.04 ± 0.02
Station 860 (31°49'N, 67°33.5'W)				
Raw Sea Water (0-1483 meters)	0.2 ± 0.2	0.8 ± 0.8	0.2 ± 0.1	0.03 ± 0.01
Acidified Sea Water	0.9 ± 0.5		0.6 ± 0.3	
Irradiated Sea Water			0.5 ± 0.3	0.06 ± 0.02
36°50'N, 65°10'W (0-1500 meters)[1]	0.5 ± 0.3 µg/kg	1.5 ± 0.7 µg/kg		
Puerto Rico Trench (*ca.*, 20°N) (0-3000 meters)[2]	*ca.*, 2 µg/kg	*ca.*, 2.5 µg/kg		
Bermuda (32°10'N, 64°30'W) (0-3000 meters)[3]			0.04-0.07 µg/kg	
Pacific (29°N and 32°N, off California) 1000 meters[4]			0.03-0.4 µg/kg	
English Channel; Irish Sea[5]				0.024-0.25 µg/l
Coastal Water, Japan[6]				0.08 -0.17 µg/l

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1) Spencer and Brewer (1969)
2) Spencer and Brewer (personal communication)
3) Chow and Patterson (1966)
4) Tatsumoto and Patterson (1963b)
5) Mullin and Riley (1954; 1956)
6) Ishibashi *et. al.* (1962)

good, and the lower concentrations suggest that organically complexed Cu may be present at Station 858.

6.8.1.2 Zinc

It is not possible to obtain a completely independent check of the Zn results, because only data from raw sea water analyses are available. However, an estimate of the reliability is possible. For example, at the 1500 meter station (36°50'N, 65°10'W) sampled and analyzed by Spencer and Brewer, the average Zn concentration was 1.5 ± 0.7* µg/kg, whereas, the mean quantity of Zn at Station 860 was 0.8 ± 0.8* µg/l (Table 6-7). The lower mean amounts of Zn in raw sea water again suggesting the presence of organically complexed metal; in this case Zn.

There does not appear to be any real difference between the amount of Zn estimated (in the same manner as Cu) for the Puerto Rico Trench and the mean amounts found at Station 860 (Table 6-7). This agreement is quite good, and indicates little if any of the Zn to be chelated.

6.8.2 Cadmium

No Cd data has been reported for deep ocean stations. The previous work, using extensive wet chemical procedures, has been in coastal waters. Mullin and Riley (1954; 1956) determined Cd spectrophotometrically after prior concentration employing a dithizone extraction method. They reported an average concentration of 0.113 µg/l in the waters of the Irish Sea and of the English Channel. The range was from 0.024 to 0.25 µg/l Cd.

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* Standard deviation.

Ishibashi et. al. (1962) coprecipitated Cd with CuS by passing H_2S gas through 20 liters of sea water. The Cd was later separated from Cu and Fe on an ion-exchange column and extracted from the eluent as a 1-(2-pyridylazo)-2-naphtol chelate with benzene and determined spectrophotometrically. The amounts of Cd found in coastal water off Japan varied between 0.08 and 0.17 µg/l.

Whitnack and Sasselli (1969) recently reported Cd at 1 µg/l for a surface sample off the coast of California. The concentration of Cd was determined by anodic stripping voltammetry using a hanging mercury drop electrode. This value may be in error and not directly comparable with our data.

The amounts of Cd found in this investigation are in good agreement with the lowest values reported by Mullin and Riley. A mean oceanic Cd concentration of 0.04 ± 0.02* µg/l was observed in the upper 1500 meters (Table 6-7).

6.8.3 Lead

Høgdahl (1963) has tabulated some of the results from early studies that investigated the concentration of Pb in sea water. The reported range was from 0.6 to 8 µg/l. Tatsumoto and Patterson (1963b) have noted that these high quantities were probably the result of sample contamination. Therefore, only the most recent data reported by Patterson and co-workers will be considered as an acceptable comparison for this present research.

The distribution of Pb in the eastern Atlantic Ocean has been reported by Tatsumoto and Patterson (1963). These workers (1963b) have also determined Pb in open ocean stations (29° and 32°N) off California. Chow and Patterson (1966)

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* Standard deviation.

have published the results for a concentration profile at an open station (32° 10'N, 64°30'W) off Bermuda.

The procedure used by these investigators to determine the concentration of Pb in sea water has been outlined in the Tatsumoto and Patterson report for the Pacific Ocean measurements. Briefly, the Pb is assayed by isotope dilution. A Pb^{206} spike is added to sea water acidified to pH 2 with HCl. The Pb and other heavy metals are later extracted with dithizone-chloroform from the sea water previously adjusted to pH 8.5 with NH_3. The Pb is reextracted by dithizone in the presence of ammonium citrate and potassium cyanide. The amount of Pb originally present is established from the final isotopic ratios determined by mass spectrometry.

The critical point in this procedure is the attainment of complete isotopic equilibration. The acid conditions will facilitate the exchange. However, the spike must be added immediately because Pb adsorbs on the walls of the polyethylene containers employed for sample storage. Tatsumoto and Patterson (1963 b) found that about 10 μg of a 15 μg Pb tracer (in 10 ml 8N HCl) was adsorbed on polyethylene, previously cleaned with concentrated HNO_3, after sitting for some weeks. Matson (1968) has shown that this adsorption can occur quite rapidly. For example, a solution (0.6M NaCl) containing 5.4 μg/l Pb was reduced to less than 2 μg/l Pb in 8 hours by adsorption on the walls of a polyethylene bottle previously washed with hot concentrated HNO_3.

This latter phenomenon may be important in the study of Pb in the Atlantic waters off Bermuda (Chow and Patterson). In this case, the Pb^{206} spike was added at the Bermuda Laboratory some hours after the sea water was collected. This station is approximately 200 miles northeast of Station 860 in this investigation, and these sites are suitable for comparison.

At 32°10'N, 64°30'W, the Pb concentration decreased from 0.07 µg/kg at the surface to 0.04 µg/kg at 3000 meters. At Station 860 (31°49'N, 67°33.5'W) the free Pb (raw sea water) at the surface was 0.29 µg/l and 0.050 µg/l at 4113 meters. The quantities of Pb (Table 6-4) were also more variable with depth, reaching concentrations of as high as 0.47 µg/l (1483 meters) and as low as 0.045 µg/l (104 meters). This is fair agreement. However, the Pb concentrations determined in the acidified sea water sample are the more appropriate data for comparison. On the average these quantities of Pb are high by about an order of magnitude. The results also differ at Stations 858 and 859 by about a factor of 10.

This discrepancy could be a real difference such that the waters west of Bermuda show more continental influence (e.g., industrial Pb) than the stations east of Bermuda. The quantities of Pb found in this present study display better agreement with two open ocean Pacific concentration profiles at 32°32'N, 120°30'W and 29°13'N, 120°37'W that are also closer to industrial areas. In these cases, the surface waters ($<$ 1000 meters) contained between 0.03 and 0.4 µg/l Pb with an average concentration of Pb at 0.2 µg/l (Tatsumoto and Patterson). However, this anomaly must remain undefined until further work is done using anodic stripping analysis in sea water, and until a direct laboratory comparison of the two techniques is possible.

6.9 Trace Metal Speciation

At Stations 859 and 860 the differences between raw and acidified samples suggest that a significant fraction of Cu and Pb is sequestered by weakly acidic organic ligands that form metallo-organo compounds of moderate stability (see Chapter 3). The average amount of free Cu in raw sea water represents about 30% of the Cu present when the pH of the sea water solution is adjusted to pH 3. Lead shows a corresponding change which yields an average increase of 50% in the amount of free Pb upon acidification. Moreover, the percentage of complexed Cu (ca., 70%) agrees quite favorably with the data for "off-shore" surface water obtained in the coastal water study (Chapter 5). In that investigation 70% of the Cu was complexed in moderately stable chelates.

The evidence for the presence of organically complexed Cu and Pb in open ocean water is corroborated by the analyses of irradiated samples, where an increase in free Pb was usually observed. Since the 4 hour irradiation period destroys approximately 75% of the dissolved organic carbon (Section 3.1.4), the amounts of Pb in irradiated sea water will be lower than the acidified portion if very stable Pb chelates (> Pb-EDTA) are not present. In general, the data suggests that strongly sequestered Pb is not present. However, the mixed layer samples at Station 859 and the 4000 meter sample at Station 860 show an additional release of Pb above the amount found in the acidified water. This observation is noted, but it is not emphasized because the irradiation data are based on single analyses.

It is also not possible to establish with a great degree of certainty how much Cd exists organically complexed in sea water. The slightly higher amounts of Cd observed in the photo-oxidized sea water indicates that some fraction is sequestered in organic molecules. However, further investigation is necessary to determine the absolute amounts of complexed Cd in open ocean water.

6.10 Trace Metal Distribution

Generally, the amounts of trace metals reported in this investigation for the open ocean waters of the northwestern Sargasso Sea agree favorably with other relevant studies (Section 6.8). However, it would be somewhat bold to generalize with regard to the observed trace metal distribution and its relation to the hydrography on the basis of three sampling stations taken during one season. Yet, there is a definite trend to the trace metal data which parallels the physical observations made during CHAIN Cruise 85, and this phenomenon is worthy of comment.

The increase of the free metal concentrations for raw sea water in the upper 1000 meters moving southward along the 67°30'W meridian is the most striking feature associated with the trace metal data. This fact can be illustrated by averaging the amounts of free metal species measured in the 1000 meter layer at the various stations. These median values appear in Table 6-5 (see also Table 6-7).

At first glance, the data would suggest a southward increase in free metal species, that is independent of the thermal frontal system at ca., 26°N. However, the null hypothesis test of the mean values for the upper 1000 meters indicates that Stations 859 and 860 may be sampling from the same population (Table 6-6). Whereas, both the average free Cu, Pb and possibly Zn are significantly different south of the front (Station 858) than to the north.

Hence, it can be argued that the thermal frontal system does present a barrier or a demarcation between southern and northern conditions in the northwest Atlantic

Ocean at this time of year. The trace metal distribution appears to correlate quite well with the convergence zone. Higher concentrations of free metal in the upper 300 meters at Station 858 can be considered characteristic of tropical waters, whereas the smaller amounts found for comparable depths north of the front are indicative of northern surface waters in the Sargasso Sea. As noted earlier (Section 6.8.2), these observations are supported by other work. Spencer and Brewer (personal communication) found the quantity of Cu and Zn (also Ni) to be higher in the Puerto Rico Trench (ca., 20°N) than at 36°N in the Sargasso Sea.

It is not readily apparent, nor resolvable, why the amounts of free metal differ at other depths not directly associated with the front (see Figure 6-2). Unfortunately, total metal data (i.e., for acidified or irradiated sea water) are not available for Station 858. The amounts of free metal observed for raw sea water at this site do suggest that the total quantities of metal would be greater at Stations 859 and 860. It would, however, be extremely interesting if total metal concentrations were not statistically different across the front, but only the free metal varied. This is a very good problem to further study.

6.10.1 Surface Samples

Several surface samples were collected using a glass or polyethylene bucket sampler. These were analyzed for free metal and the data are presented in Table 6-8. The amounts of free metals are low and comparable to station values, but some very small quantities of free Cd (< 0.01 μg/l) were evident. It is interesting that the surface concentrations do show variations over small ocean

TABLE 6-8

FREE METAL CONCENTRATIONS FOR SEVERAL SURFACE SAMPLES FROM THE WESTERN SARGASSO SEA

Position	Temp. (°C)	Salinity (‰)	Trace Metal Concentration (µg/l)			
			Zn	Cu	Pb	Cd
25°36'N, 66°41'W	25.14	36.618	0.2	0.5	0.32	0.03
26°16' , 66°37'			0.3	1.1	0.3	0.07
26°20' , 67°21'	24.02	36.655	0.3	0.4	0.3	<0.01
26°10' , 67°20'	24.28	36.612	0.8	0.5	0.4	<0.01
26°41' , 67°31'	23.12	36.561	1.9	0.7	0.4	<0.01
26°46' , 67°32'	23.20	36.546	0.2	0.3	0.2	0.03

areas, that is suggestive of patchiness.

6.11 Conclusions and Suggestions for Future Work

6.11.1 Introduction

There have been very few independent checks of reported data for the trace metal distribution in a particular oceanic area. Moreover, it has often been difficult to find good agreement where investigations have taken place in the same region. Unfortunately, this is a very serious problem because, in some instances, genuine trace metal variations, particularly on a small scale, are either masked or considered unreliable. This quandary presents a formidable obstacle not only toward our understanding of the general oceanic distribution of trace metals, but, also toward the recognition of the interactions (biological and geochemical) and mixing processes that may result in local or small scale variability. The latter may ultimately determine the fate of a trace metal in the oceans.

Therefore, it is gratifying to find such good agreement, with respect to the quantities of Cu and Zn present in the Sargasso Sea, between this present study and the work of Spencer and Brewer. This corroborating evidence gives additional support to the observation by the anodic stripping method, that a large fraction of the total Cu and Pb in open ocean water exists sequestered in moderately strong organic chelates. Also, the variations in the free Cu and Pb species in raw sea water across the thermal zone must be considered real and significant. This is a striking example of small scale variability.

Since the Cu and Zn data appear to be good and because the amounts of Cd measured were in agreement with the lowest quantities previously observed in sea water, the Pb data may be considered reliable. Thus, the higher Pb concentrations reported for open sea waters in this study may also represent local variability in the oceans.

6.11.2 Thermal Front Survey

The thermal front survey must be classified as a reconnaissance investigation, since further study of these phenomena would be revealing. In the western North Atlantic, thermal fronts have reported over a wide latitude range, 22°N - 32°N, at various times during the year (Voorhis and Hersey, 1964). An examination of the trace metal distribution across other fronts would be most interesting. For example, will the trace metal variations across the convergence zone be evident at other latitudes?

It appears that anodic stripping analysis of free metal in raw sea water can be used as a marker indicative of the present and past history of a water mass. This was clearly shown in the coastal water study (Chapter 5) where the offshore sea water contained 50% less free Cu, and incidentally 50% less total Cu, than the inshore water. The variations found across the thermal front zone further suggests the possible use of this type of metal data for oceanographic purposes.

Trace metal profiles should be investigated on a finer scale, and if possible, by use of an in situ monitoring instrument. Continuous analysis through the thermocline and perhaps in the deeper layers may provide new information toward the understanding of the processes governing the distribution of trace metals in the oceans. Perhaps, the effects from mixing in the thermocline (microstructure) on the local and long term spatial variability of trace metals can be established.

6.11.3 Trace Metal Speciations

Trace metal (Cu and Pb) speciation resulting from organic metal complexes was observed in open ocean waters. Perhaps, this phenomenon plays a significant role in the interactions and distribution of trace metals. The amounts of organically complexed metals was significant even in an unproductive region as the Sargasso Sea. It would be most worthwhile to study trace metal speciation in areas of high productivity (such as the upswelling zones off Peru or Africa) where the relationships between trace metal species and primary production should be reinforced because the dissolved organic matter and trace metal occur in larger quantities.

Studies of this nature may reveal whether organically complexed trace metals are available or unavailable to phytoplankton, or if trace metal chelates are metabolic by-products. The interactions between trace metals, complexing agents and phytoplankton could also be studied in the laboratory and when combined with field measurements might provide much relevant information toward the understanding of the role of trace metals as micronutrients.

The speciation observed for Cu in the coastal waters, off Falmouth, Massachusetts, also points out the importance of considering metal chelates in studies of the marine cycle of trace metals. What happens at the river-ocean interface? For example, do large amounts of trace metals in rivers enter the major ocean circulation, and if so, in what form, inorganically dissolved or organically complexed? The coastal water study indicates that strongly sequestered Cu may be swiftly deposited close to its terrestrial inputs.

Trace metal speciation studies are particularly relevant in cases of possible heavy metal pollution. Not only should the effect of uncomplexed metals to biota be measured, but attempts should be made to isolate and identify chelated metal species which could be toxic agents.

Only a limited number of photo-oxidized sea water analyses were made during CHAIN Cruise 85. These were not sufficient to demonstrate either the presence or absence of very stable organically sequestered metal in open ocean water. However, more careful work utilizing the ultra-violet photo-oxidation technique should be undertaken to establish where, and how prevalent this phenomena may be.

6.11.4 Anodic Stripping Voltammetry Utilizing the Thin Film Mercury Composite Graphite Electrode

The anodic stripping method, itself, bears further investigation. The Ni interference should be thoroughly examined not only because of its purely physicochemical interest but because the systematic nature of the interference suggests the Ni can be determined in sea water. Thereby, extending the usefulness of the anodic stripping technique utilizing the thin film mercury composite graphite electrode.

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BIOGRAPHICAL NOTE

The author, William Francis Fitzgerald, was born in Boston in 1936; the son of Thomas Francis and Julia Agnes Fitzgerald. He attended public schools in that city and graduated from Boston Technical High School in 1954. After two years, and with the funds obtained through employment as a shipper, T.V. antenna repairman, newspaper distributor and other mundane occupations, he entered Boston College to major in chemistry. He received a B.S., cum laude, in 1960. The following year, he obtained a M.S. in chemistry from the College of the Holy Cross. Whereupon, he was employed as a research assistant at the Woods Hole Oceanographic Institution. He had the most fortunate opportunity to work under the guidance of Professor Paul C. Mangelsdorf, Jr. This association culminated, when the author entered the Massachusetts Institute of Technology in 1966 to pursue a program leading to a doctorate in chemical oceanography.

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