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MASTER

A STUDY ON THE CHEMICAL BEHAVIOR OF ZINC IN CHESAPEAKE BAY WATER USING
ANODIC STRIPPING VOLTAMMETRY

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TECHNICAL REPORT 76

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ABSTRACT

Anodic Stripping Voltammetry from a thin layer of mercury was used to analyze Chesapeake Bay water for zinc directly at concentrations between 0.5 and 20 parts per billion (ppb). Interferences on the zinc signal are significant. The interference from copper can be quantitatively corrected for. Of five other metals which are potential zinc interferences only nickel and cobalt are expected to cause significant problems. In the method presented herein, the range of nickel and cobalt concentrations expected to occur in the Bay water cause suppression of the zinc signal by an amount equivalent to less than 0.4 ppb zinc. The coefficient of variation of replicate zinc analyses is 3.7% at a zinc concentration of 2.5 ppb. The thin layer mercury electrode response to zinc in solution is affected by the chemical condition of the zinc in two ways: the stripping peak potential changes and the rate of zinc plating changes. By using Anodic Stripping Voltammetry as both an analytical technique for zinc and as a device to sense the chemical condition of zinc, and in conjunction with the technique of oxidizing dissolved organic matter by high intensity ultraviolet light, a survey was conducted of the temporal and spatial distribution of the zinc concentration and of zinc sequestering by dissolved organic matter in Chesapeake Bay water.

It was found that several processes affected the zinc concentration and the extent of zinc chelation. In the upper Bay just below the outfall of the Susquehanna River zinc is desorbed from sediments freshly deposited by the spring freshet. The desorption is caused by cation exchange with the higher salinity water which intrudes over the sediments

when the freshet ceases. Variations in the aqueous zinc concentration with time at the stations samples cannot be accounted for by influx of zinc from the ocean or the tributaries. A flux of zinc from the sediments was detected. It was large enough to cause a measurable increase in the aqueous zinc concentration in a few day's time. Since a buildup of zinc in the aqueous phase was not observed, it is proposed that zinc is being cycled between the sediments and the water.

The sequestering of zinc by suspended organic matter was substantial only in late summer when phytoplankton blooms had accumulated a concentration of organic matter exceptionally high compared with the rest of the year. Different rates of reaction between zinc and chelators were found at different times of the year.

Evidence was found which indicated that naturally occurring chelators have stability constants for reaction with copper, nickel and cobalt which are higher than the stability constants for reaction with zinc.

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SYMBOLS

a	activity of the ligand (Zn) in the mercury phase
C_R^o	concentration of the reduced metal in the mercury at the start of the stripping step
C_O	concentration of the oxidized form of the metal in solution
$C_O \text{ Cu}$	concentration of copper in the aqueous phase (ppb)
$C_O \text{ Zn}$	concentration of zinc in the aqueous phase (ppb)
Cu_S	concentration of free copper in the mercury phase expresses as the ratio, moles of copper:moles of mercury (mole ratio)
Cu_T	total copper concentration in the mercury phase (mole ratio)
δ	the no - chelator classification symbol
E_p	the potential at which the stripping current maximum occurs
$E_p \text{ Zn}$	the potential at which the stripping current maximum due to the oxidation of zinc occurs; referred to as the zinc stripping peak potential
E_{pl}	the plating potential relative to the Ag/AgCl electrode
I	concentration of the copper:zinc intermetallic in the mercury
i_p	the stripping current at the maximum (μamp); referred to as the stripping peak current
$i_p \text{ Cu}$	the stripping peak current due to the stripping of copper
$i_p \text{ Zn}$	the stripping peak current due to the stripping of zinc
$i_p^+ \text{ Cu}$	the normalized stripping peak current due to copper
$i_p^+ \text{ Zn}$	the normalized stripping peak current due to zinc
k_1	the first order reaction rate constant
v	the potential sweep rate (mv/second)
$\bar{n}$	average number of ligands per central group
$\sigma = s$	the standard deviation
Zn_S	concentration of free zinc in the mercury phase (mole ratio)
Zn_T	total zinc concentration in the mercury phase (mole ratio)

1. INTRODUCTION

The demand for information regarding the concentrations and movements of trace metals in marine systems has increased in the past few years as a result of greater use of these systems for industrial and domestic waste disposal. But most techniques available to the researcher for detecting trace metals are inadequate for studying the chemistry of or estimating the concentrations of zinc at normal concentrations in natural waters. The state of the analytical art is illustrated by comparing the results of zinc analyses performed by several laboratories on one sample of seawater. Brewer (1970) reported that the mean and coefficient of variation of 40 analyses on one sample were ~ 5 ppb and 100% respectively. It is emphasized that this degree of statistical scatter was obtained by comparing the results of the analytical operation only, which is presumably carefully controlled in each laboratory so to avoid gross analytical errors due to sample contamination. The operation of sampling the environment cannot be controlled as well as the analytical operation and is often thought to be of minor importance in determining the metal concentrations in a water body. One can imagine that with today's methods of sampling and analysis, two workers could easily come to widely different conclusions about the zinc concentrations in natural waters.

The study reported here deals with variations in time and space of the total zinc concentration, the extent of zinc sequestering by suspended organic matter and the movements of zinc in the aqueous phase of water from Chesapeake Bay. In the study program, I adopted safeguards in the sample collection and handling operations which, I believe, minimized gross errors from contamination in the analytical estimate. The analytical technique used was especially developed and evaluated

for this study and is sensitive enough to analyse water samples for zinc directly without preconcentrating the sample. The technique is sensitive to the chemical form of zinc in solution and a method was developed to use these characteristics to demonstrate the sequestering of zinc by organic matter. The methods are described in detail. I will begin with a discussion of the analytical technique.

A specialized polarographic technique called Anodic Stripping Voltammetry (ASV) has been a laboratory curiosity for years (Shain, 1963). When Matson et al. (1965) developed a stable thin mercury layer cathode and produced signals of the order of microamperes (μamp) from test solutions of a few ppb, the technique appeared to be useful for direct analysis for several trace metals in natural water (Matson, 1968). Also Zirino and Healy (1971) have used hanging drops of mercury as cathodes for a differential ASV technique in which a net signal (much smaller than obtainable using thin layers of mercury) is amplified to get a signal of useable size.

In ASV using thin layers of mercury, the technique described here, metals are electroplated from the aqueous solution into the mercury phase and, after plating for an arbitrary duration, the metals are oxidized back into solution by changing the potential on the cathode in the anodic sense at a constant rate. If the plated metals do not interact with each other in the mercury phase and can oxidize at reasonably fast rates, the metals are returned quantitatively to solution and the current due to the oxidation of each metal reaches a maximum (i_p) at some potential (E_p). Ideally the metals which are plated together strip off at separate potentials depending upon the oxidation energy of the metal.

Roe and Toni (1965) developed a mathematical model which predicted i_p and E_p for the stripping of a metal as a function of the reduced metal

concentration in the mercury at the start of the stripping step (C_R^0) and of the potential sweep rate (v). They assumed that the cathode had the following physical characteristics: i) the plated metals diffuse in the mercury so fast that a gradient does not form and ii) a diffusion layer in the solution outside the mercury surface is thin enough that the flux of the stripped metal is inversely proportional to the concentration gradient across the layer. In practice the first of these is attained at specific potential sweep rates and mercury thicknesses, and the second is achieved by stirring with nitrogen gas which, additionally, purges the solution of oxygen. Their derived equations predict i) $i_p \propto v$ and ii) $i_p \propto C_R^0$. These relationships have been verified by Matson (1968) in artificially prepared solutions. I found also that within the carefully defined limits listed in Appendix Table I, the zinc stripping current maximum ($i_{p\text{ Zn}}$) was proportional to the plating time and the aqueous zinc concentration ($C_{O\text{ Zn}}$).

In this report the technique is applied to the study of zinc in Chesapeake Bay. I found four ways in which it can be used and have described each in detail. Then I have used the methods in a survey of the temporal and spatial variations in total zinc and the zinc chemical condition vis-a-vis organic chelation in the aqueous phase of Bay water samples.

2. EQUIPMENT

2.1. General

To perform the electrical functions of plating, stripping and current readout, I used the polarographic system described by Enke and Baxter (1964) and supplied by Heath-Schlumberger (Benton Harbor, Michigan). The system includes a tube type operational amplifier (CAT #EUW-19A), a stabilizer (CAT #EWA-19-4) and a unit to wire the amplifiers as a polarograph (CAT #EUA-19-2). It is a so-called controlled potential polarograph in that the reference electrode carries no current. All current passes between a counter and the cathode. The operator sets a potential between the reference and cathode, and it is maintained by the reaction at the cathode forced by an amplified potential drop between the cathode and the counter electrode. The polarograph develops a potential of 10v or 0.1v for the full scale cathode current. The 0.1v output was monitored with a Honeywell Electronix solid state y vs. time recorder. All electronic functions of the polarograph and recorder were either calibrated frequently or monitored continuously.

The reference cell was Ag/AgCl in 0.10 M NaCl.* The Ag/AgCl surface was made by anodizing a cleaned silver wire in 0.1 M HCl solution. The counter electrode was a coil of bright platinum wire. Both electrodes were isolated from the test solution by quartz tubes with an electrolyte connection through a sanded glass:teflon sleeve seal. The resistance of the electrolyte contact was small but the flow of reference and counter electrode fluids was restricted by the seal.

The sample cell was a 150 ml Teflon beaker (DynaLab Corp.) fitted with a machined Teflon head. The three electrodes and a quartz gas

* All potentials stated are relative to this cell.

Machined Teflon Head
Top View

Side View

Figure 1 The cell holder and machined Teflon head. Dimension - 2/3 actual size.

delivery tube dipped into the sample. The head was mounted on a rig (Figure 1) with a spring held moveable bottom plate which held the Teflon beaker in place. The rig was mounted to a wooden base cushioned from house vibration.

The test solutions were stirred to keep the plating rate high, and purged of oxygen. Both functions were provided by bubbling prepurified nitrogen gas directly on the cathode. The gas was dispersed through a quartz capillary tube pulled into a Shephard's crook shape. A flow rate of ~ 120 ml/minute kept the current due to oxygen reduction at < 0.1 μ amp.

2.2. The Waxed Carbon Rod Substrate

Carbon is an excellent conducting material but the pores of pressed carbon rods must be filled to prevent electrolyte intrusion. Two types of carbon rod are available from Fisher Scientific Company (CAT # 4-676-5 and - 10). The - 10 brand is harder and denser than the - 5 brand. Matson (1968) could find no difference in the electrical properties of these two types but I found that the mercury would not stick to the - 5 brand longer than a few minutes. The - 10 brand rods held mercury for several hours.

The carbon rods are cut to 3 inch lengths and submerged in a beaker of smoking hot paraffin. To degas the rods, I draw an aspirator vacuum on the beaker and repeatedly heat and evacuate until no more gas bubbles come out. Then I let the paraffin cool under normal pressure until it is just ready to solidify and withdraw the rods leaving a thin film of paraffin on each for insulation. To expose a conducting surface one polishes away the paraffin in any shape desired. I decided to blow the stirring gas vertically upward to surround the plating surface, and found

that by indenting the surface into the rod slightly, the mercury was protected from direct gas abrasion thus increasing the useable life of the electrode. To make this shape, I cut out a cylinder 4-6 mm long and about 1 mm deep into the lower end of the rod leaving a cap to shield the surface. For the initial cut, I used a high speed lathe and a sharp bit set to cut with very little drag. For final polishing I held Kimwipes to the surface while turning the rod in the lathe or a drill press. The final surface should be smooth but not glossy.

When using the rods in natural water samples, residues of organic matter gradually collect on the conducting surface and cover the plating sites. This residue can be wiped off with Kimwipes or washed off with 50% ethanol or 1 M NH_4OH . Some portion of the organic matter in natural water performs a valuable service, however. A clean, freshly polished rod cannot be used because it catches small gas bubbles which inhibit plating. Exposing the rod to raw sea or Bay water for a few moments enables it to shed the small bubbles. The same water irradiated with strong ultraviolet light to destroy the organic matter will not cause this phenomenon.

The paraffin gradually degrades with age and exposure to reagents, samples or water. Severe degradation causes stripping peak doublets and poor mercury retention. The useable life of a rod is 10-15 days under normal conditions of exposure to Bay water. After this it must be either repolished or discarded.

2.3. Mercury Plating

A mercury droplet must be attached to each exposed carbon grain of the rod to make an electrode. The only way to do this at present is to

electroplate the mercury from solution. The method used by Matson (1968), Fitzgerald (1970) and Seitz (1970) was to plate from acidified seawater with Hg(II) added at -0.1 v. The reaction energy is pH dependent; Hg° forms using acid chloride but calomel (Hg_2Cl_2) forms using neutral chloride solutions at this potential. I noticed, however, that powdery residues formed on my carbon rods which were not soluble in strong acids or bases. I was able to produce similar residues by repeatedly plating mercury from 0.1 M HCl solutions and stripping it off into 0.01 M HClO_4 . In control experiments using 0.01 M HClO_4 for mercury plating and stripping both, no residues formed. I did not identify the residue but circumstantial evidence strongly indicates that it is calomel. It is possible that calomel is produced as an intermediate product in the mercury reduction reaction, crawls onto the paraffin sites and does not reduce further. The residue caused serious electrical problems so I rejected the mercury plating procedure using acidified seawater in favor of one using 0.01 M HClO_4 solution. For mercury plating I used a 5×10^{-5} M Hg (II) in 0.01 M HClO_4 solution, plated at 0.00v and measured the coulombs of mercury deposited by integrating the plating current with time. The plating surface area was $\sim 0.5\text{cm}^2$, so $\sim 24,000$ μ coulombs of mercury were deposited to get the surface density recommended by Seitz (1970) of 2.5×10^{-7} moles/ cm^2 . This required 10-20 minutes of plating.

When the mercury was deposited, I checked the coverage by the following method: After rinsing the electrodes, I inserted a fresh 0.01 M HClO_4 solution without mercury, purged the solution, and increased the potential to -0.70v : Normally the current dropped to < 2.0 μamp in a few minutes, and then I increased the potential until the current exceeded 10 μamp : From my experience, if the coverage is suitable, the potential

at this point is at least -0.78v .

2.4. Electrode Stability

Other workers (e.g. Fitzgerald, 1970) have reported that this electrode is stable for weeks. I found unfortunately, that the sensitivity for zinc drops 20-30% in 8-12 hours of continuous use after mercury deposition (Figure 2). I varied the mercury surface density, the rod surface conditions and the chemical and electrical parameters in mercury plating but the decrease in sensitivity and the simultaneous loss of mercury could not be stopped or even slowed. Because the sensitivity decays substantially in a short time, I always plated an electrode fresh at the beginning of each work day and stripped the remaining mercury off into 0.01 M HClO_4 at the end of the day. In experiments performed during the day, I determined the electrode sensitivity and used it to normalize the signals to a standard sensitivity.

Figure 2

The changes in three analytical parameters with use of the electrode. The zinc and copper sensitivities vary but the analytical estimate by standards addition technique is constant.

3. BEHAVIOR OF THE ELECTRODE

3.1. The Stripping Curve

The stripping curve (current vs. potential) is the ASV readout data and interpreting the stripping peaks is the first step in using this technique. A stripping curve of the metals deposited from seawater is shown in Figure 3. The baseline of the curve is formed by two independent processes: i) hydrogen reduction and ii) double layer charge shifts. Stripping peaks are superimposed on the baseline. In Region I of Figure 3, the baseline is primarily formed by the rate of decrease of the hydrogen reduction. In Region II it is formed by charge shifts. The zinc peak occurs in Region I. The rate of hydrogen reduction depends upon C_R^0 so that the baseline under the zinc peak is not necessarily continuous. However, without definite proof to the contrary, the most logical baseline is a smooth curve which connects the curvature of Region I and the near linearity of Region II without noticeable discontinuities.

After trying several methods of drawing baselines I decided that the best method was to draw them freehand and adjust the curvature by visual inspection to get the smoothest fit. After considerable practice I was able to draw these lines with satisfactory consistency. Generally if the shift in baseline current was $< 2.0 \mu\text{amp}$ across the zinc curve base replicate estimates of the baseline current at $E_{p \text{ Zn}}$ varied $< 0.05 \mu\text{amp}$. A least squares fit to a plot of $i_{p \text{ Zn}}$ vs. $C_{0 \text{ Zn}}$ (Figure 9) had an Index of Determination of 0.9996 and passed through the origin so my approach to estimating the baseline current at $E_{p \text{ Zn}}$ does not introduce a measurable systematic error in determining $i_{p \text{ Zn}}$.

Figure 3

Stripping curve showing the baseline in different potential regions. Medium: sea water, $E_{pl} = -1.270$ v.

3.2. Variations in $E_{p, Zn}$ with pH

The mathematical model for thin mercury layer ASV (Roe and Toni 1965) predicts that the stripping peak potential of a metal (E_p) is a function of the redox potential of the metal in the aqueous test solution. Zirino and Healy (1970) found that by driving the carbonates from seawater, they could cause the $E_{p, Zn}$ by differential ASV to shift anodic by several millivolts. Also, I found that a cathodic shift could be caused by increasing the pH. Apparently, $E_{p, Zn}$ is at least qualitatively dependent upon the energy of the oxidation (stripping) reaction as predicted by the model.

Nicholson and Shain (1964) suggested that in the stripping reaction, changes in the potential of maximum reaction rate with changes in the activity of a complexing anion requires that the reaction between the aqueous metal cation and the anion be fast relative to the rate of supply of the metal cation from the electrode. If the reaction is not fast enough, the metal merely oxidizes as the free cation. A rough approximation of the rate constant necessary to cause this shift can be made by assuming i) all the metal strips into the 1 μ thick unstirred layer and ii) in that layer, the bulk ionic zinc activity is maintained at ~ 100 fold less than the total concentration. In the case of the observed shift in $E_{p, Zn}$, if the complexing reaction is first order, then

$$\frac{d[Zn^{2+}]}{dt} = -k_1 [Zn^{2+}]$$

Typical numbers are: The rate at which ionic zinc is stripped into solution, $\sim 0.8 \times 10^{-11}$ moles/sec; the volume of the unstirred layer $\sim 5 \times 10^{-7}$ liters; the bulk zinc activity in solution is $\sim 10^{-9}$ M. The

calculated k_1 is $\sim 10^4$ /second.

The prediction by Roe and Toni (1965) is that E_p is a function of both the redox potential and a factor which contains an unknown quantity, the diffusivity of the metal species. However, when the activity of the complexing anion is large enough that most of the metal in solution is complexed as one form, the diffusivity should be constant with further increases in the activity of the complexing anion. At constant diffusivity, changes in E_p are, by this model, equal to changes in the redox reaction energy. For the case of zinc oxidizing to form a zinc hydroxide complex of unknown stoichiometry, we can write the general reaction:

For demonstrating the method I used to mathematically predict changes in E_p Zn with pH, I here let $x = 1$. The Nernst equation for the reaction is:

$$E = E^\circ + \frac{0.059}{2} \log \frac{[\text{Zn(OH)}^+]}{[\text{Zn(Hg)}][\text{OH}^-]} \quad (3a)$$

Using the definition of the stability constant for the complexing reaction:

and the mass balance relationship

$$\Sigma(\text{Zn}) = \frac{[\text{Zn}^{2+}]}{\gamma_1} + \frac{[\text{Zn(OH)}^+]}{\gamma_2} \quad (3b)$$

where the γ 's are the respective activity coefficients of free and

complexed zinc (3a) can be expressed as

$$E = E^{\circ} + \frac{.059}{2} \log \frac{\gamma_1 \gamma_2 K \Sigma(\text{Zn})}{\{\gamma_2 + \gamma_1 K [\text{OH}^-]\} [\text{Zn}(\text{Hg})]} \quad (3c)$$

I shall specify that experimentally the terms γ_1 , γ_2 , $\Sigma(\text{Zn})$, K and $[\text{Zn}(\text{Hg})]$ will be held constant. The first derivative of (3c) is

$$dE = - \frac{.059}{2} \left\{ \frac{\gamma_1 K}{\gamma_2 + \gamma_1 K [\text{OH}^-]} \right\} d[\text{OH}^-] \quad (3d)$$

Over a finite range of pH, (3d) can be integrated to read

$$E \left| \begin{matrix} E_2 \\ E_1 \end{matrix} \right. = - \frac{.059}{2} \log \left\{ \gamma_2 + \gamma_1 K [\text{OH}^-] \right\} \left| \begin{matrix} [\text{OH}]_2 \\ [\text{OH}]_1 \end{matrix} \right. \quad (3e)$$

An analogous relationship can be derived for the general stripping reaction. It is

$$E \left| \begin{matrix} E_2 \\ E_1 \end{matrix} \right. = - \frac{.059}{2} \log \left\{ \gamma_x + \gamma_1 \beta_x [\text{OH}]^x \right\} \left| \begin{matrix} [\text{OH}]_2 \\ [\text{OH}]_1 \end{matrix} \right. \quad (3f)$$

where β_x is the stability constant for the general complexing reaction

Equation (3f) can be evaluated by inspection over two pH ranges: i) where $\gamma_x > \gamma_1 \beta_x [\text{OH}]^x$ (E) will not change with pH and ii) where $\gamma_x < \gamma_1 \beta_x [\text{OH}]^x$, (E) will change linearly with pH at a rate of $(.05916 x / 2)$ volts per

pH unit at 25 C. At the intersection of the pH dependent and pH independent portions of the E vs. pH plot, the arguments should be equal

$$(\gamma_x = \gamma_1 \beta_x [\text{OH}]^x).$$

I tested these predictions experimentally by varying the pH in 0.1 M NaCl solution containing zinc and measuring the E_p . The laboratory temperature was 20 C so the constant in equation (3f) is (.0583/2 v). The plating potential, potential sweep rate and chart speed were carefully calibrated so that the measured E_p Zn values have an uncertainty of ± 3 mv. The pH values were measured with a combination glass:Ag/AgCl electrode. I calibrated this glass electrode with Beckman buffers at 7.00, 8.07 and 9.80 units just before each experimental reading, using the buffer closest to the experimental value in pH. The combination of readout uncertainty and a drifting glass electrode limits the pH measurement to ± 0.05 units. For pH adjustments, I added increments of a 2 M NaOH solution. I checked the level of carbonate in this solution by adding barium chloride until a precipitate appeared and comparing the results with control solutions. From this test, I concluded that the carbonate concentration was $< 10^{-2}$ M. The increments of this solution added ranged 1 μ l to 1 ml in volume, totalling 2 ml. The added carbonate therefore ranged in concentration 10^{-7} to 10^{-4} M. In all cases, this is two orders of magnitude below the hydroxide concentration. The stability for ZnCO_3 is approximately $\log K_1 = 10.9$ (Sillen and Martell, 1963).

The results of this experiment are shown in Figure 4. As predicted by equation (3f) E_p is independent of pH up to some point where it increases cathodic linearly with increasing pH. A least squares fit to the sloped portion of the plot had a slope of 0.0568 v/pH unit and an index of determination of 0.997. This slope is remarkably close to that

Figure 4 The response of E_p Zn to changes in pH in 0.1 M NaCl.

predicted for the general stripping reaction with $x = 2$. The pH at the intersection of the level and sloped portions is 9.13. From the relationship $\gamma_2 = \gamma_1 \beta_2 [\text{OH}]^2$ and from supporting data listed in Table 1, I calculated β_2 and the ΔG_f° of $\text{Zn}(\text{OH})_2^\circ$. These calculated values are compared with published values in Table 1.

The calculated value of $\log \beta_2$ is smaller than $\log K$, for ZnCO_3° , suggesting that even at the concentration of carbonate in my test solution, the results could have been biased by the formation of ZnCO_3° . Two facts tend to dismiss this possibility: (1) In that case theory would predict a slope of 0.0291 v for a unit logarithm incremental addition of 2 M NaOH reagent (2) if we presume that at the intersection of the sloped and level portions of Figure 4, the reaction actually occurring is between zinc and carbonate, and using the relationship ($\gamma_2 = \gamma_1 K_1 [\text{CO}_3^{2-}]$) with $[\text{CO}_3^{2-}] = 10^{-7}$ M (i.e.) two orders of magnitude less than $[\text{OH}^-]$ at that point, we calculate $\log K_1 = 7.46$ which is in poor agreement with the published $\log K_1$.

The argument can also be made that zincate ion (ZnO_2^{2-}) forms in pH range of this experiment. Again two facts tend to dismiss this argument: (1) The reaction to form ZnO_2^{2-} requires 4 (OH^-) ions so theory would predict a slope of 0.1136 v/pH unit and (2) using the stability constant for the reaction $\text{Zn}^{2+} + 4\text{OH}^- \rightarrow \text{ZnO}_2^{2-} + 2\text{H}_2\text{O}$ as calculated from the free energy data (Garrels and Christ, 1965) the zincate ion is important only at pH > 12.

Presuming that there is no bias in this experiment due to ZnCO_3° formation we can make some general observations about the meaning of the results. The calculated $\log \beta_2$ is in poor agreement with the solubility product of amorphous $\text{Zn}(\text{OH})_2$, but in excellent agreement with Butler's

Table 1

The parameters used in calculating β_2 and comparisons of calculated and published constants.

Parameter	Value	Source
$\gamma_{\text{Zn(OH)}_2}^\circ$	1.0	Garrels and Christ (1965) p. 102
$\gamma_{\text{Zn}^{2+}}$	0.35	" " "
K_w @ 20 C in NaCl solution	0.681×10^{-14}	Garrels and Christ (1965) p. 70
$\log \beta_2$	9.86	Calculated, this work
$\log K_{so}$ of amorphous Zn(OH)_2	-15 to -17	Sillen and Martell (1964)
$\log \beta_2$	10.1	Butler (1964) p. 287
$\Delta G_f^\circ \text{Zn(OH)}_2^\circ$	-123.8 Kcal/mole	Calculated, this work. Supporting data from Garrels and Christ (1965)
$\Delta G_f^\circ \text{Zn(OH)}_2$ (amorp)	-131.9 Kcal/mole	Garrels and Christ (1965) p 428

(1964) estimate. Zirino and Healy (1970) remarked that in seawater about 75% of the zinc was Zn(OH)_2° while 4% was ZnCO_3° . They do not say precisely what constant they used for β_2 but from the proportions of Zn(OH)_2° and ZnCO_3° they calculated it seems probable that they used K_{so} for amorphous Zn(OH)_2 . It is not at all certain that this constant has any relationship to the stability constant of the true ion pair Zn(OH)_2° .

The results of my experiment are compatible with the theory that the zinc stripping reaction in solutions of $\text{pH} > 9.13$ forms the ion pair Zn(OH)_2° which has a stability constant of $\log \beta_2 = 9.86$ and exists for at least a few milliseconds in an energy state ~ 8.0 Kcal/mole higher than that of amorphous Zn(OH)_2 . Since the zinc species Zn(OH)_2° has not been reported, the chemical state suggested by this experiment may be metastable.

3.3. The Relationship Between i_p Zn and the Plating Potential E_{pl}

The second characteristic of this ASV technique which I will discuss is the relationship between the plating rate and the plating potential E_{pl} . The *plating rate* is qualitatively defined as the rate at which metal is deposited into the mercury phase per unit concentration of the metal in solution. Another term, *sensitivity*, which has been used without precise definition, is now defined as the increase in stripping peak current (i_p) caused by an increase in the aqueous concentration of the metal by 1 ppb. The sensitivity is proportional to the plating rate.

If one increases the potential on the cathode in any given solution containing zinc, first a potential is reached where zinc begins to plate out and electrons begin to flow. Further increases in potential cause it to increase until it is ultimately limited by the diffusion of the

zinc species to the cathode. The cathode has an unstirred layer of $\sim 1 \mu$ thickness through which the metals must diffuse. Conceptually the potential of maximum plating rate corresponds to the potential where the plating energy is fully supplied. To test this concept, I determined the plating rate of zinc with E_{pl} in three solutions: seawater with 6.0×10^{-8} M zinc, 0.1 M NaCl with 1.2×10^{-8} M zinc and 0.1 M NaCl at pH 11.6 with 6×10^{-8} M zinc. The results are shown in Figures 5 and 6 as changes in $i_{p\ Zn}$ with E_{pl} in each solution. The curves are shaped as we expected. The plating reactions in seawater and 0.1 M NaCl solution can be written

The Nernst equation predicts the reaction potential as

$$E = -1.044 - \frac{.059}{2} \log \frac{1}{[Zn^{2+}]} \quad (3g)$$

The constant is the sum of the zinc standard half-cell potential and the Ag/AgCl half-cell potential. The experimental and predicted values of the potential at maximum plating rate are compared in Table 2. The general plating reaction at pH = 11.7 can be written

Rather than compare experimental and predicted potentials, I calculated the standard free energy of reaction (ΔG_R°) for the zinc half-cell using the experimental measurement of the potential of maximum plating rate, and using the calculated ΔG_R° and data for the free energy of formation of hydroxyl anions, I calculated ΔG_f° for the species $Zn(OH)_x^{2-x}$ for $x = 1, 2$ and 3 . The calculated values of ΔG_f° are compared with some

Figure 5 Plots of i_p Zn versus E_{pl} : (a) in seawater, (b) in 0.1M NaCl containing $1.2 \times 10^{-8} M$ zinc.

Figure 6 Plot of i_p Zn versus E_{pl} in 0.1M NaCl at pH = 11.7.

published values in Table 2.

The experimental potential of maximum plating rate in seawater and NaCl solutions is anodic of the predicted potential by ~ 22 mv. Since I ignored the presence of zinc carbonate or zinc hydroxide species in seawater in the calculation of the predicted potential, it is remarkable that the difference between experimental and predicted potentials is the same in both media. At high pH in NaCl media, the closest agreement between my calculated ΔG_f° values and published ΔG_f° values is for $x = 1$. But the agreement between the ΔG_f° Zn(OH)_2 value calculated in this experiment and that calculated in the E_p Zn vs pH experiment is excellent. This result suggests that the ion pair Zn(OH)_2° is a stable entity in NaCl solution.

The concept formulated above probably has only limited usefulness. But it may be possible to approximate the free energy difference between the ionic and complexed forms of zinc in natural water by measuring the differences in the potential of maximum plating rate. Fitzgerald (1970) observed a change in the potential of maximum copper plating rate when he destroyed the organic chelators in seawater by high intensity ultra-violet irradiation. The change was ~ 200 mv corresponding to an apparent increase of ~ 9.2 Kcal/mole in the energy level of copper. It is well known, however, that some metal complexes are not reducible (e.g.) Zn-EDTA (Kolthoff and Lingane, 1952). Therefore, it is not safe to assume that the plating rate of any metal is the sum of terms which are functions of the diffusivity and the reaction energy only. The potential of maximum plating rate then is not necessarily a measure of the energy of the plating reaction only.

Table 2

Comparison of experimental and predicted potentials of maximum plating rate.

Sample	Zinc Concentration	Ionic Zinc Activity Coefficient	Predicted Potential	Experimental Potential
Seawater	6.0×10^{-8} M	0.30	- 1.272 v	- 1.250 v
0.1 M NaCl	1.2×10^{-8} M	0.35	- 1.291 v	- 1.268 v

Note: Ionic zinc activity coefficients from the Debye-Huckel Law (Garrels and Christ, 1965. p.63).

For the half-cell reaction		Calculated $\Delta G_f^\circ \text{ Zn(OH)}_x$	Published $\Delta G_f^\circ \text{ Zn(OH)}_x$	Comments
$\text{Zn(OH)}_x^{+(2-x)} + 2e^- \rightarrow \text{Zn(Hg)}^\circ + x(\text{OH})^-$				
$\Delta G_R^\circ = + 45.2 \text{ Kcal/mole}$	$x = 1$	- 82.8 Kcal/mole	- 78.7 Kcal/mole	
	$x = 2$	- 120.4 "	- 131.9 "	My value - 123.8
	$x = 3$	- 158.0 "	- 167.4 "	

Note: Published values are from Garrels and Christ (1965) or calculated from available stability constants in Sillen and Martell (1964) with supporting free energy data from Garrels and Christ (1965).

4. USING ASV FOR QUANTITATIVE ZINC ANALYSES

4.1. The Metals Which Form Stripping Peaks

For a metal in aqueous solution to cause a stripping peak it must plate into mercury at some potential, and oxidize out of mercury within a potential range of a few millivolts. The potential necessary to plate zinc suffices to coplate a number of other metals, of which a relative few strip off to form recognizable peaks (e.g.) zinc, cadmium, lead, copper, bismuth and thallium (Smith and Redmond, 1971). For all practical purposes in Chesapeake Bay water, the duration of plating ideal for producing zinc stripping peaks is enough to produce additional peaks only from copper. In Appendix Table II, I have summarized several measurements of the copper and zinc sensitivities by the ASV technique in Chesapeake Bay water.

4.2. The coplated Metals Which Behave Non-Ideally

Conceptually, a given plated metal will behave in one of four ways determined by combination of the stripping reaction and the reactivity with coplated metals as indicated below.

Interaction with coplated metals	Stripping Behavior	
	Forms a Peak	No Peak
Unreactive	Ideal	Non-Ideal
Reactive	Non-Ideal	Non-Ideal

It is easily demonstrated that the coplated metals which in some way behave non-ideally can interfere with the use of the ASV technique for analytical measurements. Some examples are shown in Figure 7. Inter-

Figure 7

The effects of interfering metals on the zinc and copper signals: (a) a 6.1 ppb copper addition to Bay water, (b) a 2.9 ppb cobalt addition to seawater, (c) a 6.4 ppb nickel addition to Bay water and (d) a 6.0 ppb nickel addition to Bay water with 0.01 M tartrate added.

actions of zinc with copper, cobalt and nickel cause substantial reduction in $i_{p\text{ Zn}}$ and tailing in the zinc peak. Interactions of copper with cobalt and nickel cause distortions of the copper peak, reductions of $i_{p\text{ Cu}}$ or secondary peaks. Another curious effect is demonstrated by Figure 8 where the apparent zinc plating rate decreases for E_{pl} cathodic of - 1.29 v. This effect is caused by an increase in the plating rate of the zinc interfering metals with E_{pl} .

Kemula et al. (1958) reported the nickel:zinc interaction in a hanging drop mercury electrode and Shain (1963) noted that interactions of this kind were being reported frequently. In spite of these proofs of the interaction phenomena, Matson (1968) did not pursue it and frankly stated that they were probably not important when the aqueous concentration of the interferent was $< 10^{-5}$ M. Fitzgerald (1970) realized that Matson's (1968) assertion was incorrect and that in fact the nickel in seawater ($< 10^{-8}$ M) caused measureable suppression of the zinc signals. He suggested that nickel *subtracted* current from $i_{p\text{ Zn}}$. Seitz (1970) found the interactions of zinc with copper, nickel and cobalt and of copper with nickel, cobalt and silver all at aqueous concentrations $\sim 10^{-8}$ M which is comparable to the concentrations present in natural waters.

For the purpose of demonstrating the magnitude of the interferences, I defined an interference factor as follows:

$$\Delta Z_n / \Delta X \text{ or } \Delta C_u / \Delta X = \Delta i_{p\text{ Zn}} \text{ (or } \Delta i_{p\text{ Cu}}) \div \text{zinc (copper)}$$

sensitivity $\div$ the interferent addition to the test solutions (units ppb).

This is an apparent change in the aqueous zinc or copper concentration per addition of interfering metal. A number of interference factors are listed in Appendix Table II, all determined in Chesapeake Bay water.

Figure 8 The change in i_p Zn with E_{pl} in Chesapeake Bay water for E_{pl} cathodic of - 1.27 v.

The interaction of zinc with copper is a serious obstacle to using this technique for zinc analysis because both the zinc and copper concentrations and the zinc and copper plating rates in natural waters are comparable. I measured the zinc peak current for a range of $C_0 \text{ Zn}$ in the presence of various concentrations of coplated copper. The medium used in this study was half-strength artificial seawater with 0.01 M sodium tartrate, cleaned by exhaustive electrolysis over mercury until neither zinc nor copper signals appeared from a standard plate. The electrode parameters used in this experiment are the standard parameters and are listed in Table 3. The results are shown in Figure 9. Here the total copper concentration (C_{Cu}) in the mercury phase is expressed as the ratio, moles of copper: moles of mercury. The least squares fit is to the eight points along the line where $C_{\text{Cu}} = 0.00$. Fitzgerald's supposition that the interfering metals *subtract* current from $i_{\text{p Zn}}$ (which implies that $i_{\text{p Zn}}$ is totally suppressed when the interfering metals concentration exceeds the zinc concentration) is not realized. The response in $i_{\text{p Zn}}$ with $C_0 \text{ Zn}$ curves toward the origin rather than intersecting the $C_0 \text{ Zn}$ axis. The response also becomes linear at some point with a slope identical to that of the line where $C_{\text{Cu}} = 0.00$.

The suppression of $i_{\text{p Zn}}$ is accompanied by a tailing effect suggesting that the area under the zinc stripping curve may be unaffected by interfering metals. I determined the areas of several zinc stripping curves as a function of $C_0 \text{ Zn}$ in the presence of copper and compared the values with like values of curves produced in the absence of copper. I integrated the curves by cutting out the curve shapes from clean tracing paper overlays and weighing the cutouts to the nearest 10^{-5} grams. I converted the weights to coulombs of zinc by dividing them by the ratio of a weight per a known current $\times$ time product. The results are shown

Table 3

The electrode parameters used in determining the quantitative relationships between copper and zinc.

Electrode Surface Area	0.5 cm^2
Mercury Surface Density	$< 2.5 \times 10^{-7} \text{ Moles/cm}^2$
Mercury Mass	$\sim 1.0 \times 10^{-7} \text{ moles}$
Plating Potential (E_{pl})	$- 1.270 \pm .002 \text{ v}$
Plating Interval	5.00 minutes
Voltage Sweep Rate	$16.50 \pm .05 \text{ mv/second}$
Upper Limit of Cu_{T} and Zn_{T}	$1 \times 10^{-3} \text{ mole ratio}$

Figure 9

Experimental plots of $i_{p\text{ Zn}}$ versus $C_{0\text{ Zn}}$ at various levels of Cu_T in artificial seawater.

in Figure 10. Here the total zinc under the curve is reported as the concentration in the mercury phase (Zn_T) which is the ratio moles of zinc: moles of mercury. The tailing effect increases the difficulty of determining an accurate baseline, thus, since most of the curve area is contained in the lower third of the curve, the precision of the area measurement is worsened in the presence of copper. This effect accounts for the scatter of the measurements when copper is present. Within the limits of the measurements, however, it appears that the area of the zinc stripping curve is independent of coplated copper.

These results suggest that the zinc:copper interaction can be described by the laws of mass action. Apparently zinc and copper form an intermetallic in the mercury phase by the reaction

and when the uncomplexed zinc is stripped off, the intermetallic dissociates supplying more zinc and causing the tailing effect in the zinc stripping curve. The results shown in Figure 9 indicate that the free energy of reaction is not infinity as Fitzgerald's (1970) supposition implies, but rather something less. It is possible that $i_p \text{ Zn}$ is proportional to the free zinc concentration in the mercury (Zn_S) at the beginning of the stripping step. If this is so, by knowing the stability constant for the copper:zinc interaction (K) and Cu_T (which is proportional to $i_p \text{ Cu}$) one can calculate Zn_T which is proportional to $C_0 \text{ Zn}$. To test this proposition, I derived a mathematical model for the response of $i_p \text{ Zn}$ with $C_0 \text{ Zn}$ at various levels of Cu_T and compared the curves generated from the model with the experimental curves in Figure 9. For supporting relationship, I determined the following experimentally:

- a. $Zn_T = f(C_0 Zn)$
- b. $Zn_S = f(i_p Zn)$
- c. $Cu_T = f(i_p Cu)$

For these measurements I used the same medium and electrode parameters as used in the experiments to derive Figure 9. Stripping curve areas were determined and converted to concentration units as described earlier. Relationships (a) and (b) were determined by adding small increments of zinc to a copper free sample. Since copper is absent $Zn_T \equiv Zn_S$. In Figure 11, only relationship (b) is shown. The ordinate could equally well have been $C_0 Zn$. Relationship (c) was determined by adding increments of copper to a zinc free solution. Two separate determinations were made and combined in Figure 12. The data points in both figures are fitted to straight lines by the least squares method. In both cases the fits are excellent and the intercept is within two standard deviation units of the origin.

Using the relationship determined as shown in Figures 11 and 12, I computed Zn_S and Zn_T at various levels of Cu_T from the experimental curves in Figure 9. The mass balance requires that $Zn_I = Zn_T - Zn_S$ where Zn_I is the concentration of zinc removed into the intermetallic. Rossotti and Rossotti (1961) suggest a method for determining the stoichiometry of a complex. To comply with their treatment, I calculated the following:

$$\bar{n} = \frac{Zn_I}{Cu_T} \quad \begin{array}{l} \text{the average number of ligands} \\ \text{(Zn) per central group (Cu)} \end{array}$$

$$a = Zn_S \quad \text{the free ligand activity}$$

and plotted several values of $\bar{n}$ vs. $\log a$ as shown in Figure 13. In this

Figure 10 Comparison of the values for Zn_T obtained with and without copper by integration of the zinc stripping curve.

Figure 11 Plot of $i_p Zn$ versus Zn_S in artificial seawater without copper. The integration of the zinc stripping peak was done by the cut out and weigh technique.

Figure 12 Plot of $i_p \text{ Cu}$ versus Cu_T . The integration was obtained by the cut out and weigh technique.

Figure 13 The formation curve for the zinc-copper intermetallic complex in mercury.

so-called formation curve for the complex, $\bar{n}$ approaches a limiting value of unity. The zinc:copper intermetallic complex is, therefore, mononuclear.

The intermetallic complex can be described by three equations:

$$K = \frac{I}{[Zn_S][Cu_S]} \quad (4a)$$

$$Zn_S = Zn_T - I \quad (4b)$$

$$Cu_S = Cu_T - I \quad (4c)$$

where (I) is the intermetallic complex concentration and Cu_S is the free copper concentration in the electrode before the stripping step begins. The object now is to algebraically compute curves of $i_p Zn$ vs. $C_0 Zn$ at various levels of Cu_T , assuming that $i_p Zn$ is proportional to Zn_S , and compare them with the experimental curves. The stability constant (K), however, cannot be computed independently. It is necessary, to use a value for K which elicits the best agreement between the calculated and experimental curves.

Using equation (4a), Cu_S is expressed as a function of Zn_S , K and (I). This expression is substituted into (4c) and the result solved for (I). This equation is substituted into (4b) to get

$$Zn_S^2 + \left\{ \frac{1 - K Zn_T + K Cu_T}{K} \right\} Zn_S - \frac{Zn_T}{K} = 0 \quad (4d)$$

Any other combination results in an expression wherein Zn_S is not separable. With the aid of a Hewlett-Packard 9810 Calculator, I computed Zn_S over given ranges of Zn_T , Cu_T and K. After converting Zn_S and Zn_T to $i_p Zn$ and $C_0 Zn$ respectively, I have presented the results in Figure 14. Over the range in K shown there is a substantial change in the shape of the modeled curves. A K of 1×10^5 causes the best

Figure 14 Solutions to equation 4d for $K = 1$ and 12×10^4 .

agreement between the modelled and experimental curves regarding the value of $i_{p\text{ Zn}}$ where the response of $i_{p\text{ Zn}}$ with $C_{0\text{ Zn}}$ becomes linear with a slope identical to that of the line where $Cu_T = 0.00$. No value for K predicts the *shape* of the experimental curves when $i_{p\text{ Zn}} < 1.0 \mu\text{amp}$, however. For $K = 1 \times 10^5$, the model predicts a lower $i_{p\text{ Zn}}$ than experimentally obtained. This result suggests that when $i_{p\text{ Zn}} < 1.0 \mu\text{amp}$, it is not proportional to Zn_S implying that when Zn_S is small compared to (I), the dissociation of (I) contributes significant amounts of zinc to that fraction of Zn_T which causes $i_{p\text{ Zn}}$. This concept may be expressed as follows:

$$i_{p\text{ Zn}} = \alpha Zn_S + \beta I \quad (4e)$$

which empirically describes the experimental result that when $I > Zn_S$, $i_{p\text{ Zn}}$ is a function of (I).

Apparently, over a specified range of $i_{p\text{ Zn}}$, the response of $i_{p\text{ Zn}}$ to $C_{0\text{ Zn}}$ as a function of Cu_T conforms with the model that copper and zinc form a mononuclear complex with a $K \sim 1 \times 10^5$ and Zn_S (the uncomplexed zinc concentration) is proportional to $i_{p\text{ Zn}}$. Over another range, $i_{p\text{ Zn}}$ is not so simply related to Zn_S , Zn_T and Cu_T . I did not quantify equation (4e) because the majority of natural water samples caused values of $i_{p\text{ Zn}} > 1.0 \mu\text{amp}$ under the electrode conditions specified in Table 3.

The success of the model discussed above in predicting the experimental effects of the zinc:copper interaction tempts us to extend it to include other metals which affect $i_{p\text{ Zn}}$ and $i_{p\text{ Cu}}$. These other metals, however, usually do not form observable stripping peaks so that an estimate of Co_T or Ni_T which would permit a quantitative treatment analogous to that for the zinc:copper interaction is not possible. But

it should be noted that since zinc strips off early in the potential sweep while the interacting metals come off later, the most likely effect on the zinc stripping curve is tailing accompanied by suppression of $i_p \text{ Zn}$. The same cannot be said for the copper stripping curve since the interacting metals and copper may come off in the same potential region. The effect may be to suppress, enhance or mask the copper stripping maximum. More complex types of interaction have also been observed. In one sample, an addition of nickel caused $i_p \text{ Zn}$ to *increase* suggesting that nickel had combined with a coplated metal which was interacting with zinc and so caused the release of Zn_s . In a sample containing Fe(III) with 0.01 M tartrate, an intermetallic with a unique stripping curve at the cadmium position forms and is apparently affected by zinc, copper and iron.

Of the several other metals which are potential interferers with $i_p \text{ Zn}$ and $i_p \text{ Cu}$, I have tried to quantify the effects from only six. The effects from copper, cobalt and nickel have already been discussed. Manganese (II) and chromium (III) have no measureable effect on the zinc and copper curves at the 10 ppb level. Iron (III) causes the triple complex at concentrations ~ 300 ppb. It is impossible to say if all the interferences have been discovered but since there are so many coplatable metals the chances are good that some have escaped detection.

4.3. Methods for Reducing the Interferences

The scheme of an ideal zinc analysis would somehow prevent the interfering metals from plating. This is probably not possible but I have tried several techniques for reducing the plating rate of the interfering metals and have had some success. The working potential I used (-1.270v)

maximizes the zinc plating rate while minimizing the plating rates of cobalt and nickel. I have also tried to selectively sequester the interfering metals but have had no success. At $\text{pH} > 9.5$ the potential of maximum plating rate of cobalt and nickel shifts farther cathodic than that of zinc but in seawater samples a high pH causes precipitation of $\text{Mg}(\text{OH})_2$. Some of the organic ligands used by polarographers (Kolthoff and Lingane, 1952) to shift the half-wave potential of certain metals are helpful. I had very good results with sodium tartrate at concentrations of $\sim 0.01 \text{ M}$. Appendix Table II shows the decrease in interference factors caused by tartrate.

4.4 Remarks on ASV as an Analytical Method

It is probable that the area of the zinc stripping curve is proportional to $C_{\text{O Zn}}$ and is unaffected by the interacting metals. But the confidence limits on individual measurements of the area become larger as the interfering metal concentration increases due to the tailing effects so that an accurate estimate of $C_{\text{O Zn}}$ would require several measurements. The peak current, $i_{\text{p Zn}}$, can be measured with excellent precision even when the interfering metal concentration is high. Because of the greater precision, I chose to use $i_{\text{p Zn}}$ as the primary indicator of $C_{\text{O Zn}}$ and correct the estimate for the known interferences.

The suppression of $i_{\text{p Zn}}$ from copper can be readily corrected for in each analysis. The range of interferences from other metals can be estimated from the interference factors in Appendix Table II. In Chesapeake Bay, Carpenter and Grant (1968) found that the aqueous nickel and cobalt concentrations were $< 0.5 \text{ ppb}$ and $< 3.0 \text{ ppb}$ respectively.

The cumulative suppression of $i_p \text{ Zn}$ from these two metals will be equivalent to < 0.4 ppb in 0.01 M sodium tartrate solution.

There is also an effect upon the zinc plating rate due to the E_{pl} used (-1.270 v). At this potential, equation (3g) and Figure 5 predict that the plating rate will be a maximum at $C_0 \text{ Zn} = 0.8$ ppb but will decrease to 75% of maximum at 0.1 ppb.

4.5. Correcting for the Copper Interference

Solving equations (4a), (4b) and (4c) for $Zn_T = f(Zn_S, Cu_T, K)$ we get

$$Zn_T = Zn_S \left(\frac{K Cu_T}{1 + K Zn_S} \right) \quad (4e)$$

Each parameter in equation 4e is a linear function of peak height and aqueous concentration as shown in Table 4. The coefficients come from the data in Figures 9, 10 and 11. These coefficients were obtained with one electrode in one standard solution. When using other electrodes in real samples, $i_p \text{ Zn}$ and $i_p \text{ Cu}$ must be adjusted in value to conform with the values expected under the standard conditions so that the coefficients in Table 4 can be used to convert the data to $C_0 \text{ Zn}$. Otherwise with each new electrode and solution a new set of coefficients would be needed. The proportions between the coefficients would be the same in any case but the absolute values would be different. I decided to normalize $i_p \text{ Zn}$ directly to the zinc plating rate (sensitivity) by multiplying it by the ratio of the standard zinc sensitivity to the sample zinc sensitivity. The plating rate is a function of the electrode condition and the chemical state of the metal in solution. It will be shown in a later section that chelation decreases the zinc plating rate.

Table 4

Data from the least squares fits to the calibration curves.

Relationship	Standard Deviation in i_p
$Zn_S = 1.307 \times 10^{-4} i_p Zn$	0.068
$Cu_T = 1.502 \times 10^{-4} i_p Cu$	0.072
$Zn_T = 1.307 \times 10^{-4} i_p^* Zn$	0.068
$i_p^* Zn = 1.027 C_{O Zn}$	0.057
$K = 1.0 \times 10^5$	

Note: $i_p^* Zn$ is $i_p Zn$ in the absence of copper.

By the method used here to normalize $i_p \text{ Zn}$, the final estimate of $C_0 \text{ Zn}$ will include that fraction contained within fast reacting chelators but not the fraction contained in slow reacting chelators. To correct $C_0 \text{ Zn}$ for the copper interference it is necessary to know only $C_{\text{T}} \text{ Cu}$, not $C_0 \text{ Cu}$, hence the method for normalizing $i_p \text{ Cu}$ need adjust only for the electrode condition. In this case I normalized $i_p \text{ Cu}$ to the zinc sensitivity in the absence of dissolved organic chelators. In these samples, the organic matter was destroyed by irradiating the sample with high intensity ultraviolet light, a procedure which I shall describe more fully later. The signal heights, $i_p \text{ Cu}$ and $i_p \text{ Zn}$, were normalized as follows, here (+) indicates the adjusted value:

$$i_p^+ \text{ Zn} = i_p \text{ Zn} [1.027 \div \text{the zinc sensitivity}]$$

$$i_p^+ \text{ Cu} = i_p \text{ Cu} [1.027 \div \text{the zinc sensitivity in chelator free samples}]$$

Using the relationships in Table 4 and the normalized stripping signal heights, equation (4e) is rewritten

$$C_0 \text{ Zn} = \frac{i_p^+ \text{ Zn}}{1.027} \left(1 + \frac{15.0 i_p^+ \text{ Cu}}{1 + 13.1 i_p^+ \text{ Zn}} \right) \quad (4f)$$

To use equation (4f) one needs numerical values for $i_p \text{ Zn}$, $i_p \text{ Cu}$, the zinc sensitivity and the zinc sensitivity in the chelator free sample. The first two numbers are obtained directly from the readout chart. The zinc sensitivity as defined is measured by a standard addition technique. To estimate the chelator free sample zinc sensitivity in a raw water sample, I interspersed raw and irradiated samples in sequence and interpolated between the zinc sensitivities in the irradiated samples.

4.6. The Manipulations in the Analysis

So far I have described the construction of the equipment, the care of the electrode, the interpretation of readout data and the mathematical conversions from readout to analytical estimate. I wish to briefly note the experimental manipulations which I found important in getting reliable numbers. The physical and electrical parameters used are identical to those listed in Table 3. I begin this discussion from the plating and checking of the mercury surface.

The potential is held at -0.15 v and the cell is rinsed with distilled water. A sample (118-130 ml) is then inserted, the gas inlet tube is directed away from the electrode and the gas flow rate is turned on full (~ 180 ml/min). The sample is purged of oxygen in this manner until the oxygen reduction current drops to nearly zero, then the potential is increased to -0.60 v and 1 ml of 1.0 M sodium tartrate solution is added. I found that tartrate solutions are erosive to the mercury at potentials anodic of -0.60 v. When the oxygen reduction current is nearly zero again, the gas flow is reduced to ~ 120 ml/min and the inlet tube is adjusted to blow gas directly on the electrode cap. The potential is adjusted to -1.270 v and the plating interval is completed to the nearest second. The strip is completed to -0.1 v and the plating step is repeated immediately by shorting the sweep capacitor. When the stripping signals are stable and the background current drifts < 0.1 μ amp/cycle, 500 μ l of a standard solution containing 513 ± 1 ng of zinc are added to the sample. The second or third stripping signal after the addition is used for measuring the zinc sensitivity. This minimizes the error due to electrode sensitivity drift. After this, the potential is reduced to -0.15 v, the sample

is removed and the volume measured to the nearest milliliter for calibration purposes, and the electrode and cell are rinsed with distilled water prior to another analysis.

4.7. Analytical Precision and Reagent Blanks

The precision of the $C_{O\ Zn}$ estimate depends upon the precision of each individual datum and upon the relative sizes of the zinc and copper signals. This can be seen by inspection of the copper correction portion of equation (4f).

$$\text{Correction Factor (CF)} = \frac{15.0 \ i_{p\ Cu}^+}{1 + 13.1 \ i_{p\ Zn}^+}$$

When $0 < i_{p\ Zn}^+ < 1 \ \mu\text{amp}$ and $i_{p\ Cu}^+ > 0$, the precision of an individual measurement of $i_{p\ Zn}^+$ can be $\pm 10\%$ so that CF can be large and imprecise.

If $i_{p\ Cu}^+$ is small, CF is also small. When $i_{p\ Zn}^+$ and $i_{p\ Cu}^+$ are both large, both are determined with good precision so CF is calculated precisely.

The precision of replicate analyses was determined on three Chesapeake Bay water samples. The samples were oxidized by high intensity ultraviolet light to destroy the organic chelators, and analyzed on different days with different electrodes. The third sample was divided, one-half being analyzed directly, and the other half being oxidized a second time before analysis to determine the handling blank in the oxidation procedure. The results are shown in Table 5. The calculated CF values varied over different ranges in each sample, CF generally decreasing with each successive analysis. There was no correlation between CF and calculated zinc. The coefficient of variation on the zinc estimate within each sample was 2.8 - 4.4% despite CF

Table 5

Precision of Replicate Zinc Analyses

Sample 1

C _O Zn	CF
2.34	0.24
2.41	0.24
2.52	0.22
2.65	0.20
2.44	0.18
2.62	0.18

Mean = 2.403
 σ^2 = 0.0361
s = 0.190
Coef. Var. = 4.4%

Sample 2

2.80	0.42
2.71	0.38
2.83	0.33
2.72	0.34
2.64	0.30
2.61	0.27
2.78	0.22

Mean = 2.727
 σ^2 = 0.00576
s = 0.076
Coef. Var. = 2.8%

Sample 3 - 1 Oxidation

C _O Zn	CF
2.49	0.74
2.72	0.58
2.70	0.50
2.70	0.47
2.73	0.40

Mean = 2.668
 σ^2 = 0.00806
s = 0.0897
Coef. Var. = 3.36%

Sample 3 - 2 Oxidations

2.49	0.79
2.68	0.62
2.56	0.63
2.73	0.53
2.77	0.44

Mean = 2.646
 σ^2 = 0.0111
s = 0.105
Coef. Var. = 3.98%

Combined Data - Ten Analyses

Mean = 2.657
 σ^2 = 0.00968
s = 0.0984
Coef. Var. = 3.70%

variations of a factor of 2. In Sample 3, the difference in the means of the two sets was well within one standard deviation unit of the mean of either set so the data were combined to calculate a coefficient of variation of 3.70% on 10 analyses. The agreement of the mean values for each set of Sample 3 indicates that the handling blank in the oxidation procedure is insignificantly different from zero. A coefficient of variation of 3.7% can be expected for $C_0 \text{ Zn}$ estimates where $CF < 1.0$. If $CF > 1$, replicate analyses are in poor agreement often varying 20-50% about a mean.

The only reagent which contributed a significant reagent blank was the sodium tartrate solution. I measured the zinc added in 1 ml of reagent at ~ 10 -15 ng. This blank was not corrected for in the analytical estimates.

4.8. The Effects of Organic Sequestering

Organic chelating agents can decrease the plating rate of zinc and copper. Conceptually they do this by increasing the redox reaction free energy and decreasing the diffusivity of the aqueous metal, but the two effects cannot be measured separately. The effect of chelation on the zinc plating rate is demonstrated in Figure 15 using two organic chelators, EDTA and adenine. The plating rate of the complexed metal may vary from zero to the maximum characteristic of the ionic form of the metal. The zinc in the Zn-EDTA complex has a plating rate of zero (Kolthoff and Lingane, 1952). The adenine concentration was sufficient to complex 99% of the zinc but the net plating rate in the experiment of Figure 15b decreased only $\sim 30\%$ suggesting that the plating rate of complexed zinc is greater than zero. We cannot say *a priori* what the

Figure 15 Uptake of zinc into organic phases of lower plating efficiency: (a) $4.2 \times 10^{-8}\text{M}$ EDTA, (b) three additions of adenine, $1.6 \times 10^{-7}\text{M}$, $9.6 \times 10^{-7}\text{M}$, and $9.0 \times 10^{-6}\text{M}$.

plating rate of zinc will be when it is sequestered by chelators which occur naturally in marine systems, but the ASV technique can be used to indicate differences in the zinc (or copper) plating rates in whole samples. The logic behind this technique is developed below.

In analyzing a water sample we obtain stable stripping signals to measure $i_p \text{ Zn}$ and $i_p \text{ Cu}$ initially, and then add a standard amount of zinc to the sample. The second or third stripping signal after this addition (10-15 minutes later) we use to measure the new $i_p \text{ Zn}$ from which we compute the zinc sensitivity of the electrode. Assume now that we have organic chelating agents in the sample which reduce the zinc (and copper) plating rates below that of the ionic forms. We get one set of values for $i_p \text{ Zn}$, $i_p \text{ Cu}$ and the zinc sensitivity from which we compute $C_0 \text{ Zn}$. It is worthwhile to note that the plating rate in the sample with the zinc standard addition is identical to that in the initial sample only if the added zinc is taken up by the chelator in the exact proportion as that present initially. This is unlikely since the standard zinc addition is 1.5×10^{-8} eq. while the exchange capacity of 1 mg of humic acid (which is a large amount of humic acid for a 120 ml water sample) is only $\sim 25 \times 10^{-8}$ eq. Effectively most standard additions of zinc will cause the net plating rate to be closer that of the ionic form. Suppose now that we destroy the organic chelator and redetermine $i_p \text{ Zn}$, $i_p \text{ Cu}$ and the zinc sensitivity from which we calculate a new $C_0 \text{ Zn}$. How will each of the observed parameters have been changed by destroying the chelators? Any operation which increases the plating rate will increase $i_p \text{ Zn}$ and $i_p \text{ Cu}$. But what about the zinc sensitivity and $C_0 \text{ Zn}$? To answer this question we must look more closely at the procedure for determining the zinc sensitivity. When

zinc is added to the sample, the new plating rate depends also upon how fast the new zinc is sequestered. There are an infinite number of possibilities for the reaction rate. If the reaction is very fast, with a rate constant of $\sim 10^4$ /second, chelation would cause $E_p \text{ Zn}$ to be shifted cathodic relative to the $E_p \text{ Zn}$ in a sample free of chelators. In this special case destruction of the chelator would cause $E_p \text{ Zn}$ to shift anodic. In solutions containing slower reacting chelators, however, we can recognize four groups of chelator systems as shown in Figure 16: System A, reaction completed in < 5 minutes; System B, reaction completed in 5-15 minutes; System C, the reaction is not completed but causes a decrease in the zinc signal which is faster than accountable by electrode breakdown; System D, reaction not completed and the zinc signal decrease is not measurably faster than that caused by electrode breakdown. Under each specific chemical condition, vis-a-vis the rate of zinc sequestering by the organic chelators, we will measure a different zinc sensitivity and compute a different $C_0 \text{ Zn}$. The effects upon each parameter when the chelators are destroyed are summarized in Table 6.

Table 6

The changes in $i_p \text{ Zn}$, the zinc sensitivity and the $C_0 \text{ Zn}$ estimate when the solution chelators are destroyed.

System	$i_p \text{ Zn}$	Zinc Sensitivity	$C_0 \text{ Zn}$
A	Increases	Increases proportionally	No change
B	Increases	Increases not proportionally	Increases
C	Increases	Stable signal	
D	Increases	No change	Increases

Figure 16 The rate of change in the plating rate of a zinc standard addition in a solution containing chelators with four hypothetical rates of reaction with zinc.

This fairly simple picture is complicated by the presence of metals which interfere with the zinc stripping signal. If they are in chelated form, their plating rates will increase when the chelators are destroyed. Thus without prior knowledge of the relative concentrations of zinc and interfering metals in chelated form, it is impossible to predict whether $i_p \text{ Zn}$ and $C_0 \text{ Zn}$ will increase or decrease. This situation is illustrated in Table 7. Based upon this conceptual reasoning, I have developed a scheme whereby a sample may be classified (according to the observed changes in the parameters discussed with destruction of the chelators) into categories which indicate the rate of reaction between zinc and organic chelators and the presence of chelated interfering metals. The scheme is shown in Table 8. In practice one cannot differentiate between A and B so B is discarded. The letter (δ) is used to indicate that no zinc chelators were detected.

The presence of interfering metals causes some distortion in the shape of the stripping baseline and in the shapes of the individual stripping curves. Distortion is a sensitive indicator but it is hard to quantify precisely. In experiments with nickel, cobalt and iron, I have noted that when chelators are absent, noticeable distortion can often be caused by as little as 1 ppb of the interfering metal. The following symptoms are suggestive of the presence of interfering metals in solution: 1) a background current $> 3.0 \mu\text{amp}$, 2) extreme curvature under the zinc peak, 3) spurious signals anywhere and 4) spreading of the zinc curve at the base (tailing). When these symptoms appear or when the estimate of $C_0 \text{ Zn}$ decreases when the sample is irradiated, I classify that sample as one which contains chelated interfering metals.

Table 7

Shown in plain lettering are the effects of chelator destruction on the zinc analytical parameters when interfering metals are absent. Shown in italics are the effects when the interfering metals are present in chelated form.

System	Zinc Analytical Signal	Zinc Sensitivity	^C O Zn
A	Increases	Increases - Proportionately	No change
A*	<i>Increases less or decreases</i>	<i>Increases - Same as without interferences</i>	<i>Decreases</i>
B	Increases	Increases-not proportionately	Increases slightly
B*	<i>Increases less or decreases</i>	<i>Increases - Same as without interferences</i>	<i>Indeterminable</i>
C	Increases	Stable Signal	
C*	<i>Increases less or decreases</i>	<i>Stable Signal</i>	
D	Increases	No Change	Increases most
D*	<i>Increases less or decreases</i>	<i>Same as without interferences</i>	<i>Indeterminable</i>

Table 8

The Classification System

The samples are classified according to the changes in the analytical parameters with oxidation.

Class I			Class II		
No interference change			Interferences increase		
System	Zinc Sensitivity	C _O Zn	System	Zinc Sensitivity	C _O Zn
A	Increases	No change	A*	Increases	Decreases
C	Stable		C*	Stable	
D	No change	Increases	D*	No change	Indeterminable
δ	No change	No change	δ*	No change	Decreases

Superscript notation on Class I only

β ≡ equally severe distortion

4.9. Summary

Anodic Stripping Voltammetry can be used in at least four ways to study the chemical behavior of zinc in aqueous solutions. Under certain conditions changes in the stripping peak potential, E_p , with changes in the activity of a complexing anion can be related to changes in the free energy of the stripping reaction and the resulting equations can be used to determine the stoichiometry and stability constant of the complexing reaction. The potential of maximum plating rate appears to be an indicator of the energy state of the metal in solution and may be used to estimate the extent of organic sequestering of zinc or copper in terms of the energy levels of the metals relative to the levels when chelators are absent. As an analytical method, Anodic Stripping Voltammetry can be used to estimate the aqueous zinc concentration directly in natural waters. The accuracy and detection limit of the analysis are limited by the presence of unknown amounts of interfering metals. The upper limit of uncorrectable known interferences is ~ 0.4 ppb of zinc in Chesapeake Bay water based on the analyses of Carpenter and Grant (1968). The coefficient of variation on repetitive analyses is 3.7 % at the 2.5 ppb level. Finally, this technique combined with a method for destroying organic chelators, can be used to detect chelation of zinc and to estimate the rate of reaction between zinc and the chelators.

In the study of the chemical behavior of zinc in Chesapeake Bay which is reported herein, only the latter two applications of the ASV technique are used.

5. A REVIEW OF THE CHEMICAL BEHAVIOR OF ZINC.

5.1. In General

In oceanic and estuarine systems, zinc is found in concentrations of a few parts per billion (ppb) in the water and of tens to hundreds of parts per million (ppm) in the sediments and biota, (Goldberg, 1965). The concentrations in sediments and biota are known to be highly variable but to date the variations have not been successfully correlated with any reasonable chemical parameters. Variations in the water have generally escaped detection because of inadequate analytical techniques. The best example to the contrary is Spencer and Brewer's (1969) study of trace metals in the Sargasso Sea. They found that seasonal variations were $< 20\%$.

Trace metals are exchanged between the phases of a marine system but the processes driving the transport have been studied only in the past few years. Cation exchange desorption was studied by Bachman (1963) and O'Connor (1968). The general finding was that the zinc which adsorbed on solids in freshwater was rapidly desorbed by a small concentration of sea salt equivalent to $\sim 2\%$ of full seawater concentration. Osterberg et al. (1966) noted that only 5% of the Zn-65 on Columbia River solids could be desorbed by seawater, however. It is recognized (e.g. Mortimer, 1970) that the redox potential decrease associated with low dissolved oxygen concentrations cause manganese and iron to change valence and dissolve from the solid hydrous oxide form into the overlying water. One can speculate that the manganese and iron oxide may adsorb large amounts of trace metals which can be released along with the iron and manganese but this phenomenon has not been reported. The number of cation exchange sites in soils or sediments can vary with the relative proportions of

various constituents (Bear, 1964), and with the amount of humic acid adsorbed on the solids. Rashid (1969) found that adsorbed humic acids have exchange capacities ~ 10 fold higher than organic free sediments. The contribution of humic acids to the exchange behavior of sediments can be significant.

Marine animals and plants both accumulate large amounts of zinc, far more than required for metabolic processes (Pequgnat, et al. 1969). The concentration ratio between the organism and the aqueous medium may reach 10^5 . Several workers have identified cation exchange as an uptake process in certain algae (e.g. Gutnecht, 1963; Bryan, 1969) but this is probably not universally employed. In fact results from biological enrichment studies suggest the contrary for most phytoplankton. As suggested by Provasoli (1963) and supported by Davis (1970) many phytoplankton select the chelated form of the metal over the ionic form. The uptake process is probably metabolic but the exact mechanism has not been established.

The findings noted above strongly suggest that organic chelating agents participate in the processes of metal transport. There have been some observations of metal-organic associations in the aqueous phase. Williams (1969) found copper complexes with stability constants greater than 10^{+19} and Fitzgerald (1970) noted extensive copper chelation. Since bacteria (Budd and Spencer, 1968) and phytoplankton (Hellebust, 1970) both use dissolved organic matter, it is possible that a mechanism of trace metal uptake by these organisms involves organic chelators.

Organisms higher in the food web probably get trace metals via their food, but in some cases the metals in food are rejected (Bachman, 1963; Osterberg, et al. 1964). This phenomenon has not been thoroughly studied.

Conceptually, the food of zooplankters can influence their rate of metal uptake. Bacteria, which are both predator and prey to higher organisms (Odum, 1971) may contain higher concentrations of zinc than other phytoplankton. The supplementary food source for zooplankters suggested by Fogg (1966) may be bacteria. Mechanisms for getting the dissolved organic matter energy source into edible particulate form have been suggested by Khailov and Finenko (1968), Darnell (1967) and Sheldon et al. (1967). The most cogent mechanisms involve bacterial activity.

Shellfish and fish also absorb substantial amounts of zinc but their major contribution to metal transport is probably the consolidation of edible material into feces and other waste products which drop out carrying the metal at least temporarily out of the aqueous phase.

5.2. In Chesapeake Bay

The remarks concerning the general distribution of zinc are valid for the Bay. But since the Bay is a complex system chemically, being fed by several tributaries and being strongly influenced by domestic and industrial wastes, no detailed studies of the zinc distribution in the Bay have been completed. Carpenter and Grant (1968) studied the distribution of some trace metals in water samples at the Susquehanna River outfall. Their data is shown in Figure 17. Their results emphasize that during late winter and early spring, the freshet carries large quantities of solid with a high concentration of zinc and other metals into the Bay. During the rest of the year, the input of metals is very small. This is probably the seasonal pattern for most of the tributaries. In general, the chemical behavior of zinc in the Bay is unknown.

Figure 17

The distribution of zinc, nickel, and copper in water samples at the Susquehanna River outfall. From Carpenter and Grant (1968).

Legend: SOL = solution; F.S. = filtered solids; S.S. = settled solids.

6. A SURVEY OF THE ZINC DISTRIBUTION IN CHESAPEAKE BAY WATER

6.1. The questions

The intent of this study was to analyse the aqueous phase of water samples from Chesapeake Bay for variations in time and space of the concentration and the chemical state (vis-a-vis organic chelation) of zinc. Specifically I was looking for the following information:

1. The temporal and spatial variation of the aqueous zinc concentration.
2. The temporal and spatial occurrence of organic sequestering.
3. The type of sequestering; reactive or unreactive.

This information added to a number of observations from other workers and from this laboratory permitted speculation on the following also:

1. The role of aqueous chelators in zinc uptake by the sediments.
2. The effect of cation exchange desorption on the aqueous zinc concentration.
3. The role of bacteria in zinc transport to higher organisms.
4. Cycling of trace metals between sediments and overlying water.

6.2. The Definition of the Aqueous Phase

To avoid excessive handling of the water samples, I separated the aqueous and solid phases by gravity settling. The *aqueous phase* is thus operationally defined as *the supernate liquor resulting from 5 days' gravity settling through a vertical distance of 13 cm in the dark at 3C.* Under these conditions, material with Stokes' diameters $> 0.1 \mu$ should settle out of the supernate (J. R. Schubel, pers. comm.). For a visual examination of the material remaining in the supernate, I filtered 400 ml

of it through an 0.45 μ millipore filter and examined the material collected under a phase contrast microscope. The concentration of material in the supernate was estimated visually to be <1 mg dry weight/liter. The zinc concentration contained in this material from Carpenter and Grant's (1968) analyses of suspended material would be <1 μ g/liter. The justification for using gravity settling to separate the phases is that from the experiences in this laboratory and in others (Marvin et al. 1970) contact with glass and filter surfaces in a filtering procedure introduces an intolerable uncertainty in the procedural blank. I elected to accept a less precise definition of the aqueous phase than the generally accepted definition as that which passes an 0.45 μ filter especially to avoid an unpredictable zinc blank.

6.3. Methods of Sample Collection, Handling and Analysis

Water samples were collected at three stations on Chesapeake Bay shown in Figure 18. The samples were taken between the 13th and 25th of each month from March through December 1971. The depths at Stations 914S, 858C and 818P were 11, 30 and 33 meters respectively. The range of chlorinity encountered was 0.1‰ at 914S in March to 11.9‰ at 818P in September. Three samples were taken at each station; 1, 2 and 4 meters off the bottom. For sample collection, I used one 3 liter Van Dorn bottle. The bottle was attached to the stainless steel winch wire so that it's horizontal center was the desired distance from the bottom of the lead weight. When collecting the sample, I lowered the bottle until the lead weight touched bottom, held the wire taut by hand and released the messenger. After the bottle released, I raised the sample quickly to the surface and drained it into a 1 or 2 liter Teflon bottle which I

Figure 18 The stations sampled on Chesapeake Bay.

rinsed thoroughly with the excess sample. The sample was in the Van Dorn bottle for less than one minute. The samples were refrigerated immediately and in a few hours were transferred to the main laboratory where they stood for at least 5 days in the dark at 3 C. Then the supernate was siphoned off into a plastic graduate using a Teflon tube. The empty bottle was flushed with distilled water, rinsed with a little supernate, and the remaining supernate was returned to it to await analysis.

A portion of each supernate was irradiated for three hours by a high intensity ultraviolet lamp (UV), and the raw and irradiated solutions were analysed alternately. The UV irradiation procedure was similar to that of Armstrong and Tibbitts (1968). I used a 1200 watt mercury vapor lamp (Englehard-Hanovia #189A10). This irradiation has been shown to oxidize the organic matter in solution to its elemental oxides. Fitzgerald (1970) used a less efficient lamp and still successfully broke up the suspended chelators in seawater. I found that a three hour exposure effectively destroyed the qualitative indicators of dissolved organic matter like color and the deposition of residues on surfaces, and I could detect no further changes in the zinc or copper ASV sensitivity by continued exposure to the UV lamp.

The supernate samples were analyzed by the methods described. For direct comparison of zinc and copper sensitivities in raw and irradiated supernate, the sensitivities were determined on one sample from each station. In this determination, no tartrate was added to the samples and the effects of electrode breakdown were corrected for by studying two raw samples separated by one irradiated sample and comparing the results in the single irradiated sample with the average of the results

in the raw samples.

6.4. Evaluation of the Sampling and Handling Procedure

The Bay water receives three exposures to human manipulation: 1) sampling, 2) storage and 3) analysis. There is no direct way to detect contamination at the sampling stage. However, in the vicinity of the water at the time of sampling were a stainless steel wire, a 30 pound lead weight and a chrome plated messenger. The hull of the ship is covered with tin based paint. The galvanized anchor was ~ 100 meters away. The Van Dorn sampling bottle has no metal parts on the inside. I noted also that despite the close proximity of the lead weight, the lead concentration in the samples was always near the limit of detection (< 0.5 ppb), so vertical diffusion of contaminants is probably small. Sample contamination at that stage was probably insignificant.

To detect changes in the aqueous zinc concentration during storage, I added Zn-65 to some test samples stored in either Teflon or polyethylene and measured the Zn-65 counting rate periodically, and measured changes in the aqueous zinc concentration in other samples with storage time. Non-bacterial absorption of Zn-65 on polyethylene was 5-10% of the total present. Adsorption was not detectable on Teflon. Uptake by microorganisms was insignificant over a 5 week storage period when the samples were kept at 3 C in the dark. I found no significant increases in the measureable zinc concentration in test solutions kept for several weeks in Teflon bottles, and Matson (1968) also found that Teflon bottles were inert, causing no changes in the aqueous zinc concentration at the 10^{-10} M level. The blank introduced in siphoning

off the supernate liquor could not be evaluated, but I took care to rinse all surfaces with sample or distilled water before collecting the supernate for analysis. The blank introduced by the handling involved in UV irradiation was found in Section 4.7. to be not significantly different from zero.

In the analysis, the sample was surrounded with Teflon surfaces and had only quartz or Vycor glass dipping into it. There was no measurable change in the zinc concentration during the time needed for analysis. The zinc blank from all reagents except one was insignificant. This was achieved by making microliter additions of the concentrated reagents. As noted in Section 4.7. the 1 ml tartrate addition contained 10-15 ng of zinc which amounts to a ~ 0.1 ppb blank which was not corrected for in reporting the analytical results.

By minimizing sample handling, by using Teflon storage bottles and low storage temperatures and by using an inert analytical cell, I believe that there is no measureable zinc contamination through the storage and analysis steps. But the sampling step may have a systematic error. If an error is related to the equipment used it will be hard to detect.

6.5. Results

The analytical zinc estimates are shown in Figures 19, 20, and 21. for the three stations sampled covering the 10 months from March to December 1971. The raw and irradiated sample values are both plotted and joined straight lines. The regions between the lines are shaded according to which value was larger. Vertical bars at each point indicate the range

Figures 19, 20 and 21

The calculated values of $C_{O\ Zn}$ are plotted with time at each depth and station sampled. Open circles are the values in the irradiated (oxidized) samples; solid circles are the values in the raw samples. The raw and irradiated sets are connected by lines and the spaces in between are shaded according to whether the difference is positive or negative. Vertical lines on some points indicate the range of replicate analyses. Horizontal lines on points indicate that replicate analyses were *not* done. The notation "Fe" on some points means that iron was detected as an interfering metal.

of replicate analyses. If duplicate analyses were not done, a horizontal line is drawn.

The changes in electrode sensitivity to zinc and copper with irradiation of the samples are shown in Figure 22. The percentage increase is calculated relative to the raw water sensitivity. Only one sample was done at each station. Note that the scale difference between copper and zinc is ten-fold.

In Figure 23, the larger mean zinc estimate (either the raw or irradiated sample) is plotted with distance from the bottom, and each month's values are connected by straight lines.

According to the guidelines in Table 8, to each sample I attached a label which best describes the combination of chelators and interfering metals needed to produce the observed differences in the response of the electrode to zinc between the raw and irradiated samples. These labels are presented in Appendix Table III. From the collection of such labels at each station each month, I picked a single label which most closely described the characteristics of the water at that station. These latter choices are presented in Figure 24 as time and space variations in five identifiable categories. There is overlap of the A and D and of the D and δ labels. When A and D are both noted at a station it means that the observed electrode behavior could be explained only by the presence of both types of chelators. If D and δ are both noted at a station, it means that a clear choice could not be made.

6.6. Discussion

Over 90% of the 285 recorded analyses had copper correction factors less

Figure 22 The percentage change in the zinc and copper sensitivities with oxidation. One sample was studied at each station each month.

Figure 23

The distribution of $C_{O Zn}$ with respect to the bottom. The value of $C_{O Zn}$ used is the largest one, either in the oxidized or raw sample.

Occurrence of interferences

Occurrence of C-type chelators

Occurrence of A-type chelators

Occurrence of D-type chelators

Occurrence of no chelators

Figure 24 The temporal and spatial distribution of interferences, chelators and no chelators.

than 1.0. Hence the precision of the bulk of the analyses should be excellent.

The features of Figures 19, 20 and 21 which stand out are the high zinc concentrations at Station 914S in May and the nearly complete sequestering of zinc into organic phases at all three stations in late summer. At no time was there observed a shift in $E_p \text{ Zn}$ caused by irradiation of a sample indicating that organic chelators react with zinc with rate constants less than 10^4 / second.

The high zinc concentration at 914S in May was accompanied by no chelators, no interfering metals and a change in chlorinity over the previous month's measurement (Figure 25). The water found there in May is a mixture of water from the Susquehanna River and water which could be found further south at an earlier date. Since neither source water contained zinc concentrations greater than 6 ppb, as seen from Figures 18 and 19, the zinc which caused the increase in concentration to 16 ppb must have come from the sediments. The strong increase in zinc close to the bottom supports this supposition. Carpenter and Grant (1968) found that the zinc extractable (by 1 M HCl) from Susquehanna River solids coming into the Bay with the spring runoff amounted to ~ 1000 - 3000 ppm by dry weight. The zinc concentrations in surface sediments as determined by acid extraction in this laboratory are ~ 100 - 300 ppm dry weight, so apparently a substantial amount of zinc leaves the solids before permanent burial. Schubel (1968) estimated the sedimentation rate of the northern Bay at 3mm/year . If the dry mass of new solids added is $\sim 0.10\text{g/cm}^2/\text{year}$ and the zinc lost from the solids is ~ 1000 ppm, the zinc available is $\sim 100 \mu\text{g/cm}^2/\text{year}$. I approximated the mass of zinc present in the water in excess of that in

Figure 25 The chlorinity with depth and time at Station 914S.

the source waters by integrating the zinc concentration curve with depth from the bottom to 4 meters off the bottom and between concentrations 6 and 16 ppb. I did not extrapolate the gradient near the sediment surface so this estimate is low. The mass of zinc apparently in excess is $19 \mu\text{g}/\text{cm}^2$, or about 20% of that probably available from the freshly deposited sediments.

The zinc concentration was back to 6 ppb by the June sampling. Since the appearance of the excess zinc was sudden and brief and associated with a change in ionic strength of the overlying medium, it was probably caused by desorption by a cation exchange process. The sequence of events which apparently caused this phenomena is as follows: The solids from the Susquehanna River were deposited on the bottom during the spring freshet. When the freshet subsided in May, the influx of higher chlorinity water caused a rapid desorption of zinc. This model agrees qualitatively with the results of Bachman (1963) and O'Conner (1968) who found that zinc desorption from solids equilibrated in fresh water was rapidly achieved when the solids were placed in $\sim 2\%$ seawater ($\sim 0.4\text{‰}$ chlorinity). There is a difference, as yet unexplained, between these findings and those of Osterberg et al. (1966) that only 5% of the Zn-65 on Columbia River solids could be desorbed by seawater. The process occurring at 914S did not produce observable amounts of interfering metals even though nickel and cobalt are present in the solids (Carpenter and Grant, 1968).

The nearly complete sequestering of zinc in late summer was accompanied by zinc:chelator reactions of intermediate rate (type-C). Interfering metals were not observed during the period. This complete sequestering occurred in water in which the organic matter concentration

was apparently unusually high. I have only qualitative indications to prove this statement, however: 1) the surface water at 818P and 858C were supporting a bloom of the dinoflagellate *Prorocentrum* (Gail MacKiernan, pers. comm.), 2) the collected samples were yellow in color but cleared when irradiated with UV light and 3) frothing and organic residue deposition on surfaces were both quite heavy in the raw samples.

The less obvious features of the data offer some further insight to the chemical behavior of zinc. The vertical distribution of aqueous zinc in Figure 23 shows that particularly at 818P, a gradient exists throughout most of the year. This suggests that zinc is being supplied from the sediments to the overlying water by some process. The average gradient at station 818P was 1.4 ppb/meter between 1 and 2 meters off the bottom. The eddy diffusivity values given by Pritchard (1967) are about $1 \text{ cm}^2/\text{sec}$ in the deeper layers of the Bay but the values could easily be smaller ($\sim 0.5 \text{ cm}^2/\text{sec}$). The flux of zinc necessary to maintain this gradient is $0.008\text{--}0.014 \text{ ng/cm}^2/\text{sec}$ or $0.6\text{--}1.2 \text{ }\mu\text{g/cm}^2/\text{day}$. This flux would cause an increase in concentration of 1 ppb/day in a 1 meter column. Since an increase is not observed, there must be some process returning zinc to the sediments.

The zinc concentration definitely varies with time of the year. The interferent concentration appears to vary also (Figure 24). April and May were marked by low concentrations of chelators and interfering metals both. In June and July, the interfering metals were present in chelated form but the zinc was *not* significantly chelated. August and September were marked by heavy zinc chelation but the interfering metals were undetectable. The interfering metals reappeared in October and were detected sporadically through December. The processes causing

these variations in the aqueous concentrations of zinc and the interfering metals cannot be delineated by the present data. Because the turnover time of the water in the upper Bay is long compared to the time interval between major variations in the zinc and interfering metal concentrations, however, the processes are probably confined to interactions between the water, sediment and biota. More work is needed to understand the relative importance of biological activity and mineralogical changes as metal uptake and resupply processes.

There have been several indications of a selectivity of chelators for cations: 1) it appeared that zinc was selectively desorbed from the sediments at 914S in May, and 2) according to the sensitivity bar graph (Figure 22) copper is selectively chelated over zinc. In another experiment I found that nickel could desorb zinc from organic matter deposited on the analytical cell beaker. Thus, of all the transition metals considered in this study, naturally occurring organic chelators seem to be least selective for zinc. This phenomenon is qualitatively predicted by the Irving-Williams Series (Ringbom, 1963). The position of zinc in this series is not definite. Ringbom also noted (p.9) that, "The complexation tendency of metals belonging to the Irving-Williams Series is particularly pronounced when nitrogen, carbon, or sulfur is the coordinating atom". Since the major natural chelators are humic acids which contain both nitrogen and oxygen functional groups, it is difficult to assign *a priori* a definite chelation order to the metals. It is certain that copper and nickel are more chelatable than zinc, but zinc may be more chelatable than cobalt.

The sensitivity bar graph (Figure 22) offers a qualitative indication of the selectivity of chelators for copper over zinc. The plating rate

increase with oxidation is 10 fold greater for copper than for zinc. Fitzgerald (1970) observed that the potential of maximum plating rate of copper was - 1.0 v in raw seawater, and the copper sensitivities in raw and UV irradiated seawater samples were about the same. Fitzgerald's (1970) findings are in sharp contrast with those reported here. At the plating potential used in this work (- 1.270 v) Fitzgerald's (1970) results would indicate that the copper sensitivity should not change significantly when the samples are irradiated, whereas in fact, the increase is substantial. This suggests that the bulk of the copper sequestered by chelators in Chesapeake Bay is not reducible at the mercury surface, while the bulk of copper in seawater is reducible at the mercury surface. This also suggests that the reaction rate between copper and the chelators which occur naturally in Chesapeake Bay is relatively fast (type A reaction).

Before completing this discussion, two final notes should be added. The zinc sensitivity at some stations in June and July decreased with irradiation of the sample. This cannot be satisfactorily explained. However, it was accompanied by the appearance of unusually high concentrations of interfering metals.

7. THE EXCHANGE OF ZINC WITH SOLIDS

7.1. Short Term Variations in $C_0 \text{ Zn}$

The role of solids in controlling the aqueous zinc concentration has been discussed by several workers (e.g. Bachman, 1963; O'Conner, 1968). In this work also, zinc desorption from river borne solids by cation exchange has been suggested. It is possible that the short term effects of cation exchange can be observed. The zinc transfer could be either into or out of the solids, but in either case any variations in the aqueous zinc concentration should correlate with changes in the suspended solids concentration.

To observe these hypothetical variations, I made a 16 hour anchor station just west of station 914S on August 16-17. The current speed, water conductivity and solids concentration were measured hourly, and samples for zinc analysis were taken at the peaks and troughs of current speeds, 1 and 3 meters off the bottom. These samples were treated as usual but only irradiated samples were analyzed. The measurements of suspended solids content and $C_0 \text{ Zn}$ are plotted with time in Figures 26a and b. The combination of heavy rains, a northerly wind and strong flood tides caused a continuous surface ebb current but strong flooding currents on the bottom. The resulting turbulence suspended large amounts of solids from the bottom.

The solids concentration in samples taken 1 m off the bottom varied over a much wider range than the concentration in those taken 3 m above the bottom. The results indicate that there was no short term effect upon $C_0 \text{ Zn}$ due to the solids. This is so despite a potential input of up to 15 $\mu\text{g/l}$ of zinc from the solid phase, and exposure of the water

Figure 26. The results of the anchor station analyses. (a) Estimates of $C_o Zn$ with time, (b) the suspended solid concentration with time.

to up to 4×10^{-5} equivalent/liter of exchange sites, enough to exchange 1.2 mg/liter of heavy metal cation. Apparently the water and solids are at chemical equilibrium.

7.2. The Interaction of Solids, Organics and Zinc

Several workers have discussed the effects of organic matter on the cation exchange capacity of sediments. Rashid (1969) in particular showed that adsorbed organic matter was a major source of exchange sites. The interaction between dissolved organic chelators and solid adsorption sites has not been studied. It is possible that adsorption of chelates from solution to solids removes zinc from the aqueous phase.

I designed an experiment to observe this hypothetical interaction using Zn-65. The experiment can be described by the matrix below:

	Raw Sediment Added	Oxidized Sediment Added
Raw Water	Set I	Set II
Irradiated Water	Set III	Set IV

Water was collected from near the bottom close to station 858C in July. The sample stood for 30 days in the plastic lined 50 gallon collection barrel. Then the water was filtered through a 0.6 μ membrane filter into twelve 6 liter polyethylene bottles and was stored at 3 C for 14 more days. The settled solids were recovered and dried over silica gel. The water in five of the bottles was irradiated in small batches by UV light. The other seven samples were left raw. Ten microcuries (μ c) of Zn-65 were added to each bottle. Ten 300 mg

portions of sediment were weighed out and reconstituted in 0.1 M NaCl with the aid of an ultrasonic device. Five of the sediment samples were oxidized with 30% peroxide solution, then all the sediments were added to the respective bottles according to the matrix. The bottles were shaken periodically over a three day period and then allowed to stand for 17 days refrigerated at 3 C. Two control bottles had no solids added. After 17 days, the distribution of Zn-65 in each bottle was determined by the following procedure:

- a. A 2 ml water sample was taken for direct counting.
- b. A fraction of overlying water was filtered through a pre-weighed 0.20 μ Nucleopore filter and the filtrate was sampled for a direct count.
- c. Most of the remaining water was siphoned off and discarded.
- d. The settled solids were stirred, spun down on a centrifuge and washed onto a filter.
- e. All the filters were dried over silica gel, weighed and counted.
- f. The bottles were washed with fuming HNO_3 . The acid and rinse water was evaporated to dryness in a Teflon beaker. The salt pellet formed was scraped out and counted.

All counts were normalized to the decay of a standard amount of Zn-65 and corrected for blanks and background when necessary.

The distribution of Zn-65 between the various phases in each bottle is presented in the bar graph, Figure 27. Because the sediments were radioactive, it was too dangerous to analyze them after equilibration, but the initial zinc extractable with 1 M HCl was 80 ppm dry weight. The zinc concentration before addition of the sediments was 13 ppb as determined by the ASV. The total zinc in the water was 78 μg , the added

Figure 27. The distribution of Zinc-65 within each sample bottle. The set numbers correspond to the matrix numbers discussed in Section 7.2.

radioactivity was 10.0 μC . Thus the initial specific activity in the water was $\sim 0.13 \mu\text{C}/\mu\text{g Zn}$. Assuming that the only process occurring was exchange with the sediments, loss of counts from the water indicated that the final specific activity of the water was $\sim 0.11 \mu\text{C}/\mu\text{g Zn}$. The specific activity of the sediment as calculated from the Zn-65 activity deposited and the zinc concentration of 80 ppm dry weight was $\sim 0.06 \mu\text{C}/\mu\text{g Zn}$. Apparently about half of the zinc extractable from the solids with 1 M HCl was also exchangeable with the tracer.

There is no significant difference between the sets in the distribution of Zn-65 so apparently the organic content of either the water or the sediments failed to influence the equilibrium state of the water and the solids to an observable extent.

Mention is made of this experiment for primarily one reason. In the absence of bacterial activity, the radioactive tracer exchanged with about one-half the available zinc. This agrees poorly with the results of Duke et al. (1966) who reported that in an artificial pond, 99.9% of the Zn-65 added *exchanged* with the sediments in 60 days. There is some question that the process encountered in their experiment was actually exchange. The reported specific activity of the sediments was 2 $\mu\text{C}/\mu\text{g Zn}$ at the end of the experiment. The stable zinc necessary to make this isotopic dilution is 5000 g whereas they reported only 660 g available. They also report aqueous zinc concentrations of 8-44 ppm but the concentrations computed from their data of total zinc and total water volume is 12 ppb. Since their results do not appear consistent with simply an exchange mechanism, perhaps they missed a large amount of zinc in a thin layer of sediments at the sediment water interface.

7.3. On Zinc Uptake by Microorganisms

An experiment was designed to detect processes which could remove zinc from the bulk of a sample. Water was pumped from below the photic zone at station 858C in July directly into 6 liter polyethylene bottles.

The water smelled strongly of sulfide at the time of collection, which means that living zooplankton were not present. The zinc concentration was ~ 2 ppb. To half the bottles I added enough formaldehyde to make a 1% solution. These samples were presumably bacterially dormant.

After two hours' delay (traveling to the shore laboratory), 10 μ C of Zn-65 were added to each bottle. I began sampling the water for counting purposes immediately. The bottles were stored at different temperature conditions, indicated by the matrix below:

Storage Temperature	3 C	23 C
Bacterial condition		
Dormant	Set I	Set II
Active	Set III	Set IV

The bottles were stored under the conditions indicated for up to 5 weeks. Between 17 and 35 days of storage, I removed selected bottles and determined the distribution of Zn-65 in the various phase of the sample. The procedure used was identical to that described in Section 7.2., but in this case 0.45 μ millipore filters were used for filtration.

The average Zn-65 loss with time in each set is shown in Figure 28. The distribution of the tracer at termination is presented in the bar graph, Figure 29. Only the conditions of Set IV caused substantial Zn-65 loss from the bulk solution, 55% being gone in 5 weeks. The samples in the Set IV bottles changed in appearance also. The water

Figure 28

Loss of Zinc-65 from the bulk sample. Each number is the average of counts obtained from aliquots of the samples remaining at each sampling. The set numbers correspond to the matrix discussed in Section 7.3.

Figure 29 The distribution of Zinc-65 within each sample bottle.

clarified, the bottle walls turned brown, and a fluffy brown deposit collected on the bottom. Microscopic examination of Set IV water revealed that non-photosynthetic organisms were present and active.

The counting rate of the suspended solids in each set was the same, ~ 1500 counts/minute/mg. The counting rate of the settled material was ~ 2500 in Sets I and II, ~ 4000 in Set III and ~ 15,000 in Set IV. The mass of suspended solids in Set IV was significantly less than in other sets.

Refrigeration seemed to work as well as formalin in stopping the zinc loss from the bulk of the solution but some bacterial activity is indicated still by the increase in Zn-65 on the walls and in the settled solids of Set III over that in Sets I and II.

The experiment answered three important questions. Assuming isotopic equilibrium, (a) from Sets I and II, the filterable suspended solids zinc is 5-10% of the total, (b) from Sets I, II and III, the bottle walls take up 0-2% of the total zinc by non-bacterial absorption and (c) bulk losses can be minimized by refrigeration. In the refrigerated samples, combined losses from wall exchange and bacterial uptake did not exceed 5% in one week and 10% in five weeks.

Other observations are noted below:

1. In Set II, an increase in filterable Zn-65 with time suggests non-bacterial agglomeration of filter passing material into larger particles at room temperature.
2. Microorganisms agglomerate suspended material into settleable particles as seen by a suspended solids concentration decrease in Set IV over the other sets.
3. The transfer of Zn-65 to the bottom in Set IV cannot have come about

exclusively by agglomeration of suspended material, however, because the activity per mass in suspended solids is 10 fold less than in the settled solids.

4. The dry mass of microorganisms in Set IV settled solids is 2-4 mg, as calculated from the difference in settled solids mass between Set IV and the other sets. The amount of tracer in Set IV solids over the other sets is $\sim 2.0 \mu\text{c}$. The specific activity of the water was no larger than $0.84 \mu\text{c}/\mu\text{g Zn}$. Therefore, assuming isotopic equilibrium, the microorganisms contain $\sim 2.4 \mu\text{g}$ of zinc with a concentration of .06-.12% (dry weight). This is a 5-10 fold higher zinc concentration than is usually reported for estuarine or oceanic sediments.

Some process did occur in Set IV samples which caused an accumulation of a large amount of zinc into a separate phase. The control conditions effectively prevented that process from occurring in the other sample bottles. Was the process biological or inorganic in origin? The only inorganic process possible could have been precipitation of manganese or iron oxides. The water was initially anoxic and might have contained dissolved manganese in concentrations up to 1 ppm. If the deposit seen in the Set IV bottles was the metal oxides, the same should have been observed in Set II bottles. In fact, the counting rate of the settled solids in Sets II and IV were radically different. The remaining option is that the process was biological.

CONCLUSIONS

1. The non-settleable aqueous zinc and zinc interfering metal concentrations in Chesapeake Bay vary with time of the year, distance from the bottom and position on the Bay. The concentrations are apparently controlled by the interaction of processes occurring in the sediments and the water.
 - a. Desorption of zinc from the sediments by cation exchange occurs in the upper Bay when higher salinity water intrudes over the sediments deposited by the spring freshet.
 - b. A persistent zinc concentration gradient near the sediments indicates a flux of zinc out of the sediments. The approximate average flux is large enough that measureable increases would occur if there were not an aqueous metal uptake process occurring simultaneously.
 - c. Temporal variations in the concentration of metals interfering with the zinc analysis have been observed.
 - d. The processes which caused variations in the aqueous metals concentrations throughout most of the year were apparently not cation exchange processes but slower acting biological or mineralogical processes. There is not enough information available at this time to estimate the relative importances of the biological and the mineralogical processes in controlling metal concentrations in the aqueous phase.
2. Chelated zinc was a major fraction of the total zinc only in late summer. The dissolved organic matter concentration was exceptionally high at this time and the chelators reacted with zinc with intermediate rates (Type-C). Fast and slow reacting (A and D - type)

chelating systems were observed in the spring and the fall samples. Chelation by these was more noticeable in the fall than in the spring. No vertical pattern in chelation was ever noticed. In no case did destruction of the chelators cause a shift in the zinc stripping potential, so apparently naturally occurring chelators in reacting with zinc have first order rate constants less than 10^4 /second.

3. The influence of chelators on copper and the other interfering metals was much more apparent than their influence upon zinc. The order of cation preference of naturally occurring chelators appears to be

which agrees with the Irving-Williams Series in chelating order.

4. The extent of the zinc sequestering appears to be directly related to the amount of organic matter in the water. There was no evidence that any chelator was *selective* for zinc over other transition metals.
5. Under conditions which favored bacterial growth, radioactive zinc was transferred from the aqueous phase to surfaces and to the bottom of sample bottles. The estimated zinc concentration in the solids produced by this process was 5-10 fold higher than that reported in oceanic or estuarine sediments.

Appendices

Appendix Table I

The Physical Parameters of the Mercury Covered Waxed
Graphite Electrode Required to Allow Proportional Responses

Parameter	Concerning	Upper Limit	Source
Mercury Thickness	Diffusion of plated metal	0.1 μ	Matson, 1968
Stripping Rate (v)	Diffusion of plated metal	30 mv/sec @ 0.1 μ	Matson, 1968
Mercury Surface Density	Stability of mercury droplets	2.5×10^{-7} Moles/ cm^2	Seitz, 1970
Reduced metal concentration (C_R°)	Diffusion of plated metal	1.4×10^{-2} (Mole ratio) for copper	Matson, 1968
Zinc Stripping Peak Height	Convenience	$< 10 \mu\text{amp}$ ($C_R^\circ \ll 10^{-3}$)	This work
Metal removed from solution by plating	Plating rate	$< 5\%$	Matson, 1968 and this work

Appendix Table II

Summary of Sensitivity and Interference Factor Data

		Tartrate			Nc Tartrate		
		Mean	σ	N	Mean	σ	N
Zinc Sensitivity ($\mu\text{a/ppb}$)	Oxidized	0.982	0.196	134	1.140	0.155	27
	Raw	0.958	0.159	69	1.115	0.190	29
Copper Sensitivity ($\mu\text{a/ppb}$)	Oxidized	0.501	0.264	128	1.438	0.450	24
	Raw	0.264	0.079	70	0.540	0.193	26
$\Delta\text{Zn}/\Delta\text{Cu}$	Oxidized	0.490	0.216	126	0.929	0.123	24
	Raw	0.346	0.070	70	0.430	0.076	26
$\Delta\text{Zn}/\Delta\text{Co}$	Oxidized	0.221					
	Raw	0.222	0.058	35	0.38	ID†	6
$\Delta\text{Zn}/\Delta\text{Ni}$	Oxidized	0.072	0.027	33	0.34	ID	12
	Raw				0.252	0.118	21
$\Delta\text{Cu}/\Delta\text{Co}$	Oxidized	0.257	ID	10	0.56	ID	1
	Raw	0.602	ID	10			
$\Delta\text{Cu}/\Delta\text{Ni}$	Oxidized	0.247	ID	7	0.53	ID	6
	Raw	0.084	ID	6			

† Note, ID means the data was insufficient for a variance calculation.

Appendix Table III

The distribution of the sample classifications

	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	
914 S	----	A	δ	δ	A	A + D	δ^*	A*	δ^*	A*	4 m
	δ^β	A	δ	δ^*	A	A + D	δ^*	A*	δ^*	A*	2 m
	C*	A + D [†]	δ	δ^*	A + D	A	δ	(A + D) ^{††} *	δ^*	A*	1 m
858 C	----	A	δ	δ^*	δ^*	C	C	A*	δ	A	4 m
	A	δ	δ^*	δ^*	δ^*	C	C	A*	δ^*	A	2 m
	A	A + D	δ	δ^*	δ	C	C	A*	δ^*	A*	1 m
818 P	----	----	D	D	δ^*	D	C	(A + D) *	A + D	A	4 m
	D*	δ	δ	δ	δ^*	D	C	A*	A + D	A*	2 m
	D*	D	δ	δ	δ^*	D	C	A*	A*	A*	1 m

Notes: † (A+D) implies the presence of both A and D type chelators

†† (A+D)
* implies the presence of both A and D type chelators so that increases in both $C_{O\ Zn}$ and the zinc sensitivity occurred despite an obvious increase in interferences.

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