# COMPLEXING CAPACITIES AND CONDITIONAL STABILITY CONSTANTS OF ZINC-ORGANIC COMPLEXES IN INTERSTITIAL AND ESTUARINE WATERS

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by

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# SUMMARY

The $MnO_2$ method (van den Berg, 1979) has been modified for the study of zinc-organic interactions in small sample aliquots by using Zn65 as a radioactive tracer. The $MnO_2$ is calibrated in a uv-irradiated aliquot of the sample by titration with the radiotracer. The Langmuir isotherm is used to describe zinc uptake by the $MnO_2$.

In the presence of a ligand, such as NTA, the time required for zinc adsorption onto the $MnO_2$ is considerably slower than in the absence of a ligand. The equilibration time depends on the salinity, in that the equilibration time decreases with decreasing salinity. Boric acid buffer is used to fix the pH at a value of 8.2. Furthermore, it was found that the calibrated values must be obtained over the same range of surface coverage of the $MnO_2$ by zinc as occurred during the analysis of sample, because more than one zinc-binding site of variable strength is available on the surface of $MnO_2$.

Results from the analyses of interstitial and surface waters indicate that only 1:1 complexation is predominant. The ligand concentrations in interstitial water samples are 0.016-1.99 µM. These are generally higher than those of surface waters (N.D.- 0.042 µM). The determined values for the conditional stability constant are comparable to those of zinc-humic (reported

by Matsuda and Ito, 1970) and zinc-organic (reported by Hirose et al.,1982) complexes. The values vary from 7.55 to 9.30 (log values) in interstitial waters, and from 8.52 to 8.95 (log values) in surface waters. In water of low salinity, the constants are higher than those at high salinity, which may indicate either reduced competition for ligands from major cations in seawater or that ligands in the two environments are of a different nature. In some samples, the levels of metals are in excess of the ligand concentration, possibly as a result of pollution in those waters.

The inorganic and organic zinc speciation in the samples are calculated with the determined conditional stability constants and ligand concentrations. Organic zinc appears to contribute 31-98% to the dissolved zinc in interstitial waters, whereas the contribution in surface waters is 1-16%. In the cases where the ligand concentration is less than the dissolved zinc concentration the organically-bound fractions are less than usual.

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# CHAPTER 1

# INTRODUCTION

Trace metals may exist in a number of physicochemical forms in natural waters (Florence and Batley, 1980). Natural waters contain a variety of substances capable of forming complexes with dissolved metal ions. These complexing agents can be either inorganic (e.g. $CO_3^{2-}$, $Cl^-$) or organic (e.g. amino acids, humic acids). Metal speciation is a factor which needs to be taken into consideration when the environmental impact of a metal is assessed, because the physical, chemical and biological behaviour of metal ions depends on the chemical state of metals in solution. For example, the toxicity of several transition metals to micro-organisms decreases as a result of complexation, indicating that the free metal ion is the toxic form (Allen et al., 1980); whereas, complexed forms appear to be non-toxic, or at least are considerably less toxic than the free metal ion.

Most natural waters have a capacity to reduce the toxic effects of added trace metals (Sunda and Gillard, 1976; Gächter et al., 1978). This has been attributed to the complexation of added metals by organic ligands present in the water, which is generally referred to as "complexing capacity" of the water. In dealing with unknown ligands, the term "conditional stability constant" is used to describe the strength of such complexation.

Over the last decade, a number of methods has been used to obtain information on complexing capacities and conditional stability constants of trace metals, copper in particular. The use of a weak ion-exchanger, $MnO_2$, in examining the natural water has been proposed by van dan Berg (1979), and van den Berg and Kramer (1979). The advantages of this method over other existing methods result from its weak exchange properties permitting the determination of the complexing properties of weak ligands in solution. The principle of the method is that copper ions in a water sample distribute themselves between a small quantity of added $MnO_2$ (solid) and dissolved complexing ligands. After sufficient equilibration time the sample is filtered, and total dissolved metal is determined by differential pulse anodic stripping voltammetry (DPASV).

In more recent work on the $MnO_2$ method by van den Berg (1982a and b) the use of radioisotopes of copper or other metals as tracers was suggested. Their use during the calibration of $MnO_2$ in the absence of any added complexing ligands would permit greater sensitivity - measuring $10^{-12}$ - $10^{-10}$M metal ions in small sample aliquots - and reduce the interference by contamination, from the filtration step.

Ion exchange has been proven to be a very useful technique for complexing capacity measurements as it can be applied to several metal ions. It provides information on both the complexing capacity and the conditional stability constant. In addition, only the "total" metal concentration needs to be measured because the analysis is preceded by a physical separation on the ion exchanger. This means that any of several sensitive analytical techniques, such as atomic absorption or voltammetry, can be used for the analysis of the metal.

The primary research objective of the study presented in this thesis can be broadly formulated in terms of the intention to further develop the $MnO_2$ adsorption technique, for the determination of interactions of zinc, and possibly of lead and cobalt, with dissolved organic material in interstitial and surface waters. The thesis is outlined as follows:

Chapter 2 describes the general theory of complexation and adsorption in estimating the extent and strength of metal-organic interactions.

Chapter 3 provides a brief discussion of the methods currently used in determining complexing capacity and conditional stability constants in comparison with the $MnO_2$ method, together with results determined in natural waters. The emphasis is on the $MnO_2$.

Chapter 4 reviews zinc, lead, and cobalt speciation to illustrate the possibility of trace metal-organic association in natural water systems and the significance of the role of metal-organic interactions as compared with inorganic speciation.

Chapter 5 presents the developed procedures.

Chapter 6 gives the results and discussion of the analyses of natural water samples.

In chapter 7 the results and implications of this work are summarized; and recommendations for future research are given.

# CHAPTER 2

# THEORY OF METAL COMPLEXATION AND ADSORPTION

## 2.1 THEORY OF METAL COMPLEXATION

When trace metal ions, such as $Zn^{2+}$, are added to a natural water they may become associated with the various organic and inorganic ligands and colloids. When equilibrium is established, the total dissolved metal concentration $[M_{diss}]$ is given by:

$$[M_{diss}] = [M^{2+}] + [MI] + [ML] \qquad 2.1$$

where $[M^{2+}]$ = concentration of free metal ions

$[MI]$ = sum of inorganic metal complexes

$= [MOH^{+}] + [MCO_3^{0}] + [MCl^{+}] + \ldots$

$[ML]$ = concentration of metal-organic complexes

The term stability constant which is used in describing a complex at equilibrium will be discussed in the following section.

### 2.1.1 STABILITY CONSTANTS OF CHELATES

The stability of a complex is conventionally described by its "formation or stability constant", which is the equilibrium constant in which the complex is formed from its constituents. In the case of a mononuclear complex the "stepwise stability constant", denoted by the symbol K, can be generalised:

$$ML_{i-1} + L = ML_i$$

$$K_i = [ML_i]/[ML_{i-1}][L] \qquad 2.2$$

The symbol $\beta$ is used to denote an overall stability constant:

$$M + iL = ML_i$$

$$\beta_i = [ML_i]/[M][L]^i \qquad 2.3$$

where i, in both cases, is the coordination number of the metal ion which is fully coordinated by the addition of the ith ligand, and L represents a ligand.

In the case of protonated complexing ligands, the stepwise stability constant is defined by:

$$ML_{i-1} + HL = ML_i + H$$

$$K_i^* = [ML_i][H]/[ML_{i-1}][HL] \qquad 2.4$$

and the overall stability constant is:

$$M + iHL = ML_i + iH$$

$$\beta_i^* = [ML_i][H]^i/[M][HL]^i \qquad 2.5$$

For polynuclear complexes the overall stability constants for protonated and unprotonated ligands are:

$$mM + nHL = M_mL_n + nH$$

$$\beta_{nm}^* = [M_mL_n][H]^n/[M]^m[HL]^n \qquad 2.6$$

and

$$mM + nL = M_mL_n$$

$$\beta_{nm} = [M_mL_n]/[M]^m[L]^n \qquad 2.7$$

repectively. The subscripts m and n denote the composition of the complex $M_mL_n$ formed (Meites, 1981).

By priming a symbol, one denotes a conditional constant. This means that the side reactions have been taken into consideration, for example, the priming of L (L′) means that only the side reactions of the ligand have been considered. Measures of the extent of side reactions are the so called side-reaction coefficients, or $\alpha$ coefficients, which will be discussed later on.

In this work the conditional stability constant for the formation of complex ZnL is defined as:

$$K_1' = [ZnL]/[Zn^{2+}][L'] \qquad 2.8$$

where $[L']$ is the ligand concentration not bound to $Zn^{2+}$.

On the surface of a large organic molecule, the availabilty of more than one type of site is possible. The binding of a second zinc ion is described by the stepwise conditional stability constant:

$$K_{21}' = [Zn_2L]/[ZnL][Zn^{2+}] \qquad 2.9$$

The formation of $ZnL_2$ complex ions (1:2) is described by the overall conditional stability constant:

$$\beta_{12}' = [ZnL_2]/[Zn^{2+}][L']^2 \qquad 2.10$$

### 2.1.2 THE SIDE-REACTION COEFFICIENT

The concept of the side-reaction coefficient ($\alpha$ coefficient) is very useful in analytical chemistry for simplifying equilibrium calculations. Ringbom and Harju (1972a, b and c) have suggested that the influence of practically all occuring side reactions on a certain main reaction could be taken into account by means of such coefficients. The $\alpha$ coefficient is defined by the expression:

$$\alpha_A = [A']/[A] \qquad 2.11$$

where the term $[A']$ denotes the sum of $[A]$ in every form.

For example, the term $[L']$, in equation 2.8 and 2.10, denotes the sum of $[L]$ and all $[H_nL]$ terms if L is only involved in side reactions with hydrogen or hydroxide forming $H_nL$, $M(H_nL)$ or $M(OH)_nL$.

If the reacting species does not participate in any side reaction, the $\alpha$ coefficient of the species is unity, otherwise $\alpha$ is greater. The relationship between the stability constant of ZnL and the conditional stability constant of ZnL (eq. 2.8) is:

$$K_1' = K_1/\alpha_L \qquad 2.12$$

### 2.1.3 COMPLEXING CAPACITY MEASUREMENT

The total concentration of ligand capable of binding the metal M (assuming one binding site per ligand molecule) can be expressed by:

$$[L_t] = [L'] + [ML] \qquad 2.13$$

and is often referred to as "complexing capacity" (Hart, 1981). To calculate the amount of metal complexed at a particular trace metal concentration, it is necessary to know the value of the conditional stability constant ($K'$) in addition to $[L_t]$.

Most methods of measuring the complexing capacity, $[L_t]$, and, if possible, $K'$, involve a titration of the ligands present in the water sample by additions of known amounts of metal ion and, after a suitable equilibration time, measurement of the unreacted metal ion or related quantity. The free metal ion concentration, $[M^{2+}]$, (or a value related to it) is plotted as a function of the total amount of metal added, $[M_t]$, to the sample. The inflection or change of slope in the titration curve occurs when the concentration of added metal ion is equivalent to that of the ligand. Beyond that value of added metal (metal concentration in excess of $[L_t]$), the free metal ion concentration increases rapidly because the available binding ligands have all been complexed. For the curve to have a distinct "break", the product $K'[L_t]$ must be considerably greater than unity (Shuman and Woodward, 1977; Hanck and Dillard, 1977a).

The conditional stability constant of a 1:1 complex (metal-unprotonated ligand) can be evaluated from equation 2.3 where $i=1$. The concentration of bound metal, $[ML]$, is the difference between the total metal added and the concentration of free and inorganically-bound metal, $[M_t] - [M']$. The concentration of L not bound by M at any point of the titration curve is the difference between the complexing capacity, $[L_t]$, and the amount of bound ligand (ML). Thus the conditional stability constant can be calculated from:

$$K' = ([M_t] - [M'])/[M']([L_t] - [M_t] + [M']) \qquad 2.14$$

Equation 2.14 may be rearranged to give

$$[M']/([M_t] - [M']) = [M']/[L_t] + (K'[L_t])^{-1} \qquad 2.15$$

By plotting the ratio of free to bound metal vs. the free metal concentration, both the complexing capacity (the inverse value of the slope) and the conditional stability constant can be simultaneously evaluated; the inverse value of the intercept is the product of the conditional stability constant and the complexing capacity (van den Berg, 1979, 1982a and b). This method was also adopted by Ruzic (1982). This kind of plot has the following properties:

a) if the slope is very small, the complexing capacity is very large, so the amount of titrant added (an additional amount of the metal) should be increased in order to measure the capacity more accurately;

b) if the intercept on the ordinate is very small, the value for $K_{ML}'$ is very high and measurement should be made over a lower range of titrant in order to determine $K_{ML}'$ more accurately.

For multi-ligand systems, the measured stability constant will not be that for an individual compound, but rather will be an average value based on the overall extent of complexation (Neubecker and Allen, 1983). If each ligand has a different product of the conditional stability constant and the concentration, the ligands will be titrated sequentially as demonstrated by Crosser and Allen (1977) for a mixture of glycine and EDTA. In natural waters, both 1:1 and 1:2 metal:ligand complexes of copper and lead with ligands may exist (Buffle et al., 1977). Mantoura and Riley (1975) reported the existence of several types of complexing sites on humic acid extracted from soil. However, there has been no indication that the ligands present were sufficiently different to be treated independently in interpretation.

In ligand-rich media of high ligand variety, mixed-ligand complexes can dominate the solution chemistry of trace metals (Byrne, 1983). He stated that neglecting mixed-ligand complexation in such a system may cause a substantial underestimation of the degree of metal complexation. A calculation method was also proposed.

The techniques used in measuring the extent and capacity of metal complexation in natural waters has been reviewed by Florence and Batley (1980), Hart (1981), and Neubecker and Allen (1983). However, a brief discussion will be given in chapter 3 for comparison purpose with the $MnO_2$ method.

### 2.1.4 FACTORS AFFECTING COMPLEX FORMATION

It is quite important to mention, at least briefly, some of the factors controlling the complex formation in general. The factors involved are, for example, acidity, temperature and ionic strength which will be discussed separately.

#### 2.1.4.1 EFFECT OF pH ON COMPLEX FORMATION

Ligands owe their coordination ability to the fact that they are Lewis bases (electron pairs donors). Apart from sharing their electron pairs with metal ions, they can also share these electron pairs with hydrogen ions to form their conjugate acids. Since every aqueous solution must contain some hydrogen ions, reactions like ML +

$H_3O^+ = M(OH)^+ + H_2L$ almost always have to be taken into account (competition for ligands between metal ions and hydrogen ions).

Because metal ions are acidic (electron pairs acceptors), there is always a competition for a metal ion between ligands and hydroxyl ions. This effect may be quite important since naturally occurring complexing ligands may have very high acidity constants (see Table 2.1), such as $pKa_2 = 8.8-9.5$ (Takamatsu and Yoshida, 1978) and $pKa_2 \sim 9$ for functional groups of humic acid (Perdue, 1978) so these ligands are partially protonated at the pH of natural waters. For example, equation 2.8 will be used to illustrate the effect of pH change on complex formation.

If Ka is the overall acidic constant of the protonated ligand (HL):

$$Ka = [L^-][H^+]/[HL] \qquad 2.16$$

all unbound ligand $[L'] = [L^-] + [HL]$ 2.17

By substitution of the [L'], equation 2.8 becomes:

$$K' = [ZnL]/[Zn^{2+}][L^-](1 + [H^+]/Ka) \qquad 2.18$$

or

$$K' = K/(1 + [H^+]/Ka) \qquad 2.19$$

From equation 2.19:

1) at $H^+ << Ka$, $K' = K$ (pH has no effect) 2.20

2) at $H^+ >> Ka$, $K' = K.Ka/[H^+]$ 2.21

(K' is a function of pH)

Similarly it can be illustrated, in case of complex formation of a ligand with more than one functional

Table 2.1 Acidity constants of HAs and FAs

| Constant | pKa | Reference |
|---|---|---|
| FA | | |
| $K_1$ | 2.3-2.6 | Gamble (1970) |
| $K_2$ | 5.04 | |
| HA, soil | | |
| $K_2$ | 10.5 | Perdue (1978)* |
| $K_1$ | 5.25 | Stevenson et al. (1973) |
| $K_1$ | 5.05 | Stevenson (1976) |
| $K_1$ | 4.68-5.1 | Takamatsu and Yoshida (1978) |
| $K_2$ | 8.8-9.4 | |
| HA | | |
| $K_1$(av) | 6.9 | Pommer and Breger (1960)* |
| $K_1$ | 2.8-3.4 | Boggard (1974)* |
| $K_2$ | 4.9-5.1 | |
| $K_3$ | 9.4-9.7 | |

all values at 0.1 ionic strength, 25°C
* experimental conditions unspecified

group, that protons may be exchanged for a divalent metal ion:

$$K' = K/([H^+]/Ka_1 + [H^+]^2/Ka_1.Ka_2 + 1) \qquad 2.22$$

where $Ka_2 = [H^+][HL^-]/[H_2L]$

$Ka_1 = [H^+][L^{2-}]/HL^-]$

Here, the concentration of ligand unbound to the metal ion is given by:

$$[L'] = [L^{2-}] + [HL^-] + [H_2L]$$

At:

1) $pH > pKa_1 > pKa_2$, $K' \sim K$ 2.23

(no competition by protons)

2) $pKa_1 > pH > pKa_2$, $K' = K.Ka_1/[H^+]$ 2.24

($K'$ is a function of pH)

3) $pKa_1 > pKa_2 > pH$, $K' = K.Ka_1.Ka_2/[H^+]^2$ 2.25

($K'$ is a function of $[H^+]^2$)

### 2.1.4.2 EFFECTS OF TEMPERATURE AND IONIC STRENGTH

For isothermal reactions:

$$\Delta G = \Delta H - T\Delta S \qquad 2.26$$

where $\Delta G$ is the free energy change , $\Delta H$ is the enthalpy change, $\Delta S$ is the entropy change, and T is the absolute temperature of the reaction.

The $\Delta G$ is related to the stability constant, K, by:

$$-\Delta G = RT\ln K \qquad 2.27$$

and it is also a function of temperature depending on $\Delta S$:

$$(\partial \Delta G/\partial T)_p = -\Delta S \qquad 2.28$$

We can now see that the relationship between $\Delta G$ and stability constant, K, includes the temperature as well.

However, this work has been done at a fixed temperature of 25°C and no attempt has been made to investigate the temperature effect. For more details on the temperature effect see, for example, Meites (1981), Bell (1977).

The ionic strength affects the activity of the ions. Frequently stability constants are determined at very low ionic strengths and the thermodynamic constant at infinite dilution is evaluated from extrapolation. In case of estuarine and sea water the ionic strength are too far from a medium of pure water for those constants to be applied. To correct such stability constants to the desired ionic strength the Davies equation (eq. 2.29) can be used to account for non-specific interactions:

$$\log\gamma = -0.5Z^2\{I^{1/2}/(1 + I^{1/2}) - 0.3I\} \qquad 2.29$$

where Z = ionic charge, $\gamma$ = activity coefficient and I = ionic strength.

It is used in the absence of complex forming medium ions. In practice, it can be used for mono- and di-valent ions up to I = 1M (Dyrssen and Wedborg, 1980).

Usually activity coefficients in natural waters are estimated with an ion-pairing model (e.g. Millero, 1975; Dyrssen and Wedborg, 1974; Stumm and Brauner, 1975). This model assumes the relationship:

$$a_i = [i]\gamma(i) \qquad 2.30$$

where $a_i$ is the activity, [i] is the concentration and $\gamma(i)$ is the activity coefficient of the free or un-complexed i.

The subscripts f and t may be used to indicate free metal ion and total metal repectively. The value $\gamma(i)$ is a function of the ionic strength only and is constant for a solution of fixed composition. The form of complexed species does not affect the thermodynamic activity of the free ion (Millero, 1981). The fraction of free metal ion to total dissolved metal ion is determined from:

$$[M_f]/[M_t] = (1 + K_{ML}^{*}[L_f])^{-1} \qquad 2.31$$

$[M_f]$ is the concentration of a given free metal ion, $[M_t]$ is the total concentration of the metal, $K_{ML}^{*}$ is the stoichiometric stability constant, and $[L_f]$ is the concentration of free ligand.

The thermodynamic ($K_{ML}$) and stoichiometric ($K_{ML}^{*}$) stability constants for formation of an ion pair ($M^{+} + L^{-} = ML^{0}$) are related by:

$$K_{ML} = K_{ML}^{*}(\gamma_{ML}/\gamma_{M}\gamma_{L}) \qquad 2.32$$

Millero and Schreiber (1982) have proposed a method to estimate the total and stoichiometric activity coefficients of ions in average seawater diluted with pure water. They found that the calculated values of the total activity coefficients ($\gamma_t$) are in good agreement with measured values.

They suggested the use of Pitzer's equation (1973) to estimate $\gamma_i$ for ions:

$$\log\gamma_f(i) = Z_i^{2}f + IB_i^{0} + B_i^{1}f_1 + I^{2}C_i \qquad 2.33$$

$f$ and $f_1$ are functions of ionic strength, $B_i^{0}$, $B_i^{1}$, and $C_i$ are parameters determined from the coefficients of Pitzer and Mayorga (1973) for $K^{+}$ and $Cl^{-}$ salts.

$K^*$ (the stability constant for the formation of ion-pair at I = 0.7) can be determined (up to I = 1M) from equation:

$$\ln K^* = \ln K + Z^2 f + IB^0 + f_1 B_1 + I^2 C \qquad 2.34$$

where K is the thermodynamic constant; the parameters Z, $B^0$, $B^1$, C are obtained from the Pitzer parameters for ions and ions pairs.

Millero (1981) has made a comparison between $\gamma_{\pm}$ of ions in river water and seawater diluted to the same ionic strength. This is because of the lack of reliable experimental measurements of $\gamma_{\pm}$ values. From comparison he found that calculated values for $\gamma_{\pm}$ of ions in river water are quite different from those in dilute seawater.

In presence of complex forming medium ions, the constants are determined in the medium for which they are intended to apply (the ionic medium approach). Such constants are often referred to as medium dependent or conditional constants.

## 2.2 ADSORPTION MODELS FOR HYDROUS OXIDES

There have been many adsorption models derived largely for hydrous oxides other than manganese oxide, and they have been recently reviewed by Stroes (1983). Examples of these models are the ion-solvent interaction model (James and Healey, 1972), the ion-exchange model (Kurbatov et al., 1951a and b), the surface-complexation model (Stumm et al., 1976; Schindler et al., 1976), and the site-binding model (Yates et al., 1974). The reason for the lack of adsorption models for manganese oxide may be because there are many types of manganese oxides in which the more amorphous types can be very difficult to identify. However, a number of studies on the adsorption behaviour of $MnO_2$ have been reported which will be mentioned in the following section.

James and McNaughton (1977) have summarized the adsorption behaviour of hydrolyzable metal ions on oxide and other mineral surfaces as follows (James and Healey, 1972; McNaughton and James, 1974):

- Adsorption is strongly dependent on pH and usually occurs over a narrow range of pH.

- The dependence of the fractional adsorption on pH is similar to the dependence of fractional formation of soluble and insoluble hydrolysis products on pH.

- The shape of the fractional adsorption – pH curve shows that $OH^-$ is consumed or $H^+$ is released as adsorption increases.

- The location of the adsorption region on the pH scale is characteristic of the metal ion and its complexes, and relatively insensitive to the adsorbent.

- The chemical interaction between the adsorbed ion and its host surface are similar for certain oxides and other minerals except manganese.

Adsorption data for wide ranges of adsorbate concentration are most conveniently described by an adsorption isotherm such as the Langmuir isotherm (e.g.

Morgan and Stumm, 1964; Posselt et al., 1968; Anderson et al., 1973; van den Berg, 1979), which relates metal adsorbed per unit surface (Tads) to equilibrium adsorbate concentration (C) in the bulk liquid phase. This equation is used because it has been found to provide a good fit to much experimental data even though its basic assumption - constant activity of the surface groups involved in the adsorption reactions - is not always fulfilled. The Langmuir isotherm treats surface sites in an analogous manner to the above treatment of dissolved complexing ligands. It is derived by combining an adsorption equilibrium constant with a mass balance on the total number of adsorption sites and can be described by:

$$Tads = Tmax\{BC/(1 + BC)\} \tag{2.35}$$

It is assumed that $\Delta$Gads (Gibbs free energy of adsorption) is constant, and that Tmax corresponds to monolayer coverage. Its characteristic features are that at low C, Tads is directly related to C; while at high C, Tads approaches Tmax. B is a measure of bond strength.

The Freundlich isotherm is also used to describe adsorption in which the average energy of adsorption decreases with increasing adsorption density to account for electrical interaction at the surface (e.g. Tewari and Lee, 1975; Guy et al., 1976). Benjamin and Leckie (1980 and 1981) have found that oxides such as $\gamma$-FeOOH, $\gamma$-$Al_2O_3$, $Fe_2O_3.H_2O$(am) are comprised of nonuniform adsorptive binding sites. They explained that at extremely low adsorption densities, all sites are available in excess and the surface behaves as though it is composed of identical sites. As the adsorption progresses, the strongest binding sites, which are the first to be occupied approach saturation, and more groups of relatively weak binding sites will be occupied causing the average overall binding strength to decrease. The adsorption density should reach maximum when all sites are occupied. In practice, the maximum value increased with adsorption density and never reached its limit (Benjamin and Leckie, 1981). The Freundlich isotherm should work well in describing the adsorption behaviour of this kind . However, it fails when the adsorption density is low (all sites are in excess).

Benjamin and Leckie (1981) found non-Langmuir behaviour for adsorption of Cd, Zn, Cu, and Pb onto $Fe_2O_3.H_2O$(am) only at low surface coverage and explain it in terms of nonuniform adsorptive binding sites, change in the coulombic interaction between the solid and the adsorbate, and unfavourable chemical interaction between adjacent adsorbed species.

From the above, one should note the important point that all available models assume uniform site adsorption. By doing so they fail to model adsorption accurately over wide ranges of adsorption densities. Thus, alteration should be made to include site non-uniformity for such oxides.

### 2.2.1 ADSORPTION MODELS FOR TRACE METAL ADSORPTION ONTO $MnO_2$

Adsorption reactions at hydrous $MnO_2$ surface are widely considered to be analogous to the formation of soluble complexes (Benjamin and Leckie, 1980), although surface and interfacial phenomena are not yet fully understood (Stroes, 1983). Surface binding sites can, as a result, be viewed as ligands which bind adsorbate ions to an extent dependent upon the concentration of the reacting species (adsorbent and adsorbate) and other solution conditions (e.g. pH, ionic strength or presence of competing ions). In the absence of contradicting evidence, it is reasonable to assume that all surface sites on a given solid are approximately equivalent, and a dispersion of a solid can be treated analogously to a solution with a single type of ligand, for the sake of simplicity, in most studies.

Some evidence has been found for three different types of sites which are responsible for adsorption reactions on $MnO_2$ (e.g.Loganathan et al., 1977; Anderson et al., 1973). Balistrieri and Murray (1982) have concluded that adsorption occurs by one, or a combination, of the following mechanisms:

- exchange with surface bound protons (e.g. McKenzie, 1979)

- exchange with adsorbed electrolyte ions such as Na and K (e.g. Murray et al.,1968)

- exchange with structural $Mn^{2+}$ or $Mn^{3+}$ (e.g.

Loganathan et al., 1977).
The order of decrease in sorption energies at these sites is: structural $Mn^{3+}$ > structural $Mn^{2+}$ > bound $H^+$ (Stroes, 1983). However the surface bound protons on $MnO_2$ are found to be the most abundant in seawater at pH 8 and account for ~85% of the surface sites (Balistrieri and Murray, 1982). This indicates that in order to model complex aquatic systems successfully, the multiplicity of surface sites must be accounted for.

The presence of sites of different binding strength on $MnO_2$ is obviously one of the factors responsible for deviation from the prediction of a simple adsorption model, e.g. the Langmuir model, because such models often treat a solid as an uniform surface. For example, Loganathan and Burau (1973) observed that adsorption onto $MnO_2$ departed from Langmuir linearity at low metal concentrations. They found that the adsorption of Zn and Co onto $MnO_2$ fitted a Langmuir equation only above a certain equilibrium concentration of metal in solution (e.g. > 0.1mM for Zn and Co at pH 4). In this case they proposed that this deviation from Langmuir linearity at low metal concentrations and the simultaneous release of Mn, was due to Co and Zn interchange with Mn in the disordered layer of $MnO_2$ and a double Langmuir equation should be used. The use of the Langmuir model, at high concentrations and high surface coverage, will only give a valid estimate for the maximum adsorption capacity of all available sites together.

In general, it can be concluded that, although adsorption on $MnO_2$ has been extensively studied, the models used to describe the adsorption process have been the same as those originally developed for hydrous oxides in general. However, no attempt was made to correct for the non-constant surface activity which is the basic assumption of the model. It is beyond the scope of this work to provide an improved model for adsorption of Zn onto hydrous $MnO_2$. Some suggestions will be put forward for future development (see section 2.2.3 and Appendix III).

### 2.2.2 THEORY OF THE $MnO_2$ METHOD

The theory of measuring complexing capacity of natural waters by means of weak ion exchangers was developed by van den Berg (1979, 1982a and b) and van den Berg and Kramer (1979). The method has been developed intentionally for use at the very low concentration of ligands in natural waters and can be summarized as follows (For sake of convenience, divalent metal will be represented by $M^{2+}$):

I. In the absence of organic complexing ligand

Adsorption of metal ion on $MnO_2$ is described by the linearized Langmuir isotherm:

$$[M^{2+}]/Tads = [M^{2+}]/Tmax + (B.Tmax)^{-1} \qquad 2.36$$

where Tads = concentration of metal adsorbed per mole of $MnO_2$ in mole

$[M^{2+}]$ = concentration of free metal ions in equilibrium with $MnO_2$

Tmax = maximum value of Tads

B = constant, related to energy of adsorption.

Tads is calculated from

$$Tads = ([M_t] - [M_{dis}])/[MnO_2] \qquad 2.37$$

where $[M_t]$ = initial concentration of metal present, and

$[M_{dis}]$ = total dissolved metal in equilibrium with $MnO_2$.

At very low $[M^{2+}]$, Tads = $K_R[M^{2+}]$, in which $K_R$ = Tmax.B in $mol^{-1}$. $K_R$ can be called the conditional stability constant for adsorption of $M^{2+}$ on $MnO_2$ and can be calibrated at fixed experimental conditions e.g. constant pH, temperature, and ionic strength. In the $MnO_2$ method, the amount of $MnO_2$ used in the equilibration is small (in order to obtain high surface coverage), so the Langmuir equation is used (eq. 2.36) for a good fit of the data.

The relationship between $[M_{dis}]$ and $[M^{2+}]$ can be expressed by:

$$[M_{dis}] = \alpha [M^{2+}] \qquad 2.38$$

where $\alpha = 1 + \Sigma(\beta_i[\text{inorganic } L_i]^{n_i})$ ; $\beta_i$ = the overall formation constant of complexes of each inorganic ligand (inorganic $L_i$ with $M^{2+}$), and $n_i$ = the number of ligands involved in each complex.

The reason for not including the contributions of other complexes, such as those formed with inorganic polynuclear and mixed ligand, is those complexes are assumed to be negligible at low metal concentration and at the natural pH of seawater.

If the $\alpha$ coefficient of the metal ion is not known , the conditional stability constant can be used, for example:

$$K_1'' = [ML]/[Mdis][L'] \qquad 2.39$$

where $K_1' = \alpha_M K_1''$

The constants B and Tmax can be obtained by titrating the $MnO_2$ with metal ions in water at fixed experimental conditions (25°C, pH 8.2). By using the linearized Langmuir equation (eq. 2.36), the plot of $[M^{2+}]$/Tads vs. $[M^{2+}]$ results in a straight line; where the y-intercept represents $(Tmax.B)^{-1}$ and the slope $(Tmax)^{-1}$. Another alternative is a plot of Tads vs. $[M^{2+}]$ which should yield a straight line passing through the origin with slope ($K_R$), at low values for Tads. $[M^{2+}]$ in equilibrium with $MnO_2$ can be calculated, after calibration in a solution of similar composition , by measuring $[M_{dis}]$ (i.e. by ASV or AAS) after removal of $MnO_2$ by filtration or by centrifugation. $[M^{2+}]$ is then calculated either from equation 2.36:

$$[M^{2+}] = \{B(Tmax/Tads - 1)\}^{-1}$$

or

$$[M^{2+}] = K_R/Tads$$

II In the presence of organic complexing ligands (1:1 complexation)

It is assumed that only inorganic metal adsorbs onto

$MnO_2$ and that ML and L′ do not adsorb. Van den Berg (1979) and Stroes (1983) have shown experimentally that this assumption is warranted.

A linear relationship of the following type can be derived:

A) In the presence of a complexing ligand

$$[M^{2+}]/[ML] = [M^{2+}]/[L_t] + ([L_t]K1')^{-1} \qquad 2.40$$

where $[L_t] = [L'] + [ML]$ and $[M_{dis}] = \alpha[M^{2+}] + [ML]$.

A plot of $[M^{2+}]/[ML]$ vs. $[M^{2+}]$ produces a straight line with the slope $([L_t]^{-1})$ and $K1'$ = slope/y-intercept.

B) In the presence of two complexing ligands

The mass balance of the ligands becomes:

$$\Sigma[L_t] = [L_t] + [L2_t] = [L'] + [ML] + [L2'] + [ML2]$$

where $$[L'] = [ML]/[M^{2+}]K1' \qquad 2.41$$

$$[L2'] = [ML2]/[M^{2+}]K2' \qquad 2.42$$

Substitute [L′] and [L2′] (equation 2.41 and 2.42) into the mass balance of the ligands:

$$\Sigma[L_t] = [ML](1 + 1/[M^{2+}]K1') + [ML2](1 + 1/[M^{2+}]K2') \qquad 2.43$$

Rearrangement of this equation gives:

$$[M^{2+}]/([ML] + [ML2]) = [M^{2+}]/\Sigma[L_t] + [ML]/\{([ML] + [ML2])(K1'\Sigma[L_t])\} + [ML2]/\{([ML] + [ML2])(K2'\Sigma[L_t])\} \qquad 2.44$$

where the sum of the complexed metal concentrations is obtained from the mass balance equation of the metal:

$$[ML] + [ML2] = [M_{dis}] - \alpha[M^{2+}] \qquad 2.45$$

At lower values of the amount of added titrant (metal), only the stronger complex, ML, is formed. So

$[ML] + [ML2] \sim [ML]$, and equation 2.40 is still valid in describing metal complexation by a single ligand. On the other hand a plot of $[M^{2+}]/([ML] + [ML2])$ vs. $[M^{2+}]$ will provide the conditional stability constant for the formation of the stronger complex and approximately its real ligand concentration within certain limits of plot. The difference in the products of $K'$ and $L_t$ of each complex determines the error in the detected ligand concentration.

At high $M^{2+}$ concentration, some of the metal ions are complexed by L2. Therefore, [ML] and [ML2] are of the same order of magnitude. If $K2' << K1'$ (assuming a difference of an order of magnitude between $K1'$ and $K2'$), $K2'.\Sigma[L_t] << K1'.\Sigma[L_t]$. Equation 2.43 can be simplified to:

$$[M^{2+}]/([ML] + [ML2]) = [M^{2+}]/\Sigma[L_t] + [ML2]/\{([ML] + [ML2])(K2'\Sigma[L_t])\} \qquad 2.46$$

From this equation (2.46) a plot of $[M^{2+}]/([ML] + [ML2])$ vs. $[M^{2+}]$ will curve during the formation of ML2, as the term $[M^{2+}]/([ML] + [ML2])$ is not constant. To determine values for $K2'$ and $\Sigma[L_t]$, sufficiently defined conditions can only be obtained when both ligands are saturated with metal ($[M^{2+}] > 1/K2' > 1/K1'$). A linear relationship is then obtained from equation 2.45:

$$[M^{2+}]/([ML] + [ML2]) = [M^{2+}]/\Sigma[L_t] + [L2_t]/(\Sigma[L_t])(K2'\Sigma[L_t]) \qquad 2.47$$

where $[ML2]/([ML] + [ML2]) \sim [L2_t]/\Sigma[L_t]$ (at saturation point of both ligands).

A plot of $[M^{2+}]/([ML] + [ML2])$ vs. $[M^{2+}]$ will then yield a slope which approaches $(\Sigma[L_t]^{-1})$, and the y-intercept of a line, drawn tangentially along the plot at high $[M^{2+}]$, is defined by $[L2_t]/(K2' . \Sigma[L_t]^2)$. $[L_t]$ and $K1'$ can be obtained similarly at low $[M^{2+}]$. For better precision in the $[L2_t]$ calculation the $[L_t]$ and $K1'$ are firstly determined, followed by calculation of $[ML2]$ from the mass balance equation (eq. 2.45). Values of $K2'$ and $[L2_t]$ can then be obtained from a plot of $[M^{2+}]/[ML2]$ vs. $[M^{2+}]$ for which all data can be used (rather than only at high $[M^{2+}]$).

More details are given by van den Berg (1979, 1982a and b), van den Berg and Kramer (1979), and Ruzic (1982). Van den Berg (1982a) concluded that the presence of complexes other than 1:1 is insignificant because at low metal ion and low ligand concentrations complexes with two ligands are less likely to be formed.

It is obvious that Langmuir adsorption (eq. 2.36) behaves similarly to 1:1 complex formation (eq. 2.40). Such behaviour was observed by Plasvic et al. (1980) in studying Langmuir adsorption on colloidal particles. Thus, it is reasonable to consider adsorption reactions onto hydrous $MnO_2$ surface to be analogous to the soluble complex formation. However, if the adsorption is not Langmuirian, nonlinearity of such a plot ($[M^{2+}]/Tads$ vs. $[M^{2+}]$) will be found. The nonlinear behaviour of the plot either of Langmuir adsorption or complex formation can be explained by the formation of complexes other than 1:1 by other types of adsorption; by formation of 1:1 complexes with different stability constants (different complexes of the same metal or of the same ligand) or by formation of 1:1 complexes together with Langmuir adsorption (Ruzic, 1982). In dealing with the nonlinear behaviour some suggestions have been put forward in section 2.2.3 (for adsorption), whereas more details on complex formation can be found in, for example, Ruzic (1982).

It is not the objective of this work to develop an appropriate adsorption model or modify the calculation method originally proposed by van den Berg (1982a). All the data were treated as in case of 1:1 complex formation only. The data were fitted by linear least-square regression. In some cases where the least-squares fit to the plot of Tads vs. $[M^{2+}]$ did not yield a straight line through the origin as theoretically predicted, a curve was drawn instead.

### 2.2.3 RECENT DEVELOPMENT OF ADSORPTION MODELS

In an attempt by Stroes (1983) to reproduce the adsorption parameters of $MnO_2$ obtained by van den Berg (1979) it was found that the reproducibility of Langmuir isotherms for a $MnO_2$ surface is generally poor. Another important finding was that deviation from linearity at the lower end (low surface coverage) of the isotherms almost always ocurred without exception. This nonlinear behaviour affects the adsorption parameters estimated from linear regression - particulary the B value. Stroes (1983) suggested that for accurate estimation of Langmuir adsorption parameters, a non-linear regression method should be used, so that there is no weighting of the data points such as in the method proposed by van den Berg (1979). In the Langmuir model B is estimated from the lower part (low surface coverage) of the isotherm while the upper part determines Tmax. It indicates that a proper estimation of both adsorption parameters can only be obtained from data which cover the whole of the isotherm. However, this is not always the case because the basic assumption of the Langmuir of constant adsorption capacity is violated and the deviation from linearity of the isotherm implies differences in adsorption strengths at high and low surface coverage of $MnO_2$. The use of a non-linear regression instead of linear-regression method should reveal whether the adsorption isotherms obtained from replicating experiments are identical or not (Stroes, 1983). Although the use of a non-linear regression method is an improvement in estimating adsorption parameters in the right direction, the use of the Langmuir model does not account for the influence of factors, such as various adsorption mechanisms and non constant activity of the involved surface group, on the overall binding constant.

Recently, a new adsorption model, the Implicit Langmuir model, has been developed to describe $Cu^{2+}$ adsorption onto $MnO_2$ at constant ionic strength of 0.01M $KNO_3$ in the pH range 6-8.5 by taking into account the relative surface coverage at each adsorption point, and by estimating the pH dependency of the binding constant (Stroes, 1983; see also Appendix III). The main advantage of this model over the Langmuir model is that it is able to describe adsorption of trace metals on $MnO_2$ more accurately at low solution concentrations and low surface coverage of the $MnO_2$. This, in turn, will help in determining more precise values of conditional stability constants in the $MnO_2$ method (van den Berg, 1979, 1982a and b) since the constants are derived at both low ligand and low metal concentrations. The linearized Langmuir equation (eq. 2.36) tends to overestimate the value for Tmax (at high surface coverage) and underestimate the value for B (at low surface coverage) (Stroes, 1983).

It would be useful if the Implicit Langmuir model (Stroes, 1983) was further extended to higher ionic strengths and with trace metals other than copper.

# CHAPTER 3

# DETERMINATION OF COMPLEXING CAPACITY AND CONDITIONAL STABILITY CONSTANT

## 3.1 INTRODUCTION

Metal-dissolved organic interaction have recently received considerable attention. In order to quantify complexing processes, measurements of stability constants for metal-organic complexes need to be made. However, a stability constant , which is a thermodynamic quantity based on activities, can not be used due to considerable lack of information on the chemical properties of the complexing organic matter (e.g. the concentration of the organic ligand, and the number of complexing sites available for metal complexation on these molecules). Therefore, conditional stability constants are obtained instead. Such a constant can be considered as an average stability constant for the different sites on organic material, and valid only at fixed solution conditions (e.g. pH, ionic strength and temperature) (Malcolm et al., 1968). Another parameter to be measured is the complexing capacity. This term has been used to describe the total concentration of potentially available metal binding ligands, $[L_t]$, found to be present in a particular natural water (Hart, 1981). However, the nature in which the term is used is inconsistent. The term "complexing capacity" is most often operationally defined by the measurement itself because the amount of free or labile metal may not be the same when measured by electrochemical, biological, ion exchange or other techniques (Neubecker and Allen, 1983). For example, Figura and McDuffie (1980) have shown that the results obtained from ASV and ion exchange depend on the equilibrium time of the method.

Copper is the most frequently chosen metal in complexing capacities studies, because it forms relatively stable complexes. Assuming comparable metal concentrations, transition metals such as Cu, Ni or Pb generally have greater affinities for organic and inorganic ligands than metals such as Na, Mg, Ca, or Mn. Thus, the extent of complexation will vary and is greater for the more strongly chelated metals. The use of copper will enable the estimation of the total complexing capacity because of this property. The use of this strongly chelated metal has further implications. Chau (1973) found that the metal, not only chelates with uncomplexed ligand, but also displaces metals from complexes of a weaker character. This indicates that the measured complexing capacity is a measure of all the complexed and free ligands which will preferentially form the new metal complex. Another implication is that none of the existing methods are able to distinguish between the complexing capacity of a sample which has already been expended by naturally ocurring metal ions and the unexpended fraction available for further complexation. Most of the previous work, therefore, aims to measure the reserve capacity of a water to complex metals, rather than the total complexing capacity.

The complexing capacity found in natural waters appears to be mainly associated with "dissolved" organic matter (Hart, 1981) because it is found to be significantly reduced or even removed from many waters after U.V. photolysis (Shuman and Woodward, 1977; Sukai and Healey, 1978). However, inorganic colloids may also contribute to the complexing capacity in natural waters (Florence and Batley, 1980).

Fulvic acid and organic matter of similar character are thought to be of prime importance as ligands in natural waters (Reuter and Perdue, 1977) and in sediments (Nissenbaum and Swaine, 1976). The extent of complexation of heavy metals by aquatic humic substances is dependent on the concentration of humic substances and the competition for available complexing sites between trace metals and major cations (Reuter and Perdue, 1977). The effect of ligand size on the complexing capacity for several metals in Ottawa River was studied (Ramamoorthy and Kushner, 1975a) which showed that Cu(II) and Pb(II) complexation was quite dependent on the molecular weight fractions of the complexing ligands while Hg(II) and Cd(II) showed little dependence. This indicates that different ligands preferentially form complexes with individual metals.

The values of stability constant for metal-fulvic complexes reported in natural waters vary considerably with pH and ionic strength (e.g. Schnitzer and Hansen, 1970), and with the nature of the studied humic substances (e.g. Matsuda and Ito, 1970; Shuman and Cromer, 1979). For example, the conditional stability constant of metal-humic substances was found : to decrease with ionic strength (Schnitzer and Hansen, 1970), increase with pH up to the point where metal hydroxide precipitates (Cheam and Gamble,1974), not to increase with degree of humification of HA (Ardakani and Stevenson, 1972), to increase with degree of humification (Matsuda and Ito, 1970), to be larger for isolated HA than in raw water sample (Shuman and Cromer, 1979; Saar and Weber, 1980) and in interstitial waters of freshwater lake and coastal sediment (Sohn and Hughes, 1981) while similar values were obtained between metal and fulvic acid both isolated and in natural waters (Shuman and Cromer, 1979). In addition, the nature of each metal used in the determination of stability constants has, to some extent, an effect on the determined value , i.e. gel complexometry (as used by Mantoura and Riley, 1975) often overestimates the molecular weight of complex material which is later used in the calculation of stability constant.

At high ligand concentration, the failure to include complexes other than 1:1 may introduce a serious error in the prediction of the extent of the metal-organic complexation, as the assumption that only 1:1 complex dominate is acceptable only at low metal concentrations. The presence of complexes other than 1:1 has been reported for copper by Bresnahan et al.(1978), Buffle et al.(1977), Guy and Chakrabarti (1976), Hirose et al. (1982), and Mantoura and Riley (1975), for lead by Stevenson (1976, and 1977), and Saar and Weber (1980), and for zinc by Courpron (1967), Hirose et al.(1982), and Imber and Robinson (1983). However, only 1:1 complex formation has been reported in interstitial waters (Sohn and Hughes, 1980).

The presence of strong complexing ligands (stronger than humic substances) in natural waters may be significant to the speciation of metals (Ferguson and Bubela, 1974; Guy et al., 1976; Morel et al., 1973). For example, at low copper concentration (ca. < 0.1µM) almost all copper would be bound to such ligands (Hart, 1981). Only few studies detected the presence of such ligands at very low concentrations in natural waters (Gächter et al., 1978; McKnight and Morel, 1979; Hirose et al.,1982). Such ligands may not have been observed by other studies because these ligands : (Hart, 1981)

- may exist in certain waters only,
- the size of metal addition in the titration experiment may be too large,
- alteration in molecular configuration or in the number and types of available binding sites of ligands after preconcentration as required by some methods,
- available strong ligands may already be taken up by metal naturally present, added in the blank or other

more strongly binding trace metals.

Another factor that should be taken into consideration is the rate at which trace metals added to a natural water are complexed. Most of the complexing capacity techniques employ a rather short equilibration time (10mins - 2h) between the trace metal added and the solution. It is likely that these methods measure only the short-term complexing capacity of that water and therefore, underestimate the total complexing capacity. Supporting evidence comes from studies of Sukai and Healey (1978) who found a rather slow rate of complexation between copper and organic ligands, from interstitial water (~110 mins. for 50% decrease in labile copper concentration); and Tuschall and Brezonik (1980) who found equilibration of copper spike was achieved in one hour in freshwater samples.

It can be concluded that the ability of a particular water to bind added metals depends on both ligand concentration and the strength of the complex formed. Ligands stronger than fulvic acids seem to be absent from natural waters because of the inability of current methods to detect such ligands. The values reported for complexing capacities and conditional stability constants should be viewed with great care if one tries to compare these results, since most of the reported complexing capacities represent only a fraction of the total complexing capacity of water samples and the constants are only conditional. Even though these values are not completely accurate, they permit speculation regarding the extent of complexation in natural waters. However, considerable care must be taken because extrapolation of the constants from one pH to another may not be valid, and different types of complexes may be formed at higher ligand concentration than at lower (i.e. 2:1 complexes are favoured at high ligand concentration) unless one works at very low free metal concentrations. Nevertheless, if due consideration is given to the limitations of these values, they can provide a qualitative or semiquantitative description of metal-organic interactions in natural waters (Mantoura and Riley, 1975).

## 3.2 COMPARISON OF TECHNIQUES

Several techniques for measuring complexing capacities (e.g. Chau et al., 1974; Chau and Chan, 1974; Ramamoorthy and Kushner, 1975a; Guy and Chakrabarti, 1976) and a large number of methods for determining conditional stability constants (e.g. Rosotti and Rosotti, 1961; Beck, 1970; Schnitzer and Khan, 1972; Shuman and Woodward, 1973, 1977) are available. Due to inherent definitions and assumptions, the results obtained by different methods can not be compared directly. These methods will be briefly reviewed in this section as a guide in comparing with the $MnO_2$ method which will be discussed separately.

The methods currently used in determining complexing capacity and conditional stability constants, can be catagorized into five main groups (Neubecker and Allen, 1983). The features of each methods are summarized below.

I. Voltammetric techniques

ASV and DPASV are commonly used techniques (e.g. Chau et al., 1974; Shuman and Woodward, 1977; Shuman and Cromer, 1979). The principle of the method is to titrate the sample which contains the complexing materials with a metal ion. The free or labile metal fraction is then monitored by DPASV and plotted as a function of the added total metal concentration. Both the complexing capacity and conditional stability constant can be calculated by extrapolation techniques. The main features of this method are:

- Great sensitivity and specificity towards the labile metal.
- Reasonably rapid.
- Applicable over a wide range of pH.
- Possibility of organic adsorption onto mercury electrode.
- Metal complexes may dissociate at the electrode during plating.

II. Ion Selective Electrode method

This method is similar to the voltammetric methods in that the electrode responds only to free or labile metal by measuring a change in potential, no redox reactions occur, and in general it is used to follow the course of potentiometric titration (e.g. Ramamoorthy and Kushner, 1975a,; Giesy et al., 1978). The method:

- is specific in the species being measured;
- has low sensitivity;
- has a possible drawback of organic ligand adsorption onto the elctrode's surface.

### III. Ion Exchange method

This method has been well established and used to determine a metal-ligand stability constant. It provides information on both the complexing capacity and conditional stability constant (e.g. Ardakani and Stevenson , 1972; Crosser and Allen, 1977) while only total dissolved metal needs to be measured after a separation of the ion-exchanger. The method:

- is based on thermodynamic rather than kinetic properties of the complex;
- can be used with any sensitive technique in measuring the total metal in solution after equilibration;
- can be applied successfully, providing that no metal complexes or ligands adsorb to the ion-exchanger;
- may be adversely affected by slow kinetics.

### IV. Biological method

The biological method measures both complexing capacity and conditional constants by measuring the growth rate (or any related parameters) of the tested organism as a function of added metal ions, the fraction of bioavailable (free) metal in solution will then be determined (e.g. Gillespie and Vaccaro, 1979; Gächter et al., 1978). The main features are:

- Great sensitivity towards free metals.
- Data produced are amenable to biological interpretation.
- The tested species can respond to factors other than the free metal concentration (i.e. other materials can exhibit toxic effects on the organisms).
- Nutritional requirements of the organisms and analysis time, which may be lengthy, may limit the application of method.

### V. Solubilization method

This method has been introduced by Kunkel and Manahan (1973) for measuring complexing capacities of strong ligands. The characteristics of this method are:

- Relatively simple and free of interference (i.e. only total dissolved metal needs to be measured).
- An experimental pH around 10 is required. Thus, the natural equilibrium of the sample is seriously altered.
- Insensitive to a variety of weakly complexing biogenic ligands.
- Possibility of organic ligand adsorption onto the

solid metal hydroxide.

- Solubility is operationally defined.

VI. Miscellaneous method

There are several additional techniques used to measure the amount of uncomplexed metal in solution. For example,

- The use of Chelex-100 resin to measure the concentration of strong ligands in solution. The technique does not determine weak metal complexes and the amount of metal, which is exchanged depends on the equilibration time (Figura and McDuffie, 1980).

- Gel filtration has been used to exclude complexes formed between macromolecules, transition metals and the free metal ions (e.g. Mantoura and Riley, 1975; Mantoura et al., 1978a). The technique fails to separate small metal complexes from the free metal ion.

- Dialysis has been used to determine the complexing capacity (Truitt and Weber, 1981) but is rather time consuming and requires a large sample. However, it is quite sensitive to micromolar quantities of complexing agents.

- Ligand exchange has recently been employed in measuring conditional stability constants of organic copper and zinc in seawater (Hirose et al., 1982). By inducing a ligand exchange reaction between ligands of natural origin and EDTA the complexing capacity and conditional stability constants can be calculated. The complex of the natural organic ligand is separated by adsorption on XAD2 resin.

It is obvious that each method has its own limitations on the basis of one or more of the following reasons: requirement of unnaturally high (free) metal concentrations to work with (e.g. ion selective electrode), applicable at relatively low pH values in order to keep the metals in solution (e.g. ion selective electrode), the ligand concentration needs to be very high ($10^{-3}$-$10^{-4}$M) and preconcentration of a natural sample is required (e.g. ion exchange method), the ligand concentration needs to be known (e.g. ion exchange, gel permeation), the method only works for strong complexes having high ligand concentrations (e.g. gel permeation), alterations of the sample are unavoidable through additives and concentration procedures (e.g. solubilization method), or the method is time consuming (e.g. dialysis method). Generally, it can be concluded that for most of these methods other than $MnO_2$ method, which will be discussed separately, either the complex needs to have a very high stability constant or the ligand concentration needs to be very high or known in order that the constants can be measured successfully. Artificial ligands such as EDTA and NTA form complexes with relatively high stability constants while naturally occurring ligands tend to be much weaker (Table 3.1). Although a small number of studies have reported the presence of strong complexing ligands in natural waters

(Gächter et al., 1978; McKnight and Morel, 1979; Sunda and Hansen, 1979; Hirose et al., 1982), their existence is still controversial. Most methods are not sufficiently sensitive to detect natural complexing ligands, as these often occur at very low concentrations.

It is important to discern between methods in which the ligand concentration is not limiting and is expected to be very high, and those methods which measure at the very low ligand concentration present in natural environment, when the conditional stability constants obtained from different methods are compared. The validity of the constants determined for natural material is still doubtful, although many methods have been shown to produce valid results for relatively pure compounds. In Table 3.1 a literature survey is summarized of complexing capacities and conditional stability constants for complexes of metals and natural organic matters of different sources, and of the method of determination.

## 3.3 THE $MnO_2$ METHOD

The $MnO_2$ method, originally developed by van den Berg (1979), is an indirect measurement technique that links the free metal ion concentration to the concentration of metal which adsorbs onto an inorganic oxide. A certain amount of $MnO_2$, calibrated for Cu uptake, is added to the sample to act as a weak ion exchange resin. Titrating the sample , at constant pH and fixed ionic strength with copper causes the organic

Table 3.1 Typical values of complexing capacities (C.C.) and conditional stability constants ($K'$) in natural samples.

| METAL | C.C. (µm) | log K | pH | METHOD | REF. |
|---|---|---|---|---|---|
| Lake | | | | | |
| Cu | - | 6.1($K'$)<br>3.8($K_2'$) | 6 | b | 1 |
| | - | 4.8-5.0($K'$)<br>9.5-10.1($\beta'$) | 6 | b | 2 |
| | 0.15-0.73 | - | - | a | 4 |
| | 0.52-0.70 | - | 6.8-7.8 | a | 5 |
| | N.D.-8.6 | - | 5 | b | 9 |
| | - | 8.42($K'$av)<br>8.80($K_1'$)<br>8.05($K_2'$) | 8 | f | 18 |
| | - | 5.67-5.96 | 7 | a | 24 |
| | 20-126 | 4.5-5.7 | - | a | 25 |
| | 0.2-3.0 | 7.6-8.5 | 7.6 | c | 29 |
| | 0.33-2.8 | 7.6-9.5 | 7.4-8.4 | c | 31 |
| Co | N.D. | - | - | a | 12 |
| | 0.4-1.6 | - | 7 | a | 13 |
| Cd | N.D.-0.77 | - | 5 | b | 9 |
| Ni | - | 5.14($K'$av) | 8 | f | 18 |
| Pb | - | 5.5-6.3<br>10.4($\beta'$) | 6.7 | b | 2 |
| | 3.8-16.5 | - | 5 | b | 9 |
| | - | 3.7-5.1($K_1'$)<br>8.8-10.1($K_2'$) | 4.5-6.0 | b | 23 |
| Zn | - | 2.83 | 3.5 | c | 6 |
| | - | 5.14($K'$av) | 8 | f | 18 |
| River | | | | | |
| Cu | 0.72-0.74 | - | - | a | 3 |
| | 0.44-1.0 | - | - | a | 4 |
| | 2.7 | - | - | b | 9 |
| | 0.88-1.08 | 9.9-10.7 | - | a | 15 |
| | 15-23 | - | 9.8-10.2 | e | 17 |
| | 25 | 3.53-3.82 | 7.3 | b | 22 |
| | 0.9-160 | 9.7-5.6 | 7 | b | 28 |
| | 0.21-30 | 9.5-4.9 | 6.8 | b | 28 |
| | 5-30 | ~7.8 | 7.6 | c | 29 |
| Co | 0.6-1.6 | - | - | a | 13 |
| Cd | 0.23 | - | - | b | 9 |
| | 5 | 3.58-3.75 | 7.3 | b | 22 |
| Hg | 55 | 5.9-6.23 | 7.3 | b | 22 |
| Pb | 8.2 | - | - | b | 9 |
| | 19 | 3.7-4.1 | 7.3 | b | 22 |
| Estuary | | | | | |
| Cu | 0.04-0.19 | - | - | d | 10 |

Table 3.1 cont.

| METAL | C.C. (μm) | log K | pH | METHOD | REF. |
|---|---|---|---|---|---|
| Algal exudate | | | | | |
| Cu | 0.7-6.7 | 7.7-8.6 | 7.6 | c | 30 |
| | 0.03-0.07 | 10.1-10.7 | - | d | 7 |
| | 1.8-2.6 | 7.4 | | | |
| Zn | 0.05-2(CC1) | 6.5-5.8($K_1'$) | 7.7 | a | 16 |
| | 0-4.4(CC2) | 7.2-6.2($K_2'$) | | | |
| Seawage | | | | | |
| Cu | 53 | - | 9.8-10.2 | e | 17 |
| Co | 4.1 | - | 7 | a | 13 |
| Activated sludge | | | | | |
| Cu | 47 | - | 9.8-10.2 | e | 17 |
| Aquarium water | | | | | |
| Co | 7.5 | - | 7 | a | 13 |
| Seawater | | | | | |
| Cu | 0.21(CC1) | 11.8($K_1'$) | 8.1 | f | 14 |
| | 0.007(CC2) | 13.8($K_2'$) | | | |
| | 0.11-0.17 | 9.78-9.86 | 8 | c | 32 |
| Zn | 0.008(CC1) | 9.3($K_1'$) | 8.1 | f | 14 |
| | 0.005(CC2) | 10.7($K_2'$) | | | |
| Soil, sediment and clay | | | | | |
| Cu | - | 5.6 | 7 | c | 8 |
| | - | 6.2 | 6.8 | f | 11 |
| | - | 6.23-6.56 | 8 | f | 26 |
| | - | 8.65($\beta_2'$) | 5 | a | 29 |
| Pb | - | 6.53($K_1'$) | 6.8 | f | 11 |
| | | 5.3($K_2'$) | | | |
| | - | 7.49 | 8.1 | f | 19 |
| | - | 6.3 | 6 | b | 23 |
| | - | 7.03($\beta_2'$) | 5 | a | 27 |
| | - | 8.35 | 5 | b | 28 |
| Zn | - | 3.92-10.33 | 7 | c | 20 |
| | - | 6.8 | 7 | c | 21 |
| | - | 4.59-5.51 | 8 | f | 26 |

Note to Table 3.1

Method

a: Voltammetric method inc. potentiometric tiration, amperometric titration and ASV.

b: Ion selective electrode method

c: Ion exchange method inc. $MnO_2$ method

d: Biological method

e: Solubilization method

f: Miscellaneous inc. dialysis, gel complexometry, ligand exchange etc.

References

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2. Buffle et al. (1977)
3. Campbell et al. (1977)
4. Chau (1973)
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6. Courpron (1967)
7. Gächter et al. (1978)
8. Geering and Hodgson (1969)
9. Giesy et al. (1978)
10. Gillespie and Vaccaro (1978)
11. Guy and Chakrabarti (1976)
12. Hanck and Dillard (1977a)
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14. Hirose et al. (1982)
15. Hoffmann et al. (1981)
16. Imber and Robinson (1983)
17. Kunkel and Manahan (1973)
18. Mantoura and Riley (1975)
19. Mantoura et al. (1978a)
20. Matsuda and Ito (1970)
21. Randhawa and Broadbent (1965)
22. Ramamoorthy and Kushner (1975a)
23. Saar and Weber (1980)
24. Shuman and Cromer (1979)
25. Shuman and Woodward (1977)
26. Sohn and Hughes (1981)
27. Stevenson (1977)
28. Sunda and Hansen (1979)
29. van den Berg (1979)
30. van den Berg et al. (1979)
31. van den Berg and Kramer (1979)
32. van den Berg (1982b)

material present and the $MnO_2$ to compete for the metal. The solid is removed from the sample (after allowing for a certain period of equilibration) by membrane filtration, and dissolved Cu in solution is measured by ASV. The difference between this and ordinary ion exchange methods lies in the relatively small amount of $MnO_2$ added to the sample, presumably causing an insignificant alteration in the sample composition.

Van den Berg (1979) mentioned the strong points of his method as follows:

1. The method has a sound theoretical basis and functions in a equilibrium situation with metal ions and ligands.

2. No preconcentration is required which means minimum disturbance to the natural water sample.

3. Due to the weak adsorption character of $MnO_2$, enough metal, even in such a dilute system as natural waters, is kept in solution to be measured accurately.

4. It is possible to discriminate between two sites of adsorption or two ligands, providing they are present in about equal concentrations and have sufficiently different stability constants to display their effect in the titration curve.

However, there are possible drawbacks to the method: at pH's $<$ 6 the conditional stability constants of ligands in natural waters, the binding constants and adsorption capacity of $MnO_2$ decreases greatly causing determinations to become rather inaccurate. The sample should be diluted if the natural ligand concentration exceed 5 μM because of the interference from organics adsorption onto the mercury electrode when ASV is used for the determination of the dissolved metal concentration. The measurements become inaccurate when $K_{ML}'$ is much larger than B. It may also be impossible to discriminate between 1:1 (CuL) and 2:1 ($Cu_2L$) complexes with this method (van den Berg, 1979).

Some assumptions were made in the $MnO_2$ method which are worth mentioning briefly here. The appropriateness of the Langmuir model depends upon the validity of the assumption that only a small amount of ion exchanger is in equilibrium with the metal ions, which means high surface coverage of $MnO_2$. Under these circumstances the Langmuir equation can be made to represent a good fit. However, Stroes (1983), in developing an adsorption model for Cu onto hydrous $MnO_2$, recently found that at low metal concentration the asorption of Cu departed from the Langmuir linearity. For these cases the Implicit Langmuir model was proposed as a better representation (see also section 2.2.3 and Appendix III). Another assumption is that neither the organic ligands nor the metal-organic complexes adsorb on the surface of $MnO_2$. This assumption will be discussed in more detail later in section 3.3.1.

Hart (1981) suggested that the method to determine the complexing capacity of natural waters should ideally have the following characteristics:

a) selectivity for the metal ion added.

b) a capability to measure the metal, or a related quantity, at very low concentrations around $10^{-8}$M.

c) a capability to provide information on both metal-binding ligand concentration (complexing capacity) and conditional stability constants.

d) not require addition of other reagents that may disturb the equilibrium or bind with added metal.

e) not require preconcentration that may disturb the natural equilibrium.

f) be useful over a wide range of pH values.

g) be relatively rapid.

As mentioned earlier in this section the $MnO_2$ method (van den Berg, 1979 and 1982a) appears to fall short of these ideal characteristics in only a few requirements while offering certain advantages over other techniques, such as the ability to determine simultaneously complexing capacities and conditional stability constants of natural waters with minimum disturbance to the samples. It can be seen that the $MnO_2$ method is interesting and worth further investigation to develop a suitable adsorption model and its application to other metals. The scope of this work is to apply the method to metals such as Zn, Pb, and Co. An adsorption model, which has been developed previously (van den Berg, 1982a), is used to fit the data.

### 3.3.1 ADSORPTION OF METAL COMPLEXES OR LIGANDS ON $MNO_2$

For the method to work properly it is necessary that neither organic ligands or metal-organic complexes adsorb on the surface of $MnO_2$. Adsorption of the metal-organic complexes, or part of it, on the $MnO_2$ would affect the determination of the conditional stability constants because the dissolved metal concentration is decreased. The effect of ligand sorption is unknown; it could result in reduced metal sorption if active sites on $MnO_2$ are taken up by ligand molecules (Hart, 1981) or may assist sorption `by forming ternary $MnO_2$-L-Cu complexes (Bourg and Schindler, 1978).

The adsorption of organic ligands onto $MnO_2$ seems unlikely, especially in the case of large, humic-acid type molecules which constitute the bulk of the organic matter in natural waters (Hart, 1981), because both HA-type molecules and $MnO_2$ particles have a strong negative charge at the normal pH of natural waters, and electrostatic repulsion is favoured (van den Berg, 1982a). Experiments conducted by Stroes (1983) to test the adsorption of organic ligands such as aspartic acid, NTA, and glycine on $MnO_2$ using C14 labelled compounds, at pH 6 and 7, showed negligible amount of adsorption for glycine, NTA and aspartic acid on the surface of $MnO_2$. Some apparent adsorption of glycine was largely due to adsorption by glassware and filter paper (Stroes, 1983). Van den Berg (1982b) tried to induce glycine to adsorb on the $MnO_2$ surface and found that only 20-30% adsorption occured at very low pH (pH<1.5) and no adsorption at all was observed at high pH. Observations in natural seawater samples by ASV also showed that the organic matter concentration is not affected by the presence of $MnO_2$ at the natural pH of the samples as no loss of free or complexed organic ligands occurs at varying copper concentrations, but that adsorption takes place on $MnO_2$ at very low pH (pH~1.8) (van den Berg, 1982b). It can be concluded that organics do not adsorb onto $MnO_2$, providing the pH is well above acidic values, and the results obtained with the method can be regarded as reliable in the pH range of natural waters (6-8.5).

### 3.3.2 APPLICATION AND IMPROVEMENT OF THE $MnO_2$ METHOD

In order to apply the $MnO_2$ method to metals other than copper, van den Berg (1979) suggested that the amount of $MnO_2$ used can be adjusted according to the affinity of each metal to $MnO_2$ (i.e. compared with 50uM $MnO_2$ for copper the amount of $MnO_2$ used would have to decrease with an increase in the affinity of metal to $MnO_2$). Murray (1975a) found the affinity of transition metal ions for hydrous manganese dioxide, as calculated from specific adsorption potentials, to be in the series: Co $\gg$ Mn > Zn > Ni > Ba > Sr > Ca > Mg. This series does not follow the Irving-Williams order (Zn < Cu > Ni > Co > Fe > Mn) as given by Cotton and Wilkinson (1972) and Stumm and Morgan (1981). He suggested that the factors controlling the affinity involved more than the crystal field stabilization energies, used in explaining the Irving-Williams order. The factors involve displacement of Mn from structural positions of $MnO_2$ by adsorbing metal ions (Loganathan and Burau, 1973), changes in the coulombic, solvation and specific chemical energy interactions (because coulombic and specific chemical energy interactions dominate the free energy of adsorption on $MnO_2$, due to its high dielectric constant) (James and Healey, 1972). Gray and Malati (1979)found that the adsorption capacity of $MnO_2$ increased in the series: Ni $<$ Co $<$ Cd $\overset{\sim}{\geq}$ Zn $<$ Mn with the explanation that the affinity for exchange adsorption can possibly be described as a function of the ionic radius. They admitted that their calculation procedure, using hydration enthalpies to estimate the affinity, might not be entirely correct, although they found their adsorption order coincided with the calculated hydration radii. This idea was originally proposed by Posselt et al. (1968) that within a given group of elements, the larger the ionic radius (or the smaller the hydration radius), the larger is the exchange affinity. Van den Berg (1979) found the affinity to be Pb $>$ Cu $>$ Cd which led him to suggest that it may be possible to apply the $MnO_2$ method to Cd but not to Pb. The same order of Pb $>$ Cu $>$ Zn $>$ Cd was also found by Bilinski et al.(1977). In this work the method has been applied to zinc, lead and cobalt and the results will be discussed later in Chapter 6.

Van den Berg (1982a and b) has put forward another two suggestions. Firstly there is the calibration of $MnO_2$ in the absence of any added complexing ligand, and secondly the enhancement of the sensitivity to reach the theoretical detection limit of the method. These aims may be achieved by using radio-isotope as tracers which would reduce or eliminate contamination in the dissolved metal concentration during the filtration step. The theoretical detection limit of the $MnO_2$ method can be calculated from the contribution to the dissolved metal concentration of the metal complex (ML) relative to the concentration from inorganic metal species ($[M'] = \alpha . [M^{2+}]$): measurement is feasible when $[ML] > [M']$. In the case of copper the lowest detectable ligand concentration in seawater is $10^{-10}$M (as calculated from the [M'] which is around $10^{-11}$ to $10^{-10}$M at $Cu^{2+}$ concentration between $10^{-12}$ to $10^{-11}$ M - normal values in natural seawater) provided that the conditional stability constant has a value larger than or at least equal to the ligand concentration. Unfortunately, a practical detection limit of the ligand concentration around $10^{-8}$M is obtained because of contamination during the filtration step which raises the dissolved metal concentration to around $1 \times 10^{-9}$ - $5 \times 10^{-9}$M (van den Berg, 1982b). This contamination problem seems to be very serious for some metals, such as zinc or lead, as shown by Stroes (1983); while attempting to calculate conditional stability constants of Zn with several known organics and natural ligands using Shuman's method, discouraging results emerged due partly to contamination. Radio-isotopes were adopted as tracers in this work, where applicable, in order to apply the $MnO_2$ method to metals such as zinc (Zn65 is used as a tracer), cobalt (Co60 is used as a tracer), and lead in the hope of fulfilling suggestions made by van den Berg (1982a and b). Unfortunately, in case of lead the use of the lead isotope Pb210 was not allowed due to safety regulations. The method is developed for use with small sample aliquots such as interstitial samples.

## 3.3 SUMMARY

In this chapter, various existing methods for determining complexing capacities and conditional stability constants of metal-organic complexes, along with the results obtained are briefly reviewed. Emphasis is placed on the $MnO_2$ method. The $MnO_2$ method offers a definite advantage over other techniques in its ability to measure conditional stability constant values in untreated natural water samples and over a wide range of pH. The method may have several weak points but has recently been proved to yield reliable results within the pH range of natural waters. Several adsorption models have been discussed which may describe metal adsorption by $MnO_2$ better than by the simple Langmuir adsorption model. Discussion of the scope of this work outlines the application of the method to other metals besides copper, enhancement of the detection limit of the method, and its application to small-size samples such as interstitial waters.

# CHAPTER 4

# INORGANIC AND ORGANIC COMPLEXATION OF Zn, Pb, and Co IN NATURAL WATERS

## 4.1 THE STUDY OF TRACE METAL SPECIATION

The factors controlling the chemical forms of trace metals in natural waters involve parameters such as the concentration of dissolved organic and inorganic ligands, the biological activity, the pH and Eh in the water, and also the total metal concentrations. Salinity and pH, among others, will obviously have a significant effect on the speciation (Mantoura et al., 1987a). The various chemical forms of metal ions may be classified into groups, such as those proposed by Florence and Batley (1980): free (hydrated) metal ion, labile metal complexes (organic and inorganic), inert metal complexes (organic and inorganic), and metal associated with colloidal particles (organic and inorganic). The complexes are formed as a result of substitution of one or more of the water molecules in the inner hydration sphere of the metal ion by the complexing agent or ligand. Weaker interactions between ions even of opposite charge, but not involving substitution in the inner hydration spheres, are of comparatively minor importance. The complex can have properties very different from the hydrated (free) metal ion. In most cases further chemical reaction, resulting in precipitation as an insoluble salt or adsorption onto solids, can occur only via the hydrated metal ion, and complex formation has the effect of suppressing these reactions by reducing the concentration of free metal ions (Gardiner, 1975).

There have been a number of studies directed towards differentiating the chemical forms of metals in the environment and using the data to predict speciation. The topic has recently been reviewed by Florence and Batley (1980). Chemical speciation in seawater has been reviewed also by Kester et al.(1975) and Stumm and Brauner (1975). These reviews discussed both experimental measurement of speciation and theoretical calculations.

### 4.1.1 CHEMICAL FORMS OF TRACE METALS IN NATURAL WATERS

Although the total concentration of a dissolved metal (dissolved metal is all metal species which pass through a 0.45µm filter, including colloidal particles) may be similar in two water systems, the chemical forms of that metal may be quite different. Some of the possible dissolved forms of a trace metal present in a natural water are of those mentioned in the previous section (Florence and Batley's scheme, 1980). The concentration of trace metals in natural waters are exceedingly low, and the situation becomes more problematic as each total measurement has then to be divided into several chemical forms which contribute to the total. The problems of contamination and separation of the fractions are insurmountable with techniques now available. Therefore, attention has been paid to the speciation study by using equilibrium models (e.g. Garrels and Thompson, 1962; Zirino and Yamamoto, 1972; Turner et al., 1981).

Generally, chloro complexes may be expected to be an important species in seawater, and adsorption of metal ions onto organic and inorganic colloids may occur because of relatively high pH of seawater. In freshwater, which generally has a lower pH but higher organic content than seawater, carbonate is usually more important than chloride as a ligand, and metal-organic interactions may dominate the speciation (Florence and Batley, 1980).

Breger (1970) and Sharp (1973) have pointed out that much of the organic matter in natural waters is in colloidal form. This organic colloidal matter has a widely varying origin and composition (Williams, 1971; Ehrhardt, 1977), and is likely to be a powerful agent for the adsorption and occulsion of trace metals (Ferguson and Bubela, 1974; Guy et al., 1976). Thus, it is possible that metal-organic interaction taking place between metals and organic "colloids" accounts for all metal-organic complexes in natural waters, while the metal-dissolved organic ligand interaction is insignificant (Florence and Batley, 1977; Turekian, 1977). When oxidized by uv-irradiation or chemical oxidants, the organic colloids decompose and release the associated metal. A significant fraction of trace metals like copper, cadmium and lead has been found to be associated with colloidal organic matter both in seawater (Batley and Florence, 1976a; Batley and Gardner, 1978) and in freshwater (Florence, 1977).

The adsorption process is also important in controlling trace metals speciation. In the freshwater - seawater mixing zone of estuaries, the precipitation and flocculation of humic substances and hydrous oxides of iron and manganese results in transfer of most of the dissolved heavy metals from the riverwater to the precipitated phase (Breger, 1970; Turekian, 1977). In this way the water is effectively scavenged of dissolved metals by organic and inorganic particulate matter and has been suggested to be the principal mechanism in removing trace metals from the water (Brewer, 1975; Turekian, 1977). The degree of adsorption will depend on the speciation of the metal, as some complex ions or molecules tend to be sorbed much more strongly at the interface than free metal ion (Stumm and Bilinski, 1972).

The extent of trace metal adsorption on particles in freshwater is largely pH dependent (Huang et al., 1977). A decrease as small as 0.5 pH units can cause the difference between complete adsorption and complete desorption, and most freshwaters have a pH which is in the critical range for adsorption. The James-Healey (1972) hydrolysis-adsorption model has been used frequently to describe metal ion adsorption onto inorganic particles. James and McNaughton (1977) have discussed the different interfacial models used to describe the adsorption.

In a study of some soft riverwaters, Florence (1977) found that over 50% of copper was adsorbed on organic colloids with no measurable adsorption on inorganic colloidal particles. The result indicates that colloidal organic matter may be able to compete for the adsorption of trace metals with hydrous metal oxides like manganese dioxide, which is a very efficient adsorbent of metals from seawater (Krauskopf, 1956). Many other types of organic matter in natural waters are also important collectors of trace metals. Ferguson and Bubela (1974) showed that algae can effectively concentrate Cu, Pb, and Zn from solution. $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ are strongly adsorbed by humic acid (Guy and Chakrabarti, 1976), while manganese dioxide is an even stronger adsorbent (Guy et al., 1976).

### 4.1.2 SPECIATION TECHNIQUES

There are two basic approaches used to determine trace metal speciation in natural water samples. The first is by calculation , the other is analytical.

#### 4.1.2.1 SPECIATION MODEL

This method involves calculation of the equilibrium concentrations of all the metal-ligand species, using known values for total metal and ligand concentrations, and published values of the relevant metal-ligand stability constants. Three types of constants are in common use:

a) thermodynamic constants based on activities; the activity scale being based on the infinite dilution scale,

b) apparent equilibrium constants which are expressed as concentration quotients and valid for a medium of given ionic strength,

c) conditional constants that are valid only under specified experimental conditions.

For computational purposes it is possible to use the thermodynamic constants in conjunction with activities, provided that the values of single ion activity coefficients are known. Alternatively, apparent constants can be used in conjunction with concentrations. Non-thermodynamic assumptions are involved in either case. The later approach is very attractive in speciation studies because there are no more problems besides sample collection, contamination and long working hours in the laboratory. But one must be careful not to overlook the importance of all complexing equilibria. Comparison of some recent models of trace metal speciation shows a wide variation. For example, the speciation of zinc is compared in Table 4.1 (see section 4.2.1). Differences are the result of the use of differences in published stability constants, the inclusion of additional complexes species, and to a lesser extent, activity coefficient corrections. But far more important errors are introduced by the failure to include, in the calculation, all metal-binding species, especially colloidal particles. Because of our restricted knowledge of metal ion interactions with organic and inorganic colloids and also with natural organic ligands, complexation models are still of limited value when applied to natural waters (Florence and Batley, 1977). However, the discrepancies between the results may be used to identify marine chemical processes requiring further investigation (Kester et al., 1975).

Examples of the computer programmes used in speciation calculation are HALTAFALL (Dyrssen et al., 1968) and REDEQL (Morel and Morgan, 1972). Recently in an attempt to place the results of speciation studies of various elements in their logical context in relationship to the periodic table Turner et al.(1981) have critically compiled a data base and used it to establish a relationship between stability constants and conditional stability constants at different ionic strength, thus avoiding the need for activity coefficient correction.

### 4.1.2.2 ANALYTICAL METHODS

This approach attempts to place the various species in experimentally defined "boxes", based on their behaviour during separation and chemical analysis. Few analytical techniques are "species specific", i.e. respond to only one particular chemical form of an element in solution. Stumm and Brauner (1975) and Kester et al.(1975) have reviewed some methods in use for speciation studies. These methods can be generally classified as those based on size, density and charge of species (e.g. ultrafiltration, gel filtration), and labilities of species relative to the technique employed (e.g. ion exchange, ASV). Among these methods ASV is perhaps the most promising analytical tool presently available for studying trace metal speciation, but it still has the major limitation that it can be applied to only a small number of metals (e.g. Cu, Zn, Pb) in natural waters. Batley and Florence (1976a and b) have proposed a scheme for classification of speciation, and have shown that by combining a number of techniques the nature and the relative importance of some species can be elucidated to some extent.

ASV has been applied to the measurement of total metal in the various fractions of the sample obtained by separation procedures (e.g. Florence and Batley, 1976a and b), to discriminate labile and bound metal fractions (e.g. Fukai and Huynh-Ngoc, 1975 and 1976; Duinker and Kramer, 1977), and to determine stability constants either by observation in the shift of redox potential of labile and reversible complex (e.g. Bilinski et al., 1976) or by titration of samples with added metals (e.g. Shuman and Cromer, 1979).

Total metal is determined after acid oxidation (Florence and Batley, 1977; Chau and Chan, 1974) or uv-irradiation in acid media (Batley and Farrar, 1978). This oxidative treatment is used to make the non-labile fraction detectable. Ultra violet irradiation in acid media (Batley and Farrar, 1978) is preferred for destroying organic matter and liberating total metal, because it avoids the high blanks associated with the use of oxidizing agents such as persulfate or perchloric acid. The method employed by Fukai and Huynh-Ngoc (1975 and 1976), and Duinker and Kramer (1977) for measuring the total metal in seawater by ASV after acidification is based on the fact that both complexation and adsorption reactions are pH-dependent. Upon acidification of seawater to a pH below the pH of the initial hydrolysis of the metal (pH 5-9 for most divalent metal ions), one would expect metal ions to be desorbed as the speciation changes from the hydrolyzed species to free metal ions and chloro complexes (Long and Agino, 1977). Acidification may also dissolve colloids and thus release occluded and colloidal metal (Duinker and Kramer, 1977). Both inorganically- and organically-complexed metal would be released to a certain degree by acidification (Guy and Chakrabarti, 1976) owing to pH-dependent changes in metal speciation, as well as to protonation of ligands. However, Brezonik et al.(1976) have claimed that the assumption that metal ions will be released upon acidification is not valid for all ligands. They found a decrease in labile metal after acidifying some of their metal-ligand systems to pH 3. It is possible that sorption of organic matter on the electrode surface occurs, thus decreasing the sensitivity of the electrode, making their results inconclusive.

The acidification technique like that employed by Fukai and Huynh-Ngoc (1975 and 1976) and Duinker and Kramer (1977) has been used in this work for measuring total dissolved metal concentration. Other techniques will not be discussed here. For more details see Kester et al.(1975), Stumm and Brauner (1975) and Florence and Batley (1980).

## 4.2 METAL-INORGANIC COMPLEXATION

Equilibrium models are quite successful in describing the inorganic speciation of metal ions in natural waters, particularly those of rapid chemical processes (Kester et al., 1975). Models like those of Zirino and Yamamoto (1972), Stumm and Brauner (1975), Dyrssen and Wedborg (1980) and Turner et al.(1981) produced results which constitute a useful general framework that permits a better understanding of speciation.

### 4.2.1 ZINC

Zinc is one of the essential trace metals, and its bioavailability is critically dependent on its chemical forms (Spear, 1981). In aquatic environments, the free zinc ion co-ordinates with six water molecules to form an octahedral aquo ion, $[Zn(H_2O)_6]^{2+}$, and these water molecules are replaced by other ligands during the formation of complexes (Cotton and Wilkinson, 1972).

Several discrepancies exist with regard to inorganic zinc complexes. For example, the speciation models which have used the stability constant for $Zn(OH)_2$ cited in Sillen and Martell (1964) are found to overestimate the concentration of $Zn(OH)_2$ by two or three orders of magnitude (Spear, 1981). With a revised stability constant, Mantoura et al. (1978b) expected the concentration of $Zn(OH)_2$ to be less than 1% of the total dissolved zinc. Table 4.1 shows the results of zinc speciation calculated from different equilibrium models which should, at best, be regarded as estimates of a very complicated system.

In the study of Bernhard et al.(1975) and Bradford (1973) it was proposed that at least 3 groups of zinc species exist in seawater: ionic zinc (10-20% of total zinc); particulate zinc (30-40% of total zinc); and complexed zinc (bound to unidentified organic or inorganic ligands, usually 50% of total zinc). Even though discrepencies in zinc speciation do exist, a trend has emerged from these studies. Generally in seawater, inorganic zinc is divided between free metal ion, chloro and carbonato complexes, while in a typical freshwater free metal ion, carbonato and hydroxo complexes predominate (Florence and Batley, 1980).

Zinc may be adsorbed, through ion exchange, onto negatively charged surfaces, in the electrical double layer surrounding amorphous colloids and particulates, and also onto those adsorbents having functional groups

Table 4.1 Percentage distribution of zinc between the principal inorganic species in seawater (25°C, 1 atm, 35%. salinity, pH 8).

| Reference | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9* |
|---|---|---|---|---|---|---|---|---|---|
| Species | | | | | | | | | |
| $Zn^{2+}$ | 16 | 55 | 47 | 6 | 38 | 17 | 26.6 | 46 | 14.1 |
| $ZnOH^+$ | 2 | 2 | <1 | 0.1 | - | - | 4.4 | 12 | 0.9 |
| $Zn(OH)_2$ | - | - | <1 | 72 | 30 | 62 | | | |
| $ZnCl^+$ | 44 | 31 | 20 | 10 | 18 | 6.4 | 47 | 35 | 79.5 |
| $ZnCl_2$ | 15 | - | 10 | 5 | 7 | 4 | | | |
| $Zn(OH)Cl$ | 13 | - | - | - | - | - | | | |
| $ZnCO_3$ | 3 | 6 | ~4 | 2 | - | 5.8 | 17.7 | 3 | 3.8 |
| $ZnSO_4$ | 2 | 6 | 10 | 2 | 4 | 4 | 4.3 | 4 | 1.7 |

1. Dyrssen and Wedborg (1974)
2. Ahrland (1975)
3. Mantoura et al. (1978b)
4. Florence and Batley (1976b)
5. Lu and Chen (1977)
6. Zirino and Yamamoto (1972)
7. Florence and Batley (1980)
8. Turner et al. (1981)
9. Sibley and Morgan (1975); * at pH 9.18

at the water-solid interface that are capable of chelation (chemi-sorption) (Spear, 1981). Inorganic adsorbing agents include mineral particles, amorphous and crystalline clays as well as hydrous metal oxides. Adsorption of zinc onto hydrous manganese dioxide is described by a Langmuir isotherm (Spear, 1981), in which a maximum level of adsorbed zinc is reached. The adsorption capacity of adsorbing agents for zinc is expected to decrease with increasing ionic strength (James and McNaughton, 1977) as competition from major cations would interfere with zinc adsorption and possibly promote zinc desorption (Gadde and Laitinen, 1974).

### 4.2.2 LEAD

$Pb^{2+}$ binds strongly to a number of anions but in natural waters carbonate, hydroxide, phosphate, sulfide and sulfate are the predominant inorganic ligands. Most lead salts are sparingly soluble or insoluble in water (Cotton and Wilkinson, 1972). The uncertainties in the figures for total lead concentrations resulted from its low concentration in natural waters and the ease with which samples are contaminated. Although these difficulties are now being overcome (Burnett and Patterson, 1979), attempts to split the total lead concentrations in natural waters, particularly open ocean samples, into individual species are still unsuccessful. The use of a theoretical approach in the study of lead speciation may help clarify some of the physico-chemical problems ,and indeed, a number of general points of agreement arise from the speciation studies of lead in seawater (Table 4.2). Most models consider $PbCO_3^0$ as the dominant inorganic complex in all natural waters (Nurnberg et al., 1976), with the exception of anoxic waters where lead sulfide may exist (Morel et al., 1973). All conclude that uncharged species account for more than 50% of dissolved lead at pH 8 (Whitfield and Turner, 1977). This finding may prove significant if it can be confirmed that such uncharged complexes tend to form colloidal aggregates in solution. It is also agreed that $PbHCO_3^+$ and $PbSO_4^0$ are minor species at pH 8, and that ionic lead contributes only a few percent to total lead.

In a typical freshwater (oxidizing conditions, pH 8) the major form is $PbCO_3^0$ with a few percent of $Pb^{2+}$ and $Pb(OH)^+$ (Sibley and Morgan, 1975). However, $Pb^{2+}$ becomes the predominant species when the pH decreases (Turner et al., 1981). Throughout all these observations it is important to bear in mind that only lead complexes whose thermodynamic stability constants are known are included in the calculations.

A strong positive correlation between the total lead concentration in U.S. riverwaters and water hardness was found (Masironi, 1970), indicating lead to be more soluble in soft water (Davies et al., 1976). In seawater, the presence of carbonate removes 85% of the ionic lead by complexation and precipitation or by

Table 4.2 Percentage distribution of lead between its principal inorganic species in seawater (25°C, 1 atm, 35%. salinity, pH 8).

| Reference<br>Species | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $Pb^{2+}$ | – | ~1 | 2 | 3 | 2 |
| $Pb(OH)^{+}$ | 10 | <1 | – | 9 | 30 |
| $PbCl^{+}$ | 19 | 11 | 7 | 47 | 9 |
| $PbCl_2$ | 42 | 5 | 11 | | 13 |
| $PbCl_3$ | 9 | ~1 | – | | – |
| $Pb(OH)Cl^{0}$ | 9 | – | – | | – |
| $PbCO_3Cl$ | – | – | 10 | | – |
| $PbCO_3$ | – | 76 | 55 | 41 | 44 |

1. Dyrssen and Wedborg (1974)
2. Zirino and Yamamoto (1972)
3. Whitfield and Turner (1977); other species not mentioned comprises >5% of the total.
4. Turner et al.(1981)
5. Nürnberg (1980)

complexation and adsorption on particulate matter (Hahne and Kroontje, 1973).

Lead adsorbed on inorganic colloidal particles should be an important dissolved species of lead since, at the pH of natural waters, $Pb^{2+}$ is strongly adsorbed on hydrated ferric oxide (Gadde and Laitinen, 1974), manganese dioxide (Doshi et al., 1973), and silica and soil minerals (Huang et al.,1977). Bilinski and Stumm (1973) found that lead carbonato complexes are adsorbed even more strongly than $Pb^{2+}$. Sibley and Morgan (1975) using a computer model with silica as a model adsorbent, together with the thermodynamic model of adsorption of James and Healey (1972), predicted that in a typical freshwater (pH 8) about 6 percent of total lead would be adsorbed on inorganic particles, whereas in seawater, no adsorption of lead would take place because of chloride complexation of lead and competition from major cations (e.g. $Na^{+}$, $Ca^{2+}$) for adsorption sites. However, Blustien and Smith (1975) performed lead measurements in seawater and estuarine water by ASV before and after uv-irradiation, and found that at natural pH of the samples lead is adsorbed on colloidal inorganic material (e.g. hydrous ferric oxide).

### 4.2.3 COBALT

Very little is known about the cobalt speciation and its distribution in natural waters. The concentration of cobalt in seawater is likely to be

<0.05nmol $kg^{-1}$ (Bruland, 1983). $Co^{2+}$ is the stable form of cobalt in seawater. The low concentrations found in natural waters indicate that cobalt is rapidly removed from seawater, probably in association with manganese oxide phases, and also point to the potential role of cobalt as a biolimiting element in oceans (Bruland, 1983). Modelling studies of cobalt speciation has led to widely differing predictions concerning the major species present in natural waters (Table 4.3) due partly to the lack of information on the stability of carbonato complexes (Burton and Statham, 1982).

In freshwater, cobalt is adsorbed onto a wide range of clays, quartz and hydrous metal oxides (Kharkar et al., 1968; Leckie and James, 1974), and especially strongly onto hydrous manganese dioxide (Loganathan and Burau, 1973). Desorption is known to occur on mixing with seawater (Sholkovitz, 1976).

## 4.3 METAL-ORGANIC COMPLEXATION

Trace metals in natural waters have, to a lesser or greater extent, been found to be involved in proteinous and humic macromolecular organic matter with molecular weight ranging from 1,000 to 100,000 (Sugimura et al., 1978a and b; Kremling et al., 1981; Mills and Quinns, 1981; Hasle and Abdullah, 1981). These organic materials are partially land derived and partially produced in situ by biological processes. The bulk of organic matter in most soils and waters consists of humic substances

Table 4.3 Percentage distribution of cobalt between its principal inorganic species in seawater (25°C, 1 atm, 35‰ salinity, pH 8).

| Reference<br>Species | 1 | 2 |
|---|---|---|
| $Co^{2+}$ | 54 | 58 |
| Hydroxo complexes | – | 1 |
| $CoCl^{+}$ | 31 | 30 |
| $CoCO_3$ | 7 | 6 |
| $CoSO_4$ | 7 | 5 |

Stumm and Brauner (1975) suggested that $Co^{2+}$ and $CoCO_3$ are the most probable main species.

Sibley and Morgan (1975) predicted a high proportion of chloro complexes in seawater.

Mantoura et al.(1978b) predicted $CoCO_3$ as the major species (<1% of organic complexes in freshwater with insignificant complexation in seawater)

1. Ahrland (1975)
2. Turner et al.(1981)

(Schnitzer and Khan, 1972; Gjessing, 1976) which, according to Schnitzer and Khan (1972), divide into 3 main fractions based on their solubility in base and acid: humic acid (HA); fulvic acid (FA); and humin. Fulvic acid constitutes a major fraction as dissolved organic matter in many natural waters, and closely resembles soil fulvic acid (Reuter and Perdue, 1977). The binding of trace metals with fulvic acid is thought to occur by binding with one or more of non-identical, acidic functional groups on fulvic acid. These functional groups are a highly acidic carboxyl group, a moderately acidic carboxyl group, and a weakly acidic phenolic hydroxyl group (Gamble,1970). The average molar concentration of aquatic humic substances in major U.S. rivers is calculated to be about $5\times10^{-6}$ to $3\times10^{-5}$M, whereas anthropogenic ligands such as NTA and EDTA occur at much lower levels in surface waters (Reuter and Perdue, 1977). Manning and Ramamoorthy (1973), and Ramamoorthy and Manning (1974) have studied the interactions of fulvic acid with Cu(II), Pb(II), Cd(II), and Zn(II). They reported that mixed fulvate - phosphate complexes were more important than simple metal-fulvic acid complexes for all these metals.

In oxic and anoxic interstitial waters of organic rich sediments the humic fraction of the high molecular weight (HMW) organic matter was found to be mainly fulvic acid with a small proportion of humic acid (~1%) and melanoids. This HMW organic matter accumulates as a result of condensation of low molecular weigth (LMW) organic substances by humification in interstitial water (Krom and Sholkovitz, 1977). The metal-binding functional groups of sedimentary marine humates are different from soil humates (Rashid and King, 1970, 1971; Nissenbaum and Kaplan, 1972) but quite similar to sedimentary lake humates (Ishiwatari, 1973).

Some systems may contain metal-binding compounds such as tannins and siderochrome (Neubecker and Allen, 1983). Biological ligands were classified according to characteristic of living organisms by Eichhorn (1975). These ligands exist partly because metal binding is important to living organisms and, therefore, some ligands are designed for this function (Eichhorn, 1975). For example, algae can excrete strong metal-binding ligands (Ferguson and Bubela, 1972; McKnight and Morel, 1979 and 1980; Imber and Robinson, 1983). A copper complexing ligand (called hydroxamate siderophore) when oxidized by trace metals to hydroxamate will yield even stronger ligands (McKnight and Morel, 1979 and 1980).

Humic and fulvic acids form much weaker complexes than EDTA (Mantoura et al., 1978a; Mantoura and Riley, 1975; Guy and Chakrabarti, 1976) and the existence of any natural ligands stronger than EDTA was thought unlikely by Florence and Batley (1980). However, it is possible that some natural waters contain such ligands (e.g. Kunkel and Manahan, 1973; Hirose et al., 1982) for the reasons explained in section 3.1.

### 4.3.1 ZINC

The stability constants of zinc-organic complexes are low in comparison with those of metals in the first transition series (Cotton and Wilkinson, 1972); for instance, they are usually several orders of magnitude less than those of the equivalent copper and lead complexes. Bernhard et al.(1975) pointed out that under the normal conditions present in natural water, zinc-organic complexes could not easily dissociate. However, Branica (1969) has found some dissociable chelate complexes of zinc in seawater. He explained that the chelate complex should be in equilibrium with ionic zinc _in situ_, and the dissociation rate of this complex is reasonably high at the normal pH of seawater. Zinc-organic complexes are predicted to be of little importance in seawater (Mantoura et al., 1978a and b), but recently Hirose et al.(1982) found evidence to indicate the existence of naturally-occurring organic metal complexes (for zinc and copper) which are stable species and not easily dissociated or displaced with other metals.

Similarly in freshwater, Benes et al.(1976) obtained results which suggested that some zinc is strongly associated with organic matter - particularly humic substances (Guy and Chakrabarti, 1976). The reaction of zinc with humic acids involves binding to hydroxyl and carboxyl groups (Gamble et al., 1970; Gamble and Schnitzer, 1973). The stability constants of zinc humate complexes are lower in acid waters than in neutral or slightly basic waters. In acidic freshwaters containing 3 mg $l^{-1}$ of humic acid, zinc humate complexes are expected to be less than 0.1 to 2% of the total dissolved zinc (Spear, 1981). Wilson and Kinney (1977) have predicted that even at the optimum pH for zinc-humic acid binding (pH 8.0-8.5), zinc humates are likely to be only 10-15% of the total dissolved zinc. However, in highly productive ecosystems and in natural waters supporting a substantial load of organic molecules, the ligand concentration may be sufficient to bind a greater proportion of zinc-organic complexes (Spear, 1981).

Competition for organic ligands may occur between zinc and other divalent cations which are more abundant than zinc or have stronger affinities for the organic ligands. For example, NTA introduced into a freshwater system would be preferentially bound by copper ions. Major cation (e.g. $Ca^{2+}$, $Mg^{2+}$) competition may release zinc from organic complexes (Leckie and James, 1974) such as found in the estuarine model by Mantoura et al.(1978b), where calcium and magnesium concentrations increase with increasing salinity so producing shifts in chemical equilibria favouring the dissociation of zinc humates and the formation of calcium and magnesium humates.

In contrast, organic complexation is thought to be a significant factor controlling zinc dynamics in sediments. Ong-Ling et al.(1970) concluded that it is possible, as a consequence of increased ligand concentrations, that zinc-organic complexes may be relatively stable at low pH. Zinc is found to be especially mobile in acidic soils and sediments, possibly owing to dissolved zinc humate and fulvate complexes (Banat et al., 1974; Bolter et al., 1975). Unfortunately, stability constants have not yet been determined under conditions characteristic of sediments. The humic substances found in pore waters contain significant amounts of copper, molybdenum and zinc with less significant amounts of other metals such as nickel, cobalt and lead which was thought that the metals are mostly introduced into the humates during their diagenetic formation in sediment by dissolution of metals from various mineralogical phases (Nissenbaum and Swaine, 1976).

In addition, various organic materials released by algae were also found to bind zinc quite strongly (Ferguson and Bubela, 1972; Imber and Robinson, 1983). The extent of binding is, once again, strongly influenced by hydrogen ion concentration, competition by major cations such as $Na^+$, $Mg^{2+}$ (Ferguson and Bubela, 1972) and other stronger chelated metals such as copper (the binding of metal to polyphenol extracted from brown algae was found to be a factor of fifty greater in the case of copper when compared with zinc (Ragan et al.,1979)). Imber and Robinson (1983), in a study of the zinc-binding capacity of the organic material released by

*Thalassiosira fluviatilis*, found that two types of zinc-binding ligands were released which produced equilibrium binding constants comparable to those obtained for copper with plankton exudates by van den Berg et al. (1979).

The reported observations of organically-bound zinc in natural waters are summarized in Table 4.4.

### 4.3.2 LEAD

Lead(II) forms numerous complexes which are mostly octahedral in structure (Cotton and Wilkinson, 1972). $Pb^{2+}$ was found to form complexes with soil-derived fulvic acid (Guy and Chakrabarti, 1976; Schnitzer and Skinner, 1967; Buffle et al., 1977), with aquatic organic matter (Buffle et al., 1977; Ramamoorthy and Kushner, 1975a), with algal exudate (Kushner, 1974; Ferguson and Bubela, 1972), and with corn root exudate (Gadde and Laitinen, 1973).

Much work has been done in studying lead complexation in natural waters such as those in Table 4.5. Earlier work by Matson et al.(1969), with Lake Michigan water using ASV, showed that the greater portion of trace metals was bound up in slowly dissociating forms. In particular, lead was bound up by intermediate molecular weight organic material. A major portion of the lead binding capacity of the Ottawa River waters was also found to reside in the molecular weight fraction below 1,400 g $mol^{-1}$ (Ramamoorthy and Kushner, 1975b). Florence

Table 4.4 Literature comparison of "organically-bound zinc fractions" in natural waters.

| Organically-bound zinc fraction (%) | Techniques | Reference |
|---|---|---|
| Seawater | | |
| 45.7 | dialysis, NAA | Rona et al.(1962) |
| 21.4-42.6 | dialysis | Slowey and Hood(1971) |
| 50 | ion exchange, ASV | Florence and Batley (1976a) |
| 20 | ASV | Fukai and Huynh-Ngoc (1976) |
| 60 | DPASV | Duinker and Kramer (1977) |
| 42 | Ligand exchange | Hirose et al.(1982) |
| 44-70 | Spectrophotometry with solvent extraction | Fukai and Huynh-Ngoc (1975) |
| Freshwater | | |
| 10-46 | dialysis | Benes and Steinnes (1974 and 1975) |
| 66 | ion exchange | Figura and McDuffie (1977) |
| 50 | ion exchange | Hart and Davies (1977)[1] |
| Interstitial water | | |
| 100 | solvent extraction dialysis and emission spectrography | Nissenbaum and Swaine (1976)[2] |

1. Polluted riverwater
2. From reducing sediment; particulary bound to humic acid

Table 4.5 Literature comparison of "organically-bound lead fractions" in natural waters.

| Oganically-bound lead fraction(%) | Techniques | Reference |
|---|---|---|
| Seawater | | |
| 16-53 | ion exchange | Florence and Batley (1976a)[1] |
| 87 | DPASV | Duinker and Kramer (1977)[2] |
| 8-42 | DPASV | Nilsen and Lund (1982) |
| 26-100 | ASV | Sugai and Healey (1978) |
| 12 | ion excahnge | Florence and Batley (1976b) |
| 3-12 | adsorptive-bubble separation | Wallace (1982) |
| Riverwater | | |
| 43 | ion exchange | Hart and Davies (1977) |
| Estuarine water | | |
| 35 | ASV | Batley and Gardner (1978) |

1. Lead associated with organic and inorganic colloidal particles.
2. High result may have been contributed by inert form to analytical techniques used at pH 8.1, e.g. particulate lead in the form of lead oxide that passed through the membrane filter.

and Batley (1976a and b, 1977) used an ion exchange resin to distinguish between lead species in seawater, and reported that a high proportion of dissolved lead (40-80%) was associated with colloidal inorganic particles, whereas a smaller fraction (10-35%) was adsorbed on organic colloids in both seawater and estuarine water. Molecular organic and inorganic lead complexes accounted for 0-20% and 0-30% respectively.

The presence of powerful organic complexing agents in freshwater could alter the lead speciation considerably (Ferguson and Bubela, 1972; Guy et al.,1976). Morel et al.(1973) showed that NTA ($1\times10^{-5}$M) added to a typical freshwater (pH 7) would complex essentially all lead present. The addition of NTA to natural waters can dissolve a significant amount of lead from sediments (Banat et al., 1974). In the study of lead partitioning in offshore ocean sediments, Gupta and Chen (1975) found that between 52-65% of the total lead content of the sediments was associated with organic matter, sulfides, micro nodules and amorphous iron oxides; this is termed the non-residual lead fraction. Nissenbaum and Swaine (1976) concluded that lead associated with marine humic substances in interstitial water of recent sediment is of minor importance in comparison to Cu, Mo and Zn.

### 4.4.3 COBALT

Cobalt(II) is known to form stable complexes with organic ligands, but in the presence of dissolved oxygen these will almost certainly be oxidized to their respective cobalt(III) complexes which are kinetically inert (Florence and Batley, 1980). The most common complex of cobalt is vitamin B12 (cyanocobalamin), and is found in seawater at ng level (Duursma, 1965; Carlucci and Silbernagel, 1966).

Very few studies have been carried out on cobalt complexation and the results are shown in Table 4.6. These studies show that cobalt complexation in natural waters is significant. Consequently, a lot more work should be done in order to obtain useful information for a better understanding of cobalt speciation.

## 4.4 SPECIATION MODEL AND STABILITY CONSTANTS USED IN THIS WORK

Published data on stability constants vary greatly (e.g. Sillen and Martell, 1971, 1964). Martell and Smith (1974) and Smith and Martell (1976) have published a compilation of selected values for metal-ligand stability constants. International Union of Pure and Applied Chemistry (IUPAC) has set up a Commission on Equilibrium Data to attempt to evaluate published thermodynamic equilibrium data critically. The evaluated data have now been published (Högfeldt, 1982; Perrin, 1979; Beck, 1977).

Turner et al. (1981) have proposed a refined calculation method in studying the equilibrium speciation

Table 4.6 Literature comparison of "organically-bound cobalt fractions" in natural waters

| Organically-bound cobalt fraction(%) | Techniques | Reference |
|---|---|---|
| Lake and riverwater | | |
| >60 | Dialysis | Benes and Steinnes (1975) |
| Estuarine and coastal water | | |
| 30 | AAS | Batley and Matousek (1977) |
| 35-50 | ion exchange solvent extraction | Lowman and Ting (1973) |
| Interstitial water | | |
| 30-50 | solvent extraction, dialysis, and emission spectrography | Nissenbaum and Swaine (1976) |

of dissolved components in natural water. The method induced more than 500 stability constants of complexes. Their data base on conditional stability constants were taken mostly from Baes and Mesmer (1976) for hydrolysis constants, and Smith and Martell (1976), and was supplemented, for instance, with carbonate complexation constants from Bilinski et al. (1976). The stability constants were fitted to an interpolation formula of the form:

$$\log\beta^{*} = \log\beta^{o} + 0.51[\Delta Z^{2}I^{1/2}/(1 + BI^{1/2})] + CI + DI^{2}$$

where I is the ionic strength, $\Delta Z^{2} = \Sigma Z^{2}$(products) $- \Sigma Z^{2}$(reactants)(Z representing the charge on the component and B, C and D are treated as adjustable parameters. By using this equation, the introduction of specific assumptions concerning the activity coefficients of ions and complexes can be avoided.

In this work most of the stability constants used are calculated from the interpolation formula. In cases where the complexes involved in the calculation are not included in the list of Turner et al.(1981), the stability constants required are taken directly from Martell and Smith (1974) and Smith and Martell (1976).

By introducing a boric acid/sodium hydroxide buffer to control the pH of all experiments at pH 8.2, the necessity of including all borate complexes into side reaction coefficient has been considered. Basset (1980) have critically reviewed the data available for borate complexes; however, the data is insufficient and not well defined, particularly in the case of stability constants obtained by Schigol (1959, 1963). This is probably the result of not considering the competing equilibria such as hydroxo complexes (van den Berg, 1982c). Therefore, the stability constant (conditional) values of borate complexes proposed by van den Berg (1982c) are used. All constants used will be included in Appendix IV.

## 4.5 SUMMARY

This chapter presents a general framework of trace metal speciation in natural water, concentrating in particular on zinc, lead and cobalt, and shows that there still are different opinions concerning the inorganic chemical forms of these trace metals. These differences seem to stem from the limitations in analytical techniques available and from the stability constant values reported. Therefore, it is necessary to consider every aspect of each of the studies in order to be able to understand and choose a speciation model which is a good representative of natural waters. It is also equally important to discuss the extent of metal-organic complexation, which in turn will help interpreting the data and confirming the results presented in this work.

# CHAPTER 5

# EXPERIMENTAL PROCEDURES

## 5.1 SAMPLE COLLECTION AND SAMPLING SITES

Sediment samples from the Gulf of Thailand were collected with a grab sampler, but only sediment not in contact with metal parts of the sampler was used. Later in the laboratory an MSE temperature-controlled, high speed centrifugation unit was employed in the extraction of the interstitial water from the sediment. The interstitial water samples were stored in precleaned polyethylene bottles and frozen. Seven sites from the Upper Gulf of Thailand were sampled at the Pollution Monitoring Programme's sampling stations set up by the National Research Council of Thailand (Figure 5.1). Station 1 and 2 are in the channel of the Chao Phraya River, the biggest of the four rivers that flow into the Upper Gulf of Thailand. Station 3, 4 and 5 are located offshore. Several important points should be noted here. The site of station 3 has been used as a dumping ground for untreated-organic industrial waste, particularly that from a whisky distillery. The site at Station 4 has been used as a dumping ground for dredged materials from the Chao Phraya River by the Harbour Authority of Thailand. The sites at Stations 6 and 7 are located off the east coast which is not the main industrial area, but is a holiday resort and deep-water harbour. This area is heavily affected by the load from Bang Pa Kong River.

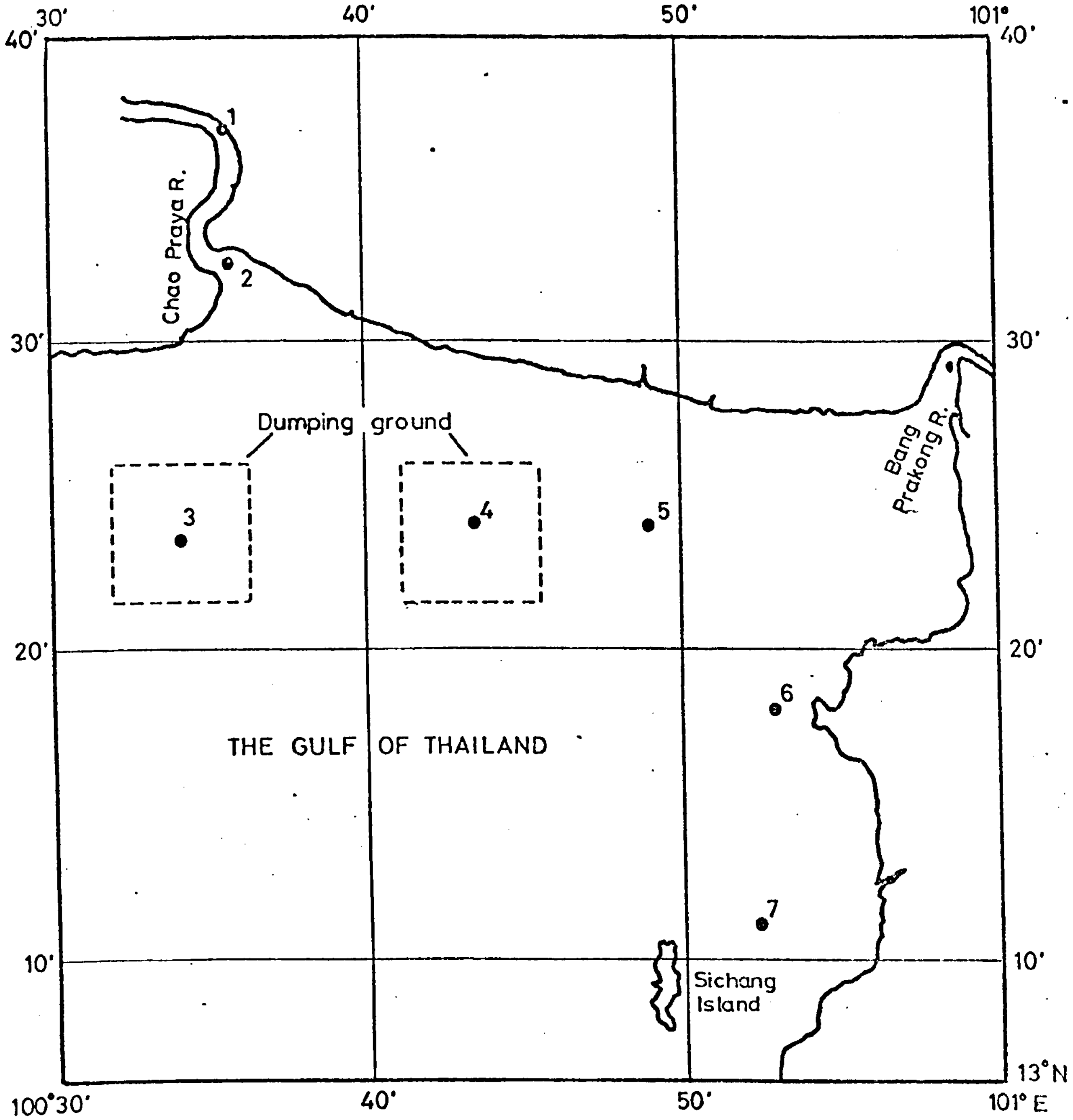

Figure 5.1 Sampling sites in the Gulf of Thailand.

The sediment samples from the Mersey River were collected at Eastham, Otterspool, West Bank and Fidler Ferry (Figure 5.2). Samples were collected with a perspex tube, of 70 mm diameter, by pushing it through the sediment column at the water edge area, and were pushed from the tube into a plastic bag by a piston made of a perspex disc, of the same diameter as the tube, attached to a wooden rod. Only the top 15 cm of the sediment was collected due to a difficulty arising from the fact that the areas near the river bank are mostly rock debris from damaged dike covered with only a thin layer of sediment. Consequently, more than two corings at the same location were needed to get enough sample. The sediment samples were centrifuged at high speed (~12,500g) to extract the interstitial water from the sediment, and the analyses were carried out immediately afterward.

Chan (1983) has reviewed the state of pollution in the Mersey estuary. The Mersey is still one of the most polluted estuaries in Britain because it is responsible for the drainage area of about 4,500 sq km of over 5 millions in population and highly industrialized areas of Merseyside, Greater Manchester, South Lancashire and North Cheshire. The effluents discharged into the Mersey include both treated, untreated domestic and industrial sewage.

Surface water samples were collected from the River Ribble, the River Dee and the North Atlantic Ocean.

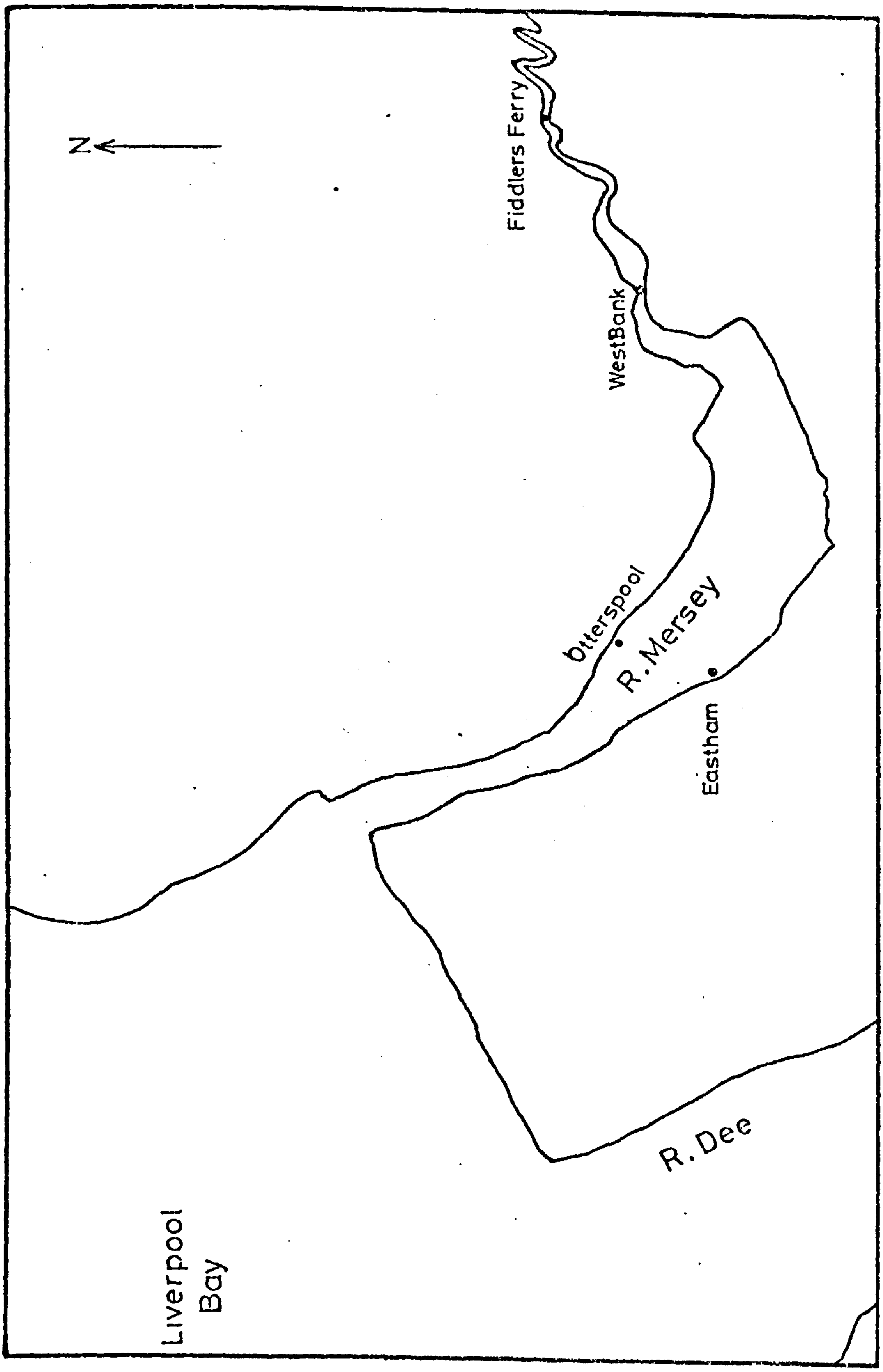

Figure 5.2 Sampling sites in the River Mersey.

The river water samples were collected during high tide at the river mouths in 1982 and 1983. The analyses were carried out immediately after they had been transferred back into laboratory. The surface water sample from the Atlantic was collected during a cruise in April 1982 and was frozen until analysis.

## 5.2 PREPARATION OF CONTAINERS

Originally, all the containers, glassware and plasticware used were soaked in 3N nitric acid for 3 hours, rinsed repeatedly with distilled water and later soaked in 0.01N nitric acid at least one week. As for the storage over a longer period, they were rinsed with distilled water before filling with very dilute nitric acid solution (~0.005N). Reaction vessels and polycarbonate tubes (Gallenkamp TUL-680-030Y) that came into contact with $MnO_2$ solutions were soaked in between experiments with 1N nitric acid containing 0.2mM oxalic acid to prevent transfer of $MnO_2$, then rinsed and soaked in 0.005N nitric acid. Those polycarbonate tubes which were used to store the filtered solutions were cleaned by rinsing with distilled water, soaking in 0.1N nitric acid overnight, and rinsing with distilled water again before filling up with very dilute nitric acid for storage. Before each analysis the reaction vessel and polycarbonate tube were equilibrated with uv-irradiated clean seawater of the same ionic strength as those of the sample overnight to condition the container walls. The polycarbonate tubes were then rinsed once with distilled water and dried at 35°C; whereas the reaction vessel was rinsed twice with the sample just before commencing the experiment.

## 5.3 MICRO CHLORINITY DETERMINATION

### 5.3.1 Reagents

a. Standard seawater (Cl%. 19.375).

b. Silver nitrate solution: prepared by dissolving 17.818 gm of $AgNO_3$ in 500 ml of distilled water.

c. Fluorescence indicator solution: prepared by dissolving 5 mg of sodium fluoresceinate in 5 litre of distilled water.

### 5.3.2 Method

The salinity could not be measured by salinometer because of the small size of the interstitial water samples. Therefore, the method chosen was the one suggested by Grasshoff (1976) for chlorinity determination in a small sample aliquot by precipitation titration using an adsorption indicator.

To 50ml of fluorescence indicator solution 25ml of distilled water was added; add 1ml of standard seawater or sample, titrate with $AgNO_3$ solution, which should be standardized daily against standard seawater, until the end point was obtained (pink colour on the precipitate). The titration was carried out with continuous stirring with a magnetic stirrer. If the chlorinity of the sample is very low, the amount of sample added to dilute indicator solution can be increased to give a more pronounced end point and more accurate reading of the volume of $AgNO_3$ solution used. The replication should be carried out for both standard and samples. The salinity was then calculated from:

$$S‰ = 1.80655\ Cl‰$$

For more details refer to Grasshoff (1976). In case of surface water samples, which could be collected in a large volume, salinity measurement was performed on a Beckman conductivity salinometer.

## 5.4 DETERMINATION OF WATER DENSITY BY CALCULATION

Millero et al.(1976) have proposed the 1-atm equation of state of seawater. Later, the UNESCO panel recommended, after examining the differences between the equation of Millero et al.(1976), their direct experimental measurements and the new measurements of Poisson et al. (1980), a requirement for a new 1-atm equation of state. Millero and Poisson (1981) have recently proposed the new equation of state of seawater at 1-atmosphere:

$$(\rho - \rho_o) = AS + BS^{3/2} + CS^2$$

where A, B, and C are functions of temperature. At 25°C the values of these coefficients are

$$A = 7.59238 \times 10^{-1}$$

$$B = -4.20204 \times 10^{-3}$$

$$C = 4.8314 \times 10^{-4}$$

$\rho$ is the absolute density in kg $m^{-3}$. The density of Standard Mean Ocean water ($\rho_o$) is calculated from Bigg's equation (1967) which yield the value of $\rho_o$= 997.047958 kg $m^{-3}$ at 25°C. More details can be found in Appendix II.

## 5.5 DETERMINATION OF MAJOR IONS CONCENTRATIONS BY CALCULATION

In order to simplify the calculation, the assumption was made that in all analysed samples all the major ions behave conservatively. All the used ratios are from Wilson (1975)(Table 5.1) and the calculation of major ion concentration in mole $l^{-1}$ can be generalised by:

$$[M] = (\text{major ion to chlorinity ratio/atomic or molecular weight of that ion})\ Cl\textperthousand.\ \rho^{-1}$$

where S‰ = 1.80655 Cl‰ and $\rho$ = density in gm $cm^{-3}$.

## 5.6 DETERMINATION OF CARBONATE CONCENTRATION

The purpose of bubbling filtered, water-saturated air through the sample is to use the carbonate system for buffering the system, and at the same time, avoid more analytical steps to be involved in the $MnO_2$ method making the method more tedious and time consuming. Carbonate is one of the important inorganic ligands that is needed in speciation calculation, and the concentration can be calculated as follows.

In a system that is in equilibrium with $CO_2(g)$

Table 5.1 Ratio of major elements in g $kg^{-1}$ to Cl%. (g $kg^{-1}$).

| Element | Ratio |
|---|---|
| Cl | 0.99896 |
| $SO_4$ | 0.14000 |
| Ca | 0.02126 |
| Mg | 0.06626 |
| K | 0.02060 |
| Na | 0.55567 |

(aqueous carbonate system open to the atmosphere with constant $P_{CO_2}$) the carbonate concentration can be calculated from:

$[CO_3^{-2}] = (K_H\, P_{CO_2}\, \alpha_2)/\alpha_0$ (Stumm and Morgan, 1981)

where $K_H$ is the Henry's law constant in M atm$^{-1}$ ($K_H = [H_2CO_3^*]/P_{CO_2}$) and is equal to $10^{-1.51}$ at 25°C;

$P_{CO_2}$ is the partial pressure of $CO_2$ and is equal to $3.2\times10^{-4}$ atm;

The ionization fraction $\alpha_0$ and $\alpha_2$ are defined by :

$$\alpha_0 = (1 + K_1/[H^+] + K_1K_2/[H^+]^2)^{-1}$$

$$\alpha_2 = ([H^+]^2/K_1K_2 + [H^+]/K_2 + 1)^{-1}$$

where $[H_2CO_3^*] = [CO_2(aq)] + [H_2CO_3]$

$$K_1 = [H^+][HCO_3^-]/[H_2CO_3^*]$$

$$K_2 = [H^+][CO_3^{-2}]/[HCO_3^-]$$

If we regard $K_H$ and $P_{CO_2}$ values as constants (under the experimental conditions which are fixed at 25°C and 1 atm pressure), the carbonate concentration is a function of pH and ionic strenght (in terms of $K_1$ and $K_2$), and can be calculated directly from experimental pH, $K_1$, and $K_2$. For more details see Stumm and Morgan (1981).

## 5.7 PREPARATION OF $MnO_2$

### 5.7.1 Reagents

a. 0.04M sodium hydroxide in 0.02M potassium permanganate: prepared from dissolving 1.5803 gm of $KMnO_4$ (Analar) with 0.8 gm of NaOH (Analar) in 50ml of distilled water.

b. Manganese solution (~0.2M): prepared by dissolving 3.958 gm of $MnCl_2.4H_2O$ in 100ml of distilled water.

c. Primary standard oxalate solution (~0.02M): prepared by dissolving 0.826 gm (accurately weighed) $Na_2C_2O_4$ in 250ml 0.1M perchloric acid.

d. Secondary standard permanganate solution (~0.02 M): prepared by dissolving approximately 24 gm of $KMnO_4$ (Analar) in 1 litre of distilled water; heating to ~90-95°C and left at that temperature for 1 hour, cooling off in the dark at room temperature for 2-3 days, and filtering using sintered glass no.4.

### 5.7.2 Method

The hydrous manganese dioxide used in the experiments was prepared by the reaction:

$3Mn^{2+} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$ (at neutral pH)

75ml of a 0.02M potassium permanganate solution, containing 0.04M sodium hydroxide is added to 50ml 0.02M manganese nitrate solution while stirring vigorously with a magnetic stirrer. During the formation of manganese dioxide, the pH drops due to the release of protons from adsorbed water. The pH is brought back to near neutral by the immediate dropwise addition of 1M sodium hydroxide solution. After the reaction is completed, the precipitated $MnO_2$ is purified by repetitive centrifugation (ca. 3 times) and resuspension with distilled water. For the greatest desorption of contaminating heavy metals, the centrifugation should be carried out on the suspension at a pH around 5. The final $MnO_2$ suspension should form a finely distributed suspension which can be pipetted reproducibly upon careful shaking of the container.

The concentration of $MnO_2$ is then measured by reducing aliquots of the suspension with a slight excess of oxalate solution. The determination of manganese is performed by graphite furnace atomic absorption spectrometry (GFAAS) and also by back titration with standardized potassium permanganate (Vogel, 1953). The results from both methods are used to confirm each other and in the calculation of the average oxidation stage of Mn. The result shows that the prepared manganese dioxide is $Mn^{3.88+}$ and the oxide is $MnO_{1.94}$ – very close to the values reported by van den Berg (1979). The concentration of the suspension is 0.0425M.

## 5.8 pH MEASUREMENT

The pH was measured by the "free hydrogen ion" scale with a Radiometer PHM 64 in conjunction with a Radiometer GK 2401C combined glass/calomel reference electrode. The electrode was filled with saturated KCl in equilibrium with KCl crystals. The electrode was calibrated at 25°C against 0.01M HCl pH 2.000; which was prepared by dilution of 0.1M HCl (BDH "Convol") with distilled water and by the addition of the appropriate amount of solid NaCl to adjust the ionic strength to that of the sample. The electrode was conditioned in this buffer overnight. After calibration the electrode was always rinsed with $MnO_2$-treated, uv-irradiated water of the same ionic strength as buffer. The electrode was then not allowed to come into contact with distilled water or solutions of different ionic strength. The pH was measured after 15-20 minutes equilibration of the electrode in the sample.

## 5.9 MEASUREMENT OF METAL-ORGANIC COMPLEXATION BY THE $MnO_2$ METHOD

### 5.9.1 Reagents

a. Distilled water: from an all silica still; double distilled.

b. Sodium hydroxide solution (~1M): prepared by dissolving an appropriate amount of NaOH (Analar) in distilled water.

c. Boric acid: from 99.5 percent $H_3BO_3$ (Analar).

d. Nitrilotriacetic acid solution (~5mM): prepared by dissolving an accurately weighed 0.1 gm of NTA in the minimum amount of sodium hydroxide solution and diluting with distilled water.

e. EDTA solution (~10 µM): prepared the same way as NTA solution.

f. Nitric acid: from concentrated $HNO_3$(Aristar).

g. "Metal free" acetate buffer (2M, pH 4.0): prepared by gradually adding 115 ml glacial acetic acid (analytical grade) to a solution of 138.2 g $K_2CO_3$

(analytical grade) in 900 ml of distilled water. The carbon dioxide was boiled off, and the solution was left to cool overnight, and made up to 1 litre. The pH was finally adjusted to 4.0 by adding glacial acetic acid, and the buffer was later cleaned by electrolysis at −1.2V in an ESA reagent cleaning system (ESA 2014 PM).

h. Zinc stock solution (0.015M): from BDH zinc standard solution (spectrophotometric grade).

i. Carrier free radioactive Zn65 (3.7 $\mu$g ml$^{-1}$, 0.77 mCi ml$^{-1}$): supplied by Amersham International Ltd., and the activity specified was for 1st December 1981.

j. "Organic matter free" distilled water: prepared by uv-irradiation of distilled water with a 1 KW lamp Hanovia unit for 3 hours.

k. Clean seawater: prepared by equilibrating filtered seawater with 15 uM $MnO_2$, stirring by a magnetic stirrer overnight, uv-irradiating by 1 KW lamp Hanovia unit for 3 hours, and filtering through acid-cleaned membrane filters.

l. Acid-cleaned membrane filter (Oxoid, 0.45 $\mu$m pore size): the filter was soaked in 0.1M $HNO_3$ overnight, and rinsed repeatedly with distilled water before use.

### 5.9.1.1 PREPARATION OF WORKING STANDARD RADIOACTIVE ZN65 SOLUTION

Three working standard solution of zinc (mixture of stable zinc and Zn65) were prepared at different stages during the project, so as to obtain different activities of radioactive tracer, and in total concentrations of zinc. The purposes of using three different working standard solutions are:

a. to optimize the level of radioactive zinc activity because of its relatively short half life (245 days) compared to the total time span of this work;

b. to find the suitable level of radioactive activity to be used in order to increase the method's sensitivity.

The working standard solutions were prepared by mixing the stock zinc solution (BDH standard, 15.298mM) with carrier-free Zn65 solution in different proportions, and diluting to around 30ml by weight with distilled water (Table 5.2). The total zinc concentration of each working standard solutions was determined by GFAAS and confirmed by DPASV determination at pH4. The results from gamma scintillation counter were used in checking the loss of zinc from working standard solution caused by improper adjustment of pH during preparation stage.

It is best to keep the pH of the working standard solutions around 4 which seems to be just acidic enough to prevent metal precipitation and adsorption onto the container walls. Apart from the reasons mentioned, it is in a matter of interest that the working standard solution should not be too acidic, thus avoiding a pH change in the sample that may result from the addition of acidic standard solution during the titration process.

Table 5.2 Concentrations of working standard solutions, activity level of Zn65 and proportion between stock zinc solution and carrier free Zn65.

| Concentration (mM) | Date | Activity ($\mu$Ci ml$^{-1}$) | Volume of stock zinc to volume of Zn65 in 30ml solution (ml:ml) |
|---|---|---|---|
| 0.0976 | Nov.'81 | ~1.92 | 0.175:0.075 |
| 0.3827 | Jun.'82 | ~3.82 | 0.800:0.150 |
| 0.1098 | Dec.'82 | ~2.56 | 0.200:0.200 |

Nitric acid (Aristar) and NaOH solution were used in adjusting the pH of the working standard solutions.

## 5.9.2 ANALYTICAL TECHNIQUES USED IN THE ZINC DETERMINATION

Three analytical techniques were employed in measuring zinc concentrations:

1) Liquid scintillation technique - used solely for the measurement of Zn65 activity;

2) GFAAS technique - used in measuring the concentration of total dissolved zinc in standard working solution;

3) ASV technique - used in measuring the concentration of total dissolved zinc in the blank and sometimes in the working standard solution.

### 5.9.2.1 LIQUID SCINTILLATION TECHNIQUE

For gamma ray measurements by scintillation counting, single large crystals of sodium iodide, containing a trace of thallium iodide as an activator, are used almost exclusively because of the high density and high atomic number of iodine which results in a high rate of adsorption of gamma rays (Friedlander and Kennedy, 1960). The scintillation system used consisted of a well type scintillation counter (a Panax USC series; NaI(Tl) crystal and photomultiplier; housed in a lead castle) and Nuclear Enterprise SR7 Scaler Ratemeter equipped with a Datac 312 printer. Zn65 emits 1.11 MeV gamma rays on a line spectrum which is quite monoenergetic and well estblished. It is also a suitable nuclide for calibrating the gamma spectrophotometor (Wilson, 1966). Other nuclides, that are also commonly used, are Caesium 137 and Cobalt 60. The SR7 Scaler Ratemeter was set in the pulse height analyzer mode, dual channel (E ± ΔE) at the base line setting (E) calibrated according to gamma energy of 1.11 MeV, and the window ( ΔE) of around 1V to obtain the width of the peak at half maximum of 4.9% of 1.11 MeV, and at the error of around 1% or less (Chase and Rabinowitz, 1966). In this mode pulses from the source with an amplitude greater or less than E ± ΔE are registered in the second channel, and the result is read from the register in the first channel. Whilst setting up the instrument, it is necessary to optimize the high voltage supply in order to get the maximum count in the first channel. Every three months the instrument was recalibrated against a standard gamma ray source to maintain maximum efficiency.

The calibration curve for liquid scintillation counting was done regularly by using freshly prepared acidic standard solutions which had been diluted from the appropriate working standard Zn65 solution. The total dissolved zinc concentration of the sample aliquots from each titration points can then be calculated. In order to correct for the dilution effect (the change in the proportion between the stable zinc and radioactive Zn65 which changes accordingly to the addition of working standard solution during titration), a correction factor was introduced at the nth addition of working standard to the sample.

correction factor = $([Zn_t]_n - [Zn_b])/[Zn_t]_n$

where $[Zn_t]_n$ is the total zinc concentration after the nth addition of the working standard and $[Zn_b]$ is the initial concentration of zinc (stable) in the sample solution before titration.

However, considerable care was taken to ensure that there is a minimal difference in volume between each filtered sample aliquot and the standard solutions used in preparing the calibration curve for the scintillation counting; similar geometrical shape of container must be used to contain the sample aliquots during counting (throughout the experiments 1.3x6.0 cm polycarbonate tubes with caps, Gallenkamp TUL-680 030Y, were used; and also the positioning of the tube itself in the well of the counter must be reproducible.

### 5.9.2.2 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

This technique was used solely for the purpose of determining the concentration of the working zinc standard solution. The instrument used was a Perkin Elmer 2280 atomic absorption spectrophotometer equipped with a Perkin Elmer HGA 400 graphite furnace unit and an AS-1 automatic sampling system. The operating conditions were those in Perkin Elmer (1980). The series of unknown and standard solutions were prepared by addition of either a fixed amount of working standard solution (concentration to be determined), or different amounts of BDH zinc standard solution to a fixed volume of acidified distilled water. The concentration of working standard solution was then calculated, after measurement by means of the internal standard (BDH) addition curve. The concentration range of additional standards was adjusted to cover the concentration level of the unknown. The concentration of the unknown itself was the average value from 5 replicated solutions.

### 5.9.2.3 ANODIC STRIPPING VOLTAMMETRY

The instruments used in this study consisted of a PAR 174A polarographic analyzer, a PAR 303 static mercury drop electrode, a PAR 305 magnetic strirrer, and a Houston Instrument 2000 omnigraphic X-Y recorder.

Dissolved zinc was determined in 5ml sample aliquots by DPASV at pH 4.0. To the sample, 0.05ml of a 2M acetate buffer was added, and the sample was deoxygenated by bubbling with Ar gas for 5 minutes. The plating potential was -1.25V against a saturated Ag/AgCl reference electrode, the plating time 150 seconds, the scan rate 5mv $s^{-1}$ and the pulse frequency 0.5 seconds. The plating was done while a magnetic stirrer provided constant stirring. The stirring was stopped at 150 seconds; the solution was allowed to stand for a further 30 seconds; and the stripping process was started. Each aliquot was measured three times, but the first measurement was always disregarded, and the average of the second and third measurement was used. If there was a difference in peak height of more than 1% between the second and third measurement, a fourth measurement was performed, and the average of the three was used.

The dissolved zinc concentration of the aliquots was calulated from the calibration curve obtained from a series of at least three internal standard additions (the standard used was the diluted BDH standard).

DPASV technique was used in determination of zinc in both the working standard solutions and the blank level in samples.

### 5.9.3 METHOD

An aliquot of ~60ml of the sample was weighed into a cleaned, conditioned 125ml polyethylene bottle. Filtered, water-saturated air from a compressed air cylinder was then bubbled for at least 45 minutes. An amount of ~0.15gm (accurately weighed) solid boric acid (Analar) was poured directly into the reaction vessel, followed by ~0.3ml of 0.6M NaOH solution to prevent the abrupt change in pH when the sample comes into contact with boric acid. The reaction vessel was a 100ml polarographic cell with water jacket which was kept at a constant temperature of 25 ±0.05°C by continuously pumping water from a temperature-controlled water bath through the water jacket. The pH was adjusted to 8.20 by addition of 0.6M NaOH solution, and was kept constant throughout the titration. A 5ml subsample was pipetted out by an Oxford Macroset pipette, and buffered to pH 4.0 with 0.05ml 2M acetate buffer to be used later for the zinc blank determination. For subsampling, an Oxford Macroset pipette was used which was calibrated daily gravimetrically with distilled water. Depending on the expected level of ligands present in the sample (to maintain the sensitivity of the method), an amount of between 0.05-0.09ml of 0.0425M $MnO_2$ was added to give a final concentration of 35-70 µM $MnO_2$. The titration was then performed by additions of 0.05ml of a suitable working zinc standard solution; the pH shift (which hardly occurred) was adjusted back accordingly to 8.20 by using 0.6M NaOH. A 5ml subsample was pipetted into a conditioned 6ml polycarbonate tube, which was then closed tightly with cap. The total of ten additions were made, varying the total added zinc concentration between 0.11 to 1.4 µM. All the subsamples were shaken overnight (for at least 20 hours) in a water bath set at 25°C. After equilibration, the subsamples were filtered through Oxoid membrane filters using a Millipore "Swinnex" filter unit (13mm diameter filter paper) directly into polycarbonate tubes, and subsequently acidified with 0.025ml conc.$HNO_3$ before closing the caps tightly and liquid scintillation counting.

As for the radioactive waste disposal, all the used membrane filters were soaked in 0.1M oxalic acid in order to dissolve the $MnO_2$ associated with radioactive zinc on the filter before disposing the liquid and solids separately.

Normally, total dissolved metal concentrations (Cu, Pb, Cd, and Zn) were measured by DPASV from a sample aliquot of each sample before metal titration. In cases of high metal concentration, for example, as in Mersey interstitial water and some surface sample, the sample had to be treated with $MnO_2$ overnight (~20-30 µM $MnO_2$), and filtered through an acid-cleaned membrane filter. The total metal concentrations were then remeasured. The pretreatment is necessary in these cases to avoid the change in charge distribution on the oxide caused by higher metal concentrations (the calibration of $MnO_2$ was always performed in low metal concentration water) which may result in the difference of metal-ion binding capacity from the calibrated value.

### 5.9.4 CALIBRATION OF $MnO_2$

It is preferable to calibrate the $MnO_2$ in water of the same composition as the sample, but from which all the complexing ligands have been removed. The calibration procedure of the exchange capacity and binding strength of the $MnO_2$ for zinc ion was carried out the same way as above. The calibration could be performed with or without a ligand of known binding strength (in the experiments NTA was used). If NTA was used, a final concentration of 20 µM NTA was selected. It is preferable to calibrate $MnO_2$ in absence of complexing ligands, provided that the method used for metal determination is sensitive enough and the metal is not strongly bound to the oxide; this was achieved using a working standard solution of the highest Zn65 activity possible, and by adjusting the $MnO_2$ concentration. Since the volumes of most obtained interstitial water samples are limited the uv-irradiated clean seawater was used as a medium. In adjusting the ionic strength of the medium to the same level as the sample, dilution was made with 1 mM bicarbonate solution (prepared by dissolving an appropriate amount of $NaHCO_3$ in "organic matter free" distilled water).

## 5.10 EQUILIBRATION TIME

The calibration experiments were set up at two different salinities of 31.83 and 8.68‰. The initial volume of the medium was around 100ml, and the amounts of all the reagents required were adjusted accordingly to give final concentrations of 70 µM $MnO_2$, 0.04M buffer, 20 µM NTA, and 0.75 µM zinc. The subsamples were taken at the different time interval, filtered, acidified and counted. Finally, a plot of Tads vs. time was made.

## 5.11 TEST OF ZINC ADSORPTION ON CONTAINER WALLS

The study was carried out using uv-irradiated, $MnO_2$-treated water of salinity 25‰. To 100ml of the medium 0.1ml of 0.1098mM working zinc standard solution was added. The final concentration of added zinc was

~0.1098 µM in the presence of 0.04M boric acid buffer (pH 8.20). The total zinc concentration of the sample had been previously measured by DPASV at pH 4.0, and found to be very low ($10^{-9}$M). At different time intervals (e.g. 0.5, 1 or 3 hours), subsamples were taken and the dissolved zinc concentrations were measured by DPASV at pH 8.20. Each subsample was later acidified and submitted to liquid scintillation counting, thus providing an internal check for the reliability of the result.

## 5.12 SUMMARY

In determining a complexing capacity and conditional stability constant by the $MnO_2$ method, the data obtained from each experiment (e.g. salinity, dissolved metal and total metal concentrations) have to be processed in several steps. In order to illustrate how both the complexing capacity and the conditional stability constant are calculated the calculation steps can be summarized as follows:

1) Calculation of the density from the Millero-Poisson equation of state (see section 5.4 and also Appendix II); and was later used in both calculation of major ion concentration and estimation of the sample's volume.

2) Calculation of major ion concentrations (see section 5.5).

3) Calculation of ionic strength, including the

increase in ionic strength from borate buffer.

4) Calculation of the carbonate concentration (see section 5.6).

5) In speciation calulation, it is necessary to include all possible side reactions. Firstly, all stability constants of each side reactions are corrected to the desired ionic strength either by Davies equation or by using the model of Turner et al. (1981) (see section 4.4). Secondly, the corrected stability constants are used in calculation of the side reaction coefficient ($\alpha_M$) of metal-inorganic complexes (including borate complexes introduced into the system by the use of buffer), and the side reaction coefficient of ligands ($\alpha_L$) used in the calibration of $MnO_2$ such as NTA.

6) The data of total and dissolved metal concentrations, in conjunction with the side reaction coefficients and concentration of $MnO_2$, are used to calculate Tmax and B in the calibration experiment, or $[L_t]$ and $K_{ML}'$ for the natural water samples as described in section 2.2.2.

# CHAPTER 6

# RESULTS AND DISCUSSIONS

## 6.1 EQUILIBRATION TIME

It is important to have an estimate for the time required to obtain equilibrium between metal ions, complexing ligands and $MnO_2$ as measurement prior to equilibrium will lead to a wrong interpretation of the result and to poor reproducibility. The equilibration time (the time required for metal to reach maximum adsorption on $MnO_2$ surface) was tested for the NTA-$MnO_2$-zinc system at various salinities. At a salinity of 31.8‰ the amount of zinc adsorbed on $MnO_2$ reached a maximum value within 15 hours (Figure 6.1) and at a salinity of 8.7‰ in only 9.5 hours (Figure 6.2), while 50% of zinc adsorption occurred within 15 and 10 minutes respectively. Therefore, the equilibration time allowed in all experiments of at least 20 hours is quite sufficient to obtain equlibrium between metal ions, complexing ligands and $MnO_2$. Equilibration times varying from less than an hour to several days to reach adsorption equilibrium between free metal ions and $MnO_2$ have been reported in the literature (Table 6.1). The presence of a ligand seems to slow down the adsorption considerably.

Adsorption of cobalt onto $MnO_2$ should reach equilibrium faster than zinc because of its stronger affinity for $MnO_2$ (Loganathan and Burau, 1973; Murray, 1975a).

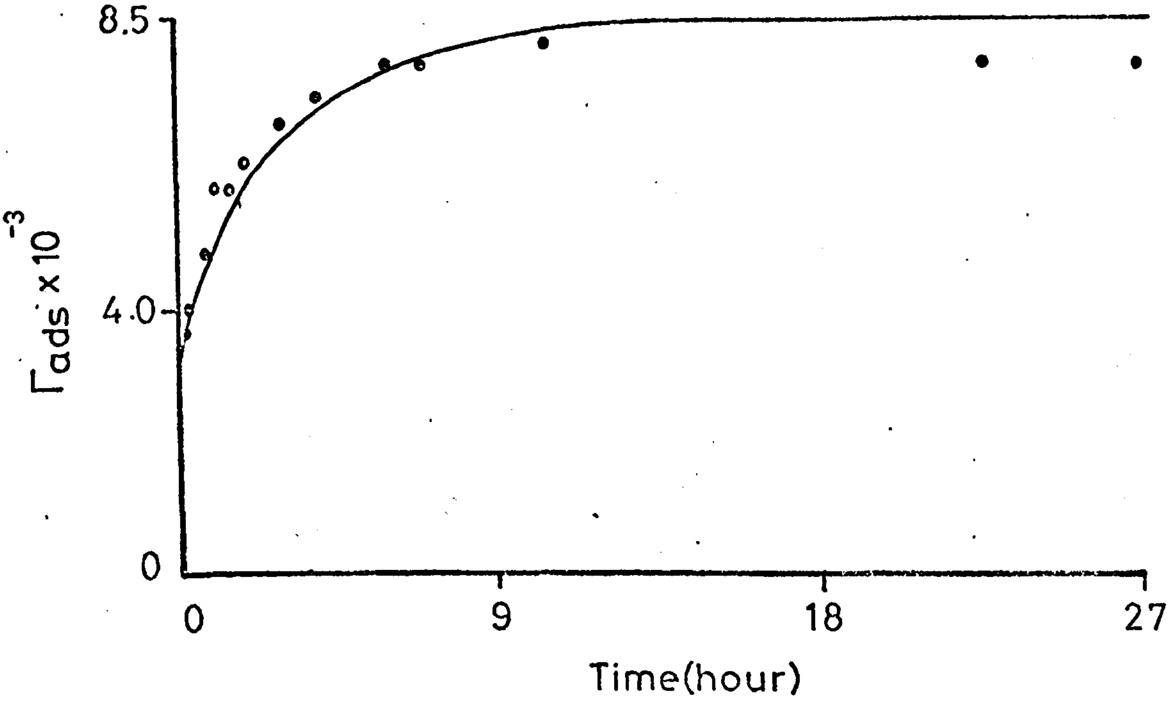

Figure 6.1 Kinetics of zinc adsorption onto the $MnO_2$ surface in presence of 20 µM NTA at 31.83%. (at 25°C, pH 8.20, 70 µM $MnO_2$).

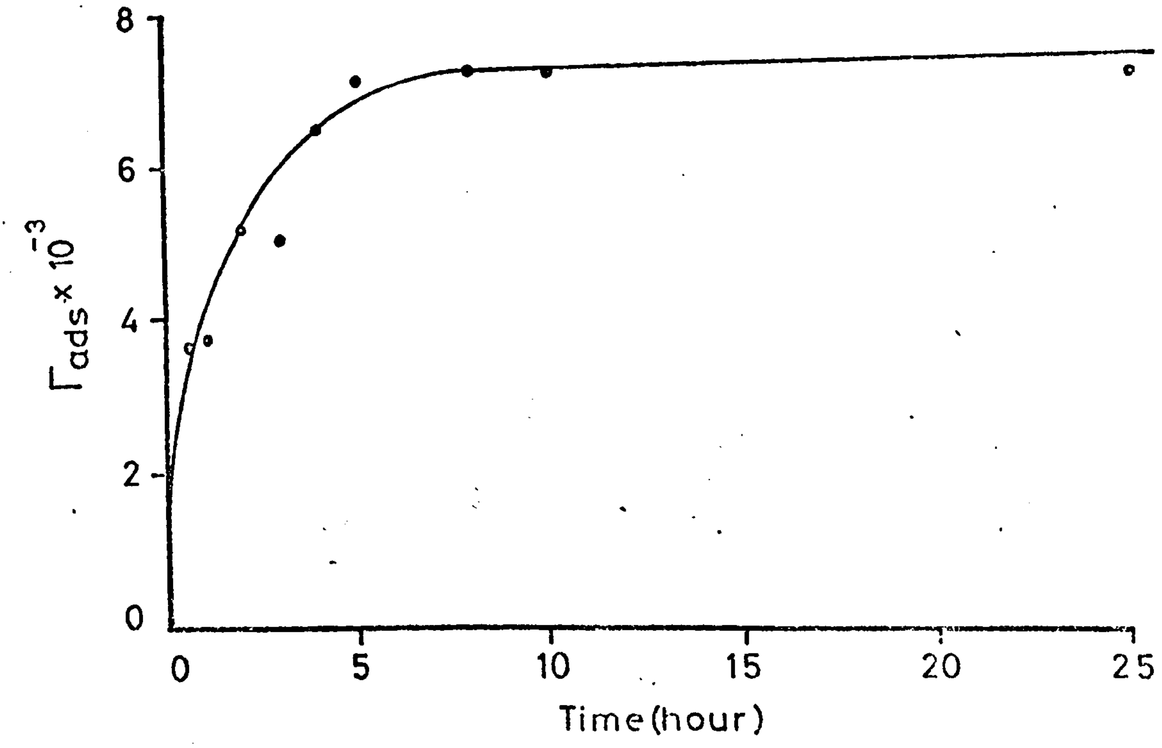

Figure 6.2 Kinetics of zinc adsorption onto the $MnO_2$ surface in presence of 20 µM NTA at 8.7%. (at 25°C, pH 8.20, 70 µM $MnO_2$).

Table 6.1 Adsorption of trace metals on $MnO_2$; time required to reach equilibrium (at 25°C)

| Reference | Adsorbed metal | pH | I | Time |
|---|---|---|---|---|
| Loganathan and Burau (1973) | Co, Zn | 4 | 0.001 | 1 hour |
| Gadde and Laitinen (1974) | Pb, Zn | various | not reported | 3 hours |
| Murray (1975a) | Co, Zn | various | 0.1 | 1 hour |
| Loganathan et al. (1977) | Co, Zn | 3.5-10.0 | 0.001 | 2 days |
| Dempsey and Singer (1980) | Zn | 6.0-8.5 | 0.01 | 0.5 hour |
| this work* | Zn | 8.2 | 0.15<br>0.60 | 9.5 hours<br>15 hours |

* in presence of NTA

The NTA-$MnO_2$-Co system was tested at 14‰ salinity (Figure 6.3). Adsorption of cobalt was found to increase abruptly within the first hour (~50% in 10 minutes and upto ~80% in 1 hour) and then gradually increase for upto 6 hours. After 6 hours the amount of dissolved cobalt was very close to the detection limit (by measuring the activity of Co65 with scintillation counting), even in the presence of 20 µM NTA, and became undetectable after 24 hours. It is possible that the used level of $MnO_2$ (70 µM) is too high, and overcomes the ability of NTA to retain cobalt in solution. Also it is possible that cobalt(II) is oxidized by the $MnO_2$ to cobalt(III) (Murray, 1975b), which then adsorbs irreversibly onto the surface of $MnO_2$. Thus, the large adsorption capacity of $MnO_2$ for cobalt could be explained. No further attempt was made to apply the $MnO_2$ method to cobalt. Another technique for measuring cobalt complexing capacity has been demonstrated successfully by Hanck and Dillard (1977a and b).

An equilibration time similar to that for zinc was selected for experiments with lead, though equilibrium is reached faster because of the greater affinity of lead for $MnO_2$.

## 6.2 EFFECT OF ZINC ADSORPTION ON CONTAINER WALLS

Adsorption of inorganic dissolved zinc on container walls was tested by measuring, as a function of time, the dissolved zinc concentration at pH 8.2 by DPASV, and

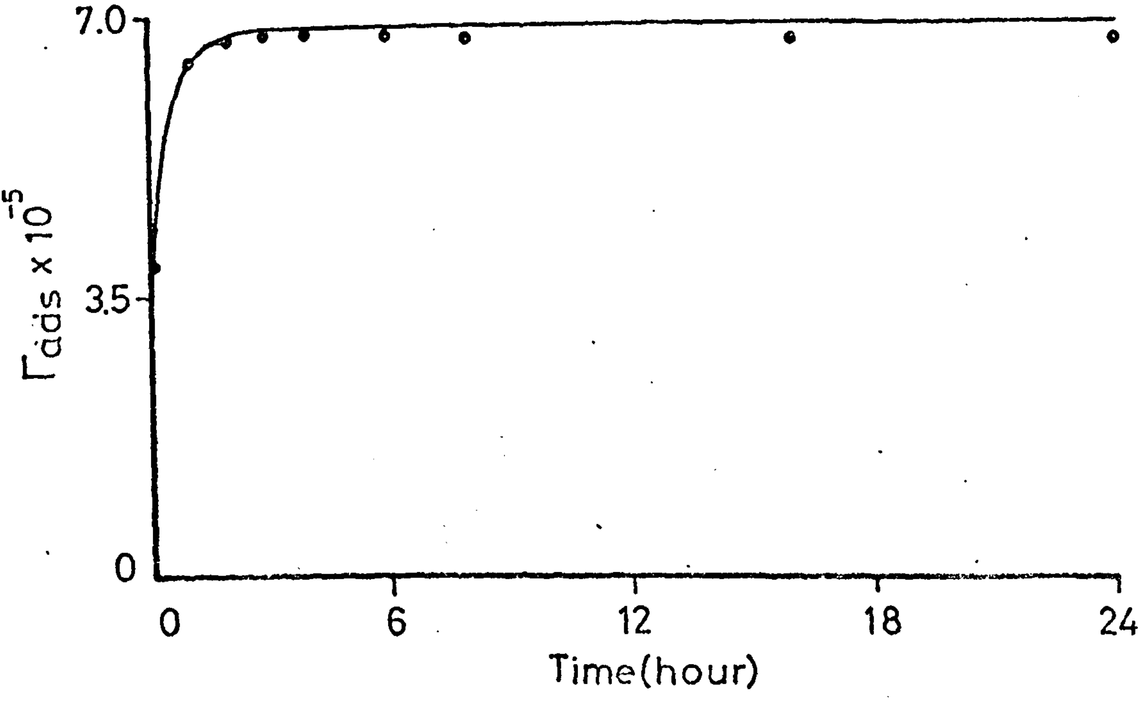

Figure 6.3 Kinetics of cobalt adsorption onto the $MnO_2$ surface in presence of 20 μM NTA (at 25°C, pH 8.20, 70 μM $MnO_2$).

by scintillation counting of added tracer as described in section 5.11. In this experiment the dissolved zinc concentration (inc. tracer) was 0.1 μM (Figure 6.4). It was found that about 5% of zinc was adsorbed after 24 hours, and the amount adsorbed increased to ~16% over the period of 48 hours. Adsorption of zinc on $MnO_2$ is a lot faster than adsorption onto container walls, so most of inorganic dissolved zinc is removed from solution in a very short time in presence of $MnO_2$. For example, about 50% adsorption of zinc on $MnO_2$ is achieved within 3 minutes in absence of ligand (Dempsey and Singer, 1980) and within 10 minutes in presence of 20 μM NTA (This work). Adsorption on container walls, therefore, is negligible and does not cause an error in the determination by the $MnO_2$ method because the dissolved inorganic zinc concentration in presence of $MnO_2$ is generally low, and the $MnO_2$ acts as a dissolved zinc buffer.

## 6.3 CALIBRATION OF $MnO_2$

The adsorption parameters, Tmax and B, in the Langmuir equation (eq.2.36) were calibrated, for the zinc experiments, over a narrow pH range (pH 8.00-8.35), over a wide range of salinity (1.75-35.0‰) and in presence and absence of NTA and boric acid buffer. The calibration experiments for lead were carried out in presence of NTA and boric acid buffer at various $MnO_2$ concentrations. All experimental data in this work are reported with the

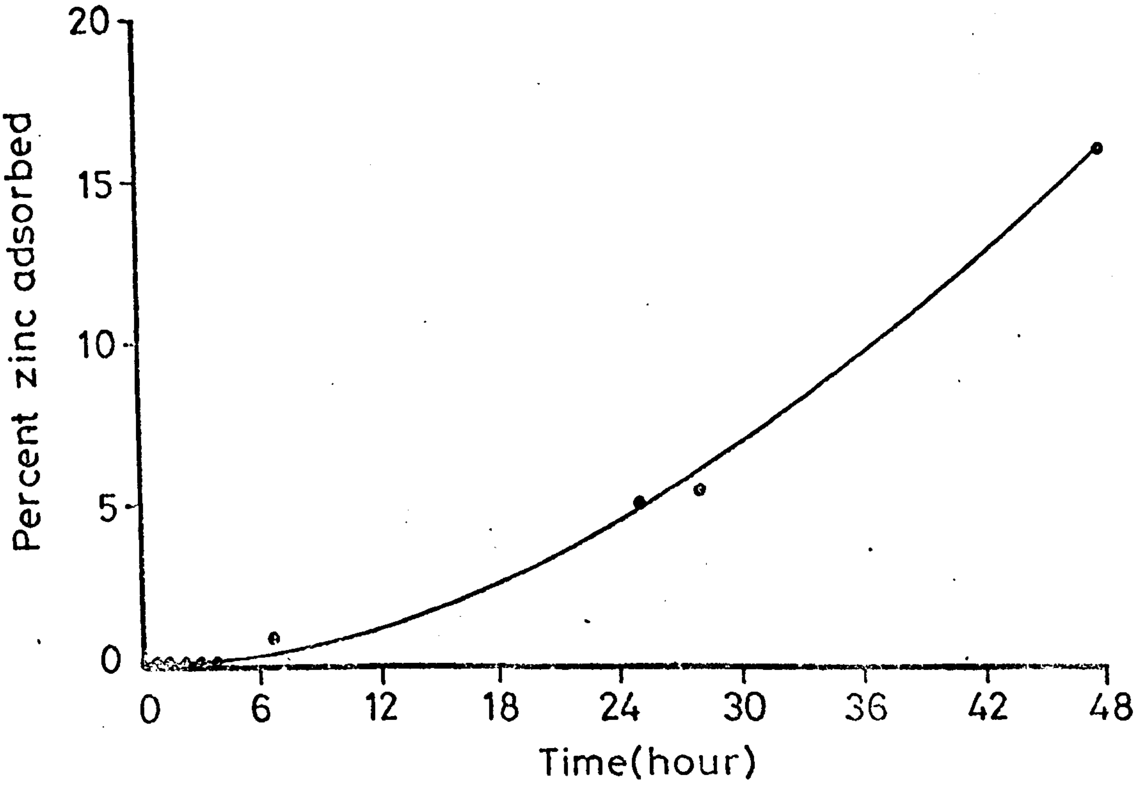

Figure 6.4 Rate of zinc loss from solution via adsorption onto container walls.

standard error calculated at 95% confidence limit (see Appendix I: Regression analysis).

### 6.3.1 ZINC

The $MnO_2$ method (van den Berg, 1982b) proposed the bubbling of filtered, water-saturated air through the media until a constant pH is obtained. Unfortunately, it was found to be difficult to get exactly the same pH in water samples as obtained in calibration experiments done in the waters of the same composition, and so the effect of pH was studied in the narrow range of pH likely to be obtained. During these experiments the zinc concentration was varied between 0.1 and 1.3 µM, and the concentration of $MnO_2$ was 70 µM. The results are shown in Table 6.2 and can be compared with the data of Dempsey and Singer (1980). The trend seems to show a slight decrease in Tmax with increasing pH, whereas the B values increase with pH. Dempsey and Singer (1980) studied zinc adsorption onto $MnO_2$ in 0.01M $NaNO_3$ medium and carried out their experiments at zinc concentrations upto $2\times10^{-5}$M in presence of a $10^{-4}$M $MnO_2$. They allowed $MnO_2$ to equilibrate with zinc for 40 minutes and the amount of adsorbed zinc was measured instead of dissolved zinc. Their $MnO_2$ was prepared following the recipe of van den Berg and Kramer (1979), and was, therefore, similar to the $MnO_2$ used in this work. They obtained higher (~10 times) Tmax values for the Langmuir isotherm and smaller B values (~2.5 times, log unit) than this

Table 6.2 Effect of pH on the adsorption of zinc onto $MnO_2$ (at 25°C).

| pH | logB | Tmax |
|---|---|---|
| This work; in absence of ligand, at ~0.62 ionic strength | | |
| 8.04 | 6.94 ±0.04 | 0.035 ±0.003 |
| 8.09 | 7.65 ±0.06 | 0.034 ±0.004 |
| 8.25 | 7.43 ±0.04 | 0.031 ±0.005 |
| 8.34 | 8.36 ±0.06 | 0.025 ±0.003 |
| Dempsey and Singer (1980); in absence of ligand, at ~0.01 ionic strength | | |
| 6.0 | 6.13 | 0.100 |
| 7.0 | 6.27 | 0.136 |
| 8.0 | 5.78 | 0.253 |
| 8.5 | 5.74 | 0.396 |

work. It is likely that more adsorption sites will be occupied as the amount of adsorbed zinc increases (which causes Tmax to increase in magnitude), whereas overall binding strength decreases (Benjamin and Leckie, 1980). More results in the use of Langmuir isotherm in studying adsorption behaviour of the oxide of nonuniform surface sites will be presented later on. Dempsey and Singer (1980) found that Tmax increased with increasing pH while B decreased. However, their experiment were performed at much greater zinc concentration than this work, which may explain the different results.

Van den Berg (1979) calibrated the surface of $MnO_2$ for copper adsorption under conditions (i.e. level of metal added and $MnO_2$ concentration) similar to this work and observed an increase in Tmax with pH which leveled off at pH>8. The B value was found to increase at pH>6.5 but it was constant at lower pH. Stroes (1983) used the same conditions as van den Berg (1979) and found that Tmax does not change with pH but B increases with pH (Figures 6.5, 6.6). Therefore, it is possible that at low metal concentration, particularly at high pH (>8), Tmax is not affected by pH while B increases with increasing pH.

Thus, it is necessary that an adsorption model, such as the Langmuir model, must be applied at constant pH. It was, therefore, decided to make use of a pH buffer. Boric acid buffer was used to control the pH at 8.2. It is very important that all side reactions of

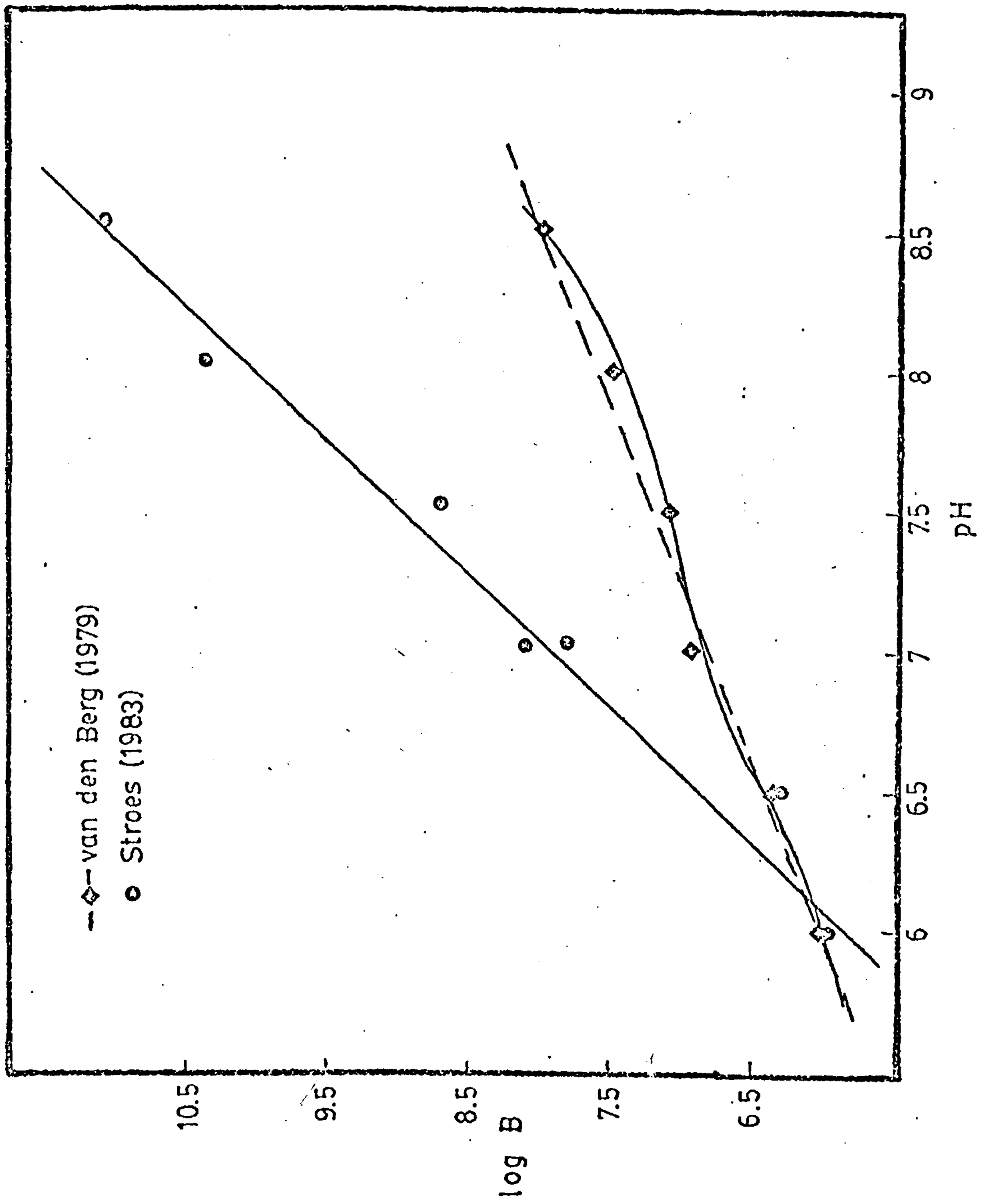

Figure 6.5 Effect of pH on the Langmuir adsorption parameter B (after Stroes, 1983).

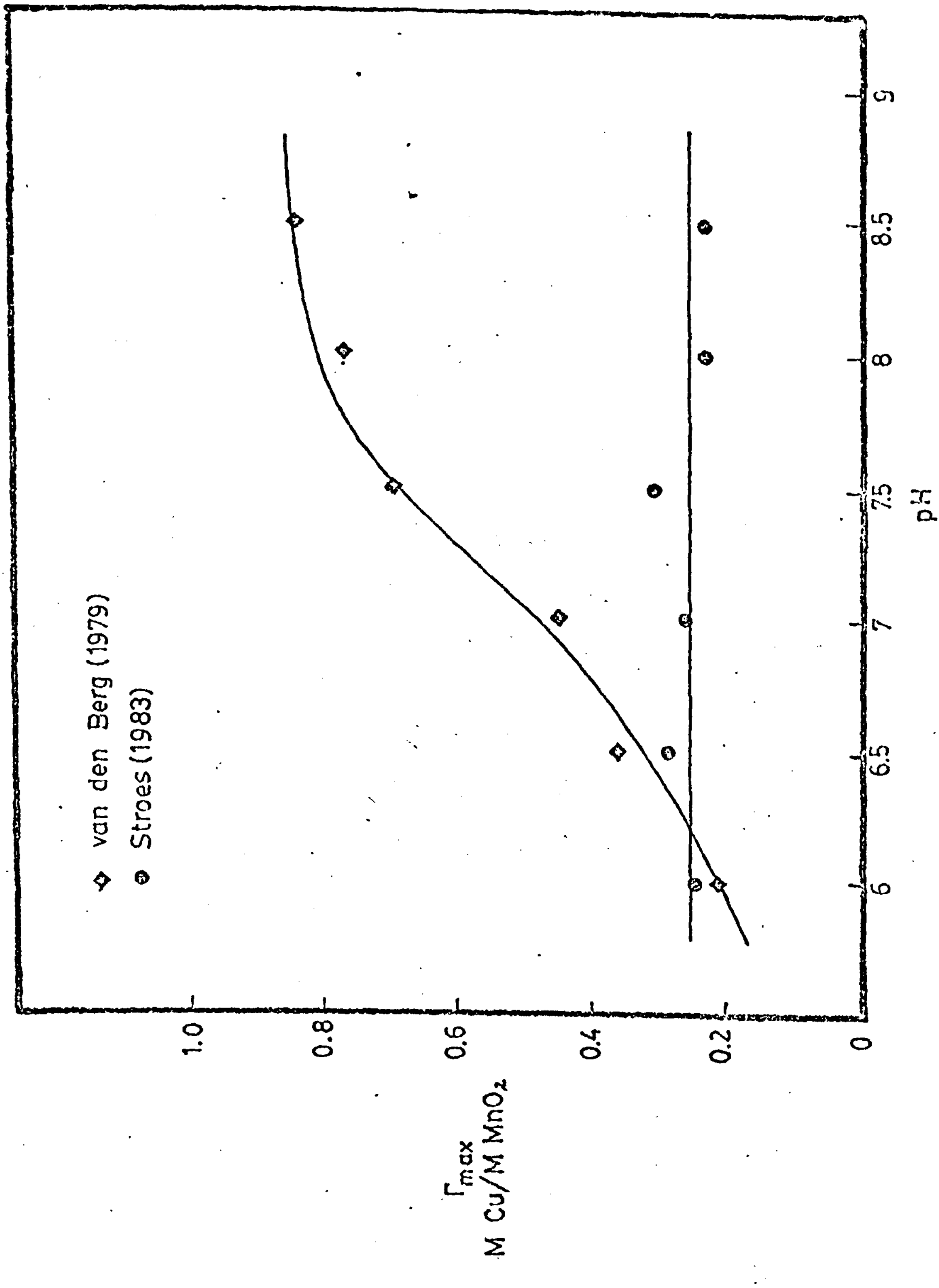

Figure 6.6 Effect of pH on the Langmuir adsorption parameter Tmax (after Stroes, 1983).

borate ion are included in the speciation calculation. Stability constants of borate complexes, as reviewed by Basset (1980), were used first, but the borate fraction of metal ion speciation was found to be unrealistically high. Recently, van den Berg (1982c) has determined these stability constants again. The new constants of borate complexes, when used in the speciation calculation, showed that, after side reactions of borate complexes were accounted for, the adsorption parameters were the same in the absence and presence of various buffer concentrations (Table 6.3). A concentration of 0.04M boric acid buffer was selected for the experiments, because it provides sufficient buffering capacity while the concentration is low enough so as not to alter natural equilibria.

The constants in the Langmuir equation for adsorption of zinc onto $MnO_2$ were calibrated in seawater at various salinities. In some cases a known complexing ligand ($1.5\times10^{-8}$-$2\times10^{-8}$ MNTA) was added in order to increase the dissolved zinc concentration in equilibrium with $MnO_2$, while keeping the free $Zn^{2+}$ concentration low. The results are given in Table 6.3. Seawater was diluted with $10^{-3}$ M $NaHCO_3$ at salinities below 33%.. The free zinc concentration was varied between $2.5\times10^{-9}$ to $3.4\times10^{-8}$ M in these experiments. Values for B and Tmax were generally found to increase with decreasing salinity: logB inthe presence of NTA, for instance, increased from 7.65 at a salinity of 32%. to 8.8 at

Table 6.3 Calibrated values of logB and Tmax for adsorption of zinc onto $MnO_2$ (at 25°C, 70 µM $MnO_2$, pH 8.20).

| Salinity | logB | Tmax | $\log\alpha_{Zn}$ | Buffer concentration (M) |
|---|---|---|---|---|
| I. Effect of buffer (in presence of ~20 µM NTA)[1] | | | | |
| 31.2 | 8.26 ±0.05 | 0.017 ±0.002 | 0.319 | - |
| 31.8 | 8.20 ±0.09 | 0.020 ±0.004 | 0.328 | 0.005 |
| 31.8 | 8.17 ±0.05 | 0.019 ±0.002 | 0.358 | 0.08 |
| II. Effect of salinity | | | | |
| - in absence of ligand[1] | | | | |
| 32.8 | 7.14 ±0.09 | 0.015 ±0.002 | 0.321 | - |
| 25.0 | 7.70 ±0.19 | 0.024 ±0.008 | 0.290 | - |
| 20.0 | 7.39 ±0.09 | 0.032 ±0.006 | 0.260 | - |
| - in presence of ~20 µM NTA[2] | | | | |
| 31.8 | 7.65 ±0.04 | 0.061 ±0.005 | 0.349 | 0.04 |
| 8.7 | 7.74 ±0.05 | 0.048 ±0.005 | 0.254 | 0.04 |
| 1.8 | 8.80 ±0.04 | 0.040 ±0.003 | 0.228 | 0.04 |

1. 0.1-1.2 µM added zinc concentration; 0.0976 mM (total) zinc standard solution with 1.92 µCi $ml^{-1}$ tracer.

2. 0.3-4.0 µM added zinc concentration; 0.3826 mM (total) zinc standard solution with 3.83 µCi $ml^{-1}$ tracer.

2%., while values for Tmax only varied between 0.04 and 0.06, at zinc concentrations between 0.3 - 4μM.

LogB values, obtained from calibrations in the absence of NTA, may not represent the trend due to the salinity effect accurately. This is because the activity of the tracer used in the experiments was low, thus reducing the accuracy of the values comprising the lower section of the isotherm used in the estimation of these three values for logB.

The shift in logB may possibly represent reduced competition from major cations in seawater of lower salinity for adsorption sites on the $MnO_2$. A similar trend was observed for adsorption of copper on $MnO_2$ (van den Berg, 1982b) where logB was found to increase upon dilution of the sample to lower salinity. Competition by major cations is, therefore, an important factor which determines the extent of trace metal adsorption on $MnO_2$. A similar effect was observed by Murray (1975b), and Dempsey and Singer (1980). High concentrations of competing cations (e.g. 0.47 M Na, 0.055 M Mg and 0.01 M Ca) were sufficient to decrease the adsorption of $Co^{2+}$ by $MnO_2$ (Murray, 1975b). Using the competitive Langmuir model, Dempsey and Singer (1980) concluded that large concentrations of major cations, such as calcium alone, do not prevent adsorption of trace concentrations of Zn by $MnO_2$ (at $1\times10^{-3}$M Ca and 5 μM Zn), and competition is insignificant at pH values greater than 7. At higher trace metal concentrations, negligible competition was also observed by Tewari et al.(1972) and Murray (1975b).

The values of Tmax from the calibrations in the presence of NTA can be compared with values obtained in absence of NTA. Tmax increases by a factor of almost 4 times in absence of NTA in seawater of 32‰ salinity, when the studied range of added zinc concentrations is increased by a similar factor. A similar effect was found when the $MnO_2$ concentration is varied but the range of zinc concentration is kept constant: higher values for Tmax were obtained at lower concentration of $MnO_2$ (Table 6.4).

It may, therefore, be concluded from the above findings that a number of sites with different binding strengths exist on the surface of $MnO_2$. Thus, it is necessary to calibrate metal adsorption onto $MnO_2$ under the same conditions of surface coverage as occurs during sample analysis. The following considerations need to be taken into account for a proper application of the Langmuir model (Benjamin and Leckie, 1980, 1981):

- the binding strength decreases successively when more sites are occupied, even though the overall surface is still capable of binding more metal;

- the average overall binding strength at very low adsorption densities is less than that of the strongest binding sites which are firstly occupied;

- the adsorption parameters, Tmax and B, are estimated over different ranges of adsorption densities.

Table 6.4 Calibrated values of logB and Tmax for adsorption of zinc onto $MnO_2$ at different $MnO_2$ concentrations (at 25°C, 0.04M buffer of pH 8.20, and 20 μM NTA).

| Salinity | logB | Tmax | $\log\alpha_{Zn}$ | $MnO_2$ (μM) |
|---|---|---|---|---|
| I. 0.3-4.0 μM added zinc concentration; 0.3826 mM (total) zinc standard with 3.83 μCi $ml^{-1}$ tracer. | | | | |
| 35.0 | 7.68 ±0.05 | 0.070 ±0.007 | 0.369 | 35 |
| 35.0 | 7.53 ±0.02 | 0.056 ±0.007 | 0.369 | 70 |
| II. 0.1-1.5 μM added zinc concentration; 0.1098 mM (total) zinc standard with 2.56 μCi $ml^{-1}$ tracer. | | | | |
| 22.7 | 7.88 ±0.08 | 0.061 ±0.007 | 0.301 | 35 |
| 22.7 | 7.88 ±0.06 | 0.039 ±0.005 | 0.301 | 70 |

Apparent B values are greater when estimated from the lower part of the isotherm (low coverage of adsorption sites), and are correlated with smaller values for Tmax, because Tmax is related to B through Tmax = (y-intercept.B)$^{-1}$.

A number of sites with different binding strengths on the surface of $MnO_2$ was also observed by other workers (e.g. Loganathan and Burau, 1973; Balistrieri and Murray, 1982).

Calibrations in the presence of NTA produced similar values for Tmax at different salinities, probably because of the metal-buffering effect of the NTA - there is less variability in the range of free $Zn^{2+}$ concentrations, so the obtained values for Tmax are more similar. However, the values calculated for logB in the presence of NTA are significantly greater than those obtained without (~0.5 log unit). This difference may well be the result of uncertainty in the value of the stability constant for complex of zinc with NTA. This constant has, therefore, been redetermined with the $MnO_2$ method and the result is given in section 6.4.

### 6.3.2 LEAD

The use of a radiotracer such as Pb210 was not possible due to its high level of alpha radiation being above the safety limit permitted in this department. Therefore, it was necessary to use another sensitive method (i.e. DPASV) in measuring dissolved lead. The procedure used is the same as used in the zinc experiments, but less $MnO_2$ was used in accordance with the greater affinity of lead for $MnO_2$. The calibrated values of Tmax and B at different $MnO_2$ concentrations in waters of various salinities are summarized in Table 6.5. Interestingly, the concentrations of dissolved lead in equilibrium with $MnO_2$ were much greater in all experiments than those of dissolved cobalt, even at 70 µM $MnO_2$, and could be determined easily by DPASV with the HMDE. This indicates that affinity of lead for $MnO_2$ surface is lower than cobalt but still higher than zinc (if one compares the level of dissolved metal after equilibration with $MnO_2$). An increase in Tmax when the adsorption density increases (by decreasing the $MnO_2$ concentration) is observed. The results are not directly comparable as the salinities of the experiments at different $MnO_2$ concentrations are not the same. Nevertheless, the magnitudes of Tmax and B are generally higher than those of zinc, thus showing that lead has a stronger affinity for the $MnO_2$ surface (Figures 6.7a and b). In addition, it is also possible that lead is bound preferentially to a different group of sites on the oxide surface (Benjanmin and Leckie, 1981).

The reproducibility of the isotherms was generally not as good as for zinc; data obtained from replications tend to differ from each other in term of dissolved lead concentrations in equilibrium with $MnO_2$. This may be due to unsuitable amounts of $MnO_2$ for an even

Table 6.5 Calibrated values of logB and Tmax for adsorption of lead onto $MnO_2$ at different $MnO_2$ concentrations (at 25°C, pH 8.20).

| Salinity | logB | Tmax | $\log\alpha_{Pb}$ | $MnO_2$ (μM) |
|---|---|---|---|---|
| 35.0 | 8.62 ±0.03 | 0.114 ±0.016 | 1.56 | 70 |
| 14.0 | 9.03 ±0.05 | 0.098 ±0.01 | 1.41 | 70 |
| 6.0 | 8.98 ±0.06 | 0.280 ±0.03 | 1.49 | 35 |
| 23.0 | 9.35 ±0.09 | 0.570 ±0.10 | 1.44 | 15 |

N.B. 0.3-4.0 μM added lead concentration in presence of 20 μM NTA and 0.04 M boric acid bufer.

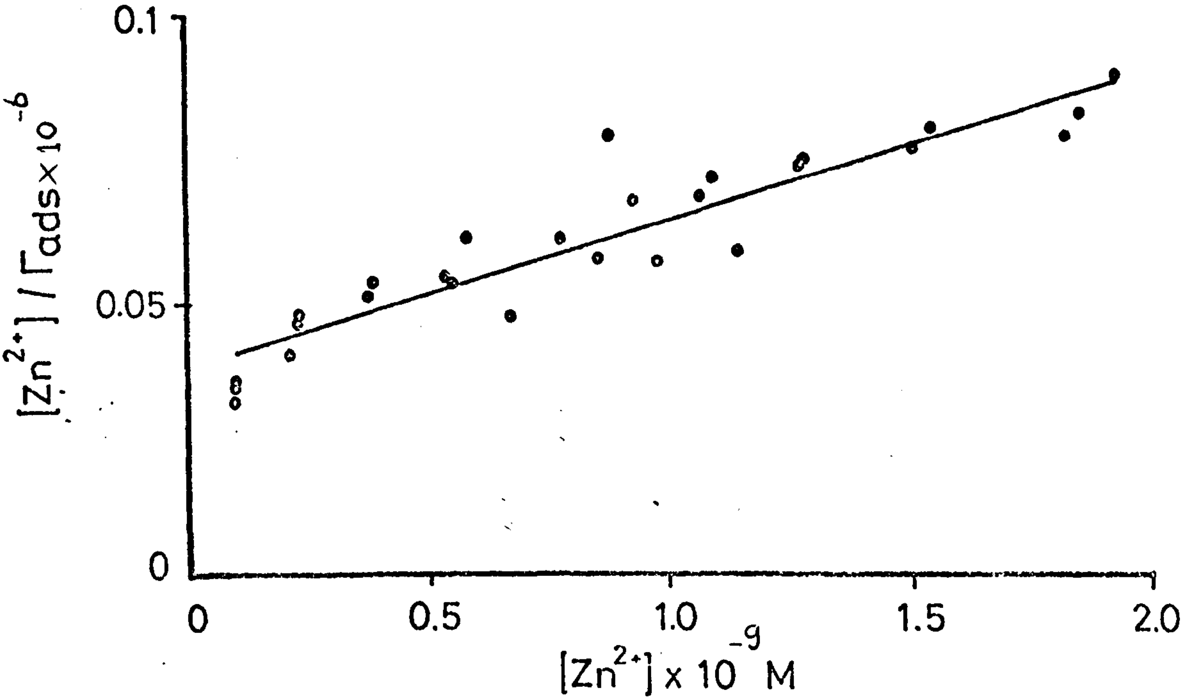

Figure 6.7a Typical calibration plot of zinc experiment (pH 8.20, 70 μM $MnO_2$, 0.3–4 μM added zinc).

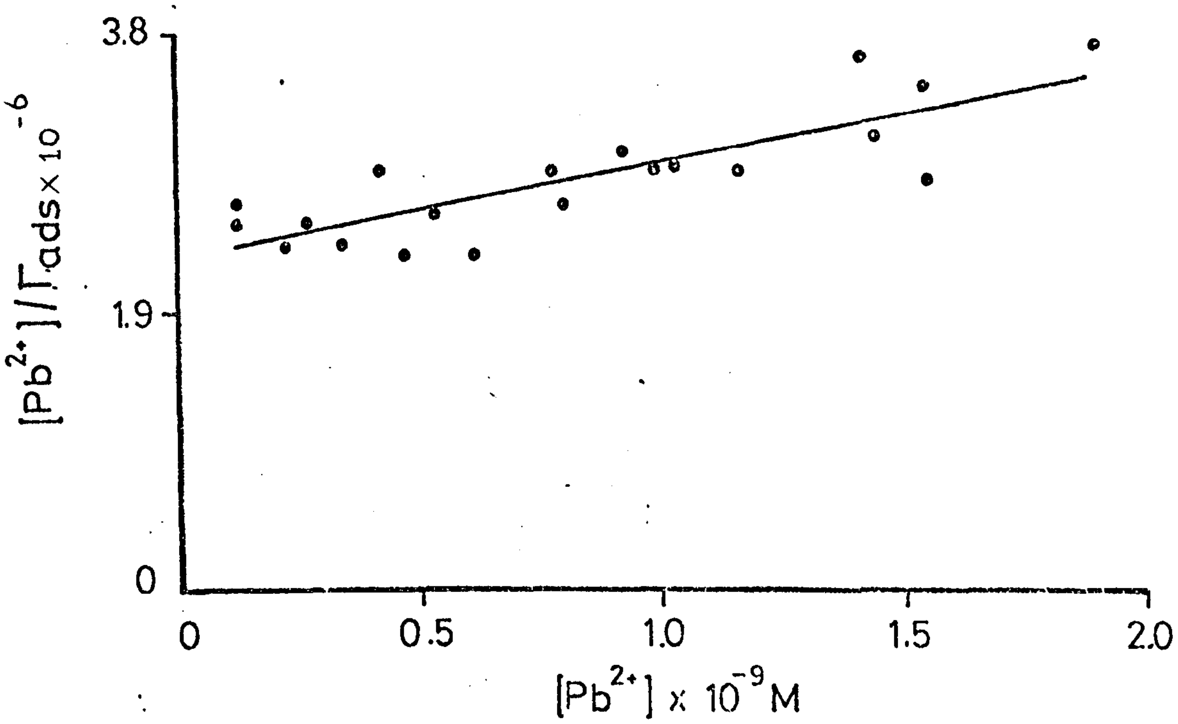

Figure 6.7b Typical calibration plot of lead experiment (pH 8.20, 70 µM $MnO_2$, 0.3-4 µM added lead).

distribution of lead between them; the equilibrium was heavily biased on the side of $MnO_2$. Other possible causes are contamination and the loss of lead from solution by adsorption onto the container walls, even though the container had been conditioned before use.

## 6.4 DETERMINATION OF STABILITY CONSTANTS OF KNOWN LIGANDS BY THE $MnO_2$ METHOD

To evaluate the $MnO_2$ method for Zn and Pb, NTA and EDTA are treated as models for unknown ligands. The determined stability constants are compared to the published literature values.

The values of Tmax and B determined from the calibration in the absence of a known ligand were used, where applicable, whereas, in presence of a known ligand, stability constants of Zn-NTA and Pb-NTA complexes from Smith and Martell (1976) were used in calculations. A number of experiments were carried out to determine stability constants of Zn-NTA, Zn-EDTA and Pb-EDTA at low concentration of ligands (i.e. µM level), and the results can be compared with literature values in Table 6.6. Values for the stability constant were calculated from, for example:

$$K_{ZnNTA}' = [ZnNTA]/[Zn^{2+}][NTA]$$

$$[NTA_t] = [L_t] = [NTA^{-3}]\,\alpha_{NTA} + [ZnNTA^-] \text{ and}$$

$$[Zn_{dis}] = [Zn^{2+}]\,\alpha_{Zn} + [ZnNTA^-]$$

at each added zinc concentration, and the mean value is reported. It was found that the obtained stability

Table 6.6 Comparison of stability constants determined by the $MnO_2$ method with literature values (at 25°C).

| Complex | logK | I | Reference |
|---|---|---|---|
| Zn-NTA | 10.808 ±0.019 | 0.45 | This work |
| | 10.321* | 0.45 | Martell and Smith (1974) |
| | 9.33* | 0.45 | Raspor et al. (1981) |
| Zn-EDTA | 16.211 ±0.045 | 0.62 | This work |
| | 16.109 ±0.042 | 0.70 | This work |
| | 16.070* | 0.62 | Martell and Smith (1974) |
| | 14.379* | 0.62 | Raspor et al. (1981) |
| Pb-EDTA | 16.003 ±0.025 | 0.45 | This work |
| | 17.43* | 0.45 | Martell and Smith (1974) |

* corrected to the same ionic strength as this work with the Davies equation.

constants agree well with the literature values: the calculated values are slightly larger than the literature values for zinc complexes and slightly smaller for lead complexes. However, it should be noted that the literature values are normally obtained from experiments under different conditions (e.g. very low or very high ionic strength media, simple component electrolyte solution, so comparison with these published values is difficult to make. For example, the values reported by Raspor et al. (1981) were determined in freshwater conditions (where ionic strength approaches zero). In addition, the adjustment of these values to the desired ionic strength is only approximate, although done by means of a standard method, and may be subject to error. Therefore, it is likely that adjustment of these values to the desired ionic strength causes some uncertainty.

## 6.5 COMPLEXING CAPACITIES AND CONDITIONAL STABILITY CONSTANTS OF NATURAL WATERS

The method has been applied to a number of interstitial waters and surface waters to study complexation of zinc by organic material. The results are summarized in Table 6.7. In all cases, only 1:1 complexation was found as indicated by straight lines in the plots of $[Zn^{2+}]/[ZnL]$ vs. $[Zn^{2+}]$ (Figures 6.8a and b).

Interstitial water samples from the Gulf of Thailand were found to contain zinc-binding ligands of

Table 6.7 Complexing capacities and conditional stability constants for organic complexes of zinc in natural waters, determined by the $MnO_2$ method (at 25°C, pH 8.20).

| | S%. | [Lt] (μM) | logK′ | zinc concentration (μM) |
|---|---|---|---|---|
| I. Interstitial water | | | | |
| The Gulf of Thailand | | | | |
| St.1 | 8.7 | 0.53 ±0.03 | 8.18 ±0.05 | 0.066 |
| St.2 | 1.8 | 0.016 ±0.003 | 9.03 ±0.30 | 0.082 |
| St.3 | 29.2 | 1.22 ±0.09 | 7.57 ±0.04 | 0.086 |
| St.4 | 29.1 | 1.02 ±0.10 | 7.55 ±0.06 | 0.024 |
| St.5 | 29.5 | 0.80 ±0.06 | 7.67 ±0.06 | 0.125 |
| St.6 | 30.6 | 0.66 ±0.04 | 7.71 ±0.05 | 0.058 |
| St.7 | 31.2 | 0.44 ±0.05 | 7.62 ±0.07 | 0.019 |
| River Mersey | | | | |
| Eastham | 14.2 | 1.99 ±0.31 | 7.72 ±0.07 | 0.064* |
| | | 1.68 ±0.67 | 7.80 ±0.16 | 0.068 |
| Otterspool | 14.2 | 0.34 ±0.17 | 8.50 ±0.22 | 0.006* |
| West Bank | 5.3 | 0.20 ±0.07 | 8.77 ±0.14 | 0.024* |
| Fidler Ferry | 6.4 | 0.05 ±0.02 | 9.30 ±0.15 | 0.014* |
| II. Surface water | | | | |
| N.Atlantic | 35.0 | N.D. | - | 0.036 |
| River Dee | 22.7 | 0.006 ±0.001 | 8.52 ±0.25 | 0.105* |
| River Ribble (I) | 13.9 | 0.042 ±0.003 | 8.95 ±0.28 | 0.321 |
| (II) | 25.0 | 0.018 ±0.002 | 8.67 ±0.30 | 0.049* |

* $MnO_2$-treated samples.

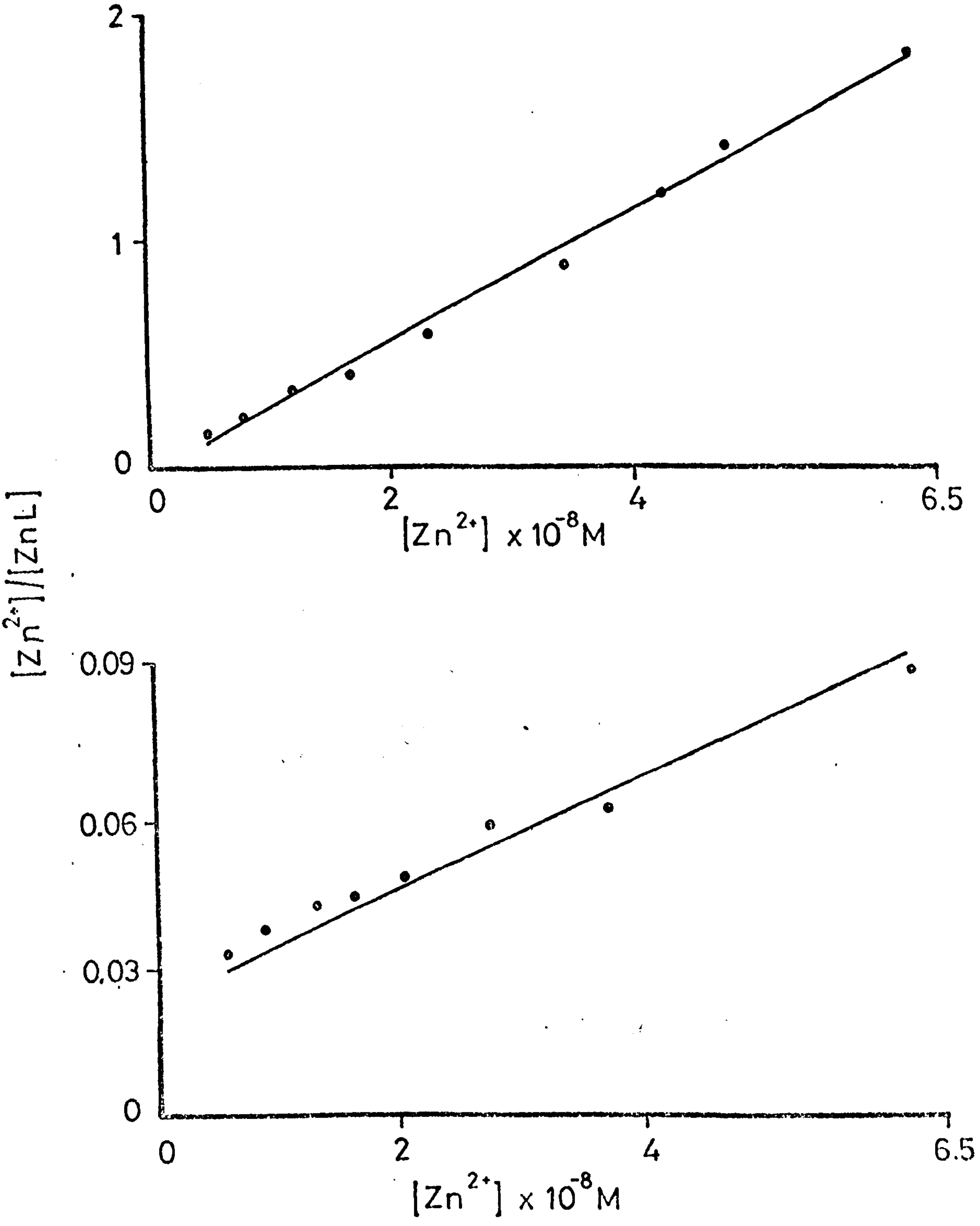

Figure 6.8a Typical plot of zinc complexing capacity determination in surface water (above).

Figure 6.8b Typical plot of zinc complexing capacity determination in interstitial water (below).

concentrations varying from 0.016–1.2 μM. Values for $K_{ML}'$ are generally less than 8 (log value), particularly in high salinity interstitial waters from offshore sediments. In interstitial waters of low salinities from the Chao Phraya River channel $K_{ML}'$ are much higher (>8.2 log unit). This may indicate the reduced competition for ligands from major cations in seawater. It is also possible that ligands in offshore sediments are of different nature from those in river sediments (Rashid and King, 1970 and 1971; Nissenbaum and Kaplan, 1972). Generally the complexing capacities are less than $10^{-6}$M. However, values greater than this were found in samples from Station 3 and 4. This high complexing capacity is to be expected in those two samples because both sites have been in regular use as dumping grounds for untreated organic wastes and dredged materials (as explained in section 5.1). Zinc concentrations are less than about $10^{-7}$M in all samples. The complexing ligands in the interstitial waters of the Gulf Thailand are apparently not saturated with zinc; and spare complexing capacity is still available.

The zinc concentrations in interstitial waters of the Mersey were very high (>$10^{-7}$M): the highest being 8 x $10^{-7}$M in a sample at Otterspool. It is likely that in samples containing high concentration of zinc the unexpended complexing capacities in such waters might be very low and too difficult to detect. Therefore, the binding ability, of samples containing high concentration of zinc was determined after treatment with $MnO_2$ to reduce the initial total zinc concentration. Thus, the concentrations of free, detectable ligands are increased. A good example is the experiment performed in untreated and treated samples from Eastham. By decreasing the initial dissolved metal concentration the detected ligand concentration increased considerably, while $K_{ML}'$ seemed to be unaffected. The complexing capacities found in treated Mersey samples are quite low for interstitial waters (0.05-0.34 µM) when compared with the Gulf of Thailand samples; the exception being the Eastham sample. Values for $K_{ML}'$ are greater than 8.5 (log unit), except in the sample of Eastham (7.7 log unit), which contained a very high concentration of zinc-binding ligands (>1.7 µM). This is possible because this area receives periodically a large quantity of both sewage sludge and industrial wastes from the ship canal through the Weaver Sluices (Chan, 1983), whereas other areas are not directly located at waste outfalls. It is likely that some of the zinc-binding ligands found in the Mersey may, therefore, not be naturally occurring ligands but rather ligands from domestic and industrial wastes. The values determined for complexing capacities and the initial concentrations of zinc in each sample indicate that sedimentary ligands in the River Mersey have already lost their binding ability with respect to zinc.

Samples of the Mersey River in comparison contained less zinc complexing ligands than the samples of the Gulf of Thailand. This is probably because the River Mersey is responsible for the drainage of a more heavily industrialized area containing a higher load of various metals which in turn reduce the reserve metal-binding ability to a very low level. $K_{ML}'$ values determined in the River Mersey are quite comparable to those of the Chao Phraya River. This may confirm the reduced major cation competition for complexing ligands at lower salinities. In samples suspected to contain ligands other than humic substances (i.e. Station 3 of the Gulf of Thailand, and Eastham) the $K_{ML}'$ values are very similar to those of natural ligands.

The ligand concentrations found in surface water are very low ($4\times10^{-8}$M) and undetectable in oceanic surface water. The values of $K_{ML}'$ in river surface waters are high (>8.5 log unit) and quite comparable to those found in interstitial waters of river sediments. Samples of the Dee and the Ribble (II) contained ligands already oversaturated with zinc and other metals such as Cu and Pb of which the concentrations were found to be very high ($>10^{-6}$M). Only 1:1 complexation was found as in the interstitial waters. Only the River Dee sample, however, showed some evidence of complexes other than 1:1, as the plot of $[Zn^{2+}]/[ZnL]$ vs. $[Zn^{2+}]$ is curved. Not enough data points were available for determination of the second site or ligand in the sample. Generally, most zinc was found to be unassociated with organic substances in natural surface waters. These results confirm the findings of Florence (1977) and Hirose et al. (1982). Chelation in interstitial waters was found to be more important than in surface waters.

$K_{ML}'$ values determined in samples of marine origin were similar to those obtained by Hirose et al. (1982) in surface seawater and are within the range of stability constant values of Zn-humic, and - fulvic complexes (Matsuda and Ito, 1970; in Table 3.1). Unfortunately, no conditional stability constants of zinc-organic complexes are available in interstitial waters or river waters. Thus, it is premature to conclude that the detected ligands resemble those of humic substances; even ligands suspected to be other than humic substances produced similar $K_{ML}'$ values.

Attempts to measure lead complexing capacities and their conditional stability constants in natural waters were less successful. The method was applied to Atlantic water, interstitial Mersey waters, River Dee and River Ribble (II) waters. In all cases it was found that the measured dissolved lead concentrations in solution in equilibration with $MnO_2$ were randomly scattered, probably as a result of contamination. Generally, the measured values should increase with the increase in the amount of added lead; however, in some samples, the measured concentrations of subsequent additions showed no significant increase, or might even decrease. This suggests the possibility that the ligands were saturated with metal ions, as is the case for samples from polluted areas, or that the free ligand concentrations were below the detection limit of the $MnO_2$ method for lead (e.g. in Atlantic water). The extent of lead complexation by sedimentary organic substances has been reported to be less than zinc (Nissenbaum and Swaine, 1976). Also it is possible that the balance of the system (15-70 µM $MnO_2$) was not suitable, due to the high affinity of lead for the surface of $MnO_2$. Nevertheless, the method appeared to work when tested with 0.09 µM EDTA in presence of 15 µM $MnO_2$; as the estimated value of $[L_t]$ (0.07 ±0.01 µM) is very close to the added EDTA concentration (0.09 µM). Therefore, it may be possible to apply the $MnO_2$ to lead by lowering the concentration of $MnO_2$.

## 6.6 SOME SUGGESTIONS TO IMPROVE THE DETECTION LIMIT OF THE ZINC COMPLEXING CAPACITY DETERMINATION

Van den Berg (1982b) suggested that the theoretical detection limit of the $MnO_2$ method can be calculated from the contribution of MeL to the dissolved metal concentration relative to the contribution from inorganic metal species: the concentration of [MeL] should be greater than [Me-inor.]. The use of radioactive tracer was suggested. The practical limit as found by van den Berg (1982b) is about $10^{-8}$M. From this work the lowest measured zinc complexing capacity was 0.006 ±0.001 µM. The dissolved zinc concentrations measured ($<10^{-9}$M) were quite easily detectable and low levels of zinc were also observed in calibration experiments in absence of the added known ligand. The addition of the radiotracer, therefore, lowered the detection limit considerably.

Use of a higher tracer concentration does not necessarily improve the detection limit. It is necessary to retain zinc in the solution at a detectable level after equilibration with $MnO_2$, which can be achieved either by decreasing the $MnO_2$ concentration or by using higher tracer concentration. For example, the results from the calibrations at different levels of $MnO_2$ (Table 6.4) show that more zinc is retained in the solution at lower $MnO_2$ concentration as the Tmax increases, while the binding strength appears to be unaffected. It is advisable to optimize the $MnO_2$ concentration for each range of ligand concentration by calibrating the $MnO_2$ in presence of a variety of known ligands of comparable binding strength to zinc-natural ligand complexes, or without added ligand in the case of very low ligand concentrations.

## 6.7 CALCULATED ORGANIC SPECIATION OF ZINC IN THE NATURAL WATER SAMPLES

In the previous section values for ligand concentrations and conditional stability for complexes of $Zn^{2+}$ with organic substances in the natural water samples have been reported. These values, together with the calculated side reaction coefficient of zinc ($\alpha_{Zn}$)

and dissolved zinc concentrations, were used to calculate the zinc speciation in the presence of organic ligands. The results are given in Table 6.8. The organically-bound fraction of zinc, as indicated by $[ZnL]/[Zn_t] \times 100\%$, amounts to 89-97% of total dissolved zinc in interstitial waters from the Gulf of Thailand with the exception of one sample (St.2), 31-98% in interstitial waters from the Mersey, and 1-16% in surface waters. The samples of the Gulf of Thailand generally have low apparent ligand concentrations, considering the sizable amount of organic material which is usually present in interstitial waters. It is possible that a large fraction of these ligands is already bound by stronger complex forming cations such as $Cu^{2+}$. In the sample of St.2 the dissolved zinc concentration is greater than the ligand concentration, and organic complexes of zinc, therefore, only represent 19% of dissolved zinc in this sample.

Dissolved zinc concentrations were high in Mersey interstitial waters and all surface river waters, except Atlantic water, with the result that zinc-binding ligands are saturated and cannot bind any additional zinc. The organically-bound zinc, therefore, represents only 31-98% and 1-16% of dissolved zinc respectively. A much greater fraction of zinc is bound by dissolved organic material if surplus inorganic metal is removed from solution by treatment with $MnO_2$. In that case ~98% of dissolved zinc is organically bound in the Mersey interstitial

Table 6.8 Speciation of $Zn^{2+}$ into organic, [ZnL], and inorganic components in natural waters; $[Zn_t]$ is the total zinc concentration (at 25°C, pH 8.20).

| | $[Zn_t]$ (µM) | $\log \alpha_{Zn}$ | $[Zn^{2+}]$ (nM) | [ZnL] (µM) | $([ZnL]/[Zn_t])$ × 100% |
|---|---|---|---|---|---|
| I. Interstitial water | | | | | |
| The Gulf of Thailand | | | | | |
| St.1 | 0.066 | 0.254 | 1.003 | 0.064 | 97 |
| St.2 | 0.082 | 0.228 | 39.28 | 0.016 | 19 |
| St.3 | 0.086 | 0.349 | 1.880 | 0.082 | 95 |
| St.4 | 0.024 | 0.349 | 0.627 | 0.026 | 94 |
| St.5 | 0.125 | 0.349 | 3.671 | 0.117 | 93 |
| St.6 | 0.058 | 0.349 | 1.746 | 0.054 | 93 |
| St.7 | 0.019 | 0.349 | 0.958 | 0.017 | 89 |
| River Mersey | | | | | |
| Eastham | 0.064 | 0.264 | 0.719 | 0.063 | 98* |
| | 0.068 | 0.264 | 0.762 | 0.067 | 98 |
| Otterspool | 0.006 | 0.264 | 0.056 | 0.0059 | 98* |
| | 0.371 | 0.264 | 33.81 | 0.309 | 83 |
| West Bank | 0.024 | 0.247 | 0.226 | 0.0236 | 98* |
| | 0.642 | 0.247 | 251.5 | 0.198 | 31 |
| Fidler Ferry | 0.014 | 0.249 | 0.192 | 0.0137 | 98* |
| | 0.106 | 0.249 | 32.02 | 0.049 | 46 |
| II. Surface water | | | | | |
| River Dee | 0.105 | 0.301 | 49.7 | 0.006 | 5* |
| | 0.898 | 0.301 | 446 | 0.006 | ~1 |
| River Ribble (I) | 0.321 | 0.264 | 152 | 0.042 | 13 |
| (II) | 0.049 | 0.310 | 16.2 | 0.016 | 32* |
| | 0.11 | 0.310 | 45.5 | 0.017 | 16 |

* calculated from $MnO_2$-treated blanks.

samples, whereas 5-32% is bound in surface waters. Generally, these samples not only contain high concentrations of zinc, but also of other metals such as Pb and Cu, indicating a state of pollution in these environments, because the ligands, which are capable of complexing these toxic metals, are overburdened. However, only River Ribble(I), even though the dissolved zinc concentration was higher than ligand concentration, the untreated sample is still capable of binding more zinc.

In comparing the results from this work with values reported for organically-bound zinc in natural waters (Table 4.4) some conclusions can be drawn:

- The values obtained in this work are comparable to those reported values.

- In surface water, only a small fraction of zinc is bound by organic substances. However, in rivers responsible for an industrialized drainage area, more zinc can be bound. The extent of zinc-organic complexation is likely to depend on the load of other complex forming cations and the amount of the ligands.

- In interstitial water, chelation of metals may be of great importance in controlling the geochemistry of trace metals in sediments.

## 6.8 SUMMARY

The time required for equilibrium of zinc adsorption onto $MnO_2$ in the presence of a ligand was found to be around 15 hours (at 31.8‰) and less at lower salinities or in absence of complexing ligands. The adsorption of inorganic dissolved zinc on container walls is far slower and negligible.

Tmax and B were found to be pH-dependent. The use of boric acid buffer minimized this effect. The calibrated values were similar to those obtained in absence of buffer after correction for the side reactions of borate ion using stability constants of borate complexes reported by van den Berg (1982c).

Generally, the calibrated values of Tmax and B increased with decreasing salinity. An increase in these values might represent reduced competition by major cations in seawater for adsorption sites on the $MnO_2$ surface. An increase in Tmax was observed at high added zinc concentrations and at low $MnO_2$ concentrations. This indicates that a number of sites with different binding strengths exist on the surface of $MnO_2$. Therefore, calibration of metal adsorption onto $MnO_2$ under the same condition of surface coverage as occurs during sample analysis is necessary. The Langmuir isotherm may not be an ideal model to describe adsorption behaviour of a nonuniform surface. Nevertheless, it can be properly applied if considerations such as those put forward by Benjamin and Leckie (1980 and 1981) are taken into account.

At the investigated level of $MnO_2$, it is likely that the balance for an even distribution of lead between

$MnO_2$ and NTA was unsuitable, due to strong affinity of lead for $MnO_2$ surface. However, testing the method with 0.09$\mu$M EDTA produced an estimated value which is in good agreement with added values. It may, therefore, be possible to apply the method to lead by lowering the concentration of $MnO_2$.

In determining stability constants of NTA and EDTA complexes with zinc and lead the values show a very good agreement with literature values. Thus, proving the ability of method to produce reliable results when applying to natural samples.

Only 1:1 complexes were found, in both interstitial and surface waters only one surface sample from River Dee revealed the possible existence of complexes other than 1:1, but not enough data points were available for the determination of the second site or ligand in the sample. The determined complexing capacity values could be related to the locations of the sampling sites. The conditional stability constants are found to be comparable to those of soil humic substances (i.e. reported by Matsuda and Ito, 1970) and natural ligands (i.e. reported by Hirose et al., 1982); however, ligands suspected to be other than humic substances produced similar values.

Reduced competition for ligands from major cations affects the magnitude of $K_{ML}'$: values for $K_{ML}'$ are larger at low salinity (river samples) than at high salinity (marine samples). It is also possible that the ligands found were of a different nature.

Some suggestions to further extend the detection limit of the $MnO_2$ method have been put forward.

Calculation of the organic and inorganic zinc speciation indicates that the major part of dissolved zinc is present in organic complex ions, unless the ligands are saturated by high concentrations of zinc and other trace metal ions, such as present in polluted environments.

# CHAPTER 7

# SUMMARY AND GENERAL IMPLICATIONS OF THIS STUDY

## 7.1 CONTEXT OF THIS WORK

In recent years a growing number of studies have been, and are currently, directed toward the prediction of the behaviour of trace metals in natural waters. The work presented in this thesis forms a contribution to a knowledge of the interactions between trace metals and dissolved organic substances in the natural aquatic system. Interactions of metals and organic matter exert a strong influence over the biogeochemical cycle of such metals. For example, a trace metal bound in strong complexes, particularly with organic ligands, will generally remain unavailable for uptake by marine organisms. Furthermore, the occurrence of certain organically bound trace metals in natural waters can now be regarded as an established fact,even though in earlier studies they have frequently been ignored.

To evaluate the importance of trace metal interactions in natural waters, one has to be able to measure the extent and strength of such interactions and to express these in measurable units. Generally, trace metal-ligand associations are assessed by stability constants, while concentration and stoichiometry are a measure of the extent of such interactions. The terms "conditional stability constant" and "complexing capacity" replace stability constant and concentration because of their suitability in describing interactions between trace metals and unknown ligands in natural waters.

## 7.2 THE $MnO_2$ METHOD

Several techniques are currently in use for the measurement of conditional stability constants and complexing capacities. Each technique has its own advantages and disadvantages over the others, and among these techniques is the $MnO_2$ method.

The $MnO_2$ method possesses a definite advantage over other methods in its capability to measure both conditional stability constants and complexing capacities in filtered, unconcentrated natural water samples over a wide range of pH (e.g. 6-9), while other methods either can only be applied at unrealistic pH (i.e. very low or very high pH) or require sample preconcentration. Dissolved metal concentrations are measured after equilibration with the $MnO_2$. Firstly, the surface of $MnO_2$ is calibrated for metal uptake in a uv-irradiated sample. Secondly, the untreated solution is titrated with the metal in the presence of $MnO_2$ which causes the unknown organic material and the $MnO_2$ to compete for the metal. After a certain equilibration period (i.e. 15 hours), during which time the temperature and pH are kept constant, the $MnO_2$ is removed by means of filtration using 0.45 $\mu$m pore size filter. Finally, the total dissolved metal concentration in the filtrate is determined by a sensitive analytical technique such as DPASV, scintillation spectrometry (together with a use of radioactive tracer). From the total amount of metal added, and the free metal concentration (calculated from the amount of adsorbed metal on the calibrated $MnO_2$ surface), one can plot free metal concentration vs. the ratio of free metal/metal-ligand and hence calculate the ligand concentration and the metal-ligand conditional stability constant. In case of 1:1 complexation, a straight line is obtained, and the ligand concentration can be calculated from the slope, while the conditional stability constant is calculated from the intercept and slope.

To be able to obtain reliable results from the $MnO_2$ method, ligands or metal-organic complexes should not adsorb on $MnO_2$. It has been shown by a recent study of Stroes (1983) that such adsorption does not occur at the natural pH of the water samples; therefore, the $MnO_2$ method will, under these conditions, be able to yield reliable results .

It is necessary that metal uptake by the $MnO_2$ surface should be described accurately because the oxide surface may possess nonuniform sites of different binding strengths. The use of simple adsorption models, which generally assume constant adsorption capacity, may not be ideally suitable. Nevertheless, the Langmuir isotherm seems to be capable in describing zinc uptake onto the $MnO_2$. Some recent developments in adsorption models are presented in Appendix III.

Originally the $MnO_2$ method (van den Berg, 1979) was proven to work successfully for copper complexes with weak ligands at low concentration. The method has been tested in this work with moderate (NTA) and strong (EDTA) zinc-binding ligands, and works well with both kind of ligands, at low ligand concentrations ($10^{-7}$-$10^{-6}$M).

The use of a buffer though inadvisable (van den Berg 1979), has proved to be very useful, providing that all possible side reactions by the buffer are taken into account. A concentration of 0.04M boric acid buffer appears to be most suitable.

Application of the $MnO_2$ method to other metals with stronger affinity than copper to the $MnO_2$ surface (Pb and Co) was not successful. However, by optimizing the balance between ligand-$MnO_2$-metal one might be able to apply the method more successfully.

Use of a radioactive tracer improved the detection limit of the method, and also allowed the use of small sample sizes, which is of importance in the study of interstitial waters.

## 7.3 GENERAL IMPLICATIONS OF THIS STUDY

Analysis of various natural waters revealed that:

- Generally, most of the water samples contain a surplus of complexing ligands for zinc.

- It was found that some waters have already lost their capability to complex additional amounts of metal possibly as a result of pollution in those environments.

- Sedimentary organic substances in river and marine environments may be different in nature because of the apparent difference in strength of the complexes in each environment: the strength tends to be higher in rivers. This difference may also indicate a reduced competition for ligands by major cations.
- 1:1 complexation is predominant in all interstitial waters and surface waters, except in one case (River Dee surface water).
- Complexation by organic substances in sediments may be very important in controlling the geochemistry of trace metals as most of the metals are complexed. Complexation by organic material in surface water, appears to be less significant for zinc.
- The values of conditional stability constants of zinc-organic complexes found in both interstitial waters and surface waters are generally comparable to those of humic substance complexes. Some samples, suspected to contain ligands other than humic substances, yielded constants of similar strengths.
- The complexing capacities found in interstitial waters are generally higher than those in surface waters. Thus, in combination with the results on the degree of complexation, it is possible that trace metal-organic interaction in sediments is quite important in controlling the level of metals present in natural aquatic systems.

## 7.4 RECOMMENDATIONS FOR FUTURE RESEARCH

The description of metal uptake onto a nonuniform oxide surface may not be ideally suitable; however, it is beyond the scope of the work to develop a suitable adsorption model. The use of the Langmuir model has been shown to be quite successful in this work. It is possible to improve the method by applying other adsorption models which take the various adsorption mechanisms and nonuniform sites of different binding strength into account. An example of such models is the Implicit Langmuir model (Stroes, 1983) and is included in Appendix III.

Application of the method to other metals with stronger affinity for $MnO_2$ surface than copper (e.g. Pb) is possible by adjusting the balance of the system in terms of $MnO_2$ concentration to suit the strength and level of metal-binding ligand present in the water sample.

The presence of naturally-occurring ligands is indicated in aquatic systems at low concentrations. The $MnO_2$ can, therefore, best be calibrated in absence of a known ligand, thus assuring that the adsorption density in the sample is over the same range. If calibration in the presence of a known ligand is unavoidable (i.e. the necessity to maintain the metal concentration at detectable level according to its affinity to the $MnO_2$ surface), one can adjust the $MnO_2$ concentration accordingly to compensate for the competition for the metal of such ligand and maintain the adsorption density of calibrated values over the same range as the sample. Another alternative is to vary the amount of known ligand used in calibrations.

To achieve the theoretical detection limit, it is necessary to optimize the $MnO_2$ concentration according to the ligand concentration or to adjust the radioactive tracer concentration.

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# APPENDIX I

## REGRESSION ANALYSIS

(Wonnacott and Wonnacott, 1977 and Meites, 1981)

Regression analysis is used here to calculate the best values of coefficients in an equation which relates the dependent variable to the independent one. When fitting a linear regression line, $y = a + bx$, the values a and b can be calculated from:

$$a = (\Sigma y - b\Sigma x)/n$$

$$b = (n\Sigma xy - x\Sigma y)/\{(n\Sigma x^2 - (\Sigma x)^2\}$$

Where n is the number of measurements, x and y are the independent and dependent variables repectively. The subscripts have been dropped, but each summation is still understood to include all individual values.

To evaluate the sample standard deviation, $S_y$, we use the equation:

$$S_y = \{(\Sigma[y_{meas} - a - bx]^2)/(n-2)\}^{1/2}$$

or

$$S_y = \{(\Sigma[y_{meas} - y_{calc}]^2)/(n-2)\}^{1/2}$$

The true value of the y intercept, $\alpha$, and the slope, B, are approximated by the value of a and b obtained from a finite sample. Confidence intervals can be attached to $\alpha$ and B by:

$$\alpha = a + tS_y\{1 + 1/n + \bar{x}^2/\Sigma(x - \bar{x})^2\}$$

or

$$\alpha = a + tS.E.(a)$$

and

$$B = b + tS_y/\{(n - 2)\Sigma(x - \bar{x})^2\}$$

or

$$B = b + tS.E.(b)$$

Where $\bar{x}$ is the mean of the n values of x, and, for example, S.E.(q) is the standard error of q. The required values of t can be obtained for the desired level of confidence from any Student's t table of critical points.

The variance of a and b, V(a) and V(b), which are the square of their standard error, are used in the calculation of confidence interval of K′ and $[L_t]$. The calculation of K′ is performed by dividing the slope, b, by the y-intercept, a.

From the method of root mean square error:

$$S.E.(b/a) = (b/a)\{V(a)/a^2 + V(b)/b^2\}^{1/2}$$

and

$$K' = (b/a) + tS.E.(b/a)$$

The ligand concentration is calculated from the inverse of slope, 1/b. Thus,

$$S.E.(1/b) = V(b)^{1/2}$$

and

$$L_t = 1/b + \{tS.E.(1/b)\}^{-1}$$

# APPNDIX II

# MILLERO-POISSON INTERNATIONAL EQUATION OF STATE OF SEAWATER AT ONE ATMOSPHERE (1981)

UNESCO panel recommended the equation of state of seawater at one atmosphere, from 0 to 40°C and 0.5 to 43%. salinity as follows:

$$\rho = \rho_o + AS + BS^{3/2} + CS^2$$

where $A = 8.24493\times10^{-1} - 4.0899\times10^{-3}t + 7.6438\times10^{-5}t^2$

$- 8.2467\times10^{-7}t^3 + 5.3875\times10^{-9}t^4$

$B = - 5.72466\times10^{-3} + 1.0227\times10^{-4}t - 1.6546\times10^{-6}t^2$

$C = 4.8314\times10^{-4}$

t°C; S is the salinity in parts per thousand; $\rho$ in kg m-3; and $\rho_o$ is the density of water (after Biggs, 1967):

$$\rho_o = 999.842594 + 6.793952\times10^{-2}t - 9.095290\times10^{-3}t^2 + 1.001685\times10^{-4}t^3 - 1.120083\times10^{-6}t^4 + 6.536336\times10^{-9}t^5$$

with the standard error of $3.6\times10^{-3}$ kg m$^{-3}$.

This new equation will replace the equations proposed by Millero et al.(1976) and Poisson et al.(1980).

As all the experiments in this work were done at 25°C the parameter A, B and $\rho_o$, which are the function of temperature, are:

$A = 0.75924$

$B = -4.2020\times10^{-3}$

$\rho_o = 997.04796$ kg m$^{-3}$

# APPENDIX III

## THE IMPLICIT LANGMUIR MODEL FOR ADSORPTION OF TRACE METALS ONTO MnO (after Stroes, 1983)

Stroes (1983) has developed the Implicit Langmuir model to describe the adsorption behaviour of $Cu^{2+}$ onto $MnO_2$:

$$\log(Tads/[M^{2+}]) = npH + \log B + \log\{(Tads - Tmax)/e^{-(Tads/Tmax - 1)}\}$$

where the term $[H^+]^n e^{-(Tads/Tmax - 1)}/B$ represents the overall binding energy involved; Tads (= mol Madsorbed/ mol $MnO_2$) and the free $M^{2+}$ concentration in solution are calculated. Tmax, B and n are the adsorption parameters. The model predicts the observed deviation from linearity at low surface coverage when the data is fitted to the Langmuir isotherm. The binding energy depends on the pH, the $[H^+]/[M^{2+}]$ exchange ratio (n), the surface coverage (Tads/Tmax) and a constant B.

The parameter n can be estimated in many ways. For example, the use of Kurbatov plots (1951a and b) of $\log M_{sorbed}^{n+}/[M^{n+}]_{solution}$ vs. pH should yield a straight line with a slope, indicating the parameter n, and a intercept which depends on the value of Tads. However, this parameter is not constant during increasing adsorption (Stumm and Morgan, 1964; Posselt et al., 1968). By including the term $e^{-(Tads/Tmax - 1)}$ in the Implicit Langmuir model, this effect can be corrected (Stroes, 1983).

Practically, the data should be fitted to the model by a non-linear regression, and the adsorption parametrs Tmax, B and n can be estimated. For further details of this model refer to Stroes (1983).

# APPENDIX IV

## STABILITY CONSTANTS OF COMPLEXES (FORMATION CONSTANTS)

### I. TRACE METALS WITH MAJOR CATIONS IN SEAWATER (after Turner et al., 1981)

| Complex | $\log\beta^{o}$ | B | C |
|---|---|---|---|
| $Co^{2+}$ | | | |
| $Co(OH)^{+}$ | -9.65 | 2.02 | -0.03 |
| $Co(OH)_2$ | -18.80 | 2.01 | -0.12 |
| $Co(OH)_3^{-}$ | -31.50 | -0.07(D) | -0.09 |
| $Co(OH)_4^{2-}$ | -46.30 | * | -0.34 |
| $CoCl^{+}$ | 0.57 | 1.57 | 0.17 |
| $CoSO_4$ | 2.36 | 1.63 | 0.05 |
| $CoCO_3$ | 4.91 | 1.63 | 0.05 |
| $Pb^{2+}$ | | | |
| $Pb(OH)^{+}$ | -7.71 | 17.71 | -0.02 |
| $Pb(OH)_2$ | -17.12 | 35.73 | -0.09 |
| $Pb(OH)_3^{-}$ | -28.06 | -0.22(D) | 0.51 |
| $PbCl^{+}$ | 1.58 | 1.29 | 0.22 |
| $PbCl_2$ | 1.82 | 2.90 | 0.26 |
| $PbCl_3^{-}$ | 1.71 | 3.13 | 0.35 |
| $PbCl_4^{2-}$ | 1.40 | 3.65 | 0.47 |
| $PbSO_4$ | 2.75 | 1.63 | 0.05 |
| $Pb(SO_4)^{2-}$ | 4.51 | 1.61 | -0.22 |
| $PbCO_3$ | 7.00 | 1.63 | 0.05 |
| $Pb(CO_3)^{2-}$ | 10.29 | 1.61 | -0.22 |
| $Zn^{2+}$ | | | |
| $Zn(OH)^{+}$ | -8.96 | 2.17 | 0.12 |
| $Zn(OH)_2$ | -16.90 | 2.05 | 0.01 |
| $Zn(OH)_3^{-}$ | -28.40 | -0.07(D) | 0.06 |
| $Zn(OH)_4^{2-}$ | -41.20 | * | -0.20 |
| $ZnCl^{+}$ | 0.49 | 1.20 | 0.21 |
| $ZnCl_2$ | 0.62 | 2.86 | 0.03 |
| $ZnCl_3^{-}$ | 0.51 | 0.65 | 0.77 |
| $ZnCl_4^{2-}$ | 0.20 | 3.65 | 0.47 |
| $ZnSO_4$ | 2.36 | 1.49 | 0.12 |
| $Zn(SO_4)_2^{2-}$ | 3.63 | 0.83 | 0.02 |
| $ZnCO_3$ | 4.75 | 1.63 | 0.05 |

* denotes case where B = 1 and D = 0, whereas other cases D = 0 and B, C $\neq$ 0 or B = 0 and C, D $\neq$ 0.

The stability constant ($\log\beta^*$) is calculated from:

$$\log\beta^* = \log\beta^\circ + s\Delta Z^2 I^{1/2}/(1 + BI^{1/2}) + CI + DI^2$$

where s is 0.511 $mol^{1/2}\ l^{1/2}$ at 25°C; $\Delta Z^2 = \Sigma Z^2(\text{products}) - \Sigma Z^2(\text{reactants})$; and I is the ionic strength. B, C and D are constant for each complex and are presented in the table above.

The stability constants for hydrolysis are from the reaction:

$$M^{n+} + yH_2O - yH^+ = M(OH)_y^{(n-y)+}$$

and calculated from:

$$\log\beta^* = \log\beta^\circ + s\Delta Z^2 I^{1/2}/(1 + I^{1/2}) + bI$$

where the constants and symbols are the same as the previous equation, except B = b and both C and D = 0.

Other stability constants data are compiled below. When correcting these constants to the desired ionic strength the Davies equation (eq. 2.29) was used.

II. Other complexes

| Complex | logK | I | References |
|---|---|---|---|
| $HNTA^{2-}$ | 9.33 | 0.5 | 1 |
| | 9.65 | 0.1 | 1 |
| $MgNTA^{-}$ | 5.47 | 0.1 | 1 |
| $CaNTA^{-}$ | 6.39 | 0.1 | 1 |
| $HEDTA^{3-}$ | 10.17 | 0.1 | 1 |
| $MgEDTA^{2-}$ | 8.83 | 0.1 | 1 |
| $CaEDTA^{2-}$ | 10.61 | 0.1 | 1 |
| $H_2CO_3$ | 10.329 | 0 | 2 |
| | 10.0 | 0.1 | 2 |
| | 9.57 | 1 | 2 |
| $HCO_3^{-}$ | 6.352 | 0 | 2 |
| | 6.16 | 0.1 | 2 |
| | 6.02 | 1 | 2 |
| $CoNTA^{-}$ | 10.38 | 0.1 | 1 |
| $CoNTA_2^{4-}$ | 14.33 | 0.1 | 1 |
| $PbNTA^{-}$ | 11.34 | 0.1 | 1 |
| $PbEDTA^{2-}$ | 17.88 | 0.1 | 1 |
| $ZnNTA^{-}$ | 10.66 | 0.1 | 1 |
| $ZnNTA_2^{4-}$ | 14.24 | 0.1 | 1 |
| $ZnEDTA^{2-}$ | 16.44 | 0.1 | 1 |
| $HB(OH)_4^{-}$ | 8.924 | 0.7 | 3 |
| $CaB(OH)_4^{+}$ | 0.99 | 0.7 | 3 |
| $MgB(OH)_4^{+}$ | 0.82 | 0.7 | 3 |
| $NaB(OH)_4$ | -0.47 | 0.7 | 3 |
| $ZnB(OH)_4^{+}$ | 1.87 | 0.7 | 3 |
| $Zn(B(OH)_4)_2$ | 2.90 | 0.7 | 3 |
| $PbB(OH)_4^{+}$ | 3.04 | 0.7 | 3 |
| $Pb(B(OH)_4)_2$ | 4.10 | 0.7 | 3 |
| $Co(B(OH)_4)_4^{2-}$ | 10.03 | 0 | 4 |

1. Martell and Smith (1974)
2. Smith and Martell (1976)
3. van den Berg (1982c)
4. Basset (1980)