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"EFFETS DU PH SUR LE DOSAGE DES METAUX TRACES PAR LA METHODE DE LA POLAROGRAPHIE INVERSE"

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LIST OF SYMBOLS / LISTE DES SYMBOLES

i_e	electrodeposition current
C_a	metal amalgam concentration, sometimes represented by $[M_{Hg}]$
t	plating time
n	number of electrons transferred
F	Faraday's constant
V	volume of mercury drop
D	diffusion coefficient
C_c	bulk solution concentration of the metal ion
A	electrode area
δ	thickness of the diffusion layer
m	mass transport coefficient
r	radius of HMDE
E^0	standard reduction potential of the metal versus the saturated calomel electrode
E	peak potential
SCE	saturated calomel electrode
v	potential sweep rate
i_f	faradaic current
i_c	charging current
i_b	background current
C_T	total inorganic carbon concentration
Q_p	integrated current peak
$\hat{\sigma}$	standard deviation
μ	ionic strength
DOM	dissolved organic matter

EDTA	ethylenediamine tetra-acetic acid
NTA	nitrilotriacetic acid
DTPA	diethylenetriamine penta-acetic acid
EDDHA	ethylenediamine - di - orthohydroxy - phenylacetic acid
K	stability constant
K_f	formation constant
M	molarity
$[M]_T$	total metal concentration
$[M^{+z}]$	ionic metal concentration
L	ligand concentration
β_j	stability constant of the metal ion with "j" ligands
k_f	complex formation rate constant
k_d	complex dissociation rate constant
DME	dropping mercury electrode
HMDE	hanging mercury drop electrode
ASV	anodic stripping voltammetry
DPASV	differential pulse anodic stripping voltammetry
PASV	pulse anodic stripping voltammetry
i_p	peak height
E_p	peak potential
DPP	differential pulse polarography
PP	pulse polarography
MFE	mercury film electrode
MA	modulation amplitude
z	valence of metals

RESUME

Des études de métaux traces par la polarographie inverse ont démontré que pour des échantillons filtrés d'eau naturelle, l'intensité de courant des pics (i_p) augmente pour plusieurs métaux (Zn, Pb, Cu, etc) à la suite d'une acidification. On constate également que le potentiel des pics (E_p) se déplace en direction anodique à la suite de l'acidification.

Pour un milieu artificiel inorganique, O'Shea (1972) a montré que de grandes augmentations de i_p et de forts déplacements anodiques de E_p peuvent être provoqués par l'acidification d'un échantillon. D'autre part, il existe des expériences qui démontrent que i_p peut avoir une valeur maximum à un pH de 5.5 (Lewin et Rowell, 1973) et que la capacité apparente de complexation est indépendante du pH dans la gamme de pH 4 à 8, pour certains échantillons (Chau et al., 1974).

Il était donc souhaitable de vérifier les résultats quelque peu contradictoires trouvés dans la littérature afin de mieux évaluer l'importance du pH dans la distribution des espèces métalliques solubles. Le but de ce travail est donc de vérifier les résultats de O'Shea (1972) concernant les intensités de courant et les potentiels de pics et de mieux évaluer la valeur de la polarographie pour l'étude de la distribution des espèces métalliques.

Une série d'expériences préliminaires a été effectuée afin d'améliorer la sensibilité et la fidélité de la méthode analytique employée. Les renseignements fournis par ces expériences préliminaires ont aidé par

la suite à la conception des expériences pour étudier l'influence du pH et à l'interprétation des résultats. Pour ces expériences, le protocole expérimental a essentiellement consisté à déterminer i_p et E_p pour quatre métaux traces (Zn, Cd, Pb et Cu) par polarographie inverse à différentes valeurs du pH, dans des échantillons ultra-filtrés d'eau du robinet et d'eau de lac.

Les résultats montrent que l'intensité de courant augmente pour le zinc, le cadmium, le plomb et le cuivre à la suite de l'acidification de ces échantillons. Les augmentations de i_p sont relativement petites si on les compare à celles rapportées par O'Shea (1972) pour des échantillons synthétiques non filtrés ou à celles observées par d'autres chercheurs (Allen et al., 1970; Fitzgerald, 1970) pour des échantillons d'eau naturelle non filtrés. O'Shea a proposé l'existence de complexes inorganiques "non-labiles" dans ses échantillons afin d'expliquer les changements d'intensité de courant et de potentiel. La présence de complexes inorganiques "non-labiles" dans nos échantillons d'eau du robinet est cependant peu probable, car l'augmentation de l'intensité de courant en fonction du pH pour le zinc, le cadmium, le plomb et le cuivre suite à l'acidification ne correspond par au degré de décomplexation de ces mêmes métaux pour un modèle simple d'équilibres chimiques.

On constate également que les potentiels de pics se déplacent dans une direction anodique suite à l'acidification des échantillons. L'analyse de ces déplacements du potentiel, à l'aide de calculs d'équilibres thermodynamiques, fournit des renseignements utiles sur les changements qui se produisent lors de l'acidification.

La méthode de la polarographie inverse s'avère donc un outil fort utile pour l'étude de la distribution des espèces métalliques solubles.

CHAPTER 1

INTRODUCTION

1.1 Trace metals in the aquatic environment

1.1.1 Roles of trace metals

The importance of certain trace metals as micronutrients for phytoplankton and higher plants has been known for a long time. Recently, new elements have been added to the list and a greater understanding of their roles has been achieved. Macronutrients, such as C, H, O, N, P, S, K, Mg, Ca and Na, may be present in the aquatic environment in concentrations varying from 10^{-2} to 10^{-4}M, whereas micronutrients (e.g. Fe, Mn, Zn, V, Mo, Cu, B, Si and Co) are hardly ever found at concentrations greater than 10^{-5}M. Generally macronutrients are employed as building materials (C, H, N, O) or for ionic regulation (Ca, Mg, K, Na), whereas micronutrients are often found as constituents of enzymes involved in metabolic reactions. These reactions include photosynthesis in phytoplankton and higher plants, nitrogen fixation, et caetera (Eyster, 1968). Although these micronutrients may be limiting factors to life processes at low concentrations, certain of them (e.g. Zn, Cu) may also become toxic if present at too high a concentration. Other trace metals (e.g. Pb, Cd, and Hg) do not appear to be required for any plant life and are extremely toxic if present at concentrations above certain threshold values. Their toxicity usually depends on their chemical form, since the uptake of trace metals depends, as one might expect, on highly selective pathways.

1.1.2 Trace metal distribution

In natural waters trace metals are found in the following forms:

Soluble:	free (aquo)
	complexed
Colloidal:	organic
	inorganic
Particulate:	adsorbed
	co-precipitated (coatings)
	organic solids
	inorganic solids (crystalline)

It should be noted that the distinction between the three classes (e.g. soluble, colloidal, particulate) is necessarily operational, depending as it does upon the physical means used for separation. Within this general framework, Gibbs (1973) has studied the transport mechanisms of Fe, Ni, Cu, Cr, Co and Mn in the Amazon and Yukon rivers. He found that the distribution for both rivers was similar, with Cu and Cr transported mainly in the crystalline solids, Mn in coatings, and Fe, Ni, and Co distributed equally between metallic coatings and crystalline solids. What is surprising about his findings is the fact that very little metal is transported in solution, except for the case of Mn where soluble manganese accounts for 10-17% of total metal. In general, for both rivers no more than 5% of the total metal is found in "solution" after filtration through a membrane filter of nominal 0.45 μm pore size. These rivers, however, are little influenced by man; the soluble fraction may well increase in rivers receiving industrial and municipal wastes.

Although the proportion of total metal found in the soluble form may often be quite small, it is not unimportant. Evidence exists to show that the soluble form is directly assimilated by phytoplankton and higher plants. In the following work discussion will be limited to this important soluble form of metal, although from time to time reference will be made to the colloidal and particulate forms, because of the inevitable exchange of metal between these different phases.

1.1.3 Complexation

Soluble metal may be broken down somewhat arbitrarily into 'free' and 'complexed' metal, the latter term referring to that fraction bound to inorganic or organic ligands. 'Free' metal ions do not exist in aqueous solution. In the absence of other ligands, the metal ion is bound to water molecules and/or water derivatives (OH^-, O^{-2}) depending on pH and oxidation state. Within the pH range of natural waters monovalent ($z = +1$) metal cations tend to form aquo-complexes ($M(H_2O)_n^{z+}$); bivalent cations tend to form aquo- and hydroxo-complexes ($M(H_2O)_x(OH)_y^{(z-y)+}$); and trivalent cations form predominantly hydroxo-complexes ($M(OH)_n^{(x-n)+}$). Those cations with a charge greater than or equal to 4 generally form tightly bound oxo-complexes ($M(O)_m^{(z-2m)+}$) such as silicates, permanganates, etc.

In natural waters the common inorganic ligands (Cl^-, SO_4^{-2}, HCO_3^-, and CO_3^{-2}) compete with the water molecules for the metal cations; this competition is most effective in the case of the bivalent cations. Among the bivalent cations available, Ca^{+2} and Mg^{+2} are often present in natural waters at concentrations approximately 10^6 times greater than the bivalent trace metals.

However, the stability constants of Ca^{+2} and Mg^{+2} with the above anions are very small ($K_1 \sim 10^3$ or less) and hence an insignificant fraction of total Ca^{+2} and Mg^{+2} is bound to these ligands. On the other hand, trace metals in the form of bivalent cations do interact with the common inorganic ligands. For example, Stiff (1971a) has investigated the complexation of copper with CO_3^{-2} in inorganic waters. He found that within the range of bicarbonate alkalinities of natural waters, and a pH range of 6.5 - 8.5, $CuCO_3^o$ is the predominant form of soluble copper, the 'free' cupric ion accounting for but a fraction (0.9 - 25%) of total soluble copper.

The presence of organic ligands in natural waters complicates enormously the picture. It is estimated that almost 90% of organic matter found in the photic zone of the hydrosphere is in the soluble form. This dissolved organic matter (DOM) is present however at low concentrations in most natural waters: 0.1 - 10.0 mgC/l or 10^{-6} - 10^{-4}M, if one assumes an average equivalent weight of 100. Generally one finds three classes of DOM in the aquatic environment: the natural products of biosyntheses and biodegradation (i.e. biogenetic material: carbohydrates, proteins, lipids, amino acids, etc.), refractory organic matter (gelbstoff, humic matter, etc.), and synthetic products from industrial waste (pesticides, detergents, waxes, dyes, etc.). Much of this material has the capacity to associate with metal ions, either by complexation, chelation or peptization. The fact that the concentrations of metal ions are much greater than that of the DOM means that there ought to be very strong competition among them for the available organic ligands. One can assume that in order for trace metals to compete appreciably with

Ca^{+2} and Mg^{+2} for organic ligands, their relative stability constants must again be of the order of 10^6 times those of Ca^{+2} and Mg^{+2}.

By virtue of their particular geometry and their donor atoms, most organic ligands exhibit a certain preference for some metal cations over others. This inherent selectivity of organic ligands will thus characterize the organo-metallic interactions in natural waters. Other properties of organic ligands will likewise influence these interactions. For example, from entropy considerations alone, metal chelates are inherently more stable than their monodentate analogues. Furthermore metal chelates are more resistant to decomplexation following dilution than monodentate complexes. These properties will obviously influence organo-metallic interactions in natural waters ... but just how important are these interactions?

1.1.4 Organo-metallic interactions - physical chemical evidence

The classic argument cited in support of the hypothesis that organo-metallic interactions are of importance in the aquatic environment is that observed ferric iron concentrations greatly exceed the levels predicted from solubility product considerations, even if the formation of inorganic complexes is taken into account. Thus, it is estimated that the concentration of iron in lake and sea water is greater by about 5 orders of magnitude than that which would be predicted on the basis of the solubility product of ferric hydroxide (10^{-36}) and a pH value of 8.0 (Siegel, 1971), taking into consideration the formation of hydroxo-complexes. This suggests that the DOM plays a protective role in preventing the precipitation of ferric hydroxide. We can suppose likewise that the DOM is active in controlling the solubility of Cu, Pb, Zn and other trace metals in natural waters. As outlined below, considerable research exists in support of this hypothesis.

Slowey and coworkers (1967) have extracted copper from Gulf of Mexico samples with chloroform and subsequently analysed the copper by neutron activation techniques. They found from 8-50% of total copper in their extractions and a marked increase of extractable copper with depth. The fact that less than 1% of divalent ^{64}Cu added to identical samples could be extracted indicated the presence of non-labile organic complexes of copper, possibly with extracellular biogenetic material of planktonic origin. Using perchloric acid oxidation in offshore Florida waters and a colorimetric method (neocuproine) for the extraction of copper, Alexander and Corcoran (1967) have determined spectrophotometrically the concentrations of ionic, particulate, and total soluble copper. They found that soluble copper was the predominant form and that ionic copper never accounted for more than 40% of total soluble copper. Williams (1969) has determined the copper content of unfiltered samples of Southern California sea water before and after photo-oxidation using a colorimetric method (sodium diethyldithiocarbamate followed by extraction with carbon tetrachloride). In this study organic copper accounted for 5-28% of total copper. Furthermore a control experiment using EDTA as a complexing agent indicated that, barring kinetic considerations, the copper-organic complexes must have stability constants greater than 10^{18} in order to avoid detection by this procedure. Williams proposed the possibility that copper is bound by colloidal material and surrounded by an organic sheath.

Shapiro (1964) has presented a similar explanation for the case of iron in the presence of highly colored fresh water. He assumed that the iron-color relationship was primarily one of peptization rather than chelation. Ghassemi and Christman (1969) have likewise studied the binding of iron to colored matter in natural waters using Sephadex gel filtration techniques. They found that even in the presence of strong chelating agents like EDTA a portion of the iron remained bound to the high molecular weight fractions of the colored matter. They proposed that some mechanism other than chelation must explain this. Barsdate (1970) has investigated the complexing capacity of lake water using the radioisotopes: ^{60}Co, ^{54}Mn, ^{65}Zn. He used dialysis techniques to separate his samples into dialysable (< 2μm) and non-dialysable fractions (2-500μm) and observed the retention of metal radioisotopes within the dialysis sack. His results showed that progressively more metal is retained as the colour of the water increases. He concluded that the metals were associated with organic matter rather than inorganic colloids, since these substances retained their metal-binding properties after extraction into polar solvents, removal of the solvent by evaporation and subsequent redissolution in aquous solution.

1.1.5 Organo-metallic interactions - biological evidence

Thus viewed from a physico-chemical standpoint it seems fairly certain that organo-metallic interactions must exist, but what biological evidence is available? A fact that has perhaps stimulated more interest in organo-metallic interactions than anything else is the knowledge than in laboratory experiments with phytoplankton it is more than often necessary to add a chelator (EDTA, for example) to a culture medium in order to stimulate growth. Apparently similar bodies of water containing equal amounts of inorganic nutrients and approximately the same population of phytoplankton and exposed to equal amounts of light, may differ enormously in their productivity. It has been suggested that the difference between 'good' and 'bad' waters, from the point of view of biological productivity, may depend upon the availability of essential micronutrients or, on the contrary, on the presence or absence of toxic elements.

Essentially three kinds of experiments are found in the literature to test the effect of trace metals on productivity. The first kind involves the addition of trace metals to natural waters, which are assumed to be deficient in one or another trace metal. Goldman (1965) has investigated the effect on growth of certain trace metals added to lake water. He found that the addition of Mo (10^{-6}M) gave a large increase in productivity over blank samples within a few days, but Co (10^{-7}M) on the other hand drastically reduced productivity over the same period. He suggested that the lake water was deficient in Mo, and that Co was obviously toxic at the concentrations added. In another study, Wetzel (1965) has investigated the effect of Fe and Co on two lakes - one with a very low productivity and a second with a relatively high productivity. For the first lake, his results indicated a marked increase in productivity for the addition of Fe, slightly less for the addition of Co in the form of vitamin B_{12}, and a marked reduction in productivity for the addition of $CoCl_2$ with respect to control samples. For the second lake additions of metal had no effect on productivity. It appeared from this experience that the DOM of the second lake was able to 'absorb' the $CoCl_2$ (toxic to the phytoplankton in the first lake) by complexation or some other mechanism, and thereby protect the phytoplankton population and that sufficient trace metals were available to prevent them from becoming limiting factors in the productivity experiments.

The second kind of experiment involves the addition of organic ligands, with or without trace metals, to natural waters. Johnston (1964) has made an exhaustive study of the effect of trace metals, organic ligands and vitamins on the fertility of enriched sea water. His sea water samples were enriched with phosphate, nitrate and silicate in order to give optimum growth. Comparison was made with control sea water samples enriched with EDTA (8×10^{-5}M) and the trace metals Fe, Mn, Zn, Co and Cu. The purpose behind adding chelated trace metals was to increase the supply of essential micronutrients and furthermore, to bring very sparingly soluble metals into solution with the help of EDTA. The results showed that the addition of EDTA ($\geq 10^{-5}$M) alone to samples without added trace metals compared well with the control samples with added trace metals. One can conclude that an adequate supply of trace metals existed in the original sample, but was unavailable for the growth of phytoplankton. Johnston suggested that the presence of a chelator greatly enhances the leaching of metal from particulate matter to replace uptake into algal tissue. If one assumes that the power of a chelating agent to tie up metal varies directly with its stability constant for the metal complex thus formed (neglecting kinetic considerations), then certain synthetic chelating agents would appear in the following order:

$$(\log K) \quad \text{NTA} < \text{EDTA} < \text{DTPA} < \text{EDDHA}$$

With culture assays Johnston investigated the effect on growth of these chelating agents at 2.7×10^{-5}M and 2.7×10^{-6}M. At the higher concentration EDTA, DTPA, and the control (8×10^{-5}M EDTA + trace metals) gave better growth than NTA and EDDHA. At the lower concentration only EDTA gave good growth. From the results, it appears than an <u>optimum</u> chelating power may exist.

Interpretations of this apparent optimum chelating power are numerous. It may be that there is an optimum concentration of trace metals or a balance between these metals determined by the chelating power of the organic ligand; on the contrary, it is possible that the chelating agent itself may be toxic. Johnston has pointed out that complex formation greatly modifies the behavior of metals by changing their solubility directly, and by affecting the oxidation-reduction potential and other physical and chemical characteristics of the medium.

A third kind of experiment in the literature involves the removal of the dissolved organic matter. Barber et al. (1971) have studied the effect on productivity of the removal of the DOM by activated charcoal or by photo-oxidation. The effects of adding EDTA, Fe, trace metals, and deferriferrioxamine B (a ferric specific chelator of high stability) were also investigated. In order to insure that neigher light nor nutrients would be limiting factors, nutrient rich water from an upwelling off the coast of Peru was mixed with surface water from which part of the naturally occurring phytoplankton population had been removed by filtration. The activated charcoal treatment selectively removed certain organic compounds without causing significant change in the concentration of nitrite, nitrate, silicate, and phosphate. Two types of water could be distinguished in his study: the first type contained natural organic ligands, whereas the second appeared to be lacking in these same ligands. For the first water type, growth was influenced neither by the addition of EDTA, nor by the addition of trace metals and Fe, nor by any combination thereof;

in addition, the growth rate did not depend upon the inoculum size. Treatment with activated charcoal reduced growth, but the effect could be reversed on adding trace metals and Fe, or EDTA, trace metals and Fe. The addition of deferriferrioxamine B to the charcoal treated water further reduced growth, presumably by strongly chelating iron and rendering it still less available to the phytoplankton.

In the second water type, growth was increased by the addition of EDTA, of trace metals, and any combination of the two. Treatment with activated charcoal, on the other hand, did not produce any change in growth. For this second water type, the growth rate was found to depend directly upon inoculum size. This positive dependence implies that the phytoplankton themselves are capable of synthesizing and releasing a quantity of the conditioning agents or organic ligands necessary to render the water propitious for phytoplankton growth. Watt (1966) has shown that extra-cellular release increases when phytoplankton populations are diluted with filtered water, and his results indicate that less productive waters have a higher relative release of extra-cellular products.

The simplest interpretation one can make of Barber's experiments is that chelating agents such as EDTA or naturally occurring organic ligands enhance growth by increasing the availability of the metals already present, while the addition of trace metals alone enhances growth by providing a substitute pool of available metal that phytoplankton can use. It is worth noting that freshly added trace metals have a different availability than the 'aged' metal already present in sea water.

Although the work of Johnston, Barber and others has thrown a good deal of light on the effect of trace metals and chelating agents on productivity, one may reproach them for never having measured the actual metal content of samples before additions! This information might narrow the field of interpretation. For instance, it is possible that increases in growth upon the addition of chelating agents may be due to the masking of toxic elements by chelation. No information appears to contradict this view! Stumm and Bilinski (1972) maintain that "there is circumstantial evidence, but no direct proof for the existence of soluble chelates in natural waters". Hence one may interpret the data from practically any point of view depending on whether the existence of soluble metal chelates seems plausible to one or not!

1.1.6 Soluble trace metal speciation

It seems evident that the stumbling block with regard to increasing our understanding of the biological importance of metal-organic interactions lies in our ignorance of the speciation of trace metals in solution. We need to have more information on the type of metal species or forms encountered under different chemical conditions, and their biological importance. For instance, it is generally assumed that only the ionic form of a metal is biologically active, but little or no experimental evidence exists to prove this, except for the case of copper. Manahan and Smith (1973) have provided very convincing evidence that ionic copper is required for algal growth, and that optimal growth in laboratory culture experiments is achieved at very low concentrations. Their work demonstrated the uptake of ionic copper from a well-behaved metal chelate reservoir in a synthetic medium. But what are those metal species found in natural waters, and just how well-behaved are they?

The distribution of a given metal among the various chemical forms depends on the following factors: the total metal concentration ($[M]_T$), the concentration of other competing cations ($[H^+]$, $[Ca^{+2}]$, $[Mg^{+2}]$, etc.), the concentration of reacting ligands ($[L]$), the stability constants (K) of possible metal complexes, and finally on the rate constants for the formation and dissociation of these complexes (k_f, k_d). Metal speciation in natural water samples thus depends on a delicate balance of chemical equilibria, which may easily be disturbed by the experimental approach chosen to study the metal distribution. Because of difficulties inherent in isolating the various metal complexes, most experimental approaches have been limited to determinations of the total metal concentration and several "operational" classes of metal, which rarely correspond to well-defined chemical forms. These approaches, however, do give an idea of trace metal speciation in solution. In Table 1, a resume of frequently used experimental approaches is given (Campbell et al., 1974).

Perhaps the most complete work on trace metal speciation in polluted fresh water using these techniques is that of Stiff (1971b). He investigated the soluble forms of copper, defined operationally as those which passes through a membrane filter of nominal 0.45 µm size. From a list of inorganic and organic ligands, he assumed the following to be predominant in the complexation of copper: HCO_3^-, CO_3^{-2}, CN^-, amino acids, polypeptides, and humic acids. Total soluble copper was determined using the colorimetric method of Alexander and Corcoran (1967). The concentration of "free" cupric ion was determined using the specific ion electrode for copper, and then the amount of copper complexed by the carbonate was calculated using pH values, stability constants and the bicarbonate activity.

Copper cyanide complexes were determined using a reagent with which cyanide quantitatively interferes: PHTTT*. This method, however, is unable to distinguish the cyanide complexes from other very strong complexes, such as those of cysteine, histidine, and sulfide that may interfere with the determination. Copper complexed by humic acids was found to be partly extractable in hexanol. Hexanol insoluble humic substances were determined by taking into consideration their retarding effect on the rate of formation of the copper-PHTTT complex. As copper complexed by amino acids and polypeptides could not be determined directly, their concentrations were estimated by subtracting all other forms of copper from the total soluble copper.

In applying this method to filtered river water samples, to which copper had been added, Stiff claimed that copper was present primarily in carbonate complexes and in amino acid and polypeptide material. Cupric ion accounted for less than 2% of the total added copper. The amount of copper retained in the inert and hexanol-extractable humic acid complexes was unpredictable. Sometimes it appeared as inert and sometimes as hexanol-extractable humic acid complexes, and sometimes neither appeared. In samples of filtered sewage water to which copper had been added before filtration, the "copper cyanide" fraction predominated. However, as Stiff has suggested, this fraction is probably due to the presence of colloidal copper sulfides, or histidine or cysteine complexes in these waters, because little or no cyanide should be found in domestic sewage.

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* 3-propyl-5-hydroxy-5-D-arabino-tetrahydroxybutyl-3-thiazolidine-2-thione

TABLE 1

Experimental approaches to the study of soluble trace metals and the different operational classes they determine / Approches expérimentales pour l'étude des métaux traces en solution ainsi que les différentes classes opérationnelles qu'elles déterminent.

Operational classes Classes opérationnelles	Experimental approaches Approches expérimentales	References / Références
"free" / "libre"	electrochemistry: specific ion electrodes / électrochimie: électrodes sélectives	Stiff, 1971 a, b Smith, 1973 Gardiner, 1974
"free" / "libre"	electrochemistry: anodic striping voltammetry / électrochimie: polarographie inverse	Allen, 1970 Fitzgerald, 1970 Zirino, 1970 Chau and Lum-Shue-Chan, 1974
"free" / "libre, labile, exchangeable / échangeable	colorimetry: specific reagents / colorimétrie: réactifs colorimétriques spécifiques	Williams, 1969 Shapiro, 1969
	chromatography: ion exchange or molecular exclusion / chromatographie: échange d'ions ou exclusion moléculaire	Ghassemi, 1969 Siegel, 1971
dialysable	dialysis / dialyse: membrane	Barsdate, 1970 Gibbs, 1973
ultra-filtrable	ultrafiltration: membrane	Gjessing, 1970 Wilander, 1972
extractable / extractible	extraction: organic solvent / solvant organique	Slowey, 1967 Corless, 1968

TABLE 1 (continued/suite)

Description	Experimental approaches / Approches expérimentales	References / Références
total / total	digestion in oxidizing medium followed by some method of metal determination / digestion en milieu oxydant, suivie d'une méthode de dosage des métaux	Chau and Lum-Shue-Chan, 1974 Barsdate, 1967

The analytical techniques employed by Stiff, though innovative, are open to a good deal of speculation. In the light of the importance of copper-amino acid complexes in river water samples, some adequate means of determining these complexes directly should be found. The stability constants of the copper-amino acid complexes are small ($\log K \leq 8$), except for the histidine and cysteine complexes discussed above, so any attempt at isolating these complexes would probably disturb the equilibrium of the system and invalidate the results. It is obvious that determinations of this kind will require very special techniques, that minimize disturbance of the sample equilibrium.

1.1.7 Analytical methods

Criteria for the choice of an analytical method for determining trace metals are sensitivity, selectivity, accuracy, applicability, reliability, convenience and economy. In addition, one must consider the different selectivities of the various methods: some methods determine the total metal content, whereas others are sensitive only to a particular oxidation state or to an ionic form of a metal. Many methods require preconcentration techniques, which are fine for the determination of total metal content, but inapplicable for the differentiation of metal species. When very large numbers of samples require trace metal determinations, speed and ease of operation become desirable features of an analytical method.

Although numerous methods of determining trace metals exist, the most common are optical or electrochemical in nature. Among the optical methods the most frequently employed are atomic absorption spectrophotometry and colorimetry. Conventional atomic absorption with flame vaporization is an extremely reliable, though not particularly sensitive method. It is excellent, however, for determining total metal content, if combined with some rapid means of metal preconcentration. The carbon-rod technique of atomic absorption, on the other hand, has a sensitivity of the order of 1000 times greater than that obtained with the conventional flame technique, but is somewhat less reliable due to matrix effects (organic or inorganic compounds or ions) in natural water samples. Colorimetry has historically been the most widely applied technique in trace analysis, because of its sensitivity, reliability and economy. It involves, however, more steps and complications than any of the direct procedures. A separation or preconcentration step (e.g. solvent extraction) is required and numerous reagents are used to prepare the sample. The detection limits for this method depend on the experimental apparatus and conditions, and therefore vary greatly from one laboratory to another.

Electrochemical methods include potentiometry with specific ion electrodes, and various polarographic and voltammetric techniques. Potentiometry with specific ion electrodes is a very useful direct method of determining "free" metal activities in natural waters. With constant ionic strength, electrode response for copper is Nernstian down to 50 μg/l, but below this concentration, the response becomes non-Nernstian and extrapolation of the results is required, a hazardous procedure at best.

Because of the logarithmic dependence of potential on ion activity, small errors in potential result in relatively large errors in ion activity. Hence enormous care should be taken with this method. Smith and Manahan (1973) have shown that in order to successfully measure the cupric ion activity in tap water samples, a complexing antioxidant buffer had to be added to the samples. This buffer solution served to control pH, regulate ionic strength, reduce the interference from the ferric ion, and provide a moderately reducing medium. Their work has shown that in order to have reproducible results, some understanding of the chemical behavior of the ion of interest is necessary. Used with care, the potentiometric method can give excellent results for a wide variety of metals.

Polarographic and voltammetric methods are direct techniques for determining the so-called "free" and labile metal concentrations. Labile metal is then interpreted to mean any form of the metal of interest, that will plate on the surface of a mercury electrode. This will obviously include ionic metal and some complexed species, the distribution depending on the physico-chemical conditions of the sample (e.g. pH, presence of strongly binding ligands, temperature, etc.). The polarographic method describes a technique, whereby the metal ion is selectively reduced on a dropping mercury electrode (DME) producing a rapid increase of the diffusion current for a characteristic value of cell potential. The current-potential curve is then recorded and the height of this current wave is proportional to the metal ion concentration. The method is applicable to any substance - molecular or ionic, organic or inorganic - that can be reduced on the surface of the mercury electrode. More than twenty metallic elements have been determined using this method with mercury and other electrode surfaces. Although conventional polarography (DC linear) is not the most sensitive of methods (see Table 2), considerable improvement can be gained by using square-wave potential sweep techniques such as pulse and differential pulse polarography.

Anodic Stripping Voltammetry (ASV), or inverse polarography as it is commonly called, is a simple and elegant technique in which the metal ion of interest is concentrated by electroplating on a mercury electrode for a suitable time and then measured by reversing the current and stripping the deposited metal back off into the solution. In this case, a hanging mercury drop electrode (HMDE) is often employed. In stripping voltammetry with mercury electrodes only those metals capable of forming an amalgam with the mercury can be determined: Ba, Bi, Cd, Cu, Ge, In, K, Ni, Pb, Sb, Sn, Tl and Zn (Barendrecht, 1967). As one can see from Table 2, the ASV method is extremely sensitive - often limited only by a background of trace metal impurities in reagents.

In the following work, we have chosen to explore the use of the ASV method, because of its several advantages as an analytical tool:

- high sensitivity and reliability
- possible species differentiation in the range - ionic to total metal content
- minimum tampering with environment samples - risk of contamination reduced
- simultaneous determinations of different metals
- field measurements possible
- small sample volumes

In the following section the theory of ASV will be discussed.

1.2 Theory and principles of anodic stripping voltammetry (ASV)

1.2.1 Description of the ASV technique

Anodic Stripping Voltammetry involves the following two consecutive steps:

TABLE 2

Detection limits of the various electrochemical methods of determining trace metals / Limites de détection de certaines méthodes électrochimiques de dosage des métaux traces

Analytical methods Méthodes analytiques	Detection limits / Limites de détection *
Potentiometry: specific ion electrodes / Potentiométrie: électrodes sélectives	$10^{-6} - 10^{-7}$ M
Polarography / Polarographie (DME):	
1. DC linear / en courant continu	$10^{-5} - 10^{-6}$ M
2. pulse / à implusions	$10^{-6} - 10^{-7}$ M
3. differential pulse / à impulsions différentielles	$10^{-6} - 10^{-7}$ M
Voltammetry /Voltammétrie (HMDE):	
- Single sweep / balayage simple	$10^{-6} - 10^{-7}$ M
- Anodic stripping / Polarographie inverse	
1. DC linear / en courant continu	$10^{-8} - 10^{-10}$ M
2. Pulse / à impulsions	$10^{-9} - 10^{-11}$ M
3. Differential pulse / à impulsions différentielles	$10^{-9} - 10^{-11}$ M

* Osteryoung and Osteryoung, 1972; Ellis, 1973; Princeton Applied Research Corp., 1971.

1. the preconcentration of the metal ion (or ions) of interest by controlled potential electrolysis in a stirred solution. This means that the metal ions are deposited cathodically on a solid microelectrode or reduced on a mercury drop or film electrode forming an amalgam.
2. the anodic dissolution of the concentrated metal by oxidation and its return to the solution. This is achieved by a relatively slow anodic potential sweep in a quiescent solution.

The first step is known as plating and the second as stripping. Plating is performed for a precise length of time under reproducible experimental conditions such that only a fraction of the desired metal is deposited on the mercury surface. Stirring rate, drop size, temperature, supporting electrolyte concentration, and cell geometry are held constant. Depending on the size of the drop and the volume of the sample, one is readily able to concentrate the desired metal in the mercury drop or film by a factor of a 1000 times the concentration of the metal in the solution, and often only as little as 2% of the total metal is removed from the bulk solution. It is possible by controlling the applied potential during plating to seperate metal ions on the basis of their different deposition potentials. In this case, the applied potential is set at a value cathodic to the polarographic half-wave potential of the desired metal ion, but not too cathodic as to include the half-wave potential of the unwanted metal ion. At the end of the plating step, the stirrer is stopped and a short time (30 sec.) is allowed to permit the amalgam concentration to become homogenous and to ensure that convection in the solution has ceased.

Next an anodic potential scan is applied, whereby the metal amalgam is oxidized back into the solution producing a response proportional to the metal amalgam concentration. This is called stripping, and is therefore the analytical step of interest. The resulting voltammograms (current vs potential) show current peaks whose heights are proportional to the corresponding metal concentrations in the mercury and consequently to the metal concentration in the bulk solution, if plating conditions are constant. Furthermore the peak potential of a metal is a qualitative indication of the nature of the stripping solution - the presence of metal-binding ligands can be thought of as facilitating the diffusion of the metal out of the mercury and into the solution, causing a shift in peak potential. Therefore the important characteristics of a voltammogram are peak height (i_p) and peak potential (E_p).

1.2.2 Theory

In this section, the discussion will be limited to partial plating techniques only, since total plating is evidently of less interest for the analysis of metals in states of chemical equilibrium. In partial plating one can assume that the metal concentration in the bulk solution is not appreciably changed during the electrodeposition step. Similarly, one can assume that, if plating time is sufficiently long, the electrodeposition current will reach a constant value. Therefore for the case of a hanging mercury drop electrode (HMDE) or a mercury film electrode (MFE), the metal amalgam concentration, C_a, is given by Faraday's law:

$$C_a = \frac{i_e t}{nFV} \qquad (1)$$

where i_e is the electrodeposition current, t is the plating time, n is the number of electrons transferred, F is Faraday's constant, and V is the volume of the mercury drop. The electrodeposition current (i_e) depends on mass transport phenomena such as diffusion and convection produced by stirring the solution. For the diffusion-controlled situation i_e is expressed in the following way:

$$i_e = \frac{nFDC_bA}{\delta} \tag{2}$$

where D is the diffusion coefficient, C_b is the metal concentration in the bulk solution, A is the electrode area, and δ is the thickness of the diffusion layer. In a stirred solution δ will be affected by the stirring rate, cell geometry and electrode design. If these factors are constant from one plating step to another, then equation 2 can be expressed as follows:

$$i_e = mnFDC_bA \tag{3}$$

where m is the mass transport coefficient (proportional to the square root of the stirring rate) (Ellis, 1973). By substitution, we have the following relation:

$$C_a = \frac{mDC_bt}{r} \tag{4}$$

where r is the radius of the mercury drop.

It is obvious from the equations above that the reproducibility of the plating step depends greatly on the reproducibility of the convection pattern around the mercury drop. Stirring rate and cell geometry are therefore very important, and must be held constant. In addition, other factors such as temperature, drop size, electrodeposition time, and ionic force must be controlled.

Quantitative determinations of plated metal are made during the stripping step. This step depends on the experimental parameters of electrodeposition and on certain factors inherent to stripping analysis such as sweep rate and pulse height. In addition, the type of electrode will influence the results of stripping analysis, be it a MFE or a HMDE.

At this point, it is important to introduce the notion of reversibility and irreversibility in electrochemical reactions. A reaction will appear reversible if the electron transfer rate appears infinitely fast in comparison to the technique used for measurement. Reversibility then depends on the particular technique employed. In polarography electron-transfer rate constants of 2×10^{-2} cm/s. and greater appear reversible. Those below 3×10^{-5} cm/s. appear totally irreversible (Princeton Applied Research Corp., 1971).

For the following reversible reaction in which the metal is soluble in the solution as well as in the mercury drop:

$$M^{+n} \quad ne^{-} = M_{Hg} \qquad (5)$$

the Nernst equation applies and is given by:

$$E_p = E^0 - \frac{0.059}{n} \times \log \frac{\{[M_{Hg}]\}}{\{[M^{+n}]\}} \quad (25^{\circ}C) \qquad (6)$$

where $\{[M_{Hg}]\}$ and $\{[M^{+n}]\}$ are the activities of the metal in the amalgam and the metal ion in the solution at the mercury drop surface respectively. E^0 is the standard reduction potential of the metal vs the saturated calomel reference electrode (SCE), assuming an activity for the Hg in the drop equal to unity. E_p is then the peak potential for the given solution or the potential for which any value more cathodic will reduce the metal on the mercury drop and for which any value less cathodic will oxidize the same metal.

In stripping analysis a reversible metal reaction implies that the electron-transfer rate for a metal being oxidized is faster than the rate of diffusion of the oxidized metal away from the mercury drop surface. This means that diffusion is the rate-determining step with electron transfer appearing infinitely fast. Some metal oxidations however are less reversible than others, and the degree of reversibility is then apparent from the stripping voltammogram. The current peak width increases with increasing irreversibility. Furthermore the degree of reversibility of a metal ion can be evaluated from its half-peak width ($W_{1/2}$), which corresponds to the slope of the DC polarographic wave in classical polarography (Meites, 1965).

The peak height, i_p, has been derived for the reversible stripping process with the HMDE by Reinmuth (1961). This is given as follows:

$$i_p = k_1 n^{3/2} D^{1/2} r v^{1/2} C_b t - k_2 n D C_b t \qquad (7)$$

where v is the potential sweep rate and k_1, k_2 are constants. The second term accounts for the spherical contribution to linear diffusion and, as one can see, decreases the current. It is worth noting that the peak height is not proportional to the area of the drop as is the electrodeposition current, but to its radius. For potential sweep rates of 20 mV/s. and less, this equation no longer applies, because a correction for finite electrode volume is necessary (Barendrecht, 1967). In the experimental work that follows, a sweep rate of 2- 10 mV/s has been used. This equation nevertheless gives one an idea of the dependence of i_p on factors influencing the stripping step.

The peak potential of the metal ion in ASV will be influenced by numerous factors. These include the presence of metal-binding ligands, pH, temperature, the oxidation state of the metal ion, and the character and the ionic strength of the medium. Metal-binding ligands, however, have the most profound effect on peak potential.

In general, for reversible reactions complex formation results in shifts of peak potential towards more negative values, the shift increasing with increasing ligand concentration. Note, however, that these shifts will occur only if the rate of complex formation is faster than the rate of oxidation of metal out of the mercury electrode*, and if the concentration of the reacting ligand is sufficiently high to ensure that the formation of the metal complex at the surface of the mercury electrode is not prevented by a lack of reacting ligand.

Within certain limits, the formation constants and formulae of metal complexes can be calculated from the observed shifts in peak potential for increasing concentrations of reacting ligand. One method for

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* In polarographic analysis, shifts in the half-wave potential will occur only if the rate of decomplexation is slower than the rate of reduction of the metal on the mercury drop.

simple systems is that of Ligane (1941), which applies to single complex formation with reversible metal ions. This method requires that the following conditions be fulfilled:

1. the diffusion coefficient of the complex must be the same as that of the simple metal ion;
2. the ligand concentration at the electrode surface must be equal to the bulk concentration. Thus the ligand concentration at the electrode surface (being depleted by complex formation) must be much greater than the oxidized metal concentrations in order that the above condition is fulfilled (Crow, 1969);
3. the electron-transfer rate* must be faster than the rate of diffusion of the metal species away from the electrode surface: this implies that the rate of diffusion is the rate-determining step for the reaction;
4. a single complex must predominate over a wide range of ligand concentrations.

For the following complexation reaction:

$$M^{+z} + j\ L^{-y} \rightleftarrows ML_j^{+(z-jy)}$$

with a formation constant, K_f, expressed as:

$$K_f = \frac{\{ML_j^{+(z-jy)}\}}{\{M^{+z}\}\ \{L^{-y}\ j\}} \tag{8}$$

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* The presence of certain ligands may facilitate the electron-transfer process, increasing the degree of reversibility of the electrochemical reaction for the metal ion: pyridine for Ni^{+2} (Crow, 1969), and I^- and OH^- for In^{+3} (Engel et al., 1965).

Lingane developed a relationship between the shift in half-wave potential, the stability constant and the equilibrium ligand concentration using the Nernst equation. For stripping analysis, under the conditions listed above, this becomes: (Ernst et al., 1974)

$$\Delta E_p = E_{p_0} - E_{p_1} = \frac{0.059}{n} \log K_f + j \frac{0.059}{n} \log [L] \quad (25^\circ C) \qquad (9)$$

where E_{p_0} is the peak potential of the uncomplexed metal ion and E_{p_1} is the peak potential of the metal in the presence of the metal-binding ligand. From the graph of ΔE_p versus log [L] it is a simple matter to evaluate the ligand number, j, and the formation constant, K_f, of the metal complex.

The total current flowing through the cell during stripping analysis is given below:

$$i = i_f + i_c + i_b \qquad (10)$$

where i_f is the faradaic current due to the oxidation of the species under analysis; i_c is the charging current due to the charging of the double layer at the electrode-solution interface; and i_b is the background current due to the oxidation of impurities or the decomposition of the electrolyte; i_c and i_b make up the residual current or background noise in the system. The charging current is given by the following relation:

$$i_c = A\, v \frac{dq}{dE} \qquad (11)$$

where dq/dE is the differential double layer capacity. Charging current therefore increases with r^2 and v for the HMDE, whereas peak current increases much more slowly with r and $v^{1/2}$. Thus for DC linear sweep stripping analysis little can be done to increase sensitivity, except increasing plating time. For very low level trace analysis long deposition times are required, sometimes as long as 30 minutes per sample. It is probably this aspect above all that has retarded the widespread adoption of ASV. Several techniques have been employed to minimize the effects of residual current.

Two of these are Pulse and Differential Pulse Anodic Stripping Voltammetry (PASV and DPASV respectively). They have the advantage of providing higher sensitivities by reducing the effect of charging current or capacitive current. In PASV square-wave pulses of successively increasing amplitude are applied to the HMDE (Figure 1). The Princeton Applied Research polarograph, model 174, provides pulses of 5 to 100 mv lasting 57 ms. with current sampling at the end of each pulse. The magnitude of each pulse is governed by the scan rate, v, and the pulse frequency. The voltage pulse lasting 57 ms. gives rise to a charging current spike, much like that generated when a voltage pulse is applied across a capacitor. This charging current, however, decays approximately exponentially with time. The faradaic current, on the other hand, decays approximately as $t^{-1/2}$. Hence towards the end of the pulse the system current is almost entirely faradaic, the charging current having decayed practically to zero. The current is then sampled during the final 17 ms. of the voltage pulse and a considerable gain in sensitivity is achieved. Because the potential pulse lasts only 57 ms. followed by a return to initial conditions, this allows the electroactive species that was oxidized during the pulse to be partially returned to its reduced state. This means that the concentration

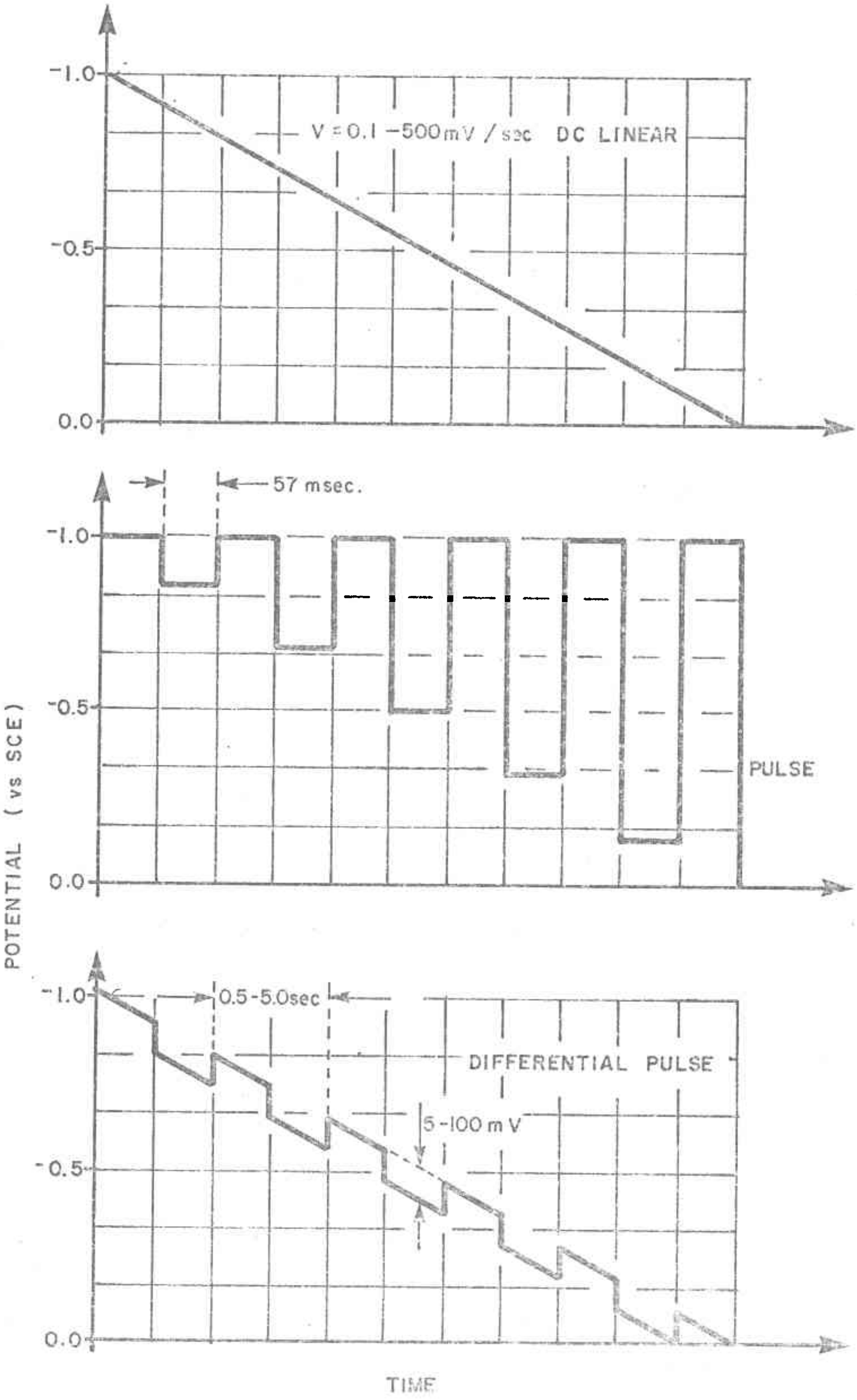


Figure I . Schematic representation of anodic stripping techniques/
Représentation schématique des techniques de polarographie inverse.

of the electroactive species in the vicinity of the electrode will be close to its starting concentration just before the next potential pulse. Hence the resulting voltammogram for PASV gives a polarographic waveform instead of current peaks as in ASV. Osteryoung and Parry (1967) have estimated that this technique increases sensitivity by a factor of approximately 5 to 7 times over the classical method.

Another technique that has been used extensively in our laboratory is DPASV. In this technique the square-wave pulses are superimposed on the conventional linear potential ramp and the magnitude of each pulse is fixed. In the same way as in PASV, the charging current is greatly reduced at the end of the pulse. Here, however, the total current is measured just before the pulse is applied and stored in a memory. Then at the end of the pulse it is measured again and the difference between the two values, which is attributable to i_f, is amplified and plotted as a function of applied potential. This method yield current peaks, whether applied to polarographic or stripping procedures, because the resulting curve is, in effect, a derivative of the polarographic curve. Differential Pulse Polarography (DPP) has been estimated to increase sensitivity by a factor of approximately 7 to 10 times over the classical method (Osteryoung and Osteryoung, 1972). Another advantage is the fact that the peaks are symmetric - an attribute of importance when it comes to estimating peak heights.

Figure 2 shows voltammograms of Cd, Pb and Cu for stripping analysis by classical ASV, PASV and DPASV. In this example, the experimental conditions were held constant in order to compare the sensitivities of the different methods. It is obvious that a plating time of two minutes is not sufficiently long for classical ASV, which requires plating times of the order of ten minutes or longer.

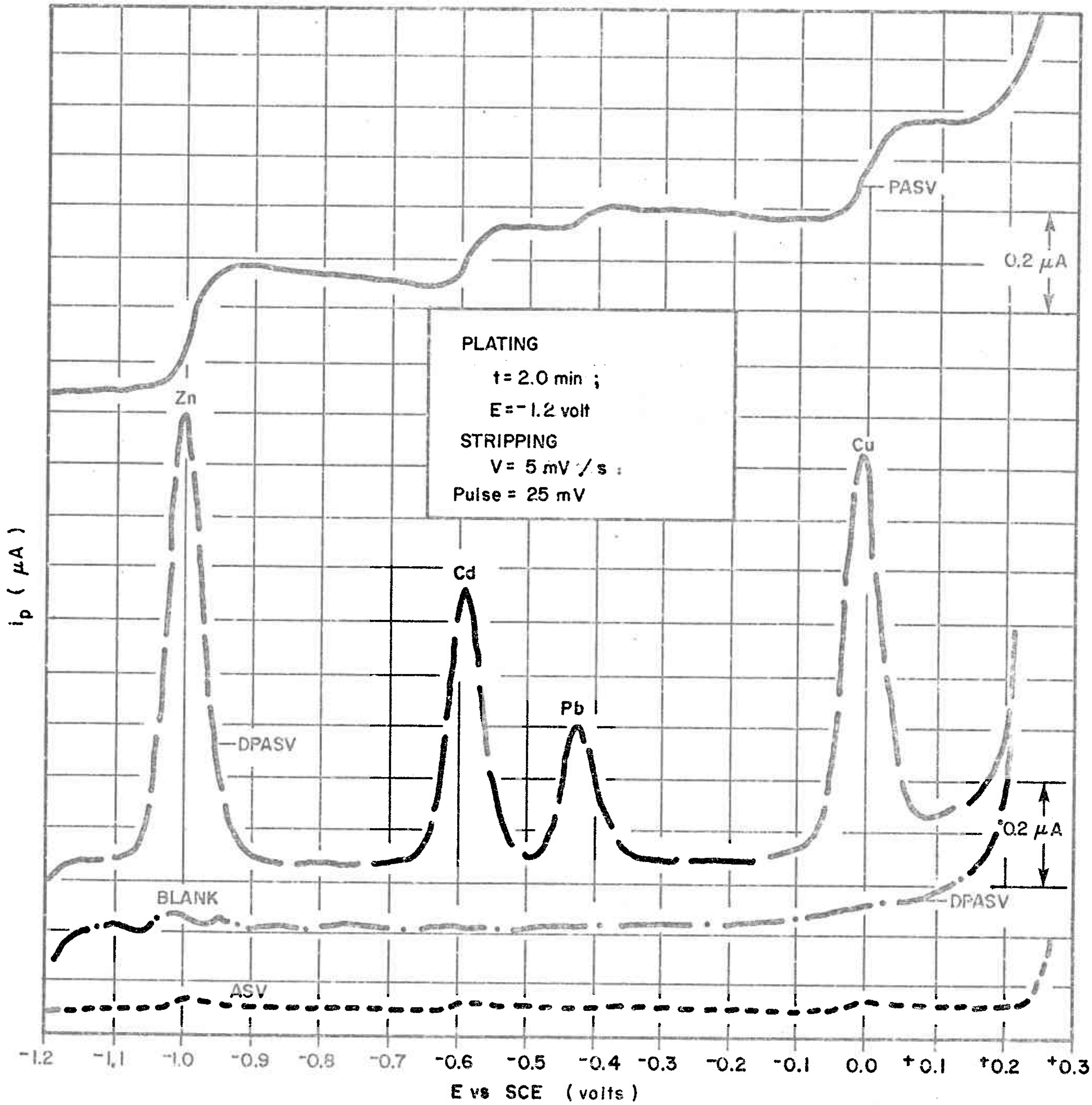


Figure 2. Comparison of anodic stripping techniques for the determination of zinc, cadmium, lead and copper / Comparaison des techniques de polarographie inverse pour le dosage du zinc, du cadmium, du plomb et du cuivre.

1.2.3 Experimental details

Three types of electrodes have traditionally been used in stripping analysis: hanging mercury drop electrodes, mercury film electrodes, and solid metal electrodes. The HMDE used in the following work was developed by Kemula (1959) and consists of a capillary tube with a mercury reservoir. The flow of mercury throught the capillary tube is controlled by a micrometer screw and piston assembly. Drops can be readily renewed and their size can be easily adjusted. This electrode gives highly reproducible results in acidic and neutral media, but is useless in alkaline media with a pH greater than 11, due to a reduction in the surface tension of the mercury drop and the penetration of the solution into the capillary. Its advantages are a high overvoltage for hydrogen evolution (characteristic of all mercury electrodes), simplicity, frequent drop surface renewal, sensitivity, and good reproducibility. The main disadvantage to the electrode is a loss of resolution due to the diffusion of metals into the drop during plating, and a subsequent broadening of current peaks during stripping analysis.

Mercury film electrodes have become very popular since the development of the composite mercury-graphite electrode by Matson et al. (1965). This electrode consists of minute droplets of mercury electroplated on a polished wax-impregnated graphite rod. The graphite provides an inert support for the mercury film. The advantages of Matson's electrode are high resolution and sensitivity - superior to results attainable with the HMDE. Its only serious limitation occurs when it is applied to environmental samples. As with the HMDE, surface-active agents in natural waters tend to be adsorbed on the mercury surface, where they may slow the rate of plating and interfere with the stripping step. Hume and Carter (1972) have noted that if a composite mercury-graphite electrode is removed from a humic acid solution and subsequently placed in a "clean" solution, it will continue to behave as if it were still in the humic acid solution. The HMDE has the advantage of a continuously renewed mercury surface, and it is for this reason and for its inherent simplicity that we have chosen to use it.

Solid microelectrodes such as platinum, graphite and glassy carbon have been employed in the past because of their greater anodic range and their ruggedness. Surface contamination and lack of reproducibility, however, are problems with these electrodes. For metals such as Au, Ag, and Hg itself, it is imperative to use solid electrodes, because oxidation potentials more positive than that of mercury are required.

Assuming partial plating procedures, polarographic and ASV techniques will determine only those metal species that will plate on the mercury electrode within the time intervals employed. In any reversible reaction, for which diffusion to the electrode surface is the rate determining step, metal aquo-complexes will always be plated on the mercury, provided the plating potential is sufficiently cathodic. For complexed metal, however, electrodeposition will depend upon several factors. Some metal complexes may plate directly, whereas others must undergo prior dissociation. In the latter case the rate of complex dissociation must be faster than the subsequent electron-transfer rate for significant plating of the complexed metal to occur. For instance in alkaline solutions, zinc (II) exists primarily in the form of the tetrahydroxozincate (II) ion - $Zn(OH^{-})_4^{-2}$. The electrodeposition of zinc then proceeds as follows (Tanaka, 1959):

$$Zn(OH)_4^{-2} \xrightarrow{k_1} Zn(OH)_2 + 2OH^-$$

$$Zn(OH)_2 + 2e^- \xrightarrow{k_2} Zn_{Hg} + 2OH^-$$

In this case the complexed zinc will plate appreciably only if the rate of dissociation, k_1, is faster than the electron-transfer rate, k_2. It is worth noting that in this case the complexed metal ($Zn(OH)_2$) can be plated directly, and does not necessarily have to pass by an aquo-complex in order to plate. Other examples of one-step electrodeposition are the reduction of $Ag(NH_3)_2^+$ and $Cd(CN)_2$ (Tanaka, 1959). The increased bulk of a complexed metal ion and therefore its slower diffusion rate can prevent complexed metal from being plated to the same degree as the aquo-complex of the same metal. For instance coordination with large ligands such as tartrate, citrate, and EDTA markedly increases the size of the diffusing species, and in such cases the diffusion coefficient (D) may be only half or less than the diffusion coefficient of the metal aquo-complex (Meites, 1959). This suggests that one should take some care in interpreting results, particularly when comparing current peaks due to primarily metal aquo-complexes with those due to metal bound to large ligands.

In the literature one stumbles inevitably across terms such as "labile" and non-labile" metal complexes. These terms are operational labels referring to those metal complexes that will plate on the mercury electrode and those that will not plate respectively. O'Shea (1972) has defined labile metal complexes as those complexes for which the rate of metal dissociation is faster than the rate of diffusion of the metal species to the electrode surface. Conversely, non-labile metal complexes are those for which the rate of metal dissociation is slower than the rate of diffusion of the metal species to the electrode surface. An obvious problem with these labels is the generality of their definitions. For instance, the degree of electrodeposition of labile metal complexes will depend on the diffusion coefficients of these complexes. Therefore some labile metal species will tend to be plated to a greater degree than others, and may likewise be interpreted to be more labile. In addition, for the case of metal complexes that are plated in one step, O'Shea's definition of labile metal complexes is quite meaningless. For such operational terms to be useful, it is necessary that they depend on fewer experimental factors and more on chemical concepts.

In the following section, applications of ASV to environmental samples will be discussed.

1.3 Applications of ASV to environmental samples

1.3.1 General applications

In the early sixties ASV began to be applied to the determination of metal ions in natural waters. Ariel and Eisner (1963) and Ariel et al. (1964) used ASV to analyse Dead Sea brine. They determined Zn, Cd and Cu with a HMDE. Then Matson et al. (1965) developed their very popular composite mercury graphite electrode, and Matson (1968) reported the determination of the Pb content of various natural waters using this electrode. Some of the problems encountered in the determination of trace metals in seawater samples were discussed in an article by Whitnack and Sasselli (1969). They determined Zn, Pb, Cd and Cu in seawater interpreting their results as an indication of the activity of the ionic form of the respective trace metals.

An ingenious method of determining ionic metal using a potentiometric method combined with ASV was described by Matson et al. (1969). This method involves the plating of a small quantity of the metal to be determined into a known quantity of mercury on the composite mercury graphite electrode. The electrode is then transferred into the sample and the applied potential is regulated at the metal peak potential. The metal remaining in the electrode is then determined by stripping analysis. Subsequent calculations using the Nernst equation permit one to determine the ionic metal in the sample. Matson et al. maintain that ionic metal in environmental samples can be determined in this way down to a phenomenal limit of 10^{-20}M. Note, however, that the proposed method is particularly laborious.

About this time attempts were made to define operationally the metal determinations made by the ASV method. For instance, Allen et al. (1970) described an ASV procedure for determining what they called free and acid-exchangeable Cu, Cd, and Pb in several lakes and rivers. Free metal in their work is understood to mean labile metal that is plated at the original sample pH; acid-exchangeable metal is defined as any metal that is released to the solution on the acidification of samples with perchloric acid (pH = 2). Their results indicated enormous increases of Cu and Pb after acidification of unfiltered samples. In addition, they monitored the lead concentration of river and lake water samples on acidification and found that acidification yielded an instantaneous partial release of lead followed by a slow leaching of the metal. They interpreted the latter phenomenon as being characteristic of metal exchange with the more stable complexes.

Acid digestion and photooxidation have been compared as methods of releasing strongly bound metal by Fitzgerald (1970). In three seawater samples he determined copper by ASV at a pH = 8, after acidification to pH = 3, and after 12 hours of photooxidation. In his first sample of filtered nearshore water 70% of total copper was found in strongly bound complexes, and determinations of copper after acidification to pH = 3 gave the same results as photooxidation at pH = 8 or pH = 3. In a second sample of filtered, relatively polluted water, photooxidation at pH = 8 gave a significantly greater current peak for copper than acidification to pH = 2.5. The results indicated that 63% of total copper was found in strongly bound complexes, of which over 50% released their metal on acidification. In a third sample of unfiltered, open ocean water acidification to pH = 3 gave significantly greater current peaks for copper and lead than photooxidation for 4 hours only. In this case the situation is reversed, but the two samples are impossible to compare because of their different photooxidation times.

Chau and Lum-Shue-Chan (1974) have defined more thoroughly the term, "labile" metal, and distinguished what they call strongly-bound metal. They define labile metal to include ionic metal, acetate-exchangeable (in their experiments 0.04M sodium acetate buffer is present as supporting electrolyte) metal, and part of the strongly bound metal in waters where the ligand to metal ratio is about one or greater. This contribution of strongly bound metal to labile metal determinations is due to the dissociation of these metals during the plating step. Chau and Lum-Shue-Chan suggest using as short a plating time as possible to minimize this contribution to the observed current peaks. Further evidence to support this theory was provided in another publication appearing the same year (Chau et al., 1974). Other authors have provided similar evidence showing that labile metal may include metal from complex dissociation. Shuman and Woodward (1973) observed that chemical dissociation of the Cd-EDTA complex occurred during plating and contributed to stripping currents. Hanck and Dillard (1973) observed similar complex dissociation of the In-EDTA complex during the plating step. They found that by lowering the sample temperature to $0^{o}C$, it was possible to reduce the contribution of complex dissociation to peak current.

Strongly bound metal is defined by Chau and Lum-Shue-Chan (1974) as the difference between total metal and labile metal concentrations. In order to determine the total metal content of samples, one must liberate all metal from complexes that will not plate. This can be accomplished by several methods: acid digestion (nitric acid, perchloric acid, etc.), ultraviolet photooxidation, persulphate and sulphuric acid digestion, cation exchange (e.g. Fe^{+3}), etc. Some of these methods release metal by simple cation exchange whereas others destroy the organic matter present in the sample. Chau and Lum-Shue-Chan found acid digestion satisfactory for releasing strongly bound metal in filtered lake water samples, but this method was not effective in samples containing sewage effluent. For these samples they used persulphate and sulphuric acid digestion, which gave complete digestion of organic matter, whereas photooxidation for two hours of similar samples gave incomplete decomposition. It may thus be wise to compare methods of releasing total metal content for different water samples, before proceeding with the method of one's choice.

Chau and Lum-Shue-Chan used DPASV to determine labile and strongly bound forms of Zn, Cd, Pb, and Cu in lake water. Their results showed that labile metal concentrations of the four metals were significant in waters of relatively low pH (4.4 to 4.6). Their data indicated that copper and lead are much more strongly bound in lake water than zinc. Cadmium was not detectable in most of the lakes studied.

1.3.2 Complexation capacity

In the last few years ASV has been used frequently in determinations of the apparent complexing capacity of natural waters. In order to better appreciate the meaning of this term, some explanation will be necessary. In any given water sample, different trace metals will be complexed to different degrees. For instance the copper and lead uptake in natural waters is found to be different from that of zinc (Chau and Lum-Shue-Chan, 1974). Disregarding the kinetic aspects of complexation, it can be shown that the degree of complexation (ΔpM) of a metal will be independent of its own concentration, provided that the ratio of available ligands to total metal is greater than one. In this case the degree of complexation can be expressed in terms of the individual ligand concentrations and their stability constants for complexation:

$$\Delta pM = \log \frac{[M]_T}{[M^{+z}]} = \log \; 1 + \sum_{i=1}^{m} \sum_{j=1}^{n} \beta_j \; [L_i]^j \qquad (12)$$

where $[M]_T$ is the total metal concentration, $[M^{+z}]$ is the ionic metal concentration, $[L_i]$ is the concentration of the i-th ligand, and β_j is the overall stability constant for the complex $M(L_i)_j$ involving complexation of the i-th ligand with the given metal. In the light of this discussion it is obvious that in order to give a complete characterization of the complexing capacity of a natural water sample a great deal of knowledge concerning the above parameters and reaction rates is required.

In view of these difficulties, and for the purposes of monitoring water quality, a general concept of "complexing ligand availability" or "apparent complexing capacity" has evolved in recent years.

A common technique used for determining the complexing capacity of a water sample is a complexometric titration procedure in which an electroactive metal ion, such as copper, is the titrant. The metal-ligand complex formation is then followed by ASV and the stoichiometric end points are determined. This method was employed by Allen et al. (1970) in following the uptake of copper by a sample of unfiltered river water. They concluded that the complexation of copper by river water followed pseudo first-order kinetics. Bender et al. (1970) used a similar method in determining the concentration of complexing ligands in filtered (0.45 μm) sewage samples by titrations with copper. They found ligand concentrations equivalent to $1 - 80 \times 10^{-6}$ moles of copper per liter. In addition, they showed that copper bound to ligands in the sewage could be released by acidification or cation exchange with iron (III).

A DPASV procedure has been used by Chau et al. (1974) to determine the apparent complexing capacity of filtered (0.45 μm) lake waters. Copper was again used as the indicator cation and was added to samples at concentrations ranging from $1.5 - 5.5 \times 10^{-6}$M. They proposed that copper complexation would be complete if the competing side reactions due to other metals were minimized. They suggested that this situation would be favored if the total copper concentration were greater than the total ligand concentration and the sum of other highly reactive metal concentrations such as Fe (III), Pb and Ni. This metal to ligand ratio should likewise minimize the effect of complex dissociation during the plating of labile copper. From measurements of the copper binding capacity of known complexing agents, they concluded that their method would only measure those copper complexing agents with log stability constants greater than about 13. Interference from Pb and Fe (III) was a problem with their method, since copper cannot displace these metals when they are present at concentrations as low as 10 μg/l and 25 μg/l respectively. Chau et al. gave values of apparent complexing capacity ranging from 0.1 - 0.7 x 10^{-6}M for lake water, 0.7 - 1.2 x 10^{-6}M for water from Hamilton harbour, and 1.8 - 2.5 x 10^{-6}M for sewage effluent (values are expressed as moles of complexed copper and all samples had been filtered through a 0.45 μm membrane filter).

A different approach has been adopted by Hanck and Dillard (1973). They had investigated the use of ASV as a means of monitoring complexometric titrations of samples containing known concentrations of EDTA, using In (III) as the titrant. They found that their results were always lower than the known added concentrations of EDTA and not very reproducible. They interpreted these results as being due to complex dissociation during the plating step, which contributed to the current peak of the "free" metal ion. High "free" metal concentrations therefore gave low complexing ligand concentrations. After some effort to rectify this situation by reducing plating time and cooling samples, they concluded that ASV was not a satisfactory method for measuring complexing capacity. Thus they opted for a DPP procedure, which minimized the problems inherent to the ASV technique. In addition they developed a method of determining complexing capacity that involved the conversion by oxidation of Co (II) - complexes to Co (III)- complexes. Aliquots of Co (II) were added to unfiltered natural water samples, which were subsequently buffered to pH 7 by adding a phosphate buffer. The Co (II) complexes were then oxidized to Co (III) complexes by adding hydrogen peroxide to the samples. Excess peroxide was removed with the enzyme catalase and the uncomplexed Co (II) was determined by DPP in the samples after the addition of ethylenediamine (0.05 M final concentration - the reduction of Co (II) is usually not observable in aqueous solutions at pH 7, but is well defined in solutions containing high concentrations of ethylenediamine). The detection limit of their method is reported to be 0.6×10^{-6} mole-equivalents Co (III) per liter, and will determine only those cobalt (III) complexing agents with log stability constants greater than 17. The practical pH range of their method is from 5 to 10, because the efficiency of catalase in decomposing hydrogen peroxide decreases rapidly below pH 5 and the catalyse molecule itself is denatured above pH 10. Unfortunately no information is given concerning the effect of pH on the sensitivity of their method. Interference by Cu and Fe (III) is possible but was not detected in the samples of natural water tested. Hanck and Dillard give values of apparent complexing capacity ranging from $0.9 - 1.6 \times 10^{-6}$ M for several rivers in North Carolina, 4.1×10^{-6}M for a sewage effluent, and 7.5×10^{-6}M for water from an aquarium (values are expressed as moles of complexed Cobalt (III) and samples are unfiltered).

Complexometric titrations monitored by ASV have also been employed in determining other experimental parameters related to the complexing capacity of a given water sample. Shuman and Woodward (1973) developed a method to determine conditional formation constants and to estimate the dissociation rate constants from the titration curve data alone.

1.3.3 Effects of pH changes on trace metal speciation

Complexing capacities of natural water samples are expected to change with changing pH (Stumm and Morgan, 1970). It is well known that metal chelates are influenced by changes in pH: their conditional stability constants are often reduced by powers of ten for pH changes within the range of natural waters. Thus sample pH is expected to exert an important influence on trace metal speciation.

From the earliest applications of ASV to environmental samples considerable effort has gone into evaluating the influence of pH on electrode response. Zirino and Healy (1970), using pH-controlled differential ASV (system combining two HMDE's) determined concentrations of labile Zn, Cd and Pb in unfiltered seawater samples. The pH was controlled by purging samples with a mixture of CO_2 and N_2. Their results showed that for decreases in pH from 8.3 to 5.6, the current peaks for Zn and Pb increased, but that of Cd did not change. Peak potentials for Zn and Pb were shifted anodically by 0.03 v, whereas the peak potential of Cd did not change. The same results were obtained with artificial seawater samples presumably free of organic matter, and with filtered seawater samples submitted to strong photooxidation. Similar findings were obtained for peak potentials of Zn, Cd and Pb in filtered (0.45 μm) open ocean water samples, which had subsequently been spiked with 4×10^{-8} M of each of these metals. They suggested that changes in peak current were due to the inorganic components of seawater.

In a later article the same authors (Zirino and Healy, 1972) studied the effects of pH changes. They found that the calibration curves of Zn and Pb at pH 5.8 had greater slopes than those produced at pH 8.3 in unfiltered seawater samples. For Cd the slope remains the same at both values of pH. They suggested that Zn and Pb combine with weak acid anions to form inert (i.e. non-labile) complexes at the higher pH. The same year Zirino and Yamamoto (1972) presented a pH-dependent mathematical model for the speciation of Zn, Cd, Pb, and Cu in the presence of inorganic ligands commonly found in seawater. Their calculations showed that three of the four metals are complexed to a considerable extent in seawater (namely Zn, Pb and Cu), and that the distribution of chemical species varies greatly with changes in pH.

The influence of pH on the stripping potential of Zn has been studied by Bradford (1972). Assuming that most of the Zn is complexed as one form only and that the rate of diffusion of this species is constant with increasing concentration of the complexing anion, Bradford calculated mathematically from the redox potential the change of zinc peak potential with pH. His predictions showed that E_p was independent of pH up to a certain pH value, above which it increased linearly in a cathodic direction for increasing pH. He tested these predictions experimentally by varying the pH in a 0.1 M sodium chloride solution containing zinc and measuring the E_p. The results of this experiment were very similar to his mathematical predictions. He concluded that the complex influencing the stripping reaction was $Zn(OH)_2^o$, with a log stability constant of 9.8. Bradford's approach is not new, since metal-ligand interactions in simple systems have been predicted mathematically from redox potentials for a long time (Crow, 1969). The results are useful, however, because reliable information on the influence of pH in natural waters may be gained from the study of simple systems.

In order to investigate the effect of pH on electrode response, O'Shea (1972) chose a synthetic medium containing known concentrations of trace metals and common inorganic ligands. His results showed that the peak current of Bi, Cd, Cu, In, Pb, and Tl decreases with increasing pH (pH from 4.6 to 8.0) in solutions of 10^{-2} M sodium carbonate prepared with double-distilled water. Each metal was present at a concentration of 2.0×10^{-8} M. Over the pH range studied, i_p decreased by a factor of more than 4 for copper, less than 2 for bismuth, cadmium, and lead, and slightly more than 2 for indium and thallium. In addition, O'Shea found that the peak potential for each of these metals was shifted cathodically with increasing pH. E_p was shifted by 0.12 v for bismuth, 0.09 v for copper, 0.08 v for lead, 0.04 v for cadmium and indium, and 0.02 v for thallium. This cathodic shift with increasing pH was interpreted as a qualitative indication of the presence of metal-binding ligands in the original sample. O'Shea further suggested that these shifts when combined with decreases in peak height, indicate the presence of non-labile complexes at the higher values of pH. Shifts in peak potential occurring without accompanying decreases in peak height were interpreted to be the result of the formation of labile complexes. This hypothesis was used to explain a rather large shift in the peak potential of cadmium (0.03 v) between a pH of 6.9 and 8.0, where peak height did not change significantly.

Some confusion is evident when one attemps to evaluate O'Shea results. His results were interpreted in terms of changes in the chemical speciation of the soluble forms of the trace metals studied, but they might also be due, at least in part, to possible changes in metal distribution between the soluble and particulate phases, and inescapably to the effects of adsorption/desorption of metals from the cell walls. The fact that O'Shea apparently did not take the precaution to filter his solutions through a 0.45 μm membrane before his experiments leaves one wondering whether some insoluble metal may have affected his results. Calculations of the free metal concentrations of Cd, Pb, and Cu for total metal concentrations of 2.0×10^{-8}M, total inorganic carbon (C_T) equal to 10^{-2} M, and pH = 8.0, and comparison of these values with the calculated solubilities for these metals, suggest that none of these metals should precipitate at this pH in aqueous solutions containing metal hydroxide and carbonate complexes. It is possible however that insoluble species were present in his samples and that some loss of soluble metal was incurred by adsorption on this particulate matter with increasing pH.

O'Shea used Pyrex glass cells in his experiments with sodium carbonate as the supporting electrolyte. It is well known that Pyrex adsorbs trace metals in the neutral pH range. Stumm and Bilinski (1972) have shown that the neutral lead carbonate complex ($PbCO_3^o$) is much more strongly adsorbed on negatively charged silica than aquo-complexes of the free metal ion. Their results showed fifty percent adsorption of a total lead concentration of 93×10^{-8} M in the presence of a carbonate ion concentration of 4×10^{-4} M after less than ten minutes (the pH is not given in their work). In addition they suggested that hydroxo-, sulphato-, carbonato-, and other complex ions or molecules would similarly be more strongly adsorbed at interfaces than aquo-complexes of the corresponding free metal ions. O'Shea's results showing a diminution of peak current for lead with increasing pH could well be explained, at least in part, by the adsorption of neutral lead carbonate onto the cell walls.

O'Shea used sodium bicarbonate (10^{-2} M) as the supporting electrolyte in order to better simulate aquatic conditions, where hydroxy and carbonato ligands are predominant. A problem that arises from this choice of supporting electrolyte is the fact that the ionic strength is not constant for the subsequent changes in pH. The ionic strength changes, because the concentrations of HCO_3^- and CO_3^{-2} vary over the range of pH employed. In O'Shea's experiments the ionic strength (μ) should increase by fifty percent for an increase in pH from 4.6 to 8.0 (μ increases from 1.0×10^{-2} to 1.5×10^{-2}). Copeland et al. (1973) have shown, for a composite mercury-graphite electrode of the type used by O'Shea, that peak potential is shifted cathodically for increases in ionic strength or decreases in cell resistance. From the results of Copeland et al., a shift in peak potential of as much as 0.02 v may be attributed to the increase of ionic strength occurring in O'Shea's work. Although this and other observations may somewhat discredit O'Shea's results, his work still merits the attention of the investigator, being one of the few in-depth studies of the effect of pH on trace metal speciation.

Using a HMDE, Ernst et al. (1974) have investigated the dependence of peak current on pH and alkalinity for Zn, Cd, Pb and Cu at concentrations of 2.5×10^{-6} M. The supporting electrolyte was KNO_3 at a concentration of 10^{-1} M. They employed DPP and DPASV in their trace metal determinations in order to compare the electrodeposition and stripping steps respectively. The pH was increased from 5.0 to 10.0 for sample alkalinities of 10^{-3}, 10^{-2} or 10^{-1} eq/l by purging the samples with a mixture of CO_2 and N_2. Using the DPP method peak current decreased gradually for all metals considered, but this decrease was more pronounced in solutions of low alkalinity than in those of high alkalinity. The decrease in peak current at the higher pH values, similar to that observed by O'Shea, was interpreted in terms of a precipitation of insoluble trace metal species. It was suggested that for the higher alkalinities the onset of precipitation was retarded and occurred at higher pH values, since the presence of carbonate and bicarbonate ions would increase the solubility of the metals by complexation.

The results for the DPASV method were similar to those obtained by the DPP method, with the exception of zinc and lead. For these metals, the changes in peak current for a given pH interval were greater for the DPASV method than for the DPP method. Ernst et al. concluded that the peak currents for the DPASV method depend on both the electrodeposition and stripping steps. The theory of ASV, however, suggests that peak current depends on the plating medium and on the instrumental parameters of plating and stripping, but not on the stripping medium itself. Unfortunately, no attempt was made by Ernst et al. to reconcile their conclusions with the existing theory of ASV.

Experiments dealing with the influence of pH on stripping currents in sewage and natural water samples have produced seemingly contradictory results. Using the composite mercury-graphite electrode Lewin and Rowell (1973) determined labile and total heavy metal concentrations in unfiltered samples of sewage effluent by ASV. The supporting electrolyte was sodium acetate and the metals of interest were Pb, Cu and Cd. Investigating the effect of pH on electrode response, they found that a pH of 5.5 gave maximum peak current for copper; the maximum was less pronounced for lead, and still less for cadmium. Peak current increased rapidly between pH 7 and 6, attained a maximum at pH 5.5 and fell off slowly for pH values below 5. This is a very unusual result, since acidification would have been expected to produce steadily increasing stripping currents due to the competition of hydrogen ions for the ligands (Allen et al., 1970; O'Shea, 1972; Ernst et al., 1974).

For high values of pH, on the other hand, complex formation may be hindered by the loss of soluble metal due to the formation of insoluble metal hydroxides. In order to evaluate the useful range of pH for their determinations of apparent complexing capacity with copper as the indicator cation, Chau et al. (1974) investigated the effect of pH on their method using filtered samples of Hamilton Harbour water. Samples with various pH values were spiked with copper concentrations of 5×10^{-6} M. These samples were equilibrated for at least 2 hours and the labile copper measured. The amounts of copper taken up were used as an estimate of the apparent complexing capacity. Their results showed that the apparent complexing capacity was independent of the original pH in the range of pH from 4 to 8. For values of pH below pH 4, the apparent complexing capacity decreases and for values of pH above pH 8 it increases. This is quite an unexpected result, since it is known that the conditional stability constant of copper with a strongly reactive ligand like EDTA decreases by 6 powers of ten on acidification from pH 8 to 4 (Ringbom, 1959). Likewise the conditional stability constants of other copper complexes with natural water ligands may be expected to change over this wide range of pH.

One may conclude from this discussion that ASV has played a prominent role in the study of trace metal speciation, complexing capacities, and pH influence in environmental samples. However, a number of seemingly contradictory results have yet to be reconciled.

CHAPTER 2

OBJECTIVES

In the summer of 1973, we received the Princeton Applied Research Polarographic Analyzer, Model 174, at our laboratory and began setting up the apparatus to do experiments in the DPASV mode. During this period, considerable time was spent setting up a laboratory for trace metal work, testing the effect of numerous experimental parameters on electrode response, and resolving the inevitable problems that arose due to lack of experience. During this time, a series of preliminary experiments designed to optimize instrumental as well as chemical parameters affecting trace metal determinations were carried out by DPASV. These experiments attempted to study the following aspects:

1. the effect of temperature changes on electrode response;
2. the reproductibility of DPASV with the HMDE;
3. the effect of mercury drop size on the stripping voltammogram;
4. the effect of plating time on peak current;
5. the effect of pulse amplitude on peak current and potential;
6. the effect of ionic strength and type of supporting electrolyte on peak current and potential.

The information gathered from these preliminary experiments was essential for the design and interpretation of the subsequent experiments.

At this time it was evident from the work appearing in the literature that pH was a very important factor controlling trace metal speciation in the soluble phase (see section 1.3). The increased current peaks and shifted potentials in stripping analysis of common trace metals on acidification had been interpreted to be due to the inorganic components of natural water samples (Zirino and Healy, 1970) and to the dissociation of non-labile complexes in inorganic solutions (O'Shea, 1972). Furthermore experiments in the literature were difficult to compare, because of the different procedures employed, and considerable confusion existed concerning the interpretation of results. The aim of our research was thus to verify the results of O'Shea (1972) and, in addition, to gain insight into the use of ASV as an analytical tool for studying trace metal speciation.

The experimental protocol involved the determination of the peak currents and potentials for four common trace metals (Zn, Cd, Pb and Cu) by stripping analysis at different values of pH in filtered samples of tap and lake water. Our experiment differred from other experiments reported in the literature in the following ways:

- the samples were left to equilibrate or "age" for a period of three days at room temperature and pH = 5.9, after the addition of trace metals, sodium bicarbonate, and supporting electrolyte (Siegel, 1971);
- the samples were then filtered (0.45 μm) and ultrafiltered (nominal molecular weight cut-off of 100,000) at pH = 5.9 before being introduced into the polarographic cell. Ultrafiltration was deemed necessary to remove any trace of particulate metal that might contaminate the samples at lower values of pH;
- trace metal determinations were made at decreasing values of pH with sample equilibration at each pH of interest.

Considerable care was taken to avoid contamination of samples by particulate matter and to allow for equilibration of samples at each pH value. These precautions were necessary in order to reduce the margin of interpretation inherent in experiments of this kind.

CHAPTER 3

PRELIMINARY EXPERIMENTS

3.1 Material and methods

3.1.1 Instrumentation

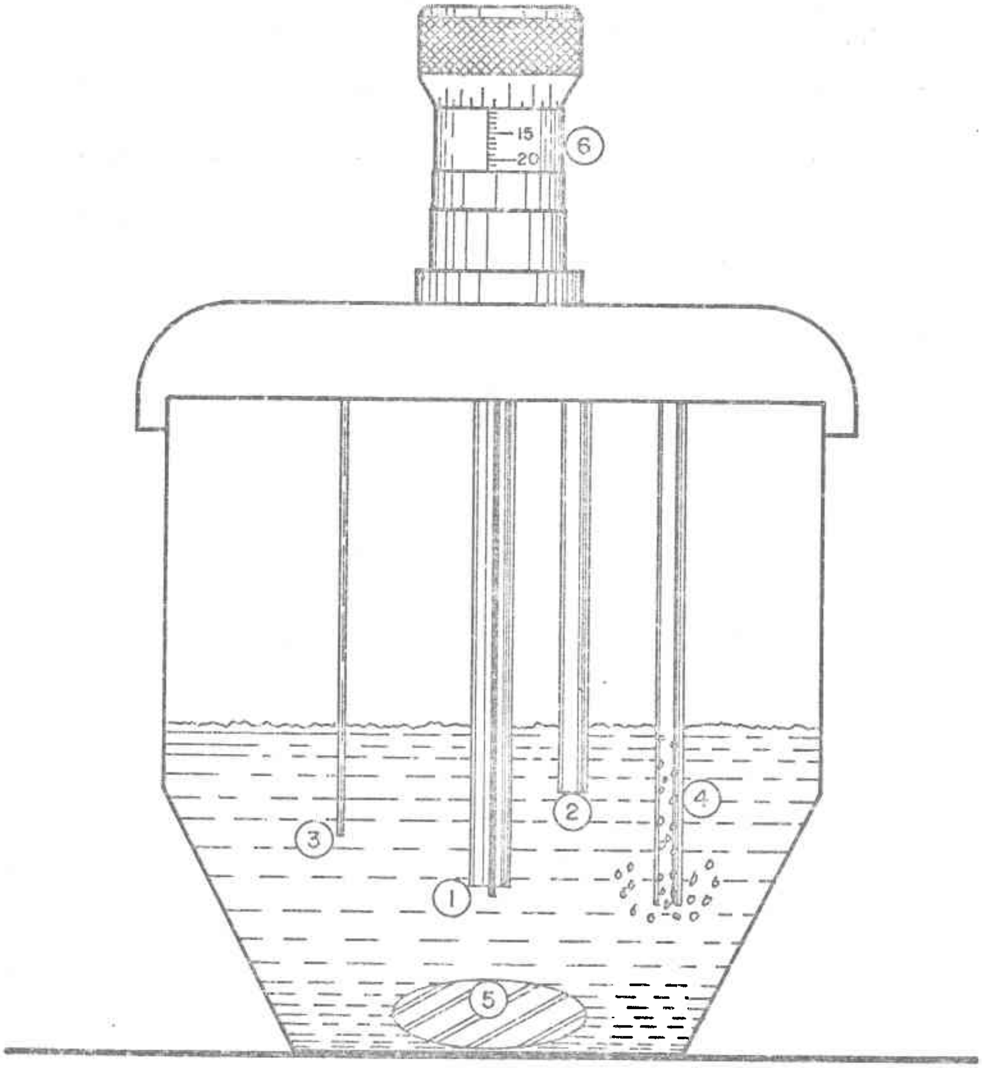
The Princeton Applied Research Polarographic Analyzer, Model 174, was used to provide controlled potential electrolysis (plating) and potential scanning (stripping). The Model 174 incorporates a potentiostat with a current capability of 20 mA, a drop timer for polarography with the DME, and the necessary controls for scanning. This instrument permits one to choose between four different potential scanning procedures: normal and sampled DC, pulse, and differential pulse. Additional instrument parameters include initial potential, scanning rate and range, current sampling rate (drop time), and pulse voltage for the differential pulse mode. The voltammograms were subsequently recorded on a Houston Instrument Model 2000 XY recorder.

3.1.2 Cells and electrodes

The HMDE used in our work was supplied by Princeton Applied Research (PAR, Model 9323) and consisted of a micrometer screwpiston assembly with glass capillary tube. In the work that follows, mercury drops with diameters not greater than 1.0 mm were employed. Experiments were performed in thermostated Pyrex cells (100 ml, Metrohm). Pyrex is not, however, the best material for ASV studies, because it is known that trace metals can be leached from the glass and significant adsorption of trace metals on container walls has been reported with this material (Stumm and Bilinski, 1972). For rapid trace metal determinations (less than 30 minutes contact time per sample) no detectable contamination by Pyrex for zinc, cadmium, lead or copper (i.e. <0.1 µg/l) has been encountered in this work. The most effective way to deal with adsorption, which is always a problem in trace metal work, is sample equilibration with all container walls. In the work described here each sample was equilibrated with the cell walls for at least fifteen minutes, then rejected and replaced by a fresh portion before metal determinations were begun.

Constant temperature was maintained with the use of the Haake Model FE Constant Temperature Circulator. For most of the following experiments, the temperature was controlled at 25.0°C with a variability of not more than 0.1°C. Figure 3 shows the cell and electrode arrangement used in our work. A saturated calomel reference electrode (SCE) was fitted to a salt bridge assembly fitted with Teflon tubing. Contact with the solution was made through a porous glass plug fixed in the end of the tubing. Potassium nitrate (2 drops of a 2M solution) was then added to the salt bridge to provide good electrical contact between the SCE and the solution. The counter electrode consisted simply of a platinum wire.

Stirring was accomplished with a Teflon coated magnetic stirring bar resting on the bottom of the cell. A Lab-Line Instruments Magnastir apparatus stirred the solution at a fixed rate for the entire experiment. A stirring rate was chosen for which little or no turbulence was evident in the solution. Stirring was started and stopped by an on-off switch, thus avoiding errors associated with resetting the stirring rate for each experiment.



1 = CAPILLARY
2 = SALT BRIDGE WITH STANDARD CALOMEL ELECTRODE
3 = PLATINUM COUNTER ELECTRODE
4 = TEFLON DEGASSING TUBE
5 = MAGNETIC STIRRING BAR
6 = MICROMETER PISTON ASSEMBLY

Figure 3. Cell and electrode arrangement / Disposition de la celiule et des électrodes.

3.1.3 Supporting electrolyte

Although it has been stated in the literature concerning ASV that the addition of supporting electrolyte to samples is unnecessary in trace metal analysis with mercury electrodes (Siegerman and O'Dom, 1972), our experience indicates otherwise. Copeland et al. (1973) have shown that both the plating and stripping processes at a MFE are critically dependent upon solution resistance. With solutions of low ionic strength, peak height increases with increased ionic strength, and peak potential is shifted cathodically. The HMDE is considerably less sensitive to solution resistance, because of the small area of the drop as compared to the thin film. Hence a larger uncompensated resistance is necessary to show peak height and potential changes with ionic strength. From our experience it would not be wise to work with an ionic strength less than 10^{-2} M in unbuffered solutions with the HMDE, because of potential drift and non-reproducible current peaks. In slightly acidic media (pH = 4) it is possible to reduce ionic strength to the 10^{-3} M level, but results become increasingly non-reproducible.

Two supporting electrolytes have been used in this work: potassium nitrate (Fisher Scientific, A.C.S. grade) and sodium acetate (Fisher Scientific, A.C.S. grade). The former has the advantage of being a truly non-reactive electrolyte with the metals under investigation, whereas sodium acetate is known to form weak complexes with several metals*. Copper

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* Concerning the copper-acetate complex, it is worth mentioning that some disagreement exists in the literature over the value of its stability constant. Smith and Manahan (1973) have suggested that the acetate ion forms a 1:1 copper complex with a formation constant of $10^{6.3}$, whereas Sillen and Martell (1964) give formation constants in the order of 10^{1-3}.

behaves rather badly in the presence of potassium nitrate (Chau and Lum-Shue-Chan, 1974); in acid solutions (pH <4) the copper peak is sharp and well defined, but it becomes progressively broader as pH increases. Quantitation of copper at the ppb level is then virtually impossible in solutions of neutral pH with potassium nitrate as supporting electrolyte. Cadmium and lead, on the other hand, give well defined peaks in acid and neutral solutions containing either electrolyte. Zinc is also well behaved in neutral solutions containing either electrolyte, but disapperas into the rising current curve for hydrogen reduction in acid solutions.

When doing straightforward trace metal determinations in neutral solutions with either electrolyte, it is extremely important to control pH with a buffer. During deaeration with nitrogen gas, the pH is unbuffered solutions may occasionally increase by two units and cause the precipitation of one or another of the trace metals (Sinko and Dolezal, 1970). In order to deal with this problem an appropriate non-reactive buffer solution with a pH between 5 and 7 should be used. Trace metal determinations in solutions with a pH greater than 7 are hazardous, because trace metal may be lost through precipitation or co-precipitation and because standard additions do not necessarily give a linear calibration curve in alkaline solutions (Sinko and Dolezal, 1970).

The deionized water used in the preparation of reagents, for cleaning glassware and plastics, and for all other needs was produced from the Millipore water deionization system (Milli-Q2 High Purity Water System and the Milli-Q3 Pretreatment System). The individual trace metal concentrations of the Millipore water were observed to be of the order of ≤0.1 μg/1.

3.1.4 Deaeration system

It is important to remove oxygen from the solution before the plating step. The presence of oxygen often interferes with polarographic determinations as it is reduced at the mercury electrode at approximately -0.05 v and -0.8 v versus the SCE. Furthermore in unbuffered solutions the accumulation of hydroxide ion, as a result of oxygen reduction, may change the pH in the vicinity of the electrode. This change of pH can interfere with the desired reaction by causing precipitation or complex formation of the electroactive substance at the electrode. Cadmium, for instance, is known to be very sensitive to the presence of oxygen in the solution during the stripping step (Barendrecht, 1967). The method generally used to remove oxygen from the solution is the bubbling of oxygen-free nitrogen through the cell during ten or fifteen minutes before the plating step.

Oxygen-free nitrogen was prepared from tank nitrogen by passing the nitrogen ghrough a bed of metallic copper (BASF Catalyst R3-11), which reacts chemically with the oxygen. Next the oxygen-free nitrogen was filtered through a membrane filter (Millipore, 0.22 μm) and bubbled through a gas washing bottle filled with deionized water to humidify the gas flow and minimize the subsequent loss of sample volume by evaporation. Gas flow was finally measured by a flowmeter (Gilmont, model F250) before passing into the cell.

3.1.5 Reagent purification

All supporting electrolytes and reagent solutions were filtered through membrane filters (Millipore, 0.45 μm) before being purified electrochemically. The PAR Electrolyte Purification Apparatus, Model 9500, was used to remove heavy metals from a liter of solution by deposition on a mercury pool electrode. This apparatus has the advantage of being designed so that it may be left unattended for long purification periods. In general 24 hours operation at a potential of -1.5 v sufficed to reduce trace metal concentrations (Cu, Cd, Pb, Zn) in the supporting electrolyte to the 1 μg/l level.

The mercury (Fisher Scientific M-141, Instrument Grade) used in this electrochemical purification procedure and for the HMDE had likewise to be purified. This was accomplished by a method described by Whitnack and Sasselli (1969) involving filtration and successive treatments with sodium hydroxide (4M), nitric acid (2M) and deionized water (Millipore).

3.1.6 Cleaning of glassware and plastics

A reasonably simple procedure was employed for cleaning containers, pipettes, cells, etc. that did not appear to introduce contamination greater than 0.1 μg/l of the trace metal of interest. All glassware and plastics were first soaked in chromic acid cleaning solution (Fisher: Chromerge) for at least ten minutes, and afterwards rinsed well in tap water. Chromic acid is a very efficient cleaning solution, but is difficult to remove from fine porosity frits and from glassware itself, and can etch glassware left in contact with it for long periods of time. Finally all glassware and plastics were soaked for several days in dilute nitric acid (10% W/V HNO_3). With new glassware and plastics this soaking lasted at least a week. Before use, all glassware and plastics were rinsed thoroughly in deionized water.

Further purity could have been achieved by infrared sub-boiling distillation (Mitchell, 1973) of the deionized water from the Millipore system, and by an additional soaking of glassware and plastics in 10^{-3} M Na_2H_2EDTA (Manahan and Smith, 1973) between the acid soak and water rinse. In principle these steps should allow one to descend to the 10 ng/l level, but in practice this is very tedious because numerous precautions must be taken such as clean air hoods to eliminate airborne contaminants, Teflon bottles for reagent and sample storage, quartz cells for stripping analysis, etc.

3.1.7 Peak height evaluation

In stripping analysis of well behaved reversible metal systems, the original metal concentration is proportional to the current peak on the stripping voltammogram. This proportionality is evaluated by standard addition techniques, which give a calibration curve for the solution. To give reliable results, at least two standard additions must be made. It is possible however to estimate the original metal concentration, C_o, from a single addition, if one assumes that the calibration curve will pass through zero for a negligible concentration value. In this case, C_o is given by the following equation:

$$C_o = \frac{i_o \, v_a \, C_a}{i_1 \, v_a \quad (i_1 - i_o) v_o} \qquad (13)$$

where i_o and i_1 are peak heights for the original solution and for the same solution after the addition of a fixed volume, v_a, of the standard addition solution having a metal concentration, C_a; v_o is then the original sample volume before addition.

Because of a rapidly rising background current or the overlap of two current peaks that hide the background current, it is not always easy to measure current peak heights. In such cases judicious estimation must be employed. Barendrecht (1967) has summarized some of these methods. In Figure 4 adapted from Barendrecht, a hypothetical stripping voltammogram with overlapping peaks is given. The curves B_1, B_2 and B_3 are current vs potential plots for solutions without any of the metals, with metal M_1, and with metals M_1 and M_2 respectively. The most reliable measurements of peak current are given by the arrows. It is obvious that measuring the i_p value from the peak to the baseline C is not to be recommended. When it is impossible to obtain a stripping voltammogram of the blanks, there are two methods open to the investigator for evaluating the i_p values.

First of all, the investigator can stop the potential sweep at the potential E_1 for a fixed time allowing the complete dissolution of the metal M_1 from the mercury drop, but sufficiently cathodic such that the metal M_2 continues to plate. The current will then reach the background level from which the i_p value of M_2 can be measured. After this step has been accomplished, the potential sweep can be continued. If standard addition techniques are being used to evaluate the metal M_2, it is necessary to repeat this step for the same length of time and at the same potential for the metal additions. The metal M_1 however is unaffected by the potential sweep hold at E_1 and repetition is unnecessary for metal additions. A similar procedure using a potential between the peaks M_2 and M_3 may be employed to evaluate the metal M_3.

A second method, used frequently in this work, is but a rough measure of the true peak height (Figure 4b). This method gives a rapid

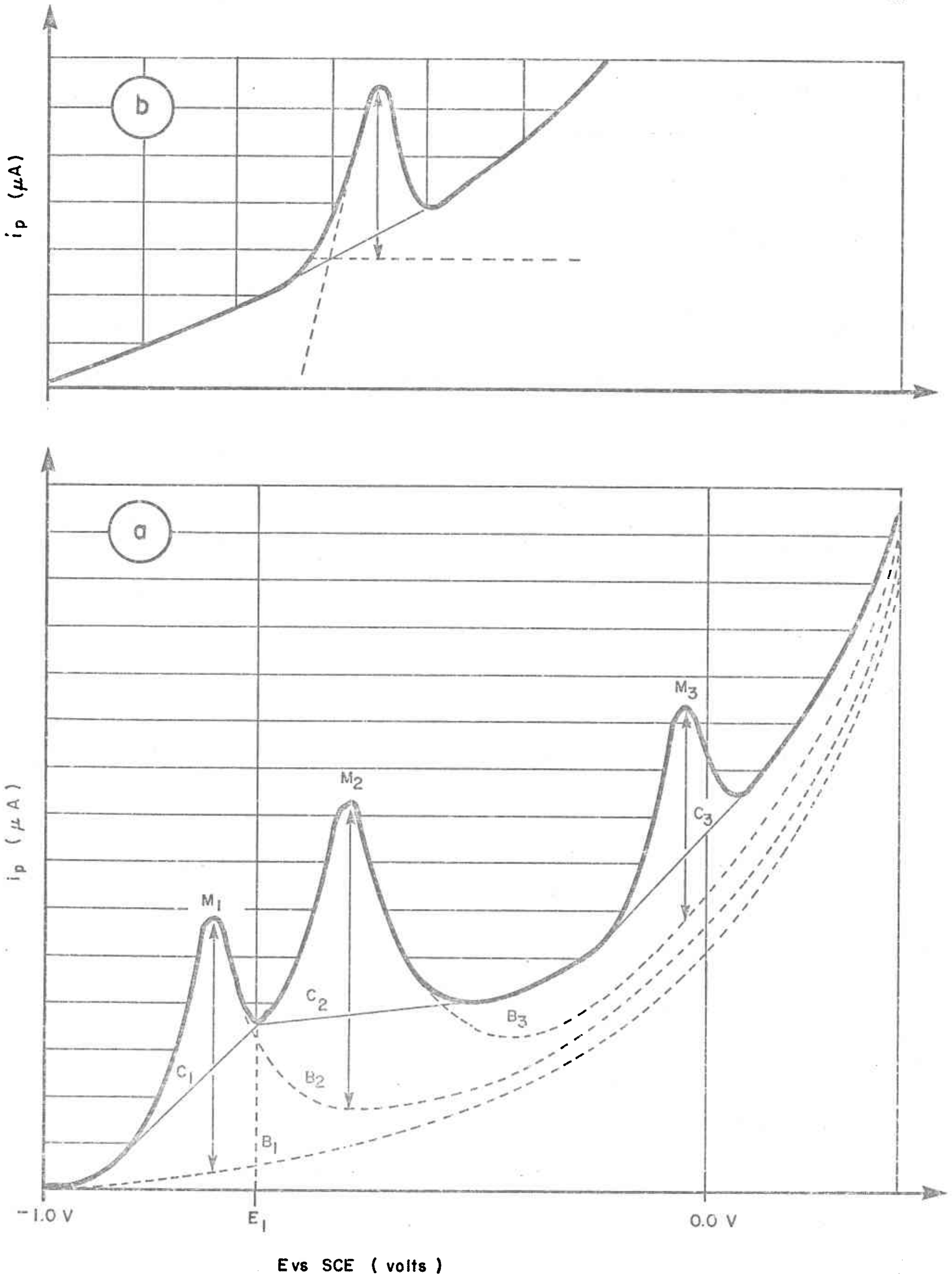

Figure 4 . Evaluation of stripping voltammogram / Èvaluation de l'intensité des pics en DPASV.

estimation of the peak current of a single metal on a sloping background current.

It is sometimes necessary to integrate the charge in coulombs represented by a current peak: $Q_p = \int i(t)dt$. This occurs when peak width varies for a change of medium, pH, supporting electrolyte, or as a result of surface active agents that suppress metal dissolution from the mercury (Barendrecht, 1967). In such cases metal concentration in the solution is proportional to the integrated charge represented by the value of Q_p.

3.2 Preliminary experiments

3.2.1 The effect of temperature variations

The effect of temperature variations on peak current was investigated by differential pulse anodic stripping voltammetry (DPASV) for the metals lead and cadmium in acidified unfiltered tap water (HNO_3, pH = 2). Cadmium had been added to the tap water to a final concentration of approximately 1 µg/l and this gave similar peak heights for the two metals. Plating was carried out at a potential of -0.7 v versus SCE for 3 minutes. Stripping was performed under the following conditions: sweep rate of 2 mv/s, pulse or modulation amplitude (MA) of 25 mv. Metal determinations were made in triplicate at each temperature, after temperature stabilization times of 15 minutes. The temperature was varied at intervals of three degrees over a temperature range from 20°C to 38°C.

3.2.2 The reproducibility of DPASV with the HMDE

A HMDE capillary was meticulously cleaned following the instructions provided by the supplier (Princeton Applied Research), and filled in the appropriate manner with mercury. Each mercury drop measured six micrometer scale divisions (approximately 0.9 mm drop diameter), and four such drops were extruded and discarded before measurements began using the fifth drop. The sample was acidified tap water (HNO_3, pH = 2) to which a small quantity of cadmium has been added to give a final concentration of approximately 1 μg/l. Plating potential was -0.7 v lasting 3 minutes at 23°C. Sweep rate was 2 mv/s with a pulse amplitude of 25 mv.

3.2.3 The effect of mercury drop size on the stripping voltammogram

The effect of mercury drop size on the stripping voltammogram was investigated for cadmium and lead in deionized water containing a sodium acetate buffer (0.1 M, pH = 5.9) using DPASV. The concentrations of added cadmium and lead were about 20 μg/l. The plating potential was -0.9 v lasting 2 minutes at 25°C. Sweep rate was 5 mv/s with a pulse amplitude of 25 mv.

Mercury drop size was varied from 1 to 8 micrometer scale divisions (drop diameters of 0.52 to approximately 1.05 mm, Metrohm) and metal determinations were made in duplicate for drops corresponding to each scale division. Note, however, that scale divisions are not directly proportional to drop diameter.

3.2.4 The effect of plating time on peak current

The dependence of peak current on plating time has been studied for DPASV determinations of cadmium and lead (concentrations of about 20 μg/l) in a deionized water sample. The supporting electrolyte was a sodium acetate buffer (0.1 M, pH = 5.9). The plating potential was -0.9 v and stripping was performed with a sweep rate of 5 mv/s and a pulse amplitude of 25 mv. Two determinations were made for each plating time, starting with a thirty second plating time in a quiescent solution and progressing to a final 11 minute plating time in a stirred solution (including as usual the required thirty second quiescent period at the end of each plating time).

3.2.5 The effect of pulse amplitude on peak current and potential

The effect of varying the pulse amplitude has been studied using DPASV for the stripping voltammogram of a deionized water sample containing zinc, cadmium, lead and copper at concentrations of 20 μg/l each. The supporting electrolyte was a sodium acetate buffer (0.1 M, pH = 5.9). Plating potential was -1.2 v and plating lasted 2 minutes. Sweep rate was 5 mv/s and pulse amplitude was varied from 5 to 100 mv, while other experimental conditions were kept constant.

3.2.6 The effect of ionic strength and type of supporting electrolyte on peak current and potential

The effect of varying the ionic strength has been investigated for the stripping voltammogram of a deionized water sample containing zinc, cadmium, lead and copper at concentrations of 20 μg/l each. The plating potential was -1.2 v and the metals were plated for 2 minutes. Sweep rate was 5 mv/s and pulse amplitude was constant at 25 mv.

It was essential to keep pH constant for all additions of supporting electrolyte, because pH changes in the solution might cause considerable variation of peak currents and potential. Hence a standard deionized water sample was prepared containing a relatively low concentration of a sodium acetate buffer (0.002 M, pH = 5.9). Starting with this standard sample, successive additions of supporting electrolyte were not expected to change sample pH significantly. This was confirmed by verifying the pH after each addition of supporting electrolyte.

In the first experiment, the ionic strength (μ) of the standard sample was increased by successive additions of sodium acetate to give final concentrations from 0.002 M to 0.122 M. A control experiment was performed to determine the degree of trace metal contamination of the standard sample due to additions of sodium acetate alone. Determinations of trace metals by DPASV were made for each addition of sodium acetate to 50 ml of the standard sample. The control sample was then rejected and a fresh portion (50 ml) of the standard sample was introduced into the polarographic cell. Trace metals were added to the standard sample volume (1 ml of a freshly prepared solution (pH = 2) containing 1 mg/1 of zinc, cadmium, lead and copper; final concentration 20 μg/1 of each metal). Determinations of trace metals by DPASV were performed twice at each concentration of sodium acetate indicated above. Thus by subtracting the increases in peak current in the control sample from those increases in peak current in the standard sample with added trace metals for successive additions of sodium acetate, it is possible to determine the effect of ionic strength on peak current.

In the second experiment the ionic strength (μ) of the standard sample was increased by successive additions of potassium nitrate to give concentrations from 0.002 M to 0.122 M. A similar procedure to that described above was followed in this experiment including the control sample and the standard sample containing the same concentrations of added trace metals.

3.3 Results and discussion

3.3.1 The effect of temperature variations

In earlier experiments Kemula (1959-60) observed that the temperature coefficient for the plating step varied from 5 to 50% per degree centigrade, depending on drop size and volume of the mercury reservoir of the HMDE. Hence one might expect peak currents to be sensitive to increases in temperature. Results obtained with our electrode showed, however, that peak current was not very sensitive to changes in temperature, and that peak potential was quite independent of this variable (Figure 5). The results for lead showed that peak current increased slowly by a factor of 3% per degree centigrade with our electrode.

No attempt was made to evaluate the effect of temperature on the electrochemical behavior of cadmium, because of the erratic results obtained with this metal. It is possible that the electrode response for cadmium was influenced by our choice of plating potential. Plating potential should always be sufficiently cathodic to the equilibrium potential of the mercury drop to assure that peak currents are independent of plating potential. If the concentration of the metal in the mercury drop is 1000 times the concentration of the metal ion in the sample at the solution-mercury interface, the equilibrium potential or peak potential will be shifted to more negative values by at least 3 x 0.06/n volts. Barendrecht (1967) suggests a choice of electrodeposition potential of 0.3 to 0.4 volts more negative than the characteristic half-wave potential. Peak potential for cadmium in an acid medium is -0.58 v, which gives, according to the approximation above, a half-wave potential for cadmium in the vicinity of -0.49 v. Thus it is apparent that the plating

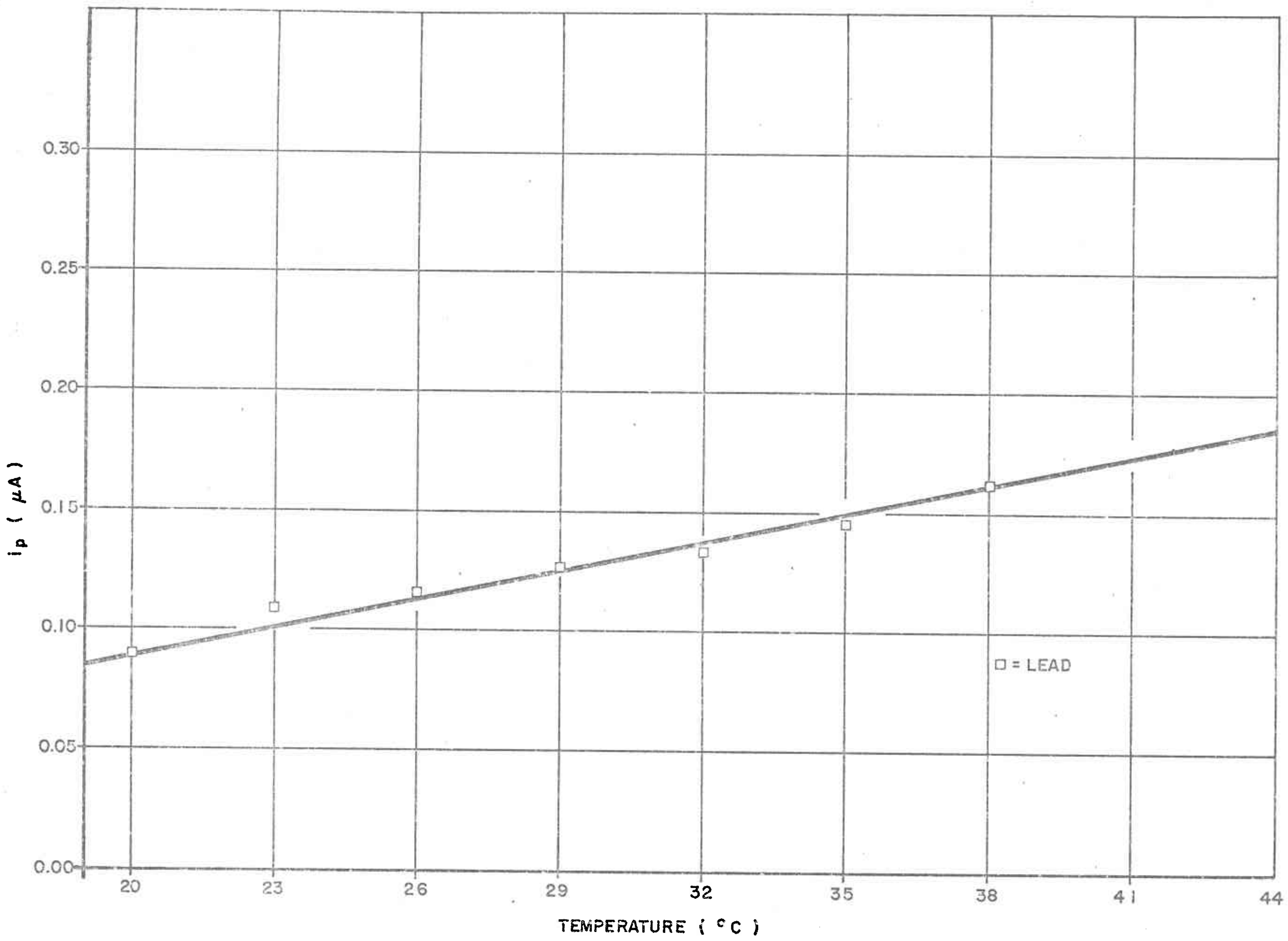

Figure 5 . The effect of temperature changes on peak current / L'effet du changement de la température sur l'intensité du courant i_p .

potential used in this experiment (-0.7 v) was only 0.2 v cathodic to the half-wave potential of cadmium in acidified tap water, and that choice of plating potential may have been the cause of the erratic behavior of the cadmium peak.

3.3.2 The reproducibility of DPASV with the HMDE

Using ASV with a HMDE of the Kemula design (micrometer drive assembly with capillary tube), Beran et al. (1971) have found a 3.0% relative deviation for the thallium current peak in an acidified solution (0.04 M HCl) for a series of ten measurements performed under constant conditions. Our results (Figure 6) were similar to those of Beran et al. For a series of 24 measurements, the relative deviation for the lead current peak was found to be 2.3% and that for cadmium, 4.5%.

It may be that the results for cadmium were affected by our choice of plating potential as in the experiment on temperature variations described above. One would expect the results for cadmium to be at least as good as those of lead, since cadmium is generally electrochemically well behaved in inorganic solutions.

3.3.3 The effect of mercury drop size on the stripping voltammogram

Several authors (Hume and Carter, 1972; Ellis, 1973) have noted a loss of sensitivity for the HMDE due to the diffusion of plated metal into the drop. From the equations describing peak current for the HMDE, it is apparent that i_p increases with drop radius (r). At the same time, the volume to area ratio of the mercury drop will increase as a function of r/3 and metal diffusion out of the mercury drop may become a problem. Evidence for metal diffusion problems will appear as a broadening of

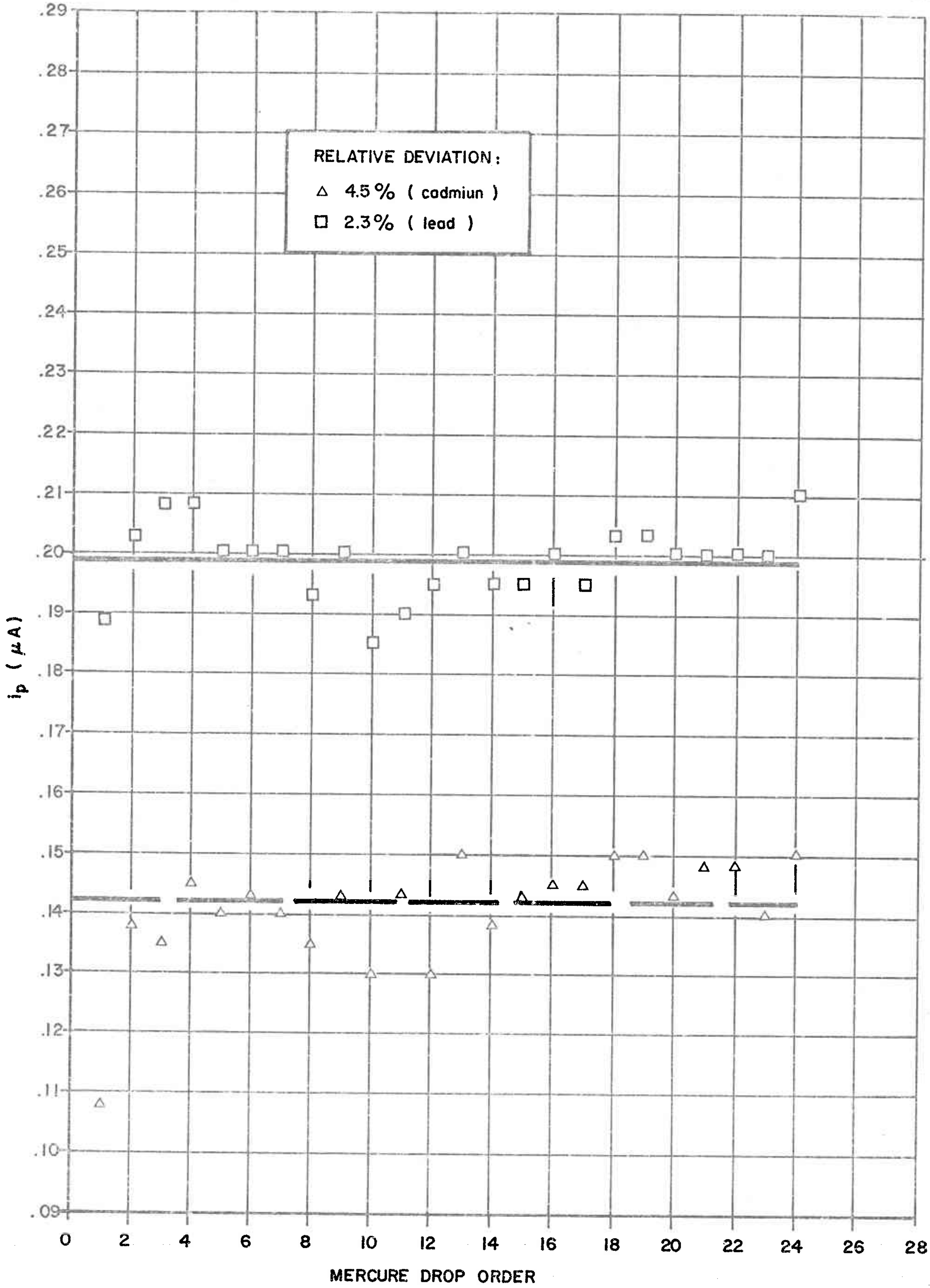

Figure 6 . Reproducibility of the DPASV method for cadmium and lead / Fidèlité de la méthode de DPASV pour le cadmium et le plomb.

current peaks, which may be evaluated by measuring the width of these peaks at half-peak height and comparing these widths for increasing drop size. The results of this experiment should therefore permit us to evaluate these diffusion problems and to select an appropriate drop size for subsequent experiments.

The results showed that peak current more than doubled for cadmium and lead over the range of drop diameters employed (Figure 7). The half-peak width ($W_{1/2}$), on the other hand, was constant for both cadmium and lead current peaks for drop sizes of 1 to 8 (0.52 - 1.05 m.) scale divisions ($W_{1/2} = 0.05$ volts). This means that under these experimental conditions, the mercury drop size can be increased to improve sensitivity without worrying about the metal diffusion problems described above.

Some restrictions on the choice of drop size do exist however. One of these is reproducibility, since to our knowledge, no information is available to the effect that reproducibility is the same for all drop sizes. The preceeding experiment has shown that current peak reproducibility was good for drops measuring six scale divisions (0.95 mm), but the reproducibility of the method for other drop sizes was not determined. The author would recommend that such verification be carried out as a matter of course by those wishing to use larger drop sizes.

Another restriction is the physical instability of larger mercury drops, which may be dislodged more easily than smaller drops in a stirred solutions during the plating step. The advantage of increased sensitivity gained by using large mercury drops may be lost through the tiresome repetition of determinations due to dislodged drops. In the following

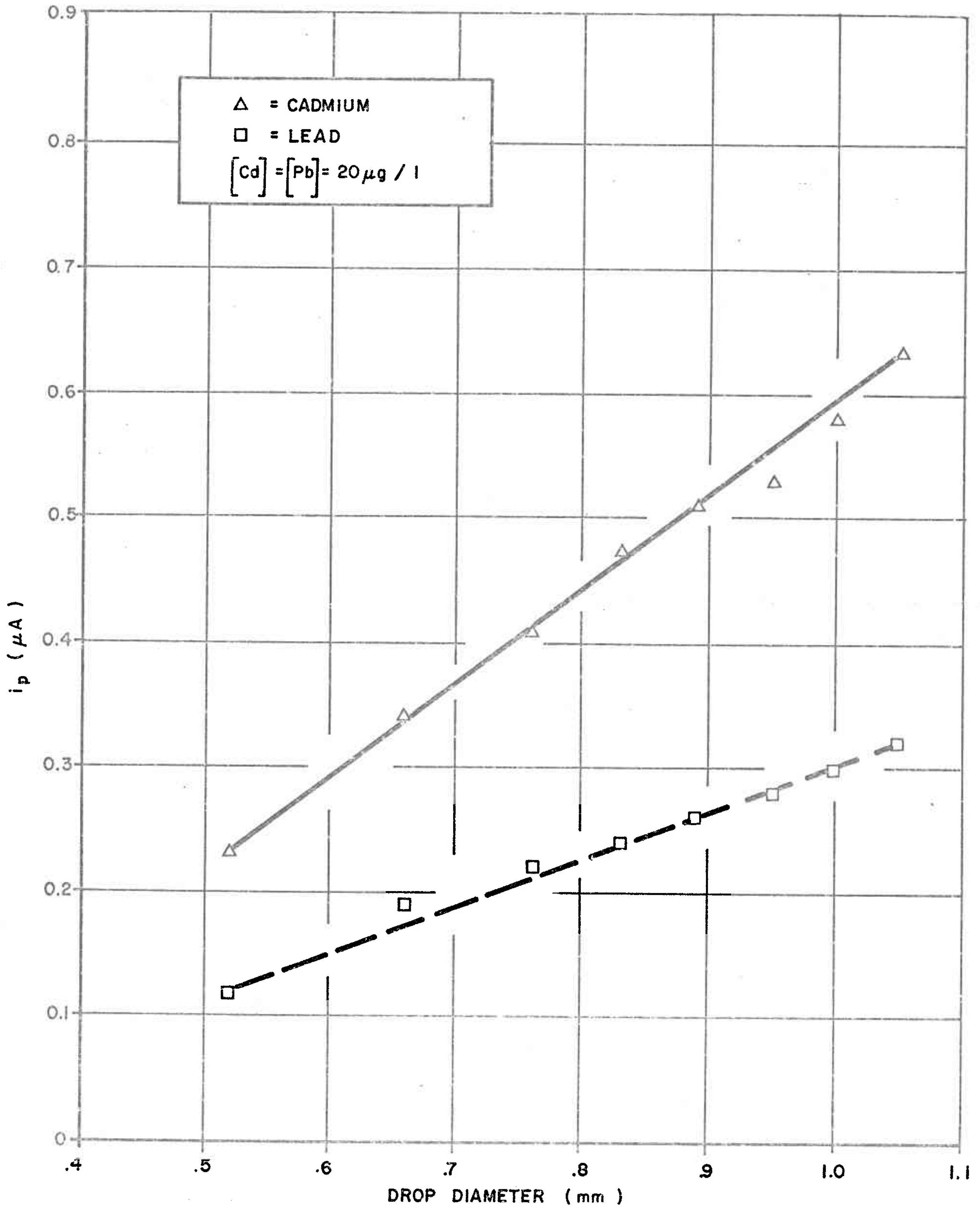

Figure 7 . The effect of mercury drop size on peak current / Effet de la dimension de la goutte de mercure sur l'intensité du courant i_p.

experiments, drop sizes from 3 to 6 scale divisions have been used, unless otherwise indicated.

3.3.4 The effect of plating time on peak current

From the theory of stripping analysis, peak current depends among other things on plating time (see section 1.2). Plating is usually carried out for a fixed time in stirred solutions followed by a thirty second interval after stirring has stopped. This interval permits the metal alamgam concentration to become homogenous and ensures that convection in the solution has ceased. Plating time then includes this thirty second rest interval.

The results (Figure 8) showed that under constant experimental conditions peak current does indeed increase linearly with plating time for intervals longer than 60 seconds. It appears from the figure that the peak current for cadmium increased at about twice the rate of the peak current for lead (0.23 μA/min compared to 0.12 μA/min respectively). This may be due to numerous factors, including the different diffusion coefficients of the two metal ions (Meites, 1965). It is interesting that a metal ion may have a characteristic slope for plots of peak current versus plating time under constant experimental conditions. Based on this fact, some means of distinguishing ionic from complexed metal may perhaps be devised.

It is obvious that increased sensitivity may be gained with longer plating times, but what is gained in sensitivity is lost in the increased analysis time per sample. Short plating times are recommended for natural water samples in order to minimize the dissociation of metal complexes

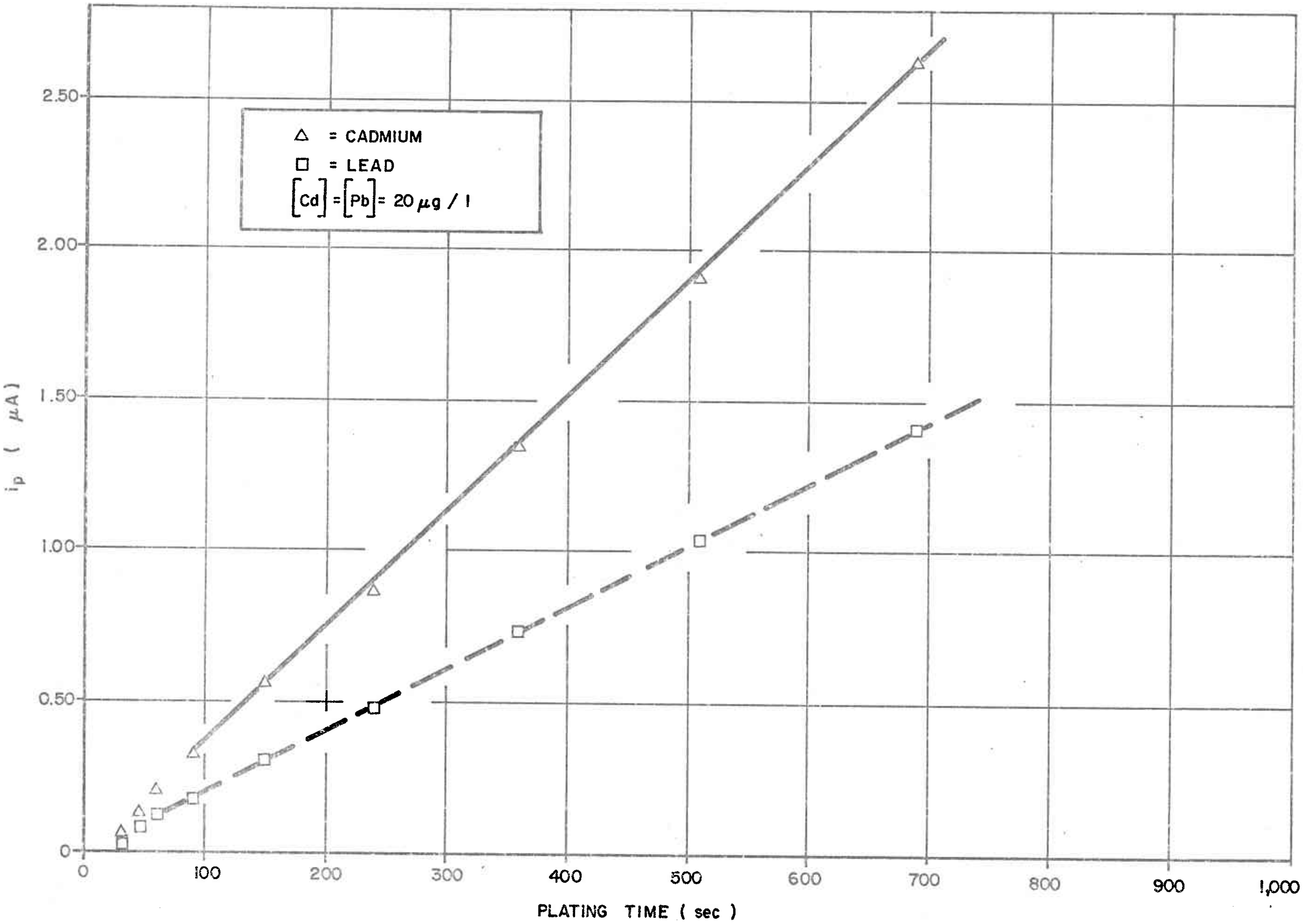

Figure 8 . The effect of plating time on peak current / Effet du temps de plaquage sur l'intensité du courant (i_p) .

during the plating step and other disturbances of initial equilibrium conditions.

3.3.5 The effect of pulse amplitude on peak current and peak potential

In the DPASV technique voltage pulses are superimposed on the conventional linear DC potential ramp. Although in principle any pulse amplitude may be employed in trace metal determinations by DPASV, some change in form and position of peak currents is to be expected on varying pulse amplitudes (Christie et al., 1973).

The results (Figure 9) showed that peak current increased by a factor of ten or more from the smallest to the largest pulse amplitude for each of the metals investigated. In addition, peak potential was shifted cathodically by 45 mv for each of the metals. This corresponds well with the theoretical prediction of the variation of peak potential given by Osteryoung and Parry (1967):

$$E_p = E - \Delta E/2$$

where ΔE is the variation in pulse amplitude. This would give a value of 47.5 mv for the same increase in pulse amplitude.

It is apparent from the figure that the form of the current peaks has changed: the peaks are appreciably broader at 50 and 100 mv than at other pulse amplitudes. An explanation for this behavior can be found in the excellent review by Christie et al. (1973) on instrumental artifacts related to the differential pulse mode of operation. They have suggested that this peak distortion is related to the number of opportunities that the memory has had to sample a non-zero current. Their work has shown

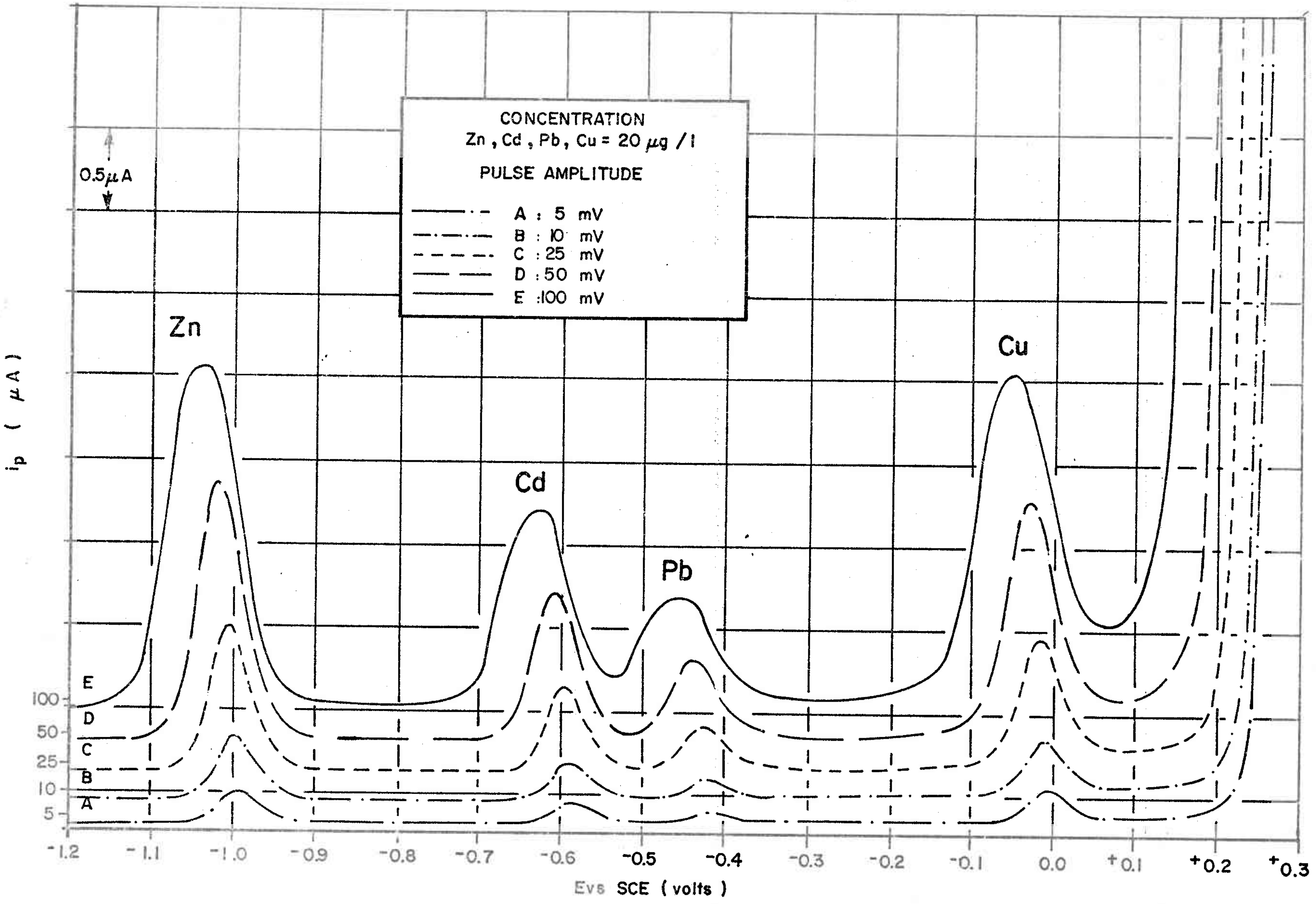

Figure 9 . The effect of pulse amplitude in DPASV on peak current and peak potential / Effet de l'amplitude de l'impulsion dans DPASV sur l'intensité du courant et le potentiel .

that if the experimental parameters of scan rate, drop time, and pulse amplitude are kept constant, the peak current is as usual directly proportional to the concentration of the electroactive species.

One may therefore conclude that, in spite of these instrumental artifacts, good results can be obtained if calibration and analysis are done under the same instrumental conditions and the investigator adheres to the principles of good analytical practice.

3.3.6 The effect of ionic strength and type of supporting electrolyte on peak current and peak potential

The work of Copeland et al. (1973) has shown that for the MFE an increase in ionic strength may cause significant increases in peak height and cathodic shifts of peak potential. This is essentially an instrumental artifact due to the effect of uncompensated resistance on electrode response. The HMDE is expected to be somewhat less sensitive to changes in solution resistance compared to the MFE.

Ionic strength may also influence peak current and peak potential in other ways. The amount of metal plated on the mercury electrode depends on the diffusion coefficient of the metal ion or species. This diffusion coefficient, however, is not constant for increasing ionic strength. The diffusion coefficient, D, varies for changes in ionic strength, μ, in the following manner (Meites, 1965):

$$D = D^{o} - s\mu^{1/2} \qquad (14)$$

where d^{o} is the diffusion coefficient at infinite dilution and 's' is constant for a particular supporting electrolyte and metal ion assuming constant temperature. Unfortunately, little or no information is available in the literature, with regard to values of diffusion coefficients for different ionic strengths and media, permitting one to quantitate this effect. The diffusion coefficient is not expected to change very much for variations in ionic strength*, so the effect on peak current should not be too important.

Varying the ionic strength of the solution obviously changes the activity coefficients of those metal ions to be plated on the mercury electrode. This change in the activity coefficient will provoke a change in the stripping potential by the Nerst equation (see section 1.2). For increases in ionic strength from 10^{-3} to 10^{-1}, the peak potential of divalent metal ions will be shifted cathodically by approximately 0.01 volts due to the reduced activity coefficients of these ions.

In the first experiment, where additions of sodium acetate were made to the standard sample, typical results (Figure 10a) showed that peak height was reduced and peak potentials for each metal were shifted cathodically with increasing ionic strength. For the case of zinc, the diminution of peak height was quite pronounced, whereas potential shift for this metal is barely visible from the figure. For the other metals a successive diminution of peak height was observed, and considerable shifts in potential were evident. In the second experiment, where additions of potassium nitrate were made to the standard sample, typical results (Figure 10b) showed a slight increase in peak height with increasing ionic strength, except for the case of copper, and peak

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* For instance, the diffusion coefficient of Tl (I) in a KCl medium changes by as little as 5% for increases in ionic strength from 0.04 to 0.16 (Meites, 1965).

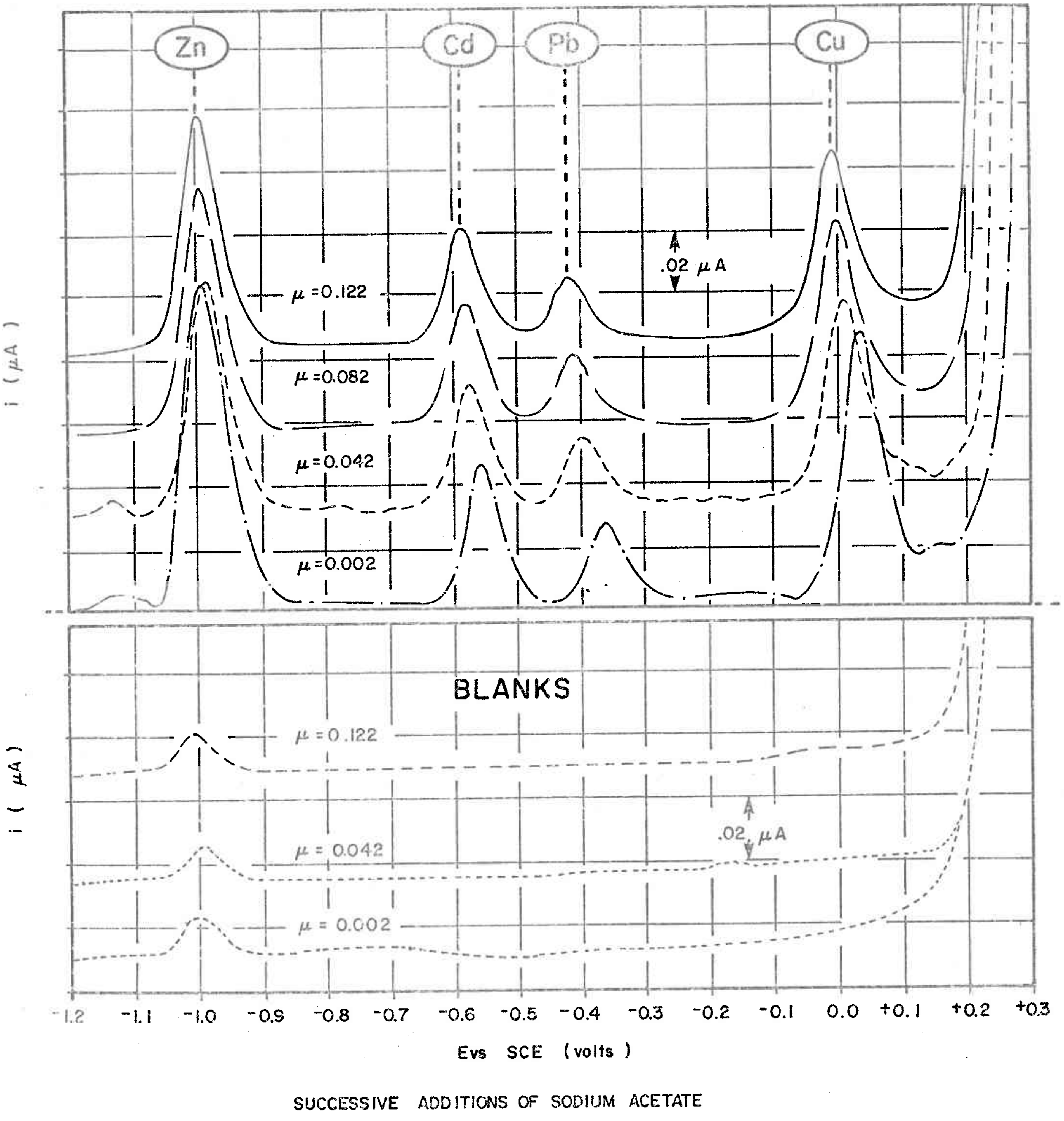
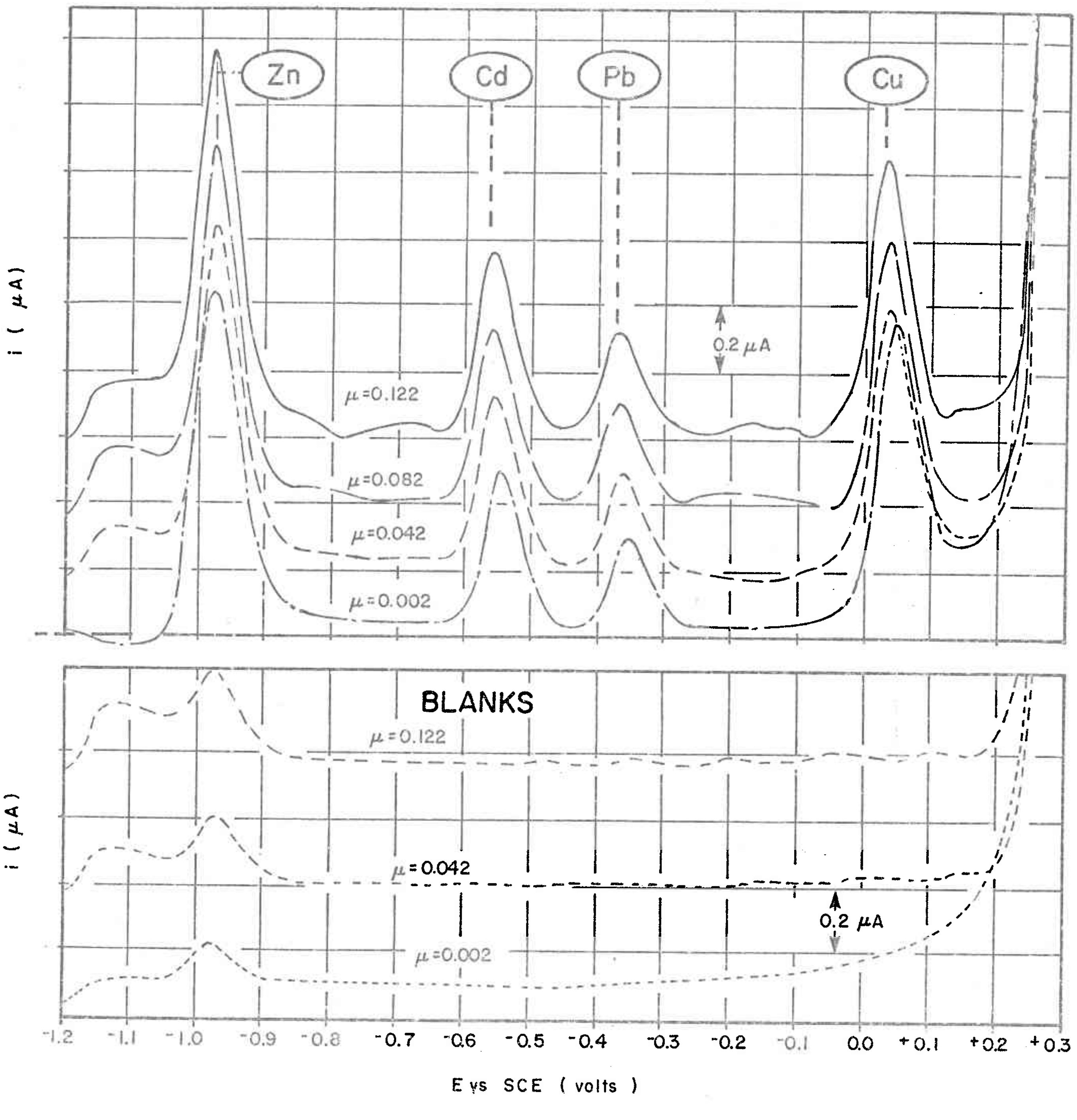


Figure 10a . The effect of ionic strength on peak current and peak potential / Effet de la force ionique sur l'intensité du courant et sur le potentiel.



SUCCESSIVE ADDITIONS OF POTASSIUM NITRATE

Figure 10b. The effect of ionic strength on peak current and peak potential/
Effet de la force ionique sur l'intensité du courant et le potentiel.

potentials were again shifted to more cathodic values. In Table 3, the average values of peak current and peak potential are given for each ionic strength.

In comparing these two experiments, it appears that sodium acetate shifts peak potentials more cathodically than potassium nitrate with increasing ionic strengths. Furthermore sodium acetate reduces peak heights with increasing ionic strength, whereas potassium nitrate leads to a slight increase in peak current values. The shifts in peak potential observed with increasing ionic strength in the sodium acetate medium may be caused by the formation of weak complexes (see section 3.1) with the acetate ion, combined with the effect of the reduced activity coefficient of the metal ion. The diminution of peak heights in the sodium acetate medium may be due to the binding of these metals to the acetate ligand to form electrochemically labile complexes with diffusion coefficients lower than those of the "free" hydrated metal cations.

The shifts in peak potential in the potassium nitrate medium are smaller than those for sodium acetate and are probably due to the effect of the reduced activity coefficient of the metal ion alone. The slight increase in peak heights is more difficult to explain. Since no contamination of the blanks is evident from the additions of potassium nitrate, it is possible that the increases in peak current are a result of the suppression of uncompensated resistance. This is improbable, however, in view of the rather insignificant shifts in peak potential obtained in this medium.

Because of the variable amount of electrolyte naturally present in environmental samples, it would be wise to add sufficient supporting

TABLE 3

Average values of peak current and peak potential for changes in ionic strength / Valeurs moyennes de l'intensité du courant et du potentiel pour des changements de la force ionique *

Successive additions of sodium acetate / Additions successives d'acetate de sodium

Ionic Strength/ Force ionique (μ)	i_p (μA) Zn	Cd	Pb	Cu	$-E_p$ (volts) Zn	Cd	Pb	Cu
0.002	0.96	0.43	0.24	0.80	0.995	0.560	0.360	-0.040
0.042	0.73	0.38	0.21	0.62	0.995	0.575	0.395	-0.020
0.082	0.77	0.37	0.21	0.62	1.000	0.580	0.410	-0.005
0.122	0.75	0.36	0.20	0.56	1.000	0.585	0.415	0.000

Successive additions of potassium nitrate / Additions successives de nitrate de potassium

Ionic Strength/ Force ionique (μ)	i_p (μA) Zn	Cd	Pb	Cu	$-E_p$ (volts) Zn	Cd	Pb	Cu
0.002	1.02	0.48	0.28	0.84	0.990	0.555	0.360	-0.040
0.042	0.97	0.50	0.28	0.75	0.990	0.565	0.370	-0.030
0.082	1.05	0.52	0.30	0.79	0.990	0.570	0.375	-0.030
0.122	1.10	0.54	0.31	0.80	0.990	0.570	0.375	-0.030

* Each value is the average of two independent determinations / Chaque valeur est la moyenne de deux mesures indépendantes

electrolyte to mask their effect on peak current and potential. Similarly, it would be wise to choose an ionic strength greater than 0.04, since the results for this experiment with the HMDE appear to be somewhat more stable above this value.

CHAPTER 4

THE EFFECT OF pH ON PEAK CURRENT AND PEAK POTENTIAL

4.1 Experimental

Two water samples were chosen for this experiment. The first sample was water drawn on March 6, 1975 from a tap in our laboratory situated in the city of Ste-Foy, Quebec. This water is drawn from the St. Lawrence River and subjected to standard filtration plant procedures. Its chemical composition resembles river and lake waters low in organic matter and ground waters containing mostly inorganic chemical species (Table 4). The tap was left running for a period of one hour (to flush the pipes of any water that had remained in copper plumbing overnight), before water was collected in a 2-liter polyethylene bottle, which was quickly closed with a tight fitting plastic screw cap. This sample was immediately employed in the preparation of the experimental solution.

The second sample was water from Lake Boivin, a small eutrophic reservoir on the Yamaska-Nord River upstream from the city of Granby, Quebec. Raw water from Lake Boivin was kindly collected in November 1974 by Benoit Belanger from a tap at the water filtration plant in Granby, ans stored at a temperature of 4°C in a large polyethylene container at our laboratory. A sub-sample was collected on March 6, 1975 in a 2-liter polyethylene bottle, as above, and employed immediately in the preparation of the experimental solution. This water has a relatively high organic matter content and resembles eutrophic river or lake water (Table 4).

TABLE 4

Chemical composition of water samples used for pH experiments / Composition chimique des échantillons d'eau employée pour les expériences de pH

PARAMETER / PARAMETRE	CONCENTRATION	
	Tap water/ Eau du robinet	Lake water/ Eau du lac
SiO_2 (mg/l)	2.4	0.2
Ca (mg/l)	34.0	13.8
Mg (mg/l)	6.0	2.3
Na (mg/l)	14.0	6.4
K (mg/l)	1.6	2.4
SO_4 (mg/l)	40.0	14.8
Cl (mg/l)	21.0	10.9
NO_3 (mg/l)	1.2	<0.1
PO_4 (mg/l)	<0.02	0.04
Conductivity/ Conductivité (μmhos cm^{-1}) (25°C)	257.0	130.0
Total inorganic carbon/ Carbon inorganique total (mg C/l)	10	3
Total organic carbon/ Carbon organique total (mg C/l)	<1	19
Zn* (μg/l)	9	17
Cd* (μg/l)	<0.1	<0.1
Pb* (μg/l)	<0.1	13
Cu* (μg/l)	20	6

* Water samples containing / échantillon d'eau contenant:

0.1 M NaOAc + 0.01 M $NaHCO_3$

Solutions were prepared in 500 ml Pyrex volumetric flasks, that had been scrupulously cleaned beforehand (for cleaning procedures, see section 3.1). These volumetric flasks were filled with approximately 300 ml of each sample, to which was added sodium acetate (25 ml of a 2M NaOAc purified solution; final concentration 0.1M). Sodium bicarbonate of a 1M $NaHCO_3$ solution; final concentration 0.01 M), and a solution of zinc, cadmium, lead, and copper (20 ml of a freshly prepared solution (pH = 2) containing 10 mg/l of each metal; final concentration of about 400 µg/l for each metal). Further additions of sample were made to complete to a final volume of 500 ml. These solutions were left to equilibrate for 3 days at room temperature in the same glass-stoppered Pyrex flasks.

The pH vas determined and each sample was filtered through a membrane filter (Millipore, 0.45 µm) that had previously been cleaned by soaking for 24 hours in deionized water and rinsing with 3 liters of deionized water. This washing procedure was found to be necessary because untreated Millipore filters contaminated the filtrate with unidentified organic material (e.g. surfactants ?) which rendered polarographic determinations impossible. The pH was determined again and each sample was subjected to ultrafiltration using a stirred filtration cell (Amicon Corporation, Model 402) fitted with a filter membrane having a nominal molecular weight cut-off of 100,000 (Amicon filter XM 100A). The pH was again measured and compared to that determined before the filtration steps.

The polarographic cell, which had been soaked in 10% nitric acid (W/V) for over 24 hours, was rinsed with deionized water to remove any trace of acid, and finally with two 50 ml volumes of the filtered sample solution. The cell was filled with a fresh portion of the filtered sample solution and left to equilibrate for 15 minutes. This sample was then rejected and a fresh 50 ml sample introduced into the cell. Again the pH was determined and compared to previous values. A mixture of nitrogen and carbon dioxide was bubbled through the cell for 15 minutes to remove dissolved oxygen. During this time changes in pH were monitored by introducing a pH-electrode into the cell in the place of the platinum counter electrode, and the $N_2:CO_2$ mixture was adjusted to give a final selected pH of 8. At the end of 15 minutes and after the final pH had been reached, the gas mixture was diverted to blow over the surface of the solution, the pH-electrode was removed and the platinum counter electrode was replaced. Under the cover of the $N_2:CO_2$ mixture the sample was equilibrated at pH 8 for 15 minutes.

Simultaneous trace metal determinations were carried out for all four metals using DPASV for values of pH beginning with pH 8.0. Plating potential was -1.2 volts and plating time lasted 2 minutes including the 30 second rest period. Stripping was performed with a sweep rate of 5 mv/s and a pulse amplitude of 25 mv. Metal determinations were made in triplicate at each pH value (8.0, 7.0, 5.9 and 4.7) and were repeated for two different equilibrium times at each pH value - once after 15 minutes and a second time after 75 minutes.

The pH was progressively reduced to 7.0, 5.9 and 4.7 using the $N_2:CO_2$ mixture, and DPASV determinations were repeated at these pH values in triplicate for the two different equilibrium times. The concentrations of each of the four metals were determined simultaneously by standard addition techniques at the end of the experiment at pH = 4.7.

The chemical composition of the original unfiltered samples of tap water and lake water were analyzed by the Ministère des Richesses

Naturelles du Québec, Service Qualité des Eaux. The total metal content of these samples was determined after acidification (HNO_3, pH = 2) by DPASV. In the case of zinc, for which determination by this method is impossible in acidified solutions, the pH of the sample was neutralized (pH = 7) by additions of sodium hydroxide (Ventron, Cat. No. 87864, ultra-pure) before DPASV determinations were begun.

In the case of the tap water sample eight successive determinations of peak current were performed under constant experimental conditions at pH 8, in order to permit calculation of the standard deviation values of peak current for this experiment*.

4.2 Results and discussion

4.2.1 Ratio of soluble metal to total metal content

A very curious and unexpected result is the observation that the ratio of soluble metal after equilibration and filtration (M_S) to total added metal before equilibration and filtration (M_T) is lower for every metal in the lake water sample compared with the tap water sample (Table 5). A great deal of experimental evidence exists to show that the dissolved organic matter (DOM) in a sample will tend to solubilize metal that would otherwise have precipitated as insoluble metal salts (see chapter 1). The loss of soluble metal through such precipitation reactions should then have been greater for the tap water sample than for the lake water sample; as shown by the M_S/M_T ratios in Table 5, the opposite result was obtained.

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* The results for the tap water sample were applied to the data for the lake water sample.

TABLE 5

Trace metal distribution in the solutions used for pH experiments / Distribution des métaux traces dans les solutions employées pour les expériences de pH

SAMPLE/ ECHANTILLON	Total added metal concentrations before equilibration and filtration / Concentrations totale des métaux ajoutés avant équilibration et filtration M_T (µg/l), pH = 2.0				Soluble metal concentration after equilibration and filtration / Concentration des métaux en solution après équilibration et filtration M_s (µg/l), pH = 4.7				Percent recovery of added metals / Récupération des ajouts des métaux en pourcentage M_s/M_T (%)			
	Zn *	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu
Tap water/Eau du robinet	409	400	400	420	90	325	95	220	22	81	24	52
Lake water/Eau du lac	417	400	413	406	50	265	75	200	12	66	18	49

* Zn was determined at an adjusted pH of 7.0/Zn a été dosé à un pH ajusté de 7.0

Several explanations may be advanced to account for this result including significant losses of soluble trace metals through adsorption on particulate matter in the lake water sample. Visual inspection of this sample, the accumulated residue on the filter membrane, and the prolonged filtration time all indicated the presence of appreciable particulate and colloidal matter in the lake water sample. On the other hand, very little evidence of this material was found in the tap water sample. Adsorption on particulate matter in the lake water sample may therefore explain the lower ratio of soluble metal after equilibration and filtration to total added metal before equilibration and filtration found for this sample. Recent research has shown that the particulate phase often accounts for a large fraction of total metal content in environmental samples. For example, Stiff (1971b) found an average of 69% of total copper in the particulate phase for five different polluted rivers in Britain. Metal displacement reactions and metal-colloid reactions are generally rather slow. For this reason, an equilibration time of 3 days was chosen to allow the sample to "age" sufficiently, to insure as complete an equilibration as possible; under such conditions, maximum losses of metal to the particulate phase are to be expected.

Verification of pH before and after filtration indicated that although pH did not increase as a result of the filtration procedures, the pH of the equilibrated lake water sample (pH = 9.2) was slightly greater than the pH of the equilibrated tap water sample (pH = 8.9). Small differences in pH in this high pH range may account for relatively large differences in the loss of metal through precipitation of insoluble metal species. From theoretical calculations, cadmium, lead and copper should be particularly sensitive to slight changes in pH, since precipitation of these metals is to be expected at pH 9 for the total metal concentrations encountered in these solutions. It is therefore possible that this difference in pH contributes to the discrepancies apparent between the results obtained for the two samples.

A further possibility is that the loss of soluble metal to the Pyrex walls of the volumetric flask during equilibration may have been greater for the lake water sample than for the tap water sample. At present such an argument is pure speculation, since, to our knowledge, little experimental evidence exists to show that adsorption losses are more important in one medium than in another at the same pH. Stumm and Bilinski (1972) have shown that the presence of carbonato ligand strongly increases the loss of lead on silica surfaces (see section 1.3). They suggested that hydroxo, sulphato, carbonato and other complex ions or molecules should be more strongly adsorbed on negatively charged silica than aquo-complexes of the same metal. In this connection, an attempt was made in our laboratory to quantitate the loss of metal to the walls of the Pyrex polarographic cell. The unfiltered lake water sample including added trace metals was equilibrated for 1 1/2 hours. The sample was rejected and the cell was rinsed rapidly with three 100 ml volumes of a deionized water sample containing the same concentrations of sodium acetate and sodium bicarbonate as the lake water sample (pH = 9). The cell was then filled with 50 ml of the deionized water sample and the background level of the trace metals was determined by DPASV. The sample was immediately acidified by additions of nitric acid (16 M HNO_3, final pH = 4) and the trace metal content was again determined by DPASV. An appreciable increase in trace metal content could be taken as evidence of prior adsorption losses during the equilibration period. However, the results showed that no detectable liberation of zinc, cadmium, lead or copper from the Pyrex walls occurred on acidification. Possible interpretations are that no appreciable adsorption occurred or that adsorbed metal was removed during the cell rinsing, or that metals were adsorbed irreversibly and were not freed by acidification. Our preliminary experiment thus proved inconclusive, and some other method would have to be used to evaluate adsorption losses. A suggestion would be the use of appropriate radionuclides, which would be easily detectable in the deionized water sample after acidification, or on the cell walls.

4.2.2 Results of pH experiments

4.2.2.1 Influence of equilibration time

The choice of two different equilibration times was motivated by the fact that rates of acid exchange are known to be relatively slow in environmental samples (Allen et al., 1970) and the time required for chemical equilibrium is not expected to be constant from one sample to another. Thus equilibration times of 15 and 75 minutes were used for constant pH. During this time, the appropriate mixture of nitrogen and carbon dioxide was passed through the cell over the surface of the sample.

It is evident from the results (Table 6) that equilibration time had no significant effect on peak potentials, but did influence peak heights. Generally the peak height tended to be greater for the longer equilibration time. Note however that with the sole exception of cadmium in the tap water sample, the shape of the i_p vs pH curve (Figures 11 and 12) is similar for the two equilibration times.

TABLE 6

The effect of pH on peak current and peak potential / Effet du pH sur l'intensité du courant et le potentiel

i_p (μA)

	Tap water / Eau du robinet					Lake water / Eau du lac			
					Equilibration time / Temps d'équilibration (1)				
pH	Zn	Cd	Pb	Cu		Zn	Cd	Pb	Cu
8.0	3.32	9.00	1.40	8.80	T	0.82	7.40	1.00	5.85
	(3.28)	(9.23)	(1.49)	(9.17)	T'	(0.92)	(7.43)	(1.00)	(5.93)
7.0	3.57	9.10	1.47	9.53	T	1.28	7.60	1.20	6.40
	(3.85)	(10.00)	(1.60)	(10.00)	T'	(1.32)	(7.57)	(1.20)	(6.73)
5.9	3.52	9.93	1.73	10.10	T	1.25	7.70	1.30	7.43
	(3.80)	(9.87)	(1.73)	(10.50)	T'	(1.35)	(7.87)	(1.30)	(7.53)
4.7	3.17	9.30	1.73	10.37	T	1.00	8.07	1.40	8.57
	(3.23)	(9.73)	(1.83)	(10.83)	T'	(1.08)	(8.23)	(1.45)	(8.67)

$-E_p$ (volts)

pH	Zn	Cd	Pb	Cu		Zn	Cd	Pb	Cu
8.0	1.010	0.600	0.450	0.040	T	1.010	0.600	0.455	0.055
	(1.015)	(0.600)	(0.455)	(0.055)	T'	(1.015)	(0.600)	(0.460)	(0.060)
7.0	1.010	0.600	0.430	0.025	T	1.010	0.600	0.435	0.025
	(1.010)	(0.600)	(0.435)	(0.030)	T'	(1.005)	(0.595)	(0.430)	(0.015)
5.9	1.005	0.600	0.425	0.015	T	1.005	0.595	0.425	0.015
	(1.010)	(0.600)	(0.425)	(0.015)	T'	(1.005)	(0.595)	(0.425)	(0.015)
4.7	1.000	0.590	0.415	0.005	T	0.995	0.590	0.415	0.005
	(1.000)	(0.590)	(0.415)	(0.005)	T'	(0.995)	(0.595)	(0.420)	(0.005)

(1) T and T' signify equilibration times of 15 and 75 minutes respectively / T et T' signifient des temps d'équilibration respectifs de 15 et 75 minutes.

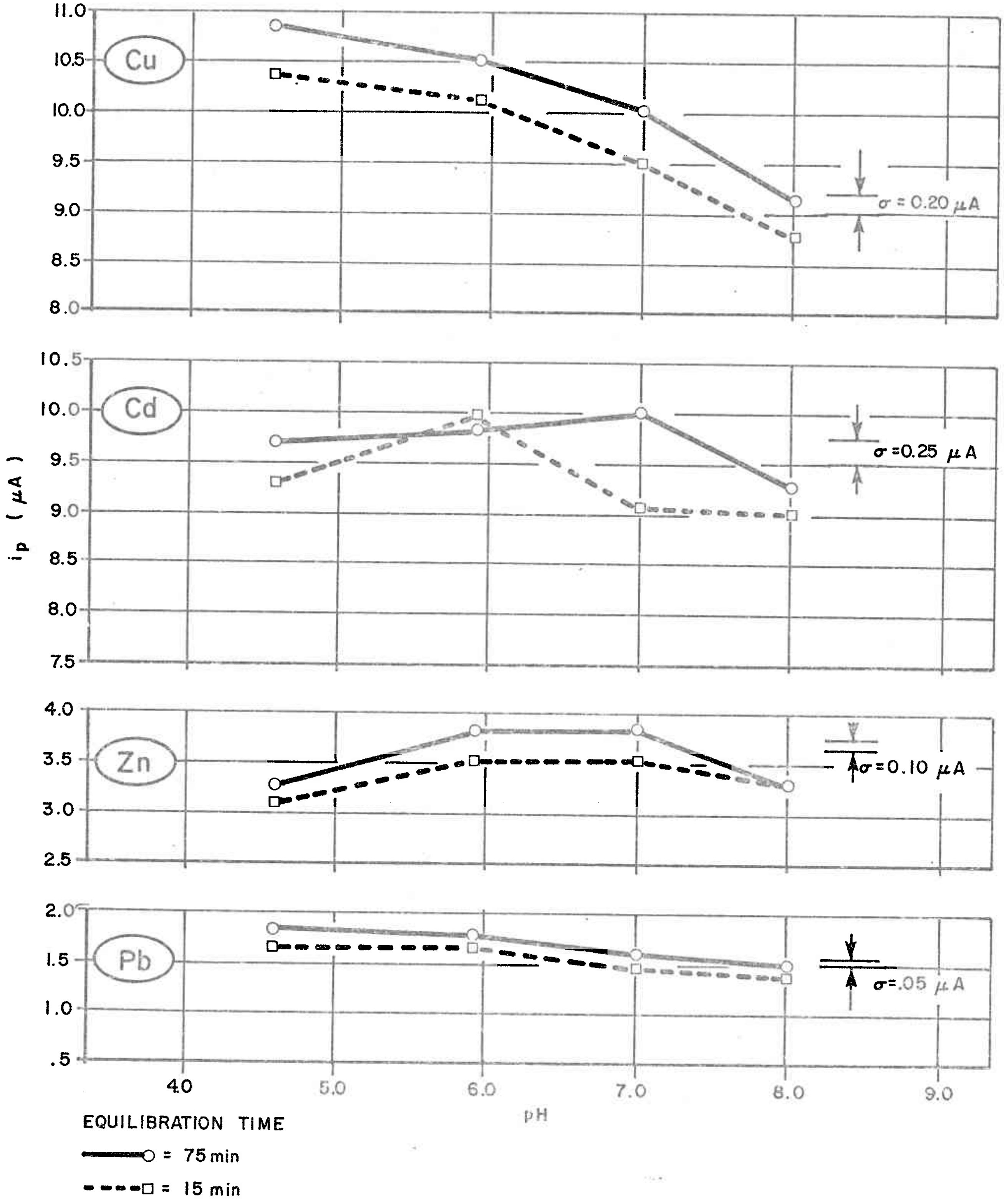

Figure 11 . Variation of peak current with changes of pH (Tap water) / Variation de l'intensité du courant avec les changements du pH (eau du robinet) .

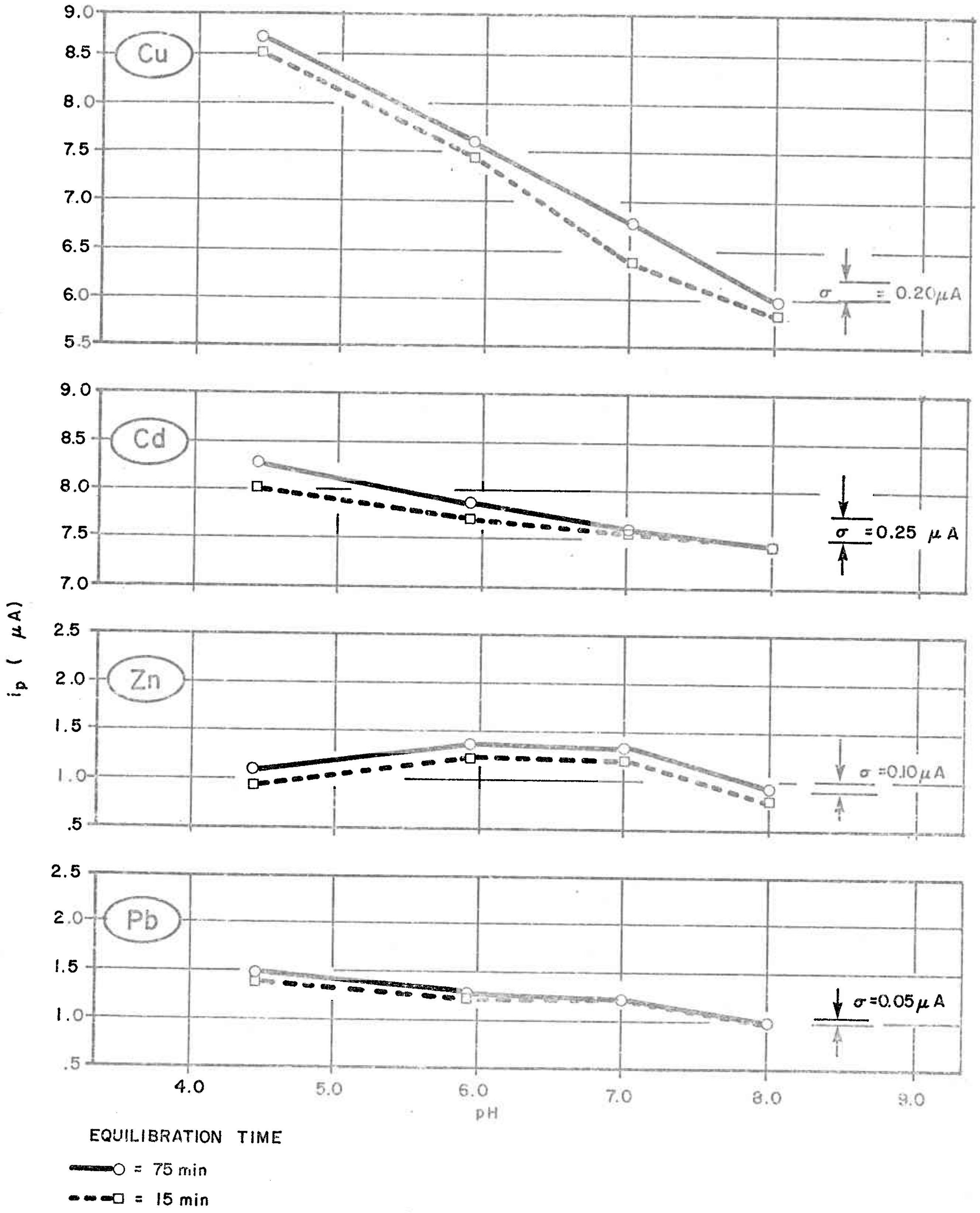

Figure 12. Variation of peak current with changes in pH (Lake water)
Variation de l'intensité du courant avec les changements (Eau du lac).

The relative deviation of the peak current values of the tap water sample at pH 8.0 was calculated from the data. The results gave values of relative deviation from 2 to 3% for each of the metals considered. The values of standard deviation are indicated on Figures 11 and 12 for the different metals.

4.2.2.2 Effect of pH on peak current

The effect of pH on peak current was somewhat irregular (Figures 11 and 12). In general, there was a significant increase of peak current on acidification of both samples for all the metals determined. For copper and lead, i_p values increased by a factor of approximately 1.2 in the tap water sample and 1.4 in the lake water sample over the range of pH from 8 to 4.7. Peak current values of cadmium increased by a factor of approximately 1.1 in the lake water sample, but behaved irregularly in the tap water sample. Electrode response to zinc rose to a plateau in the middle of the pH range studied and decreased again towards lower pH values. In the tap water sample, this plateau corresponds to an increase of i_p by a factor of approximately 1.1, whereas in the lake water sample, this factor is approximately 1.5.

These results for cadmium, lead, and copper may be compared to those of O'Shea (1972) dealing with sodium bicarbonate solutions and to previous results in our laboratory for unfiltered tap water samples. O'Shea's results show increases in peak current by a factor of slightly less than 2 for cadmium and lead, and greater than 4 for copper over the same range of pH as that studied in our experiment. Previous experimental results in our laboratory, obtained with an unfiltered ramdom tap water sample, showed that peak current increased by a factor of 1.1 for cadmium, 2.0 for lead, and 2.5 for copper for a decrease in pH from 7.0 to 4.7. Therefore it is evident that the filtration and ultrafiltration steps reduce considerably the increase of peak current due to acidification, except in the case of cadmium for which the factor remains low in both filtered and unfiltered samples. This infers that the large increases in peak current on acidification observed by O'Shea in his unfiltered samples were due, at least in part, to solubilization on desorption of particulate metal rather than to changes in soluble metal speciation.

4.2.2.3 Effect of pH on peak potential

The effect of pH on peak potential provides additional clues to the chemical changes occurring in the samples. The results (Figures 13 and 14) showed anodic shifts of peak potential on acidification for all the metals in both samples. The observed shifts were greatest for copper and lead. In the tap water sample, the anodic shifts of zinc, cadmium, lead and copper on acidification were approximately 0.01, 0.01, 0.04 and 0.04 volts respectively. The results in the unfiltered tap water sample were similar to those of the ultrafiltered sample. In the lake water sample, the results were the same except for zinc and copper which underwent slightly larger anodic shifts of approximately 0.02 and 0.05 volts respectively. For copper and lead the shift in potential is greatest between pH 7.0 and 8.0 in both samples, but this discontinuity is more pronounced in the lake water sample than in the tap water sample. For this change in pH there is no corresponding discontinuity in the i_p vs pH relation; the peak current maintains a steady increase over the entire pH range.

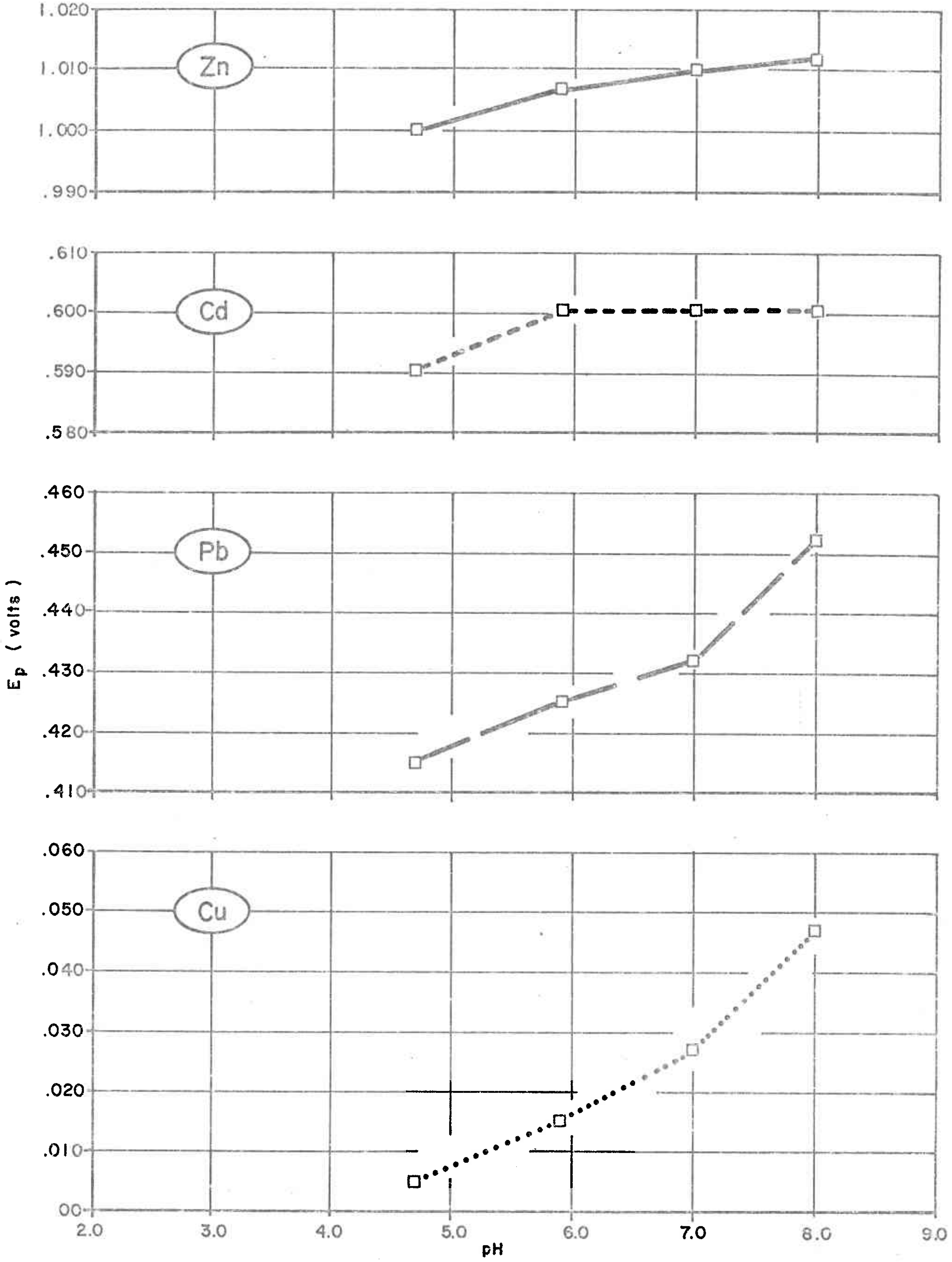

Figure 13 . Variation of peak potential with changes in pH (Tap water)
Variation du potentiel des pics avec les changements du pH (Eau du robinet) .

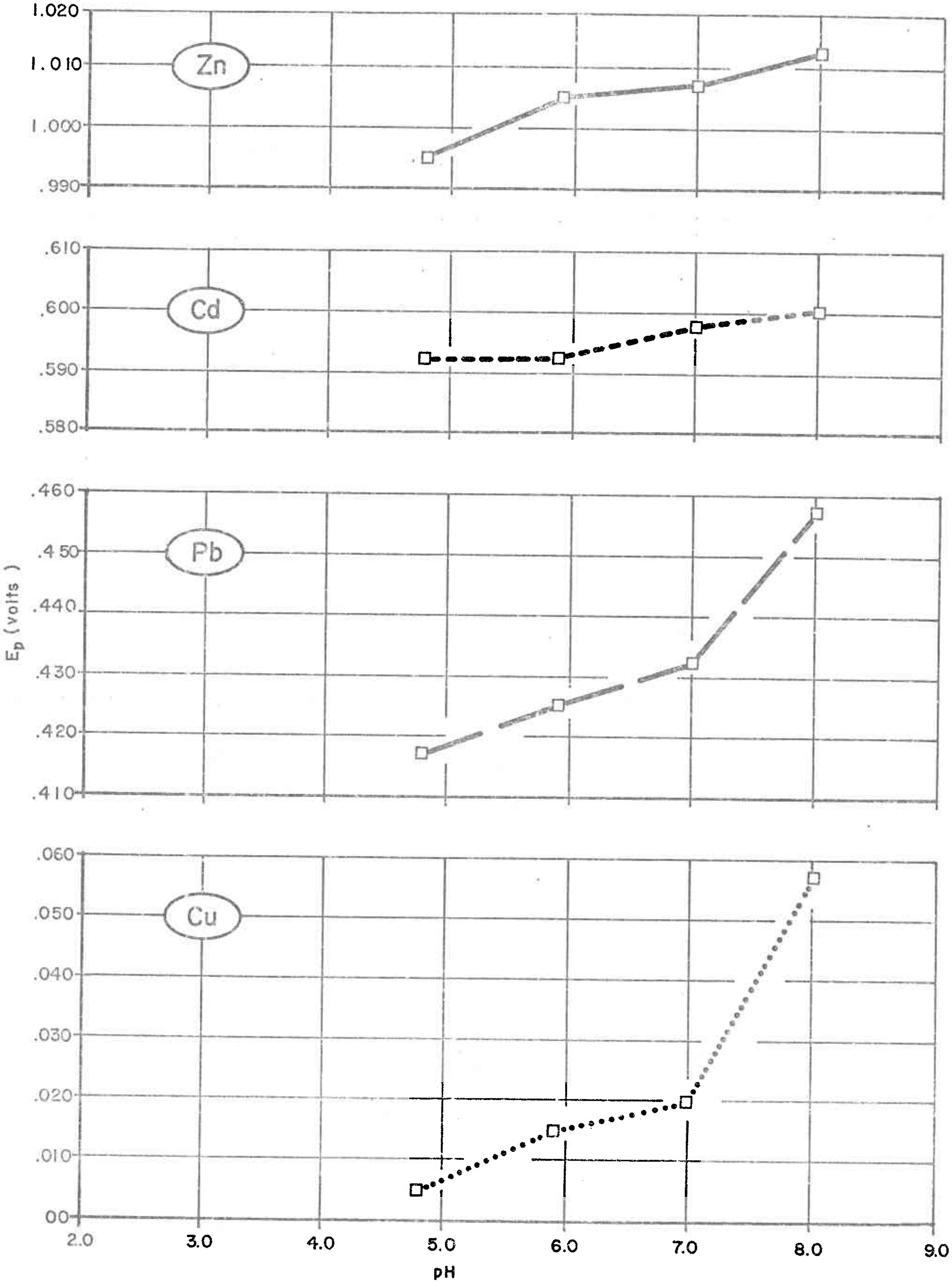

Figure 14. Variation of peak potential with changes in pH (Lake water)
Variation du potentiel des pics avec les changements du pH
(Eau du lac) .

O'Shea (1972), on the other hand, reported enormous shifts in peak potential over the same range of pH. He found anodic shifts on acidification for cadmium, lead, and copper of approximately 0.04, 0.08 and 0.09 volts respectively.

4.2.3 Discussion

4.2.3.1 Equilibrium calculations

From a simple chemical equilibrium model (e.g Zirino and Yamamoto, 1972) of the tap water sample, including inorganic species only, it is possible to draw certain conclusions concerning the results above. Metal interactions with the anions OH^-, Cl^-, SO_4^{-2}, HCO_3^- and CO_3^{-2} were considered (See Appendix 1). The chloro and sulphato complexes were eventually rejected, because these anions were not present in sufficient concentrations to complex the metals to any appreciable extent. Using this model a graph of the logarithm of $[ML]/[M^{+z}]$ vs pH was drawn to show possible complexation reactions of the metals (Figure 15). Based upon the results shown in Figure 15, the distribution of these metal species in percent of total soluble metal can be calculated (Table 7).

It is evident from Figure 15 and Table 7 that below pH 5.9, none of the metals is complexed significantly by inorganic ligands and that between pH 5.9 and 7.0 only lead and copper appear in complexed form, bound largely by the carbonato ligand. Between pH 7.0 and 8.0, lead, copper and zinc are found predominantly in complexed form, whereas no more than 15% of cadmium is found in complexed form even at pH 8.0. Among the "associated species", the carbonate complexes of lead, copper and zinc predominate; the hydroxide complexes of these metals account for a neglible fraction of the total metal concentration.

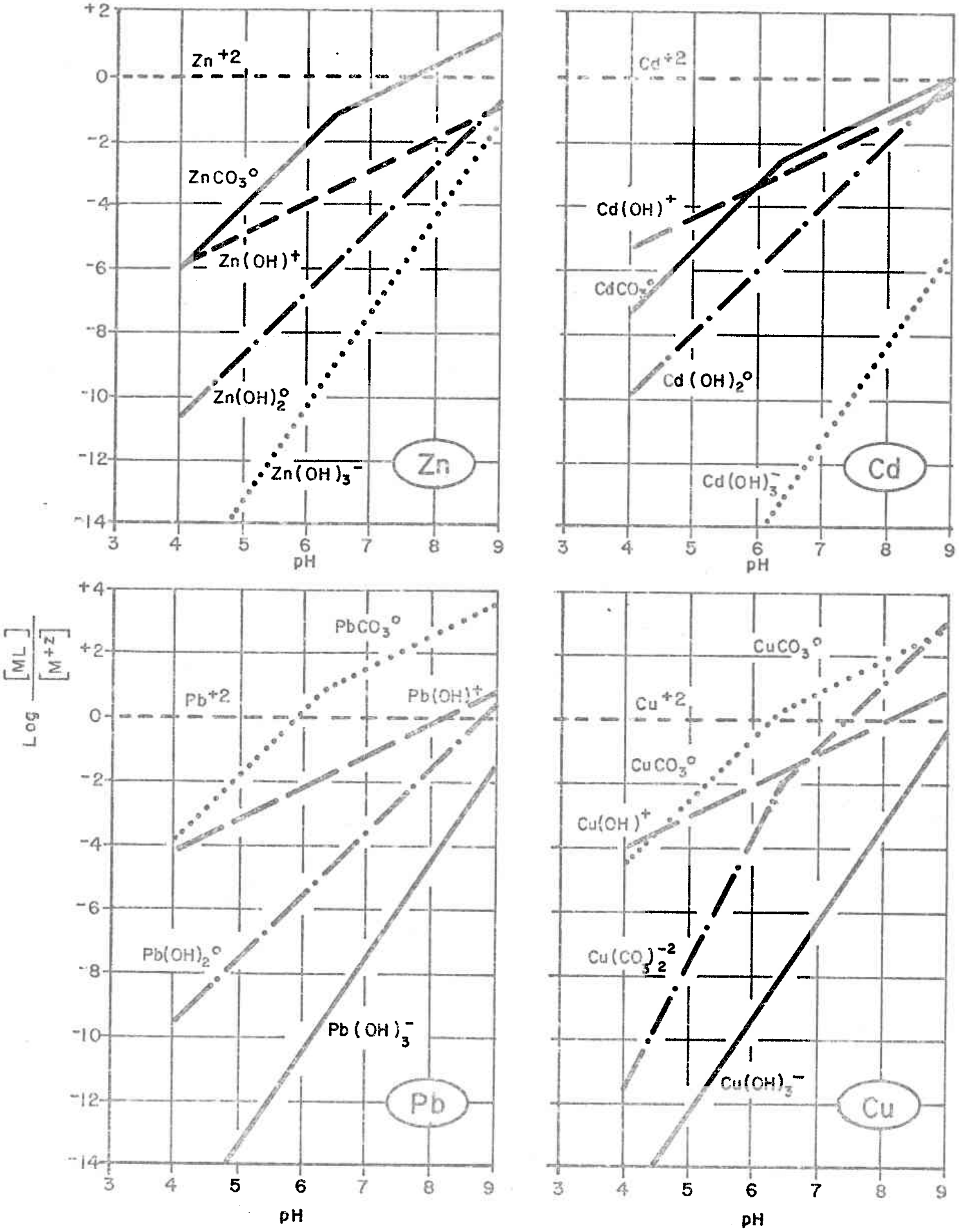

Figure 15 . The effect of pH on the log of the ratio of complexed metal concentration over the metal ion concentration / Effet du pH sur le log du rapport de la concentration des complexes métalliques sur la concentration des métaux en formes ioniques ($\log\{[ML]/[M^{+z}]\}$).

TABLE 7

Theoretical distribution of metal species, expressed in % of total soluble metal / Distribution théorique des formes métalliques exprimées en % du métal total soluble *

Zinc

pH	Zn^{+2}	$Zn(OH)^{+}$	$Zn(OH)_2^{o}$	$Zn(OH)_3^{-}$	$ZnCO_3^{o}$
8.0	30	1	-	-	69
7.0	81	-	-	-	19
5.9	99	-	-	-	1
4.7	100	-	-	-	-

Cadmium

pH	Cd^{+2}	$Cd(OH)^{+}$	$Cd(OH)_2^{o}$	$Cd(OH)_3^{-}$	$CdCo_3^{o}$
8.0	85	4	1	-	10
7.0	99	-	-	-	1
5.9	100	-	-	-	-
4.7	100	-	-	-	-

Lead/Plomb

pH	Pb^{+2}	$Pb(OH)^{+}$	$Pb(OH)_2^{o}$	$Pb(OH)_3^{-}$	$PbCO_3^{o}$
8.0	-	-	-	-	100
7.0	3	-	-	-	97
5.9	52	-	-	-	48
4.7	100	-	-	-	-

Copper/Cuivre

pH	Cu^{+2}	$Cu(OH)^{+}$	$Cu(OH)_3^{-}$	$CuCO_3^{o}$	$Cu(CO_3)_2^{-2}$
8.0	1	1	-	82	16
7.0	12	1	-	85	2
5.9	84	1	-	15	-
4.7	100	-	-	-	-

* N.B. These are approximate values calculated to the nearest percent / Ce sont des valeurs approximatives calculées au pourcentage le plus près (see Appendix; voir l'Annexe)

4.2.3.2 Peak potential

Within certain limits, graphs of peak potential versus pH will reflect the chemical changes occurring in samples (see section 1.2). Cathodic shifts in peak potential during stripping analysis require among other things that the concentration of the reacting ligand be sufficiently large to ensure rapid complexation of the oxidized metal at the mercury drop surface. Considering first the tap water sample (Figure 13), the larger shifts in peak potential between pH 7.0 and 8.0 for copper and lead may be interpreted as the result of complete complexation of these metals by the carbonato ligand at the higher pH. The peak potential of zinc, in the other hand, remain relatively unaffected by the complexation of this metal with the carbonato ligand. For values of pH below 7.0, the lack of sufficient inorganic ligands, carbonato or other, explains the smaller cathodic shifts in peak potential.

As previously mentioned, the shifts in peak potential reported by O'Shea are much greater than those observed in our experiments for the same change in pH in the tap water sample (see Figure 16).

Since the concentration of the hydroxo- and carbonato- ligands are the same for the same value of pH, the differences in the shifts of peak potential must be attributed to other factors (e.g. the use of a HMDE and a sodium acetate supporting electrolyte (0.01 M) in the present experiment). The large shifts in peak potential for cadmium in O'Shea's experiments are particularly anomolous, since no other investigator has reported shifts of peak potential for cadmium in the same range of pH.

Turning now to the lake water sample, comparison of Figures 13 and 14 reveals that between pH 5.9 and 8.0 a larger shift of the copper

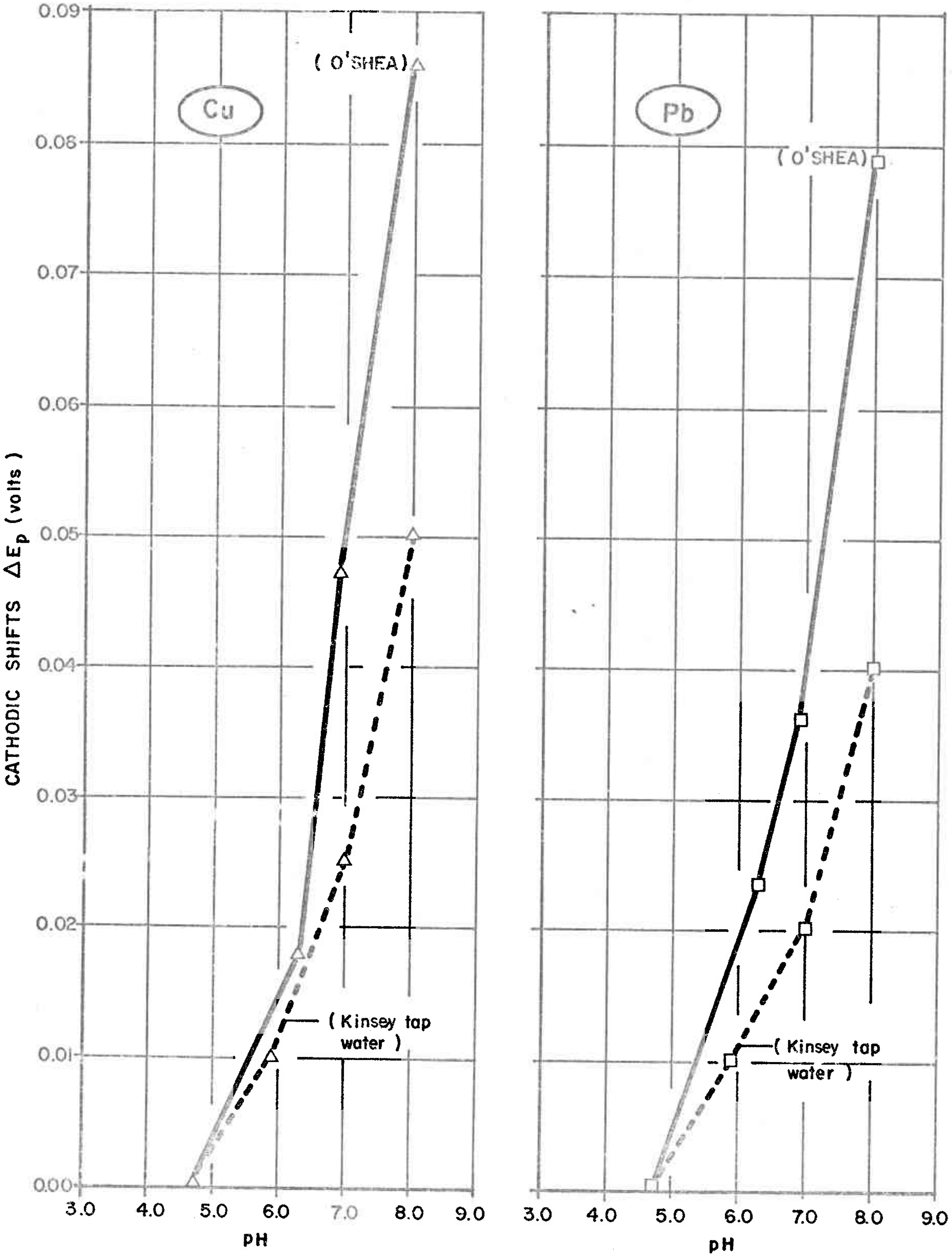

Figure 16. Cathodic shifts of peak potential with increasing pH - Comparison of available résults / Décalages cathodiques du potentiel des pics en fonction du pH - Comparaison des résultats disponibles.

and lead peak potentials occurs than in the tap water sample. The major difference between the two samples lies in the higher concentration of inorganic matter in the lake water (19 mg C/1 compared to < 1 mg C/1). From comparison of Figures 13 and 14, it is evident that at low pH the peak potentials vary in the same manner in both samples; it would thus appear that the organic ligands have no observable effect on peak potential for low pH. At higher pH, however, the appearance of the graphs of peak potential differs, suggesting that the organic matter has an important effect on copper and a somewhat less important effect on lead between pH 7.0 and 8.0. This implies that, in the lake water sample, organic complexes of copper and lead are found between pH 7.0 and 8.0, and predominantly inorganic complexes or ionic metal below pH 7.0.

4.2.3.3 Peak current

Inspection of the graphs of i_p versus pH (Figures 11 and 12) bring up several points of interest. First of all, the rather pronounced shifts in peak potential for lead and copper between pH 7 and 8 (see above) do not correspond to any well defined changes of peak current for the same values of pH. The peak currents of these metals increase steadily over the entire range of pH. Such a situation suggests that the inorganic or organic complexes responsible for the shifts in peak potential in this pH range are labile complexes, or strongly bound complexes that dissociate during electrodeposition. O'Shea (1972) has used a similar argument to define labile complexes of cadmium.

A second point of interest is the difference between the tap and the lake water sample for the increase in the lead and copper peak current on acidification. As previously mentioned, the peak current values of lead and copper increase by a factor of approximately 1.2 in the tap water sample and 1.4 in the lake water sample. This difference may be taken as further evidence for the existence of organic complexes of these metals in the lake water sample.

A third point of interest is the rise in the peak current of zinc to a plateau between pH 6 and 7. It is known that several metals, including nickel and copper, can interfere with ASV determinations of zinc when coplated together*. Thus a possible explanation of the plateau effect for zinc might be that the relatively high concentrations of copper (approximately 200 µg/1) interfere with the electrode response to zinc. Chau and Lum-Shue-Chan (1974) have noted, however, that no interference in the determination of 10-100 µg/1 of zinc was detectable for copper concentrations up to 315 µg/1. Similar results were obtained in interference studies with nickel. Therefore interference by copper and nickel can be discounted as a possible explanation of the pH effect on zinc. It has been mentioned elsewhere (Chapter 3) that the zinc peak disappears into the rising current curve for hydrogen reduction in acid solutions. It is possible that hydrogen reduction interferes with the plating of zinc in slightly acidic media for plating potentials of -1.2 volts.

4.2.4 Conclusions

The large differences between our results and those of O'Shea (1972) for the effect of pH on peak current can be reconciled by considering the differences in sample preparation. As has already been

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* Interference is caused by the formation of Ni-Zn and Cu-Zn mixed amalgams (Bradford, 1972).

discussed elsewhere (section 1.3), the fact that O'Shea's bicarbonate solutions were not filtered and that no supporting electrolyte was added to these solutions to give constant ionic strength for the experimental range of pH, should suffice to explain these differences.

Comparing O'Shea's results for shifts in peak potential with our results over the same pH interval, it is obvious that the differences cannot be explained merely by the changes in ionic strength of O'Shea's solutions, which have been shown elsewhere to account for a shift of not more than 0.02 volts (see section 1.3). It is suggested that these differences may be caused by various factors including the use of a HMDE and a sodium acetate supporting electrolyte. The large shifts in the peak potential of cadmium reported by O'Shea are assumed anomalous.

Our experimental results show that sample equilibration is important after changes in pH. It appears that in either tap water or lake water samples, a slight increase in peak current is observed between 15 and 75 minutes of sample equilibration at constant pH (the pH having decreased). A possible explanation of this phenomenon would be the slow desorption of adsorbed trace metal from the cell walls. Equilibration time, however, had no significant influence on peak potential.

From the simple chemical equilibrium model (Appendix 1), it is obvious that the carbonate complexes of all the metals except cadmium will predominate at the higher values of pH. The hydroxide complexes of the metals are shown to account for a neglible fraction of the total metal concentration.

The greater shifts in peak potential for copper and lead in the lake water sample suggested the presence of organic complexes at the higher values of pH. Comparison of the peak current and the stripping potential graphs (Figures 11, 12, 13, 14) indicated that labile complexes or strongly-bound complexes that dissociate during electrodeposition are present in the lake water sample.

CHAPTER 5

SUMMARY

The aim of our research was to investigate the effect of pH on peak current and peak potential as measured by the ASV technique, and to gain insight into the use of ASV as an analytical tool for the study of trace metal speciation.

Our results demonstrate that increases in peak current for zinc, cadmium, lead, and copper are consistently observed on the acidification of ultrafiltered natural water samples. The increases in peak current for our samples were relatively small compared to those of O'Shea (1972) for unfiltered bicarbonate solutions or to those observed by other workers (Allen et al., 1970; Fitzgerald, 1970) for unfiltered natural water samples. To explain the changes in the peak current and peak potential in his samples for changes in pH, O'Shea postulated the existence of "non-labile" inorganic complexes. The presence of "non-labile" inorganic complexes in our tap water sample seems unlikely, however, because the increase of peak current with respect to pH for zinc, cadmium, lead and copper on sample acidification does not correspond to the extent of decomplexation predicted by the simple chemical equilibrium model for these trace metals.

Changes in pH appear to influence both the polarographic reduction kinetics of the various metal species as well as their chemical distribution. Changes in pH may affect the polarographic reduction of a metal species, involving several stages of metal dissociation, by eliminating some of the intermediate steps (Crow, 1969). The polarographic reduction rate of the hydrated metal ion may be different from that of metal complexes due to slight differences in diffusion coefficients (see section 1.2). Changes in chemical distribution due to variations of pH would consequently produce changes in peak current, which might be wrongly interpreted as evidence for "non-labile" complexes.

A very rough measure of the relative polarographic reduction rate of the metal ion and its set of metal complexes in a sample is given by the slope of the graph of peak current versus plating time (see section 3.3) O'Shea (1972) produced graphs of peak current versus plating time for copper, lead, and cadmium for different values of pH. On the linear portion of these graphs, the relative polarographic reduction rates can be determined by measuring the slope. At pH 8.0, the relative polarographic reduction rates of copper, lead and cadmium were 0.5, 1.0 and 1.2 μA/min respectively increasing to 1.1, 2.0 and 2.0 μA/min respectively at pH 6.3. Although part of these increases may be caused by contamination from particulate matter present in O'Shea's unfiltered samples, significant increases may nevertheless be expected for ultrafiltered samples of tap water. The large increase in the relative polarographic reduction rate of cadmium (~1.7x), however, is unexpected, since little or no complexation of this metal is predicted in this pH range by our chemical equilibrium model (Appendix 1). No less than 90% of total cadmium will be present in the form of the hydrated metal ion for this pH range. Hence it may be suggested that the changes in peak current of cadmium are caused by the influence of pH on the polarographic reduction kinetics of the hydrated cadmium ion, and not by the presence of a "non-labile" cadmium complex at higher pH values.

The increases in the relative polarographic reduction rates of copper (2.2x) and lead (2.0x) are somewhat larger than that of cadmium. For higher pH values our simple equilibrium model predicts that copper and lead will be found predominantly as carbonate complexes. For these metals increases in peak current on acidification may be caused by the combined effect of increased polarographic reduction rates and changes in chemical distribution favorable to increased peak currents.

Our results also indicate that some information concerning trace metal speciation can be gained from the analysis of shifts in peak potential for changes in pH (e.g. Guy et al., 1975). The use of a chemical equilibrium model, however, is invaluable, if not essential, in this kind of analysis, for predicting the predominant trace metal species of simple systems, such as our tap water sample. The construction of chemical equilibrium models is all but impossible for natural water samples containing organic matter, such as our lake water sample, due to the lack of reliable information concerning stability constants and concentrations of individual organic ligands; thus, the analysis of shifts in peak potential for changes in pH alone will be difficult if not impossible. In general, pH is not a very selective variable for studying trace metal speciation by the ASV method, since changes in pH provoke widespread changes in the chemical distribution of trace metals.

ASV remains a very useful analytical tool for the study of trace metal speciation, if combined with intelligent manipulation of experimental variables. It has been suggested that the study of relative polarographic reduction rates (from graphs of peak current versus plating time) of trace metals may provide some means of distinguishing between ionic and complexed metal (section 3.3). Sample temperature can be lowered to reduce the dissociation of strongly-bound metal complexes during electrodeposition (Hanck and Dillard, 1973), thus giving a better measure of free or loosely bound metal. The plating step can be performed in one solution containing various known concentrations of trace metals and the mercury electrode may subsequently be transferred to a natural water sample to record the shifts in peak potential (Phillips and Shain, 1962; Matson et al., 1969). Electrode transfers of this kind may provide information on the complexation of the plated metal once it is released (oxidized) into the natural water sample. Complexometric titrations of natural water samples with metal or ligand as the titrant have been followed by the ASV method and have proved useful in the study of trace metal complexation (e.g.: Allen et al., 1970; O'Shea, 1972). ASV may be used in concert with ultrafiltration and dialysis techniques to determine the concentration of trace metals bound to organic matter in different molecular-size fractions of natural water samples.

These are but a few of the possible experimental manipulations with ASV that may prove useful in the study of trace metal speciation.

APPENDIX 1

A simple chemical equilibrium model

This simple chemical equilibrium model of tap water includes metal reactions with anions such as OH^-, Cl^-, SO_4^{-2}, HCO_3^- and CO_3^{-2}. The chloro- and sulphato- complexes with zinc, cadmium, lead and copper have not been calculated, because their formation constants are so small that very little metal will be bound to these anions. In a seawater sample, however, it would be important to consider these complexes due to the higher chloride and sulphate concentrations. C_T in this calculation corresponds to that in experimental media (10^{-2}M).

The formation constants for complexation of zinc, cadmium, lead and copper with these anions were given by Zirino and Yamamoto (1972) unless otherwise indicated; in some cases it was felt that the formation constants furnished by other authors were more reliable (See Table 8). Several complexes appearing in the Zirino and Yamamoto seawater model do not appear in our model. Al the metal-bicarbonate complexes have been rejected because detection of these species is not generally reported in the literature. One of these complexes, $CuHCO_3^+$, has been reported to be non-existent in sodium bicarbonate solutions (Stiff, 1971a). The complex, $Cu(OH)_2^o$, appearing in the model of Zirino and Yamamoto has also been rejected, because indirect evidence from copper titrations with carbonato ligand by Ernst et al. (1974) showed that this complex cannot be important in fresh water samples*. The tetra-ligand complexes such as $Cu(OH)_4^{-2}$ have not been considered in the model, because these

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* Voir page 52.

TABLE 8

List of complexation reactions and their formation constants / Liste des réactions de complexation et leurs constantes de formation

Réaction	log K	Reference *
$Zn^{+2} + OH^- = ZnOH^+$	4.4	
$Zn^{+2} + 2OH^- = Zn(OH)_2^o$	9.8	Bradford, 1972
$Zn^{+2} + 3OH^- = Zn(OH)_3^-$	14.0	
$Zn^{+2} + CO_3^{-2} = ZnCO_3^o$	5.3	
$Cd^{+2} + OH^- = CdOH^+$	5.0	
$Cd^{+2} + 2OH^- = Cd(OH)_2^o$	10.6	
$Cd^{+2} + 3OH^- = Cd(OH)_3^-$	10.0	
$Cd^{+2} + CO_3^{-2} = CdCO_3^o$	4.0	Gardiner, 1974
$Pb^{+2} + OH^- = PbOH^+$	6.2	
$Pb^{+2} + 2OH^- = Pb(OH)_2^o$	10.9	
$Pb^{+2} + 3OH^- = Pb(OH)_3^-$	13.9	
$Pb^{+2} + CO_3^{-2} = PbCO_3^o$	7.5	
$Cu^{+2} + OH^- = CuOH^+$	6.3	
$Cu^{+2} + 3OH^- = Cu(OH)_3^-$	15.0	
$Cu^{+2} + CO_3^{-2} = CuCO_3^o$	6.8	Stiff, 1971a
$Cu^{+2} + 2CO_3^{-2} = Cu(CO_3)_2^{-2}$	10.0	

* The formation constants are given by Zirino and Yamamoto (1972) unless otherwise indicated / Les constantes de formation sont données par Zirino et Yamamoto (1972) sauf indication contraire.

They used titration techniques to determine the stability constants and ligand numbers of the copper carbonate complexes. The linear appearance of their graph of peak potential (DPP and DPASV) versus carbonato ligand concentration in the range from 10^{-6} to 10^{-4}M and again from 10^{-4} to 10^{-2}M (corresponding to a pH range for our samples from 6 to 10) indicated single complex formation of $CuCO_3$ in the former and some unknown carbonate species in the latter range respectively.

complexes account for a negligible fraction of total soluble metal in the pH range considered.

The hydrogen and hydroxide ion activities were given directly from the reading of pH. The individual activity coefficients for the metal ions and their complexes were calculated from the Davies modification of the Debye-Huckel expression (Davies, 1962):

$$\log \gamma_i = -0.51\ Z_i^2 \left(\frac{\mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}} - 0.3\ \mu \right)$$

where z_i is the ion charge of species i and μ, the ionic strength For our samples containing 0.1 M NaOAC with an ionic strength, μ, of 0.1 (pH > 4.7), the following values of activity coefficients are obtained using the equation above:

$\gamma_I = 0.70$ for monovalent ions or complexes

$\gamma_{II} = 0.30$ for divalent ions or complexes.

At pH = 4.7, a correction to ionic strength is necessary giving $\mu = 0.075$ and values of activity coefficients of $\gamma_I = 0.74$ and $\gamma_{II} = 0.34$. Since these values are not very different from those given for $\mu = 0.1$ and since very accurate calculations are unnecessary for the needs of our model, the former values of activity coefficients have been used.

For zinc, the following metal complexes are considered: $Zn(OH)^+$, $Zn(OH)_2^o$, $Zn(OH)_3^-$, $ZnCO_3^o$. Using the formation constants and the activity coefficients above, it is possible to express the concentrations of these metal complexes in terms of the ionic zinc concentration and the pH. For example:

$$[Zn(OH)^+] = \frac{\gamma_{II}}{\gamma_I} [Zn^{+2}] \quad 10^{pH-14} \quad 10^{4.4}$$

$$[Zn(OH)_2^o] = \gamma_{II} \ [Zn^{+2}] \quad 10^{2\ (pH-14)} \quad 10^{9.8}$$

$$[Zn(OH)_3^-] = \frac{\gamma_{II}}{\gamma_I} [Zn^{+2}] \quad 10^{3(pH-14)} \quad 10^{14.0}$$

$$[ZnCo_3^o\ ] = \gamma_{II}^2 \ [Zn^{+2}] \quad \alpha_2 \ C_T \quad 10^{5.3}$$

where C_T is the total inorganic carbon concentration and α_2 is defined by the following relation:

$$\alpha_2 = \frac{K_1K_2}{[H^+]^2 + K_1 [H^+]} + K_1K_2$$

where $K_1 = \gamma_I \times 10^{-6.3}$ and $K_2 = \frac{\gamma_I}{\gamma_{II}} \times 10^{-10.25}$

For cadmium, the following metal complexes are considered: $Cd(OH)$, $Cd(OH)_2^o$, $Cd(OH)_3^-$, $CdCO_3^o$. Using the formation constants and the activity coefficients above, it is possible to express the concentrations of these metal complexes in terms of the ionic cadmium concentration and the pH. For example:

$$[Cd(OH)^+] = \frac{\gamma_{II}}{\gamma_I} [Cd^{+2}] \quad 10^{pH-14} \quad 10^{5.0}$$

$$[Cd(OH)_2^o] = \gamma_{II} \ [Cd^{+2}] \quad 10^{2(pH-14)} \quad 10^{10.6}$$

$$[Cd(OH)_3^-] = \frac{\gamma_{II}}{\gamma_I} [Cd^{+2}] \quad 10^{3(pH-14)} \quad 10^{10.0}$$

$$[CdCO_3^o] = \gamma_{II}^2 [Cd^{+2}] \quad \alpha_2 \quad C_T \quad 10^{4.0}$$

For lead, the following metal complexes are considered: $Pb(OH)^+$, $Pb(OH)_2^o$, $Pb(OH)_3^-$, $PbCO_3^o$. Using the formation constants and the activity coefficients above, it is possible to express the concentrations of these metal complexes in terms of the ionic lead concentration and the pH. For example:

$$[Pb(OH)^+] = \frac{\gamma_{II}}{\gamma_I} [Pb^{+2}] \quad 10^{pH-14} \quad 10^{6.2}$$

$$[Pb(OH)_2^o] = \gamma_{II} [Pb^{+2}] \quad 10^{2(pH-14)} \quad 10^{10.9}$$

$$[Pb(OH)_3^-] = \frac{\gamma_{II}}{\gamma_I} [Pb^{+2}] \quad 10^{3(pH-14)} \quad 10^{13.9}$$

$$[PbCO_3^o] = \gamma_{II}^2 [Pb^{+2}] \quad \alpha_2 \quad C_T \quad 10^{7.5}$$

For copper, the following metal complexes are considered: $Cu(OH)^+$, $Cu(OH)_3^-$, $CuCO_3^o$, $Cu(CO_3)_2^{-2}$. Using the formation constants and the activity coefficients above, it is possible to express the concentrations of these metal complexes in terms of the ionic copper concentration and the pH. For example:

$$[Cu(OH)^+] = \frac{\gamma_{II}}{\gamma_I} [Cu^{+2}] \quad 10^{pH-14} \quad 10^{6.3}$$

$$[Cu(OH)_3^-] = \frac{\gamma_{II}}{\gamma_I} [Cu^{+2}] \quad 10^{3(pH-14)} \quad 10^{15.0}$$

$$[CuCO_3^o] = \gamma_{II}^2 [Cu^{+2}] \quad \alpha_2 \quad C_T \quad 10^{6.8}$$

$$[Cu(CO_3)_2^{-2}] = \gamma_{II}^2 [Cu^{+2}] \quad \alpha_2^2 \quad C_T^2 \quad 10^{10.0}$$

By expressing the ratio of the concentration of each metal complex over the concentration of its ionic species ($[ML] / [M^{+z}]$), it is possible to construct a graph of $[ML] / [M^{+z}]$ versus pH over a pH range of 4 to 9 for each of these metals. These graphs are drawn in Figure 15.

Now the total soluble metal in our model is equal to the sum of all the soluble metal species including ionic metal. For instance, this can be expressed in the following manner for zinc:

$$\begin{aligned}[Zn]_T &= [Zn^{+2}] + [Zn(OH)^+] + [Zn(OH)_2^o] + [Zn(OH)_3^-] + [ZnCO_3^o] \\ &= [Zn^{+2}]\left(1 + \frac{[Zn(OH)^+]}{[Zn^{+2}]} + \frac{[Zn(OH)_2^o]}{[Zn^{+2}]} + \frac{[Zn(OH)_3^-]}{[Zn^{+2}]} + \frac{[ZnCO_3^o]}{[Zn^{+2}]}\right)\end{aligned}$$

Using the $[ML]/[M^{+z}]$ values from Figure 15 and the total soluble metal concentrations after equilibration and filtration (M_s) from Table 5 for the tap water sample, we can calculate the ionic metal concentration for any pH value from the equation above. From this ionic metal concentration it is possible to calculate the concentrations of all the soluble metal species for the same pH.

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