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Studies of Mercury Film on Carbon Electrode
for Metal Ion Analysis Relevant to Natural Waters

by

Ibrahim K. Alzand, B.Sc., M.Sc.

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

Feb. 1981

The undersigned recommend to the Faculty of Graduate Studies
acceptance of this thesis:

"Studies of mercury film on carbon electrode for metal ion analysis
relevant to natural waters"

Submitted by Ibrahim K. Alzand, B.Sc., M.Sc., in partial fulfilment
of the requirements for the degree of Doctor of Philosophy.

Thesis Supervisor

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ABSTRACT

The project reported in this thesis originated from an interest in development of an electrode which might be used for field sampling by electrodeposition followed by stripping analysis in the laboratory after storage and transport using the sensitive differential pulse anodic stripping voltammetry (DPASV). Since stability of DPASV electrodes with time and handling is unknown, the approach to the problem has involved several preliminary stages. In particular, we assume that successful storage for reasonable time periods would be achieved, if at all, by using an enclosed "flow through" design. Thus, attention was directed to carbon electrodes which can be used to fabricate such designs.

The study includes three stages. They are:

- (1) evaluation of carbon and mercury film on carbon electrodes for analysis of Zn, Cd, Pb and Cu;
- (2) study of river-water samples at these electrodes;
- (3) study of electrode stability, especially that of the reticulated vitreous carbon, RVC, flow through electrode. On the basis of the results from these three stages a design for a field electrode has been developed which will undergo evaluation in an "in the field" instrument performance study organized by Dick, Rye and Verschingle for the summer of 1981.

For each of the first two stages of the study, interesting issues, very important to the operating performance of a large surface area electrode, such as the one in our field samples, were raised.

A detailed study of Cu at the mercury film electrode, MFE, and with a hanging mercury drop electrode, HMDE, showed that the two peaks observed in the voltammograms are due to the limited solubility

of copper in mercury. The more negative cathodic peak, labelled "I-Cu" below, is assigned to undissolved copper, the second peak at the more anodic potential which we call "II-Cu" is assigned to amalgamated copper. The height of each of these two copper peaks and their relation to each other proves to be a function of the Cu^{2+} concentration, the plating time, deposition potential, the thickness of the mercury film (in case of MTFE), the chloride concentration present in the solution and presence of organic matter in river-water samples. A detailed examination of these variables has been made with a HMDE's and MTFE's. Numerous ambiguities in recent literature are resolved.

A survey of DPASV signals for copper in a variety of conditions distinguish the circumstances which are associated with two problems in copper determination. The affect of Cl^- on the mercury wave (which in turn effects the relative apparent peak heights, peak potentials and widths of the two copper signals) is distinguished from the Cl^- role at higher concentrations in producing chlorocopper complexes. Errors of earlier papers are corrected. Data are presented on two related issues: the factors in a natural water sample that confuse the use of ASV as a probe for Cu speciation; and the effect of high Cl^- concentration on Cd and Pb signals.

Some observations on ASV signals from a natural water sample subjected to various pretreatments reveal a variety of effects related to the medium effects which were identified in the synthetic samples. It is interesting that the effects attributed to " organic " matter in

the natural sample are sufficiently qualitatively similar to those of Cl^- that the work on Cl^- provides a good background for understanding the effects of organics in natural samples. The results emphasize the adsorption of organics on the electrode rather than their role in forming complexes in solution.

The following are the scientific contributions emerging from the work reported :

- (a) The phenomena of dual copper signals have been accounted for in suitable detail.
- (b) The causes leading to peak shift, peak broadening and variable peak heights have been identified. This has implications in differentiation of trace metal species in natural waters.
- (c) An electroanalytical method has been developed which has a sensitivity higher than the conventional techniques.
- (d) Utility of the method for field sampling followed by storage has been indicated. The method allows a simple device to be used in the field while retaining sophisticated DPASV for the analysis.

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Finally, I should like to dedicate this thesis to my family, first my wife, Maysoon, and to my children, Khotiaba, Enass, Jumana and Aseel.

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(I.1) Introductory Remarks

Concern over environmental pollution has increased the need for accurate, precise and simple means for the chemical analysis of trace constituents in natural waters. Emphasis is shifting towards "in situ" or "on site" probes in order to avoid expensive sample collection and time delays, with consequent degradation of grab samples intended for laboratory based analysis. This is particularly important where monitoring of potentially toxic materials is required [1].

Similarly, it is increasingly realized that total concentration measurements are only of limited use and that toxicity and geochemical activity are critically dependent on the speciation of the various solutes. Electrochemical techniques are sensitive to the chemical environment of the metal ions to be analysed and often provide a more useful analysis [2]. In this regard anodic stripping voltammetry, ASV, has proved to be a remarkably sensitive tool for the determination of heavy metals or anions at trace and microtrace concentrations.

(I.2) The Anodic Stripping Method

The sensitivity of ASV is achieved through a preconcentration process in which the electro-active species is reduced by an applied potential more negative than the voltammetric half-wave potential of the species, and the reduced metal is deposited onto solid electrode or by formation of an amalgam in a mercury electrode. At sufficiently large over-potential, the rate of deposition of various metal ions is determined by their respective concentrations, the diffusion and hydrodynamic

properties of the electrolytic solution, and the electrode surface area that has been used [3-5]. The deposition time can be adjusted to produce the required sensitivity. The metals are oxidized (stripped) from the electrode by scanning the potential anodically. The resulting voltammogram exhibits an anodic peak at a potential which identifies the metal ion. The peak height is a quantitative measure of metal ion concentration in the solution [4]. The stripping step may be implemented with any one of several voltage scan routines including linear sweep, pulse, and differential pulse. Similar information is obtained in each case but pulse techniques can improve signal-to-noise ratio and enhance sensitivity in appropriate circumstances. If a linear potential scan is used, the stripping peak current, i_p , for hanging mercury drop electrode, HMDE, is given by [6].

$$i_p = 2.72 \times 10^5 n^{3/2} A D^{1/2} C_R v^{1/2} \quad (1)$$

where C_R is the concentration of the analyte in the mercury drop (mole cm^{-3}), v is the scan rate (volt s^{-1}), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and A is the electrode surface area (cm^2). The peak potential, E_p , is

$$E_p = E_{1/2} - \frac{1.1 RT}{nF} \quad (2)$$

where $E_{1/2}$ is the voltammetric half-wave potential, and n , F , R and T have their usual meanings in standard physical chemistry texts. As equation (2) shows, E_p is independent of the instrumental parameters or the concentration of reducible substance, and is 0.028/ n volt more cathodic than $E_{1/2}$ at 25° [6].

For mercury thin film electrodes, MTFE's, the theory developed by de Vries and Van Dalen [7] characterizes a reversible process of the dissolution of metal for a very thin film, and may be applied under condition of a slow linear potential scan. The relationships for the stripping peak current, i_p , peak potential, E_p , and the peak width at half height, $b_{1/2}$, are given by:

$$i_p = 1.1157 \times 10^6 n^2 A C_R L v \quad (A) \quad (3)$$

$$n(E_p - E_{1/2}) = -1.43 + 29.53 \log H \quad (mV) \quad (4)$$

$$nb_{1/2} = 75.53 \quad (mV) \quad (5)$$

where L is the mercury film thickness in (cm) and H is dimensionless parameter defined by:

$$H = (L^2/D) (nF/RT) v \quad (6)$$

The equation (3-5) should be accurate for H values $\leq 1.6 \times 10^{-3}$.

Roe and Toni [8] have also derived peak current (i_p) and peak potential (E_p) equations for ASV from MTFE under similar conditions of a slow linear potential scan. Their assumptions include negligible diffusion in the mercury film and good solution stirring. Further approximations are made in the derivation to yield:

$$i_p = nFALC_R v \phi e^{-1} \quad (7)$$

$$E_p = E^0 + \frac{2.3}{n} \log \frac{\delta L v \phi}{D} \quad (8)$$

where $\beta = nF/RT$, e is the base of Napierian logarithms, E^0 is the formal electrode potential, and δ is the thickness of the diffusion layer. In stirred solution, " δ will be affected by the stirring rate, cell geometry and electrode design" [4].

As can be seen from equations (3) and (7), the peak current (i_p) is a function of the scan rate v . Thus increased scan rate should result in higher sensitivity and improved resolution [3].

However, increasing the scan rate severely degrades the signal-to-noise ratio of the response. The total current flowing through the system is [9].

$$i_t = i_f + i_c + i_b \quad (9)$$

where i_f is the faradaic current due to the oxidation of the species being analyzed, 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 oxidation of impurities or decomposition of the electrolyte. It is evident that both i_c and i_b contribute to electrochemical noise in the system. The charging current is given by [6]

$$i_c = A v \, dQ/dE \quad (10)$$

where dQ/dE is the differential double layer capacity. Thus, increasing v and/or A to maximize the absolute signal, induces an increase in the charging current as well. "This imposes a practical limitation on the improvement that can be realized by increasing A and v " [3] in linear sweep techniques.

Recently, various wave form techniques have been used with the aim of enhancing the sensitivity of ASV. These include the use of phase-sensitive ac [10,11], square wave [12,13], stair case [13,14] and pulse and differential pulse techniques [13,15-17]. Among these, Differential pulse anodic stripping voltammetry, DPASV, is the most sensitive. The increase in sensitivity is based on the high level of discrimination against the charging current and this enhances the signal-to-noise ratio.

Differential pulse anodic stripping voltammetry (DPASV) consists of superimposing short potential pulses of 5 - 100 mV amplitude on a slow linear potential ramp. Generally the pulses have a duration of 50-100 ms and a repetition rate of 0.5-10 s. The linear potential scan rate is of the order of $2-10 \text{ mV s}^{-1}$ so that the ramp potential does not change significantly during the life of the pulse. The current is sampled just before the application of the potential pulse and again near the end of the pulse. As noted earlier the current in each instance consists of charging, faradaic and background components. If the applied pulse changes the potential to a value where equilibrium between oxidized and reduced species is shifted, the two sampled currents will differ mainly in the faradaic components. A plot of Δi (difference between second and first current samples) vs. potential is analogous to a differential polarogram where the peak potential is diagnostic of the electroactive species and the peak height is proportional to its concentration. Thus the noise due to capacitive and background currents is minimized, improving the signal-to-noise ratio and consequently enhancing the sensitivity [4,5]. Moreover, the analyte oxidized during the

pulse may be redeposited at the end of the pulse if the potential returns to a level at which reduction occurs. Thus a significant portion of the stripped analyte can make repetitive contributions to the measured signal, further enhancing the sensitivity [3].

(I.3) Choice of Working Electrodes

A number of materials have been used as working electrodes for ASV. The most popular systems use mercury in some form. Solid electrodes of platinum, gold, silver, and carbon have been used [9]. Generally poor results are obtained from depositing samples on solid metal electrodes. Reproducibility is poor due to surface contamination and if more than one metal is deposited problems arise due to peak overlapping [4,18]. Moreover, difficulties may arise from the tendency of some noble metal electrodes to form intermetallic compounds [3]. However solid electrodes have been used for the determination of metals that have oxidation potential more positive than that of mercury (e.g. Ag) [18] and for the determination of mercury as well [19,20].

The hanging mercury drop electrode is one of the most popular electrodes for ASV. This electrode offers simplicity and reproducibility when properly used [21-24]. Several advantages of the HMDE make it a desirable electrode for DPASV. Generally, the peak height is less dependent on composition of supporting electrolyte, reproducible results can be obtained [21,24], and fewer interferences are seen because the greater volume of the hanging mercury drop which leads to less intermetallic compound formation [9].

Mercury thin film electrodes were first developed by Matson et al. [25]. These electrodes offer a higher plating efficiency and sensitivity than can be achieved with HMDE owing to a large surface area-to-volume ratio and to the efficient transport related to relatively higher rates of solution stirring or electrode rotation. Also they offer the same potential range as the HMDE [24]. In addition to having higher sensitivity, mercury films can provide better resolution since diffusion from the bulk of the film is fast [25].

Several solid materials have been used as substrates for mercury films in ASV. These include Pt, Au, Ag, Ni and carbon. Carbon is preferred compared to metallic materials whose behaviour is complicated by their finite solubility in mercury and the tendency of the metal to form intermetallic compounds [21,26]. Widely used forms of carbon for mercury thin film substrates include wax-impregnated graphite, glassy carbon and vitreous carbon electrodes [25,27-31] some examples follow. Matson et al. [25] succeeded in plating a stable mercury film on wax-impregnated graphite and optimum conditions were established from examining the mercury film by microscopic measurements. Crosman et al. [27] reported a mercury film on wax-impregnated graphite electrode not subject to memory effect and with sensitivity to metal ions dependent on the thickness of the mercury film. Florence [28] described a method of forming a mercury film "in situ" with a glassy carbon electrode. This electrode improved resolution of Cd^{2+} , In^{3+} , Pb^{2+} and Cu^{2+} peaks compared with the results obtained at HMDE and MTFE prepared "in situ" at pyrolytic graphite electrode. Copeland et al. [29] examined six types

of graphite having diverse physical properties as substrates for a mercury film, they reported that non-impregnated vitreous carbon is the most suitable.

For the analysis of acidic solutions, graphite electrodes have been modified by epoxy resins [30], impregnated with polymer resins cured under radiation [31], or impregnated with styrene followed by irradiation with ^{60}Co [32].

Tubular mercury-covered graphite electrodes designed for ASV to suit the analysis of flowing solutions have been the subject of several recent studies [33,34]. The effects of several variables such as plating potential, plating time, and flow rate were studied on the determination of Zn in seawater [33] and Thallium in the presence of EDTA to mask other metals [34]. Graphite cloth as a substrate for mercury film has been exploited by Wang and Ariel [35] for monitoring of traces of copper and cadmium in flowing solution. Recently, flow-through electrodes have been fabricated from reticulated vitreous carbon, RVC, [36,37]. This material has low electrical resistance, large surface area, and physically continuous structure [36]. ASV has been accomplished using a porous mercury-coated electrode of RVC in a flow-through configuration [38].

(I,4) Speciation in Water and ASV Studies

The chemical speciation of trace heavy metals in the aquatic environment plays a significant role in many chemical and biological studies. In this regard, emphasis has been placed on trace metal complexation by various organic and inorganic compounds and the distribution

and availability of these complexes either in a soluble form or adsorbed on colloidal particles [39,40]. Electrochemical methods can indicate such speciation [40] although aqueous solution phase speciation is not the only factor when a metal also exists in reduced form in the electrode during some part of the analysis process.

Various separation methods have been used to separate dissolved metal ions from metal associated with colloids in natural waters. Many workers [41-44] have studied a large number of elements in river, lake, and seawaters using dialysis, ultrafiltration, centrifugation and electrophoresis. Their results indicated that the chemical form and the distribution depend mainly on the oxidation state of these metals, concentration of ligands present, and the pH of the sample. Thus, most of the low oxidation state metals exist in water predominantly as simple cationic species. In contrast, the high oxidation state metal ions (e.g. Al^{3+} , Th^{4+}) are mostly adsorbed on or in colloidal particles.

Ion-exchange techniques have been applied to study metal speciation in natural waters. The most interesting work is associated with studies involving chelating resins (e.g. chelex-100). Florence and Batley [45,46] studied the retention of Zn, Cd, Pb and Cu from seawater on a chelating resin (Chelex-100). The results indicated that a significant fraction of these metals is not retained by a chelating resin. ASV results led them to the conclusion that most of the trace metals which are not removed by the resin are associated with organic and inorganic colloidal particles [45].

The chemical speciation of trace heavy metals in natural water is quite obviously a very difficult analytical problem. Sensitive analytical techniques such as neutron-activation analysis and atomic-absorption spectrophotometry (AAS) determine the total concentration of the metal available in the natural sample. Accordingly these techniques are not applicable to differentiate the chemical forms of trace metal in natural waters without prior separations [39]. Electrochemical techniques, particularly potentiometry with selective-ion electrodes and anodic stripping voltammetry are applicable to speciation studies [40] without prior separations.

Few potentiometric studies have been made on trace metal complexation in natural waters. This is due to the limited sensitivity of selective-ion electrodes, which respond only to uncomplexed metal ions and at a level of concentrations higher than the level of trace heavy metal found in most natural water [40]. A comprehensive study in this field was done by Stiff [47], which presented an analysis scheme for copper complexation in the soluble forms present in polluted fresh waters using a copper ion-selective electrode. He reported that "much of the copper present in river-water was associated with suspended solids and that soluble copper would consist almost entirely of complexed forms" [47]. Gardiner [48] used a cadmium ion-selective electrode to study the labile complexes of cadmium in synthetic and real samples. The concentrations usually encountered in natural waters are generally lower than the detection limit of the cadmium ion-selective electrode but the extrapolation

of the conclusions to lower concentrations was believed to be reliable.

Recently, much of the work concerned with the speciation of trace metals in natural waters has been done with ASV. Most studies have used a procedure to differentiate between the "labile" (electro-active) and the strongly "bound" (electro-inactive) metals in water samples [39,45,46,49]. The "labile" form of Zn, Cd, Pb and Cu can be measured directly by ASV after adjustment of the sample with an appropriate amount of buffer at its original pH or in acidic solution. The measured signal is then assumed to be related to a sum of the simple hydrated metal ion and the weak complexes and colloids which are dissociated at the electrode surface. The total metal is usually measured by ASV after digesting the sample by UV irradiation [49], persulphate oxidation [39], or acid digestion [45,46]. The difference between total and labile metals represented the "bound" form which may be regarded as strong inorganic and organic metal complexes and metal adsorbed on colloidal particles [50] which are not dissociated at the electrode surface.

There is, of course, a potential flaw. Factors associated with the amalgam phase or with interference by material adsorbed on the electrode can mask metals and lead to an erroneous assignment of some of the total metal to "bound" forms. Clear recognition of some instances of this flaw forms the subject of a significant part of the report below.

Florence and Batelly [50] developed a model for chemical speciation of Cu, Pb, Cd, and Zn in natural waters using ASV in conjunction with simple sample treatment schemes. They have thus classified metal species into seven discrete groups. The sample treatment scheme is meant to reduce the ambiguities we mentioned above.

Ernst, Allen, and Mancy [75] summarized the use of ASV for study of speciation in 1975. They note that equivalent medium effects on differential pulse polarography, DPP, and DPASV signals would indicate an effect only on the cathodic step, such an effect is retained in the "memory" of the film to affect the anodic stripping since it reflected the elimination of metal in "un-labile" and non-reducible metal complexes with ligands, colloids and particles from the cathodic deposition. It is a fairly simple effect and, if isolable, is an instance where the speciation information from ASV is straightforward. The "labile" forms of Zn, Cd, Pb and Cu can be measured directly. "Non-labile" metal is estimated only after sample pre-treatment. Unfortunately, Ernst, Allen and Mancy [75] showed that significant medium effects occur during the anodic step as well as the cathodic step. This would not produce a serious limitation if only solution species were at issue. However, one of the main points raised by some of our work reported here is that effects in the mercury phase and on the electrochemistry of mercury are important. These effects are not simply related to solution speciation and greatly complicate interpretation of ASV results in terms of speciation. Caution about such specious arguments is one of our clear messages.

(I.5) Problems and Prospects of ASV

In preparation for presentation of our results we give a brief summary of problems we may encounter using ASV. A few words about the scope of ASV will also help to put our subject matter in perspective. All ASV techniques involve analysis in a supporting electrolyte. The electrolyte may be simply an acid medium, or it may be a buffer system particularly when control of pH is essential. Supporting electrolyte concentrations which are consistent from sample to sample are generally essential. Lower ionic strengths should be avoided because the large potential drop across solution of high resistance may lead to incomplete plating of some metals [51]. Supporting electrolyte concentrations of 10^{-2} - 10^{-3} M are sufficient in DPASV [52].

ASV suffers the same interferences as direct polarography. Overlapping peaks cause problems in the determination of two metal ions having similar peak potentials (e.g. Bismuth and Antimony) [53]. The stripping potentials can be modified to some extent by the choice of the supporting electrolyte and/or the choice of electrode [53]. Intermetallic compounds formed in the mercury electrode may cause low stripping current [27,54]. These effects are most noticeable in MTFE systems. Metal with the most negative deposition potentials (e.g. Zn, In) are most severely affected. Modulated stripping procedures help to reduce this problem because their enhanced sensitivity enables lower amalgam concentration to be used. Several reports [9,55-58] have dealt with the well known problem of copper-zinc intermetallic formation. Kemula *et al.* [55] were the first to recognize that Cu-Zn compounds interfered with the ASV

analysis of Cu and Zn. The observed effect was a decrease in sensitivity of ASV for Zn when Cu was present. Most of the reports in this area estimated that the formation of the Cu-Zn compound causes a reduction in the zinc peak and an enhancement of the copper peak. This is due to the fact that the Cu-Zn intermetallic strips at a potential which cannot be resolved from that of Cu. Copeland *et al.* [58] suggested the addition of metal (e.g. Gallium or Thallium), which appears to form intermetallic compounds itself but not to cause interference.

Recently ASV performed in a twin-electrode thin layer cell [59,60] eliminated Cu-Zn interference by exhaustive deposition of Cu on one electrode, the second electrode was used to complete the Zn or Zn and Cd determination.

ASV provides an analytical method capable of measuring ions in solution at concentration as low as ng ml^{-1} . This is the level of concentration of most of the heavy trace metals in natural waters, and direct determination of some of them may be possible by this method. The simultaneous determination of Zn, Cd, Pb, and Cu in a variety of natural waters by ASV has been studied at various pH [61,62]. The results indicated that the determination of zinc ions in acid solution is not feasible because the potential for the reduction of zinc ions at the HMDE or MTFE is more negative than, or equal to, the potential for the reduction of hydrogen ions. They suggested a neutral or alkaline medium be used for the simultaneous determination of Zn, Cd, Pb and Cu. On the other hand Batley and Florence [63] found that the sensitivity of the ASV method for Zn, Pb and Cu will be enhanced in acidic solution

and decreases at high pH. They suggested a seawater buffered with acetate to pH 4-5 to be a convenient medium to measure labile metal concentration. Studies of Cd determination in aqueous solution of humic acid in weak basic, acidic and weak acidic media showed that ammonium acetate-acetic acid buffer is most suitable for ASV [64].

The analysis of Cu is often complicated by halide ions in the sample or chloride ions from the reference electrode or the salt bridge. The copper dissolution peak may be obscured or partly obscured by the anodic dissolution of mercury [65]. In such instances the determination of copper requires either a change of medium or the addition of a strong complexing agent specific to copper. The addition of 1×10^{-4} M thiocyanate solution permits copper to be determined in the presence of halide ions. Ariel *et al.* [66] used a modified procedure in which Cu from Dead Sea brine was stripped after transfer of mercury drop electrode into a second medium. Medium-exchange was employed to reduce the possibility of interference of elements having similar peak potentials in sea water.

An interesting approach has been achieved by extracting copper from seawater through a reduction onto HMDE, the mercury drop content of copper was analyzed within a filament atomizer [67] of atomic absorption spectrometer. Edwards and Bregioni [68] presented another procedure in which copper was plated on MTFE and completely stripped into a small volume of distilled water. This water was then analyzed for Cu by flameless AAS providing yet another illustration of the use of a combination of techniques for achieving better sensitivity.

A survey of metals and samples analyzed using HMDE and MTFE combined with DPASV [22,29,60,69-71] reveals the enormous possibilities of analysis of trace constituents in a wide variety of samples including seawater, environmental samples, and biological samples. Pretreatment of the samples does not always constitute an essential step in these measurements. The inclusion of such a step becomes necessary generally depending upon the nature of the ions, presence of possible interfering ions or some interfering organic matter.

DPASV with HMDE has been used for the direct and simultaneous determination of Zn, Cd, Pb, Cu, Sb and Bi at their natural levels in seawater [69]. The optimal instrumental parameters were described. The determination of Bi in seawater is made possible by applying an initial potential of -0.150 V, which is sufficiently negative for enrichment, while reduction of Cu is negligible. For more negative deposition potential, there is simultaneous reduction of Cu, Sb and Bi. Lund and Onshus [22] have used DPASV with HMDE and MTFE prepared "in situ" for investigation of various instrumental parameters and established optimized conditions for the direct determination of Cd, Pb, and Cu in seawater. The results compared favourably with those obtained using linear sweep stripping voltammetry.

As we approach the present experiments, we recall once more that DPASV with MTFE's has been widely used for the determination of trace heavy metal ions in a variety of samples [29,60,70,71]. Copeland *et al.* [29] have investigated and optimized instrumental and chemical conditions for the direct determination of Pb and Cd in natural waters, blood, blood plasma, and urine. Lund and Erikson have also used DPASV for simultaneous

determination of Cd, Pb and Cu in different types of urine samples [70]. The results indicate that urine can be analyzed directly for Cd and Pb without pretreatment of the sample. DPASV at thin layer electrodes was demonstrated with Pb, Cd, Zn, Cu and Tl [60]. Typical calibration curves are linear over a range of 30 to 600 ng ml⁻¹. With a detection limit of 10 ng ml⁻¹ samples of blood, soybean and oyster were analyzed for Pb [60]. DPASV was used for the determination of Cu in palm oil after pretreatment [71].

MEDIUM EFFECTS ON DETERMINATION OF COPPER BY DIFFERENTIAL PULSE
ANODIC STRIPPING VOLTAMMETRY (DPASV)

(II.1) Introduction

A survey of DPASV signals for copper in a variety of conditions distinguish the circumstances which are associated with two problems in copper determination. The role of Cl^- in influencing the mercury wave (which in turn affects the relative apparent peak heights and widths of the two copper signals arise from Cu(Hg) and undissolved Cu (metal)) is distinguished from the role at higher chloride concentrations in solution in producing chlorocopper complexes. Data are presented as two related issues : 1. The factors in a natural water sample that confuse the use of ASV as a probe of Cu speciation; and, 2. the effects of high Cl^- concentration on Cd, Pb and Zn signals.

In a number of studies, problems with multiple signals for Cu in anodic stripping voltammetry have been recognized [24, 56, 72]. Peak shifts, widths, and doubling have been associated with two distinct phenomena. The first is formation of chloride complexes [56, 72], the second is the limited solubility of Cu (metal) in Hg (liq.) [24, 72]. Discussion of the first factor has recognized problems with exact stoichiometry and raised questions about the reaction. Discussion of the second factor has not included exploration of ranges of medium composition that leads to domination

by one factor or the other. The present work explores the role of medium when hanging mercury drop electrode, "in situ" deposited thin mercury film, and preformed thin film electrodes are employed for ASV determinations of Cu, Pb, Cd, and Zn in the differential pulse mode. In particular, the role of Cl^- in changing the Hg waveform is documented and its effect on Cu signals from both $\text{Cu}(\text{Hg})$ (amalgam) and $\text{Cu}(\text{m})$ (the solid metal) is documented. The importance of changes in Hg waveform is an important additional influence that has not previously been discussed.

The results of the exploration of medium effects are important to understanding the use of ASV in speciation studies on natural waters. Some observations on ASV signals from a single natural water sample subjected to various pretreatments reveal a variety of effects related to the medium effects on synthetic samples. The explanation for these parallels is not obvious.

(II.2) EXPERIMENTAL

(II.2.1) Apparatus. Differential pulse anodic stripping voltammetry (DPASV) was carried out in a conventional manner using a PAR 364 Polarographic Analyzer equipped with a standard PAR cell for 3 electrodes and nitrogen purge. Voltammograms were recorded using a Fisher recordall (Series 5000).

Three types of working electrodes were employed.

- (i) hanging mercury drop electrode (HMDE, PAR model 9323),
- (ii) mercury thin film electrode (MTFE) with 'in situ' mercury deposition (MTFE in situ) and
- (iii) MTFE predeposited (MTFE preformed).

The films were deposited on wax impregnated graphite supplied by PAR instruments (model 9319). This electrode has a diameter of 0.625 cm (0.30 cm^2 surface area). The end was polished and the remainder of the lower half of the rod was covered with a tight fitting teflon tube pressed on from the polished end. The electrode was polished before each use with fine emery paper, washed with ethanol and wiped with lens tissue. The reference electrode was SCE connected to the cell via a salt bridge filled with either 1M KNO_3 or 0.5 M NaNO_3 and terminating at a vycor frit sealed into a length of heat shrinkable teflon tubing. The counter electrode was a Pt wire. pH was measured with an Orion Model 701A digital analyzer.

(II.2.2) Materials: Mercury was triply distilled and was transferred only with a clean, dry siliconized capillary. Hydrochloric and nitric acids were Ultrex grade (J.T. Baker). KCl , KNO_3 , NaNO_3 , sodium acetate, acetic acid, citric acid, and ammonium hydroxide were reagent grade.

All solutions were prepared from deionized water purified from "tap" distilled water by passing through a high efficiency mixed bed ion exchanger followed by distillation from alkaline permanganate in all glass apparatus. Solutions were stored in preleached linear polyethylene bottles.

The Hg(II) plating solution was prepared by dissolution of triply distilled Hg in a minimum amount of Ultrex HNO_3 and dilution with deionized water to give $0.01\text{M Hg}(\text{NO}_3)_2$ stock. Stock standard solutions of metals were prepared by dissolution of one gram of pure metal $> 99.9\%$ (previously cleaned with acid and dried) in a minimum amount of 8M Ultrex HNO_3 followed by dilution with $1\% \text{ V/V HNO}_3$ to $1000 \mu\text{g ml}^{-1}$.

More dilute secondary stock solutions were prepared by diluting these solutions just prior to use. N_2 gas was scrubbed of residual O_2 by passage through a gas washing bottle containing V(II) and a second containing the supporting electrolyte of the experiment in question. Supporting electrolyte and standard solution were transferred to the cell using Eppendorf 500-1000 and 20-200 μl pipettes with disposable tips. All glassware was leached with 6M HNO_3 between uses.

(II.2.3) Mercury Film Deposition and Procedures: Mercury films were preformed on polished graphite electrodes from well-stirred 0.02M acetate solutions containing 1×10^{-4} M Hg^{2+} by depositing at -0.8V for periods depending on the mercury film thickness required. After plating, the electrode was held at -0.02V for 10 mins with stirring. This was to ensure that any contaminants co-deposited with mercury were stripped.

The preformed mercury films appeared to remain stable and to yield reproducible results during the course of a day, perhaps because the electrodes were kept in distilled water (oxygen free) between experiments without exposing the electrodes surface to air. The mercury film could be removed at the end of a series of experiments by wiping the electrode surface with a paper tissue, followed by polishing the electrode for the next plating.

The average mercury film thickness was estimated by using the relation [53]

$$L = i_l t W / n F A d \quad (11)$$

where i_l = limiting mercuric ion deposition current in μA

W = atomic weight of mercury (200.6)

t = deposition time (s)

n = number of electrons involved in reduction (2)

A = electrode surface area (0.30 cm^2 for PAR electrode model 9319)

d = density of mercury (13.56 g cm^{-3}).

From the limiting current of $19.6 \mu\text{A}$ obtained for the electrode, the average mercury film thickness after plating for 10 mins was estimated at $300 \text{ \AA}$.

MTFE's were also prepared "in situ" by adding $100 \mu\text{l}$ of 0.01M Hg^{2+} to 25 ml of the buffered sample pH 5.5 (final Hg^{2+} concentration $4 \times 10^{-5}\text{M}$). Prior to plating and during deaeration, the electrode was held at $+0.5\text{V}$ to prevent gas bubbles adhering to the electrode surface. Plating of mercury and the metal ions being studied was carried out at -1.0V or -1.25V for periods depending on the concentration of the metal ions. After the stripping process the electrode was held at $+0.5\text{V}$ for 2 min, following which the electrode was wiped with tissue paper and was then ready for the next determination.

From the limiting current of $11.2 \mu\text{A}$ obtained for the electrode with $4 \times 10^{-5}\text{M}$ Hg^{2+} solution, the average mercury film thickness estimated from equation (11) after 5 min plating was $85 \text{ \AA}$.

In the case of the HMDE, the siliconized capillary was filled with triply distilled mercury before each experiment and 0.03 cm^2 mercury drop was used for each run. Relatively short deposition time was used to avoid penetration by test solution.

With all types of electrodes, deposition of Cd, Pb, and Cu was made at -1.0V and at -1.25V for Zn with stirring for 5 min. The DPAS voltammograms were recorded from a quiet solution after 30s using 5 mV s^{-1} scan rate and 50 mV modulated amplitude.

During the stripping process, N_2 gas was continuously passed

over the solution. All peak currents reported in this study have been corrected for the additional factor of 10 gain of the PAR Polarograph Model 364 operating in the differential mode. Thus, a nominal peak current of $50 \mu\text{A}$ is reported in this study as $5 \mu\text{A}$.

(II.3) Results

In early experiments, KCl was used in the salt bridge. A change from saturated KCl to 1M KNO_3 or 0.5M NaNO_3 affect the copper in MTFE's. Two Cu peaks appear: The first (cathodic side) at -0.21V has a half width, $b_{1/2}$, of 50 mV ; the second or more anodic potential at -0.08V has a half-width of 45 mV . The height of each of these two Cu peaks and their relation to each other proves to be a function of the thickness of the mercury film, the plating time for "in situ" electrodes, deposition potential, the chloride ion concentration, and the Cu^{2+} concentration. These observations stimulated a review of the literature and a detailed examination of these variables at HMDE's and MTFE's.

Figure 1 shows the dependence on Cu concentration at MTFE. Note that the -0.08V peak (II-Cu) dominates at low (1 ng ml^{-1}) concentration but that the -0.21V peak (I-Cu) grows in faster as the concentration rises. Behaviour on the HMDE is similar (Fig. 2) but with lower sensitivity [73]. An analysis of the contribution to the total Cu signal from each peak as Cu concentration rises on both MTFE and HMD electrodes is given in Figures 3 and 4 respectively. Note that the sum of peak currents, i_p , for the two peaks (I-Cu + II-Cu) is linear in added Cu.

POTENTIAL, E/V

Figure 1. DPAS voltammograms obtained at MTFE's prepared "in situ" for synthetic samples containing 1, 4, 8 and 16 ng ml^{-1} $[\text{Cu}^{2+}]$ from a to d respectively. 0.3 cm^2 electrode area, 85A MF thickness, 5 min. deposition time, -1.0V initial potential, 5 mV s^{-1} scan rate.

Figure 2. DPAS Voltammograms obtained with a HMDE for synthetic samples. 0.03 cm^2 drop area, 5 min. plating at -1.20V, 5 $mV\ s^{-1}$ scan rate.

Figure 3: Calibration curves of I Cu, II Cu and total Cu obtained at MTFE for synthetic samples. 0.3 cm^2 electrode area, 85A MF thickness, 5 min deposition time, -1.0 V initial potential, 5 mVs^{-1} scan rate.

Figure 4: Calibration curves of ICu, IICu, and total Cu obtained with HMDE for synthetic samples. 0.03cm^2 drop area, 5 min-plating at -1.20 V .

Mercury film thickness in MTFE's was also a parameter. When copper at 1 ng ml^{-1} is deposited for 5 min. at -1.0 V in a preformed MTFE of approximately $60 \text{ \AA}$ thickness, the peaks of I-Cu and II-Cu have i_p values of 0.70 and $1.30 \text{ \mu A}$, respectively. As the film thickness was increased to $420 \text{ \AA}$ in 4 steps between 60 and $420 \text{ \AA}$, the height of the I-Cu peak decreased reaching "zero" at $420 \text{ \AA}$ as illustrated in Fig. 5. conversely, the II-Cu peak height increased to a maximum value of $2.30 \text{ \mu A}$ (the sum increased slowly from 2.00 to $2.30 \text{ \mu A}$). When "in situ" film formation is used, film thickness and quantities of copper plated increase together. Fig. 6 shows that the second factor ultimately dominates. The change in peak height with plating time for $1 \text{ ng ml}^{-1} \text{ Cu}$ is similar to the change of peak height with copper concentration (long plating times finally can deplete Cu). Note the non-linearity beyond 60 mins.

The dependence of I-Cu and II-Cu peak current on deposition time at a HMDE's of identical surface area was also studied. Table I and Fig. 7 illustrate the results obtained for three concentrations of Cu with various deposition times. The peak currents of the solid phase (I-Cu) grow faster compared to those from amalgam phase (II-Cu) as the deposition time increases. The Fig. shows that the ratio of $i_p(\text{I-Cu})/i_p(\text{II-Cu})$ for each copper concentration increases linearly with increasing deposition time, where the slope of $i_p(\text{I-Cu})/i_p(\text{II-Cu})$ increases steeply with concentration. These observations support our previous conclusion about the limited solubility of copper in mercury. The ratio of precipitate to amalgam may be determined by the solubility.

POTENTIAL, E_p , V

Figure 5: DPAS Voltammograms obtained with a preformed MTFE's for $1 \text{ ng ml}^{-1} [\text{Cu}^{2+}]$ with different film thicknesses 60, 120, 180, 300, and 420 Å respectively. 5 min-plating at -1.0V.

Figure 6: Dependence of peak current on deposition time obtained with a MTFE's prepared "in situ" for 1 ng ml^{-1} Cu in acetate buffer at pH 5.6.

Table I

Dependence of I-Cu and II-Cu peak currents and their ratio on deposition time. The results obtained with a HMDE for synthetic samples contain 3, 5 and 8 ng ml⁻¹ of Cu. 0.03 cm² drop area, -1.0 V initial potential and 5 mV s⁻¹ scan rate.

Dep. time, min.	$i_p(\text{ICu}), \mu\text{A}$	$i_p(\text{IICu}), \mu\text{A}$	$i_p(\text{ICu})/i_p(\text{IICu})$	$[i_p(\text{ICu})/i_p(\text{IICu})]/\text{min}$
a) 3 ng ml ⁻¹ Cu				
2.5		0.060		
5.0	0.054	0.085	0.63	0.126
7.5	0.070	0.092	0.76	0.101
10.0	0.110	0.115	0.96	0.096
15.0	0.185	0.150	1.23	0.082
20.0	0.240	0.160	1.50	0.075
			average	0.096
b) 5 ng ml ⁻¹ Cu				
2.5	0.072	0.110	0.65	0.260
5.0	0.145	0.158	0.91	0.182
7.5	0.190	0.170	1.11	0.148
10.0	0.270	0.195	1.38	0.138
15.0	0.400	0.218	1.83	0.122
20.0	0.570	0.260	2.19	0.110
			average	0.160
c) 8 ng ml ⁻¹ Cu				
2.5	0.170	0.190	0.89	0.356
5.0	0.310	0.235	1.32	0.264
7.5	0.480	0.280	1.71	0.228
10.0	0.600	0.300	2.00	0.200
15.0	0.970	0.350	2.77	0.184
			average	0.246

Fig. 7: Dependence of the current ratio ($i_p(\text{ICu})/i_p(\text{IICu})$) on deposition time. The results obtained with a HMDE for 3, 5, and 8 ng ml⁻¹ of copper. 0.03 cm² drop area, -1.0 V initial potential and 5 mV s⁻¹ scan rate.

if the rate of attainment of equilibrium is fast, in a thin layer at the surface of the mercury drop. However, the overall values are determined by the rate of diffusion into the mercury drop bulk.

Later, for example, we report that the ratio of solid to amalgam decreases after storage. This is a consequence of redissolution after the an amalgam concentration becomes uniform. similar effect is seen in the last column of Table I where values of $[i_p(\text{I-Cu})/i_p(\text{II-Cu})]/\text{min.}$ decrease with increasing deposition time.

Now the effect of chloride ion must be examined. In the case of "in situ" MTFE analysis, the most revealing experiment is presented in Fig. 8 where the effects on copper peaks of 0.0 , 5.0×10^{-4} , 1.0×10^{-3} and 2.0×10^{-3} M KCl are recorded. The I-Cu peak is affected slightly at most. The II-Cu peak "disappears". A little careful inspection of the figure, however, reveals that it is disappearing into the large mercury wave which is advancing cathodically with increasing Cl^- concentration. There is no evidence available for a change in the II-Cu height because that peak cannot be resolved clearly from the cathodic wave of mercury at Cl^- concentration $\geq 5 \times 10^{-4}$ M. In this concentration range, there is little evidence for Cl^- complexation of Cu (see nearly constant I-Cu peak height). Rather, there is loss of information concerning the quite probably nearly constant II-Cu peak height which is a consequence of Cl^- "complexing" Hg not Cu.

The observation, of course, do not deny the effect that Cl^- complexation can exert on voltammograms. At higher Cl^- concentrations,

POTENTIAL, E_p , V

Figure 8: Effect of chloride concentration on the peak currents of I Cu, and II Cu. a) DPAS Voltammogram obtained with a MTFE prepared "in situ" for a synthetic sample contain 20 ng ml^{-1} Cu and $4 \times 10^{-5} \text{ M-Hg}^{2+}$ 5 min-plating at -1.0 V . b, c and d recorded after addition of 5×10^{-4} , 1×10^{-3} and $2 \times 10^{-3} \text{ M}$ chloride.

the peak potential, E_p , peak current, i_p , and width at half height, $b_{1/2}$, for the well resolved Cu signal at the cathodic side (II-Cu) become a function of chloride ion concentration. Relevant results, in this case at an HMDE, are collected in Table II. Results involving Cd, and Pb are also included. The effect of Cl^- on E_p , i_p , and $b_{1/2}$ of the well resolved I-Cu begins to be significant at $1.2 - 1.5 \times 10^{-3} M$ KCl. E_p showed a progressive cathodic shift with increasing Cl^- concentration and i_p diminished steadily to a minimum value at 0.01 M Cl^- concentration but increased slightly again at the highest Cl^- concentrations. The $b_{1/2}$ also showed a progressive increase with increasing Cl^- concentration which stabilized after 0.1 M Cl^- concentration. For Cd and Pb both i_p and $b_{1/2}$ are not affected up to 1.0 M Cl^- concentration, where cathodic shift in the peak potential of Cd is observed at $5 \times 10^{-3} M$ KCl and for Pb it emerges at 0.10 M KCl.

The shift in peak potentials may be understood from the equation [53] relating E_p to the polarographic half-wave potential ($E_{1/2}$) in DPASV mode

$$E_p = E_{1/2} - 1.1 \frac{RT}{nF} - \frac{\Delta E}{2} \quad (12)$$

where E = modulated amplitude (V). For Cd and Pb, $E_{1/2}$ is shifted cathodically with increase in chloride concentration from 0.1 to 1.0 M [74].

In MTFE's prepared "in situ" the results with successive addition of Cl^- to the sample containing mercury plating solution

Table II

Effect of chloride concentration on i_p , $b_{1/2}$, and E_p for I-Cu and II-Cu and on E_p for Cd and Pb in simultaneous determination at HMDE. 0.03 cm² drop area, 3 min. plating at -1.20 V, 5 mV s⁻¹ scan rate. 25 ml buffered sample (pH 5.5) contains 10 ng ml⁻¹ Cd and Pb and 15 ng ml⁻¹ Cu.

KCl conc. mol/l	Cd	Pb	I-Cu			II-Cu		
	E_p, V	E_p, V	$i_p, \mu A$	E_p, V	$b_{1/2}, mV$	$i_p, \mu A$	E_p, V	$b_{1/2}, mV$
0	-0.650	-0.500	0.160	-0.160	80	0.135	-0.080	60
2×10^{-4}	-0.650	-0.500	0.165	-0.160	80		-0.080	
4×10^{-4}	-0.650	-0.500	0.163	-0.160	80		-0.080	
6×10^{-4}	-0.650	-0.500	0.161	-0.160	80			
8×10^{-4}	-0.650	-0.500	0.162	-0.160	80			
1.2×10^{-3}	-0.650	-0.500	0.145	-0.165	83			
1.5×10^{-3}	-0.650	-0.500	0.130	-0.170	85			
5×10^{-3}	-0.655	-0.500	0.100	-0.180	95			
1×10^{-2}	-0.660	-0.500	0.090	-0.210	110			
5×10^{-2}	-0.665	-0.500	0.110	-0.260	120			
1×10^{-1}	-0.673	-0.505	0.120	-0.275	115			
5×10^{-1}	-0.690	-0.520	0.140	-0.320	115			
1.0	-0.700	-0.530	0.140	-0.340	115			

are collected in Table III. The results indicated that the peak currents decreases not only for I-Cu but also for Cd and Pb with increasing Cl^- concentration. This is related to the diminishing thickness of Hg-film with increase of Cl^- . $E_{1/2}$, Hg^{2+}/Hg shift cathodically with addition of Cl^- thereby decreasing the overpotential at which deposition is carried out.

The table also shows that the peak potentials for metals shift cathodically with increasing Cl^- concentration. However the magnitude of shift is different from that observed with HMDE, this is because in addition to the change of $E_{1/2}$ there is also a change in film thickness with increasing Cl^- concentration. The dependence of E_p on film thickness in DPASV is given by [17].

$$n(E_p - E_{1/2}) \propto \log L^2/D_R t \quad (13)$$

where L = film thickness (cm), D_R = diffusion coefficient of metal in mercury ($\text{cm}^2 \text{s}^{-1}$), and t = pulse width (sec).

Finally, the two Cu peaks, I-Cu and II-Cu can be altered relative to each other and absolutely by the choice of plating potential in the absence of Cl^- . An example of this is shown in Figure 9 which refers to an experiment conducted on an Ottawa drinking water buffered with sodium acetate/acetic acid ($\text{pH} = 5$) (it contains approximately 20 ng ml^{-1} of Cu) and which utilized a preformed MTFE of $300 \text{ \AA}$ thickness. It is seen that I-Cu peak is strongly favoured by more cathodic deposition potential.

Table III

Effect of chloride concentration on i_p and E_p for Cd, Pb, I-Cu and II-Cu in simultaneous determination at MTFE prepared "in situ". 0.3 cm^2 electrode surface area, 5 min. plating at -1.0V , 5 mV s^{-1} scan rate, 25 ml buffered sample (pH 5.5) contains 5 ng ml^{-1} Cd and Pb and 20 ng ml^{-1} Cu and $4 \times 10^{-5} \text{ M Hg}^{2+}$

KCl conc. mol/l	Cd		Pb		I-Cu		II-Cu	
	$i_p, \mu\text{A}$	E_p, V	$i_p, \mu\text{A}$	E_p, V	$i_p, \mu\text{A}$	E_p, V	$i_p, \mu\text{A}$	E_p, V
0	10.20	-0.725	8.75	-0.570	34.50	-0.200	11.25	-0.07
5×10^{-4}	10.10	-0.725	8.70	-0.570	34.00	-0.200		-0.07
1×10^{-3}	9.90	-0.725	8.60	-0.570	32.40	-0.205		
2×10^{-3}	9.65	-0.725	8.50	-0.570	28.50	-0.210		
6×10^{-3}	9.10	-0.730	8.00	-0.575	24.00	-0.217		
1×10^{-2}	8.00	-0.730	7.50	-0.575	20.30	-0.230		
2×10^{-2}	7.00	-0.735	7.00	-0.580	17.25	-0.245		
5×10^{-2}	6.00	-0.745	6.25	-0.585	16.35	-0.280		
1×10^{-1}	5.84	-0.750	6.00	-0.590	15.00	-0.305		
5×10^{-1}	5.70	-0.775	5.80	-0.610	13.50	-0.380		
1.0	5.50	-0.790	5.50	-0.615	12.70	-0.405		

Figure 9: Effect of initial potential on the peak currents of I Cu, II Cu.
20 $ng\ ml^{-1}$ $[Cu^{2+}]$ in drinking water buffered with acetate (pH 5).
0.3 cm^2 electrode area, 5 min deposition time, 2 $mV\ s^{-1}$ scan rate.

(II.4) Interpretation

The results presented in Figures 1-7 cannot be associated with complex formation and clearly reflect the ASV consequences of the limited solubility of copper in mercury [24]. The I-Cu peak (at the cathodic side) is that for particles of solid copper suspended in or plated on the mercury electrode. The II-Cu peak (at the anodic side) is the peak for a copper amalgam. The results presented to give a clear idea of a cross section of our experiments. Double peaks for copper at all three electrode types are observed, but, of course, the I-Cu (solid) is most prominent at low mercury film thickness.

The conclusion is reinforced by data in Figure 9. There it is obvious that " fast " deposition at highly cathodic voltage favours, precipitation of Cu where as " slow " deposition at voltages much nearer the reversible values favours Cu atom formation and amalgamation.

A confusion appears to have affected some earlier discussions with respect to the role of Cl^- . It is apparent that Cl^- complexing of Cu is not the only way Cl^- can affect Cu signals. Rather, Figure 8 shows that the major effect can be on Hg. Since ASV studies are frequently directed to identification of speciation in a sample [50], it is especially important to be aware of the circumstances where properties of mercury not the analyte are at issue. Chloride can mask " labile " Cu by the shift of the Hg wave. This is the effect reported in ref. [56]. Two final points need to be made. First, the effect of complexing follows usual inorganic chemical complexity constant sequences.

Second, the effect appears only at relatively high Cl^- concentration except in the case of the high concentration metal, Hg.

A somewhat discouraging cautionary tale related to the effect discussed in this study on the interpretation of natural water samples is briefly told in Figure 10. This figure compares DPAS voltammograms for a sample of water from the Rideau River in Ottawa. The sample was adjusted to $\text{pH} = 5.6$ with acetate buffer. The two scans refer to deposition (plating) at -1.00 V and -1.25 V respectively for 5.0 min. Beyond the trivial (if spectacular difference) that a Zn peak accompanies those for Cd, Pb and Cu when deposition occurs at -1.25 V , we see the peak for Cu(solid) is enhanced by the higher deposition (plating) voltage. Existing theory [75] could have been used to attempt to attribute this peak to a new dissolved Cu species and the change greatly affects, at the very least, the determination of "labile" Cu in a scheme such as that given in ref.[50]. Clearly the change has nothing to do with parameters of the aqueous sample. It reflects parameters of the Hg phase. Thus, a speciation study must, at the least, include careful evaluation of effects of plating potential and other parameters.

Figure 10: DPAS Voltammograms obtained with a preformed MTFE for 25 ml river-water sample buffered with acetate to pH 5.6. 5 min plating a) at -1.0V and b) at -1.25V.

ANALYSES OF SAMPLES FROM THE RIDEAU RIVER
BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

(III.1) Introduction

Following a study of medium factors influencing signals for Cu, Cd, and Pb in DPASV analysis at wax impregnated graphite electrodes with thin Hg films and at the HMDE, we have examined a fresh water sample. DPASV has been extensively discussed as a method for species identification in natural samples. Some medium effects of our previous study could confuse issues in species identification. These effects and additional ambiguities are observed in the studies of a fresh water sample. We find the MTFE electrode with "in situ" deposition of the Hg film is the most sensitive for analysis of the river water samples.

A number of papers [39,40,45,46,49,50,75,76] have discussed the application of anodic stripping voltammetry to differentiation of trace metal species in natural waters. The idea is sufficiently accepted that it has recently appeared in a review for the chemical general reader [77]. All popular electrode types including HMDE, and MTFE's on graphite substrate either predeposited or formed "in situ" have been exploited. The basic idea is to associate changes in peak positions, peak multiplicities, and peak widths with changing speciation in the sample. The preceding chapter illustrated effects of this type on Cu signals that arose from the behaviour of the copper amalgam and the oxidation of mercury itself. We have extended

the study to a natural water sample to explore the ambiguities that can arise in assignment of species from these effects.

III.2 Experimental

Preparation of Samples: Samples of surface water were collected from the Rideau River at Ottawa near the Department of the Environment gauging station. The containers were 1 l. high-density polyethylene bottles which had been leached with 3M HNO_3 for at least 2 weeks and then rinsed with doubly distilled water followed by river water. River water was allowed to stand in the bottles for one half-hour before a fresh sample was collected. Samples were filtered through acid washed millipore 0.45 μm membrane filters. Analysis was normally completed on the same day.

Procedure for "UV digestion" involved addition of 50 μl of 30% H_2O_2 to a 25 ml aliquot of sample which had been acidified to $\text{pH} = 2$ with 2 M Ultrex HNO_3 . The irradiation was carried out with a 1 KW medium pressure mercury vapour lamp for 4 hours with stirring. A final 5 min irradiation with purified N_2 bubbling removed residual peroxide.

Acid digestion of samples was carried out as follows: Aliquots (25 ml) of filtered river water were acidified to $\text{pH} = 0.7$ and reduced, to very small volume on a hot plate (without boiling). This residual sample was diluted with deionized water and brought to $\text{pH} 5.0$ with acetate buffer.

Insoluble particles retained on the millipore filters from 1.00 l of river water were dissolved for analysis by wet ashing. Filters plus 10 ml of 2M ultrex HNO_3 were heated for "one half" hr. at 70°C . The solutions were filtered through $0.45\ \mu\text{m}$ membrane filters and the filters were washed with deionized water and the resulting solution finally diluted to 50.0 ml. 1.25 ml aliquots were transferred to the electrolysis cell and diluted with deionized water and acetate buffer to give 25.0 ml and $\text{pH} = 5.0$.

DPASV runs were done as described in Chapter II.

(III.3) RESULTS

(III.3.1) HMDE

Figure 11 shows a DPASV run on an untreated river water sample. A "blank" is presented which corresponds to stripping without deposition. We note a Hg stripping wave in the background which is similar to that found to be a consequence of the presence of Cl^- in the previous chapter. This makes Cu determination very insensitive and one could not resolve II Cu peak. Here the effect cannot come from Cl^- . Curiously, as the figure shows, it can be reduced by cycling the pH down to 2 then back to $\text{pH} \approx 5$. What this does to Hg oxidation is not by any means obvious. But, the effect on Hg oxidation wave arises from a sample component, probably organic.

What can be reported is that UV digestion of the sample as shown in Fig. 12 reduces the Hg background signal. Moreover, once the background has been reduced, the Cu signal at the anodic side

Figure 11: DPAS Voltammograms obtained with aHME for 25 ml river-water samples a) buffered with 0.025M acetate to PH 5.6. b) acidified with 2M nitric acid to PH 2 before addition of the buffer to raise the PH to 5. 10 min plating at -1.20V. The dotted lines represent blank solution.

Figure 12: DPAS Voltammograms obtained with a HMDE a) U.V. digested river-water sample. b) after addition 2 ng ml⁻¹ of Zn, Cd, Pb and Cu. 6 min-plating at -1.20V. Dotted lines represent blank soln. passed through same digestion procedure and recorded after deposited for the same time.

(II-Cu) is well resolved. That is, both amalgam and solid Cu are present but the background effect appears to obscure one of these signals. The peak potential of Zn, Cd, Pb, I-Cu and II-Cu are -1.01, -0.65, -0.50, -0.160 and -0.08V respectively. The largest signals for all metals were obtained after digestion in acid.

(III.3.2) MTFE

Measurements of Cd, Pb, and Cu were conducted with plating at -1.00V. Zn was determined by plating at -1.25V. This is because of a metallic interference between Cu and Zn which arises in MTFE's. The DPAS voltammograms obtained on a 150Å⁰ (Fig.10) preformed mercury film with untreated water is very similar to that shown in Figure 11 for the HMDE. The same problem discussed above effects Cu determinations. Blanks were again recorded by "stripping" without deposition. The peak potentials for Zn, Cd, Pb, I-Cu and II-Cu are -1.07, -0.73, -0.58, -0.30 and -0.12V respectively. Because of the slow sweep rate of DPASV (5 mV s^{-1}) and the high surface to volume ratio of the MTFE, deposition occurs during stripping and significant peaks are found in blanks. This is especially the case when standard addition methods are used. This blank effect becomes more severe, quite obviously, as the initial potential becomes more cathodic. It is for this reason that scans for Cd, Pb, and Cu were initiated from -1.00 V and only Zn scans were initiated from -1.25 V.

Beyond the blank effect, there is an additional peak which arises in the Cu region if deposition is carried out at -1.25 V. Figure 13 shows this effect at an MTFE deposited "in situ". A peak of $0.8 \mu\text{A}$ height appears at -0.30 V when deposition is carried out at -1.25 V. This peak compares to a Zn peak of $5.4 \mu\text{A}$. The comparison suggests that the $0.3 \mu\text{A}$ peak seen when deposition takes place at -1.00 V. This peak could be attributed to a Cu-Zn intermetallic.

The presence of "Cu-Zn intermetallic" in the I-Cu region, affected not only the peak current but also the peak half-width, $b_{1/2}$. Figure 14 illustrates this result by recording the voltammograms of spiked river-water with MTFE prepared "in situ" and have $170 \text{ \AA}$ mercury film thickness. When the deposition initiated at -1.0 V, the I-Cu peak have a half-width of 50 mV (curve b), where the half-width increase to 58 mV when the deposition and the stripping carried out at -1.25 V (curve a). Moreover, the $b_{1/2}$ continues to increase with the mercury film thickness. This is consistent with the theory of DPASV [17] that the peak potentials of intermetallic Cu-Zn and I-Cu may be unequally shifted, thus causing a further separation of the two peaks with an increase in the apparent $b_{1/2}$ of the unresolved overlapped peak.

For quantitative determinations, the Zn concentrations are corrected for appearance of the -0.30 V peak as appropriate.

Table IV finally collects the analytical results for the river water by the various methods and with the various methods of sample treatment, little difference among the three types of electrodes is observed in the table. As the previous work indicated

a) 25 ml buffered River Water pH 5.6
10 min. dip, at -1.0 V

b) Same as a, dip, 1 min. at -1.25 V

Figure 13: DPAS voltammograms obtained with a MTFE prepared "in situ" for 25 ml river-water sample buffered with acetate to pH 5.6. $4 \times 10^{-5} M Hg^{2+}$ was added. 10 min-plating a) at -1.0V and b) at -1.25V

Figure 14: DPAS Voltammograms obtained with a MTFE prepared "in situ" for 25 ml river-water sample spiked with 5 ng ml^{-1} of Zn, Cd, Pb, and Cu in addition to $4 \times 10^{-5} \text{ M Hg}^{2+}$ and 0.025M acetate to adjust the pH to 5.6. 10 min-plating a) at -1.20V and b) at -1.0V.

Table IV : Analytical results of the Rideau river samples by DPASV with HMDE, preformed MTFE and MTFE prepared "in situ" with various methods of sample treatment.

Sample treatment	HMDE				preformed MTFE (600A)				MTFE prepared "in situ" (170A)			
	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu
	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹	conc. in ng ml ⁻¹
Filtered River Water	2.79	0.12	0.27	0.11	2.80	0.11	0.30	0.20	3.08	0.12	0.31	0.20
Acidified Filtered River Water	3.45	0.15	0.36	0.37	3.20	0.15	0.38	0.32	3.50	0.16	0.37	0.29
Digested River Water by U.V.	3.64	0.19	0.43	1.60	3.90	0.20	0.42	1.79	4.80	0.25	0.49	1.55
Digested River Water in Strong Acid	4.30	0.20	0.46	1.80	4.50	0.23	0.48	1.87	4.90	0.28	0.53	1.64
Metals in particulate	2.10	0.18	0.32	1.00	2.25	0.22	0.32	1.08	2.40	0.23	0.37	1.07

Note: Relative standard deviation ranging from 2 to 5% in all the three modes.

most of the disconcerting features of the determination are shown by all electrodes and the results are quite similar on all three types. However, pretreatment is clearly critical. This is reinforced by Table V which indicates how the sample divides in percentage terms, what is the total concentration identified by each method, and the sensitivity for each metal ion expressed as peak current per concentration unit, for a given deposition time ($i_p/C_b t_{dep.}$) are determined in each type of electrode.

(III.4) INTERPRETATION

The signals observed in river water samples do not precisely mirror the medium effects found (especially for Cu) in synthetic solutions discussed in the preceding chapter. However, they reveal qualitative parallels. In the synthetic solutions Cl^- was implicated in alterations of the Hg stripping background which affected all types of electrodes. In particular, it masked the peak for "amalgam" Cu. In the river water samples, a parallel effect arises which cannot be attributed to Cl^- . This effect is altered by UV digestion which leads us to attribute it to organic matter. Quite probably the main component of this material is humic [78, 79].

In reference [76] effects of an isolated fulvic acid on the Cu signal were reported. The total concentration of Cu was near 60 ng ml^{-1} , more than an order of magnitude higher than in this study. In Fig. 2 of reference [76] a peak for "solid" Cu is well defined and only a small peak for "amalgam" Cu can be seen on the anodic

side of the solid peak at a zero fulvic acid concentration. Addition of fulvic acid leads to increase of background very like that which is described here and supports the present assignment of the origin of the effect. Also, a peak grows in the position appropriate for "amalgam" Cu. This illustrates of central point of this and the preceding chapter. The effect of FA reported in ref. [76] is to alter the deposition kinetics of Cu in such a way as to lead (at least in part) to formation of "amalgam" Cu in preference to deposition of Cu into the crystal phase in the Hg. This could arise either from complexing Cu in solution or adsorption of fulvic acid on the mercury film surface.

The number of peaks is also influenced by the choice of the deposition voltage. In preformed MTFE's or MTFE's prepared "in situ" the peak near -0.30 V is associated with efforts to deposit Zn at -1.25 V. This has been associated with a Cu/Zn intermetallic phase. As Florence observed [53] , an intermetallic should suppress a signal at more cathodic potentials but should not affect signals at more anodic potentials when "no other metals remain in the Hg". If the Cu/Zn intermetallic assignment is to be understood, it must be related to the existence of solid Cu phase in the Hg film. Kinetics of formation and dissolution of crystalline alloys of Cu/Zn can be slow at Zn oxidation potentials and not become rapid until potentials near Cu oxidation potentials. This assignment is demanded for the -0.30 V peak by the clear correlation with deposition of Zn.

Moreover the broadening of -0.30 V peak also indicated the overlapping of Cu and Cu/Zn peaks. The "irreversibility" of Cu (II) waves has been demonstrated [80].

Generally, the important consequence for the uses of DPASV method in "speciation" studies that arises from this study is that factors of the "medium" that are associated with speciation in the Hg phase are of an importance similar to factors controlling speciation in the aqueous phase. The study of Cu speciation in the presence of soil organics is a clear example. The factors identified in the study of carefully constructed synthetic samples in the preceeding chapter are parallel to those seen in the river water "medium" containing some complexes and poorly characterized constituents.

Finally, these results confirm the conclusion obtained by Batley and Florence [53,56,63], using sea-water samples, and by Stojek and Kublik [73] using synthetic samples, that MTFE's prepared "in situ" were most sensitive for all metals studied. These factors influence designs for a "field oriented" device for carrying out the deposition step.

Differential Pulse Anodic Stripping Voltammetry in a flow-through cell with Mercury-Coated Reticulated Vitreous Carbon electrodes (MCRVE's).

(IV.1) Introduction

DPASV at a porous mercury-coated electrode of reticulated vitreous carbon (MCRVCE) has been adapted for use in a flow-through cell. The design and construction of the system are described. The system is characterized by extreme simplicity, stability and high sensitivity. For quantitation of concentration ranging from 10^{-10} to 10^{-1} ng ml⁻¹, a 1 to 10 min. deposition is sufficient with continuous cycling of the solution during the stripping process. The system seems to be suitable for use "on site" for plating trace metal ions.

This device should be put into the context of recent work. A variety of flow systems and cells designed for ASV [33,34,38,81-88] has been reported. These include cells in which the solution flows through an open tubular electrode [33,34,81-83] or onto a fixed [38,84,85] or rotating disk [86-88] electrode. A tubular platinum electrode flow system was first reported by Blaedel *et al.* [89]. Osterling and Olson prepared and evaluated a mercury-coated tubular platinum electrode [90]. A flow cell with a tubular gold electrode in connection with ASV has been employed [81] to detect Se(IV) in a chromatographic effluent. A tubular carbon electrode (TCE) was reported first by Sharma and Dutt [91] and one was described in detail by Mason and Olson [92].

The use of solid electrodes as a substrates for mercury films in connection with ASV has gained popularity recently. Carbon is preferred compared to metallic materials like platinum or gold

because the metals have finite solubility in mercury and tend to form intermetallic compounds [81]. Tubular mercury covered graphite electrodes (TMCGE) have been recently adapted in a flow system to measure metal ions by ASV [33,34]. Sensitivity was improved over the stationary system due to increasing mass transport to the electrode with a fast flow rate [33]. The report indicated that the system could be used for continuous measurements in the field. Schiefel and Blaedel [82] recently described the design and construction of a flow system containing a pair of tubular glassy carbon electrodes in series for ASV with collection on mercury film. The work was extended by testing the system with battery operated equipment [83] for the analysis of Cd, Pb and Cu in tap water at subnanomolar levels.

A flow system with rotating disk electrode for automatic ASV analysis, was discussed by Wang and Ariel [87]. The system allows the simultaneous determination of metals at the ng ml^{-1} level, at a rate of 10 samples per hour.

Reticulated vitreous carbon (RVC) in a flow through electrode was first reported by Strohi and Curran [36]. RVC is glassy carbon fabricated in porous blocks typically 100 pores per inch (ppi), with very large internal surface area and little resistance to flow. This electrode was tested with ferricyanide ion and ascorbic acid. RVC was found to have a low electrical resistance, large surface area, and physically continuous structure [36]. Blaedel and Wang [37] investigated the dependence of limiting currents on the flow rate

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and on the number of RVC disks employed.

ASV has been conducted with a porous mercury-coated RVC electrode in a flow-through configuration [38] for convenient determination of Cd and Pb. Because of a large surface area of RVC electrode, high background currents were observed when linear sweep ASV was used [38].

Recently, Blaedel and Wang employed an RVC disk as a rotated mercury-coated disk electrode [88] in conjunction with DPASV for the determination of Cd and Pb in nM level. They found that the high background current accompanying a large surface area RVC electrode can be minimized by using DPASV mode.

The microscopic surface area of the RVC is very low compared to conventional porous graphite, therefore surface adsorption and background currents are comparatively low, the matrix is rigid. RVC is extremely inexpensive, and it is quite easily machined and mounted in various cell designs. The physical properties of RVC are described in ref. [36].

The purpose of the present work was to employ mercury-coated reticulated vitreous carbon electrodes, MCRVCE's, in conjunction with DPASV to investigate the efficiency of this type of electrode for the determination of trace heavy metal ions in synthetic and natural samples and to study the utility of the MCRVCE's for electrodeposition of trace metals directly in the field with storage followed by analysis in the laboratory.

(IV.2) Experimental

(IV.2.1) Apparatus

The configuration used with the flow-through electrodes is shown schematically in Figure 14, A. The electrochemical cell consisted of two sections held together by a polyethylene tube. This design was chosen to facilitate the replacement and storage of the RVC electrodes. The upper section, constructed from a pyrex tube 7 mm i.d., housed the reference electrode salt bridge and the Pt counter electrode. The RVC disk (Chemotronics International Inc., Ann Arbor, Mich.) was fitted in the lower section. This section was constructed from plastic tube (7 mm i.d. at the upper end, 2 mm i.d. at the lower end). The electrical contact was made through a Pt wire sealed from outside by epoxy glue. Details of the electrochemical cell are shown in Fig. 14, B and the lower section (RVC unit) in C. The reference electrode was SCE (equivalent to one used in the earlier study) connected to the electrochemical cell through a salt bridge containing 1 M sodium nitrate. The counter electrode was Pt wire. The RVC disks were punched out from blocks of 100 pores per inch (ppi). Each disk was (7 mm) in diameter (5 mm) in length. The disk had a calculated volume of 0.19 ml and a surface area of 12.7 cm^2 . The peristaltic pump (Markson Scientific, N.Y.) was placed downstream from the cell to pull solution through the RVC electrode, thus minimizing the possibility of air entering the cell by diffusion through the Tygon tubing required by the pump. Precautions were taken to prevent gas bubbles from being trapped in the flow system.

Figure 15: A- Diagram of flow system used for DPASV at MCRVCE; Detail B shows flow cell 1) electrical contact 2) counter electrode (Pt-wire) 3) the salt bridge of the reference electrode 4) inlet of sample solution 5) outlet. Detail C shows the RVCE unit.

Electrode potential was controlled by PAR 364 polarographic analyzer. Current voltage curves were recorded on a Fisher Recordall (Series 5000).

(IV.2.2) Reagents and Solutions: All solutions were prepared from analytical grade chemicals and deionized water. Standard metal solutions were prepared from one gram pure metal > 99.9% (previously cleaned with acid and dried) in a minimum amount of 8M Ultrex nitric acid followed by dilution with 1% V/V nitric acid to $1000 \mu\text{g ml}^{-1}$. The solutions were stored in polyethylene bottles. Portions of these solutions were diluted as required for standard addition just prior to use. The mercury plating solution was prepared by dissolution of triply distilled mercury in a minimum amount of Ultrex nitric acid and dilution with deionized water to give $0.01 \text{ M Hg(NO}_3)_2$ stock. All samples were prepared in a supporting electrolyte that contained 0.012 M sodium acetate /acetic acid (pH 5.5). The concentration of the supporting electrolyte was a compromise between two conflicting requirements namely to minimize the IR drop and to prevent the mercury wave from interfering with copper peaks. The studies with standard solutions were made by adding aliquots (in μl from an Eppendorf pipet) of freshly prepared $1 \mu\text{g ml}^{-1}$ standard solution to the supporting electrolyte to give the desired concentration. Collection, filtration and digestion procedure of river-water samples were as described earlier.

(IV.2.3) PROCEDURE

100 ml of 0.012 M acetate buffer containing 1 ml of a 0.01M Hg^{2+} solution was introduced into the cell bottom (final Hg^{2+} concentration $\sim 1 \times 10^{-4}\text{M}$). The mercury film was deposited by holding the potential of the RVC at -0.8V and passing the deaerated mercury solution through the electrode at 4.8 ml min^{-1} for 20 min. After plating the mercury film, the flow was stopped and the cell bottom was replaced by another containing blank solution which was previously deaerated with nitrogen. The flow of solution was restarted for 15 min. During this period the MCRVCE was held at +0.05 V for the first 10 min., followed by 2 min. at -1.0 V before stripping anodically to 0.0 V. The above procedure was found to be sufficient for removing any contaminants which may have co-deposited with the mercury, to remove traces of oxygen that may remain in the electrode and to clean up the flow system by discarding the remaining mercury plating solution to the waste. The sample solution buffered with 0.012 M acetate (pH 5.5) was allowed to flow through the cell after purging with N_2 for 15 min. During deaeration the electrode was held at 0.0 V. The metal ions, Cd^{2+} , Pb^{2+} and Cu^{2+} were plated at -1.0 V for a period depending on their concentrations (1-10 min for concentration ranging from 10 to 0.1 ng ml^{-1}).

The oxidation step (stripping) of the reduced metals in the mercury film was performed by applying DPASV with a 5 mVs^{-1} scan rate and 50 mV modulation amplitude. The DPAS voltammogram

was recorded simultaneously while the sample solution flowed through the electrode and N_2 gas continued passage through the solution throughout all subsequent steps. The scan was stopped at 0.0V, and this potential was maintained for 1 min, after which the MCRVCE was ready for the next determination.

(IV.3) Analytical Application:

Figure 16 illustrates typical differential pulse stripping voltammograms recorded with standard samples containing Cd^{2+} , Pb^{2+} and Cu^{2+} at the 0.5 ng ml^{-1} (Curve a) and 6 ng ml^{-1} (Curve b) levels, obtained at the MCRVCE by employing relatively short deposition time. The peak potentials for Cd, Pb, I Cu, II Cu were -0.73, -0.57, -0.21, -0.11 V, respectively. High sensitivity and well defined peaks with half width, Cd (55 mV), Pb (57 mV) and I Cu (80 mV) were obtained for the determinations of the three metals.

The slow scan rate required for DPASV ($2 - 10\text{ mV s}^{-1}$) tend to prolong the duration of the determination relative to a short deposition time. Because the sample solution still flowed through the electrode during the stripping process, part of the DPASV analytical signal is derived from ions deposited during this interval (time it takes for the potential to scan from the deposition potential to the peak potential) [84].

Figure 16: DPAS Voltammograms obtained with a MCRVCE for a) 0.5 ng ml⁻¹ of Cd, Pb, and Cu plated at -1.0V for 5 min. b) 6 ng ml⁻¹ of the same metals plated at -1.0V for 2 min ($t_{dep.}$)

Accordingly the peak current of each metal ion was corrected by a factor $[38] \frac{t_{\text{dep}}}{t_{\text{dep}} + t_p}$, where t_p was the time taken to scan from the deposition potential to the peak potential [28,38] or the peak currents calculated related to the total deposition time for each metal $t_{\text{dep}} + t_p$.

From the view point of sensitivity, the MCRVCE in a flow-through cell compares favourably with other flow-through electrodes suggested to date [34,38,85]. Deposition periods required for well defined peaks range from 1 min. for 5 ng ml^{-1} , through 5 min. for 0.5 ng ml^{-1} and 10 min. for a 0.1 ng ml^{-1} for the metal ions under discussion, except copper which needs relatively longer deposition time particularly in very low concentration (in sub ng ml^{-1} level).

A linear correlation between peak currents and concentration, as shown in Fig. 17 for concentration of Cd, Pb and Cu ranges from 0.5 to 6 ng ml^{-1} for 2 min. deposition time, and allows straightforward quantitations. Fig. 18 shows the DPAS voltammograms obtained during successive runs after addition in steps of 0.5 ng ml^{-1} standard solution of Cd^{2+} , Pb^{2+} and Cu^{2+} to the blank with 5 min. (t_{dep}) plating at -1.0 V , 5 mV s^{-1} scan rate and 4.8 ml min^{-1} flow rate. The total deposition times, $t_{\text{dep}} + t_p$, are 5.9, 6.43, 7.63, and 7.97 min. for Cd, Pb, I Cu and II Cu respectively. The blank levels correspond to $1 \text{ } \mu\text{A}$ (Cd), $0.8 \text{ } \mu\text{A}$ (Pb), and $0.6 \text{ } \mu\text{A}$ (Cu) calculated from the same deposition time (i.e. 5 min.).

Figure 17: Calibration curves of Cd, Pb, ICu, IICu and total Cu obtained with a MCRVCE. 2 min-plating at $-1.0V$, $5\ mV\ s^{-1}$ scan rate and $4.8\ ml\ min^{-1}$ flow rate. All currents corrected to 2 min. deposition. (For statistics see Table VII).

Figure 18: DPAS Voltammograms obtained with a MCRVCE for synthetic samples contains Cd, Pb, and Cu. a) 0.5 ng ml^{-1} b) 1 ng ml^{-1} c) 1.5 ng ml^{-1} d) 2 ng ml^{-1} . Deposition at -1.0V for $5 \text{ min}(t_{\text{dep}})$ $t_p + t_{\text{dep}}$ are 5.9, 6.43, 7.63, and 7.97 mins for Cd, Pb, ICu, and IICu respectively.

Table VI shows the dependence of the peak current upon the deposition time for 1 ng ml^{-1} Cd^{2+} , Pb^{2+} and Cu^{2+} under the same conditions described before. The dependences were linear for deposition time ranging from 2 to 16 min. In higher concentration of the metal ions i.e. 4 ng ml^{-1} the linearity was achieved between 1 to 10 min. (the deposition times were corrected for the time required to scan the potential to the stripping peak). It was apparent that the peak current was directly proportional to deposition time.

The sensitivity for each metal ion expressed as peak current per concentration unit, for a given deposition time ($i_p/C_b t_{\text{dep}}$) was very high, the average being 126, 185, and 60 nA/nM min. , for the Cd, Pb and Cu respectively. The enhanced sensitivity as compared to a stationary system was due to increased mass transport to the electrode.

(IV.4) Analysis of River Water

Characteristic DPAS voltammograms recorded with river water samples (buffered with acetate to pH 5.5) using MCRVCE's are shown in Fig. 19. The metal ions, Cd^{2+} , Pb^{2+} , and Cu^{2+} are present at their "natural" levels (curve a), using 10 min deposition time (time for stripping is not included) at -1.0 V , 5 mV s^{-1} scan rate, and 4.8 ml min^{-1} flow rate. Concentrations are estimated by appropriate spiking (curve b). The peak potentials of Cd, Pb, I Cu, and II Cu are -0.73 V , -0.59 V , -0.30 V , and 0.11 V respectively.

As the Fig. shows the copper signals (i.e. II-Cu and I-Cu) and to a degree the Pb signal are affected by the cathodic shift in the Hg

Table VI

Dependence of peak current on deposition time. Initial potential -1.0V,
 5 mV s^{-1} scan rate and 4.8 ml min^{-1} flow rate.

$t_{\text{dep}}, \text{min.}$	Cd		Pb		Cu	
	$i_p, \mu\text{A}$	i_p/t_{dep} $\mu\text{A/min}$	$i_p, \mu\text{A}$	i_p/t_{dep} $\mu\text{A/min}$	$i_p, \mu\text{A}$	i_p/t_{dep} $\mu\text{A/min}$
a) 1 ng ml^{-1} Cd, Pb and Cu						
2	2.5	1.25	2.2	1.10	2.3	1.15
4	4.7	1.18	4.0	1.00	4.2	1.05
6	6.8	1.13	5.7	0.95	5.9	0.98
8	8.9	1.11	7.3	0.91	7.8	0.97
10	11.0	1.10	9.1	0.91	9.5	0.95
12	13.0	1.08	10.7	0.89	11.2	0.93
16	17.3	1.08	14.1	0.87	14.6	0.91
	average	1.13	average	0.95	average	0.99
b) 4 ng ml^{-1} Cd, Pb and Cu						
1	4.7	4.70	3.6	3.60	4.0	4.00
2	9.0	4.50	6.9	3.45	7.6	3.80
3	13.8	4.60	9.8	3.27	11.4	3.80
4	18.0	4.50	13.4	3.35	15.0	3.75
5	22.9	4.58	16.5	3.30	18.3	3.66
7	29.5	4.21	22.5	3.21	24.7	3.53
10	42.0	4.20	31.5	3.15	35.0	3.50
	average	4.47	average	3.33	average	3.72

i_p for Cu represents the i_p 's of I-Cu and II-Cu

The peak currents of the three metals were corrected by a factor $t_{\text{dep}}/t_{\text{dep}} + t_p$

Figure 19: DPAS Voltammograms obtained with a MCRVCE for river-water sample a) buffered with 0.012M acetate to pH 5.5. b) After addition 0.5 ng ml⁻¹ of Cd and 1 ng ml⁻¹ of Cu. Deposition was carried out at -1.0V for 10 min.

oxidation wave; this interference becomes more severe after successive measurements when a large volume of river-water has passed through the MCRVCE. The II-Cu peak is the most affected while the I-Cu peak decreases only gradually and the Pb peak is just reduced slightly. This is related as we mentioned before to the medium effect, presence of organic matter in river-water samples which adsorb on the mercury film and increase the background current. The adsorbates present in the mercury film combined with the presence of the complexing agents in the sample may be responsible for hindering the electro-deposition and/or reducing the rate of redox reactions of the metals, particularly those on the more anodic side. The effect found in the flow system with a porous RVC electrode plated with mercury is more severe than the effect at stationary electrodes (e.g. HMDE's and MTFE's). This is probably related to the larger quantity of organic material in the large volume of river water passing through the MCRVCE's.

Successive DPAS voltammograms recorded on Cd, Pb and Cu after spiking river water sample are shown in Fig. 20. The MCRVCE is equilibrated with sample before adding the standard solution (from 1 to 10 ng ml⁻¹) for seven measurements under conditions indicated before (2 min. plating at -1.0 V with addition to the time taken during the stripping process). The total deposition times ($t_{\text{dep}} + t_{\text{p}}$) are 2.9, 3.36, 4.33 and 4.93 min. for Cd, Pb, I-Cu and II-Cu respectively. These measurements indicated that the peak currents, peak potential, and the peak half-widths for Cd are uncomplicated. The peak currents for Pb spikes are reduced slightly and the peak potential is shifted cathodically

Figure 20: DPAS Voltammograms obtained with a MCRVCE for a successive addition of standard solution of Cd, Pb, and Cu to the river-water sample buffered with 0.012M acetate to pH 5.5. 2 min-plating at -1.0V, 5 mV s⁻¹ scan rate, 4.8 ml min⁻¹ flow rate.

Figure 20. Continued.

with concomitant increase in the peak half-width. The measurements on Cu spikes indicated that the II-Cu peak appears only after the addition of 6 ng ml^{-1} standard solution at -0.11 V . The appearance of II-Cu peak, of course, is a function of concentration and deposition time. The I-Cu peak appears in the low Cu concentration at -0.30 V and grows slowly with successive addition of standard solution. The growth is accompanied by peak broadening.

The peak currents for Cd, Pb and Cu on spiking river water are plotted against concentrations in Fig. 21 and compared with the results measured on synthetic samples (organic free). All the measurements of the peak currents for the three metals from both samples are corrected to 2 min. deposition time. The results for Cd indicated that the peak current - cadmium concentration relationship in both river water sample and synthetic sample are similar and have approximately same slope (currents from river water samples are probably slightly higher than those from synthetic samples due only to the original concentration of Cd in river water). The peak current for lead from river water samples are lower than those from synthetic samples. The calibration plot for Cu in river water consists of two linear regions. This is related to the fact that II-Cu peak appears only at concentrations higher than 6 ng ml^{-1} . The currents of Cu are much smaller than those observed with synthetic samples.

The plots of peak currents versus deposition time for periods ranging from 2 to 16 min. for river water spiked with 1 ng ml^{-1} of Cd, Pb and compared with those in synthetic sample are shown in Fig. 22. The plots

Figure 21: Calibration curves of Cd, Pb, and Cu obtained with a MCRVCE's for synthetic and spiked river-water samples. All currents corrected to 2 min deposition. (For statistics see Table VII).

Figure 22: Comparison between peak currents Vs. deposition time obtained with a MCRVCE's for synthetic sample contains 1 ng ml⁻¹ of Cd, Pb, and Cu and for spiked river-water sample with 1 ng ml⁻¹ of the same metal ions. (For statistics see Table VII).

indicated that a linear correlation is obtained for Cd and Pb in both samples. The slope value of Cd from spiked river water is relatively higher than that from synthetic samples and this probably related to the original quantity of Cd present in river water (approximately 0.2 ng ml^{-1}) and also related to the fact that Cd signals are less affected by the higher background currents in river water samples. In contrast, the slope value of Pb from synthetic samples is slightly higher than that from river-water, a consequence of the medium effect on the Pb signals. The plot of Cu (I-Cu + II-Cu) in spiked river-water consisting of two linear regions is similar to results previously obtained in the calibration plot (Fig. 21). That is, the appearance of II-Cu signal depends on concentration and deposition time. Thus, the II-Cu peak appears only after 12 min. deposition. As the plot shows (Fig. 22), the currents for Cu in river-water sample are much smaller than those observed with synthetic sample .

Typical voltammograms recorded with U.V. digested river-water using MCRVCE's are shown in Fig. 23. Curve (a) represents the run with fresh MCRVCE, the dashed line indicates the voltammogram recorded with deionized water containing the same quantity of the reagents used for the sample digestion passed through the same procedure. The symmetrical shape of the curve and the appearance of the II Cu signal is due to decrease of the background current. The peak potentials are -0.73, -0.57, -0.21 and -0.11V for Cd, Pb, I-Cu and II-Cu respectively.

Figure 23: DPAS Voltammograms obtained with a MCRVCE's for a) UV digested river-water sample
 b) same sample with another electrode equilibrated previously with untreated river-water. 10 min-
 plating at -1.0V. Dotted lines represent blank solution passed through the same digestion procedure
 and deposited for the same time.

To study the effects of adsorbates on the electrode without the effect of dissolved complexing agents, the MCRVCE was equilibrated with untreated river water samples. This was followed by rinsing the electrode with blank solution (organic free) for 10 min, during which time the potential of the electrode was held at 0.0 V. The blank solution was replaced with the U.V. digested river water and the voltammogram recorded (Fig. 23, curve b) under conditions similar to that in (curve a). The results indicated that the behaviour of the mercury stripping wave is similar to that found with untreated river water. That is some of the adsorbed organic in the mercury film is stable and is neither removed by rinsing the electrode with blank solution nor stripped under the applied potentials. The unsymmetric shape of the voltammogram and the shift in I-Cu peak potential (appear at -0.27 V) and the insensitivity of I Cu and II-Cu signals clearly illustrate this behaviour. This establishes adsorbed material rather than solution species as the interference source.

Another example illustrating the influence of the adsorbates on the background currents is shown in Fig. 24. Six successive runs were carried out on a 20 ml sample of untreated river water spiked with 6 ng ml^{-1} of Cd, Pb and Cu at the MCRVCE. The stripping was initiated at -1.0 V after 6 min deposition ($t_{\text{dep.}}$) for each run (time for stripping is not included). Curve a represents the sixth voltammogram recorded. The peak potentials of Cd, Pb, I-Cu, and II-Cu are -0.73, -0.59, -0.30 and -0.11 V respectively. Curve b is recorded from the same solution after replacing the MCRVCE with fresh one. The voltammogram shows that some discrimination against the background current

Figure 24: DPAS Voltammograms obtained with a MCRVCE's for 20 ml river-water spiked with 6 ng ml⁻¹ of Cd, Pb, and Cu. Initial potential -1.0V, total deposition time ($t_{dep} + t_p$) are 6.9, 7.37, 8.33, and 8.97 min for Cd, Pb, ICu, and IICu respectively, 5 mV s⁻¹ scan rate, 4.8 ml min⁻¹ flow rate. a) represented the sixth run, and b) same sample with another fresh electrode.

occurs. Thus enhancing the peak currents for II-Cu, I-Cu, and Pb. Moreover, the peak potentials of those metals are shifted anodically to appear in positions which are approximately similar to those in digested river water or synthetic samples (e.g. Pb, -0.575 V, I-Cu, -0.22 V, and II-Cu, -0.11 V). That is, the adsorption of the organic on the first electrode minimizes the quantity available for the second electrode and thus enhances the sensitivity to the metal ions. Again, the source of interference is shown to be the adsorbed layer.

(IV.5) Study of the effect of purified fulvic acids on the metal signal from synthetic samples.

In order to understand the features of voltammograms recorded with river-water samples, several experiments were performed with the MCRVCE's to study the metal signal from synthetic samples after addition of purified fulvic acid, FA. The fulvic acid used is a well characterized sample from a "Bh horizon of a podzol" collected at Armadole, P.E.I. Its properties have been extensively examined. See ref. [93] and earlier work cited there.

Fig. 25 shows the DPAS voltammograms recorded with MCRVCE for synthetic sample containing a known concentration of Cd, Pb and Cu after addition of various amounts of FA. As Fig. 25 shows, Cd is little affected by the addition of FA. The Pb signal shifts very slightly to more cathodic potentials and the peak current diminishes with increasing FA concentration. Copper signals are the most affected, the II-Cu peak becomes difficult to resolve at only $4 \mu\text{g ml}^{-1}$ FA concentration. The composite copper signal

Fig. 25: Effect of fulvic acid on metal signal. a) DPAS voltammogram recorded with a MCRVCE for a synthetic sample contains 1 ng ml^{-1} of Cd and Pb and 1.5 ng ml^{-1} Cu. The b, c and d recorded after addition of 1, 4 and $8 \mu\text{g ml}^{-1}$ of FA: 8 min-plating at -1.0 V , 5 mV s^{-1} scan rate and 4.0 ml min^{-1} flow rate.

diminishes gradually and shifts slightly to more cathodic potentials with consequent peak broadening. These observations are qualitatively similar to those found with river-water samples, suggesting perhaps that organic constituents similar to fulvic acids may be responsible for the features observed with natural waters.

The effects observed do show that the organic material has effects on both, the plating step where it prevents some metal deposition in consequence of inhibition of reduction kinetics and in the stripping step where potentials for oxidation of the analytes and mercury may be affected.

The change in the position and shape of the copper peak as the FA/Cu ratio increases indicate that Cu is bound more strongly to fulvic acid as the fraction of the fulvic acid sites occupied by Cu decreases. This corresponds to the result reported for potentiometric titration of FA with Cu at a copper ion selective electrode [93].

Table VII

Statistical Parameters of the Analytical Curves

Given in Figures 17, 21, and 22

Fig. No.	Sample	Metal	Regression Coefficient $\mu\text{A}/\text{ng ml}^{-1}$	Intercept [*] / μA	Goodness of Fit, R^2
17	synthetic	Cd	2.2949 ± 0.0221	0.523 ± 0.111	0.99944
"	"	Pb	1.9365 ± 0.0175	0.295 ± 0.088	0.99951
"	"	ICu	1.3920 ± 0.0331	0.024 ± 0.166	0.99661
"	"	IICu	0.5725 ± 0.0495	0.470 ± 0.249	0.95668
"	"	Cu (total)	1.9646 ± 0.0171	0.494 ± 0.086	0.99954
21	synthetic	Cd	2.3044 ± 0.0092	0.564 ± 0.074	0.99990
"	"	Pb	1.9486 ± 0.0237	0.321 ± 0.191	0.99910
"	"	Cu	1.9940 ± 0.0143	0.443 ± 0.115	0.99969
"	river-water	Cd	2.3513 ± 0.0210	1.179 ± 0.169	0.99952
"	"	Pb	1.7319 ± 0.0050	0.216 ± 0.040	0.99994
"	"	Cu	0.9291 ± 0.0187	0.744 ± 0.151	0.99756
$\mu\text{A} / \text{min}$					
22	synthetic	Cd	1.0518 ± 0.0044	0.456 ± 0.052	0.99989
"	"	Pb	0.8465 ± 0.0047	0.571 ± 0.055	0.99981
"	"	Cu	0.8774 ± 0.0079	0.658 ± 0.093	0.99951
"	river-water	Cd	1.2451 ± 0.0212	0.983 ± 0.250	0.99826
"	"	Pb	0.7706 ± 0.0073	0.585 ± 0.086	0.99954
"	"	Cu	0.6828 ± 0.0260	0.074 ± 0.306	0.99135

* The $\pm$ values given in this column are standard deviation of residuals. They indicate the noise level for all current values. They are given in this column because they have the dimension of current. Formally, detection limits are $2 \times$ these values.

(IV.6) Interpretation

Earlier we noted that some organic substances present in the natural water may be adsorbed on the mercury electrode and consequently may considerably affect the redox properties of the trace metal ions present in the solution, particularly Cu. Many authors [94-96] have reported that fulvic acids and humic acids, HA, are not reducible at a mercury electrode, at least for $E > -1.0$ V. Buffle and associate [97,98] reported that FA and HA may be adsorbed on the mercury electrode and thus causes an increase in the capacitative current.

Theory [99] predicts that if a surface-active substance adsorbs on the electrode as a non-electroactive substance it may influence the rate of the reduction process of the metal complexes in two ways. The first is [99]:

"- by a "steric" effect (uncharged adsorbates), if the reduction rates are different on the covered (the chemical reaction may be slowed to such an extent that it becomes the rate-controlling step) and uncovered surfaces (controlled by diffusion). Although this effect often inhibits the charge transfer, it may also accelerate this process. The increased " irreversibility " in the presence of an adsorbate may be evidenced by a decrease in limiting current (or even the elimination of the signal), a shift of the signal, or the formation of a new diffusion-controlled signal at a more negative potential."

22

OF/DE

The second is [99]:

"- by an "electric" effect (change of, ψ , potential) reinforcing the steric inhibition when the charges on the metal complexes and the adsorbed layer have the same sign and opposing it when the signs are different".

In order to explain some features of DPASV curves obtained for Cd, Pb, I Cu and II Cu from river-water samples, it is important to discuss the features using the above theory and the theory recently developed for differential pulse polarography (DPP) [100]. It was confirmed that with increasing irreversibility, the peak current decreases, the peaks are broadened and the peak potentials are shifted to negative values. This was demonstrated by [100] plotting numerical values of the current response, $\Delta i/i_d$, against potential for various values of the standard charge-transfer rate constant, K_s . For the totally reversible case, where $K_s > 2 \times 10^{-2} \text{ cm s}^{-1}$, the peak currents have the largest values, the peak half-widths have the smallest values and the peak potential is independent of K_s . As the value of K_s decreases, the peak half-width increases and the peak current decreases toward constant values at $K_s < 1 \times 10^{-3} \text{ cm s}^{-1}$ corresponding to the totally irreversible case.

On the basis of this theory, we may be able to explain some of the behaviour and the shape of the peaks of Cd, Pb, I-Cu and II-Cu obtained in river-water samples with MCRVCE's by DPASV.

First, we consider the peak current of II-Cu obtained from untreated river-water sample. A shoulder peak appears at -0.11 V (Fig. 19) which was affected by the shift in the background Hg signal and partially inhibited by the adsorbed substances on the electrode. This peak disappears with successive runs on the same electrode and appears only after long deposition time or after spiking the sample with appropriate amounts of ionic copper (Fig. 20, curves e-g).

The peak current of the solid copper (I-Cu) from river-water sample appears at -0.30 V and grows slowly with increasing Cu^{2+} concentration (Fig. 20, curves a-g). The shape of the peak was unsymmetrical and broadened. The shift in the peak potential was too high compared with that from U.V. digested river-water or from synthetic sample (e.a. -90 mV). This may be attributed to increased complexation in the presence of river-water.

The shape of the stripping curve obtained for Pb from spiked river-water (Figs. 19, 20) is not perfectly symmetrical and is spread out from the descending portion of the curve; the peak width at the half-height was 68 mV compared with the value of 57 mV obtained with synthetic sample. A similar observation was reported by Buffle and associates [97,98] for the reduction wave of Pb in the presence of humic acid using DPP. They attributed it to the increase in the capacitative current caused by the presence of humic acid.

From the plot of current height vs. concentration (Fig. 21) and from current height vs. deposition time (Fig. 22), the slope

values of Pb from spiked river-water samples were slightly lower than those obtained with synthetic samples measured under the same conditions. Moreover, the peak was observed at -0.59 V (e.a. -20 mV shift). All these observations indicate complexation of Pb^{2+} and inhibition of charge-transfer due to presence of organic adsorbates.

In the case of Cd, the peak currents, peak potentials and the peak half widths obtained from river-water samples are similar to those observed in synthetic samples. This indicates that most of Cd-complexes are "labile" and that electrode reactions remain reversible.

We discussed previously the effect of the adsorbed film and the metal complexes in the solution on the peak currents, peak potentials and the shapes of the metal curves. The influence of the adsorbates may be seen by examining a U.V. digested river-water samples using an electrode equilibrated with untreated river-water followed by rinsing with blank solution (Fig. 23, curve b). As the results indicated, some of the features of natural samples still exist. This proves that some of the adsorbed species on the mercury film are stable and not stripped during the applied potential or desorbed by rinsing the electrode with blank solution. It emphasizes the role of the adsorbed layer rather than solution species in the origin of interference. The comparison between the results obtained with river-water samples and synthetic samples gives an idea of the relative importance of the various factors which may effect the redox reaction of the metal complexes.

There is no doubt that, among these factors, the adsorbates on the mercury film electrode plays the predominant role, at least in the level of metals and reagents present in natural water and with mercury coated porous electrodes in the mode that we used.

STUDIES OF ELECTRODES FOR STORAGE OF METAL IONS

(V.1) Introduction

In recent years several attempts have been made to perform water analysis in the field, thus ending the transportation of large volumes of sample [101] and reducing opportunities for sample contamination and preserving the sample integrity. Concern for both analytical sensitivity and sample integrity recommends the use of on-site sampling/preconcentration techniques. This is because a concentrated sample in controlled chemical form will be more stable and because minor contamination will be less significant for a concentrated sample than for a trace sample.

Because natural water is not homogeneous, two factors deserve special attention in the design and testing of water sampling procedures. First, parameters of sampling such as filtration, acidification, addition of other reagents, etc. must be explored for their effects on particle size distributions. Second, collection efficiencies ("recoveries") must be examined from the point of view of "natural" or "real" samples.

A variety of materials have been used as water insoluble carriers to bring trace metals into a phase that can be easily separated in small quantities from large amounts of water by filtration, centrifugation, or flotation. This last technique of separation, flotation, has some special appeal for possible development of field instrumentation because it is an established process stream technique in the metallurgical industry which runs conveniently on a continuous basis.

Ordinary anion and cation exchangers are of limited use for concentration of trace elements from natural water because of their lack of selectivity against major ions [102]. But, the "chelating resins" have made it possible to concentrate trace metals from natural waters, and, indeed, even to separate trace metals from major ions in sea water [103]. The chelating ion exchange technique can be used to concentrate much larger volumes of water than can be conveniently handled by solvent extraction but the limitation is a slow flow rate dictated by kinetics of exchange from solution complexes and colloids and swelling of chelex-100. Chelex-100 appears to be able to remove metal ions quantitatively from soluble "labile" complexes but not from particulates [46]. Given the rising interest in speciation, the limits implied for chelex-100 may actually be turned to advantage in future. It could provide species specific sampling.

The major problems that must be faced by any system for collection, preconcentration, and transport of a trace metal sample by electrodeposition are those of mutual interferences by constituents of the analyte, and stability and reproducibility of the electrode. Electrodes of Au, Ag, Pt, C, Bi, W, and metal films on carbon have been used [3]. Of these, certain forms of carbon based electrodes are the most promising with respect to production of a stable reproducible electrode for use in field sampling. ASV is noted for the very great sensitivity achieved, as a result of the

preconcentration in the electrodeposition step. In this respect, as well as others, thin mercury film on RVC is especially notable as we have seen above.

(V.2) EXPERIMENTAL

(V.2.1) Apparatus: The flow system and the RVC electrode have been described in detail previously (Fig. 15). The lower sections (RVC electrode units) of the electrochemical cells were constructed from plastic tubes having the same dimensions (see Fig. 14, Detail C). Each unit contains a single RVC disk of 100 pores per inch (ppi). The disk had a calculated volume of 0.19 ml and surface area of 12.7 cm^2 . The overall capacity of the flow system including tubes connection, pump tube (except the solution in the cell bottom) is 5.2 ml. All experiments are performed with the PAR model 364 mentioned above and the potential are given with respect to the SCE as before.

(V.2.2) Reagents and solutions: All reagents and solutions were prepared in the same way as described previously.

(V.2.3) Mercury plating procedure: Plating of mercury films on the RVC electrode was carried out in the flow system under similar conditions to those described previously. After removing the contaminants, blank solution (0.012M acetate buffer, oxygen free) was allowed to flow through the electrode to replace all the mercury plating solution. The MCRVCE unit can be replaced with another one or used directly for measurements. Several RVCE's were plated with mercury and stored in the covered units under 2 ml blank solution. Each unit can be used for

measurements on the same day as required.

(V.2.4) Storage and Analysis procedure: Plating of Cd, Pb and Cu on the MCRVCE was done with a synthetic sample at -1.0V for 6 min deposition time and at 4.8 ml min^{-1} flow rate. The DPAS voltammogram was recorded at 5 mvs^{-1} scan rate, while the sample still flowed through the electrode. The scan was stopped at 0.0V , and this potential was maintained for 1 min, after which the MCRVCE was plated again with the metals for the same deposition time. The flow of solution was stopped and the sample solution was replaced directly with a blank deaerated previously with N_2 . The blank was allowed to flow through the electrode to remove all the sample from the electrochemical cell, during that time the electrode was still held at -1.0V . After removing the sample, the connection tube in the up stream of the electrode was locked, followed by disconnection of the MCRVCE unit which was then covered directly. This unit contains 2 ml blank solution under storage. Several MCRVCE's were plated with the metal ions under study and stored in the same manner.

For stripping of the metal ions from the stored electrode, the MCRVCE unit was connected with the flow system and a potential of -1.0 V was applied at the electrode for 5 min to replate some of the dissolved metal ions from the stored solution. During that time 8 ml of blank solution purged with N_2 was allowed to flow through the electrode (total volume = 10 ml) while the electrode was still held at -1.0V . Afterward, the scan was applied and the DPAS voltammogram recorded.

(V.3) Analysis Results

Peak currents obtained from seven MCRVCE's plated for 6 min. at -1.0V under conditions mentioned previously with synthetic sample contains 6 ng ml^{-1} of Cd^{2+} , Pb^{2+} , and Cu^{2+} and stored for periods ranging from 12 to 96 hr. are presented in Table VIII. The peak current for Cd shows a successive decrease in sensitivity with increasing storage time, while Pb peak current shows a slow decrease in sensitivity up to 24 hr. storage time, thereafter the sensitivity becomes quite constant. The Cu peak currents show a slight decrease in sensitivity during all storage periods, indicating the "stability" of Cu in the mercury film.

The behaviour of these metal ions during the storage time may be related to

1. The oxidation potential of each metal ion under discussion, that is the more cathodic metal peak potential the most affected with increasing storage time due to relatively fast stripping of the metal to the surrounding solution (dissolution) under uncontrolled potential.
2. The coalescence of mercury droplets during the storage time lowered the response to cadmium, in contrast Cu showed the highest response.

Fig. 26 (Curve a) shows the signals of Cd, Pb, I-Cu and II-Cu at zero storage time (direct run), (curve b) show the signals of these metals after 72 hr. storage time. The peak current of Cd is

Table VIII: Recovery of metal ions after storage on MCRVCE's plating from synthetic samples contain 6 ng ml⁻¹ of Cd, Pb and Cu for 6 min.

t/hour	CADMIUM				LEAD				COPPER			
	peak curr- ent before storage	peak curr- ent after storage	percentage recovery i_{Po}/i_{Ps} $\times 100$	peak curr- ent before storage	peak curr- ent after storage	percentage recovery i_{Po}/i_{Ps} $\times 100$	peak curr- ent before storage	peak curr- ent after storage	percentage recovery i_{Po}/i_{Ps} $\times 100$	peak curr- ent before storage	peak curr- ent after storage	percentage recovery i_{Po}/i_{Ps} $\times 100$
12	35.6	29.5	82.9%	28.8	24.7	85.8%	31.7	29.0	91.5%			
18	34.5	27.0	78.2%	28.6	23.8	83.2%	31.0	28.5	91.9%			
24	37.0	25.0	67.5%	28.0	22.1	78.9%	34.4	31.2	90.7%			
36	37.2	21.6	58.1%	28.5	20.6	72.3%	32.5	28.8	88.6%			
48	38.0	20.0	52.6%	29.0	22.2	76.6%	32.7	28.0	85.6%			
72	37.5	18.0	48.0%	27.2	20.6	75.4%	34.0	30.5	89.7%			
96	35.0	15.9	45.4%	29.3	22.0	75.1%	31.5	28.0	88.9%			
	36.4±3.7%				28.3±2.7%				32.5±3.9%			

Figure 26: DPAS Voltammograms obtained with a MCRVCE for synthetic sample contains 6 ng ml⁻¹ of Cd, Pb, and Cu. 5 min- plating at -1.0V. a) Direct run and b) after storage 72 hr.

diminished to less than 50% from the original peak current, while Pb shows more than 75% recovery. The peak widths at the half-peak height are broadening. Cu response is the highest, the recovery approaches 90%. Also Curve b shows that the II-Cu signal increases compared to one obtained from the direct measurement (zero storage time), thus the coalescence of the mercury droplets causes a shift in the copper metal, amalgam phase equilibrium toward the amalgam side.

Dissolving of stored metal ions in a small volume blank solution (total 10 ml) and replating on the same electrode Fig. 27, (Curve a) shows small increase in Cd peak current after long deposition time (ca. 20 min), but low recovery of Cu. This is related to the higher sensitivity of Cd in a mercury film compared to copper.

Replating the dissolved metal ions for 20 min on freshly prepared MCRVCE followed by stripping (Curve b) improves the sensitivity and the peak half-width for Cd and Pb but not for Cu.

Fig. 28 presents analytical curves for Cd, Pb, and Cu from six MCRVCE's plated previously for 5 min. at -1.0V with buffered synthetic samples which contain Cd, Pb and Cu ranging in concentration from 1 to 6 ng ml⁻¹ after storages for 48 hr. The measurements were carried out at the same electrode and the results compared with those from the direct measurements (zero storage time). The calibration curve may be used for the estimation of the labile metal ions in unknown samples using identical experimental conditions.

Figure 27: DPAS Voltammograms obtained with a MCRVCE's for synthetic sample contains 6 ng ml^{-1} of Cd, Pb, and Cu. 6 min- plating at -1.0 V and the electrode stored 72 hr. a) stripping curve of the replated metal ions for 20 min on the same electrode. b) stripping curve of the replated(20 min) metal ions on fresh electrode.

Figure 28: Comparison between the calibration curves of Cd, Pb, and Cu from synthetic samples for direct runs and the runs after storages 48 hr. plated with a MCRVCE's at -1.0V for 5 mins.

(V.4) Design of Flow System for use "on site" for plating trace metal ions

The configuration of the field flow system is shown schematically in Fig. 29, A. The electrochemical cell is connected to the container and pump by teflon tubes (2 mm i.d.). The peristaltic pump (Markson Scientific, N.Y.) is operated at 12V D.C. using a D.C. motor (Hansen Mfg. Co., Inc., IMC Magnetic Corp., Princeton Indiana). The pump is placed downstream from the cell to pull the sample through the RVC electrode as this will minimize the possibility of air entering the cell by diffusion through the Tygon tubing. Timer control is used to measure the deposition time.

A diagram of the two electrodes system electrochemical cell is given in Fig. 29, B. The electrical contact is made through the graphite tube. The counter electrode is Pt wire. The RVC disks were punched from blocks of 100 (ppi). Each disk is 7 mm in diameter, 5 mm in length, and has a calculated volume of 0.19 ml and a surface area of 12.7 cm^2 .

The potential is controlled by a variable power supply and digital voltmeter [104]. Block diagram is shown in (Fig. 29, C). Plating current can be measured with a microammeter.

(V.4.1) Suggested Procedure

Plating mercury film on the RVCE can be done on site using the two electrode system under experimental conditions similar to those used in the laboratory. Plating of metal ions also can be done in similar manner. The sample should be filtered before addition of buffer and deaeration.

Figure 29: A) Diagram of flow system that can be used "on site" for plating of trace metal ions at the MCRVCE. B) Electroanalytical cell, 1) graphite tube 2) two teflon tubes 3) two teflon plug valves 4) RVC disk 5) electrical contact with the graphite tube 6) counter electrode (Pt-wire). C) Detail of the variable power supply and the digital voltmeter.

Determination of total heavy metal ion content can be done by digestion of the sample. The digestion of the sample can be performed continuously using standard accessories [86] prior to the filtration stage. Several MCRVCE's can be plated in the similar manner and stored for further analysis in the laboratory using three electrode system.

(VI) SIGNIFICANCE OF THE PROJECT.

(VI.1) Origin of the project

A major problem related to trace analysis of natural water samples is associated with collection and transportation of samples. Losses of trace components occur easily and contamination is serious. These problems may be relieved to a significant extent by pre-concentration. Electrolytic pre-concentration has been used for flameless atomic absorption spectroscopy. For example, Newton and Davis[105] report pre-concentration of Cd, Pb, As, Hg, Se and Zn by electrolytic reduction on a tungsten wire loop produces efficient sample collection. The AA detection limits for the metals are superior to those obtained using 5 μ l solution samples in a graphite tube furnace. Lund and Larsen[106] carried out a similar study for Cd only and established agreement between their flameless AA method and ASV at approximately 0.2 μ g. Gold and platinum electrodes have also been used for pre-concentration of mercury samples [107, 108].

Several electrode geometries have been developed for concentration of metal ions. Tubular electrodes discussed above share the advantages of rotating electrodes when they are employed in a flow system. Seitz et al. [34] and Schieffer and Blaedel [82,83] have discussed the preparation and properties of these devices. Preformed mercury films appeared to be stable and the mounting geometry of these devices protects them well.

This led to the hope that an electrode could be built for electrodeposition of metals directly in the field which would allow the sensitive and valuable DPASV technique to be used in the analysis step.

The problem is that nobody has ever reported a procedure for handling and storage of plated ASV electrodes. Standard procedures tend to emphasize their fragility. Commonly, the use of any solid electrode (particularly carbon) requires that precise electrode cleaning, polishing and pretreatment procedures be used to obtain reproducible results. The nature and the extent of these procedures depend on the material involved.

The possible opening for a new behaviour seemed to be flow through electrodes. Various solid materials have been used as a substrates for mercury film in ASV. These include gold [81], platinum, [90], and carbon [91,92]. Carbon is preferred compared to metallic materials like Pt or Au whose behaviour is complicated by their finite solubility in mercury and the tendency of the metal (e.g. gold) to form intermetallic compounds [81]. Several different forms of carbon have been used as electrodes in flow-through configuration. Reticulated vitreous carbon, RVC, is a new form of carbon which possesses high surface area in addition to several practical and electrochemical advantages. This makes it suitable as an electrode in flow through systems [36-38]. RVC is extremely inexpensive and it is quite easily fabricated in various cell designs. No polishing or impregnation is required.

The RVC electrode provided high analytical currents due to its high surface area. The high analytical currents are usually accompanied by high background currents. However, the use of differential pulse anodic stripping voltammetry discriminates against the background currents, and that permits the determination of very low concentrations of heavy metal ions without prolonged deposition.

(VI.2) Analytical performance of the MCRVCE

The utility of the MCRVCE system for the analysis of synthetic and river water samples has been demonstrated. From an electrochemical point of view the behaviour of the MCRVCE system is similar to that of conventional MTFE and HMDE systems. However, the former offers a considerable improvement in that samples can be changed without exposure of mercury film to atmosphere, thus prolonging the life of the electrode and facilitating medium exchange [33,66]. Moreover the MCRVCE system offer a higher analytical response owing to increased mass transport to the electrode.

From the view point of sensitivity, MCRVCE in a flow-through system compares favourably with the other flow-through electrodes in connection with ASV assemblies that have been suggested to date [34,38,84,85]. Deposition periods required for well defined peaks range from 1 min. for 5 ng ml^{-1} , through 5 min. for 0.5 ng ml^{-1} and 10 min. for 0.1 ng ml^{-1} for the metal ions under discussion, except copper which needs relatively longer deposition time particularly at very low concentrations.

(VI.3) Stability studies

The use of the MCRVCE in a flow system for monitoring heavy metal traces requires electrode stability for adequate precision of results, as well as the storage stability we studied. The behaviour of the MCRVCE has been discussed recently [38]. Blaedel et al. have shown that the mercury on RVC electrode is stable under repetitive measurements over several hours of use. The stability of the RVC electrode itself was shown

by the fact that the sensitivity did not change appreciably over a period of 10 days [38].

In our studies, the stability of the MCRVCE after plating of the heavy metals is demonstrated by Fig. 30. It can be seen that over several independent measurements the percentage recovery changes in reproducible fashion with storage. Fig. 28 shows that even though there is loss on storage, the peak current varies linearly with concentration and as such storage does not seriously detract from the utility of this technique for quantitative determination.

A comparison of (curve b) Fig. 26 and (curve a and b) Fig. 27 shows the sensitivity for determination of Cd improves if the heavy metal is dissolved and replated on the fresh electrode. However this procedure gives only a slight improvement in the sensitivity for Pb and is deleterious for Cu.

(VI.4) Projected mode of operation of field system

The electrochemical procedure to be followed is basically the same as that used in laboratory studies. The absolute concentration of metals in the environmental samples may not be measureable by voltammetry because only a fraction of the total metal present are reducible at the electrode [33], and the determination may be subject to organic interference. Accordingly chemical pretreatment is required for the determination of the total heavy metal ion content by subjecting the sample to acid digestion procedure [50] prior to filtration. The digestion of the sample can be performed continuously using standard accessories [86] prior to the filtration stage. The reference describes a suitable field device.

Figure 30: Effect of storage on percentage recovery.

The calibration curves for "treated" field samples can be obtained using a synthetic standard. An estimate of "labile" metal can be made by comparing the current obtained from "untreated" samples with the calibration curves as above. However it must be borne in mind that interference due to organics is not always limited to metal complexing. The concept of "labile" components of natural samples is not at all unambiguous as chapters II and III have shown.

The protocol recommended for the field trial is analysis of three samples for each site. The first is a synthetic solution to serve as a standard. The second is a filtered undigested sample which will measure the "labile" metal-however poorly defined that quantity is. The third is a filtered sample acid digested, using the device of ref. [86]. The three samples should be deposited within one hour. The electrodes are to be stored as follows. After plating the metals at appropriate potential for a certain deposition time, the flow of solution is stopped and the sample solution is replaced directly with a blank deaerated previously with N_2 . The blank is allowed to flow through the electrode to remove all the sample solution from the electrochemical cell, during that time the electrode is held at the deposition potential. After replacing the sample with blank, the cell is locked from upstream and downstream and disconnected. Finally, they should be returned to the laboratory for the DP stripping run within 96 hours of deposition. Elapsed time should be noted.

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