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## POSSIBILITIES OF VOLTAMMETRIC METHODS FOR SPECIATION IN THE PRESENCE OF PARTICLES

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# ABSTRACT

Differential pulse polarography and anodic stripping voltammetry can be used directly in suspensions without pre-filtration; heavy metals like copper(II) and lead(II) adsorbed on hydrous oxides such as silica and  $\alpha$ -goethite are not being released during the time scale of the techniques and are thus not sensed by these techniques.

In samples with colloids and organics such as EDTA and NTA in the presence of heavy metals, when the complexes are non-labile but electrochemically reducible at a more negative potential, one can determine the ligand concentration and the binding capacity of the colloid from the voltammetric measurements of individual batches with different amounts of cations like copper(II) and lead(II).

From the differential pulse measurements of solutions with heavy metals and the organic ligands EDTA and NTA, it is possible to know directly the amount of metal bound to each one of the ligands and the free cation. This can also be determined by anodic stripping voltammetry at different deposition potentials.

These conclusions can be used for speciation studies in natural waters without using filtration; more work has to be done with other types of organic ligands and colloids and possible effects of adsorption need to be investigated.

## 1. INTRODUCTION

As it is well known, speciation is important in terms of chemical reactivity, bioavailability and toxicity. The heavy metals can exist in solution as different species. Some of the metal complexes may, from an electrochemical point of view, be non-labile, which means that they are non dissociable during the time scale of the technique, i.e., the measurement. In natural waters metal ions can also be incorporated or adsorbed on particles or colloids. This is a very important fraction since more than 95% of heavy metals that are transported from land to sea are in particulate form<sup>1</sup> which, in principle, can be separated from the soluble fraction using filtration techniques.

In this work we used voltammetric methods directly in the presence of the suspension of particles or colloids<sup>2</sup> without pre-filtration. In these systems of metals, ligands and colloids, as they may occur in natural waters, we attempted to interpret the concentrations of the various species that could be measured electrochemically. So, we avoid filtration that is an operational technique since it divides the species mainly according to their size (normally 0.45  $\mu$ ) and have some limitations such as contamination problems, adsorption loss, changes of concentration during the operation and finally electrostatic effects, when the filters or the colloids to be removed are electrically charged.

## 2. EXPERIMENTAL

An ionic strength of  $10^{-2}$  M  $\text{KNO}_3$  has been used. All solutions were  $5 \times 10^{-4}$  M in TRIS buffer. The temperature was  $25 \pm 2^\circ\text{C}$ ; in the presence of colloids we always made analytical determinations of individual batches waiting between 1 and 2 hours for attainment of equilibrium. This has been checked since we had the same results 24 hours later.

Different voltammetric techniques were used, such as differential pulse polarography (DPP) and anodic stripping voltammetry in d.c. (ASV) or differential pulse mode (DPASV) with hanging mercury drop electrode (HMDE), the deposition time being always 2 minutes and rest time 30 s. The counter and reference electrodes were always Pt and Ag/AgCl, respectively. The equipment was Methrom E506 or PAR-174A polarographs. The colloids used were  $\text{SiO}_2$ , the commercial product Aerosil 200 (Degussa) with a specific surface area of  $200 \text{ m}^2/\text{g}$  and  $\alpha\text{-FeOOH}$  (goethite) prepared according to Atkinson et al<sup>3</sup>, with a specific area of  $14.7 \text{ m}^2/\text{g}$ . The concentrations used in the adsorption experiments were respectively  $16 \text{ mg/dm}^3 \text{ SiO}_2$  and  $80 \text{ mg/dm}^3 \text{ FeOOH}$ .

The suspensions with NTA or EDTA and colloids were kept in the dark 1 or 2 hours before the measurements.

The heavy metals used were copper(II) and lead(II) in the form of nitrates. The concentration of the labile fraction of the heavy metals determined in suspension by voltammetric methods was always estimated from the calibration plots obtained for each technique in the absence of colloids. In the anodic stripping voltammetry experiments two deposition potentials were used (according to DPP peaks or the pseudopolarograms), in one case only the free or/and hydrolysed species having been reduced, and in the other these species plus the complexed forms.

### 3. RESULTS AND DISCUSSION

Theoretically one could anticipate that heavy metals adsorbed on colloids should be physically non-labile, since according to the Stokes-Einstein equation, the diffusion coefficient of a particle of 100Å radius is 100 times smaller than that of an inorganic complex with 1Å radius. This means that for the heavy metal adsorbed on a particle of that size the current obtained by DPP should at best (i.e., if the metal-particle complex were fully labile) be ten times smaller. If the particles are larger the current should be even smaller. Probably the surface complexes are also chemically non labile, which means that the cations are not released from the surface fast enough to become available to the electrode.

In order to check experimentally the non-labile behaviour of the surface complexes, suspensions with pure colloids, and heavy metals have been used and two approaches have been considered.

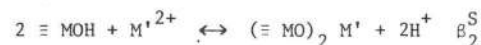
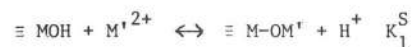
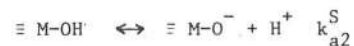
- 1) the calculation of conditional surface complex formation constants assuming that the heavy metal measured by voltammetric method is only the soluble fraction.
- 2) Comparison of the results obtained by different time scale techniques.

In the first approach we have determined the conditional surface formation constants of  $Pb^{++}$  and  $Cu^{++}$  with some hydrous oxides (Table I) for a fixed pH value, different metal concentrations and different time scale techniques such as differential pulse polarography (time scale of about 50 ms) and anodic stripping voltammetry (time scale of about 1 s).

TABLE I  
Conditional Surface Complex Formation Constants of  $Pb^{2+}$  and  $Cu^{2+}$   
with Hydrous Oxides

Colloid	$C_{Pb}$ (M)	$C_{Cu}$ (M)	pH	$pk_{a1}^S$	$pk_{a2}^S$	$\log K_1^S$	$\log \beta_2^S$
Goethite $1.5 \times 10^{-5}M$	$2 \times 10^{-6}$ to $10^{-5}$	-	7.25 $\pm 0.05$	$6.4^S$	9.25	$-2.0 \pm 0.2$ (DPASV) $-1.8 \pm 0.2$ (DPP) $-1.8 \pm 0.2$ (ASV)	
$1.0 \times 10^{-5}M$		$4 \times 10^{-6}$ to $1.5 \times 10^{-5}$	7.13 $\pm 0.05$			$-1.6 \pm 0.1$ (DPP)	
Silica $2.6 \times 10^{-5}M$	$2 \times 10^{-6}$ to $10^{-5}$		7.23 $\pm 0.02$	$7.3^6$	-		$-4.4 \pm 0.1$ (DPP)
$1.5 \times 10^{-5}M$		$2 \times 10^{-6}$ to $2 \times 10^{-5}$	6.56 $\pm 0.06$				$-3.2 \pm 0.2$ (DPP)

The stability constants of Table I correspond to the surface equilibria:



and have been determined from the mass law equations assuming that there is no dissociation of the surface complex during the time scale of the technique. The concentration of the surface groups can be estimated from the difference between the calibration plot and the parallel straight line obtained in the presence of the colloids with the heavy metal in excess (Figs. 1,2,3,4).

From the results obtained with different techniques one can see that the values of the stability constants agree within the experimental errors and are of the same order of magnitude as the literature values<sup>6,7</sup>. These are conditional constants for a certain ionic strength and pH; they have not been extrapolated for zero charge and zero coverage, and so they are not intrinsic constants corrected for electrostatic interactions:  $K_{a1}^S (\text{intr.}) = K_{a1}^S \exp(-F\psi_s/RT)$ ,  $\psi_s$  being the inner potential of the surface. We have assumed the species presented in the table and the hypothesis is checked from the constancy of the values of the formation constants for each point.

Considering the second approach to check the non lability of the surface complexes we can see from Fig. 1 that when, for example, Pb(II) has been added to goethite in individual batches and the residual lead has been determined, after attainment of equilibrium, the same concentration levels are obtained with techniques of different time scale:

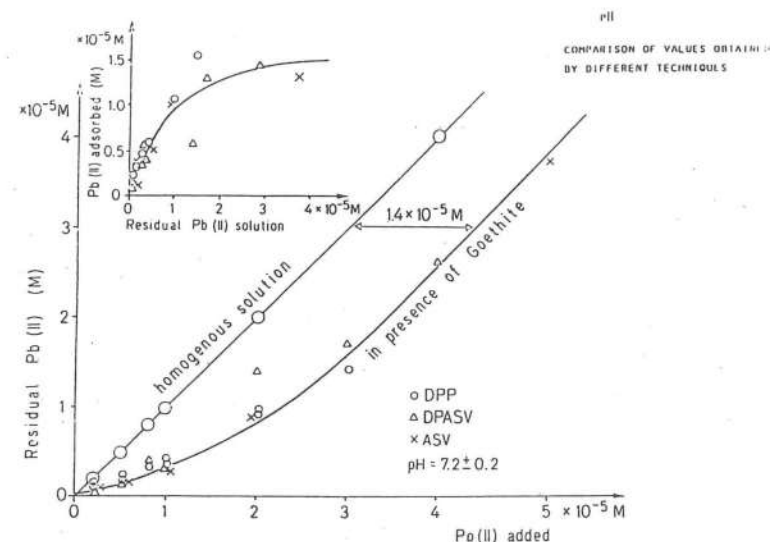


Fig. 1 - "Lead determined" in a goethite suspension of  $80 \text{ mg dm}^{-3}$  at  $\text{pH} = 7.25 \pm 0.05$  versus "lead added". The residual Pb(II) concentrations in solution were measured by different voltammetric techniques. As shown by the small figure on the top, the data can also be plotted as a Langmuir type of adsorption isotherm.

differential pulse polarography and anodic stripping voltammetry. This is well illustrated in this figure since we can fit the points obtained with different techniques to the same curve.

On the other hand, the peak potential ( $E_p$ ) and half width ( $w_{1/2}$ ) have not been influenced by the presence of the colloid and the binding capacity of goethite is  $1.9 \times 10^{-4} \text{ mol/g}$ , which is in good agreement<sup>5</sup> with a capacity of  $2 \times 10^{-4} \text{ mol/g}$  determined by adsorption of  $\text{H}^+$  and  $\text{F}^-$ .

Thus, one may infer there is no dissociation of the heavy metal

adsorbed on the colloid during the measurement, since otherwise the fraction would certainly be different for the several time scale techniques. This has been noticed for goethite and for silica with the cation Pb(II) and with Cu(II).

Thus, we conclude that voltammetric methods can be used in the presence of colloids and are expedient for:

- 1) Evaluating the partition between particles and solution
- 2) Determining surface coordination equilibrium constants.

However, since in natural waters the particles often coexist together with organic ligands, mixtures of colloids and well-defined organics such as NTA and EDTA were analysed. Different amounts of Pb(II) or Cu(II) were added to individual batches and after the equilibrium was attained in the dark during 1-2 hours (which has been checked by the similarity of results obtained for 2 or 3 days) the voltamograms obtained by DPP or ASV were recorded.

The DPP behaviour of the different species is presented in Table II and we have noticed that PbNTA, CuNTA and CuEDTA, although not labile at the reduction potential for  $\text{Cu}^{2+}$  during the time scale of the technique, can be directly reduced on the electrode at more negative potentials than the aqueous metal ion. The PbEDTA complex is also non labile, but cannot be reduced directly on the electrode, probably due to its high irreversibility, which means that for the reduction it would be necessary to use very negative potentials and before these the reduction of hydrogen ion takes place. All the surface complexes are not reducible at more negative potentials, because the interaction of the colloids with the electrode is difficult and their deposition is slow compared with the time scale of the technique.

Table II  
DPP Behaviour of the Different Species. Ionic medium  $10^{-2}\text{M KNO}_3$

Species	$E_p$ (mV) *	$W_{1/2}$ (mV)
$\text{Pb}^{2+}$	- 348	$60 \pm 2$
$\text{Cu}^{2+}$	+ 50	$60 \pm 2$
PbNTA	- 816	$75 \pm 2$
CuNTA	- 120	$70 \pm 2$
CuEDTA	- 300	$78 \pm 2$

\* The same values have been obtained in the presence and absence of the colloids.

In terms of ASV the complexes PbNTA, CuNTA and CuEDTA are non labile in the deposition step, but directly reducible at more negative potentials. During the stripping step the complexes are not labile and so only the peak of the free metal has been obtained. The complex with PbEDTA is non labile in the deposition step and not reducible at more negative potentials as also happened in DPP.

This means that in terms of ASV, two different deposition potentials, according to DPP peak potentials, or according to a pseudopolarogram, can be chosen, in such a way that at one value only the free metal can be deposited and at the second value both the free metal and the complex can be reduced. Thus, one can determine the percentage of the heavy metal and that of the ligand. This can be seen in Fig. 2 for the system NTA + Pb(II) at  $\text{pH} = 7.15$  analysed by ASV at two deposition potentials. So, at  $E_d = -1.20\text{ V}$ , both the labile and not labile species are being reduced and at  $E_d = -0.60\text{ V}$  only the labile species are being deposited. However, for Pb(II) concentration higher than NTA concentration, the straight line obtained at  $E_d = -1.20\text{ V}$  does not fit exactly the calibration plot without ligand, which is due to the dif-

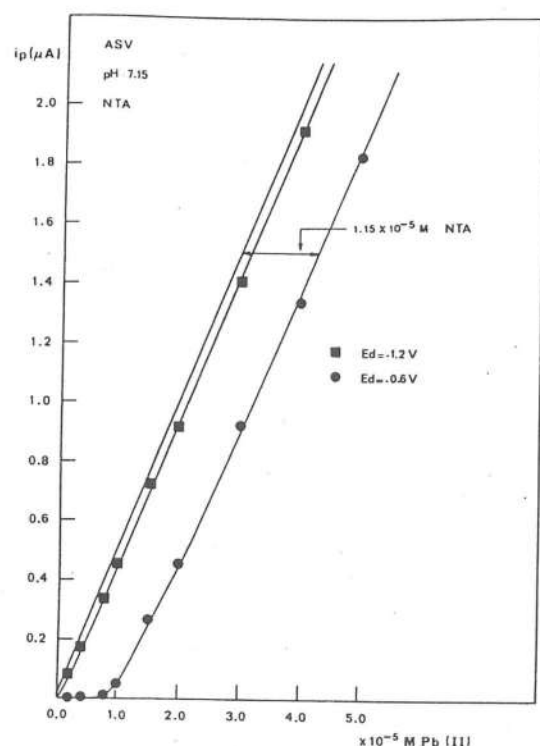


Fig. 2 - Pb(II) to NTA solutions at constant pH (pH = 7.15) followed by ASV at two different deposition potentials. At  $E_d = -1.2 V$   $Pb^{++}$  and NTA +  $Pb^{++}$  complex are being reduced, contrarily to  $E_d = -0.6 V$  where only  $Pb^{++}$  is reduced. The calibration plot within NTA is also included.

ference of the diffusion coefficient of PbNTA and free Pb(II). From this difference, a value of  $D = 1.2 \times 10^{-6} cm^2 s^{-1}$  has been calculated for PbNTA, considering (according to Buffle<sup>8</sup>) that the diffusion coefficient of the lead is  $D = 8.28 \times 10^{-6} cm^2 s^{-1}$ . With this value and from the dif-

ferent slopes of the calibration plots of Pb(II) and Cu(II) in the medium studied, the diffusion coefficient of free copper  $D = 7.56 \times 10^{-6} cm^2 s^{-1}$  has been determined, which has been used to determine the diffusion coefficient of CuEDTA complex,  $D = 5.94 \times 10^{-6} cm^2 s^{-1}$ , from the results of ASV, in the same way as has been done for lead.

After considering the behaviour of the organic complexes in terms of ASV which has been exemplified in detail for the mixtures  $Pb^{++}/NTA$  (Fig. 2), the same systems have been studied in the presence of a colloid. Again, the suspension was analysed voltammetrically without pre-filtration. This has been studied for Pb(II) and Cu(II) in the presence of NTA or EDTA with  $SiO_2$  or goethite and is illustrated with the system EDTA + goethite + Cu(II) (Fig. 3). From a plot of the peak current versus the added Cu(II) at  $E_d = -0.50 V$  (where the CuEDTA complex and the free copper is being reduced), the binding capacity of the colloid  $0.85 \times 10^{-5} M$  was determined, i.e., copper bound to goethite. However, from the same type of plot but  $E_d = -0.20 V$ , where only the free copper is being deposited, the concentration of EDTA can be determined and a value of  $0.75 \times 10^{-5} M$  was estimated which agrees with the added concentration.

However, if one uses DPP to analyse a mixture of a colloid and an organic ligand with a heavy metal, the behaviour of the plot  $i_p$  versus  $M^{++}$  added is different from that obtained by ASV. Indeed, when the heavy metal is in a lower concentration than that of the ligand, only the peak of the complex is obtained, but for higher concentrations of the heavy metal the peak of the complex is constant and the peak of the free metal increases in the same way as in the calibration plot without organic ligand and colloid. From the curve obtained with the peak current of the complex the ligand concentration can be known ( $1.05 \times 10^{-5} M$ )

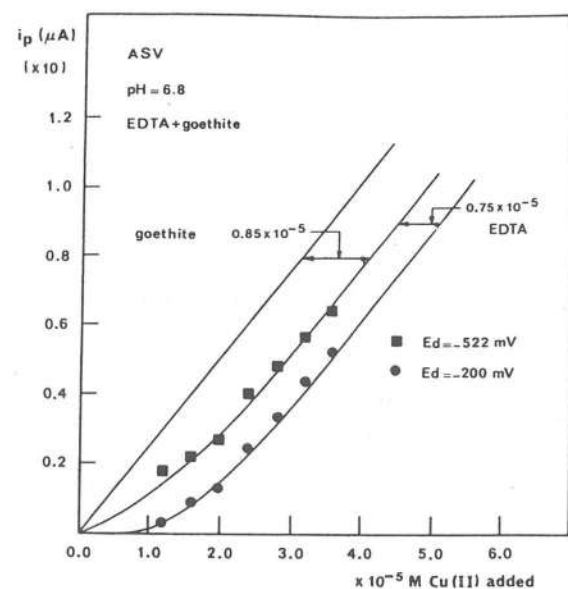


Fig. 3 - Cu(II) addition to a suspension with EDTA and goethite ( $80 \text{ mg dm}^{-3}$ ) at constant pH ( $\text{pH} = 6.8$ ) followed by ASV at two different deposition potentials. At  $E_d = -0.5 \text{ V}$   $\text{Cu}^{++}$  and  $\text{Cu}^{++} + \text{EDTA}$  complex are being reduced, contrarily to  $E_d = -0.2 \text{ V}$  when only  $\text{Cu}^{++}$  is reduced. The calibration plot without EDTA and goethite is also included.

and from the peak current of the free metal the concentration of the binding groups of the colloid plus the organic ligand can be determined using the difference of the calibration plot and the parallel through the last three experimental points ( $1.80 \times 10^{-5} \text{ M}$ ) as shown in the systems  $\text{NTA} + \text{SiO}_2$  and  $\text{Pb(II)}$  (Fig. 4).

From the results obtained for the ligand concentrations that agree with the concentrations of the organics added, one can conclude that NTA and EDTA were not adsorbed on the surface of silica or goethite

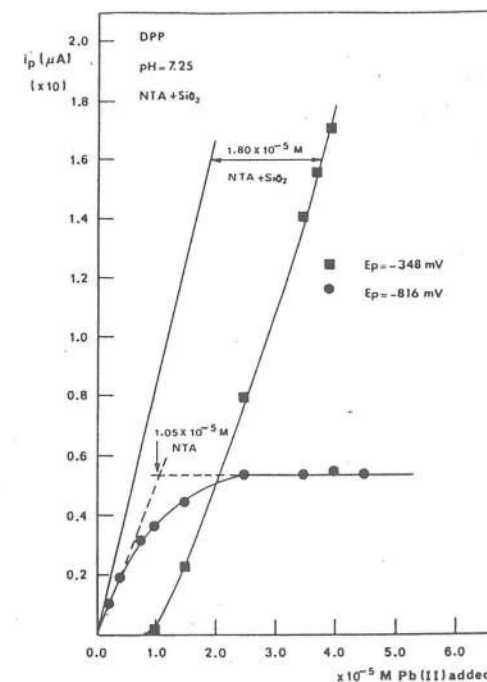


Fig. 4 - Pb(II) addition to a suspension with NTA and silica at constant pH ( $\text{pH} = 7.25$ ) followed by DPP. The reduction peak of the free lead ( $E_p = -0.35 \text{ V}$ ) and the reduction peak of the complex ( $E_p = 0.8 \text{ V}$ ) are being considered. The calibration plot without NTA and silica is also included.

under these conditions, since the heavy metal bound to the organic ligand adsorbed on the colloid should be inert.

So one can conclude that, in principle, voltammetric techniques can be used to analyse suspensions with particles such as hydrous oxides in the presence of organic ligands such as EDTA and NTA, together with labile species in solution.

As an example, Fig. 5 shows the voltammogram of a solution with



CuEDTA and CuNTA complexes together with free and hydrolysed copper where all the three peaks are well defined, from which the concentration of the respective species in solution can be determined.

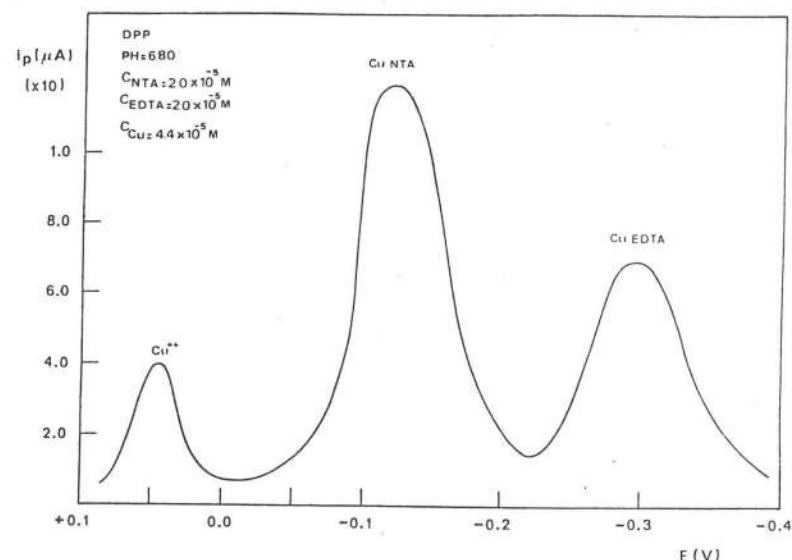


Fig. 5 - DPP polarogram obtained at  $pH = 6.80$  for a solution with  $C_{NTA} = 2.0 \times 10^{-5} M$ ,  $C_{EDTA} = 2.0 \times 10^{-5} M$  and  $C_{Cu} = 4.4 \times 10^{-5} M$  in  $KNO_3$   $10^{-2} M$  buffered with TRIS.

From the several experiments we have tried, one can conclude that in conditions where only ASV can be used - and not DPP due to the lower detection limit of the first technique - NTA can be determined with a titration adding  $Pb(II)$ , but not in a titration with  $Cu(II)$ ; this is due to the higher irreversibility of the  $PbNTA$  complex. Indeed the peak potentials of free copper and of  $CuNTA$  complex are so close to one another ( $\Delta E_p < 0.2$  V) that it is difficult to use two different deposition potentials to quantitatively separate the reduction of the two species. On the other hand, EDTA can be determined adding  $Cu(II)$  and not  $Pb(II)$ , since the  $PbEDTA$  complex is not reducible directly on the

mercury before the reduction of hydrogen ion.

If DPP can be used, NTA can be determined by titration with  $Cu(II)$  or  $Pb(II)$ , because this technique gives a higher resolution than that of ASV. However, EDTA can only be determined with  $Cu(II)$  but not with  $Pb(II)$ , for the same reason as pointed out before for ASV.

Although NTA and EDTA can exist in natural waters due to pollution, specially because they are added in some countries to the detergent powders, they are not in general the dominant organics. In non-polluted waters the main organic ligands are the humic and fulvic acids, resulting from the degradation of vegetation. These are mixtures of polymers where the dominant chelating groups are carboxylic and phenolic groups, but with nitrogen and sulfur in minor quantities. These ligands form complexes with heavy metals like  $Cu(II)$  and  $Pb(II)$  that have different degrees of lability and stability constants, according to the ratio  $C_L/C_M$ , where  $C_L$  and  $C_M$  are the total concentration of the ligand and the metal ion<sup>9</sup>. Adsorption problems on mercury are important and can be avoided in the polarographic method extrapolating to zero drop time<sup>8</sup>.

More studies need, therefore, be done before applying these results directly to natural waters. However, possible speciation schemes for different types of natural waters can be anticipated as follows.

For interstitial waters with high levels of organics and heavy metals DPP can often be used directly in the sample without filtration; a titration in batch solution can be done directly with different heavy metals such as  $Cu(II)$  or  $Pb(II)$ , the labile species and the different non labile complexes, including the surface complexes, being determined separately. The non labile complexes in solution and surface complexes



can be differentiated if the organic complexes with the heavy metals can be reduced directly on the electrode at more negative potentials.

The possibility of adsorption problems on mercury can always exist in natural waters, but this can be checked from the shape of the peak or using, for example, different drop times in DPP technique. If adsorption exists there is, in principle, the possibility of trying to minimize the problems by using normal pulse polarography with a convenient initial potential and duration of the pulse<sup>10</sup>.

In water that contains lower concentrations of metal ions, ASV can be used directly in the presence of the suspension, but different deposition potentials should be used for different heavy metals. However, in order to choose the adequate values of the deposition potentials, a pseudopolarogram needs to be established; this is a time consuming technique, and due to the presence of labile species in solution a surface effect can occur which distorts the plot of  $i_p$  versus added metal<sup>11</sup>. So, often ASV could only be used in such a way that the medium is exchanged subsequent to the deposition step or with values extrapolated to zero deposition times, to avoid the surface effect that can lead to erroneous results. The plots of peak potential versus deposition time can also give an idea if there is adsorption<sup>12</sup>.

For this reason DPP is, in principle, a more adequate technique than ASV for doing speciation studies in natural waters, but due to the higher detection limit of DPP, it can probably be used only in some types of natural waters, like interstitial waters. In this situation a DPP polarogram of the type of Fig. 5 should be useful.

Still within the analytical scheme that includes the direct analysis of the natural waters without filtration, it is useful to

determine the total metal concentration after destruction of the organic matter. The total metal concentration could be determined by voltammetric methods, or atomic absorption, which is probably more convenient due to the smaller influence of traces of organic matter.

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# DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF SOME 6-ACYL-2 (3H)-BENZOXAZOLONE DERIVATIVES

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## SUMMARY

The synthesis and the differential pulse polarographic analysis of ten 6-acyl-2(3)-benzoxazolone derivatives are presented. pH 3.00 Britton-Robinson buffer was found to be the best supporting electrolyte. The electrochemical determination is based on the reduction of carbonyl group present in all molecules. Linear response was observed from 0.2-2 to 25-65 mg.L<sup>-1</sup> depending on the molecules.

Key Words: Benzoxazolone derivatives, synthesis, analysis, differential pulse polarography.

## INTRODUCTION

Benzoxazolinones have been associated with various type of biological properties. Lespagnol and his co-workers (1,2) prepared and tested a number of derivatives of benzoxazolin-2-ones for their analgesic (3,4), antipyretic (3,4), anticonvulsive and hypnotic effects (1). Analgesic and antipyretic activity have been described in 6-acyl-benzoxazolin-2-ones (4,5) and in 3-aminoalkylbenzoxazolin-2-ones (6,7). Antibacterial (8,9) and fungicidal (10) activities have also been reported for benzoxazolin-2-ones. The pronounced biological activity of many 2-benzoxazolinone derivatives (4) and medicinal value of 5-chloro-2-benzoxazolinone (11) prompted the investigation of 3-substituted-2-benzoxazolinones.