Applicability of potentiometric stripping analysis to the speciation of lead–humic acid complexes using potassium permanganate as oxidant


Potentiometric stripping analysis (PSA) using potassium permanganate as an oxidising agent during the stripping step was applied to the measurement of the lead complexation properties of pyridine-2,6-dicarboxylic acid and humic acids (HA) at pH 6.2 and 0.1 mol l\(^{-1}\) ionic strength (K\(\text{NO}_3\)). Values of the conditional stability constants (\(\beta\)) of the well defined 1 : 1 and 1 : 2 lead(II)–pyridine-2,6-dicarboxylic acid complexes, which are labile within the time-scale of the technique, were determined by the DeFord–Hume method. The study was repeated by using differential-pulse anodic stripping voltammetry (DPASV) for comparison. The results obtained by both techniques are consistent among themselves and in accordance with the literature, which shows that permanganate was suitable as an oxidant during the stripping step of PSA measurements. A study of the lead(II)–HA (6.6 and 39.7 mg l\(^{-1}\) total organic carbon) complexation properties was performed using both PSA and DPASV. It was observed that the average stability constant (\(K\)) obtained by DPASV was much higher than that determined by PSA. This result suggests that HA adsorption phenomena at the mercury electrode interfere more markedly with lead(II)–HA stability constants determined by DPASV than with those obtained by PSA.

**Keywords:** Potentiometric stripping analysis; anodic stripping voltammetry; ion-selective electrodes; pyridine-2,6-dicarboxylic acid; humic acids; lead(II) complexes.

Anodic stripping voltammetry (ASV) and related techniques have been widely used for speciation studies,\(^{1–13}\) mainly to determine the stability constants of complexes, owing to their high selectivity and sensitivity.\(^{14,15}\) Potentiometric stripping analysis (PSA) has been applied mainly to the determination of the total concentration of heavy metals in various types of samples\(^{16–28}\) and more rarely for speciation studies.\(^{29–33}\) However, the similarity between PSA and ASV suggests that PSA may also have potential for speciation purposes.\(^{2}\)

PSA features some advantages over voltammetric techniques. It is advantageous when redox couples exhibit sluggish electrochemical charge transfer kinetics but rapid chemical charge transfer\(^{34}\) and can be implemented by using straightforward equipment such as a three-electrode cell, a high-impedance operational amplifier, an x–t recorder and a potentiostat.\(^{35–37}\) In addition, times can be measured more readily and precisely than micro currents and no potential ramp need be used (in contrast to ASV), which results in lower instrumental costs. Some workers have reported that PSA is much less affected by surface-active substances\(^{33,38–40}\) than are other stripping techniques, such as ASV. However, other workers found that adsorption of surfactants on a mercury electrode has a greater impact on PSA stripping times.\(^{41,42}\)

In addition, in PSA, an oxidizing agent [mercury(II) in many cases] must be present in the solution during the stripping step. In metal speciation studies of inert systems (determination of the free metal fraction), its presence does not interfere with the response. This probably explains why, apart from the work of Soares and Vasconcelos\(^{32,33}\) the technique has only been applied for the speciation of inert systems.\(^{29–31}\) The usefulness of PSA for speciation studies of labile systems is severely limited owing to the presence of mercury in the cell, which might interfere in the chemical equilibrium in both deposition and stripping steps. Additionally, it has been shown that PSA can be an alternative technique\(^{32}\) and more accurate than DPASV, when adsorption phenomena occur,\(^{33}\) for speciation of copper(II) labile systems. However, in those studies mercury(II) was used as an oxidant, whose presence in the solution, under the experimental conditions used, had no significant effect on the analytical signal.

The aim of this work was to study the suitability of permanganate anion as oxidising agent in PSA for speciation studies of labile systems. Permanganate anion does not compete with metal(s)–ligand(s) complexation equilibria. The method was applied to the complexation of lead with two different ligands: pyridine-2,6-dicarboxylic acid, which does not adsorb at a mercury electrode under the conditions used in this work,\(^{43}\) and commercial humic acids, which are markedly adsorbed. Lead was chosen because we intend to investigate if the application of PSA could also be extended accurately to speciation studies of metals other than copper(II) when adsorption phenomena occur.

**Experimental**

**Reagents and materials**

All solutions were prepared with analytical-grade reagents or equivalent and were used without further purification, together with deionized and doubly distilled water with a resistivity > 14 MΩ cm. Pyridine-2,6-dicarboxylic acid (Aldrich, Milwaukee, WI, USA) and HA (Fluka, Buchs, Switzerland) were used. HA solutions were prepared as follows: a suitable amount of solid HA was dissolved in water with agitation for 1 d and the solution was filtered through a 0.45 μm pore size filter; the dissolved organic carbon in the solution was measured. The solution was then diluted twofold with an appropriate background solution containing K\(\text{NO}_3\) and 2-(N-morpholino)-ethanesulfonic acid (MES) in order to obtain final solutions...
containing 0.1 mol l\(^{-1}\) KNO\(_3\) and 10 mmol l\(^{-1}\) MES at pH 6.2.

For PSA and DPASV experiments, a lead nitrate intermediate standard solution of \(4.83 \times 10^{-3}\) mol l\(^{-1}\), prepared weekly by diluting a lead nitrate stock standard solution of \(4.83 \times 10^{-3}\) mol l\(^{-1}\), (Merck, Darmstadt, Germany), in high purity water, was used. For lead ion-selective electrode potentiometry (ISE), two lead standard solutions of \(9.66 \times 10^{-3}\) and \(4.83 \times 10^{-2}\) mol l\(^{-1}\), prepared by diluting a blister of lead nitrate (Merck, Titrisol), directly in 0.1 mol l\(^{-1}\) potassium nitrate (KNO\(_3\)) solution were used.

Mercury for the working electrode was purified by washing with 10% nitric acid (HNO\(_3\)) and by double distillation under reduced pressure.

All material was cleaned by soaking in 20% HNO\(_3\) for 1 d and then rinsing several times with water.

**Apparatus**

PSA and DPASV experiments were carried out using an Ecochemie (Utrecht, Netherlands) Autolab multimode polarography with an IME module connected to an MTEK computer. A Metrohm (Herisau, Switzerland) E506 polarograph was used for the studies of adsorption phenomena by phase-selective voltammetry (ACV). Both polarographs were coupled to Metrohm 663 VA devices with a multimode electrode.

Three electrodes, a hanging mercury drop electrode (HMDE) for ACV and a static mercury drop electrode (SMDE) for PSA and DPASV, together with a glassy carbon electrode and a Ag/AgCl(s), 3 mol l\(^{-1}\) KCl electrode were used as working, auxiliary and reference electrodes, respectively.

A PC-controlled system assembled with a Crison (Modena, Italy) MicropH 2002 pH meter, a Crison MicroBU 2030 microburette, an Orion (Cambridge, MA, USA) 90-02-00 (double junction) reference electrode and a Radiometer (Copenhagen, Denmark) Model 3012 electrode (pHb) activated with a sensor of Ag2 S/PbS (prepared as described previously) \(^4\) were used for ISE measurements.

Total organic carbon (TOC) was measured with an Ionics (Massachusetts, USA) Model 1258 total organic carbon analyser.

**Procedure**

All measurements were performed at 20 °C in background solutions of 0.1 mol l\(^{-1}\) KNO\(_3\) at pH 6.2 buffered with 0.01 mol l\(^{-1}\) MES, except in ACV experiments, which were carried out in 0.5 mol l\(^{-1}\) KNO\(_3\) (in order to obviate the resistance of the cell and the influence of the diffuse layer). MES is a pH buffer with a sensor of Ag2 S/PbS (prepared as described previously \(^4\) ) for ACV and a static mercury drop electrode (SMDE) for PSA and DPASV experiments were carried out using an Ecolab multimode polarography.

**Calculations**

**Determination of conditional stability constants**

For labile complexes (ML\(_j\)), the potential shifts (\(\Delta E_p\)) obtained from a solution with a metal ion, M\(^{ii}\), in the presence and absence of a ligand, L, gives information about the extension of complexation according to an equation similar to that of DeFord and Hume: \(^{46}\)

\[
\Delta E_p = E_p^{ii} - E_p^{ii} = (2.303 RT/nF) \log \alpha + \log (i_p/i_p^*)
\]

(1)

where \(\alpha = [M][L]/[M][L]\) (\([M]\) and \([L]\) represent the total and free metal ion concentrations, respectively), \(E_p^{ii}, i_p^{ii}, E_p^a\) and \(i_p^a\) represent the peak potential and current intensities in the presence (p) and absence (a) of ligand, respectively, and \(R, T\) and \(n\) have their usual meanings.

By considering the similarities between ASV and PSA, in the latter the values of \(i_p^a\) and \(i_p^a\) could be changed by (\(d\delta/dE_p\)) and (\(d\delta/dE_p\)) respectively.

The conditions of the validity for eqn. (1) have been well described in the literature. \(^{47}\)

For simple (monomeric) and small ligands, such as inorganic ligands and amino acids, the fit of the experimental results with the theoretical results obtained by the polynomial, whose degree gives the number of complexes while the coefficients correspond to the overall conditional stability constants, \(\beta^{ii}\): \(^{32}\)

\[
\sum \beta_i [L]^i = 10^{(\Delta E_p - \delta_{c0})/nF} - 1
\]

(2)

For heterogeneous ligands (polymeric and polyfunctional), such as HA, which have a large number of different sites of coordination for the metal, the free and bound (\([M]\)) metal ion concentrations, for each point of the titration, can be calculated by eqn. (1) and the material balance of the metal [eqn. (3):]

\[
[M]_b = [M]_b + [M]_f
\]

(3)

An average stability constant (\(\overline{K}\)), expressed by

\[
\overline{K} = [M]_b/[M][L] = \overline{\Sigma} ([M]_b/[M][L])\overline{\Sigma} ([M]_f/[M][L])
\]

(4)

can be estimated from the slope of the Scatchard graph, \([M]_b/\overline{[M]}\), which is a method for linearization for the 1:1 complex formation model but it can provide information about two different types of coordination sites if the respective stability constants are sufficiently different to be distinguished.
Determination of complexation capacities

Owing to the heterogeneity of humic acids, whose composition and molar concentration are unknown, it is usual to estimate the overall concentration of sites of coordination via the complexation capacity (CC).

In this work, CC was calculated by the method described by Ruzic\(^{49}\) assuming the formation of 1:1 complexes. In this method, CC is calculated from the slope of the \([M]/[M]_0 = f \left([M]_0\right)\) curve.

Results and discussion

Pyridine-2,6-dicarboxylic acid studies

Pyridine-2,6-dicarboxylic acid was chosen as a ligand because it forms complexes whose stoichiometric stability constants have been well described in the literature\(^{50}\) and it does not adsorb at the mercury electrode under the conditions used in this work.\(^{45}\) Also, pyridine-2,6-dicarboxylic acid can be used as a simple model of humic acids.\(^{43}\)

Determination of diffusion coefficients of the complexes

Lead forms 1:1 (log \(\beta_1 = 8.70\)) and 1:2 (log \(\beta_2 = 11.57\)) complexes with pyridine-2,6-dicarboxylic acid. In order to verify the distribution of these complexes with the ligand concentration, computational simulations of chemical equilibria were performed with the speciation computer program MI-CROQL\(^ {31}\) by imposing a variation of the ligand concentration between \(2.2 \times 10^{-4}\) and \(7.7 \times 10^{-3}\) mol l\(^{-1}\) for a lead concentration of \(9.7 \times 10^{-7}\) mol l\(^{-1}\) at pH 6.2. For this purpose, stoichiometric stability constants from the literature\(^{50}\) for lead–pyridine-2,6-dicarboxylic acid complexes were used. Fig. 1 shows the distribution of these complexes with ligand concentration and indicates that for ligand concentrations lower than \(10^{-3}\) mol l\(^{-1}\) the 1:1 complex is dominant. For higher ligand concentrations, the 1:2 complex predominates. To test if the diffusion coefficients of the complexes, namely when the 1:2 complex predominates, were similar to or lower than that of the metal, the values of the normalised current \(I_{p} / I_{pa}\) determined by DPASV for pyridine-2,6-dicarboxylic acid concentrations were calculated. The values of the normalised currents were similar and close to unity in the range of ligands embraced (data not shown), which demonstrates that \(D_{ML}, D_{MRL}\) and \(D_{M}\) represent the diffusion coefficients of the 1:1 and 1:2 complexes and of the metal ion, respectively.

Complexation studies

The similarity of \(I_{p} / I_{pa}\) values obtained in the absence and presence of pyridine-2,6-dicarboxylic acid also indicates that lead(ii)–pyridine-2,6-dicarboxylic acid complexes are labile within the time-scale of the technique used. Further, \(E_{p}^0\) became more cathodic when the ligand concentration increased. These cathodic shifts resulted from the fast complexation of lead(ii) by pyridine-2,6-dicarboxylic acid during the stripping step.\(^ {52}\)

Previously, it was shown that PSA is suitable for determining the stability constants of metal–organic complexes under conditions of application of the DeFord–Hume method.\(^ {32}\) In that study, mercury(ii) cation was used as an oxidising agent, which might interfere in the chemical equilibria under study. As permanganate anion does not compete with metal(s)–ligand(s) complexation equilibria, it can be a good alternative if it is not able to oxidise the ligands in the solution. Therefore, we decided to study the suitability of using it as an oxidant during the stripping step for the PSA speciation studies. For this purpose, experimental \(\Delta E_{p} = f [\text{pyridine-2,6-dicarboxylic acid}]\) for \(9.7 \times 10^{-7}\) mol l\(^{-1}\) lead(ii) ion were obtained by both PSA and DPASV at pH 6.2 (Fig. 2). The two techniques provided virtually identical results. The values of \(\Delta E_{p}\) fitted a curve due to the presence of 1:1 and 1:2 complexes and the function described by eqn. (2) follows well a second-degree polynomial, from which the overall conditional stability constants were determined (Table 1). Table 1 also includes comparable overall conditional stability constants calculated from the stoichiometric values selected from the literature. The results obtained in this work were in accordance with those obtained previously.\(^{50}\) These results indicate that permanganate anion is a suitable oxidant for PSA under the present experimental conditions.

Humic acid studies

Quantification of HA concentration

Since HA have undefined molecular mass and are not totally soluble at a pH near neutrality, their concentrations in the solutions were estimated in two ways: through the TOC and the respective CC. To determine CC, ISE titrations of the various HA solutions were performed with lead(ii) ion solution (for a typical example, see Fig. 3). The experimental results were treated by the Ruzic method\(^{49}\) for the determination of CC. The values of CC (mean values of at least three determinations were obtained for each HA solution) were plotted as a function of the

![Fig. 1](image1.png)

**Fig. 1** Theoretical simulation of the influence of pyridine-2,6-dicarboxylic acid (L) concentration on the fraction of the total lead (α\(^p\)) in the form of (— —) PbL₁ and (—— —) PbL₂ complexes.

![Fig. 2](image2.png)

**Fig. 2** Mean values and standard deviation (\(n = 4\)) of \(\Delta E_{p}\) versus pyridine-2,6-dicarboxylic acid concentration for \(9.7 \times 10^{-7}\) mol l\(^{-1}\) lead(ii) obtained by (●) PSA and (○) DPASV at pH 6.2.

<table>
<thead>
<tr>
<th>Log (\beta_1)</th>
<th>Log (\beta_2)</th>
<th>Technique</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.06 ± 0.38(^*)</td>
<td>11.96 ± 0.22(^*)</td>
<td>PSA</td>
<td>This work</td>
</tr>
<tr>
<td>9.30 ± 0.31(^*)</td>
<td>11.46 ± 0.33(^*)</td>
<td>DPASV</td>
<td>This work</td>
</tr>
<tr>
<td>8.69</td>
<td>11.57</td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) Mean values and standard deviation for \(n = 4\).
TOC values (Fig. 4). It must be pointed out that the CC values are strictly valid only for the system studied (Pb–HA). In fact, different values of this parameter can be obtained for complexation of the same ligand with different metals. Fig. 4 shows that for HA concentrations lower than 23.8 mg TOC l$^{-1}$ the CC varied almost linearly with the concentration of TOC \( (CC (mol \ l^{-1}) = 1 \times 10^{-2} [HA, \ mg \ TOC \ l^{-1}] - 2 \times 10^{-4}, r = 0.96, n = 3). \) For higher HA concentrations, the slope of the function \( CC = f \) [TOC] decreased, which was probably due to conformational changes in the HA. This intermolecular aggregation can be explained as a result of cross-linking of separate macromolecules by metal complexation. Pinheiro et al. have also verified aggregation with the same HA as used in this work, whose diameter of aggregates was larger than 30 nm. As HA aggregation was verified, in the following experiments HA concentration is reported with respect to TOC.

### Adsorption effects

In previous work, HA adsorption studies performed by measuring \( i_{ac} \) versus \( E \) showed a maximum adsorption at −0.4 V versus Ag/AgCl(s), 3 mol l$^{-1}$ KCl, but a marked effect was also verified for more cathodic potentials. In this work, the adsorption kinetics of HA at the mercury electrode were studied at a potential of −0.7 V versus Ag/AgCl(s), 3 mol l$^{-1}$ KCl by ACV, which was chosen as the deposition potential for subsequent complexation studies. Solutions without ligand and with HA concentrations ranging from 6.6 to 39.7 mg TOC l$^{-1}$ were used. For this purpose, curves of \( i_{ac} = f (t) \) with a phase angle of 90° in stirred solutions were recorded. At this phase angle, \( i_{ac} \) is capacitive in nature and the capacitive current is proportional to the capacity of the electrode double layer if no faradaic reactions are present and the resistance of the cell is negligible. As Fig. 5 shows, an almost instantaneous (≤9 s) decrease in \( i_{ac} \) was observed for HA concentrations > 14.7 mg TOC l$^{-1}$. For a 6.6 mg TOC l$^{-1}$ HA concentration, the dependence of \( i_{ac} \) on time indicates that equilibrium is reached after about 60 s. Furthermore, the equilibrium condition is very close to saturation for the HA concentrations used, since all curves tend, within experimental error, to the same values of the limiting current.

### Complexation studies

It is well known that the adsorption of organic matter on the working electrode affects the peak potential values if the adsorption with adsorbed ligands is not negligible compared with the complexation in the bulk solution, giving higher values of stability constants. These facts prompted us to investigate the accuracy of lead(ii)-HA complexation parameters determined by PSA when adsorption phenomena occur. For this purpose, the values of \( \Delta E_p = f \) [HA] in the presence of 9.7 × 10$^{-7}$ mol l$^{-1}$ lead(ii) were measured by PSA and DPASV (Fig. 6). For each batch of solution, at least two cycles of deposition and stripping were performed; the values of \( \Delta E_p \) obtained in the two cycles (data not shown) were identical, which excludes the possibility of HA oxidation by permanganate anion during the period of the electrochemical measurements. Under the experimental conditions used in the stripping techniques (deposition time, stirring rate and potential), ac experiments (Fig. 5) showed that the
mercury electrode was saturated with adsorbed HA molecules for all HA concentrations used. For each [HA]t/[Pb], ratio, it was verified that the values of $\Delta E_p$ obtained by DPASV were much higher than those given by PSA (Fig. 6). Fig. 6 also shows that the values of $\Delta E_p$ increased with increasing [HA]t/[Pb], ratio, which confirmed the liability of Pb–HA complexes within the time-scale of the analytical techniques used. Additionally, the results obtained by both techniques fit well a second-order polynomial: for DPASV, $E_p = 17.8 + 2.9$ [HA] - 4.7 [HA]$^2$, $r = 0.999$. These curves show that for a zero organic carbon concentration, $\Delta E_p$ is close to zero for PSA and much higher, 17.8 mV, for DPASV, whose values should be close to zero for both cases within experimental error.

It should be mentioned that, we also tried to estimate $\Delta E_p$ under conditions such that adsorption phenomena do not interfere with the complexation parameters. For this purpose, two other independent techniques, ISE (more details of the methodology can be found elsewhere[33]) and differential-pulse polarography (in this case after extrapolating the values of $\Delta E_p$ to zero drop time[60]), were used but, owing to the lower sensitivity of the techniques, it was not possible to determine the complexation parameters. The experimental data were used to calculate the $K$ values by the Scatchard method[48] (see Determination of conditional stability constants). From the data, average stability constants with the values log $K = 10.06 \pm 0.54$ and 8.37 $\pm$ 0.16 were obtained by DPASV and PSA, respectively. This set of results seems to suggest that adsorption phenomena interfere markedly with the DPASV but not the PSA results.

**Conclusion**

This work has shown that permanganate anion can be used as an oxidising agent during the stripping step for PSA speciation studies of labile complexes of lead(II)–pyridine-2,6-dicarboxylic acid and lead(II)–HA instead of mercury(II) ion, with the advantage of not competing with metal(s)–ligand(s) complexation equilibria.

The results also suggest that HA adsorption phenomena at the mercury electrode interfere markedly with the Pb–HA stability constants obtained by DPASV but not by PSA for HA concentrations ranging from 6.6 to 39.7 mg TOC l$^{-1}$, which embraces the levels of dissolved organic matter present in fresh waters.6162 This behaviour is in agreement with previous results obtained for the Cu–HA system.33

These results seem to suggest that PSA may be an alternative and more accurate technique for speciation studies of labile systems when there is adsorption of organic matter at the mercury electrode. However, as electroanalytical techniques are generally very sensitive to many effects occurring at the electrode–solution interface, the present results concern only the Pb–HA system. For other systems, it will be necessary to check the suitability of PSA.

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**References**

51 Westall, J. C., MICROQL, a Chemical Equilibrium Program in BASIC, Internal Report, Institut for Water Resources and Water Pollution Control (EAWAG), Dubendorf, 1987.

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