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Optoelectrochemical Sensor for Lead Based on Electrochemically-Assisted Solvent Extraction

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ABSTRACT

A thin film containing the complexing agent 2-(5-bromo-2-pyridylazo)-5-(diethylamino)-phenol deposited on the surface of an ITO electrode has been used as a colorimetric sensor for lead. The sensor is based on a new electrochemically assisted solvent extraction method. When an anodic potential was applied to the thin-film sensing layer, lead ions were extracted from aqueous solution into the film resulting in an increase of absorbance at 550 nm. The magnitude of the absorbance change was linearly dependent on the concentration of lead in the range 0-5 ppm with an estimated limit of detection for a simple spectrophotometric method better than 250 ppb. The sensor was reset for a fresh measurement by applying a cathodic potential. The prospects for using this electroassisted extraction method in conjunction with optical waveguide evanescent field detection as a new integrated sensor for trace analysis are discussed.

Keywords: optoelectrochemistry, sensors, liquid/liquid electrochemistry, lead, waveguides, evanescent field.

INTRODUCTION

Electrochemical sensors that rely on the measurement of current[1,2] or a change in potential[3,4] are well known. More recently, sensors in which an electrochemical reaction contributes to an optical response have been reported.[5-10] These optoelectrochemical sensors retain the advantages of electrochemical control, such as spatial and temporal organisation of the reaction and fine control over the signal, but are free from disadvantages such as interference from electrochemical background noise.[8-9] In the first example of this kind of sensor an ITO electrode sandwiched between a thin film of lutetium biphthalocyanine and a planar waveguide was used to detect dissolved chlorine in water.[5,6] The spectral changes which occurred when chlorine oxidised lutetium biphthalocyanine were measured through evanescent field absorption in the film; electrochemical control was used to restore the film to its original state ready for a new measurement. More recently, electrochemical control has been used to generate the substrate for a chemiluminescent reaction in enzyme assays[7,8] and immunoassays,[9] with the potential to detect more than one analyte in the same sample. In the present paper interfacial potential control has been used to extract lead from aqueous solution into a film containing an appropriate ligand for absorbance detection, and to reset the sensor for a new measurement.

PRINCIPLES OF THE METHOD

The method is based on the electrochemistry of liquid-liquid interfaces.[11] Briefly, the partition coefficient between an aqueous and an organic solvent which is immiscible with water depends on the applied interfacial potential.[12,13] For example, the equilibrium distribution of an ion i between the aqueous and the organic (sensing film) phase is described by the two-phase Nernst equation:[11]

$$\Delta_o^w \phi = \Delta_o^w \phi_i^o + \frac{RT}{z_i F} \ln \frac{a_i^o}{a_i^w} \qquad (1)$$

where $\Delta_o^w \phi$ is the Galvani potential difference between the aqueous (w) and the organic phase (o), a_i is the activity of metal ion i, z_i is its charge and R, T and F have their usual meanings; the chelation constant is included in $\Delta_o^w \phi_i^o$. In what follows, the activity is taken as the concentration. When a chelating agent is present in the organic phase, equation (1) is only valid when the metal chelate carries a charge, in which case, the concentration ratio of metal ion will be strongly dependent on the applied potential. This electroassisted extraction differs from traditional solvent extraction of metal ions. In this case, proton exchange with the metal ion of interest takes place, as indicated by the extraction equilibrium:

$$2LH_{(o)} + M^{2+}_{(w)} \rightleftharpoons L_2M_{(o)} + 2H^+_w \qquad (2)$$

No charge separation takes place and therefore the position of the equilibrium is unaffected by the interfacial Galvani potential difference. The extractant used in the present work, 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (BrPADAP), forms a positively charged metal chelate with Pb^{2+} and hence the ratio of the concentrations of Pb^{2+} in the aqueous and organic phases will be determined by the applied interfacial potential as given by equation (1). Thus, relatively modest changes in $\Delta_o^w \phi$ will result in a very large concentration change of Pb^{2+} in the sensing film. For instance, a shift in $\Delta_o^w \phi$ of 300 mV should lead, in principle, to a change in the concentration ratio of Pb^{2+} of 10 orders of magnitude.

In order to achieve extraction into the organic phase, a suitable ligand for Pb^{2+} must be present in the film.[12,13] This fulfils two functions, to decrease the Gibbs energy of transfer of the hydrated ion to a non-aqueous environment and to provide a spectroscopic probe for quantifying the transfer of the metal ion. The chelating agent chosen, BrPADAP, belongs to a class of azo reagents forming the largest group of compounds used in spectrophotometric analysis. Their popularity is due to their high absorption coefficients (up to 1×10^5 mol dm^{-3} cm^{-1}) which make them suitable for sensitive analytical determinations. Chelation of ions occurs through the pyridinium and azo nitrogen, and the phenolic oxygen atoms. The geometry of the complex is determined by the ratio of BrPADAP to metal cation. For a 1:1 stoichiometry a square planar complex is formed with the fourth site on the metal being co-ordinated by a monodentate ligand such as water. An octahedral complex is formed when the ratio of BrPADAP to metal cation is 2:1.[14] In aqueous solution the pyridinium, azo and hydroxyl groups have pK_a values of 1.0, 3.0 and 11.2 respectively. In the pH range 3-11 the main species present is the yellow uncharged form which is soluble in non-polar solvents. BrPADAP chelates a wide range of metal ions including most of the transition metals, group IIIB, IVB and VB metals, and thorium and uranium. It has been used for the detection of lead by spectrophotometry and by adsorption stripping voltammetry.[12]

The speciation of Pb(II) is important since it determines its state of charge and therefore, the possibility of using electroassisted extraction as described by equation (1). Aqueous Pb(II) is mainly present as the hydrated Pb^{2+} and the $PbCl^+$ complex ions in chloride containing solutions,[15] i.e. as cationic species.

EXPERIMENTAL SECTION

Materials.

An indium tin oxide (ITO) electrode was used as the substrate since this constitutes a convenient optically transparent electrode for spectroelectrochemical experiments.[16] Glass coated with 20 nm thickness ITO, supplied by Balzers Ltd (Buckinghamshire, UK), was cut into electrodes that measured 25 x 9 x 1 mm thick. Poly(vinyl chloride) (PVC; inherent viscosity 1.115), 2-nitrophenyl octyl ether (NPOE), and 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (BrPADAP) were obtained from Aldrich. Tetraoctadecylammonium tetraphenylborate (TODA-TPB) was precipitated by mixing aqueous sodium tetraphenylborate (Aldrich) with tetraoctadecylammonium bromide (Aldrich) in acetone; the precipitate was recrystallised twice from acetone. Lead ion solutions were prepared by dissolving lead (II) nitrate in 10 mM NaCl.

Preparation of the sensing film electrode.

Metal ion sensors were made by depositing a sensing film on an ITO electrode. The composition of the sensing film was similar to that which has previously been used in ion selective electrodes[12,13,17] and in ion transfer studies.[15] Ionic conductivity within the film was ensured by incorporating a hydrophobic quaternary salt, TODA-TPB, within the film. PVC (50 mg), TODA-TPB (5 mg), BrPADAP (10 mg) and 0.1 ml of NPOE were dissolved in 10 ml of THF. The solution was stable and could be stored at room temperature in darkness for at least one year. The films were prepared by spreading 25 µl of this solution over an area of 1.5 x 0.9 cm on an ITO-coated glass wafer and allowing it to dry for five minutes at room temperature. Films became detached from the ITO electrode unless the perimeter was sealed with epoxy resin after deposition, because aqueous solution percolated into the interface between the film and the electrode. After preparation the electrode was cured at 75°C for one hour. The completed sensors were used on the day of preparation.

Spectrophotometric measurements.

Absorbance spectra of 0.1 mg cm^{-3} BrPADAP in NPOE were obtained with a Hewlett Packard 8452A Diode Array Spectrophotometer before and after sonicating the solution over lead (II) nitrate crystals. All other absorbance measurements were taken in a three-electrode cell made from a standard 4.5 ml cuvette using the same spectrophotometer. The reference electrode was a silver chloride coated silver wire and the counter electrode was a platinum wire; both electrodes were located in the cell behind the ITO working electrode coated with the sensing film. Potentials were controlled with an in-house built potentiostat and a waveform generator (PPR1, Hi-Tek Instruments, Buckinghamshire, England). All potentials were measured with respect to the Ag/AgCl reference electrode in 0.01 M NaCl.

Prior to carrying out measurements, the ITO electrode coated with the PVC-BrPADAP-TODATPB film was allowed to stand in the electrochemical cell for thirty minutes to allow equilibration and stabilisation of the absorbance. Lead was detected by measuring the absorbance changes for this electrode when placed in contact with Pb^{2+} solutions after applying a cathodic potential of -500 mV and resetting it by applying an anodic potential of +750 mV. The absorbance spectra were measured for a 10 ppm lead solution after applying a cathodic potential for one minute and an anodic potential for one minute. Repetitive electrochemical resetting of the sensing film in contact with a 1 ppm lead solution was demonstrated by following the change in absorbance when a series of cathodic potentials were applied for one minute followed by an anodic potential for 6 seconds. Detection of lead in the range 0 to 10 ppm was carried out with the same sensor, which was electrochemically reset at the end of each measurement. The refractive index of the films was measured with a computer controlled ellipsometer at a wavelength of 633 nm and at an angle of incidence of 70°. The refractive index was employed in the modelling of the optical response of the waveguide overlaid with the sensing film.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of the BrPADAP-Pb^{2+} chelate. The spectrum shows an absorbance maximum at approximately 550 nm and this wavelength was selected for subsequent measurements in real-time. The electroassisted extraction of Pb^{2+} in the sensing film led to clear changes in its absorption spectrum. Figure 2 shows the change in absorbance for a film electrode between the anodic and the cathodic potentials used after 1 min. of polarisation. These results clearly indicate the incorporation of Pb^{2+} within the film. There is a clear similarity between the results in Figures 1 and 2, although for the latter, Pb^{2+} had not been completely stripped from the film during the anodic cycle.

Figure 3 shows the changes in absorbance of the film electrode in contact with solutions of different concentrations of Pb^{2+} when the potential was stepped from 0.75 to –0.5 V. Stripping the Pb^{2+} from the film was carried out by applying an anodic potential of 0.75 V. The change in absorbance was proportional to the concentration of lead ions in solution, as shown in Figure 4, with a limit of detection for Pb^{2+} better than 250 ppb. This is a remarkable result considering that these were single absorption measurements carried out with a thin film electrode having an estimated thickness of 20 μm.

An electrochemical extraction coefficient can be calculated from the results shown in Figure 4. Taking the extinction coefficient for the BrPADAP-Pb^{2+} complex as $8.4\text{x}10^3$ mol^{-1} dm^{-3} cm^{-1}, and a film thickness of 20 μm, an extraction coefficient of 100 can be calculated from the changes of absorbance measured for the experimental conditions employed.

A value of 1.566 was found for the real part of the refractive index of the sensing films, n_f'. The imaginary part of the index was deduced from the absorbance measurements, resulting in a complex refractive index $n_f^u = 1.566 - j5.6 \times 10^{-4}$ for the film with no lead present and $n_f^p = 1.566 - j8.1 \times 10^{-4}$ for the film with lead present, assuming negligible dispersion between 550 and 633 nm. In order to project the performance of these films when applied to an optical waveguide sensor the transmission of a waveguide coated with a PVC-BrPADAP sensing film was computed using the four-layer waveguide model described in detail in Ref. 6 as a function of film length and thickness. Evanescent sensing in a film substantially thicker than the evanescent penetration depth was modelled, as the effect of manufacturing variations in film thickness on sensor response would thereby be minimised. Under these conditions evanescent field sensing using films on a waveguide requires the refractive index of the waveguide to be greater than that of the film. Calculations were thus based around a glass substrate with an index, n_s, of 1.569 at 589 nm (Schott BaK4) and a waveguide having an index, n_g, of 1.579. The changes in the imaginary part of the refractive index to be sensed are small and one of the distinct advantages of using a waveguide is that small changes can be detected in thin films, offering rapid sensor response due to the possibility of using long interaction lengths.

Although channel waveguides will be used in practical devices, a 1D planar model is used here as this approach has been found to model experimental ion-exchanged devices satisfactorily.[6] The ITO film is not considered in the waveguide model since an electrode geometry that does not overlay the channel waveguide is expected to be used in practice. The superstrate (cover) index was taken to be that of water, $n_c = 1.33$, and the TE polarisation for the mode propagating in the waveguide was assumed. First, the waveguide thickness giving maximum response to changes in absorption at 550 nm was determined to be 0.68 μm and this thickness was used for subsequent calculations.

Figure 5 shows the calculated response transmission of the waveguide sensor to changes of the complex film index from n_f^u to n_f^P, representing the change upon chelation with lead, as a function of the PVC–BrPADAP film thickness. The length of the polymer-coated region of the waveguide is taken to be 10 mm. The response is shown as the ratio ΔP/P expressed as a percentage, where P is the power at the output of the waveguide without lead ions present and ΔP is the change in that intensity due to the incorporation of lead ions in the film. It is evident from Fig. 5 that the response becomes insensitive to the thickness of the sensing layer and hence, to the superstrate index, for film thicknesses greater than approximately 1.2 μm, since the film thickness starts to exceed the evanescent field penetration depth. The target thickness for the PVC-BrPADAP films was therefore chosen to be 1.5 μm to allow for fabrication tolerances. Assuming that the change in transmitted power which may be detected is limited to 0.1%, due to instrumental stability, it may be deduced that, from the absorbance measurements, about 1 ppm of bound lead may be detected within the film overlaying the waveguide. Using this value and the experimental value of 100 obtained for the electroassisted partition coefficient it is estimated that the concentration of lead in solution that can be detected is of the order of 10 ppb. While Figure 5 shows near extinction of the transmitted power in the presence of lead, the absolute transmittivity of the coated waveguide in the absence of lead is 30 dB for a 1 cm long film which may lead to a poor signal to noise ratio. To obtain a more accurate estimate for the potential limit of detection for such a sensor it is necessary to consider the signal, noise and detector bandwidth of the system in detail. Reducing the length of the film would result in improved transmission but at the expense of $\Delta P/P$. For example, the use of a 5 mm long film would result in a 15 dB background attenuation, P, and a maximum $\Delta P/P$ on binding lead of 78%. These theoretical projections show that PVC-BrPADAP is a promising material for application to electroassisted lead ion sensing on channel optical waveguides, and that careful design will result in a very low detection limit, certainly well below the 10 ppb level calculated for a non-optimised system.

The stripping of Pb^{2+} from the sensing film was achieved by applying a positive potential, reversing the electroassisted metal ion extraction process and hence the absorbance change. The effect of a succession of cathodic and anodic potentials on the absorbance at 550 nm is shown in Figure 6 demonstrating that these sensors can be reset many times.

The changes in $\Delta_o^w \phi$ do not necessarily follow those of the total applied potential. This would only occur if the Galvani potential difference between the ITO electrode and the polymer film remained constant. The experiments described here were aimed primarily at demonstrating that electroassisted solvent extraction could be used, together with thin film technology, for a new family of optical metal ion sensors. In spite of the lack of control over the ITO sensing film Galvani interfacial potential difference the absorbance results were surprisingly time invariant, indicating that this potential difference assumed a constant value for each applied potential. The acid-base properties of the ITO layer are probably responsible for this effect, which greatly simplifies the operation of the devices since an internal reference electrode, although desirable, does not appear essential to achieve metal ion extraction. From a practical point of view, although the system never reaches the equilibrium conditions predicted by equation (1), provided the current integration time is kept constant, practical analytical determinations can be carried out.

Although BrPADAP is a sensitive reagent it lacks specificity because it chelates a large number of different heavy metal ions. Some metals, such as cobalt,[14] can be distinguished spectrophotometrically, but the majority of metals form a red chelate with an absorbance spectrum similar to that of lead. More recently, therefore, analytical methods employing BrPADAP have used other techniques such as capillary electrophoresis to resolve different metal ions prior to photometric detection. The advantages of BrPADAP as a chelating agent in electrochemically assisted solvent extraction sensors are stability, a high extinction coefficient and the positive charge of the metal chelate. The latter makes it possible to reset the sensor electrochemically. Very small amounts of metal chelate could leach from the membrane into the aqueous solution when the sensor is reset and ultimately can limit the useful life of the film electrode. Further work is required to assess these effects, but for the basic structure of BrPADAP it should be possible to overcome this problem by extending the alkyl chains attached to the 5-amino position of the phenol ring.

In common with other complexing agents BrPADAP is prone to two main types of interference: positive interference from substances that induce a similar change as the analyte, and negative interference from substances that compete with the complexing agent for the analyte. To eliminate these sources of interference it is often necessary to use procedures that are time consuming and technically demanding. An alternative approach is to accept that all complexing reagents are prone to interference, but to recognise that different reagents can lead to different levels of interference. The response of multiple sensing elements containing ligands specific to different metal ions in the same sample can be studied by multi-variate analysis.[18,19] This approach has already been used for conventional metal ion analysis and also for multianalyte immunoassays. Parallel arrays of channel waveguides in association with electrodes, where each one is derivatised with a sensing films that contains a different complexing reagent, would be ideally suited to extend this approach to multianalyte sensors.

CONCLUSIONS

The principles of an electroassisted metal ion extraction method for optoelectrochemical analyses have been demonstrated. The preliminary results presented show clearly that an optically transparent electrode surface can be used to transfer Pb^{2+} into a thin film attached to it, provided that the film is made ionically conducting using a hydrophobic salt and that a ligand specific to the metal ion of interest is present in it. The prospects for applying this method to evanescent absorption on a waveguide are discussed and optical attenuation calculations show that this approach can combine great sensitivity with integration of optical and optoelectrochemical methods. The device can be reset and used pseudo-continuously by employing the applied potential to carry out the metal ion concentration step and measuring this change optically.

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LEGENDS TO FIGURES

Figure 1 Absorbance spectrum of a solution of the free ligand and of the Pb^{2+} chelate in NPOE obtained by reacting a 0.1 gm cm^{-3} solution of the free ligand with solid $Pb(No_3)_2$.

Figure 2 Absorbance spectrum of a sensing film cast on ITO containing B_2 PADAP in contact with a 10 ppm Pb^{2+} solution at two different potentials.

Figure 3 Time evolution of the absorbance on applying a potential of -0.50V from a baseline value of +0.75V. The transients were finished by applying the original baseline potential. The different concentrations of Pb^{2+} in the solution are indicated in the Figure. The absorbance changes were measured at 550 nm. The base electrolyte was 0.01 M NaCl.

Figure 4 Dependence of the changes in absorbance after 1 min. of polarisation at -0.50V on Pb^{2+} concentration. Data taken from Fig. 3.

Figure 5 Theoretical dependence of the attenuation of the power transmitted through the waveguide as a function of thickness of the PVC-BrPADAP-Pb^{2+} film, calculated using a four-layer model.[6]

Figure 6 Absorbance-time transients for the response of a PVC-BrPADAP film as the potential was cycled between the anodic and cathodic limits.

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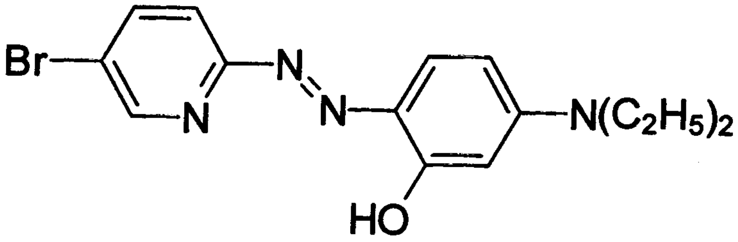
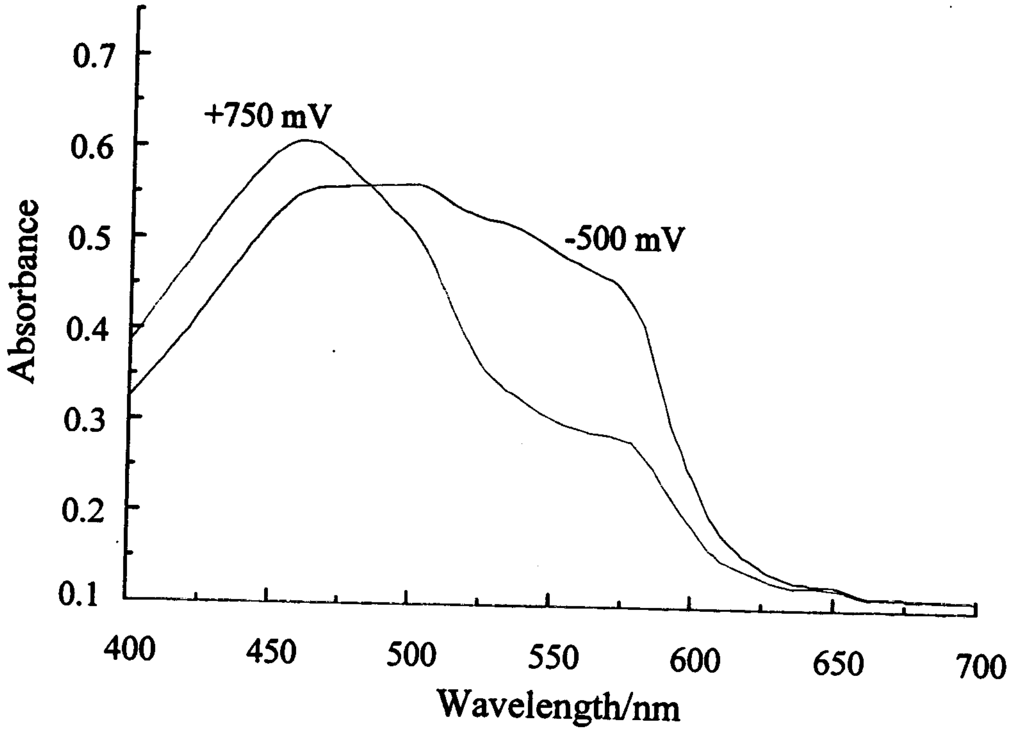


2-(5-Bromo-2-Pyridylazo)-5-(Diethylamino)Phenol

Fig 1



0.7
0.6
0.5
0.4
0.3
0.2
0.1
Absorbance
+750 mV
-500 mV
400
450
500
550
600
650
700
Wavelength/nm

Fig 2

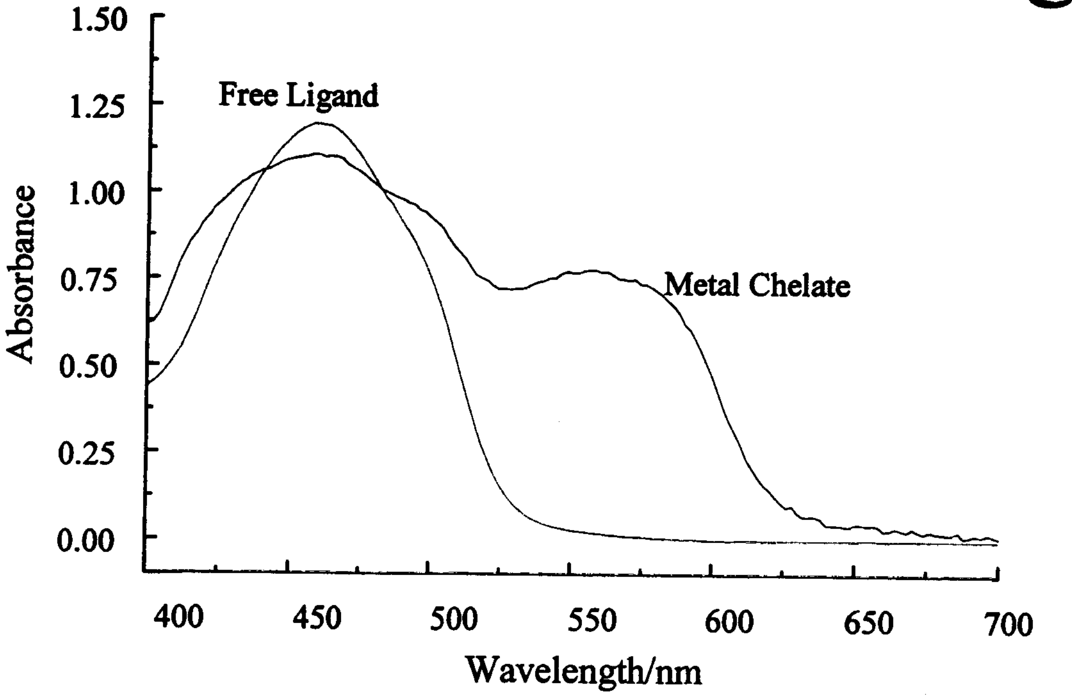
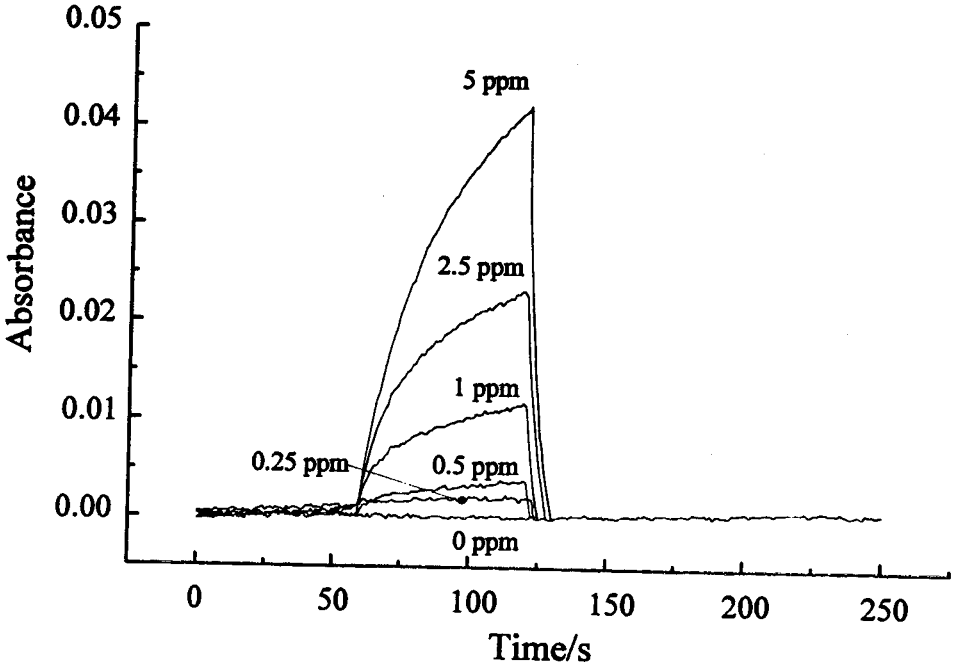

Free Ligand
Metal Chelate
Absorbance
1.50
1.25
1.00
0.75
0.50
0.25
0.00
400
450
500
550
600
650
700
Wavelength/nm

Fig 3



0.05
0.04
0.03
0.02
0.01
0.00
Absorbance
5 ppm
2.5 ppm
1 ppm
0.25 ppm
0.5 ppm
0 ppm
0
50
100
150
200
250
Time/s

Fig 4

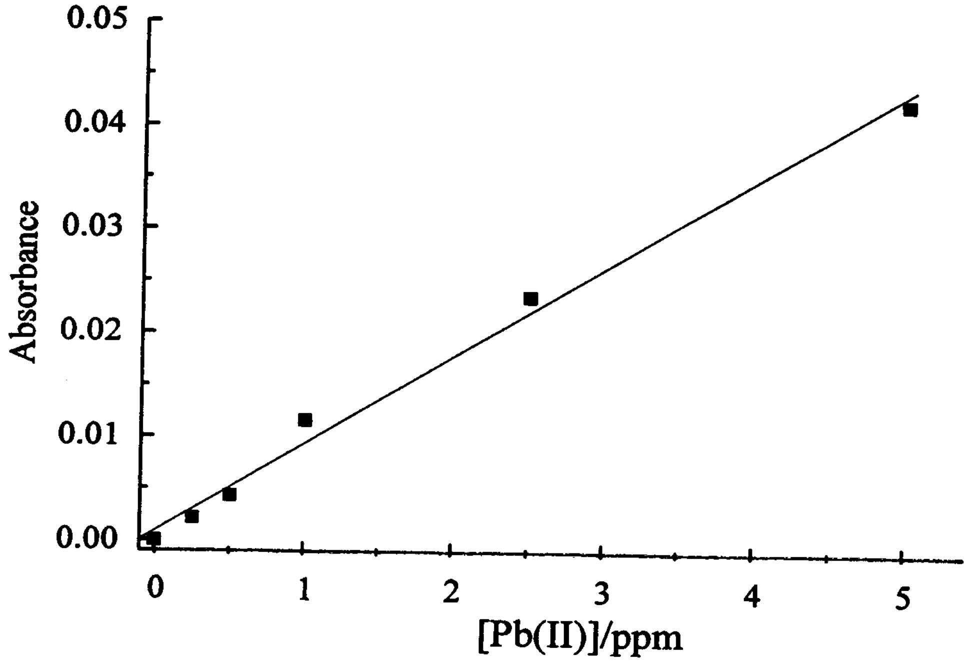


Fig 5

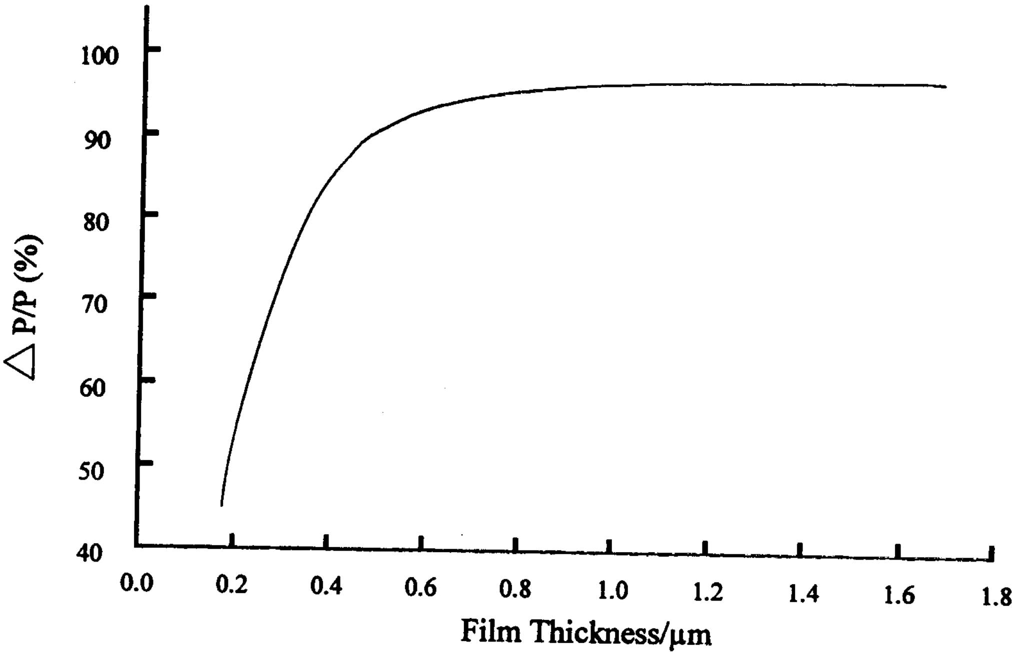
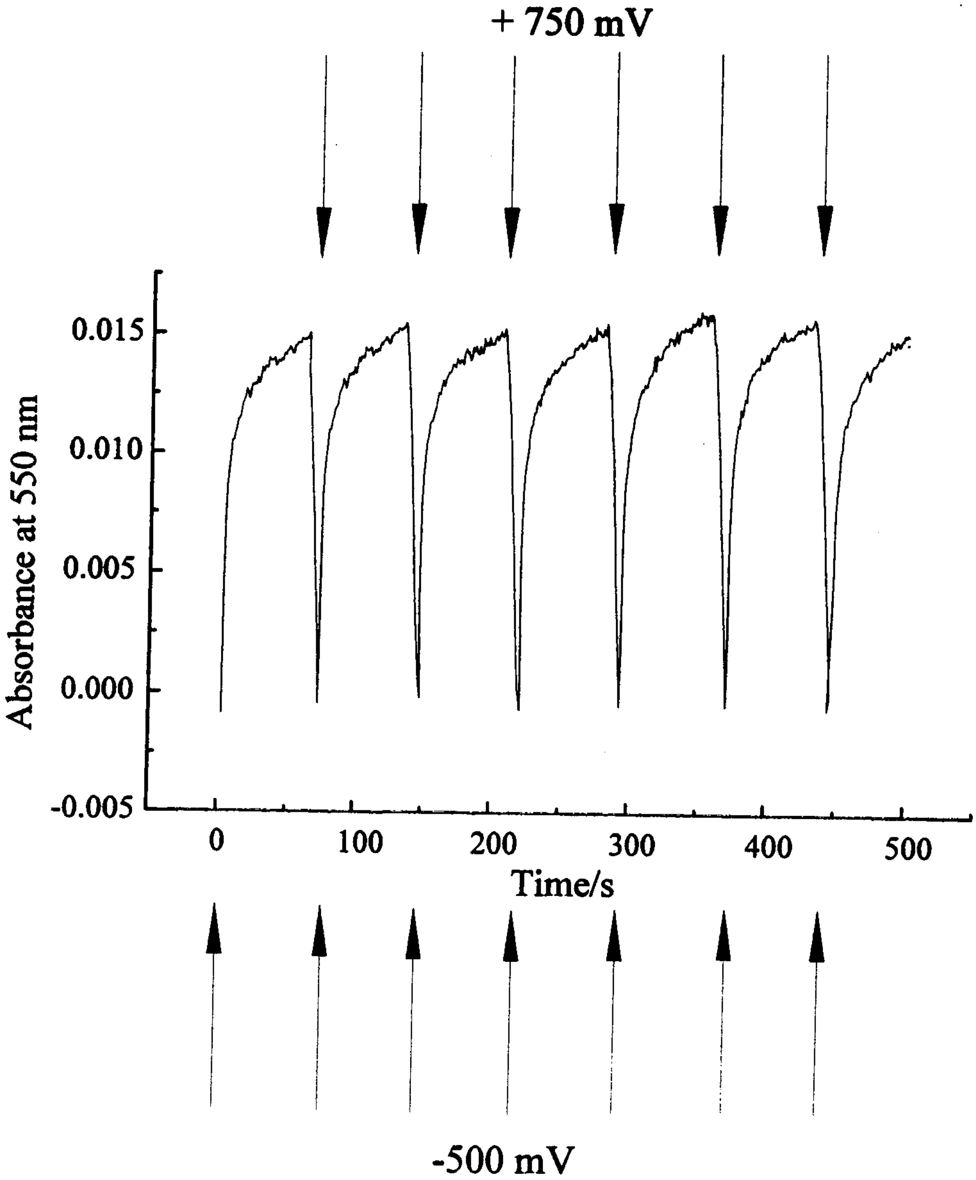

100
90
80
70
60
50
40
△ P/P (%)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
Film Thickness/μm

Fig 6


+ 750 mV
0.015
0.010
0.005
0.000
-0.005
Absorbance at 550 nm
0
100
200
300
400
500
Time/s
-500 mV