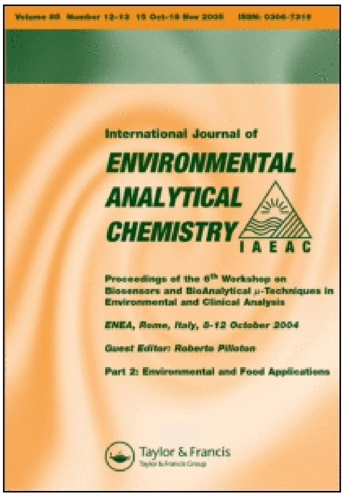

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A robust spin-coated optical sensing device for rapid determination of predominant metal ions in wastewater streams

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A ROBUST SPIN-COATED OPTICAL SENSING DEVICE FOR RAPID DETERMINATION OF PREDOMINANT METAL IONS IN WASTEWATER STREAMS

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The potential of an optical sensing material for determination of metal ions in wastewater streams is presented. The initial results in the development of a chromo-ionophore-based optical sensor for metal ions are detailed. An azo dye species, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP), together with an ionophore and plasticiser was immobilised in a film of poly(vinyl chloride) (PVC). Initial investigations using the dye-impregnated sensing film showed a reproducible and reversible response to Pb(II) ions in aqueous solution. The response of this sensing film to Pb(II) at pH 6 was found to be linear in the 0.1–10 mg/L range, with a %RSD of 1.55%. The film can be regenerated by immersion in a low-pH buffer solution. The authors demonstrate how this method shows potential for analysis using once-off sensing probes. The sensing film response for Pb(II) occurs within 30 s.

Keywords: UV-Visible spectroscopy; Metal ion sensor; Chromophore; Ionophore; Pb(II)

INTRODUCTION

Heavy metals are ubiquitous in the environment, so their quantitative determination at trace levels is very important in the field of environmental analysis. They are toxic to humans at high concentrations, and continuous exposure to low concentrations can have mutagenic effects. They have many adverse accumulative effects, including poisoning, brain damage and cancer [1].

Current laboratory-based techniques used for the detection of heavy metals in water samples include atomic absorption spectrometry (AAS) [2], inductively coupled plasma emission spectrometry (ICP-ES) [3] and anodic stripping voltammetry (ASV) [4]. These methods provide good limits of detection and wide linear ranges. They are often capable of multielemental analysis in the parts-per-trillion range. However, their expense and labour-intensive sample preparation procedures limit their overall throughput.

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Also, these methods do not lend themselves easily to miniaturisation, which is necessary for use in a sensor design.

Optical chemosensors for the determination of heavy metal ions are receiving increased attention from researchers, and are the subject of this article. The use of fibre optics in the development of chemical sensors has increased because of to their simplicity, flexibility and robustness [5,6]. They are capable of monitoring chemical concentrations *in situ* and on a real-time basis [7]. Plasticised PVC membranes with immobilised reagents have been used in the fabrication of optical heavy-metal sensors [7–15]. The practicability of using PVC membranes in these sensors is due to their homogeneity, ease of preparation and optical transparency [7]. Simon and co-workers [10–15] have shown the potential of PVC membranes for use in bulk optodes. Some studies show the potential of plasticised PVC membranes that incorporate a highly lipophilic ion-selective neutral ionophore [11] and H^+ selective chromo-ionophore, for sodium determination in human blood plasma. The work shows selective and reversible recognition of ions and optical transduction of the recognition process. An optical sensing system described by Hauser *et al.* [13] relies on ion extraction into a bulk polymer membrane, yielding a high absorbance change on interaction with nitrate. The membranes rely on the coextraction of proton/anion pairs into a membrane and selectivity is determined by the lipophilicity of the anions and the optical transduction due to the protonation–deprotonation reaction of a pH indicator. The selectivity of bulk optode membranes was investigated by Seiler and Simon [14]. The membranes incorporate an ion carrier, complexing agent, ionophore, ligand and chromoionophore. It was shown that membrane thickness and homogeneity are important parameters in the response of a membrane. Single-path absorbance measurements were used to probe samples using the optode membranes. Results were found to be reliable and comparable to conventional methods, although the optodes suffered from a limited lifetime.

A lead-selective bulk optode was described by Lerchi *et al.* [8], which was plasticised PVC membrane incorporating a metal-selective ionophore, chromoionophore and an anionic site. The system involves an ion-selective chromoionophore which is competing with a lead-selective ionophore, giving charged complexes. Lipophilic counter-ions are included for electroneutrality. In a study of selectivity it was found that the membranes showed good selectivity over calcium, magnesium, sodium and potassium. However, interference from transition metals was noted.

The development of sensors based on novel materials that are capable of interacting sensitively and selectively with a particular metal ion in aqueous solution is a subject of growing interest. Indicator dyes are used in the qualitative and quantitative analysis of metal ions. This is due to the potential availability of dye indication reaction and dye-coupled reaction for analytical measurement [10]. These dyes form strong complexes with a large number of metal ions and can be used in the fabrication of chemical sensors, as they bring about a change in specific colour or optical absorption when they interact with the metal ions [10].

In the study described in this paper, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (BrPADAP) was immobilised in a plasticised PVC membrane. The structure of the ligand is shown in Fig. 1 [11]. This membrane is being investigated as a sensing phase for use in a UV-Visible spectrometry-based optical sensor. The effect of an ionophore or ion carrier [12,13] in the sensing film is also investigated. The sensor will have potential for use in waste streams where particular metal ions form a

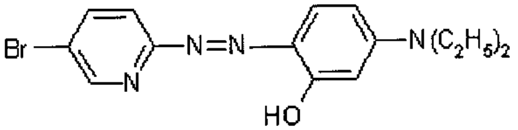

FIGURE 1 Structure of BrPADAP.

significant portion of the waste stream. Optical transduction methods offer the advantage of simple and cost-effective on-site screening for industries with metals in wastewater streams.

This article describes the initial studies in the development of the BrPADAP-based sensing film for Pb and other metal ions. A number of chemical parameters were varied to determine the most satisfactory sensing-film characteristics for Pb determination in this case, e.g. metal solution pH, film conditioning time, calibration of sensor response, reproducibility and repeatability and sensing-film regeneration.

EXPERIMENTAL

Reagents

The chromophoric dye BrPADAP, hydrochloric acid (HCl), ethylenediamine tetraacetic acid (EDTA), tributyl phosphate (TBP), potassium tetrakis (4-chlorophenyl) borate (KTCPB), tetrahydrofuran (THF), ethanol, the buffer salts sodium phosphate, sodium acetate, sodium tetraborate, 4-(2-hydroxyethyl) piperazine-1-ethanesulfonic acid (HEPES) and 3-(cyclohexylamino)-propan-1-sulfonic acid (CAPS) and metallic salts were purchased from Sigma-Aldrich, Tallaght Dublin. Stock metal solutions (1000 mg/L) were prepared by dissolving the required amount of metal salt in ultrapure water (18 MΩ). Nitrate salts of Pb(II), Cu(II), Co(II) and Cr(III) were used to prepare 1000 ppm stock solutions of the metal. Zinc sulfate was used to prepare Zn(II) and ammonium iron(II) sulphate was used to prepare Fe(II). The chlorides of Ni(II), Ba(II), Fe(III) and Sb(III) were used.

Immobilisation of the Sensing Film onto a Substrate

A 0.25% m/v solution of BrPADAP in THF (10 mL) was mixed with PVC (0.4 g), TBP (800 μL), and KTCPB (0.0075 g). An aliquot of this solution (350 μL), was spin-coated onto a glass substrate using a KW-4A spin coater from Chemat Technologies Inc., set at 1000 rpm, for 20 s.

Measurement Protocol

The glass substrate coated with the sensing film was placed in the sample compartment of a Hitachi U2000 UV/Vis spectrophotometer for measurement. Measurements were taken with an uncoated glass substrate in the reference cell. Analytes were measured by immersing the sensing slide (Fig. 2) into the sample solution for a designated time period (30 s). The exposed slide was removed from the solution and placed in the sample compartment of the UV-Vis spectrometer.

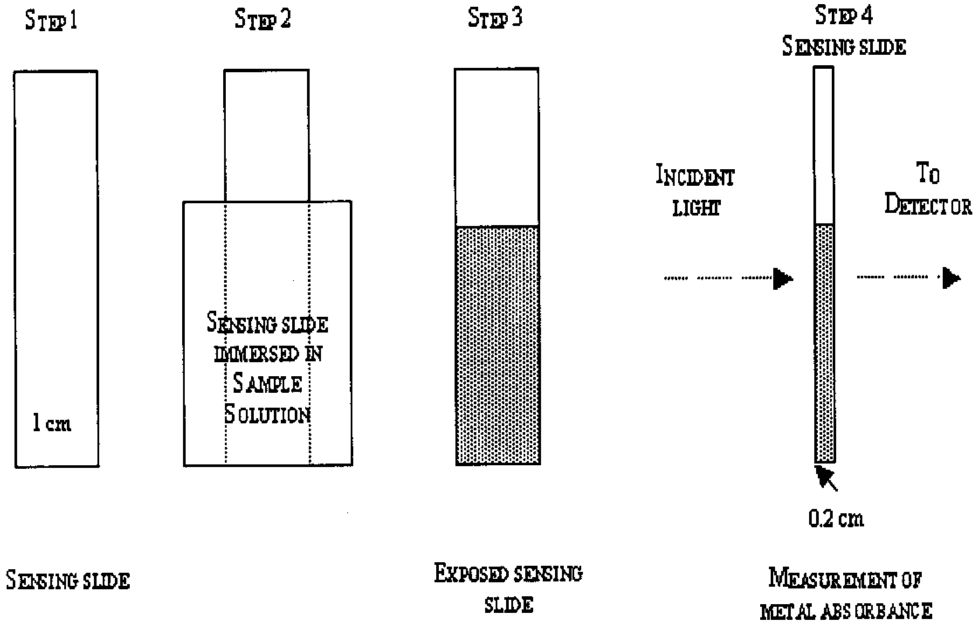

FIGURE 2 Schematic diagram showing steps involved in measurement of metals.

RESULTS AND DISCUSSION

To illustrate proof of principle of the optical sensing film, Pb(II) was used as a test analyte for all the investigations described. A number of parameters were varied to determine the most satisfactory sensing-film characteristics for Pb determination in this case, e.g., film component composition, metal-solution pH, film conditioning time, calibration of sensor response, reproducibility and repeatability, sensing-film regeneration and interference studies.

Development and Optimisation of Sensing Films

Sensing films were prepared by spin-coating a glass substrate with an aliquot of the film-generating solution. A number of parameters were varied to determine the optimum sensing-film components, e.g., quantity of film-generating solution coated onto the glass substrate, spin speed and the concentrations of BrPADAP, TBP and KTCPB.

The amount of film-generating solution coated onto the glass substrate was varied from 250 to 350 μL. Comparable absorbances were obtained for each amount. 350 μL was chosen as it gave the best %RSD of the coating weight (3.33%, $n = 3$), and a good %RSD of the response at 575 nm due to the complex (3.99%, $n = 3$).

The spin speed used for coating the glass substrate with the film-generating solution was also varied. Speeds in the range 200–1000 rpm were investigated. Upon comparison of the %RSD of the coating weights, the reproducibility of the response at 575 nm and the absorbance at 575 nm, 1000 rpm was chosen.

The next stage of the optimisation involved varying one of the film components while the others were kept constant. The first variable investigated was the concentration of BrPADAP. It was varied from 0.15 to 0.35%. The highest absorbances at 5 min were obtained with 0.25% and 0.35% BrPADAP. 0.25% BrPADAP gave better reproducibility of the response at 575 nm.

The amount of ionophore and plasticiser present in the sensing film were also optimised. The absorbances and %RSDs obtained were compared. It was found that 0.0075 g of KTCPB and 800 µL of TBP should be used. These values were selected based on the highest absorbance values obtained by measuring the band due to the complex. The most satisfactory sensing film was thus generated by mixing a 0.25% m/v solution of BrPADAP in THF (10 mL), with PVC (0.4 g), TBP (800 µL), and KTCPB (0.0075 g). An aliquot of this solution (350 µL), was spin-coated onto a glass substrate using the spin coater, set at 1000 rpm, for 20 s. For all further investigations outlined here this optimised sensing film was used. The reproducibility (%RSD) of preparing 10 films was determined to be 4.88%. As a result of this, it was possible to compare results from different films.

pH and Time Optimisation

The pH at which optimum complexation occurred for Pb and the dye species was investigated. Two film types were investigated in this pH study: (1) a PVC film containing dye and plasticiser and (2) a PVC film containing dye, plasticiser and an ionophore. To determine the most suitable pH for measurement, the absorbance of the metal : dye complex was monitored at pH values in the range 4–9. Figures 3 and 4 illustrate the results obtained. The effect observed was such that the absorbances were comparable for both film types but in the presence of ionophore the response was more rapid. In the film containing the ionophore, the most suitable pH for complexation was found to be pH 6 and the response time was 5 min in comparison to 20 min at pH 9 in the ionophore-free film. The effect of adding the ionophore was such that it allowed a more rapid transport of the metal species into the film, thereby allowing more metal to interact with the ligand. This resulted in higher absorbance values and a more

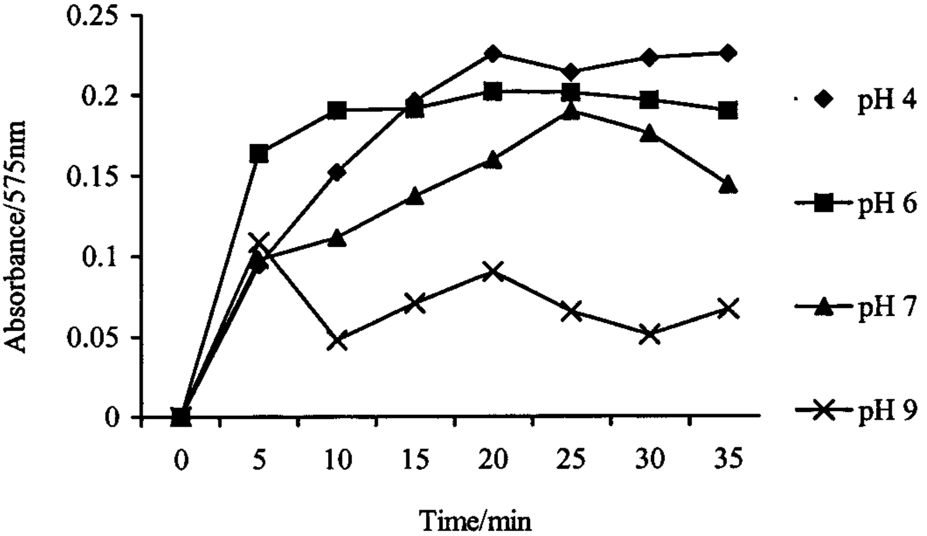

FIGURE 3 Time response of complexation of the BrPADAP/PVC/ionophore sensing film with 10 mg/L Pb(II) in buffered solution: (◆) pH 4; (■) pH 6; (▲) pH 7; (×) pH 9.

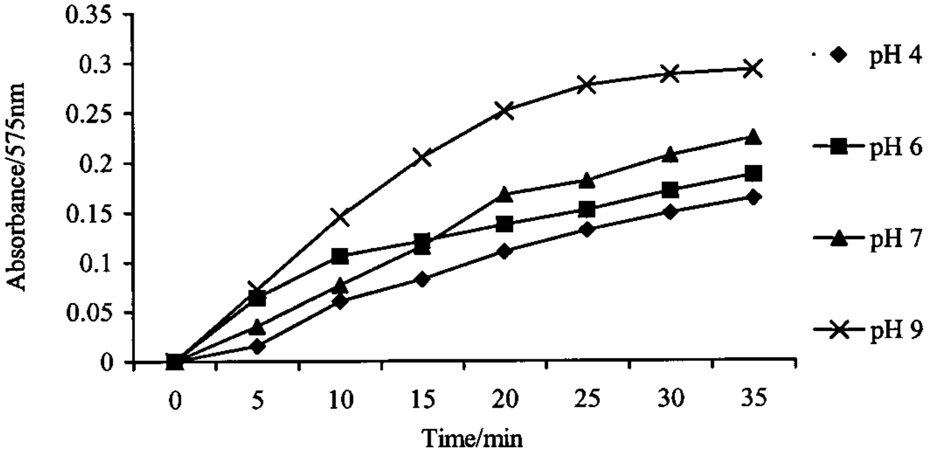

FIGURE 4 Time response of complexation of the BrPADAP/PVC sensing film after contact with 10 mg/L Pb(II) in buffered solution: (◆) pH 4; (■) pH 6; (▲) pH 7; (×) pH 9.

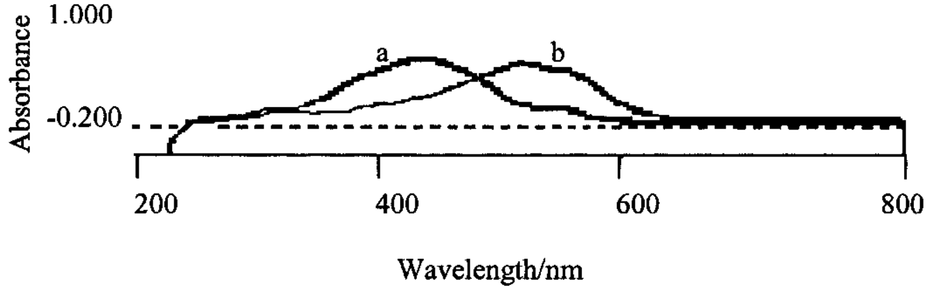

FIGURE 5 UV/Vis absorbance spectrum showing complexation of the BrPADAP/PVC/ionophore sensing film with Pb(II): (a) BrPADAP/PVC/ionophore sensing film; (b) sensing film after reaction with 10 mg/L Pb(II) at pH 6.0 for 5 min.

rapid sensing-film response. All further experiments were carried out using the BrPADAP/PVC/ionophore sensing film as it gave higher absorbance values, shorter response times and better %RSD values.

A number of reports have shown that components of a film can leach out, thus limiting the sensor lifetime. Where adequate ionophore is used, this leaching effect can be eliminated. Studies were carried out to determine the optimum concentration of ionophore for use in the film. Molar excesses of 2, 4, 6 and 8 were studied. It was found that four-fold molar excess gave the highest absorbance, complete correction of leaching effects and the best %RSD. Also, using this ionophore concentration, maximum sensor response occurred at 30 s, thereby significantly reducing the measurement time from 5 min to 30 s.

UV/Vis Absorbance Spectra

Figure 5 shows the UV/Vis absorbance spectrum of the BrPADAP/PVC/ionophore film, prior to and after the reaction with 10 mg/L Pb(II) at pH 6. It was found that the band due to the sensing film showed decreased absorbance on reaction with

Pb(II). A new band due to the complex was observed at 575 nm with the absorbance at this wavelength increasing by 0.16 absorbance units upon addition of 10 mg/L Pb(II). The band due to the complex (575 nm) was used to monitor sensing-film performance throughout these studies.

Calibration Curves

A key factor in development of a sensing system for quantitative measurements is the ability to show response over a dynamic range suited to the application. Figure 6 shows the calibration curve obtained with different concentrations of Pb(II) buffered to pH 6. A new sensing film was used for each calibration point. For each measurement the film was placed in contact with the buffered Pb(II) solution for 5 min. A regression coefficient of 0.9374 was obtained for the range 0.1–10 mg/L Pb(II) at pH 6. The %RSD for four repeated calibration curves was 1.55%. This regression value could be improved if a regenerated film was used as opposed to a new film for each calibration point. A new film may not possess exactly the same characteristics as the previous one, thus adding a degree of variability. For successful and continuous monitoring, regenerated sensing phases are desirable. The limit of detection for Pb(II) using the sensing film was found to be 0.1 mg/L ($S:N=3$), (%RSD = 1.55%, $n=4$).

Sample Analysis

To show proof of principle of the sensing slides, two industrial samples were analysed from two different waste streams. The samples selected for this investigation, are known to contain high concentrations of lead, with lower concentrations of barium and antimony. The latter two do not interfere with the measurement; therefore lead measurements can be made without interference, using such a sensing film. According to routine sample analysis results, the expected lead concentrations were in the region of 1–5 mgL Pb. Samples were measured directly without pH modification and following pH adjustment to 6.0. From the analysis it was possible to measure the sample directly without pH adjustment but higher absorbances were noted for samples adjusted to pH 6.0 (Table I). For on-site measurements it is possible to apply an absorbance correction factor to avoid sample pH adjustment, thereby obtaining an immediate result.

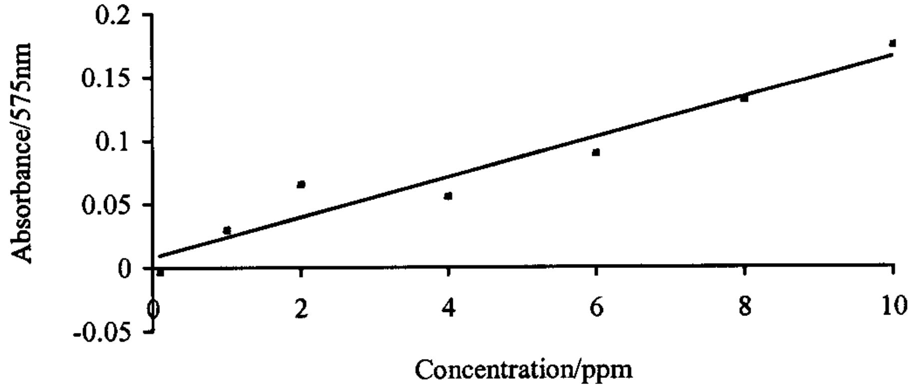

FIGURE 6 Calibration curve for BrPADAP/PVC/ionophore reacted with 0.1–10 mg/L Pb(II) at pH 6 for 5 min. A new sensing film was used for each calibration point. R^2 0.9374 ($n=4$), %RSD 1.55%, $n=4$.

Regeneration of the Sensing Phase

Reversibility of a sensing response is a desirable characteristic in the design of a sensing material. Various solutions were investigated to regenerate the BrPADAP/PVC/ionophore sensing film after it had reacted with Pb(II) in buffered solution. These regenerating agents included HCl, EDTA, KTCPB, and buffers of pH 2 and pH 10. Promising results were observed with 0.1 M HCl, 0.01 M EDTA, and pH 2 buffer. The success of HCl and pH 2 buffer is due to the fact that metal complexation is inhibited at low pH values. EDTA operates by extracting the Pb(II) from the BrPADAP complex.

Acidic conditions are reported as being unfavourable for complexation with this ligand [7]. At low pH values, the nitrogen atom in the diethylamino group is readily protonated. However, the cobalt complex of this reagent is reported to be stable in acidic solutions while other metal complexes are completely decomposed under these conditions [20]. High pH increases the ionisation of BrPADAP and may cause hydrolysis of metals [21]. This is the reason why pH adjustment shows promise for regeneration.

The most satisfactory regenerating solution was determined to be pH 2 buffer. The sensing film was regenerated by placing it in a buffered solution for a period of 5 s. Figure 7 shows the regeneration of the film after complexation with 10 mg/L Pb. It demonstrates how the film can be fully renewed after contact with Pb (II). Figure 7(a) shows the spectrum of the film alone, Fig. 7(c) shows the change in the spectral response upon contact with the metal ion and Fig. 7(b) shows the effect of regeneration with buffer pH 2 where the film again shows the original spectral response of the film alone.

TABLE I Real sample analysis using sensing films. Measurement of band at 575 nm

Sample	*Concentration* (mg/L)	
	Direct measurement	*pH adjusted to 6.0*
A	1.8	2.3
B	0.8	1.9

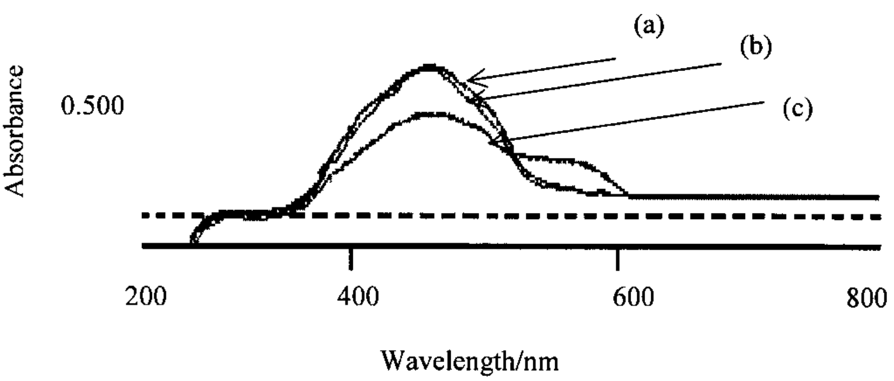

FIGURE 7 UV-Vis absorption spectra showing complexation of BrPADAP/PVC/ionophore with Pb(II), and regeneration after treatment with pH 2 buffer: (a) sensing phase only; (b) sensing phase regenerated using pH 2.0 buffer for 5 s; (c) sensing phase after contact with 10 mg/L Pb(II) at pH 6 for 5 min.

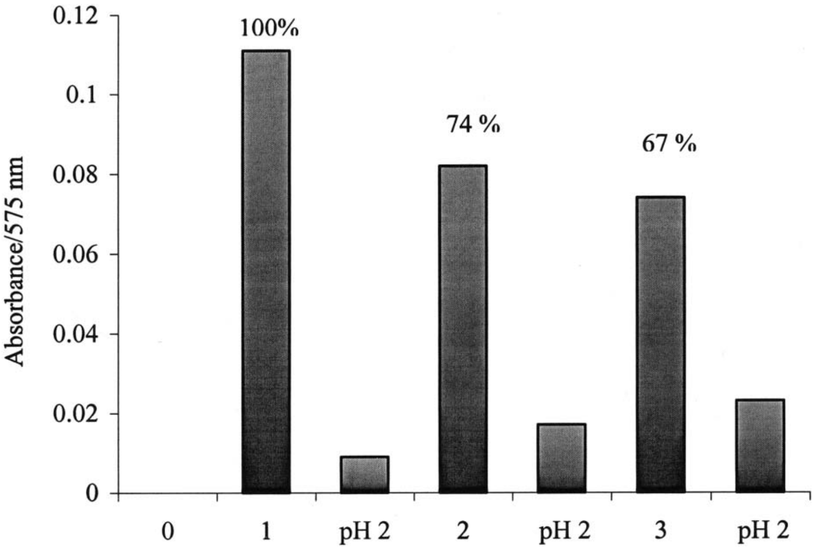

FIGURE 8 Reversibility and repeatability of sensing film response after treatment with pH 2.0 buffer: (0) initial sensing film; (1) first Pb(II) measurement; (2) second Pb(II) measurement after regeneration with pH 2.0 buffer; (3) third Pb(II) measurement after a second regeneration step with pH 2.0 buffer.

However, Fig. 8 shows that the same absorbance response was not observed for repeated measurements of Pb(II) following regeneration. The sensing phase was found to be only partially renewed when it is re-exposed to Pb(II) for the second and third time. To determine the reproducibility of the regeneration procedure, three repeated measurements were taken using three separate films. The absorbance measurements (at 575 nm) taken following a second regeneration proved to a have poorer %RSD (45%) than the first set of measurements (10%) and measurements taken after a third regeneration showed even poorer %RSDs (64%). This indicates that while regeneration achieves removal of the metal ion each time it also results in degradation of the film.

Interference Studies

In designing sensors for environmental determinations, interference from other species in the sample poses a challenge to the analyst. Promising results for a selective Cu(II) optical sensor membrane using pyrocatechol violet have been reported recently [22]. However, much of the work to date on bulk optodes has shown that interference-free metal ion determinations are not trivial. Simultaneous determinations of three metal ions were achieved, using artificial neural networks [23] to aid selective determinations.

Depending on the proposed end-use of the sensor, interferences can cause problems for measurement. However, in industrial waste streams, where only certain metals are known to be present, this may not pose a concern. It is useful to determine the effect of interference from other metal ions on this Pb sensing film using a series of divalent and trivalent metals. Divalent Cu, Co, Ni, Zn, Fe, Ba and Mg, and trivalent Fe, Cr and Sb were investigated as possible interferences. Cu, Co, Ni, Zn, and Fe(II) were found to generate the same visible absorption bands due to the complex as Pb(II) and therefore interfered with the BrPADAP/Pb reaction when they were present at the same concentration as Pb in the sample solution.

TABLE II Spectral characteristics of each metal after complexation with the sensing film

Metal	*New band* (nm)	*Absorbance at new band*
Pb(II)	575	0.094
Cu(II)	530	0.494
Co(II)	548	0.528
Zn(II)	530	0.591
Ni(II)	530	0.593
Fe(II)	548	0.378
Fe(II)	755	0.138

Metal concentration = 10 mg/L.

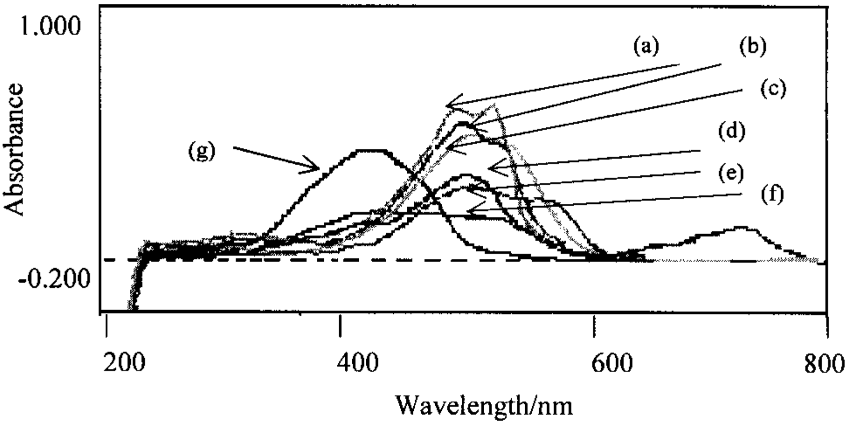

FIGURE 9 Interference study showing the response of the sensing phase to metal ions. Sensing phase after contact with 10 mg/L metal ion at pH 6.0: (a) Pb(II); (b) Cu(II); (c) Co(II); (d) Ni(II); (e) Zn(II); (f) Fe(II); (g) sensing phase without metal.

Table II details the observed spectral characteristics due to each metal ion individually in the sensing film. Figure 9 shows an overlay of the metal complexes illustrating how they interfere with the Pb response. All the metal ions tested resulted in new bands in the visible range 530–575 nm. Modifying the ionophore may combat interferences from other metal ions [14], though success in this area has been limited. Investigations are currently being carried out into film selectivity. This sensing film shows promise for measuring total metal concentration or for the quantitation of metal ion that occurs in high concentrations in a wastewater. It gives a rapid response with no sample pre-treatment necessary and is cheap to prepare.

Using this film design, the sensor response to Fe(II) shows great potential for selectively monitoring this species at 755 nm in an environmental or biological sample in the presence of other metals.

CONCLUSIONS

The potential of a novel visible-sensing film for determination of metal ion concentration in wastewater streams was shown. The organic dye BrPADAP was immobilised in a plasticised PVC membrane together with an ionophore. A UV/Vis sensing film was generated that was found to be sensitive to low levels of Pb(II). Quantitative determination of Pb(II) was practicable in the range 0.1–10 mg/L. The studies showed that the sensing film reacted with Pb reproducibly (%RSD 1.55%, $n = 4$), with a short response time (< 5 min) and good limit of detection (0.1 mg/L). The non-selective nature of BrPADAP resulted in interference by divalent Cu, Co, Ni, Zn and Fe. Rigorous investigations are being carried out to deal with interferences.

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