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CAPILLARY OPTODE: DETERMINATION OF MERCURY(II) IN AQUEOUS SOLUTION

Key words: Capillary optode, Mercury determination, Immobilised reagent,
4-(2-thiazolylazo) resorcinol (TAR).

Bambang Kuswandi and Ramaier Narayanaswamy*

Department of Instrumentation and Analytical Science, UMIST,
P.O. Box 88, Sackville Street, Manchester, UK M60 1QD.

ABSTRACT

A capillary optode for determination of mercury(II) in aqueous solution has been developed. The sensors are composed of the capillary glass tubes with a chemically sensitive coating on the inner surface, consisting of a 4-(2-thiazolylazo) resorcinol (TAR) and Nafion[®] composite thin film. When a sample solution is passed through a capillary tube, the mercury(II) ions forms complexes with the immobilised TAR resulting in a change of the colour of the inner surface

* Author for correspondence

of the capillary which, in turn, can be monitored spectrophotometrically. The characteristics of these sensors including effect of flow-rate and pH, reproducibility, sensitivity, linear range, life time and selectivity are discussed.

INTRODUCTION

Globally, there is a growing awareness of the need to reduce environmental pollution. Monitoring and quality control of drinking water, waste water and other aquatic samples, are certainly required using simple and inexpensive analytical methods. The demand for chemical sensors of high selectivity and low detection limits, e.g. for toxic metal ions such as mercury(II), therefore is on the increase. In recent years, a number of optical fibre sensors or "optodes" employing different chemical transducers and optical principles have been developed in order to fulfil such demand. This is due to the fact that optodes can offer advantages in terms of size, electrical safety, costs and no need for a separate reference.

Generally, optical metal ions sensing is based on a complex formation reaction between immobilised indicators and metal ions which, in turn, cause changes in their optical properties. Parameters such as absorbance¹, reflectance², fluorescence³, swelling⁴ and refractive index⁵ have been employed as sensing principles in optical sensors. In most cases, polymeric membranes or films containing immobilised indicators are the core elements of such sensors, which act as chemical transducers. In this case, the polymeric membranes are placed in a cell or flow-cell adopted in a planar configuration.

Usually planar configuration in terms of an optode, comprise the light source and the detector along with optical fibres which guide light from the source to the cell, containing the immobilised indicator, and back to the detector, the response of which is used for further signal processing using optoelectronic instruments. The immobilised indicator interfaces are well known sources of error due to indicator leakage, matrix swelling or matrix scratching.

Alternatively, the immobilised indicators have been interfaced to optical fibres by outer coating systems using dip coating procedures^{4,6,7}, so that they can be placed directly in the sample. However, this approach has several drawbacks including mechanical disruption, fibre bending effect and interference by ambient light as a result of inadequate optical isolation and poor reproducibility of the coating thickness on the optical fibre tips. Therefore, these drawbacks result in serious problems in reproducibility in coupling light into and out of the tip coating, which in turn, can result in poor reproducibility in optode responses.

Another alternative, which is also applicable in an optode, is the use of inner coated systems utilising plastic or glass capillary tubes for making an "integrated sensor" which can act as sampling device and optical element. A small capillary covered with a dye has been used to sense ammonia in air⁸⁻⁹ and in another instance, it has been filled with porous sol-gel powder doped with a complexing agent which produces a colour with analyte¹⁰. Subsequently, the capillary tubing has been coated by a reversed pumping technique with a chemically sensitive dye on the inner surface to sense carbon dioxide either in gas or in water¹¹.

In this work, the use of small capillaries has been explored in order to make an integrated sensor for mercury(II) ions, which has led to a new design of flow-cell and immobilisation technique. The attractive novel features of this system include the use of capillary as (a) a new support for immobilised indicator, (b) a disposable sampling vessel and (c) a micro-flow-cell.

EXPERIMENTAL

Reagents

4-(2-thiazolylazo) resorcinol (TAR, Sigma) was used as purchased. Nafion[®] (Aldrich) was obtained as 5% m/m solution in a mixture of lower aliphatic alcohols. The pH buffer solutions (pH 3-10) were prepared by adjusting HCl-KCl, Na₂HPO₄-KH₂PO₄ and CH₃COOH-NaOH solutions; in all cases, the concentration of each component in mixtures was 0.1 M and the ratios of these

components were adjusted to give the required pH. A stock solution of 1000 $\mu\text{g/ml}$ Hg^{2-} ion was prepared by dissolving 0.1355 g of HgCl_2 (Aldrich) in 100 ml of buffer solution. Sample solutions were prepared by appropriate dilution. All reagents and inorganic salts were of analytical grade and their solutions were made using deionised water (Elgastat Spectrum, UK).

Preparation of the Capillary Optode

The capillary optode was prepared from a mixture, which was casted from a solution made by dissolving 2 mg of TAR in 2 ml of 5% Nafion solution. Disposable glass micropipettes with an inner diameter of 1mm (Sigma) were used in this work. In order to deposit the sensor material inside the glass capillary, an appropriate volume (100 μl) of the mixture was first filled in the glass capillary and then sucked through the tube. Afterwards, the capillary was dried by aspirating air through it. Finally, the capillary was placed in a chamber (Thermotron, USA) at 50°C for approximately 5 hours until the inner coating was completely dry. The capillary was then stored in a dry and clean ambient air condition until use. The mixture deposited in the inner surface of the capillary has a thickness of about 2 μm as estimated using a microscope and by comparison with a plastic thin film of defined thickness.

Alternatively, the optode can also be prepared by filling the capillary with immobilised indicator in the polymeric resins. In this case, TAR immobilised on XAD-4 (<70 μm , Aldrich) by physical adsorption has been used in order to compare the performance of the nafion coated capillary optode with this other established immobilisation technique. The procedure for the physical absorption method used in this work has been described elsewhere¹².

Optical Arrangement and Instrumentation

Fig. 1a shows a typical arrangement for monitoring the change in the absorbance of the capillary optode coated with chemically sensitive material in its inner wall, while Fig. 1b shows an optical arrangement for monitoring the

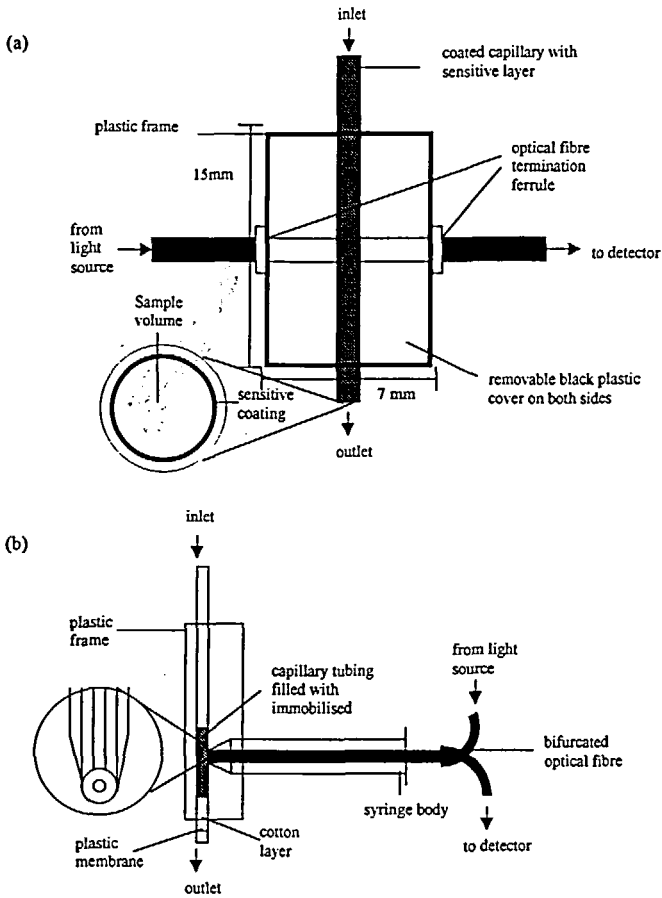


Fig. 1. (a) The capillary optode arrangement for absorbance measurements. In this system the light passes through two coating of sensing layer (coated in the inner surface). (b) The capillary optode arrangement for reflectance measurements. Both arrangements may be used for fluorescent measurements.

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change in the reflectance of the capillary optode filled with immobilised indicator. In the first arrangement [Fig. 1a], a $15 \times 7 \text{ mm}^2$ plastic block was used as a support for the capillary and two holes of 1.5 and 2 mm diameter were drilled through the sides of the block for insertion of the capillary and the single plastic optical fibre (core diameter 1mm), respectively. The block was also covered with a detachable black cloth to protect the capillary optode from ambient light interferences. The arrangement with the filled capillary optode was similar to that of the coated capillary optode, except for the positioning of the optical fibres. In this case, a bifurcated optical fibre supported in a syringe body was used (Fig. 1b). Here, the optical fibre probe consisting of either a two single fibres or bifurcated fibre bundle, was positioned perpendicular to the capillary surface. One set of fibre was then connected to light source (four LEDs: blue, yellow, red and IR) and the other to the detectors (two photodiodes).

The instrumentation used was a novel solid-state instrument, which has been designed using a state-of-the-art digital system. The arrangement of the instrument has been described in more detail elsewhere¹³. A peristaltic pump (Watson-Marlow) was used in this work for introducing sample and regenerating solutions into the capillary optode.

RESULTS AND DISCUSSION

Capillary Optode Response

The TAR-Nafion composite thin film coated in the inner surface of capillaries, showed the orange colour of TAR under dry condition. The sensitive layer can be conditioned using an acid solution (0.1M HCl) by making the sensor fully protonated and can be tested immediately at room temperature. The colour of sensitive layer changes from yellow to dark red via dark orange when Hg(II) ions are introduced.

The sensing mechanism is based on an ion exchange system, where Hg(II) ions are extracted into the film and attached to the hydroxyl sites of the ligand (TAR).

Once in the membrane, Hg(II) ions react with TAR-Nafion, forming a complex in the ratio of metal: reagent of 1:1 as TAR has two hydroxyl groups in its benzene ring¹⁴. On reversal process (by introducing an acid solution), the acid re-protonates the TAR and removes the Hg(II) ions in the complex, and the Hg(II) ions in the acid is sent to the waste.

Fig. 2 shows the changes in absorbance intensities recorded in the absence and presence of Hg(II) ions; in this case, the yellow LED (590nm) produces a good signal response when compared to other LEDs (blue LED, 460 nm; red LED, 660 nm; and IR LED, 920 nm). Thus, the yellow LED was selected as the wavelength of measurement for the TAR-Nafion composite thin film and used throughout this study. The filled capillary type optode was also tested using the reflectance mode and the results are shown in Fig. 3. In this case, again the use of yellow LED showed good reflectance signal responses for TAR/XAD-4 in the presence of Hg(II) ions. Due to the fact that the first type of coated capillary optode gives more sensitive responses with very low noise than the filled capillary optode, the former optode type was used for the remaining work involving the determination of Hg(II) ion in aqueous solution, as described below.

Optimisation Parameters

Two parameters that have been optimised in this work include the pH and the flow-rate, while other parameters such as temperature (~25°C), concentration of indicator dye and thickness of sensing layer were maintained as constants. Fig. 4 shows the effect of pH in the range 3 to 10 on the sensor response to Hg(II) ions (20ppm). In this study, pH 7 was selected as optimum pH for the capillary optode, as it provided maximum change in absorbance intensity of the sensing layer in the presence of Hg(II) ions. Also at pH ≥ 8 leaching of the TAR-Nafion composite thin film was observed.

Fig. 5 shows the effect of sample flow-rate on the capillary optode response; the flow-rate only slightly affects the sensor response time, but the magnitude of response is similar, where at high flow-rate the response is slightly faster than at

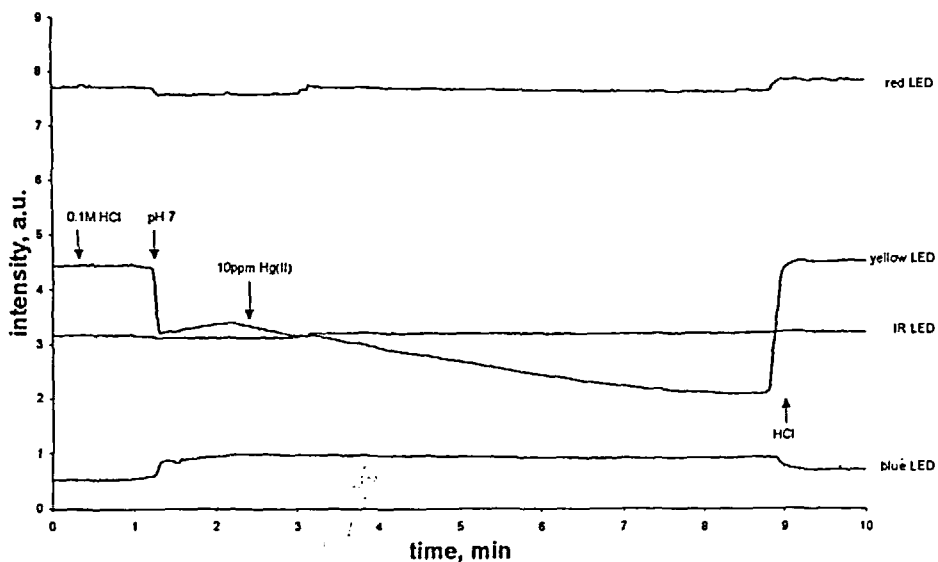


Fig. 2. Response of the capillary optode coated with TAR-Nafion to Hg(II) ions using absorbance mode.

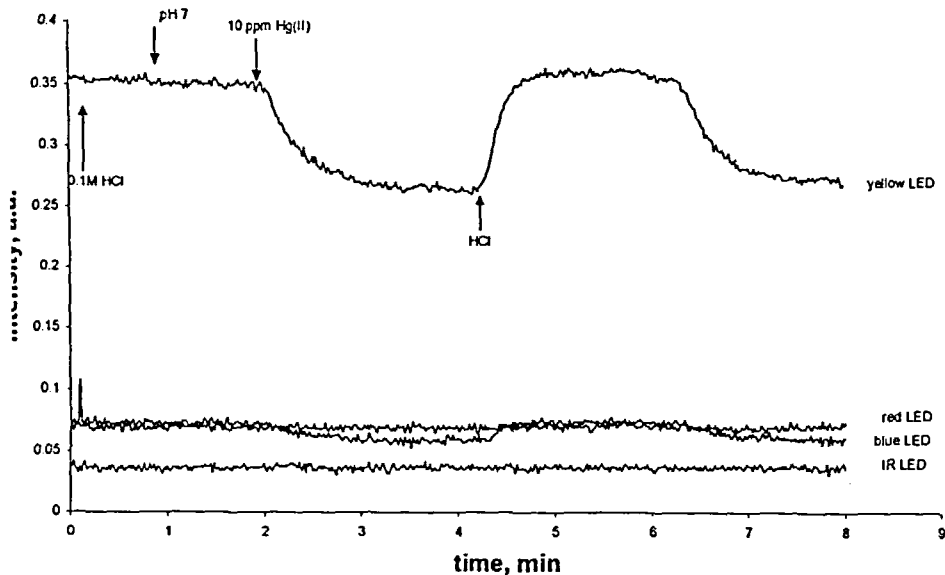


Fig. 3. Response of the capillary optode filled with TAR/XAD-4 to Hg(II) ions using reflectance mode.

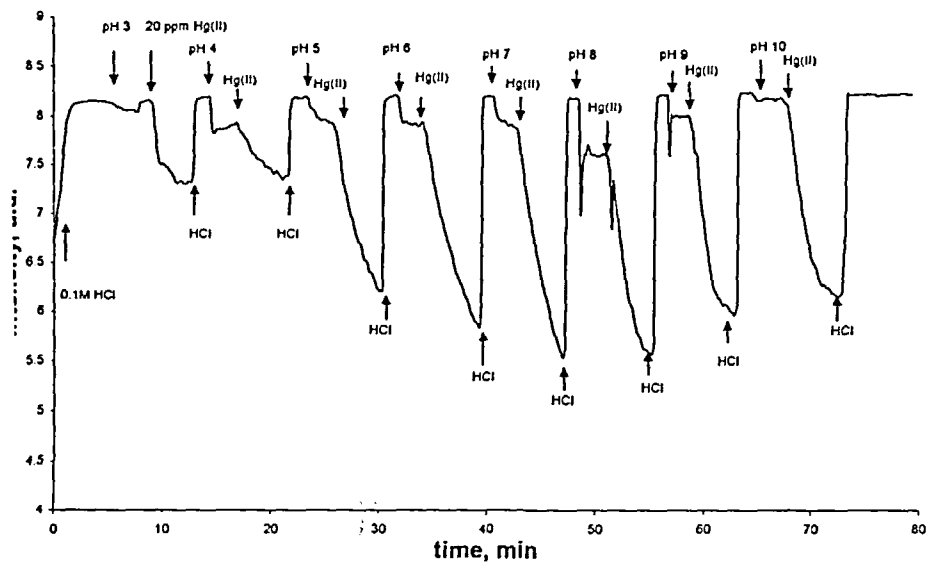


Fig. 4. Effect of pH to the capillary optode response in the pH range 3-10.

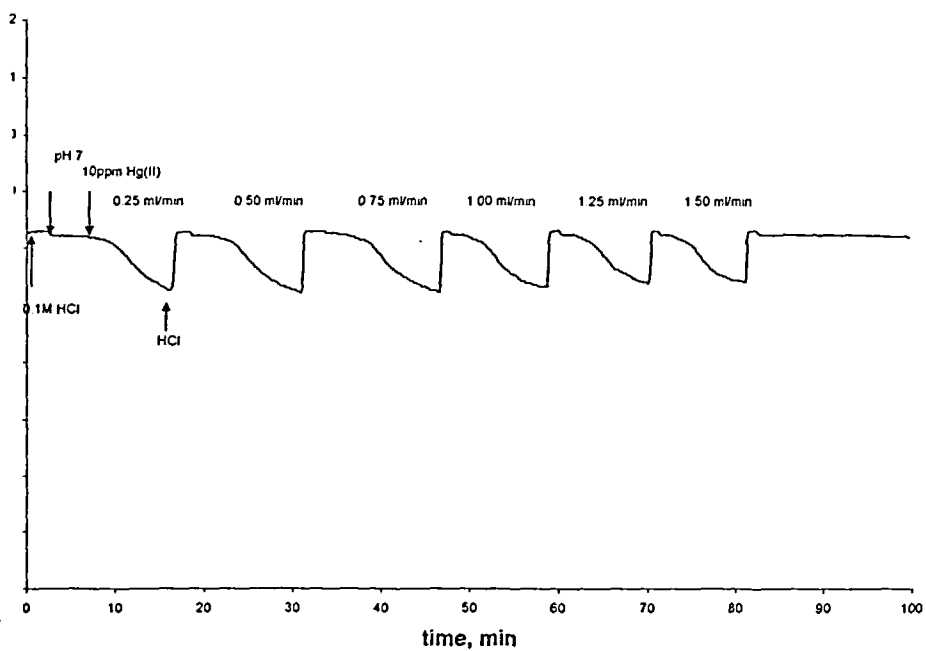


Fig. 5. Effect of flow-rate on the capillary optode response (0.25-1.50 ml/min).

the low flow-rate. Thus a peristaltic pump may not be needed here and sample flow by gravity force can be used instead. However, in this system fast flow-rate might cause abrasion of the sensing layer, as it produces high pressure of solution through the capillary. Hence, a flow-rate of 0.75 ml/min was used throughout, as a compromise between relatively rapid sample introduction time and low sample consumption.

Calibration

A calibration curve for Hg(II) ions can be constructed readily by introducing ion solutions of various concentrations into the capillary optode. The results are shown in Fig. 6. The capillary optode is capable of detecting Hg(II) ions down to 0.1 ppm with the limit of detection (defined as the concentration of sample yielding a signal equal to three times the standard deviation of the blank signal) estimated to be 0.08 ppm.

By using a kinetic method, where a time of 7.5 min to reach 95% of the final signal (t_{95}) was chosen, a calibration graph for Hg(II) ions in the range 0.1 to 20 ppm was obtained and is shown in Fig. 7 (correlation coefficient (R^2) of 0.9769). The solid line represents the fit to a typical equation for a sigmoidal response curve. The sigmoidal shape is quite reproducible in this system and also been observed in reactions in the thin films, the membrane or bulk optodes¹⁵.

Reproducibility and Stability

By the use of the kinetic method, the reproducibility of the optode film was carried out using 10 ppm of Hg²⁺ at t_{95} approximately 7.5 min as shown in Fig. 8. The mean of relative intensity change (N=7) and their standard deviations were found to be reproducible at 0.6440 ± 0.0060 . Other approaches to test the reproducibility of the capillary optode, were performed by inserting and removing of the capillary into the block (see Fig. 1a) ten times and also by the use of 10 different capillary optodes. It was found that the error due to insertion was 7.77%, while the error due to variation in fabrication was 10.04%.

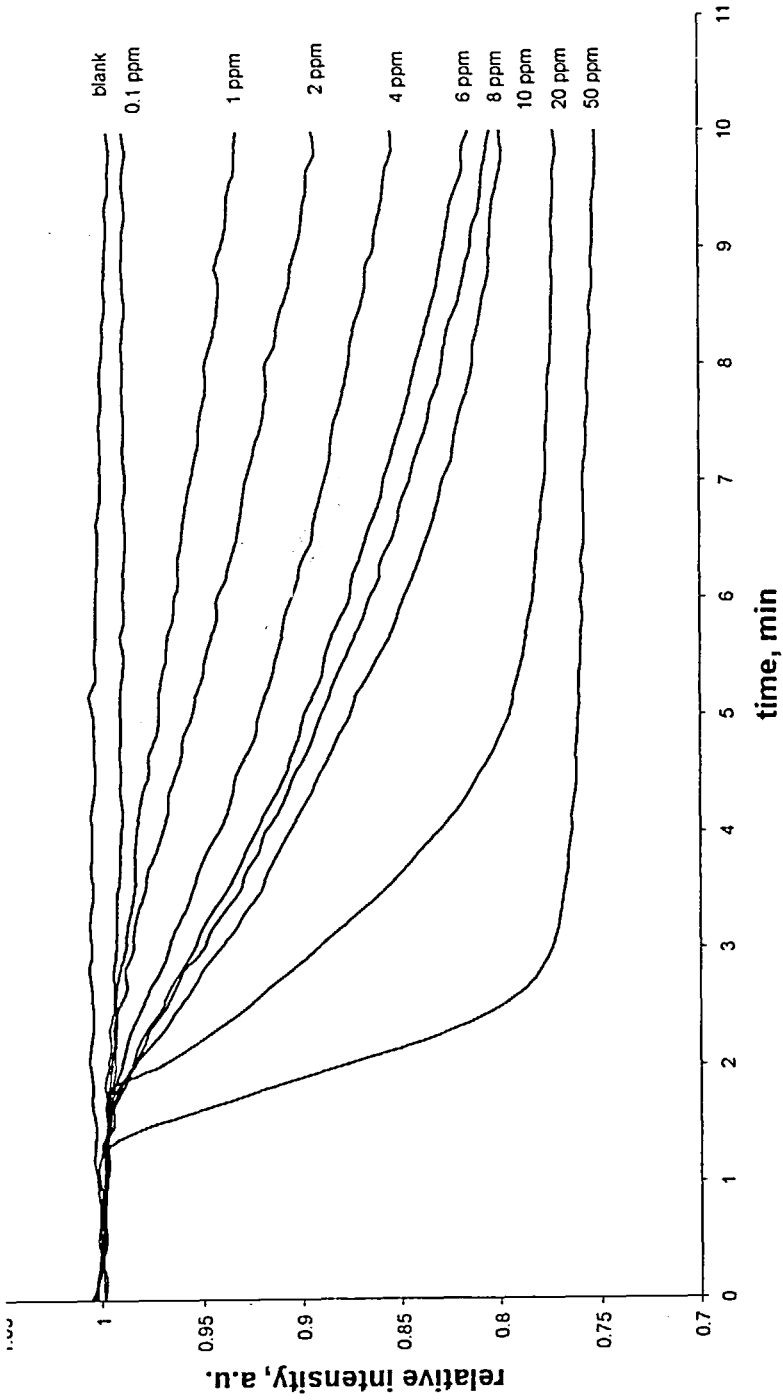


Fig. 6. Response of the capillary optode to various Hg(II) ion concentrations in the range 0-50ppm.

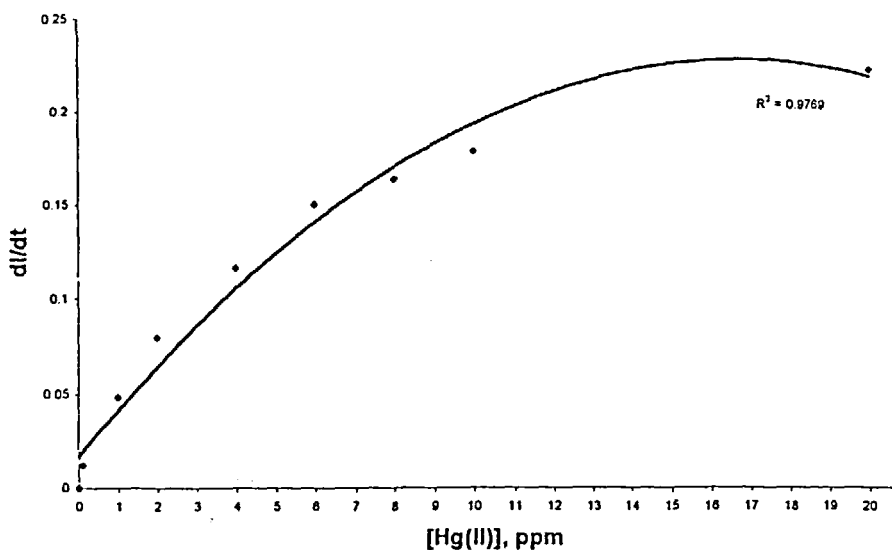


Fig. 7. Typical plot for linear range of the capillary optode in the range 0.1-20 ppm

The stability of the capillary optode was also tested by pumping 0.1M phosphate buffer solution (pH 7) for a long period of time (14 h). It was found that no significant loss of the sensing layer was observed during this period of time and the capillary sensor produced relatively stable and similar signals throughout this period of time. Therefore, one capillary optode would be sufficient for complete determination of Hg(II) in aqueous solution or it can also be used as a disposable sensor.

Selectivity

The selectivity of the capillary optode coated with TAR-Nafion composite thin film is expected to have similar selectivity behaviour as used in the conventional extraction system. The sensitivity of the optode to other metal ions is presented in Table 1, from which it can be deduced that Ni(II), Cu(II) and Co(II) are the main interfering ions in the Hg(II) determination.

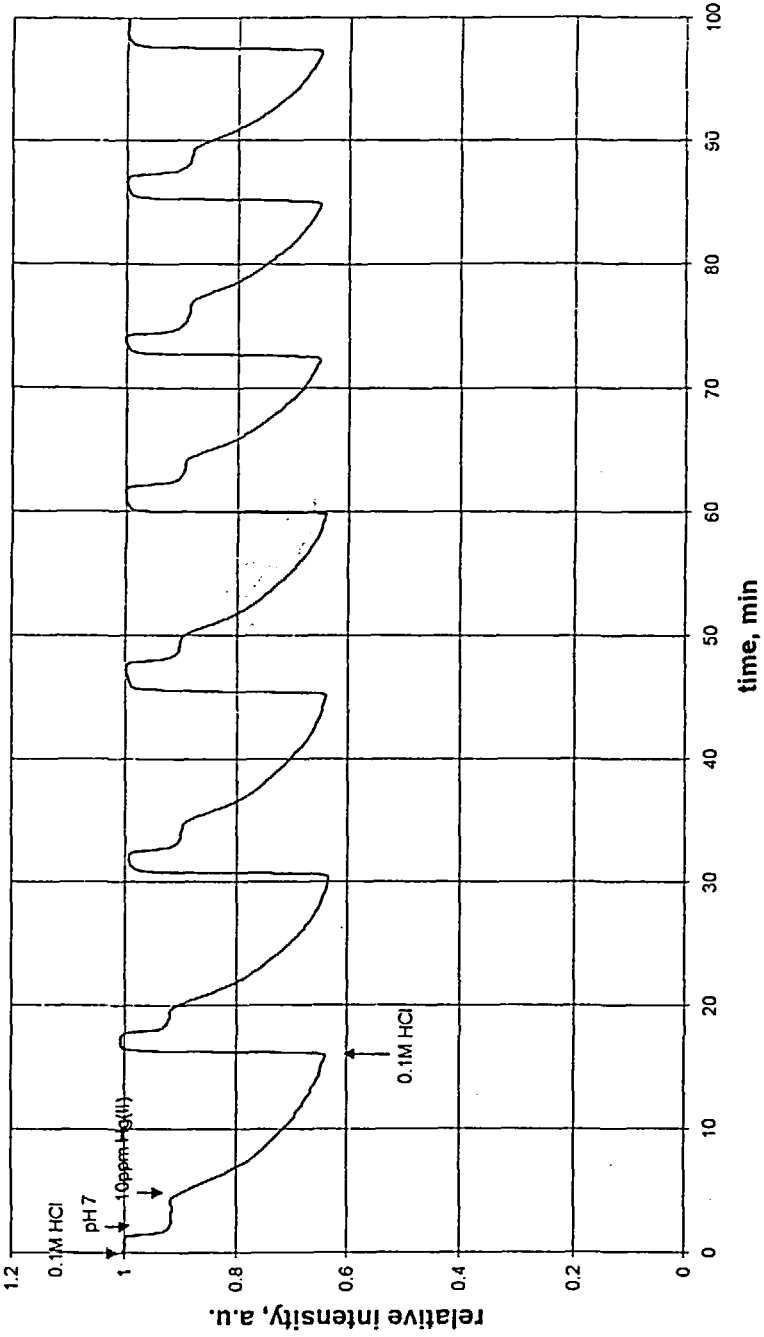


Fig. 8. Typical reproducibility response of the capillary optode.

TABLE 1

Effect of Potential Interference on the Reflectance Signal
of the Capillary Optode.

(The Reflectance intensity was recorded after 5 min of introducing the respective solution to the sensor).

Metal ions	Amount/ppm	Reflectance intensity/a.u.
Hg(II)	10	0.2585
Zn(II)	10	0.0142
Pb(II)	10	0.0214
Mg(II)	10	0.0274
Ag(I)	10	0.0420
Cd(II)	10	0.0182
Ni(II)	10	0.1924
Cu(II)	10	0.2195
Co(II)	10	0.1802

The description of the selectivity of the capillary optode here is limited. It is only been given for the metal ions of the same charge and forming chelates with similar stoichiometry and spectral properties as those for Hg(II) ions. However, by analogy with conventional extraction systems, the interference from other metal ions can be reduced by their prior extraction or by masking with certain ligands¹⁶. Therefore, two capillaries can be used in such a system, with one used as a capillary masker and the other as a capillary sensor. Other approaches can also be applied by using two sensing layers coated in one capillary, the first coating as sensitive sensing layer and the second as masking and protecting layer, so the sensing system could be made more selective to Hg(II) ions in the presence of large amounts of interferences such as Cu(II) and Co(II) ions.

CONCLUSIONS

The capillary optode presented in this work has a number of novel features. These include the attractive multifunction of capillary tube, e.g. as a new support

for immobilised indicator, as a sampling vessel, as well as a micro-flow-cell. Furthermore, it has a simple and reproducible procedure of immobilisation, and the sensing layer is mechanically protected without any air bubbles on it (which often occurs in conventional flow-cells), due to no permeation of air through the tubing.

In this study, a sensor with good reproducibility and a wide linear range of 0.1-20 ppm has been realised for the determination of Hg(II) ion. The detection limit estimated is also low at 0.08 ppm for Hg(II) ions. The capillary can also be used as disposable optode, as the sensor can be readily fabricated with high reproducibility and at low-cost. Though this work has demonstrated the use of non-fluorescent reagents in the absorbance and reflectance mode of measurement, the procedure can also be adopted with other spectroscopic modes including fluorescence.

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REFERENCES

1. A. Morales-Bahmik, R. Czolk, J. Reichert and H. J. Ache, *Sensor and Actuators B*, **13-14**, 424 (1993).
2. M. Ahmad and R. Narayanaswamy, *Sci. Total Environ.*, **163**, 221 (1995).
3. T.E. Brook and R. Narayanaswamy, *Sensor and Actuators B*, **38-39**, 195 (1997).
4. Z. Shakhster, K. D. Legg and W. R. Seitz, *Anal. Chem.*, **66**, 1731 (1994).
5. D. Clerc and W. Lukosz, *Sensor and Actuators B*, **11**, 461 (1993).
6. C. Munkholm and D.R. Walt, *Talanta*, **35**, 109 (1988).
7. A. Lambert, PhD Thesis, Umist, England, 1995.

8. J. F. Giuliani, H. Wohltjen and N. L. Jarvis, *Opt. Lett.*, **8**, 54 (1983).
9. V. Chernyak, R. Reisfield, R. Gvishi, and D. Venezky, *Sens. Mater.*, **2**, 117 (1990).
10. I. Kuselman and O. Lev, *Talanta*, **40**, 749 (1993).
11. B. H. Weigl, and O. S. Wolfbeis, *Anal. Chem.*, **66**, 3323 (1994).
12. D. P. Naughton, M. Grootveld, D. R. Blake, H. R. Guestrin and R. Narayanaswamy, *Biosens. Bioelectron.*, **10**, 325 (1993).
13. B. Kuswandi, M. N. Taib and R. Narayanaswamy, *Proc. Euroensors XII*, **1**, 343, (1998).
14. R. H. Hovind, *Analyst*, **1196**, 769 (1975).
15. M. Lerchi, E. Reitter, W. Simon, E. Pretsch, D. A. Chowdhury and S. Kamata, *Anal. Chem.*, **66**, 1713 (1994).
16. D. D. Perrin, *Organic ligands*, Pergamon Press, Oxford, 1979.

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