Investigation of a fibre optic copper sensor based on immobilised α-benzoinoxime (cupron)

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Abstract

α-Benzoinoxime, a highly selective reagent used for the gravimetric and colorimetric determination of copper, was successfully immobilised on XAD-2 and coupled with optical fibres to investigate a sensor-based approach for determining copper. Reflectance measurements were used to quantify sensor response. Optimum response was obtained at a wavelength of 560 nm and at a solution pH of 7. Using a kinetic approach in which the rate of change of reflectance is measured over a 4-min period, the response was found to be linear in the range 5–127 ppm. After measurement, the sensor can be regenerated for reuse by immersing the probe in 0.1 M HCl. With continuous use, the sensing layer was found to be stable for at least 3 days. The advantages of using α-benzoinoxime in this way are compared with its use in the traditional gravimetric and colorimetric way.
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1. Introduction

Many developing countries usually do not have sufficient financial resources to purchase technologically advanced analytical equipment and therefore the nature of the analytical work that can be performed is limited. For these countries, the development of alternative techniques which are low-cost and simple, such as of fibre optic-based sensors, would considerably enhance analytical capability. The advantages associated with fibre optic-based sensors are well known—besides being low-cost and simple, they are also capable of rapid real-time monitoring and have a number of other attractive features which make them a desirable option even if cost were not a concern [1–3]. But if they are to find application in countries such as those mentioned earlier, then it is necessary that they are simple in design and are fabricated from materials that can be acquired easily.

Gravimetry and colorimetry are methods used widely in places where sophisticated instrumentation is not easily available and these techniques usually employ reagents that are highly selective for the analyte of interest. These traditional techniques, however, involve time consuming laboratory procedures, which is a distinct disadvantage when rapid assessment is required and large number of samples have to be analysed. With the inherent advantages of fibre optic chemical sensors, there is much merit in exploring whether reagents used for gravimetry and colorimetry can be coupled with optical fibres for a sensor-based approach. Our investigations are focussed on conducting such tests for the measurement of heavy metals, and this paper is concerned with the detection of copper in aqueous environmental samples. Levels of Cu(II) expected in aqueous environmental samples can vary from sub ppb levels to the ppm range depending on the level of contamination but deleterious effects can occur at concentrations in the ppb range and therefore ability to detect at these levels is desirable [4]. Fibre optic-based copper sensors using various chromogenic and fluorogenic reagents have been reported before [5–12] but many of these whilst providing good sensitivity, are not selective for copper and also rely on more complicated measurement technologies.

Several highly selective reagents for copper are available and are recommended for its gravimetric and colorimetric determination using routine methods. A number of such reagents are being investigated by our group as possible chemical transducers for copper and the results for fast sulphon black F (FSBF) were reported in a recent paper

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[13]. In this paper, we report the results for another such reagent, α-benzoinoxime (cupron), a highly selective reagent for the determination of copper in ammoniacal solutions [14]. Other ions with which α-benzoinoxime can complex are molybdenum(VI), tungsten(VI) and vanadium(V) but these are generally not expected to be present together with copper in environmental samples.

2. Experimental

2.1. Reagents

α-Benzoinoxime (Fig. 1) and metallic salts were purchased from Sigma. Distilled deionised water was used throughout for the preparation of solutions and all chemicals used were of analytical grade. Concentrated hydrochloric acid (HCl) was diluted to 0.1 and 0.5 M for regeneration studies.

A stock solution of 635 ppm of Cu(II) was prepared by dissolving the required amount of dried copper sulfate salt in 5 cm^3 ammoniacal tartrate solution followed by dilution to 100 cm^3 with distilled deionised water. Solutions containing the working range of concentrations of Cu(II) were prepared daily by diluting the stock solution with distilled deionised water.

2.2. Immobilisation

Amberlite XAD-2 polymer (<200 μm, a macroporous cross-linked polystyrene-divinylbenzene co-polymer) was soaked in methanol for 5 min and then washed with water to wet it. Thereafter, an ethanolic solution of α-benzoinoxime (10 cm^3 of a 0.01 M solution) was mixed with the washed XAD-2 polymer (0.25 g) and contact was maintained overnight with continuous stirring of the mixture. Following this, the XAD-2 resin was separated through filtration, thoroughly washed with distilled deionised water and stored under water. No attempt was made to determine the α-bezoinoxime loading on the resin because of the difficulty of finding a suitable quantification method for it. But exposure to a solution containing Cu(II) even several months after preparation still produced a green colour indicating that α-benzoinoxime had been immobilised on the resin.

2.3. Sensor design

The sensor design was similar to that described by Ahmed and Narayanaswamy [15]. An approximately 0.5 mm thick layer of the immobilised reagent was placed at the terminal end of a bundle of plastic optical fibres (purchased from Ocean Optics, Florida, USA), covered by a nylon membrane ('Normesh' 39 μm mesh size), and held against the fibre bundle with an "O" ring. This design is economical and simple since it produces a disposable sensor tip.

2.4. Instrumentation

Fig. 2 shows a schematic of the fibre optic-based spectrometer used to monitor the optical signals from the sensing layer. The instrument, available commercially from Ocean Optics (Florida, USA), consisted of a tungsten halogen lamp as the radiation source, a CCD array detector, optical fibres
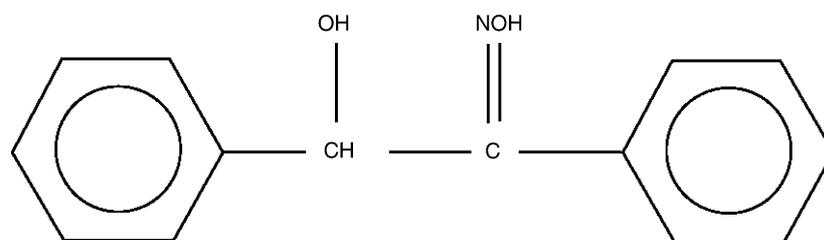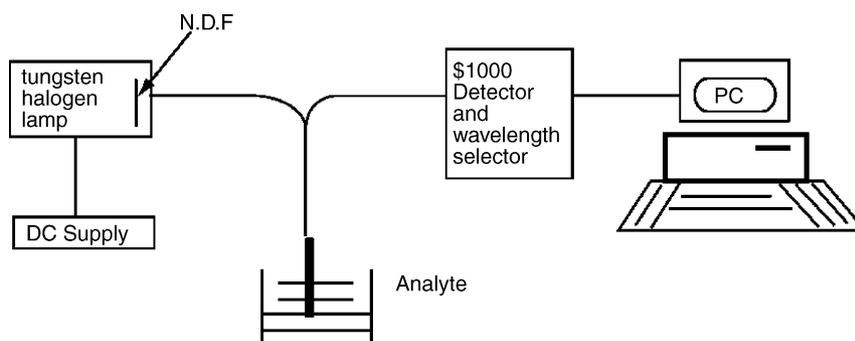

Fig. 1. Structure of α-benzoinoxime.

N.D.F = Neutral Density Filter

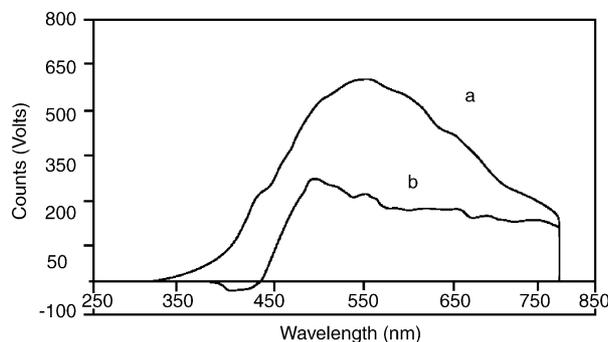Fig. 2. Schematic of the instrumentation used for reflectance measurements.

Fig. 3. Reflectance spectra of immobilised α-benzoinoxime (a) before and (b) after reaction with Cu(II).

Fig. 5. Effect of stirring on sensor response.

as light guides between components, and software for data acquisition. The optical fibre bundle to which the sensing layer was interfaced consisted of seven fibres (200 μm in diameter) of which six were connected to the light source and one to the detector.

2.5. Reflectance measurement

The optical signal recorded by the detector as counts is indicative of reflectance of the incident light by the sensing layer. The measurement of the reflectance spectrum before and after contact with 63.5 ppm Cu(II) (Fig. 3) showed that the greatest divergence between the two spectra occurred at 560 nm and all subsequent measurements were made at this wavelength.

3. Results and discussion

3.1. Optimising sensor response

The sensor response was governed by the pH of the solution (Fig. 4). At pH values lower than 7, there was very little response. At higher pH, the reflectance signal decreased possibly due to the formation of hydroxy species of Cu(II). The optimum response was obtained between 7.0 and 7.5 pH, thus all measurements were done at pH 7.2. It was also found
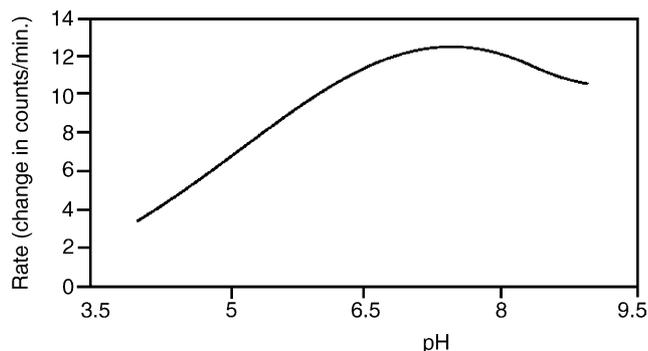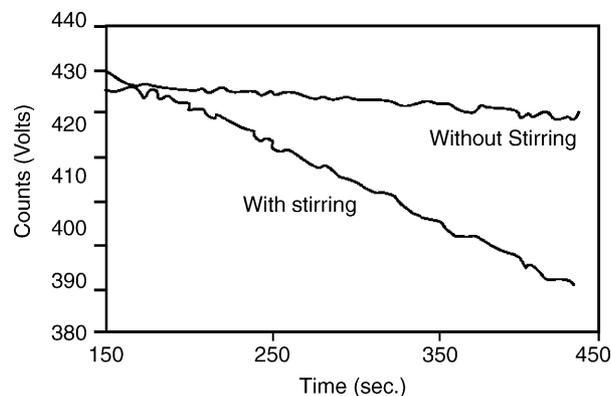
that the use of a buffer was not necessary for an ambient pH of 7.2 in the Cu(II) standard samples in which the sensor was tested. This was because the stock solution from which they were prepared was in an ammoniacal nitrate medium and dilution with deionised water to obtain lower concentrations maintained the pH around 7.2. The application of the sensor to other samples with pH values different from 7.2 however will necessitate the use of a buffer.

Stirring of the Cu(II) solution in contact with the sensing layer was found to increase the response rate by a factor of about 10 over unstirred solutions (Fig. 5) This observation is not uncharacteristic of sensor designs such as the one used in this study where optimum contact between the immobilised reagent and the analyte is prevented by physical barriers such as the resin beads and the nylon membrane. Stirring increases the rate at which equilibrium is attained and was utilised for all further measurements.

3.2. Response range

The reflectance readings against time after contact with varying concentrations of Cu(II) are shown in Fig. 6. The reflectance measurements appear to approach a steady state signal which is not different for the varying concentrations

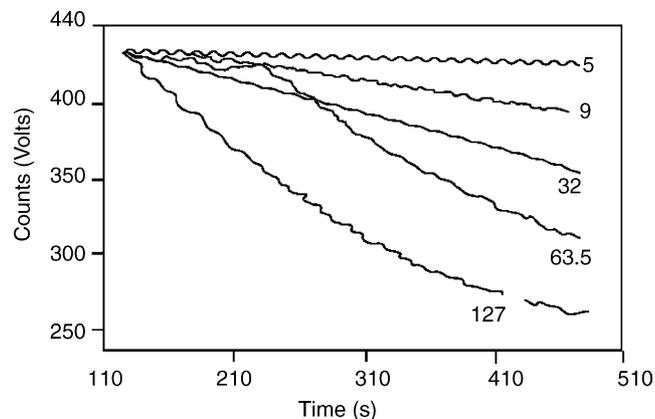Fig. 4. Effect of pH on sensor response.

Fig. 6. Reflectance measurements against time for varying concentrations (ppm) of Cu(II).
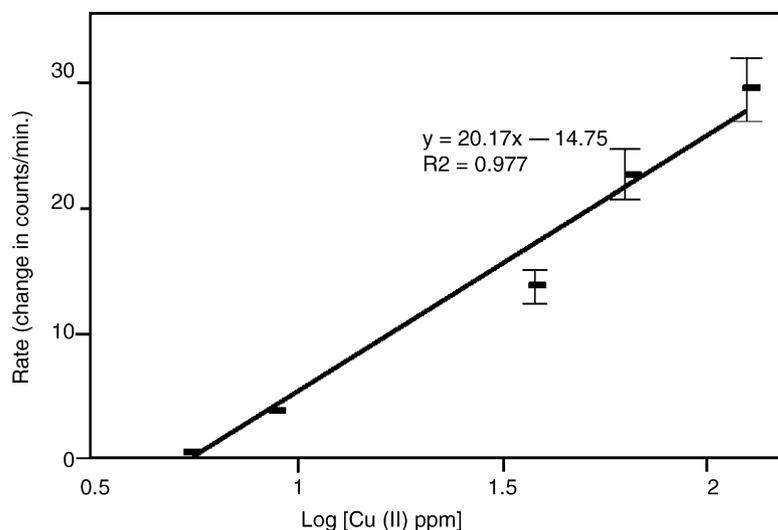
Fig. 7. Calibration curve for Cu(II).

of Cu(II), although the rate at which this steady signal is approached appears different. In such a case, the rate of change of reflectance rather than an absolute reflectance value is a better parameter for differentiating the sensor response at different concentrations. The rate of change of reflectance over the first 4 min of contact was thus calculated and plotted against the log Cu(II) concentration to obtain the calibration curve shown in Fig. 7, which is linear from 5 to 127 ppm. The LOD, defined as the concentration corresponding to a signal equal to the mean plus 3 standard deviations of the signal of a blank solution, was 5 ppm.

3.3. Reversibility

An ideal sensor should respond to changing copper concentrations in both directions. This however, is not always achievable, and regeneration of the reagent phase before the next determination is essential unless a new sensing layer is to be used for each analysis. Each fresh new layer may not be exactly the same as the previous one and this can introduce an added degree of variability that can not usually be easily accounted for. Following the reaction of immobilised α-benzoinoxime with Cu(II), regeneration by treatment with 0.1 and 0.5 M HCl was attempted (Fig. 8). Treatment of the

layer with 0.1 M HCl resulted in a steady state response identical to the original baseline. The use of 0.5 M HCl, however, resulted in a dramatic increase in reflectance beyond the original baseline. The reason for this is not very clear. It did not appear to be the result of denaturing or leaching of the immobilised reagent. This is because the original baseline could be regained by reimmersing the sensor in distilled deionized water for a sufficiently long time and after this the same response to copper as before could be obtained. The regeneration time of the sensing layer using 0.1 and 0.5 M HCl were 30 and 600 s, respectively. The use of 0.1 M HCl was therefore considered to be the best for quick regeneration of the sensor.

3.4. Reproducibility

The precision of a single layer of immobilised α-benzoinoxime was tested over 3 days. The relative standard deviation (R.S.D.) was less than 9% over this period with the sensor being used for about 5–6 h every day which shows the high degree of stability of the sensing layer. Very few workers report reproducibility of their developed sensors over such time periods and under such intensive use and direct comparison of the R.S.D. value with those of others is
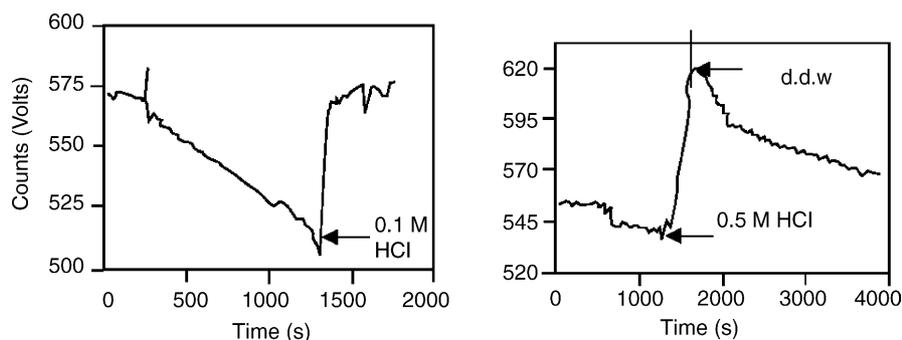

Fig. 8. Regeneration of sensor using 0.1 and 0.5 M HCl.

therefore not possible. However, R.S.D. values of between 5 and >10% in general are not uncommon [16–18].

3.5. Advantages of using α-benzoinoxime in a sensor-based approach

In this section, a discussion is presented of whether the above results show that there is significant advantage to be gained by using α-benzoinoxime coupled with fibre optics as against using it in the traditional approaches. The main advantage is in the ease with which detection is possible with the fibre optic approach. In a matter of minutes, measurement can be completed and the sensor made ready for another measurement. On the other hand, the tediousness of the laboratory procedures associated with gravimetric work is well known and does not need elaboration. For colorimetric determination, the precipitated copper complex has to be extracted into chloroform and this introduces another degree of complication.

As far as detection limit is concerned, an LOD of 5 ppm with fibre optics does not present a significant advantage over gravimetric and colorimetric methods but further lowering of the LOD with fibre optics can be possible with using other kinds of sensor designs. This could be immobilisation of α-benzoinoxime on thin film resins which would mean that the reaction with copper is no longer diffusion controlled. In terms of reversibility, the sensor as developed is not reversible but it can be regenerated for use for a period of about 3 days. Therefore a small amount of the α-benzoinoxime reagent can be used repeatedly many times. This is not the same in gravimetric and colorimetric techniques where the reagent once spent has to be discarded. This could be quite desirable from the point of view of safe use and disposal of chemicals.

4. Conclusion

The work described here demonstrates a fibre optic reflectance sensor that is rapid, reasonably sensitive and selective for Cu(II). The sensor can be used at a pH of 7.2 for quantitative determination of labile forms of Cu(II) in the concentration range of 5–127 ppm, and can easily be regenerated in 30 s by treatment with 0.1 M HCl. A LOD of 5 ppm, however, restricts the use of the sensor to samples that are reasonably contaminated with copper. High detection limits are one of the drawbacks of the kind of design used in this study in which a membrane physically separates the immobilised reagent on the resin phase from the test solution. The response pattern then becomes dependent on diffusion of the analyte across the membrane. The challenge in improving detection limits lies in developing designs that are able to achieve optimum contact between the analyte and the colorimetric reagent instantaneously. An application could be in using the sensor as an alert in the waste stream of a copper-based industry where the concentration of copper is not allowed to exceed 5 ppm. At concentrations of less than 5 ppm, the sensor does not respond and this should be sufficient indication that the waste stream is of acceptable quality.

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