An investigation of the performance characteristics and operational lifetimes of multi-element thick film sensor arrays used in the determination of water quality parameters

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Abstract

An investigation of the useful lifetimes of thick film sensors suitable for the measurement of various aqueous parameters is reported. Batches of sensor arrays designed to simultaneously measure temperature, conductivity, pH, dissolved oxygen and redox potential were investigated. In particular the device to device repeatabilitys of the pH and dissolved oxygen sensor elements were studied as it was found to be the characteristics of these elements that limit the device lifetimes. Errors of less than 5% for pH sensors and 10% for dissolved oxygen sensors were observed over periods of several months continuous immersion in water. An assessment of useful continuous immersion lifetimes was made for the sensors and possible sensor failure mechanisms are postulated. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Thick film technology is a long established technique for the fabrication of miniature, rugged, low cost electronic subsystems. The technology is extensively described in the literature [1] and essentially consists of the sequential screen printing and firing of layers of various materials to produce the electrical interconnect, dielectric isolation between layers and resistors required to form electronic circuits. In more recent years thick film technology has been successfully employed in the realization of a variety of solid state sensors endowed with the same desirable attributes of ruggedness, small size and low cost [2,3]. A particularly interesting aspect of thick film technology is the ease with which multiple instances of sensors can be simultaneously fabricated onto a common substrate. This significant advantage has led to the exploitation of thick film technology as a suitable medium for the implementation of a variety of integrated chemical and physical sensor arrays [4–6].

An integrated sensor array containing elements capable of sensing a variety of different measurands is shown in the schematic diagram of Fig. 1, where sensors for five distinct water quality parameters have been included onto one double sided assembly measuring 25×50 mm. The schematic shows both sides of a double sided assembly which has a thickness of 1 mm when the two sides are mounted back to back.

The schematic in Fig. 1 shows the underlying metalization layers only. The actual sensors are in fact rather more complex structures consisting of several layers of different materials which are deposited onto these underlying metal layers. The construction of the individual sensing elements of the array are described in more detail in the following sections.

The devices reported here were fabricated as part of a long term project concerning an investigation into the feasibility of using thick film technology for the realization of water quality sensors. The project, known as CENSAR (chemical and environmental sensor arrays), was funded by the UK EPSRC and DTI and involved a consortium of industrial and research partners. A major topic for investigation concerned the issue of sensor cost versus lifetime and accuracy. Whilst thick

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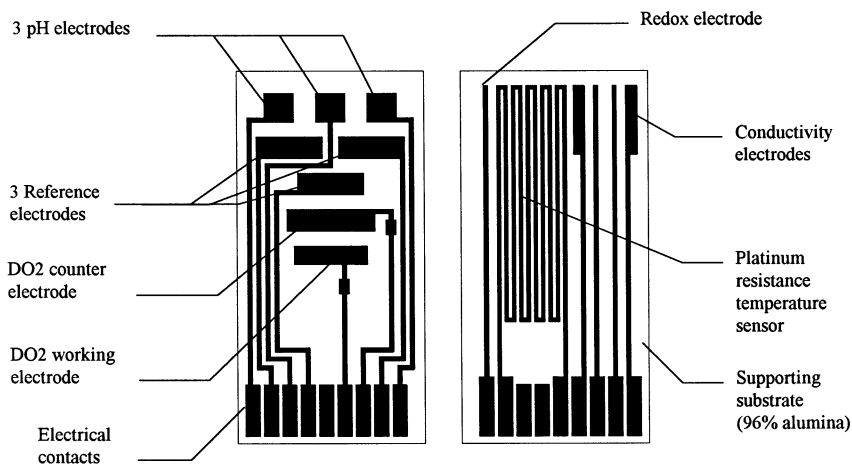*E-mail address:* jka@soton.ac.uk (J.K. Atkinson)

Fig. 1. Integrated sensor array for the measurement of pH, conductivity, temperature, redox potential and dissolved oxygen concentration. Both sides of a double sided array are shown, although only the underlying metalization layer on each side is shown.

film technology is known to be an attractive option in the fabrication of certain 'one shot' sensors [7,8], largely due to its cost advantages, it was felt that its suitability for the production of sensors with any degree of operational longevity had not been investigated fully.

2. Device fabrication details

2.1. Temperature sensor fabrication

The temperature sensor incorporated onto the array shown in Fig. 1 consists of a screen printed platinum resistance thermometer (PRT). It is constructed as a submicron thick layer of platinum deposited onto the supporting substrate in a meandering pattern to give a measurably high value of resistance (typically 500 Ω) between the two end contacts of the PRT. The platinum used was a screen printed and fired organo-metallic thick film resinate (Heraeus RP10001-145B). On immersion the platinum layer is shielded from direct contact with the water by a superimposed layer of glass ceramic dielectric (ESL 4608-CFB).

The fact that the platinum layer has a repeatable and linear temperature coefficient of resistance of ca 3600 ppm per 1°C can then be used to enable temperature to be measured to a high accuracy. The accuracy of the sensor is in fact only limited by the precision with which the electronic instrumentation can measure the resistance of the PRT. This in turn is likely to be governed by the level of electronic circuit noise encountered in the instrumentation circuits.

2.2. Conductivity sensor fabrication

The conductivity sensor reported here consists of a sub-micron thick layer of platinum (Heraeus RP10001-

145B) deposited as four electrodes which are exposed to the water through a window in the same glass ceramic dielectric layer used to cover the temperature sensor. The conductivity is measured using a four point probe method whereby an ac excitation signal is applied between the two platinum outer electrodes with the inner pair of platinum electrodes being used to measure the resulting field. The ratio of the signal detected on the inner electrode pair to the excitation signal is then a function of the conductivity of the medium into which the probe has been placed.

The sensor's accuracy is primarily determined by the quality of the electronic instrumentation making the measurement. The particular design illustrated here exhibited a measured cell constant of approximately 0.8 and was found to be linear over the range of conductivities from 50 μS cm^{-1} to 5 mS cm^{-1}.

2.3. Redox/reference electrode fabrication

Arguably, a somewhat less than accurate indicator of water quality, redox potential is none the less a useful measurement in many applications. The method for its determination in the device described here simply consists of the measurement of the potential on an immersed platinum electrode with respect to a reference electrode. Consequently, the functionality of the refer-
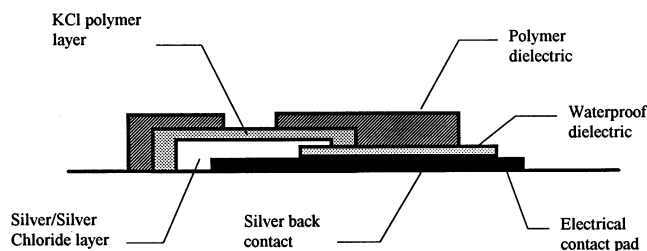

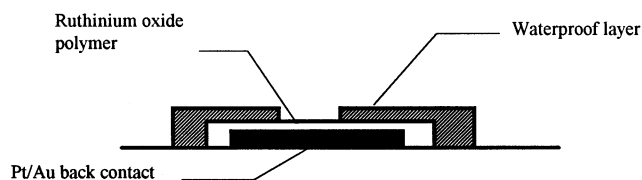Fig. 2. Cross-section of reference electrode showing individual layers.

Fig. 3. Cross-section of pH electrode showing construction.

ence electrode is the major determinator of accuracy. The platinum redox electrode was fabricated simultaneously with the temperature and conductivity electrodes using the same platinum and dielectric materials as for those sensors.

There are three separate reference electrodes on the array shown in Fig. 1, which can be used as the reference elements for redox potential, pH and dissolved oxygen measurement in a variety of different combinations. The exact choice of the number of reference electrodes in this particular application is arbitrary but majority voting to determine functionality of the electrodes can be employed with a minimum of three devices. This possibility always assumes that the electronic instrumentation can switch between electrodes. Fig. 2 shows a simplified cross-section of an individual reference electrode.

The device consists of a silver/silver chloride electrode covered by a potassium chloride containing, polymer reservoir which hydrates on contact with liquid. An optional porous plug can be printed over the potassium chloride containing layer to reduce the rate of salt loss at the expense of increased hydration time.

The devices reported in this evaluation consisted of two different types of reference electrode. Both types were fabricated as an initial layer of printed and fired silver (ESL 9912-A) which forms the electrical back contact. Onto this silver layer is then deposited a low temperature curing silver/silver chloride containing epoxy (GEM C50627R1) for one type of reference electrode and a high temperature firing, purpose made silver chloride and glass frit based material for the other.

A layer of polymer dielectric (ESL 240SB) was then deposited primarily to seal the edges of the underlying reference electrode material. This layer was also used to colour code the two different devices, a green polymer

Fig. 4. Cross-section of dissolved oxygen sensor showing construction.

dielectric layer was used for the polymer silver/silver chloride electrodes and a yellow polymer dielectric layer for the silver chloride glass electrodes

2.4. pH sensor fabrication

There are three individual pH sensors on the particular array described here. Again the exact number of devices is arbitrary although three is the minimum number for the utilization of a majority voting technique for the detection of an electrode that has gone out of calibration. The individual pH electrodes consist of a metal oxide salt bound to a metal back contact which is then connected by a waterproofed lead-in to the edge connector of the array. In the devices reported here the metal back contact used was platinum gold (ESL 5837) and the metal oxide salt was Ruthinium Oxide mixed with an acrylic binder (GEM C50502D7). A layer of polymer dielectric (ESL 240SB) was deposited on top of this structure for the purpose of sealing the edges of the polymer metal oxide layer. All thick film materials were processed according to manufacturer's instructions. Fig. 3 shows a simplified cross-section of an individual pH electrode.

Various metal oxides are suitable for use as the pH sensitive layer [9] and the use of different types of metal oxide in the same array offers the possible use of signal processing as a means of compensating for ionic cross-sensitivity. This possibility stems from the fact that the different metal oxides do not generally share the same ion cross-sensitivities. Although arrays employing combinations of different metal oxide pH sensors had been investigated previously, for the purposes of the investigation reported here it was decided to fabricate three identical pH electrodes that had been printed simultaneously. For this reason the RuO_2 ink was chosen as it was readily available and had the best known characteristic.

2.5. Dissolved oxygen sensor fabrication

Fig. 4 shows a simplified schematic diagram of the dissolved oxygen sensor in cross-section. The device consists of a salt electrolyte gel covered by a cellulose acetate membrane which is deposited onto a pair of gold electrodes. The gold electrodes were deposited as a printed and fired layer of gold paste (Dupont 5715-H) onto which a layer of 1 M potassium nitrate solution and gelatine in a weight ratio of 1:4 was subsequently screen printed and air dried to form an electrolyte approximately 8 μm thick. The membrane was screen printed on top of the electrolyte gel using a purpose made air drying solvent based ink consisting of cellulose acetate dissolved in ethyl glycol diacetate in a weight ratio of 1:4 to give a membrane thickness of approximately 10 μm.
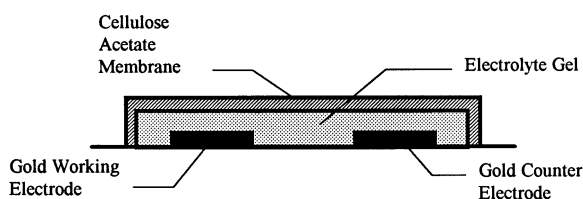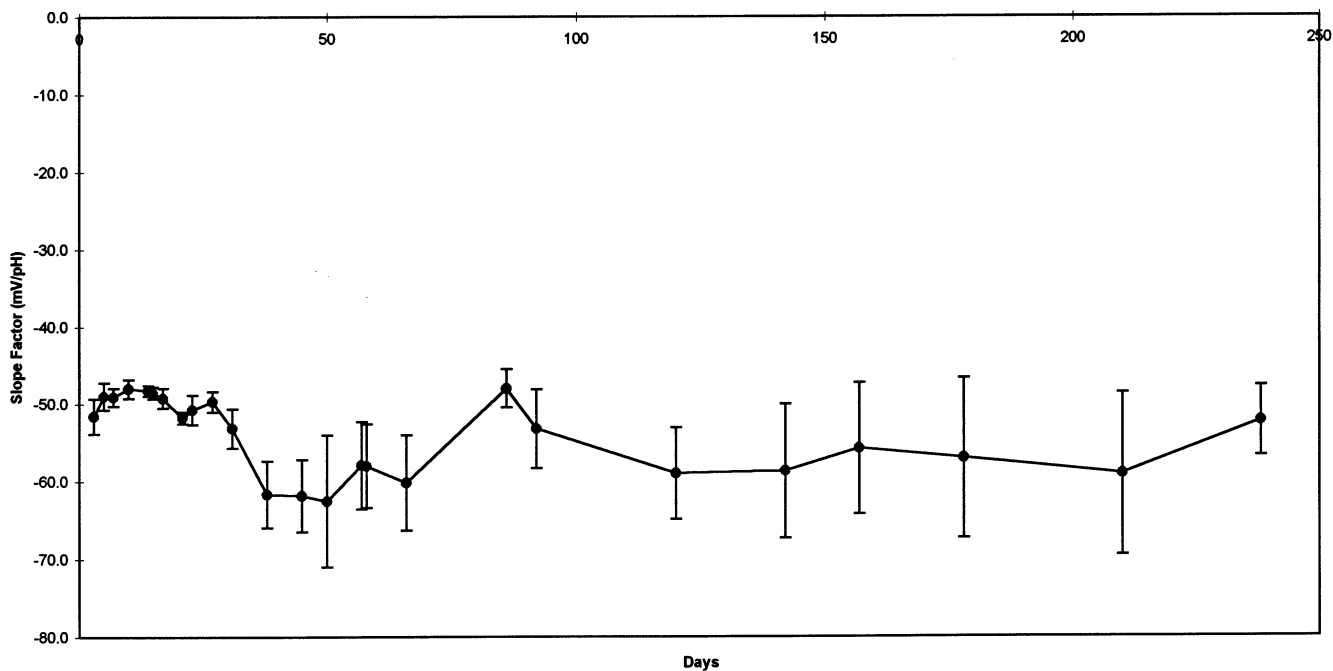
Fig. 5. Average slope factors of pH sensors (polymer based reference electrodes batch) versus integral reference electrodes.
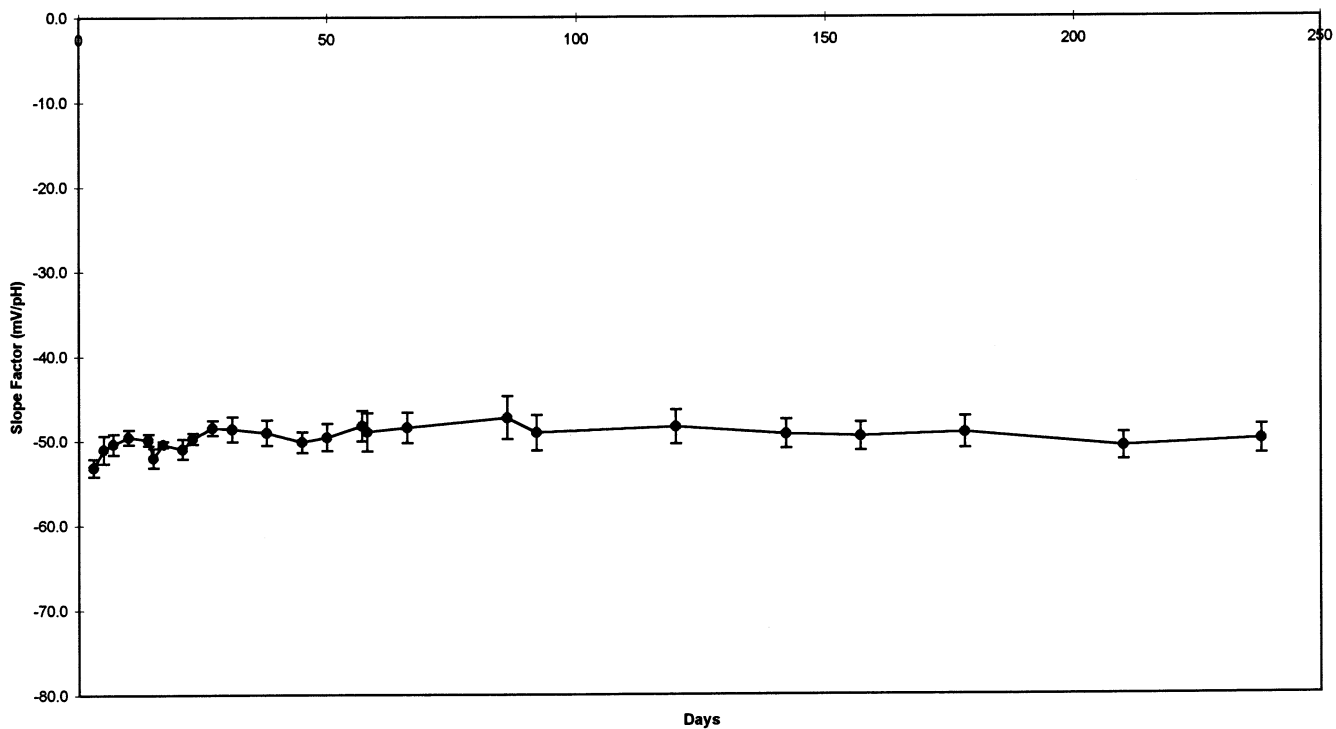
Fig. 6. Average slope factors of pH sensors (polymer based reference electrodes batch) versus external calomel reference electrode.

The gold electrodes form the working and counter electrodes for a three terminal potentiostat with one of the previously described reference electrodes on the array forming the third electrode. This structure gives a sensitivity of typically 2 μA ppm^{-1} of dissolved oxygen with approximately zero offset current and was found to respond very rapidly to changes in dissolved oxygen level.

3. Experimental

In order to determine the operational characteristics and the typical lifetimes of the sensors, a long-term test and evaluation programme was devised and implemented. Two separate batches of sensor arrays were fabricated and tested, one batch incorporating reference

electrodes fabricated with the polymer based silver/silver chloride reference electrode material (colour coded green) and the other batch incorporating the purpose made glass frit based silver chloride reference electrode material (colour coded yellow).

It was known from previous testing programmes that there was no appreciable change in the sensors measuring temperature and conductivity with continuous immersion over periods of many months. The sensors which did show a noticeable time dependency however were those for pH and dissolved oxygen and, in particular, their reference electrodes. For this reason the long term testing programme concentrated solely on the measurement of pH and dissolved oxygen.

3.1. Evaluation of sensor operational lifetimes

The evaluation of useful sensor lifetimes involved the continuous immersion in water of batches of sensor arrays and the periodic monitoring of their performance over a period of several months. Six individual sensor arrays were selected from each of the two batches fabricated and subjected to the following procedures.

In order to facilitate measurement of the sensor responses, a test rig was constructed in which the sensors were connected to their measuring instruments via multi-way switch boxes and cables. In this way it was possible to subject a complete test batch to a common test medium and environment and easily switch between individual devices to record their readings. Following immersion in each different test medium a suitable settling time was allowed for the sensors to react to the test medium before the readings were recorded. It was also necessary to allow a suitable settling time between switching each individual sensor and taking a reading to allow the instrumentation circuits to stabilize.

Provision was made for the reference electrode connection for the pH and dissolved oxygen sensor measurements to be switched between the solid state reference electrode on the array and a commercial calomel reference electrode (ABB Kent Taylor 1431-210). In this way changes in the sensor responses due to ageing of the array reference electrodes could then be monitored.

Between tests the sensors were maintained in continuous immersion in de-ionised water obtained from filtered tap water using a commercial resin filter de-ionising unit (Permutit CD250). When test readings were
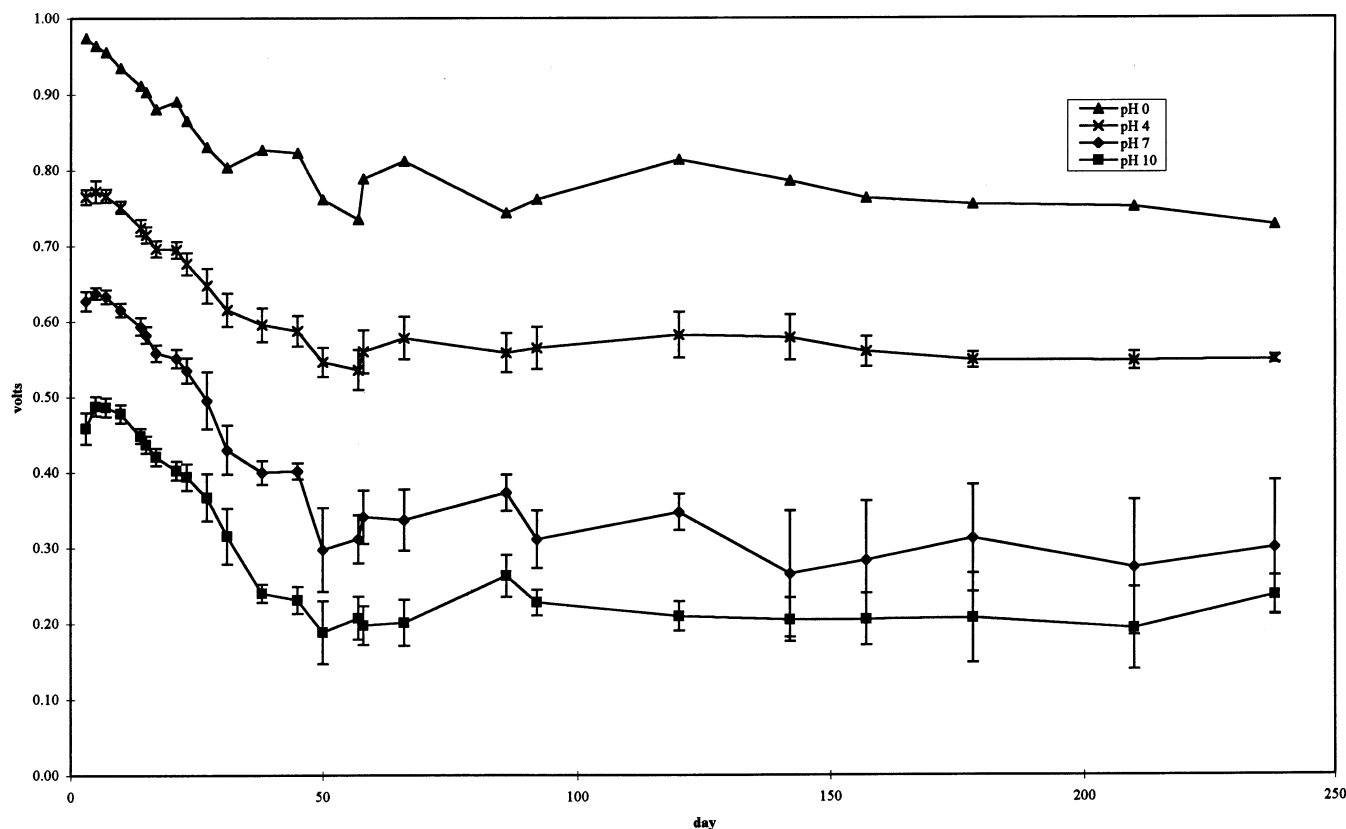

Fig. 7. Average electrode potentials of pH sensors (polymer based reference electrode batch) at pH 4, 7 and 10 versus integral electrodes with an extrapolated value for pH 0.
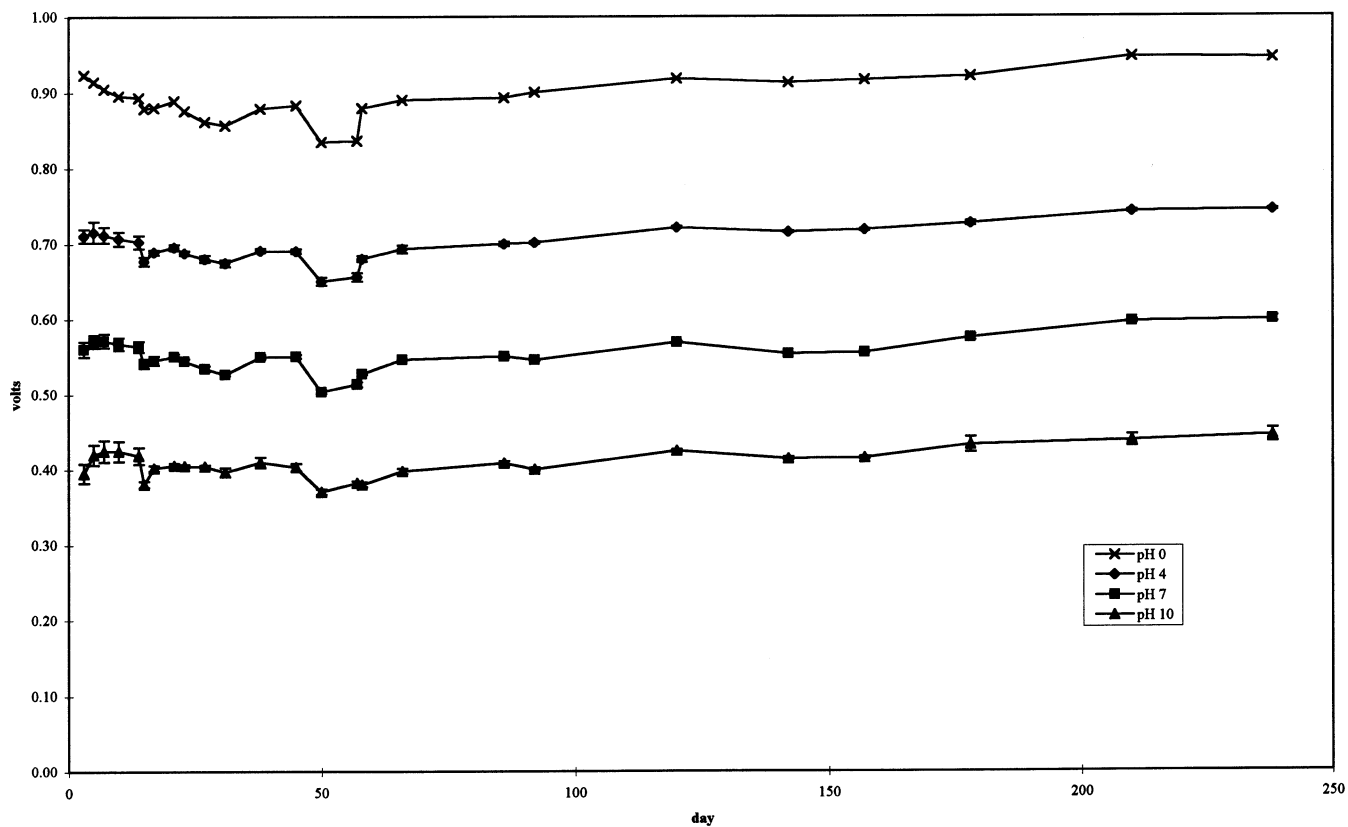
Fig. 8. Average electrode potentials of pH sensors (polymer based reference electrode batch) at pH 4, 7 and 10 versus external calomel electrode with an extrapolated value for pH 0.
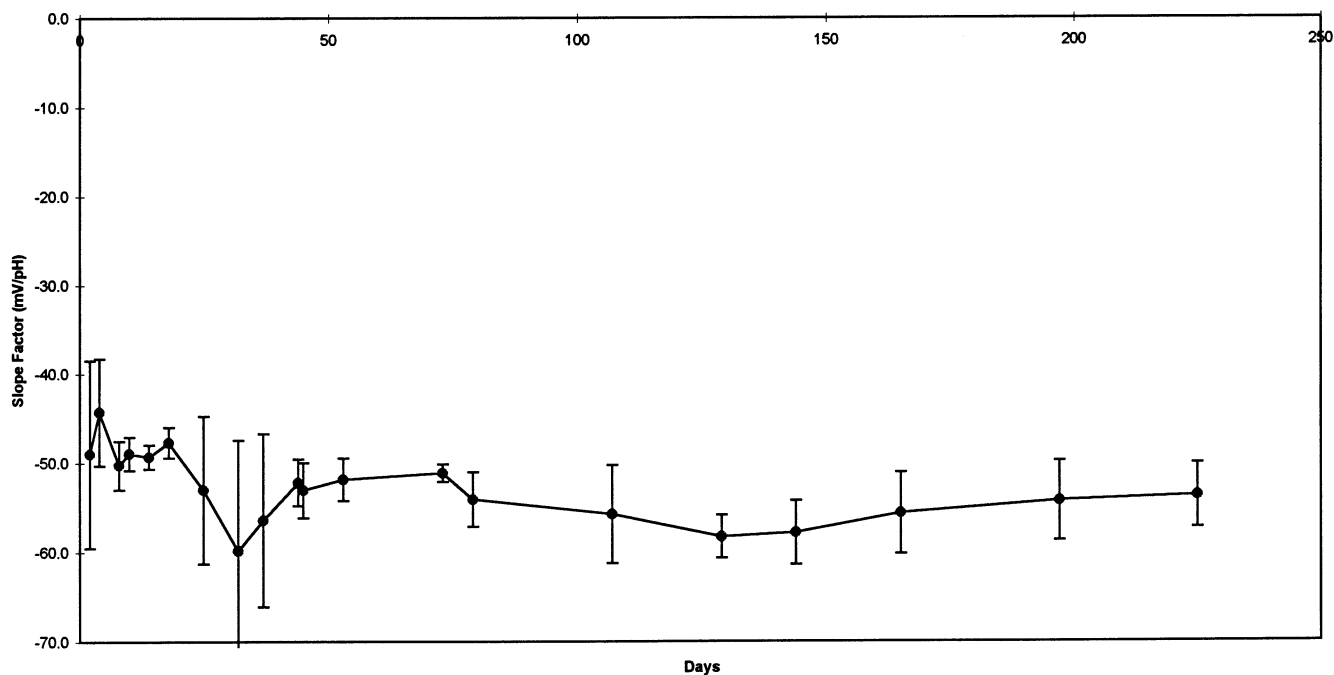
Fig. 9. Average slope factors of pH sensors (glass based reference electrode batch) versus integral reference electrodes.

taken both the sensors and the test media were maintained at a constant temperature of 20°C using a thermally-controlled water bath. This was achieved by placing the sensors in the test media in glass containers which were placed in the water bath and allowed to thermally equilibrate before readings were taken.

A further provision of the test rig was for two sensor arrays from each batch to have their dissolved oxygen sensors permanently powered in order to observe the effect on response. Between tests the permanently pow- ered sensors were held separately in glass containers of de-ionised water in order to avoid any polarization effects between sensors. The permanently powered sen- sors were disconnected from their individual power
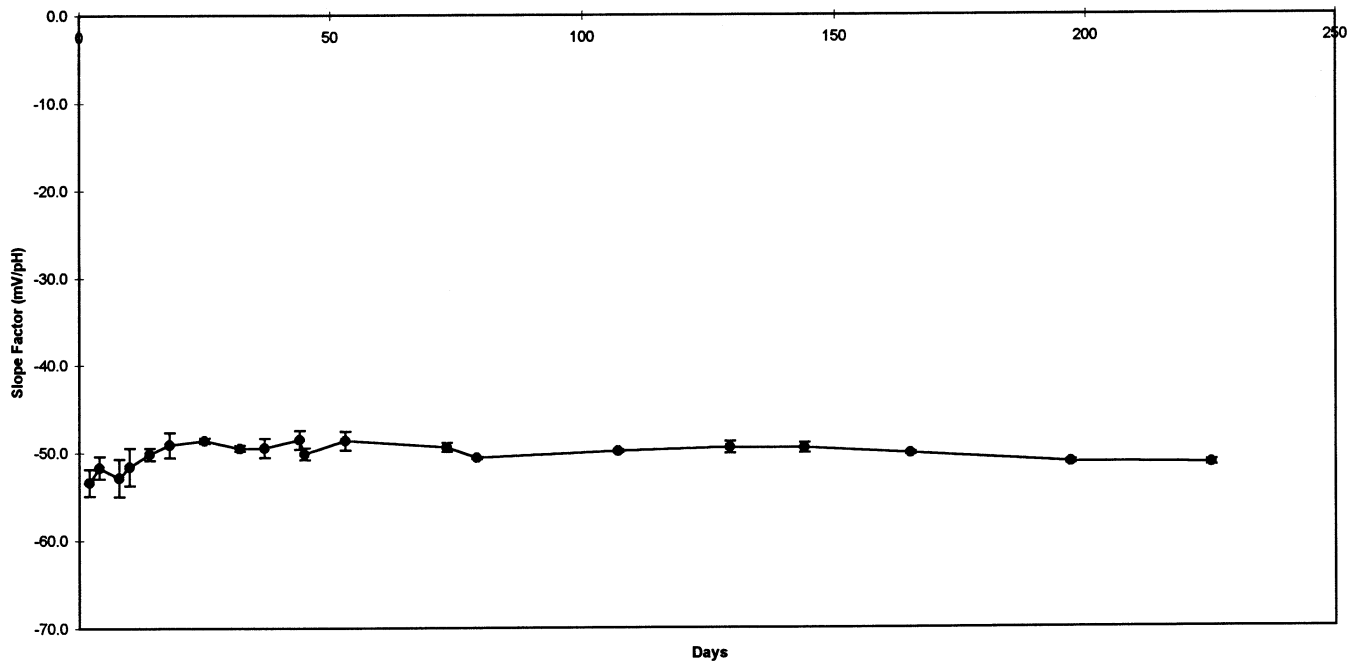

Fig. 10. Average slope factors of pH sensors (glass based reference electrodes batch) versus external calomel reference electrode.
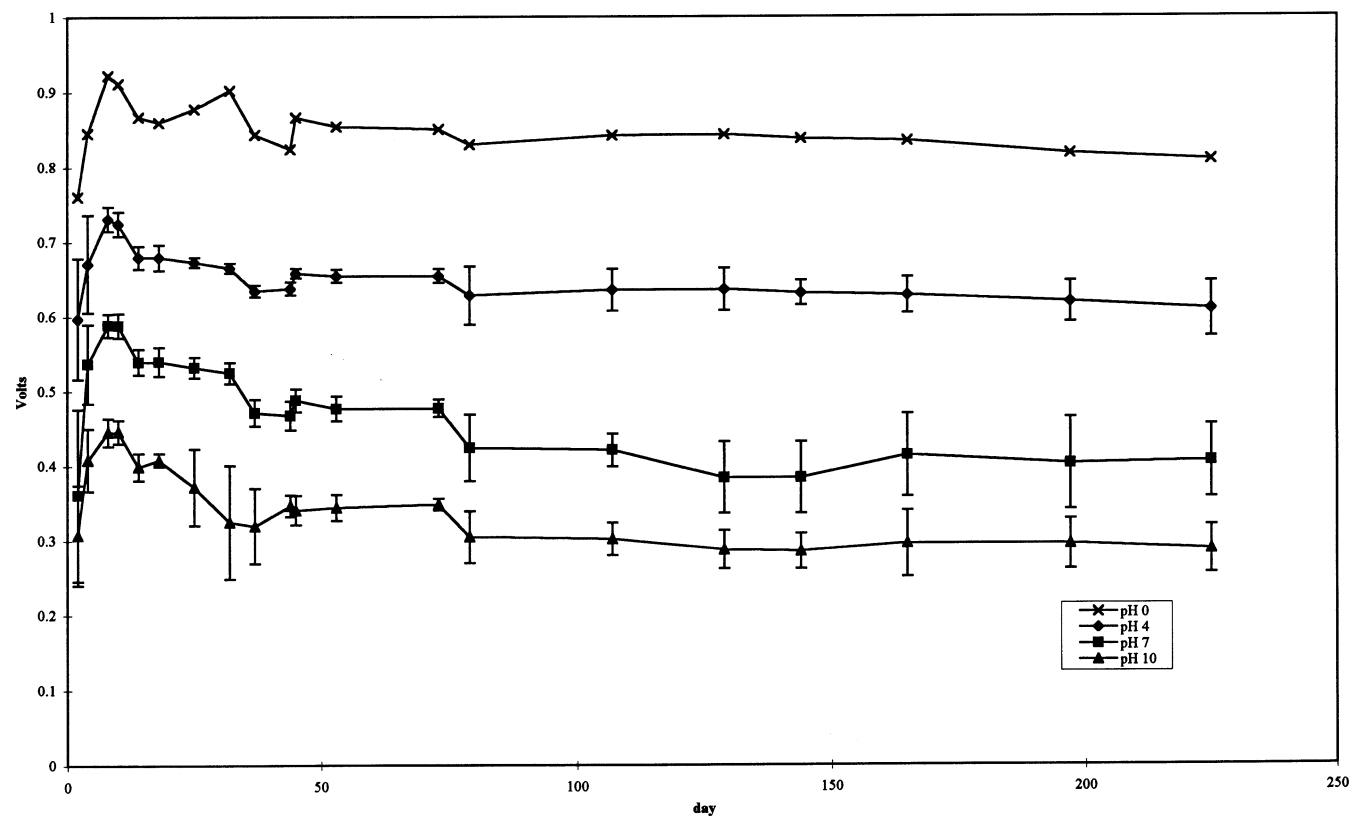

Fig. 11. Average electrode potentials of pH sensors (glass based reference electrodes batch) at pH 4, 7 and 10 versus integral reference electrodes with an extrapolated value for pH 0.

supplies when the sensors were all placed together into the various test media and reconnected after each test was complete.

The electronic instrumentation to which the sensors were connected varied according to the devices being tested. The pH sensors and their reference electrodes
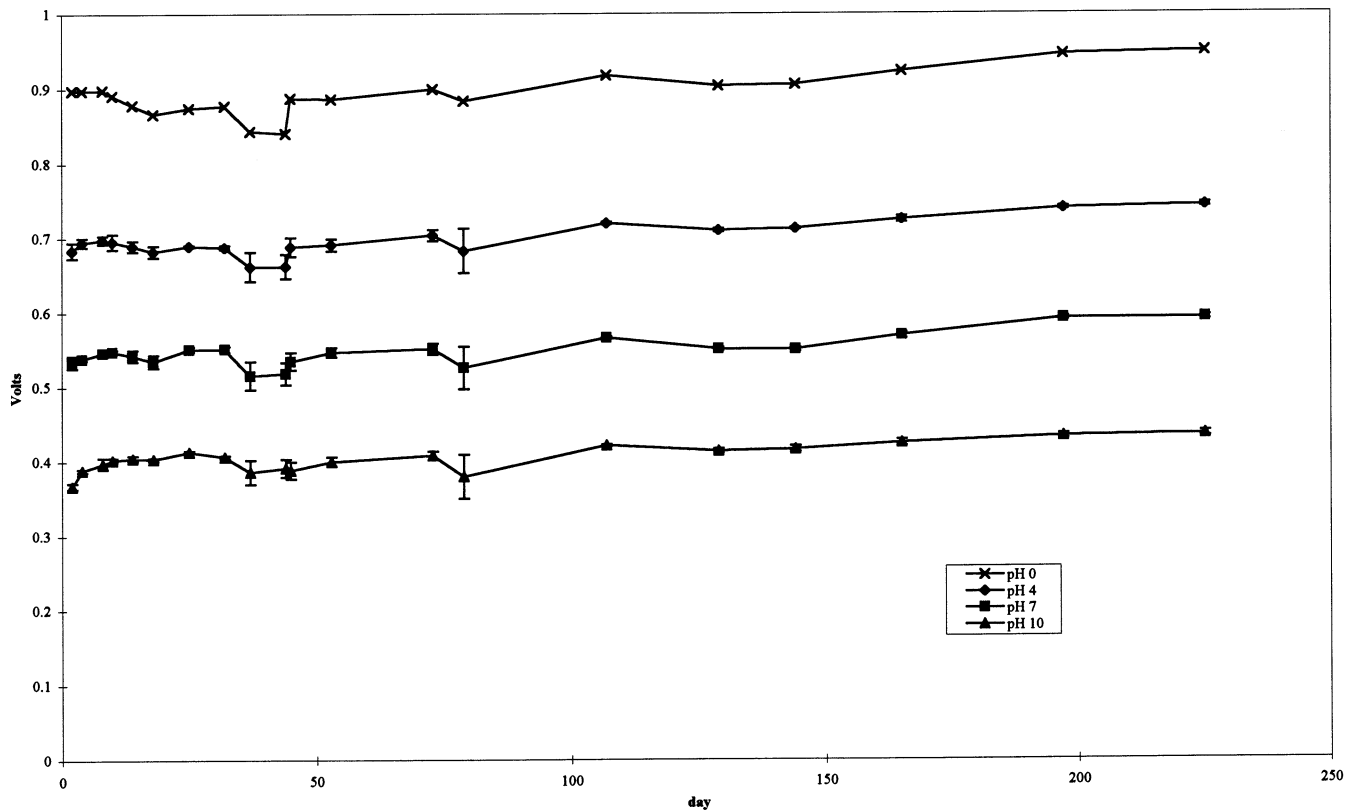

Fig. 12. Average electrode potentials of pH sensors (glass based reference electrodes batch) at pH 4, 7 and 10 versus external calomel reference electrode with an extrapolated value for pH 0.
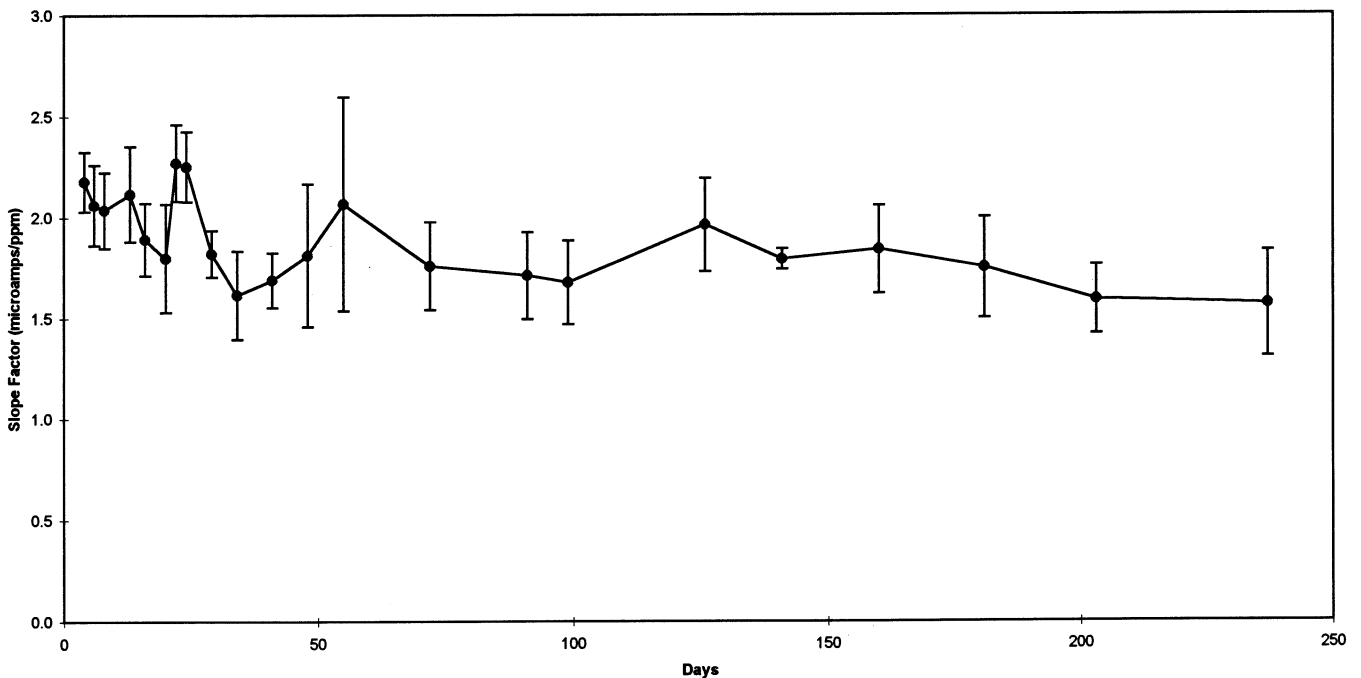

Fig. 13. Average slope factors of intermittently powered dissolved oxygen sensors using integral reference electrode (polymer reference electrode batch).

were directly connected to a purpose built high input impedance amplifier the output of which was connected to a digital voltmeter(Keithley 2000 DVM). The dissolved oxygen sensors used a simple purpose built potentiostat circuit to simultaneously hold the working electrode at -0.6 V with respect to the test solution and monitor the working electrode current. The output of this potentiostat circuit was connected to the digital voltmeter for the purpose of recording the sensor signal.
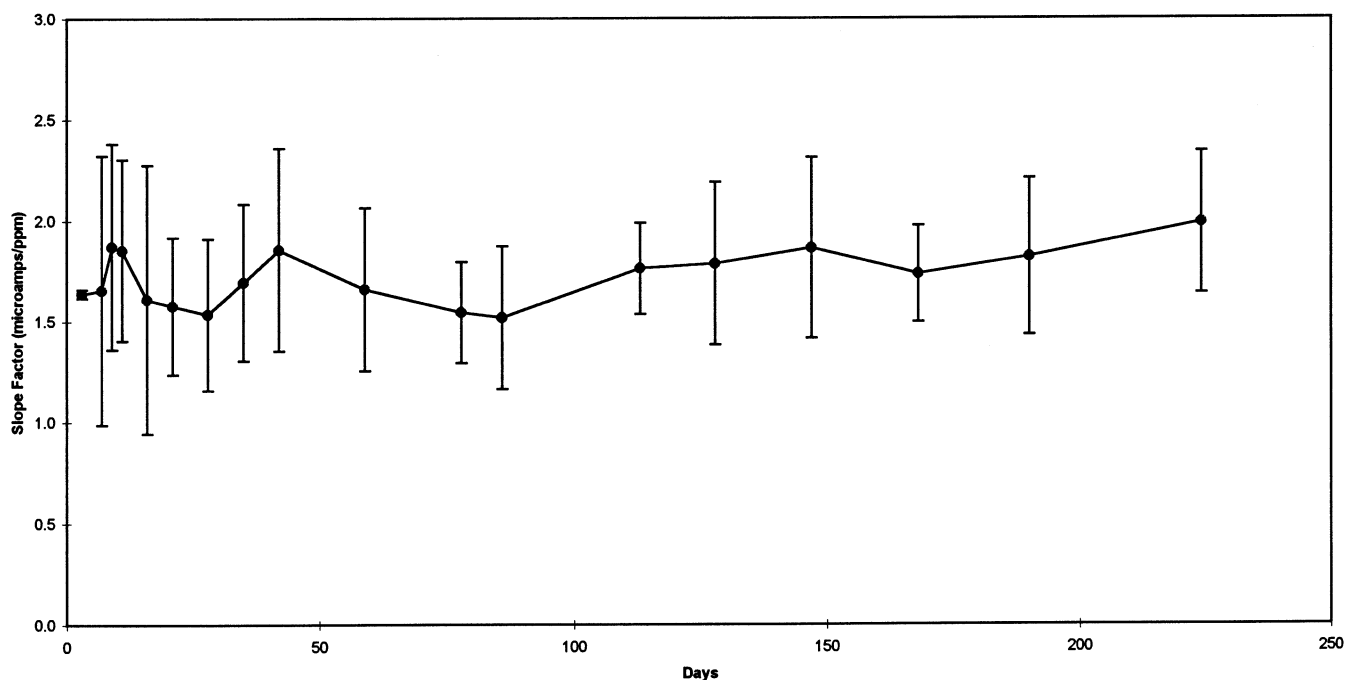

Fig. 14. Average slope factors of intermittently powered dissolved oxygen sensors (glass based reference electrodes batch).
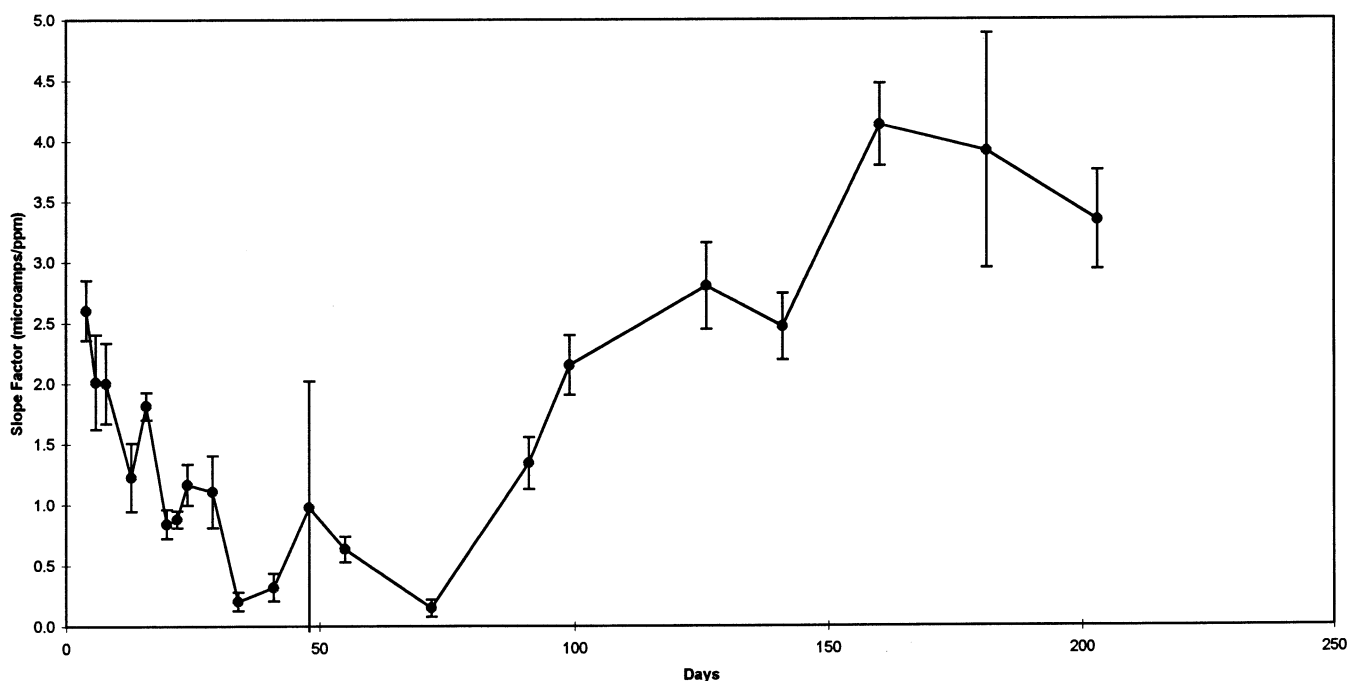

Fig. 15. Average slope factors of permanently powered dissolved oxygen sensors using integral reference electrode (polymer based reference electrode batch).
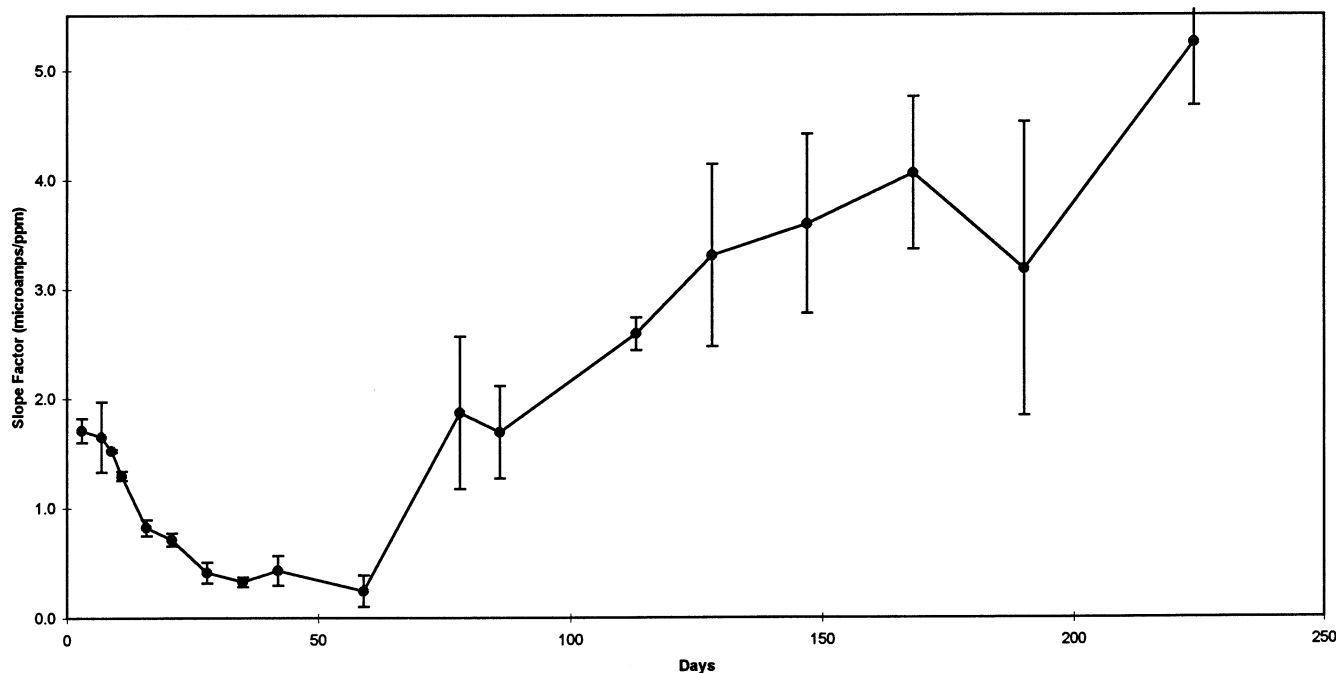
Fig. 16. Average slope factors of permanently powered dissolved oxygen sensors (glass based reference electrodes batch).

3.2. pH sensor lifetime test procedure

The pH sensors were subjected to periodic testing in three separate buffer mediums of pH 4, 7 and 10. The sensors were rinsed in de-ionised water between each immersion in a pH test buffer. Allowed settling times were typically 30 min between buffer changes and 2 min between switching devices. This method appeared to give a reading stable to 1 mV corresponding to a change of less than 0.02 pH.

The sequence in which the test devices were subjected to the different pH buffers did not have any noticeable effect on the response of the devices. This was probably due to the fact that the sensors were not left to stand for extended periods in any of the buffer solutions. A parallel programme of research [10] has however found evidence that the devices possess a 'memory effect' whereby the response of the sensors can in fact be modified if stored for long periods in media having extreme pH values.

3.3. Dissolved oxygen sensor lifetime test procedure

The dissolved oxygen sensors were tested by initially immersing the sensors in a stirred solution of de-ionised water into which air was continuously bubbled to give a level of dissolved oxygen at nominally 100%. The sensors were then left to stabilize for 1 h prior to their readings being recorded. A simultaneous measurement of dissolved oxygen concentration was made using an air calibrated commercial oxygen probe (YSI Model 57). The individual sensors were allowed to settle for 2

min between connection to the measurement circuit and recording of their readings.

The air line was then removed and oxygen free nitrogen was bubbled through the solution for approximately 30 min until a reading of ca 4 ppm dissolved oxygen was achieved on the YSI oxygen probe. At this point the nitrogen line was removed and the sensors were read. The presence of a blanket of floating plastic balls on the surface of the test solution ensured that the dissolved oxygen level did not change significantly during the period of time taken to switch between the individual sensors and record their readings.

The nitrogen line was then reintroduced into the solution and a further period of bubbling of approximately 1 h duration was allowed to remove any remaining dissolved oxygen from the solution. A set of readings was then obtained at this the nominal 0% dissolved oxygen level and the reading on the YSI oxygen probe was also recorded for comparison.

3.4. pH sensor device to device repeatability test procedure

The evaluation of device to device repeatability involved batches of individual sensor arrays of both types (green and yellow) being subjected to a range of values for each of the measurands and their responses recorded.

Then, 12 pH sensors from each batch were sequentially immersed in buffer solutions of pH 4, 6, 7, 8 and 10 (with a rinse in de-ionised water between each buffer) and their potentials were recorded. These tests

were carried out early in the sensors' operational lifetimes when any effects of reference electrode ageing were not yet apparent.

Consequently there was little difference between the results obtained with the sensor array internal reference electrodes and an external commercial reference electrode. This was ascertained by making all measurements using both the integral solid state reference electrodes on the arrays and the external calomel electrode and recording both sets of results for comparison.

3.5. Dissolved oxygen sensor device to device repeatability test procedure

In order to determine the device to device repeatability of the oxygen sensors it was necessary to simultaneously subject a batch of sensors to a stirred solution containing a known dissolved oxygen concentration and then compare the sensor responses. In practice this proved very difficult to achieve since it is not easy to uniformly control the dissolved oxygen concentration in a solution held in a thermally controlled water bath containing a large number of sensors. This problem undoubtedly caused some local variations in oxygen concentration and hence the repeatability test of the dissolved oxygen sensors almost certainly produced a figure somewhat worse than the actual device to device repeatability of the sensors.

The test procedure adopted was to bubble air through a stirred solution of deionised water for approximately 2 h until a stable reading was obtained on the YSI oxygen probe which was then recorded. The sensor readings were also then recorded at this the nominal 100% dissolved oxygen level. The air line was then removed and nitrogen was bubbled through the stirred solution until the YSI probe reading fell to approximately 75% of the air saturated reading. The readings of eight individual sensors from each batch and the corresponding YSI probe readings were then recorded. This procedure was then repeated at the 50 and 25% intervals until a final nitrogen purge of the solution was carried out to establish the nominal 0% dissolved oxygen level.

4. Results

4.1. pH sensor lifetimes

Fig. 5 shows the pH sensor slope factor plotted as a function of time obtained by taking the average slope of the electrode potentials between pH 4 and 10 for all six sensor arrays from the batch of sensors fabricated with polymer based reference electrodes. An average slope factor of 54 mV pH^{-1} ($\pm 10\%$) was obtained over the 6 months duration of the testing when using
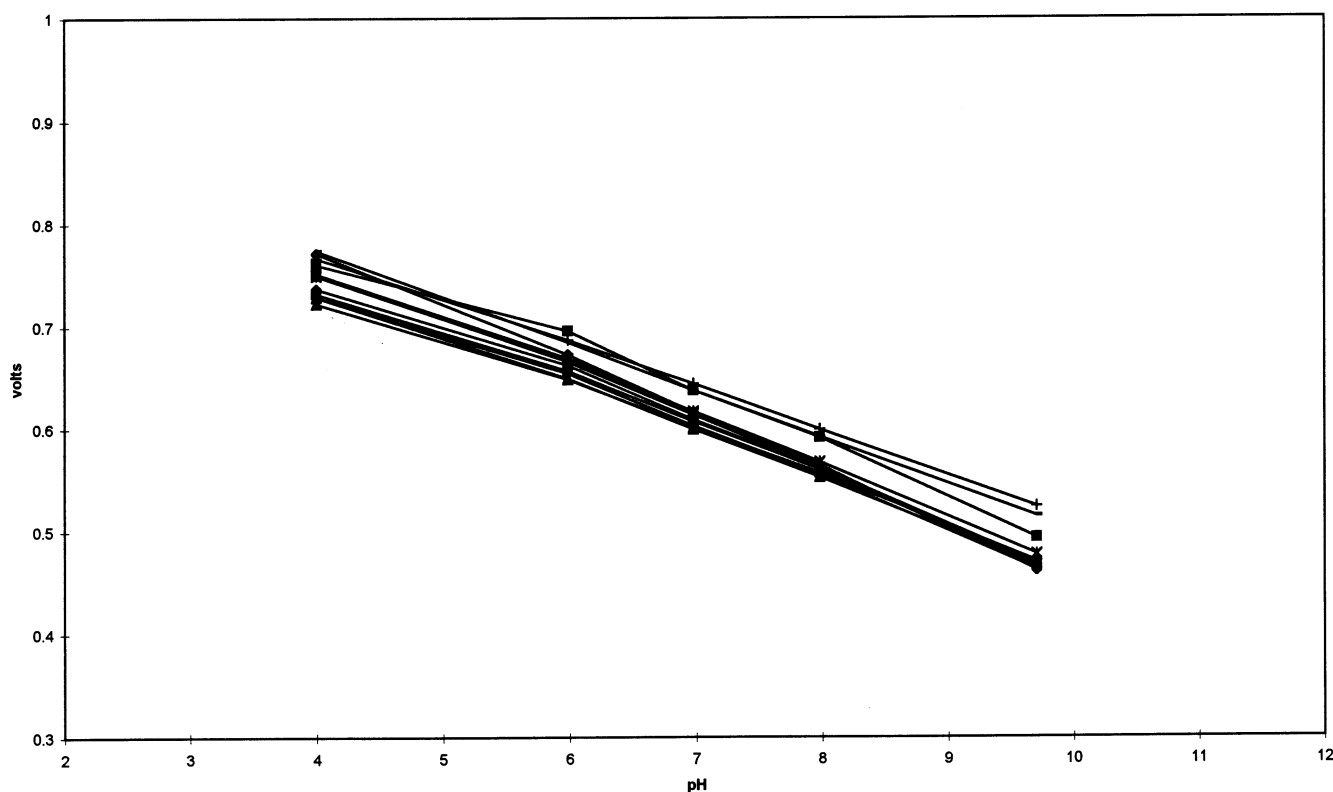

Fig. 17. Repeatability test for pH sensors, potential measured versus integral reference electrode (polymer based reference electrode batch).
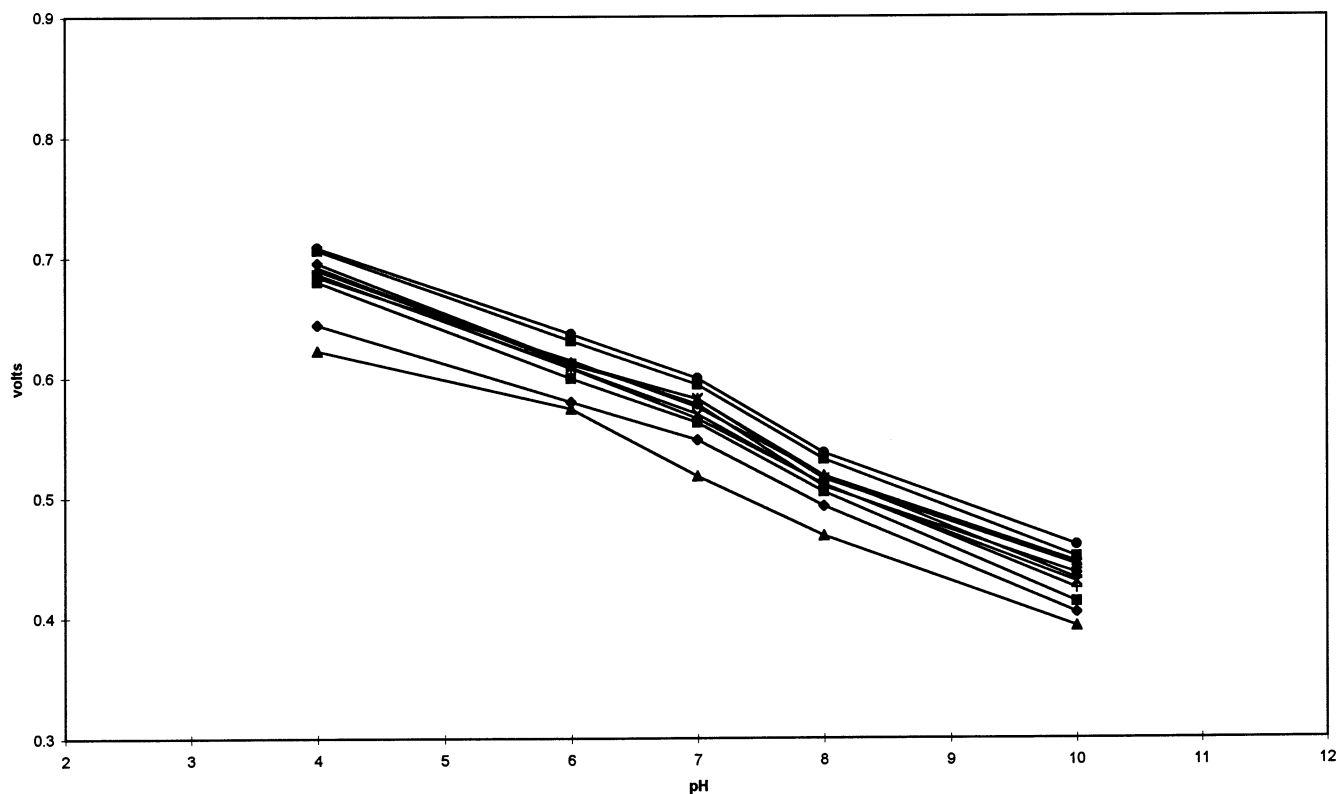
Fig. 18. Repeatability test for pH sensors, electrode potentials measured versus integral reference electrodes (glass based reference electrodes batch).

the sensor's integral reference electrodes. Fig. 6 shows an average slope factor of 50 mV pH^{-1} ($\pm 2.5\%$) for the same sensors using the external commercial saturated calomel reference electrode to make the measurements of pH response. The error bars represent the standard deviation of the slope factors for the six different sensors during each of these tests.

The average values of the actual electrode potentials of the six sensors in the polymer based reference electrode batch for pH 4, 7 and 10 versus their own integral reference electrodes are plotted as a function of time in Fig. 7. Again the error bars show the standard deviation for the complete set of six individual sensors. An extrapolated value for pH 0 is also shown, which has been calculated as the intercept of the linear regression of the average electrode potentials at pH 4, 7 and 10.

An initial drift in this average potential of approximately 5–7 mV day^{-1} is apparent in the devices which flattens out after approximately 50 days. Fig. 8 shows the same data but using the commercial calomel external reference electrode to measure the electrode potentials. Here there is no significant drift of the average electrode potentials throughout the entire 6-month period.

Figs. 9 and 10, respectively, show the average slope factors of the pH sensors from the glass based reference electrode sensor batch to be 53 mV pH^{-1} ($\pm 7.5\%$)

using the sensors' integral reference electrodes and 50 mV pH^{-1} ($\pm 2.5\%$) against the commercial calomel external reference electrode.

Figs. 11 and 12, respectively, show the average values of the actual electrode potentials of the six sensors from the glass based reference electrode batch for pH 4, 7 and 10 (plus an extrapolated pH 0 value) versus their own integral reference electrodes and versus the commercial calomel external reference electrode. There is significantly less drift in the electrode potentials during the 6-month period of testing when compared with the results for the polymer based reference electrodes, although Fig. 11 does show a period of initial instability that is quite marked.

4.2. Dissolved oxygen sensor lifetimes

Figs. 13 and 14, respectively, show the slope factors of the non-permanently powered dissolved oxygen sensors from the two batches (polymer and glass based reference electrodes), plotted in μA ppm^{-1} dissolved oxygen as a function of time in continuous immersion. These devices were only powered-up, that is connected to a potentiostat, for the time it took them to stabilize and their readings to be recorded during each of the periodic tests. For the remainder of the time in between tests they were left to soak in the Permutit filtered (nominally de-ionised) tap water.

The plots shown in Figs. 13 and 14 show the standard deviation of the slope factors of the individual sensors within the batches as error bars. The plot shown in Fig. 14 for the glass based reference electrode sensor batch is slightly misleading however since the devices in this batch had consistently disparate sensitivities which individually did not vary significantly from test to test. Hence the standard deviation of the average slope factor is a better measure of device repeatability over the 6-month testing period. Calculated on this basis the average slope factor for the polymer based reference electrode batch was 1.87 μA ppm^{-1} of dissolved oxygen ($\pm 5\%$) and the corresponding figure for the glass based reference electrode batch was found to be 1.72 μA ppm^{-1} dissolved oxygen ($\pm 7.5\%$).

Figs. 15 and 16, respectively, show the slope factors of the permanently powered sensors from the polymer and glass based reference electrode sensor batches plotted versus time. It can be seen that the slope factors of the devices falls from an initial value of approximately 2.5 μA ppm^{-1} dissolved oxygen to approximately 0.5 μA ppm^{-1} over the first 30 days. Thereafter, the devices continued to function at this much reduced sensitivity until about the 60-day mark.

At this point the experimental procedure was altered in that a small amount of sodium chloride was added to the test media to raise the conductivity to ca 500 μS when making dissolved oxygen measurements. This was done to compensate for the loss of potassium nitrate from the sensors' gel electrolyte via diffusion through the cellulose acetate membrane. It was thought that this salt loss had resulted in the potentiostat being unable to maintain the 0.6-V working electrode potential due to the very low conductivity of the de-ionised water. This addition of salt to the test media resulted in the sensor response subsequently increasing with time as can be seen in Figs. 15 and 16. Some explanations for this rather unusual pattern of response are postulated in the discussions below.

4.3. Device to device repeatability of pH sensors

Figs. 17 and 18, respectively, show the repeatability results for pH sensors from the two batches of sensors (polymer and glass based reference electrodes) versus their integral reference electrodes. The batch of pH sensors with the polymer based silver/silver chloride reference electrodes exhibited an average slope factor of 47.41 mV pH^{-1} ($\pm 6.3\%$) whilst the yellow batch incorporating the glass based silver chloride reference electrodes gave an average slope factor of 43.59 mV pH^{-1} ($\pm 3.8\%$).

Against an external commercial calomel reference electrode, the same devices exhibited slope factors of 48.29 mV pH^{-1} ($\pm 6.2\%$) for the polymer based reference electrode batch and 46.84 mV pH^{-1} ($\pm 1.5\%$) for the glass based reference electrode batch.
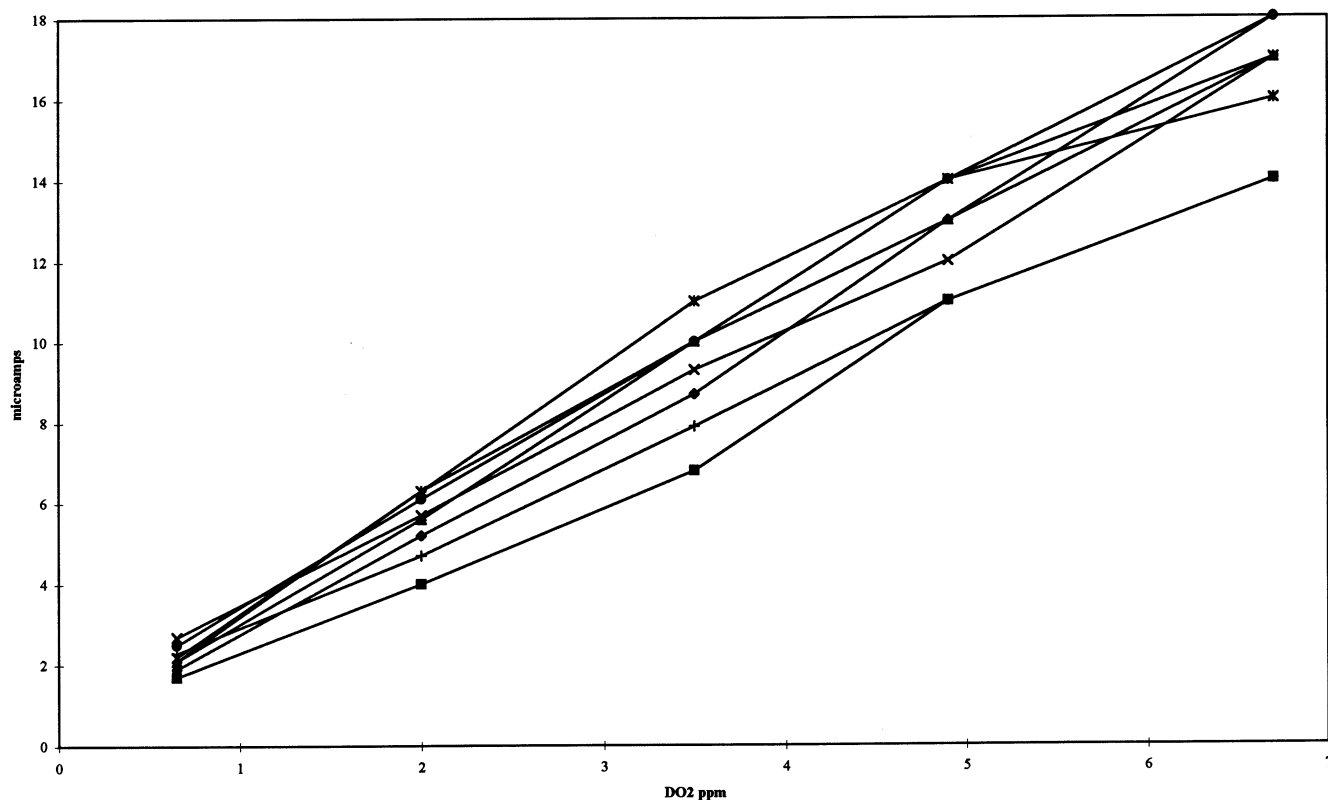

Fig. 19. Dissolved oxygen sensor repeatability test using integral reference electrode (polymer reference electrode batch).
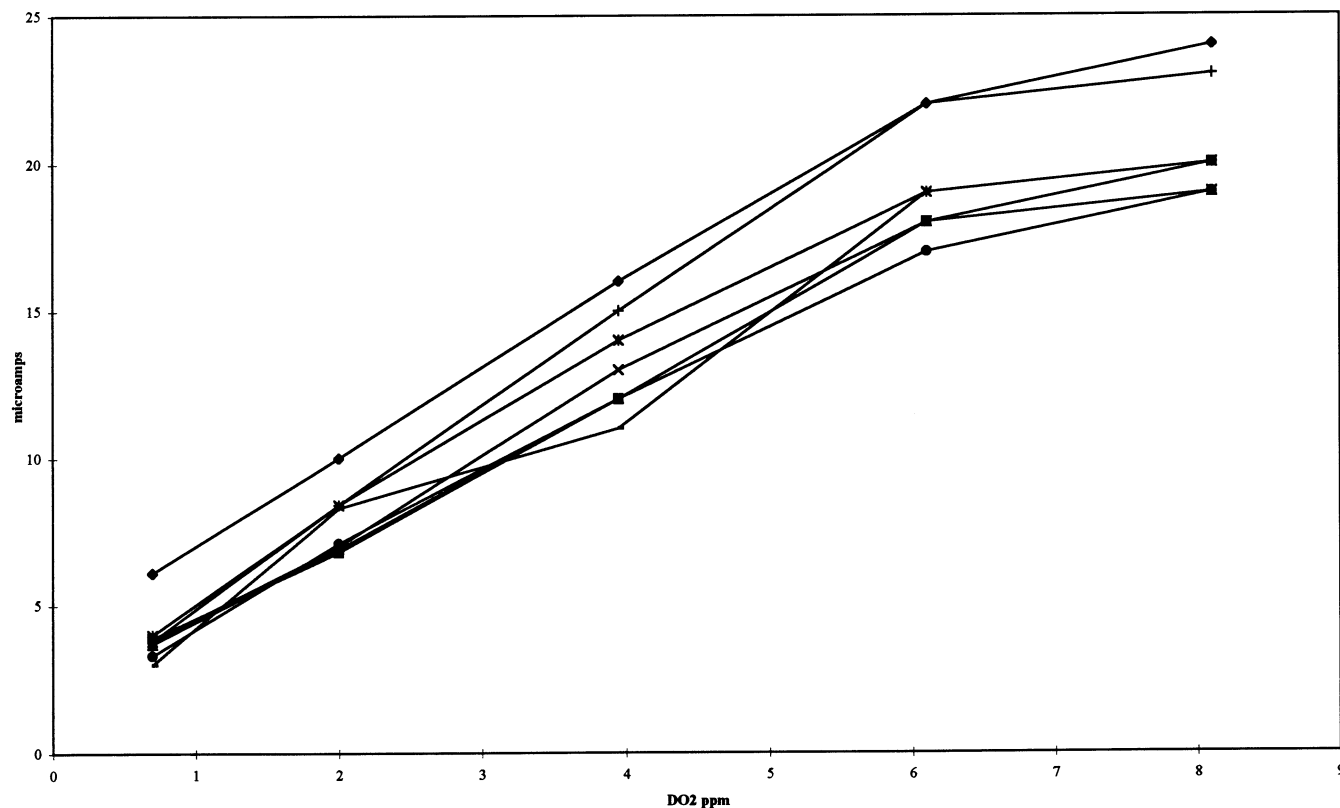
Fig. 20. Dissolved oxygen sensor repeatability test using integral reference electrodes (glass based reference electrodes batch).

## 4.4. Device to device repeatability of dissolved oxygen sensors

Figs. 19 and 20 show the dissolved oxygen sensor responses for the two batches, using their integral reference electrodes to make the measurements. As expected, there was little difference between the two batches as the choice of reference electrode type appeared to have negligible effect on the operation of the potentiostat. The polymer based reference electrodes batch showed a slope factor of 2.37 μA ppm^{-1} dissolved oxygen ($\pm 10\%$) compared with the glass based reference electrodes batch figure of 2.33 μA ppm^{-1} dissolved oxygen ($\pm 8.5\%$).

5. Discussion

5.1. pH sensors

The slope factors of both batches of pH sensors appear to show good repeatability versus time in continuous immersion. This is in keeping with the theory of operation of the sensors with the potential of the pH sensitive electrode varying in a near Nernstian manner giving a change in electrode potential of approximately 50 mV pH^{-1}.

It is generally agreed that for a ruthinium oxide electrode in equilibrium the following redox reaction occurs [11,12]:

$$RuO_x(OH)_y + \delta H^+ + \delta e^- \Leftrightarrow RuO_{x-\delta}(OH)_{y+\delta}. \qquad (1)$$
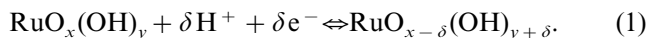
According to the Nernst equation this reaction gives rise to an electrode potential of:

$$E = E_0 + RT/F \ln a[H^+] \text{ volts}, \qquad (2)$$

where $a[H^+]$ represents the level of proton activity in the solution.

Substituting the numerical values for the constants in Eq. (2) gives a theoretical pH response at 25°C of:

$$E = E_0 + 0.059 \text{ pH volts.} \qquad (3)$$

Allowing for the fact that all the measurements of pH response were actually carried out at 20°C reduces the anticipated slope factor to approximately 58 mV

Table 1
Magnitudes of reference electrode impedance as measured using an impedance bridge circuit operating at 100 Hz

Reference electrode type	Impedance (Ω)
ABB Kent Taylor 1431-210	2000
Polymer silver/silver chloride	150 000
Glassy silver chloride	3 000 000

pH^{-1}. The actual slope factors obtained were significantly less than this theoretical value however.

It is, consequently, believed that the mechanism by which the ruthinium oxide electrodes respond to pH changes involves a combination of reactions. For example a double proton, double electron process such as:

$$2RuO_2\,2H_2O + 2H^+ + 2e^- \Leftrightarrow Ru_2O_3\,3H_2O + 2H_2O \tag{4}$$
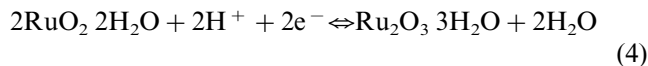
giving a sensitivity of 59 mV pH^{-1}, could be combined with a double electron, single proton reaction such as:

$$Ru_4O_6(OH)_3(OH_2)^+ + H^+ + 2e^- \Leftrightarrow Ru_4O_4(OH)_6 \tag{5}$$
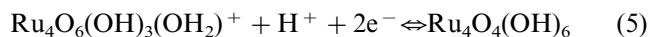
having a response factor of approximately half this value, i.e. 29.5 mV pH^{-1}. In Eq. (5) it has been assumed that surface acid groups have previously been formed due to adsorption of protons and evidence to support this theory has been obtained from a parallel programme of research [10].

Hypothesising that both these reactions are occurring simultaneously, the resulting slope factor would be due to a combination of the two and hence somewhat less than the 59 mV pH^{-1} predicted by Eq. (3). The exact value of the slope factor obtained will consequently be determined by the relative ratios of the different ruthinium oxides present at the surface.

The effect on the slope factor when changing between using the devices' own integral reference electrodes and an external calomel electrode appears relatively minimal. The use of the integral reference electrodes resulted in a slight increase in the variation of device to device response for both batches which was accompanied by noticeably 'noisier' electrode potentials. This increase in noise is perhaps only to be expected when the electrical impedances of the respective electrodes are compared. Measured values of the magnitude of impedance at 100 Hz for the various reference electrodes used are shown in Table 1.

The changes in the absolute electrode potentials versus time are attributed to changes in the operating potential of the integral reference electrodes which are discussed in the next section.

5.2. Reference electrodes

The behaviours of the two types of reference electrode employed in the evaluation were noticeably different. The polymer silver/silver chloride electrodes appeared to exhibit a rapid initial attainment of stability but then exhibited a steady drift in potential over the next 50 days of continuous immersion, as evidenced in Fig. 7. The glass silver chloride electrodes by comparison took several days to attain their initial stability but then maintained a rather more stable potential over the next 50-day period, as seen in Fig. 11.

These results are consistent with a loss of salt from the electrode resulting in a change in electrode potential, as defined by the Nernst equation. A faster rate of salt loss appears to result from the polymer bound silver/silver chloride electrode material used in the green batch than from the glass bound electrode material of the yellow batch.

Further studies of the reference electrode behaviours are being undertaken in order to better understand their mechanism of response and eventual failure mode. For the purposes of the pH sensor measurements made in this study however both sets of reference electrodes continued to function throughout the duration of the test period. The useful lifetimes of the electrodes for the measurement of pH is determined by the media in which the measurements are to be made since the reference electrodes tend to lose their insensitivity to chloride ions with continuous immersion and salt loss. Hence operation in the presence of variable chloride concentrations would cause errors that would increase with time.

5.3. Dissolved oxygen sensors

Inspection of the dissolved oxygen sensor responses versus time reveals some interesting phenomena. The intermittently powered devices continued to give good repeatability in their response over the full 6-month testing period. The permanently powered devices however showed quite a dramatic fall in their sensitivity with time. These characteristics are independent of the type of reference electrode employed, as was expected, and would, therefore, appear to indicate changes at the working electrodes as being the likely contributing factors.

Oxygen reduction at the working electrode is known to be capable of following more than one route [13] with both a direct four electron, single stage process and a two stage process being possible. The two stage process commences as shown in Eq. (6) below:

$$O_2 + 2H_2O + 2e^- = H_2O_2 + 2OH^-. \tag{6}$$
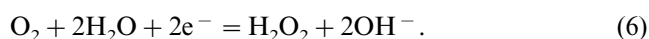
A subsequent reduction of hydrogen peroxide to hydroxil ions then follows to complete the process.

$$H_2O_2 + 2e^- = 2OH^-. \tag{7}$$

This second stage process can however be inhibited by any build-up of hydroxil ions in the locality of the working electrode. This situation was in fact found to occur during a parallel programme of research activity [14] and also in the results of other investigators [15,16]. Hence, unless the OH^- build-up is prevented, the electrode reduction current will fall with time.

The design of the dissolved oxygen sensors employed here is such that the working electrode is covered by a salt gel and a cellulose acetate membrane. Hence, hy-

droxil ions will accumulate under the membrane unless there is a sufficient diffusion gradient for them to disperse. During the first 2 months of the testing programme the sensors were stored in filtered tap water of approximately 500 μS cm^{-1} conductivity. When the sensors were subsequently stored in de-ionised water from this point onwards, a significant increase in their sensitivity occurred. This is thought to be due to the fact that the low ionic strength storage medium allowed the outward diffusion of hydroxil ions between tests such that the normally inhibiting build-up of the ions was prevented.

Further testing of the sensors beyond this point showed a steady increase in device sensitivity which was considered to be due to the accumulation of cation deposits on the working electrode increasing the catalytic activity of the electrode. Subsequent elemental analysis of the surface of the working electrodes using an electron microscope showed the presence of silver. The source of this silver deposit is not entirely clear but the presence of silver in some of the thick film conductor pastes used in the device fabrication is a distinct probability.

Thus the continuous powering of the dissolved sensors is fraught with difficulty since whilst the build-up of hydroxil ions inhibits the response, the deposition of cations can significantly enhance the response to the point of instability. Intermittently powered devices are clearly acceptable in terms of their long term response characteristics but the maximum duty cycle would need to be determined in order to allow the problems associated with permanent powering to be avoided.

Clearly the potential for commercial exploitation of thick film technology in the fabrication of these types of sensors is great. It is likely however that before this can be realized further work will be required concerning device development. In particular a means to give greater stability of the reference electrode potentials on continuous immersion must be explored if frequent calibration is to be avoided. Similarly the change in sensitivity of the dissolved oxygen sensors when continuously powered may preclude their use in several applications, unless of course they also are regularly calibrated. Also the effect on the pH electrodes of long term exposure to extremes of pH must be quantified in order to define their operational range.

Acknowledgements

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Biographies

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