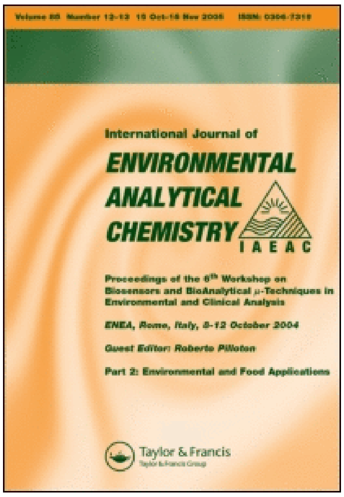

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APPLICATION OF A CYLIC POLYAMINE IONOPHORE IN PHOSPHATE SELECTIVE ELECTRODES FOR ENVIRONMENTAL ANALYSIS

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The application of macro- and micro-electrodes constructed using the new ionophore were tested in a range of solution compositions reflecting concentrations found in fresh waters, and containing Cl^-, NO_3^-, SO_4^{2-}, HCO_3^{2-}, H_4SiO_4 and a natural humic acid. The inhibition of the electrode responses to these ions was quantified using a mixed-solution method by optimising the agreement between the measured potentials and predictions from the Nicolsky-Eisenman equation. In addition, measurements were made in separate solutions of KCl to enable results to be compared with the literature. Apart from the results obtained for humic acid, mean selectivity coefficients for 16 macro- and 21 micro-electrode experiments are given. The results indicate inhibition of the electrode response to phosphate for all the anions in the concentration ranges of 0.05–1 mM Cl^-, 0.1–1.0 mM NO_3^-, 0.1–10.0 mM HCO_3^- and 0.1–1.5 mM SO_4^{2-} with high selectivity for HPO_4^{2-} in the presence of both dissolved silicon and a standard humic acid. This means that the application of the electrodes to hard waters is impracticable although studies of soft waters and laboratory studies in controlled conditions, e.g. calcium phosphate precipitation experiments, are feasible.

Keywords: Phosphate; sensor; microelectrode; selectivity coefficients

INTRODUCTION

The importance of phosphorus as a limiting nutrient in some aquatic systems has stimulated research into examining the pathways of phosphorus in the environment[1]. This has included research on transfers of dissolved phosphorus from land to water bodies, and the subsequent processes that govern its partition

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between the biota and sediments during its transport to estuaries and near coastal waters[2]. In such studies there is often a need to measure dissolved phosphorus *in-situ* and so avoid many of the problems associated with sample degradation[3]. In addition, work on natural sediments and associated algal biofilms has highlighted the importance of phosphate concentration changes in a surface "micro-layer" in controlling exchange with the overlying water[4,5]. In this situation, the direct probing of the concentration changes in the surface sediment and algal biofilms using microelectrodes[6] will enable a better understanding of the underlying mechanisms that control inorganic phosphorus fluxes.

There have been several recent endeavours to produce phosphate sensors[7–14]. Carey and Riggan[7] developed an ionophore, 3-decyl-1,5,8-triazacylodecane-2,4-dione (N_3-cyclic amine) that exhibited a linear electrode response between 1 and 0.1 μM dihydrogen phosphate activity with a near-Nernstian slope. Several interfering substances were tested *viz*: chloride, nitrate, sulphate, lactate, thiocyanate, acetate, BIS-TRIS propane and HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulphonic acid) and the selectivity pattern was found to be:

$$HPO_4^{2-} \gg SCN^- \approx Cl^- > NO_3^- > SO_4^{2-} \approx \text{lactate} \gg \text{acetate ion}$$

Other solutes that are important in applications in natural waters were not tested including dissolved silicon, natural humic acids and HCO_3^-. The latter is usually the dominant anion in hard waters and their associated sediment porewaters. The aim of the present work was to repeat the preparation of the N_3-cyclic amine and test its performance in both macro and micro-electrodes, by determining the effects of potential interfering substances (Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, H_4SiO_4 and humic acid), over concentration ranges that occur in fresh waters.

EXPERIMENTAL

Preparation of the N_3-cyclic ionophore

All chemicals were obtained from Aldrich (Gillingham, Dorset, UK). The method used followed closely that given Carey and Riggan[7]. The most notable change was that the final product was allowed to recrystallize overnight before the addition of acetonitrile for the last stage of purification.

Precursor preparation

373 ml of sodium ethoxide was slowly added to 127 ml of absolute ethanol, which was stirred by a magnetic follower, in a vessel held in a water bath at 45 °C. Diethyl malonate, 176.19 g, was slowly dripped into this solution over a

period of 25 min (still at 45 °C). The solution remained brown while this was added. 1-Bromodecane, 221.19 g, was slowly dripped into this mixture over a period of 30 min, and the solution became an opaque yellow colour. The mixture was then refluxed for 2 hours during which time the colour remained opaque pale yellow. The mixture was rotary evaporated to remove ethanol with the water bath at a temperature of 45 °C. The cooled mixture separated into a golden oily liquid and cream/whitish powder.

The mixture was placed in a separation funnel with 550 ml of distilled water, shaken gently until mixed, and allowed to separate for 30 min. The mixture separated into 2 layers, a golden brown oily layer and golden brown aqueous layer. The top layer was retained and 550 ml of distilled water was added, and the mixture was again shaken gently. After 30 min the mixture had separated into a golden oily layer, and an aqueous layer which was very pale, almost colourless. The procedure was repeated twice more (4 separations in total) with the final mixture left to separate overnight. The final oily layer obtained was a bright golden colour and opaque.

Synthesis of the ionophore

23.7 g of the precursor was added to absolute ethanol, and this dissolved completely to produce a clear and almost colourless liquid. 7.74g of diethylenetriamine was then added slowly. The resultant solution was a very pale straw colour. This was refluxed for 4 days, then allowed to re-crystallise overnight in a frigerator at 4° C. A reflux time of 4 days was sufficient to produce a yield > 80 % (Carey[7], pers. comm.). The product was re-crystallised six times in boiling acetonitrile to remove impurities. A white powdery product was obtained.

Construction of phosphate macroelectrodes

Disposable plastic pipette tips (5 ml Gilson) were used to form the macroelectrode bodies, and dipping the narrow end of the tubing into the ionophore mixture formed an ion-selective membrane. The membrane was a mixture of 80 mg ionophore, 130 mg of PVC, 140 mg of dibutyl phthalate (Carey[7], pers. comm.), and 3 ml tetrahydrofuran (Fluka, Gillingham, Dorset, UK). The electrodes were allowed to dry in a vertical position, before being stored in a desiccator for a minimum of 24 hours, the electrodes were then back-filled with 0.2 M KH_2PO_4 / 0.164 M KOH (AR Grade) at pH=7.2, and their tips left submerged in a beaker containing the same solution. They were allowed to soak for a minimum of 24 hours, but best results were usually obtained after several days of soaking. The electrode was completed by the insertion of a micro-reference electrode

(Microelectrodes Inc., Londonderry, USA model MI 401F) into the backfill solution. This was connected to a Mettler pH meter (Delta 340), set to mV mode and used as an ion-meter, in conjunction with a Ag/AgCl reference electrode (Radiometer, Copenhagen, model 201)

Construction of microelectrodes

The electrodes were constructed of 2 mm diameter glass capillaries, each pulled to a fine point, and silanised to render them hydrophobic[15]. The tip of each electrode was broken back to approximately 100 μm before being front-filled with ionophore mixture. The proportions of PVC, tetrahydrofuran, dibutyl phthalate and phosphate ionophore were the same as for the macroelectrodes. After 24 hours the microelectrodes were back-filled with 0.2 M KH_2PO_4 / 0.164 M KOH (AR Grade). They were connected to a Biologic IS100/C Ion selective dual electrometer and VF102 Dual Probe Amplifier, by means of SM200 microelectrode holders in HS111 headstages. Reference electrodes were constructed using 5% KCl in agar (Agar Technical, No. 3, Unipath Ltd) in vinyl tubing, 1.5 mm diameter, into which a chlorinated silver wire (0.25 mm silver wire, 99.99% pure, Goodfellows) was inserted. The microelectrode measurements were obtained in a Faraday Cage to reduce electrical interference, and the output from the electrometer monitored by a chart recorder.

Dihydrogen phosphate and chloride standards

All solutions were prepared using single distilled water of conductivity < 1.5 μS cm^{-1} at 20 °C. All chemicals were AR Grade. A stock solution of 0.05 M KH_2PO_4 and 0.041 M KOH was prepared and a series of 9 standards of concentration: 12.5 and 2.5 mM, 500, 250, 125, 50, 25, 5 and 2.5 μM respectively were prepared by dilution. The standards were in a background solution of 5.2×10^{-5} KOH, to keep the pH close to 8.0. The pH was measured after each determination.

A series of 8 potassium chloride standards was also made to test the response of the electrodes to chloride ions in isolation and to compare with results reported by Carey and Riggin[7]. The concentrations were respectively 12.5 and 2.5 mM, 500, 250, 50, 25, 5 and 2.5 μM KCl.

Mixed solutions containing phosphate and interfering ions

When making solutions to test the effect of interfering ions, the same KH_2PO_4 stock and KOH background solutions were used. For each concentration of interfering ion, a series of five phosphate standards was prepared with the concentrations: 12.5 and 2.5 mM, 250, 25 and 2.5 μM. The concentrations of interfering ions were chosen to reflect their occurrence in UK fresh waters[16] and were:

KCl: 0.05, 1 and 4 mM

KNO_3: 0.1, 0.5 and 1 mM

K_2SO_4: 0.1, 0.5 and 1.5 mM

$KHCO_3$ 0.1, 5 and 10 mM.

Two further interfering ions were tested using the same phosphate stock solution, but without the KOH background electrolyte. These consisted of 0.1, 1 and 10 mg l^{-1} humic acid (Swannee River HAS standard), and 10, 200 and 350 μM dissolved silicon. A stock silicon solution was prepared by the dissolution of fine quartz (C800, British Industrial Sand Ltd.) in distilled water at room temperature and the concentration of silicic acid measured by the colourimetric method given by Mullin and Riley[17].

Single solutions containing phosphate and chloride ions

Additional tests with single solutions of potassium hydrogen phosphate and potassium chloride were completed to enable comparison with results that have been published elsewhere for this ionophore[7]. Three different macroelectrodes were used and one microelectrode. The solutions consisted of:

a) nine solutions of potassium hydrogen phosphate with concentrations of 2.5, 5.0, 25.0, 50.0, 125, 250, 500, 2500 and 12500 μM respectively corresponding to a range of $pHPO_4^{2-}$ of 2.36 to 5.95, and

b) eight solutions of potassium chloride with concentrations of 2.5, 5.0, 25.0, 50.0, 250, 500, 2500 and 12500 μM respectively corresponding to a range of $pCl^-=1.95$ to 5.60.

Testing procedure

All macro- and micro-electrodes were tested initially to check the electrode response down to 25 μM KH_2PO_4 and to assess the electrode drift rate. Selected electrodes were then used in the main experiments described as follows. The tips of the macroelectrodes were submerged in 50 ml of test solution at room temperature and the solution agitated using a magnetic stirrer and follower for 30 seconds. The stirrer was turned off and the electrode signal recorded after a period of 2 minutes. Similarly, the microelectrodes were held by a micromanipulator and the electrode tips were lowered into the solution to cover the tip. The signal was allowed to stabilise for 2.5 – 3 min before recording. The solutions used to test microelectrodes were not stirred. In both instances the pH and temperature of the solution were measured immediately after each determination using a Jenway pH meter (Model 3320) and these values used to determine the chemical speciation in each solution as described below.

THEORY

The calculation of selectivity coefficients is a difficult issue and has been the topic of much discussion in the past [18,19]. The Nicolsky-Eisenman equation remains a popular choice because it is relatively simple to apply and has been used widely in the past. In this work the response of each electrode was tested using the Nicolsky- Eisenman equation with other approximations applied to the results from the single solution experiments.

The Nicolsky- Eisenman equation is defined by[18]:

$$E(E^0, K_{i,j}) = E^0 - 2.303RT1000 \times \log(a_{HPO4} + K_{i,j}a_{inh}{}^{r})/2F \qquad (1)$$

where E^0 is the standard potential for the cell (mV), T is the temperature (Kelvin), $K_{i,j}$ the selectivity coefficient, a_{HPO4} and a_{inh} the activities of hydrogen phosphate (i, primary ion) and inhibitor ions (j), E is the electrode potential in mV, r is the ratio of the ion charges (primary ion charge/inhibitor ion charge), and R and F are the Gas and Faraday constants respectively. This equation corrects for difference in charges of the ions without taking into account that the response slope of the interfering ion is not necessarily the same as the primary ion. However despite this limitation, the equation is widely used to compare electrode performance. The selectivity coefficient for each electrode- inhibitor-ion combination was calculated by a method of least-squares similar to that adopted by Wilson *et al.*[19] but using an algorithm written in Mathcad[20] to optimise E^0 and $K_{i,j}$ to obtain a minimum value of:

$$\Delta = \sum_{n} \left\{ \left[E_{\exp(n)} - E(E^0, K_{I,J}) \right] / E_{\exp(n)} \right\}^2 \qquad (2)$$

where $E_{\exp(n)}$ is n th experimental electrode potential and E is the predicted value from equation (1). The activities of hydrogen phosphate and inhibitor ions were calculated using a similar method to Hartley *et al.*,[21] with the activities given by the Davies equation[22]:

$$\log \gamma_i = -A_{DH} \times z_i{}^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.30 \times I \right) \qquad (3)$$

where γ_i and z_i are the activity and charge of the i th ion, A_{DH} is the Debye-Huckel constant and I is the ionic strength of the solution calculated from a solution speciation program[15]. The temperature dependence of the dissociation constants for phosphoric acid were taken from Bates[23], Bates and Acree[24] and Bjerrum and Unmack[25] and yielded $pK_1=2.127$, $pK_2=7.215$ and $pK_3=12.42$ for the first, second and third dissociation constants at 20 °C ($pK=-\log(K)$).

Various other methods are available to calculate selectivity coefficients[18,26] including the matched potential method, separate solution method and algebraic method of Srinivasan and Rechnitz[27]. The separate solution method was used by Carey and Riggan[7] in the form:

$$\log K_{i,j} = (E_j - E_i)/S_i \qquad (4)$$

where E_i is the electrode potential in response to a fixed activity hydrogen phosphate, E_j is potential for the same activity of the inhibiting-ion alone, and s_i is the slope of the calibration line for the electrode response to hydrogen phosphate in the absence of inhibiting ions. Equation (4) applies to electrolytes with $z_i=z_j$ (where z is the charge of the ion) and may be written in more general form as derived form the Nernst equation[18, 26]:

$$\log K_{i,j} = (E_j - E_i)/S_i + (1 - z_i/z_j)\log a_i \qquad (5)$$

Although equations (4) and (5) are frequently used[26], they are not appropriate descriptors of selectivity for ions of different charge and electrode slope[28], and are included here strictly for comparison purposes.

RESULTS AND DISCUSSION

Electrode response to phosphate

Examples of the response of macroelectrodes to Cl^-, NO_3^-, HCO_3^- and K_2SO_4 are shown in Figures 1 and 2. The limit of detection of the electrodes used in the single-solution experiments was calculated from the intersection of the lines extrapolated for the Nernstian response and none response ranges[26]. These electrodes gave a limit of detection of 20.6, 12.0 and 22.4 µM for the macroelectrode and 11.1 µM for the microelectrode. Electrode response times of both the macro- and micro-electrodes were less than 2 minutes when calculated as the time to reach 90 % of the final electrode potential after changing the hydrogen phosphate activity by a factor of 10. In fact microelectrodes reached 90% of their final electrode potential within an average of 50.33 (±27.35) seconds. The mean

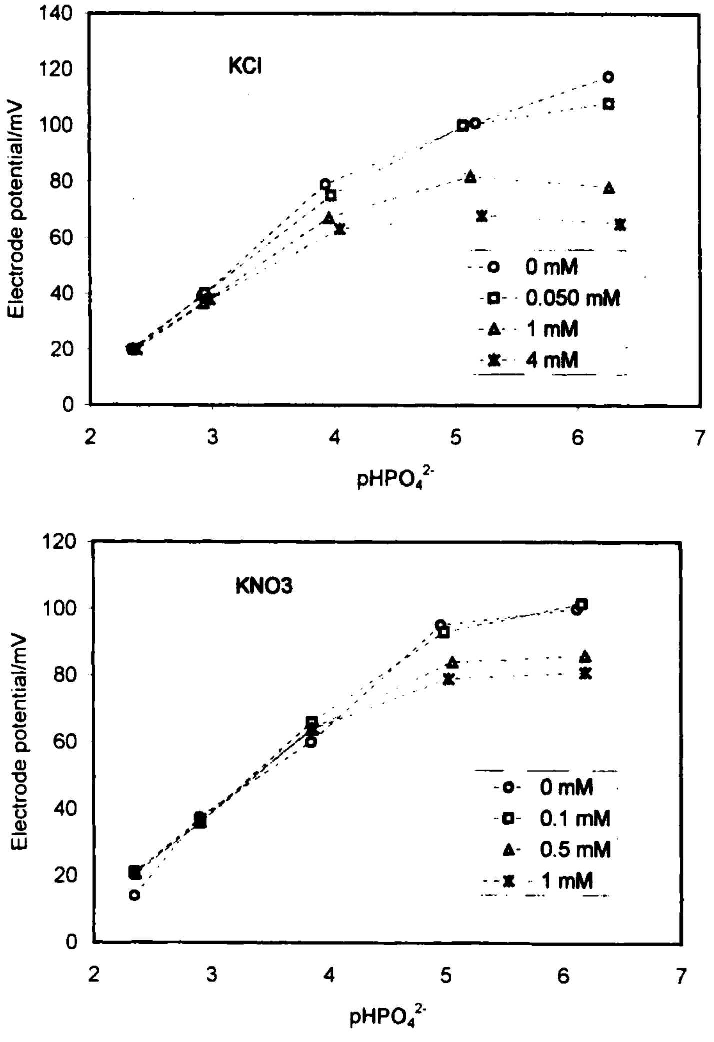

FIGURE 1 Comparison of the electrode response of two of the macroelectrodes in solutions of KCl and KNO_3 of concentrations shown, and over a range of concentrations of KH_2PO_4 from 2.5 μM to 12.5 mM at *ca* 20 °C. Key: $pHPO_4^{2-} = -\log(a_{HPO4})$

drift rate for 18 micro-electrodes calculated from calibration data in single phosphate solutions at the beginning and end of the experiments (a period of approximately 1 hour) was 0.053 (±0.033 SD) mV min^{-1}. The drift rate for the macro-electrodes was less: 0.011 (±0.009 SD) mV min^{-1}, calculated from calibration data in single phosphate solutions at the beginning and end of 11 macro-electrode experiments (a period of approximately 2 hours).

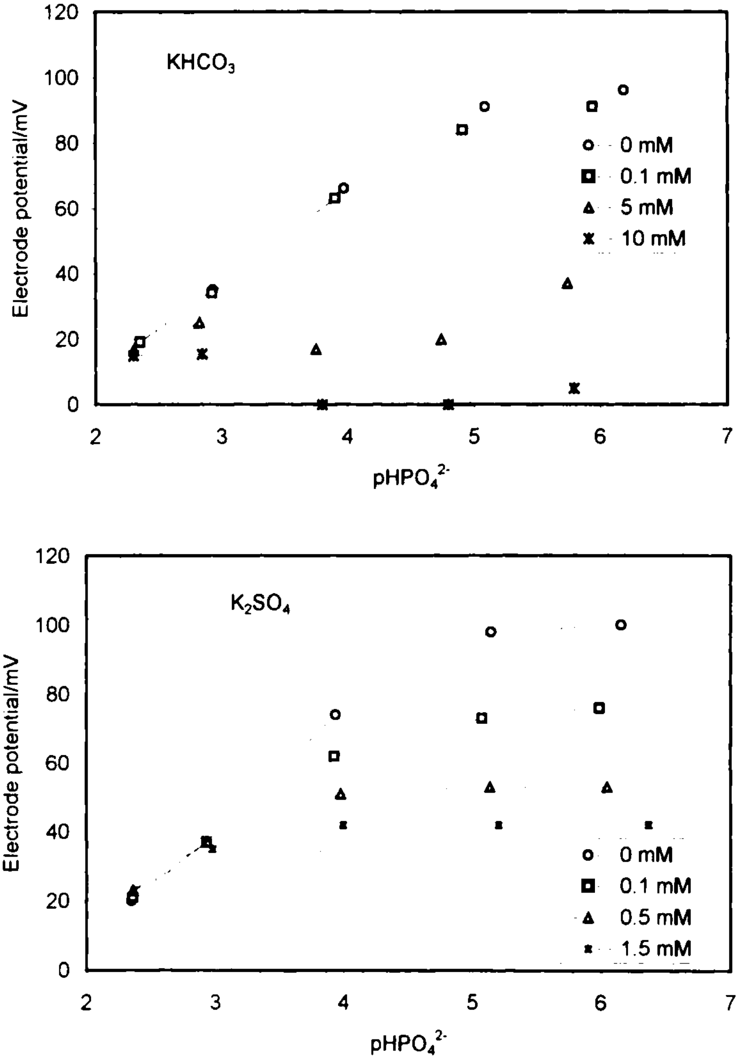

FIGURE 2 Comparison of the electrode response of two of the macroelectrodes in solutions of $KHCO_3$ and K_2SO_4 of concentrations shown, and over a range of concentrations of KH_2PO_4 from 2.5 μM to 12.5 mM at *ca*20 °C. Key: $pHPO_4^{2-}$=-log(a_{HPO4}).

When the macroelectrodes were tested initially using the phosphate standards down to a concentration of 25 μM KH_2PO_4, they gave a mean gradient of 29.7 ± 1.9 with an average r^2 value of 0.992 ± (.009) for 12 macroelectrodes. The microelectrodes gave an average gradient of 34.5 ± (4.8) and a r^2 value of 0.986

± (0.010) for 18 microelectrodes (figures in brackets are the standard deviations, SD). The reason for the deviation from a Nerstian response is unknown. The macroelectrode gradient is close to the ideal Nernstian slope of approximately 29.1 mV for divalent ions at 20 °C.

Determination of the selectivity coefficient for chloride by the single-solution method

The results were analysed by four methods: Method 1, a modified single-solution method used previously with the potentials determined at $pHPO_4^{2-}$=4.5 (see reference 7 and equation 4); method 2, the single-solution method taking account of the differences in the charge of Cl^- and HPO_4^{2-}(equation 5) with the potentials also determined at $pHPO_4^{2-}$=4.5; method 3, the single-solution method with the activity determined at the mid-point of the linear region found in this work ($pHPO_4^{2-}$=3.6), and method 4, the least-squares optimisation method with 17 points from measurements in the separate solutions of KH_2PO_4 and KCl. The results of the calculations for the four methods are given in Table I. Method 1 is that used by Cary and Riggan[7] with the electrode potentials determined using interpolation by cubic polynomials at their fixed activity of 30 µM of HPO_4^{2-} ($pHPO_4^{2-}$≈4.5). The mean value of log $K_{HPO4,Cl}$=-2.17 compares with a value calculated by Cary and Riggan[7] of -2.35 and demonstrates reasonable agreement in the performance of the electrode towards Cl^- in the two studies. The selectivity coefficients derived from the other methods are much higher in comparison to method 1. The results from methods 2 and 3 demonstrate the effects of the additional ion-charge and activity term in equation (5). The results show that it makes a small difference if the fixed activity for $Cl^-$and HPO_4^{2-} used in the method is $10^{-4.5}$ or $10^{-3.6}$ i.e see the comparison of the results from methods 2 and 3 shown in Table I. The results obtained by the least-squares method in the Mathcad computer program (method 4) are closest to method 3 but with a lower standard deviation about the mean.

Determination of the selectivity coefficient for chloride, nitrate, hydrogen carbonate and sulphate in mixed-solutions

Mixed-solution methods are always preferred to single-solution (or separate-solution) methods as they entail measuring the effects of inhibitors in the presence of the primary ion[26,27] in conditions similar to those in which the electrode will be used. In this work the range of concentrations of the inhibitors was chosen to reflect the occurrence of the solutes in fresh waters[16].

TABLE I Comparison of selectivity coefficients, expressed as $\log(K_{HPO4,Cl})$ values, calculated from the results of the single-solution method using KH_2PO_4 and KCl solutions

Electrode number	*Type*	*Temperature / °C*	*Method 1*	*Method 2*	*Method 3*	*Method 4*
1	Macro	22.5	−1.59	2.92	2.33	1.67
2	Macro	20.5	−2.92	1.59	1.49	1.27
2	Macro	20.5	−2.01	2.49	2.10	1.60
3	Macro	21.0	−2.96	1.54	1.45	1.34
3	Macro	21.0	−1.85	2.64	2.23	1.70
1	Micro	24.2	−1.55	2.96	2.31	1.72
Mean			−2.17	2.36	1.98	1.55
Standard Deviation			0.64	0.64	0.41	0.19

TABLE II Comparison of the selectivity coefficients expressed as $\log K_{HPO4,j}$ were j is the inhibitor ion, computed by the least-squares method from the Nicolsky and Eisnman equation in the program Mathcad[20]. The asterisk denotes that only data for 0 and 0.1 mM concentrations were used in the optimisation. The mean and standard deviations for the macro- and micro-electrodes are shown

Anion	*Cl^-*		*NO_3^-*		*SO_4^{2-}*		*HCO_3^-*	
	Macro	Micro	Macro	Micro	Macro	Micro	Macro	Micro
	1.281	0.858	1.698	1.510	−0.099	−0.080	1.808	2.176
	0.942	1.219	1.760	1.581	−0.127	−0.068	1.823	2.173
	1.045	1.089	1.678	2.353	0.148	−0.590	1.720*	3.114*
	1.094	0.861	1.843	2.242	−0.124	0.012	2.920*	1.720*
	–	1.112	–	2.019	–	−0.405	–	2.778*
				1.359				
Mean Temperature/°C	20.5	22.0	20.8	22.2	21.8	22.1	20.4	22.3
Standard deviation	0.9	1.7	0.9	1.6	1.1	1.9	1.3	1.9
Mean	1.090	1.028	1.745	1.844	−0.050	−0.226	2.068	2.392
Standard deviation	0.142	0.161	0.074	0.416	0.133	0.258	0.570	0.551

Typical responses obtained with the mixed-solution method with macro- and micro-electrodes are shown in Figures 1 and 2. The lowest concentrations of KCl (0.05 mM), KNO_3 (0.1 mM) and $KHCO_3$(0.1mM) had little effect on the electrode response. In contrast, the results for K_2SO_4 indicate a substantial effect even at the lowest concentration (0.1 mM). The inhibition by Cl^-, NO_3^- and

SO_4^{2-} ions was progressive with a diminishing response to HPO_4^{2-} as the inhibitor concentration increased. The results obtained for the interference by hydrogen carbonate show a different trend typified in Figure 2. No response to hydrogen phosphate was detected in the presence of 5 or 10 mM $KHCO_3$.

The results from the least-squares analysis of the data from the macro- and micro-electrode measurements for four ions are shown in Table II. An example of the agreement between the experimental data and the predicted value from equation (1) for the optimum E_0 and $K_{HPO4,SO4}$ is shown in Figure 4. The mean result for the selectivity coefficient for $Cl^-$is lower than the value found using the single-solution method, i.e $pK_{HPO4,Cl}=1.55$ in Table I in comparison with 1.09 for the macroelectrodes using the mixed-solution method. Only the lowest concentration of HCO_3^- was used in the majority of the determinations of the selectivity coefficient. There was no significant difference in the log $K_{HPO4,j}$ values for the four anions (independent t-test, 95 % confidence limits) for the macro- and micro-electrodes.

In the concentration range of ions studied, the membrane is sensitive to Cl^-, NO_3^-, SO_4^{2-} and HCO_3^- to an extent that is likely to interfere with HPO_4^{2-} determination in many hard waters. This result is in contrast to that obtained by Carey and Riggan[7], reflecting the differences in the range of inhibitor concentrations that have been studied and the method of calculation of the selectivity coefficients. This is demonstrated for single-solution measurements using chloride for which the equation used by Carey and Riggan[7] leads to much lower selectivity coefficient compared with the least-squares algorithm, and the results obtained here with the mixed-solution method. The results obtained for chloride with the single-solution method are in agreement with the electrode selectivity for chloride described by Carey and Riggan[7]. However, the application of the mixed-solution method and derivation of the selectivity coefficients as described here is more realistic for potential applications and measurements in natural waters.

Response of the electrode to dissolved silicon and humic acid

The concentration of dissolved silicon in fresh waters is controlled through the dissolution of quartz, silicates and amorphous silicas from diatom frustules and concentrations rarely exceed 350 μM[6,29]. It is the anion, $H_3SiO_4^-$ that is likely to inhibit the response of the membrane to hydrogen phosphate. The first dissociation constant of silicic acid at 20 °C is $10^{-9.88}$ and therefore dissolved silicon occurs mainly as silicic acid at neutral pH[30]. In the present work, the inhibiting ion was taken as the anion and its activity was calculated from the total dissolved silicon concentration and pH with the first dissociation constant, K_1, calculated

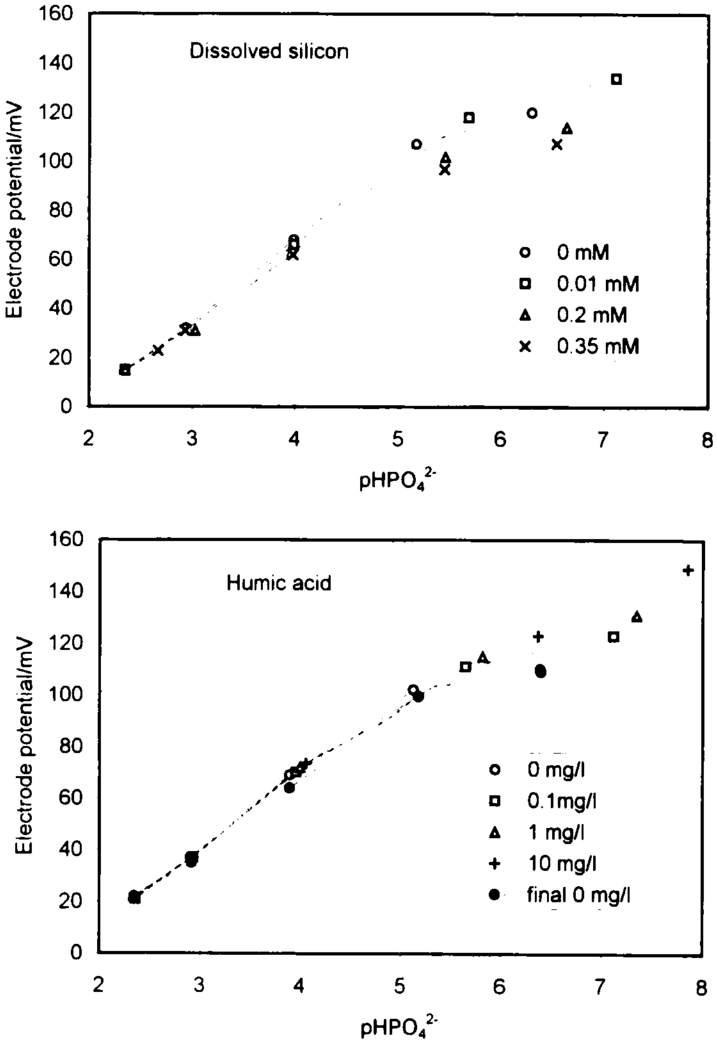

FIGURE 3 Comparison of the electrode response of two of the macroelectrodes in solutions of H_4SiO_4 and a standard humic acid of concentrations shown, and over a range of concentrations of KH_2PO_4 from 2.5 μM to 12.5 mM at *ca* 20 °C. The results obtained at the end of the experiment, here labelled as the final 0 mg/l, are shown for comparison. Key: $pHPO_4^{2-} = -\log(a_{HPO4})$

from $pK_1=-3.543+3885/T$ where T is the temperature in Kelvin between 288 and 308 K [30]. The electrode showed little response to dissolved silicon over the concentration range investigated e.g. Figure 3. The calculated selectivity coefficients of the macroelectrodes, $K_{HPO4,H3SiO4}$, were approximately $10^{-6.3}$ and much smaller than values from the other ions tested.

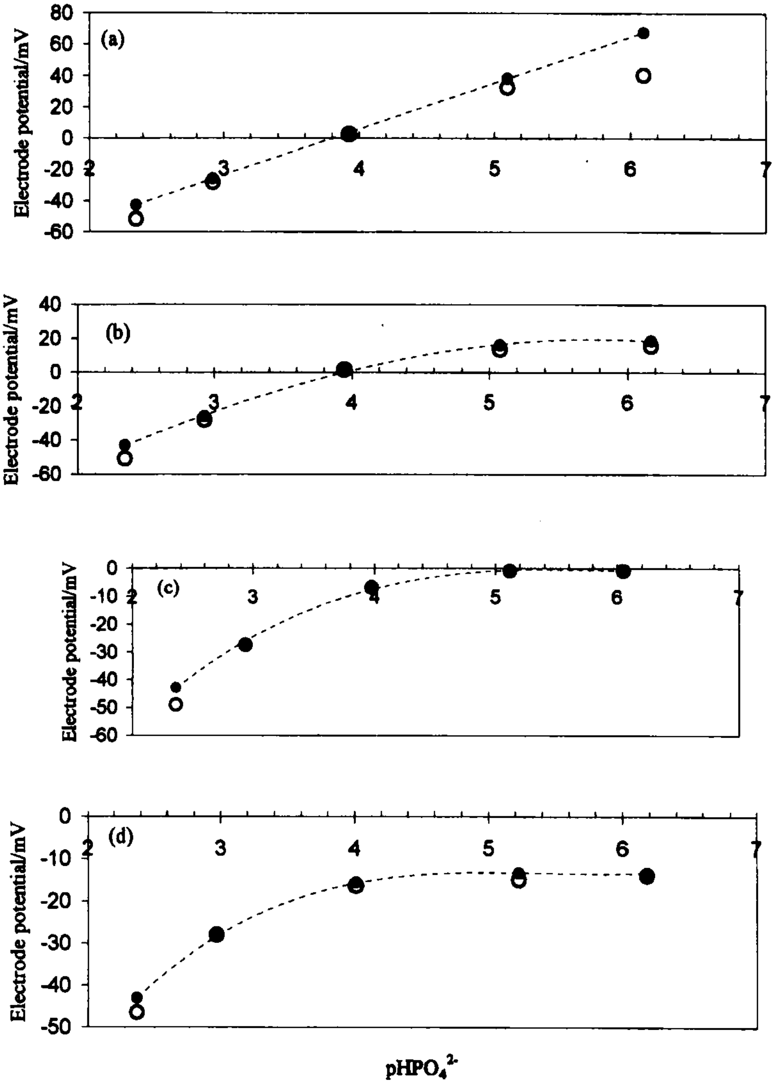

FIGURE 4 Example of a comparison of the measured electrode potential (o), and predicted (•) of a microelectrode using optimised parameters: $\log(K_{HPO4,\ SO4}) = -0.405$ and $E^0 = -112$ mV. Dotted lines show the cubic trend line for the predicted values. Key: (a) no K_2SO_4 present, (b) 0.1 mM K_2SO_4, (c) 0.5 mM K_2SO_4 and (d) 1.5 mM K_2SO_4

Similar results were obtained for the sample of standard humic acid that was tested (see Figure 3). The complexity of the humic acid molecule, both in terms of structure and charge, prohibits a detailed assessment of the selectivity coefficient. The results obtained with both the macro and micro-electrodes demonstrate that the inhibition of the electrode response is small.

CONCLUSIONS

Measurement of the selectivity coefficients by optimisation of parameters in the Nicolsky – Eisenman equation using a least-squares procedure indicates the limitations of the electrode response to hydrogen phosphate in the presence of several different inhibitors. The choice of the concentration range of the inhibitors tested was guided by their occurrence in fresh waters. A total of 320 measurements were made with macroelectrodes in mixed-solutions of the major anions (Cl^-, NO_3^-, HCO_3^- and SO_4^{2-}), a further 120 in dissolved silicon and a standard humic acid, and 51 measurements were made in single solutions of KH_2PO_4 and KCl. A slightly larger number of measurements were made with microelectrodes and these gave responses that were not significantly different from those of the macroelectrodes.

The inhibiting effect of hydrogen carbonate is a severe restriction to the application of the hydrogen phosphate selective electrode to measurements in hard waters. However, the results indicate that with low concentrations of the inhibiting ions, e.g. in some soft waters, the electrode may be a useful ancillary tool, particularly in measuring concentration gradients near interfaces. Possible environmental applications of the macroelectrode include studies of the precipitation of calcium phosphate minerals in synthetic solutions. The microelectrode has potential for studies of phosphorus fluxes in laboratory algal biofilms, and measurements of the diffusion and adsorption interaction of hydrogen phosphate in the porewaters of mixtures of sand and clay where major-anion concentrations are low and dissolved silicon is not an important inhibitor.

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