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COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

**PROCEDURES FOR TESTING pH
RESPONSIVE GLASS ELECTRODES AT 25,
37, 65 AND 85 °C AND DETERMINATION OF
ALKALINE ERRORS UP TO 1 mol dm⁻³ Na⁺,
K⁺, Li⁺**

Prepared for publication by

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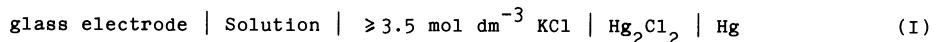
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Procedures for testing pH responsive glass electrodes at 25, 37, 65 and 85 °C and determination of alkaline errors up to 1 mol dm⁻³ Na⁺, K⁺, Li⁺

Abstract - A new method has been developed for testing glass electrodes over the pH range 0 - 14 at 25 °C in the absence of alkali metal ions, in the presence of Na⁺, K⁺, Li⁺ at high pH, and extended to 37 °C for clinical usage and to higher temperatures (65, 85 °C). The method is based on indirect comparison with results for hydrogen gas electrodes but uses silver-silver chloride reference electrodes in cells without liquid junction. With specially developed chloride-containing test buffers, it is now possible to determine the errors of glass electrodes with an accuracy of ± 1.2 mV (± 0.02 pH) over the normal pH range at 25, 65 and 85 °C and to measure Na⁺, K⁺, Li⁺ errors at up to 1 mol dm⁻³ cation at constant pH for pH > 6.5 at 25 °C. Examples are given from results of testing commercial electrodes.

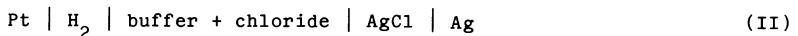
1. INTRODUCTION

It is current practice to use a glass electrode to measure the pH of a test solution (X) after the system:



has been subjected to either (a) a single point calibration involving a standard buffer S₁ of assigned pH(S) or (b) a two-point calibration (ref. 1) involving standard buffers S₁ and S₂ each of assigned pH(S), which bracket the pH of the test solution (X). In case (b), a linear variation of emf with pH is assumed but the proportionality factor may not necessarily be $(RT/F) \ln 10 = 59$ mV at 25 °C, as required theoretically.

pH(S) values are established from measurements on cells without liquid junctions containing hydrogen gas electrodes



using the Bates-Guggenheim convention (ref. 2) for the activity coefficient of chloride ion (γ_{Cl}) to obtain pH(S) = $-\log m_{\text{H}}Y_{\text{H}}$ from the experimental quantity $-\log m_{\text{H}}Y_{\text{H}}Y_{\text{Cl}}$ given by cell II. Because of the liquid junction, values of pH(X) determined using cell I (operational pH values) differ from pH(S), certainly at high and low pH (1 > pH > 9) (ref. 3). In the same regions of extreme pH, the glass electrode may show deviations from the (theoretical) hydrogen electrode function, the so-called acid and alkaline errors, which can be regarded as a mixed response to hydrogen ions and to anions or alkali metal cations, respectively (ref. 4). Poorly constructed electrodes may even show deviations in the pH region 1 - 9.

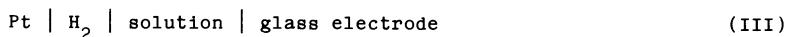
To test the performance of glass electrodes, cell I is commonly used with standard pH buffers (ref. 3). Outside the regions covered by these, certain other solutions can be used, such as 0.1 mol dm⁻³ HCl and 0.1 mol dm⁻³ NaOH. All these solutions contain varied amounts of Na⁺, which with the uncertainties arising from irreproducibility of the liquid junction potential, makes the method of testing using cell I imprecise and unsatisfactory.

Some manufacturers check all or representative samples of their glass electrodes by the two-point calibration method (or sometimes three points at 4, 7 and 9 pH) before dispatch. Sometimes nomograms or nomographs are included in the literature which accompanies the electrode indicating the likely errors in Na⁺-containing solutions at high pH. Such data are a rough guide to performance, because the errors depend on the age and previous usage of the electrode. What is required is a separate method of testing glass electrodes independently of reference electrodes with liquid junction.

In Newcastle a new method of testing the performance of glass electrodes was developed (refs. 5,6) using buffer solutions in the pH range 0 - 14, with those above 6 containing no sodium ion. Sodium ion was then added to each of the solutions of pH > 6.5 at three different Na^+ concentrations to test the pH-response of glass electrodes in the presence of this cation. The method is based on indirect comparison of glass electrodes with the hydrogen gas electrode, using silver-silver chloride electrodes in cells without liquid junction. It was designed to be simple, accurate and rapid so that it can be easily employed by manufacturers and users with the resources available in most analytical laboratories. The method has been extended to the determination of errors due to other alkali metal ions (ref. 7) and to higher temperatures (ref. 8).

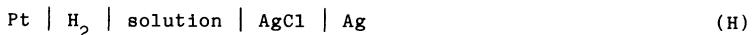
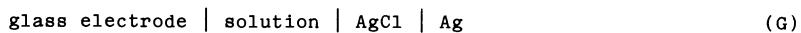
2. METHOD

The criterion of perfect behaviour of a hydrogen-ion responsive glass electrode is that the emf of the cell



should be constant independent of solution composition. Departure from this behaviour, or error, is indicated by the difference between emf values obtained with two different solutions.

For practical reasons the following glass (G) and hydrogen (H) cells, which correspond to the invariant cell (III) if the solution used is identical, are set up:



Denoting the emf of the cell III when a reference solution R is employed by E_{III}^R , then

$$E_{\text{III}}^R = E_H^R - E_G^R \quad (1)$$

where E_H^R , E_G^R are the emfs of cells H and G, respectively, with a reference solution R. Replacing solution R, in which the glass electrode is assumed to be error-free, by another solution (T) of different pH gives, in general, new values E_{III}^T , E_H^T , E_G^T so that

$$E_{\text{III}}^T = E_H^T - E_G^T \quad (2)$$

The error of the glass electrode ΔE is defined by (ref. 6)

$$\begin{aligned} \Delta E &= E_{\text{III}}^T - E_{\text{III}}^R \\ &= (E_H^T - E_G^T) - (E_H^R - E_G^R) \\ &= (E_H^T - E_H^R) - (E_G^T - E_G^R) \end{aligned} \quad (3)$$

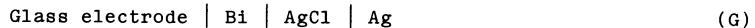
Thus the error of a glass electrode, relative to a solution where it is assumed to be error-free, can be obtained by subtracting the difference between the two values obtained for cell G from the corresponding two values for cell H, which have been determined for specially devised buffer solutions in this work. The reference solution coded B6 is chosen to be a neutral pH buffer for tests over the range 0 - 14. For direct measurement of the sodium ion error in the alkaline region the chosen reference solution has the same pH (± 0.02) as the test solution but the latter contains sodium ions.

Buffer solutions are coded Bi or BiNaj ($j = 0, 1, 2$) where j indicates $p\text{Na} = -\log \{\text{Na}^+\}$. Thus B12 means the pH of this solution lies between 12 and 13 and B12Na0 that its pH lies between 12 and 13 and also its sodium ion concentration is 1 mol dm^{-3} .

Assuming the glass electrode is error free in B6, the error in any other solution is obtained by subtracting the observed emf difference, $E_G^{\text{Bi}(i \neq 6)} - E_G^{\text{B6}}$, from the corresponding difference

for the hydrogen gas electrode, $E_H^{Bi(i \neq 6)} - E_H^{B6}$ (eqn. 3).

To determine the sodium error, the difference between the electromotive forces of cells



with $i = 12, 13$ or 14 and $j = 0, 1, 2$ is measured. Since the solution in cell G contains no sodium, the error is obtained by subtracting the emf difference between the two cells G and G', $E_{\text{G}}^{\text{BiNaj}} - E_{\text{G}}^{\text{Bi}}$, from the corresponding difference when the hydrogen gas electrode replaces the glass electrode (eqn. 3).

Compositions of the special buffer solutions are given in Table 1. Buffers BiNa2, Na1 and Na0 containing Na^+ are made from buffers B6, B7, B9 and B11 by adding sodium perchlorate monohydrate. For buffers B12, B13 and B14, perchlorate will precipitate so sodium chloride is used. However, it is not possible at these high pH values to make up the sodium-containing buffers by direct addition of sodium chloride, and they have to be prepared separately. The pH values of all Na^+ -containing buffers differ from that of the corresponding Na^+ free buffer by no more than ± 0.2 pH.

The buffer solutions may be used in either of two ways:

- (A) for testing the response at decreasing or increasing pH in the absence of sodium ions (B6 into B0 - B14).

Notes: (i) It is recommended that B6 be used as a reference solution. Direct transfers between acid and alkaline solutions may lead to greater time variation of the glass electrode readings. However, values for such transfers are given in Table 2.

(ii) Commercial samples of tetramethylammonium hydroxide may contain small amounts of Na^+ and K^+ ions as impurities, so buffers prepared from it may not be entirely free of alkali-metal ions.

(iii) The Na^+ ions present in B4 and B5 have no adverse effect as in this pH region the sodium error of glass electrodes is negligible.

- (B) For testing the response to increasing concentrations of Na^+ at constant pH (Bi into BiNa0,1,2 where $i = 6, 7, 9, 12, 13, 14$). Values for such transfers are given in Table 3.

3. PROCEDURE

(a) Glassware. Open beakers are suitable for containing solutions for short-term tests but for extensive tests of long-term, more elaborate closed vessels with necks to support the electrodes are necessary.

Pipettes 10 cm^3 , 20 cm^3 , 25 cm^3 , 50 cm^3 and 100 cm^3 (grade B) or smaller designations if desired.

One mark volumetric flasks 200 cm^3 , 250 cm^3 , 500 cm^3 and 1000 cm^3 (grade B), or smaller sizes if desired.

(b) Solutions. Select buffer solutions of the desired pH and sodium ion concentration (if required). Make up solutions in good quality laboratory distilled water. All (except B13, B14) may be stored in closed Pyrex flasks for periods up to 1 month. Sodium ion-free solutions can be stored for longer periods. B13 and B14 buffers should be stored in polyethylene bottles. All buffers from B6 - B14 will absorb carbon dioxide if left exposed to the atmosphere, but rigorous precautions to exclude it need not be adopted. The use of rubber stoppers and tubing in dispensing vessels should be avoided.

(c) Reagents. Hydrochloric acid. Volumetric reagent solutions are available commercially at 1 mol dm^{-3} . These may contain a small amount of Hg(II) , which is not detrimental for the present purpose.

Tetramethylammonium hydroxide is available commercially as a $25 \pm 1.5\%$ w/w aqueous solution. 25% corresponds to $2.792 \text{ mol dm}^{-3}$. This solution should be titrated with 0.1 mol dm^{-3} HCl to an endpoint of pH $3.5 - 4.5$ and weights given in Section (d) divided by the factor: (determined molarity)/2.792. Analysis shows typically $5 \times 10^{-4} \text{ mol dm}^{-3} \text{ Na}^+$ and

TABLE 1. Buffer composition

Solution No.	Buffer Composition	pH
B0	1 mol dm ⁻³	0.06
B1	0.1 mol dm ⁻³ HCl	1.09
B2	0.05 mol dm ⁻³ glycine hydrochloride + 0.05 mol dm ⁻³ glycine	2.49
B4	0.02 mol dm ⁻³ succinic acid + 0.02 mol dm ⁻³ sodium hydrogen succinate + 0.1 mol dm ⁻³ NaCl	4.21
B5	0.02 mol dm ⁻³ sodium hydrogen succinate + 0.02 sodium succinate + 0.1 mol dm ⁻³ NaCl	5.64
B6	0.05 mol dm ⁻³ Bis-Tris hydrochloride + 0.05 mol dm ⁻³ Bis-Tris	6.58
B7	0.1 mol dm ⁻³ Tris hydrochloride + 0.05 mol dm ⁻³ Tris	7.90
B9	0.03 mol dm ⁻³ ethanolamine hydrochloride + 0.03 mol dm ⁻³ ethanolamine	9.39
B11	0.05 mol dm ⁻³ piperidine hydrochloride + 0.075 mol dm ⁻³ piperidine	11.34
B12	0.05 mol dm ⁻³ tetramethylammonium hydroxide + 0.1 mol dm ⁻³ tetramethylammonium chloride	12.61
B13	0.19 mol dm ⁻³ tetramethylammonium hydroxide + 0.1 mol dm ⁻³ tetramethylammonium chloride	13.3
B14	0.8 mol dm ⁻³ tetramethylammonium hydroxide + 0.1 mol dm ⁻³ tetramethylammonium chloride	14.0

TABLE 2. Observed emf differences (mV) for hydrogen gas electrodes transferred between buffer solutions

To: B0	B1	B2	B4	B5	B6	B7	B9	B11	B12	B13	B14
<u>From:</u>											
B0	0	120.2	219.9	294.7	374.5	461.8	523.3	640.0	743.2	802.6	843.4
B1	-120.2	0	99.7	174.5	254.3	341.6	403.1	519.8	623.0	682.4	723.2
B2	-219.9	-99.7	0	74.8	154.6	241.9	303.4	420.1	523.3	582.7	623.5
B4	-294.7	-174.5	-74.8	0	79.8	167.1	228.6	345.3	448.5	507.9	584.7
B5	-374.5	-254.3	-154.6	-79.8	0	87.3	148.8	265.5	368.7	428.1	468.9
B6	-461.8	-341.6	-241.9	-167.1	-87.3	0	61.5	178.2	281.4	340.8	381.6
B7	-523.3	-403.1	-303.4	-228.6	-148.8	-61.5	0	116.7	219.9	279.3	320.1
B9	-640.0	-519.8	-420.1	-345.3	-265.5	-178.2	-116.7	0	103.2	162.6	203.4
B11	-743.2	-623.0	-523.3	-448.5	-368.7	-281.4	-219.9	-103.2	0	59.4	100.2
B12	-802.6	-682.4	-582.7	-507.9	-428.1	-340.8	-279.3	-162.6	-59.4	0	40.8
B13	-843.4	-723.2	-623.5	-584.7	-468.9	-381.6	-320.1	-203.4	-100.2	-40.8	0
B14	-896.3	-776.1	-676.4	-601.6	-521.8	-434.5	-373.0	-256.3	-153.1	-52.9	0

TABLE 3. Observed emf differences (mV) for hydrogen electrodes transferred between solutions of various Na⁺ concentrations of approximately constant pH

From Bi/To	BiNa2	BiNa1	BiNa0
B6	1.1	6.2	23.7
B7	0.3	3.1	9.7
B9	1.2	6.7	20.8
B11	0.7	5.0	20.9
B12	-2.5	-0.5	-3.0
B13	-	-	-6.2
B14	-3.7	-3.2	-17.5

10^{-4} mol dm⁻³ K⁺ in prepared B12. Sulphate, bromide and iodide may also be present and are not detrimental in small amounts.

Succinic acid. Use recognised analytical reagent grade. Dry at 80 °C.

Glycine. Use recognised analytical reagent grade. Dry at 80 °C.

Bis-Tris. Bis(hydroxyethyl)iminotris(hydroxymethyl)methane. (M.S. = 209.25.) Dry at 80 °C.

Tris. Tris(hydroxymethyl)aminomethane. (M.W. = 121.05.) Dry at 80 °C.

Piperidine is a volatile liquid commercially available at ~ 98% which, from a freshly opened bottle, can be used without further purification. Lower grade material should be distilled (b.p. 106 °C) from over sodium hydroxide pellets and a middle fraction collected.

Ethanolamine is a liquid commercially available at ~ 99% which can be used without further purification. Lower grade material should be distilled (b.p. 171 °C) and a middle fraction collected.

Sodium hydroxide is available commercially as a 4 mol dm⁻³ aqueous solution 'carbonate-free'.

Sodium chloride. Use recognised analytical reagent grade. Dry at 110 °C.

Sodium perchlorate is available as monohydrate. Do not dry. Analysis shows that the variation from monohydrate composition is insufficient to affect sodium ion concentration significantly.

(d) Preparation of solutions

B1. Dilute 100 cm³ of 1 mol dm⁻³ HCl to 1000 cm³ with water.

B2. Dissolve 7.507 g glycine in water, add 50 cm³ of a mol dm⁻³ HCl and make up to 1000 ml with water.

B4. Dissolve 4.724 g succinic acid and 5.844 g NaCl in a little water, add 20 cm³ of 1 mol dm⁻³ NaOH and make up to 1000 cm³ with water.

B5. Dissolve 4.724 g succinic acid and 5.844 g NaCl in a little water, add 60 cm³ of 1 mol dm⁻³ NaOH and make up to 1000 cm³ with water.

B6. Dissolve 20.924 g Bis-Tris in a little water, add 50 cm³ of 1 mol dm⁻³ HCl and make up to 1000 cm³ with water.

B7. Dissolve 18.171 g Tris in a little water, add 100 cm³ of 1 mol dm⁻³ HCl, and make up to 1000 cm³ with water.

B9. Mix 3.054 g ethanolamine with 30 cm³ of 1 mol dm⁻³ HCl, dilute with some water (care: volatile liquid, fumes with HCl) and make up to 1000 cm³ with water.

B11. Mix 10.644 g piperidine with 50 cm³ of 1 mol dm⁻³ HCl, dilute with water and make up to 1000 cm³ with water.

B12. Add 100 cm³ of 1 mol dm⁻³ HCl to 54.7 g of 25% TMAH* solution and make up to 1000 cm³ with water.

B13. Add 100 cm³ of 1 mol dm⁻³ HCl to 105.73 g of 25% TMAH* solution and make up to 1000 cm³ with water.

B14. Add 100 cm³ of 1 mol dm⁻³ HCl to 328.1 g of 25% TMAH* solution and make up to 1000 cm³ with water.

Solutions BiNa2 where i = 6, 7, 9 and 11. Take 0.351 g sodium perchlorate‡ and make up to 250 cm³ with primary buffer Bi.

Solutions BiNa1 where i = 6, 7, 9 and 11. Take 3.511 g sodium perchlorate‡ and make up to 250 cm³ with primary buffer Bi.

Solutions BiNa0 where i = 6, 7, 9 and 11. Take 35.11 g sodium perchlorate‡ and make up to 250 cm³ with primary buffer Bi.

B12Na2. Dissolve 0.146 g NaCl in 25 cm³ of 1 mol dm⁻³ HCl. Add 14.23 g of TMAH* and make up to 250 cm³ with water.

- B12Na1. Dissolve 1.461 g NaCl in a little water, add 4.74 g of 25% TMAH* and make up to 250 cm³ with water.
- B12Na0. Mix 30 cm³ 1 mol dm⁻³ NaOH, 20 cm³ of 1 mol dm⁻³ HCl and some water. Add 23.877 g sodium perchlorate[‡] and make up to 200 cm³ with water.
- B13Na0. Mix 75 cm³ 1 mol dm⁻³ NaOH, 25 cm³ of 1 mol dm⁻³ HCl and add water to make up to 250 cm³.
- B14Na2. Dissolve 0.146 g NaCl in 25 cm³ of 1 mol dm⁻³ HCl. Add 82.03 g of 25% TMAH* and make up to 250 cm³ with water.
- B14Na1. Dissolve 1.461 g NaCl in a little water, add 72.91 g of 25% TMAH* and make up to 250 cm³ with water.
- B14Na0. Mix 125 cm³ of 4 mol dm⁻³ NaOH, 50 cm³ of 1 mol dm⁻³ HCl and some water and make up to 500 cm³ with water.

(e) Measuring equipment. Measurements may be made with a pH meter on its mV scale to avoid complications arising from slope factor variation and temperature compensation. Recalling that 0.01 pH = 0.6 mV, a scale interval of 1 mV or discrimination of 0.1 mV is desirable, even though reproducibility at this level is not achievable.

(f) Glass electrodes. The glass electrode should be conditioned before use as stated by the manufacturer. In transferring a glass electrode between solutions (and the reference electrode if transferred; see below) the procedure of washing with a little of the solution into which the electrode is to be transferred is the most satisfactory. Swabbing with tissue may lead to carry-over from one solution to the next unless an intermediate wash with distilled water is employed, but introducing this may have an adverse effect on the time response of the electrode.

(g) Reference electrodes. Silver-silver chloride electrodes are available commercially. Alternatively these electrodes may be prepared as described below. Their standard potential is unimportant, but if desired it can be determined in solution B1 against a hydrogen gas electrode taking 0.796 as the value for the mean ionic activity coefficient of HCl at 0.1 mol dm⁻³ at 25 °C. One reference electrode only is needed if this is transferred together with the glass electrode between solutions. Using this procedure, however, it is not possible to ascribe a slow response solely to the glass electrode unless preliminary tests have been made on the time-response of the reference electrode. It is preferable to use reference electrodes for each buffer solution allowing them time to reach equilibrium before the glass electrode transfers are commenced. With this procedure the bias potentials (intercomparison potentials in a common electrolyte) of the silver-silver chloride electrodes should be measured beforehand in B1, and should not exceed \pm 0.2 mV.

If not available commercially, silver-silver chloride electrodes may be prepared by one of the following three methods:

- (i) Electrolytic type. Anodize pure silver wire suitably sealed into glass tube supports in 0.1 mol dm⁻³ potassium chloride or hydrochloric acid for 1 h at a current density of 1 mA cm⁻². Use platinum wire as cathode.
- (ii) Bi-electrolytic type. Cathodize pure platinum wire (1 mm) suitably sealed into glass tube supports in 1% potassium argentocyanide solution for 25 h at a current density of 1 mA cm⁻². Wash thoroughly in distilled water. Convert part of the deposited silver to silver chloride by anodizing in 0.1 mol dm⁻³ potassium chloride or hydrochloric acid for 1 h at a current density of 1 mA cm⁻². Use platinum wire as the other electrode in both electrolyses.
- (iii) Thermal-electrolytic type. Dissolve 28 g silver nitrate in 250 cm³ distilled water and heat to 50 °C - 60 °C. Add drop by drop with vigorous stirring a solution of 6 g sodium hydroxide in 25 cm³ of distilled water. Cool and filter the precipitated silver oxide on a sintered glass funnel. Wash very thoroughly with distilled water, preferably by shaking with twenty changes of 100 ml of distilled water in a stoppered bottle. Filter but retain as a thick paste.

* Mass requires adjustment if TMAH is not 25%. Divide mass given by (determined molarity/2.792).

[‡] Solutions containing perchlorates should be discarded after use and not permitted to form solid residues, which are likely to be highly explosive.

Wind lengths of 1 mm platinum wire into helices 2 mm diameter and 5 mm long and seal a protruding length into glass tube supports. Apply silver oxide paste to each helix and heat in a small tube furnace at 450 °C until white. Add further coats as necessary until no platinum wire in the helix remains exposed. Convert part of silver to silver chloride as for type (ii).

Electrodes should be stored in fresh 0.1 mol dm⁻³ KCl for 24 h before use. Bias (inter-comparison) potentials then do not usually exceed \pm 0.1 mV. Method (i) may not yield electrodes of this quality because of strains present in drawn wire. Further details on preparation are available (ref. 9).

4. TREATMENT OF RESULTS

The error of the glass electrode on transferring between any two solutions is given by comparing the difference in observed potentials with the appropriate value derived from Table 2 or 3. The error can only be ascribed to the second solution if the electrode is known (or assumed) to be error-free in the first buffer. Values in Tables 2 and 3 refer to 25 °C, but no serious inaccuracy is expected if tests are made in a draught-free atmosphere at temperatures \pm 2 °C from this, provided all solutions are at the same temperature.

Examine 1. A glass electrode was transferred between B6 and B12 yielding an emf difference of 332.6 mV. Comparing this with the entry (6th row, 10th column) in Table 2 of 340.8 mV, then the error is 8.2 mV = 0.14 in pH at pH = 12.6.

Example 2. A glass electrode was transferred between buffers B9 and B9NaO yielding an emf difference of 18.0 mV. Comparing this with the entry 20.9 (3rd row, 3rd column) in Table 3 then the error is 2.8 mV = 0.047 in pH at pH = 9.4

With use, the performance of a glass electrode may fall, as shown by an increased response time, increased Na⁺ error, and perhaps errors in transfer between buffers in the medium pH range (3 - 9). Gross errors may originate from cracks in the pH-sensitive region or at its junction with the glass stem. Such defects will be shown up by detecting a drop in membrane electrical resistance.

5. APPLICATION TO THE PHYSIOLOGICAL pH RANGE (pH 6.4 - 7.6) AND PHYSIOLOGICAL Na⁺ CONCENTRATION (0.15 mol dm⁻³)

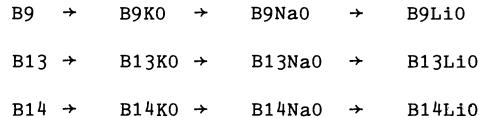
Small errors of the glass electrode of 0.01 have been observed in the physiological range (ref. 10). For practical reasons in the design of blood pH sensors, glasses of less than the optimum glass composition for low Na⁺ error are used. It is therefore essential to have a method which determines the performance of the glass electrode when it is to be used for pH measurement in blood as proposed by IFCC (ref. 11).

The method was therefore adapted (ref. 12) to 37 °C and physiological pH (5.4 - 7.6) and Na⁺ concentration (0.15 mol dm⁻³). Buffers B6 and B7 were used and a new sodium-containing buffer B7NaO.8 of pH 7.58 at 37 °C prepared by dissolving 10.534 g NaClO₄.H₂O in 500 ml of B7. For the transfer of perfect glass electrode at 37 °C, B7 \rightarrow B6, $\Delta E = 56.7 \pm 0.2$ mV and for B7NaO.8 \rightarrow B7, $\Delta E = 4.0 \pm 0.2$ mV.

One glass electrode tested yielded errors of -0.1 and 0.2 mV respectively, clearly within experimental error. Another showed a sodium error of 0.3 mV, in accord with a rough estimation from the manufacturer's monograph.

6. EXTENSION TO SOLUTIONS CONTAINING K⁺, Na⁺ AND Li⁺ AT 25 °C

The method was adapted (ref. 7) to permit determination of errors due to other alkali metal ions. Additional solutions were prepared according to Table 4. Potassium hydroxide is available as AVS ampoules from BDH (Poole, U.K.) but lithium hydroxide was prepared from Analar reagent LiOH.H₂O. Tests were made in the sequences



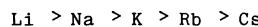
No studies were carried out, unlike the case of Na⁺, on the reproducibility of solution preparation. This is not expected to be good in the case of Li⁺ solutions in the absence of

TABLE 4. Preparation of buffer solutions containing alkali ions

Solution	Components	Final volume/cm ³
B9K0	21.7837 g K ₂ SO ₄ + B9 to	250
B9Na0	35.115 g NaClO ₄ .H ₂ O + B9 to	250
B9Li0	15.995 g LiSO ₄ .H ₂ O + B9 to	250
B13K0	25 cm ³ 1 mol/dm ³ HCl + 75 cm ³ 1 mol/dm ³ KOH + H ₂ O to	250
B13Na0	25 cm ³ 1 mol/dm ³ HCl + 75 cm ³ 1 mol/dm ³ NaOH + H ₂ O to	250
B13Li0	25 cm ³ 1 mol/dm ³ HCl + 3.147 g LiOH.H ₂ O + 11.1965 g Li ₂ SO ₄ .H ₂ O + H ₂ O to	250
B14K0	25 cm ³ 1 mol/dm ³ HCl + 125 cm ³ 2 mol/dm ³ KOH + H ₂ O to	250
B14Na0	25 cm ³ 1 mol/dm ³ HCl + 125 cm ³ 2 mol/dm ³ NaOH + H ₂ O to	250
B14Li0	25 cm ³ 1 mol/dm ³ HCl + 10.4900 g LiOH.H ₂ O + H ₂ O to	250

commercial ampoules for the preparation of hydroxide solutions of known concentration as for Na⁺ and K⁺. Hydrogen electrode transfer values will not be given but the errors of six commercial glass electrodes are given in Table 5.

At pH 13 and 14, all six electrodes show Eisenman's order XI, (ref. 13)



in agreement with the high anionic field strength of the lithium-containing glasses. Consequently the ions in solution must be dissociated from their hydrating water molecules as they approach the anionic sites and they penetrate the glass as the bare cation.

TABLE 5. Errors (mV) of pH glass electrodes transferred between buffer solutions of approximately same pH and added alkali ion of decreasing atomic number

Buffer	Error/mV						
	Electrode:	A	B	C	D	E	F
B9K0		-0.8	0.7	0.4	-0.9	-1.6	-0.7
B9Na0		-3.1	-1.9	-1.1	-1.7	-3.0	-2.8
B9Li0		-0.9	-1.1	-0.3	-0.9	-1.8	-1.0
B13K0		0.8	0.4	0.9	0.6	0.6	-0.1
B13Na0		4.5	1.7	6.0	4.3	2.9	3.1
B13Li0		9.1	8.1	16.8	11.9	9.1	19.7
B14K0		1.5	2.0	-0.3	0.9	3.4	1.2
B14Na0		7.0	4.8	9.4	10.6	8.5	7.0
B14Li0		16.3	14.0	25.0	21.8	20.9	42.0

Temperature variation, solution contamination with CO_2 and uncertainties in the concentration of the solutions result in the small negative errors observed in B9. Errors of glass electrodes at this pH, if they were present, would be expected to be positive. Better control of these afore-mentioned variations would lead to increased precision of the method.

pH sensitive glass electrodes containing lithia as the principal alkali oxide have been commercially produced since the 1940's. They are more durable and show smaller errors in solutions containing Na^+ and K^+ than sodium electrodes. However, they do show larger errors in solutions containing lithium but that is not a drawback because solutions containing Li^+ ions are less used than those containing Na^+ and K^+ . Sokolov and Passynsky (ref. 14) introduced pH responsive lithium glass containing 18.1 mol % Li_2O , 9.6 CaO and 72.3 SiO₂. From their graphs, Isard (ref. 15) obtained errors at pH = 13 of 120 mV in LiOH, 10 mV in NaOH and 0 mV in KOH at 17 °C. So the same order of alkali ion selectivity was observed as for the compositions used in the present work.

7. EXTENSION OF THE METHOD TO HIGH TEMPERATURES (65 AND 85 °C)

Currently, hydrogen responsive (pH) glass electrodes are available from several manufacturers in both laboratory and industrial forms which are stated to be usable in the temperature range 0 - 100 °C or higher. These statements are not, however, based on tests of the pH response of these electrodes at high temperatures but on durability tests. In such tests, the electrode is subjected to the high temperature for successive periods of time, say, 30 minutes and after each exposure retested at 25 °C. This situation is unsatisfactory but reasons for it are understandable. Little data are available on the pH values of standard buffers at high temperatures. Of the seven standard solutions currently adopted by the National Bureau of Standards, data are available only for tartrate, phthalate, phosphate and borate buffers above 50 °C and stop at 95 °C. Some other workers (refs. 16-17) have provided pH data for three of these buffers, determined by a slightly different procedure, at 100, 125 and 150 °C. Even with the availability of limited data on pH standards at these high temperatures, checking of glass electrodes under these conditions using saturated calomel reference electrodes presents formidable problems with respect to maintaining the liquid junction and the effects of the disproportionation of calomel which lead to temperature hysteresis problems. The alternative of using a remote reference electrode at 25 °C is unattractive.

It is therefore important to attempt (ref. 8) to extend the new method of testing to higher temperatures. Industrial interest extends to temperatures of 130 °C but, prior to the development of specialised apparatus, it was decided to make measurements at 65 and 85 °C thus requiring only minor changes in technique.

The temperature range 65 - 85 °C was chosen as being easily attainable in a water thermostat with the use of polystyrene balls to cut down evaporation losses. Also 65 °C can be obtained in an air thermostat while retaining the ability to make manual transfers of the glass electrodes without special precautions. Use of an air thermostat means that the whole of the glass electrode, cap and stem, is at 65 °C.

Initially, measurements were made in a three-limbed cell with stopcock which permitted a glass electrode to be mounted in the third limb. The volume of this vessel was 250 cm³ and since a hydrogen gas presaturator was also used, a total volume of 300 cm³ was required per run. This was reduced to 200 ml by a redesign of cell vessel into a single pot-shaped vessel incorporating three B19 sockets for electrodes and a Grade 1 sintered glass disc for hydrogen gas bubbling. In order to keep the dissolved silver chloride from reaching the hydrogen electrode the silver-silver chloride was separated from the bulk of the solution by inserting it in 10 mm diameter glass tube sealed at its lower end with a ceramic 'stone' of the same porosity as those used for calomel reference electrodes with liquid junction. After cooling from 85 °C overnight, a colloidal brown colour (presumably Ag_2O) was noted in some of the more alkaline buffer solutions. It was found essential that an adequate amount of silver chloride was present on the electrodes, and they were periodically subjected to additional chloridising.

In transferring glass electrodes, it was not convenient because of the higher temperature to use the technique of washing with a little of the new solution, so instead the glass bulb was lightly touched with filter paper. This led to longer times to achieve steady readings.

The emf differences for a perfect glass electrode (that is for a hydrogen gas electrode) when transferred between B6 and any other at 65 °C are given in Table 6. Values are given only to the nearest mV as some larger scatter in the readings than expected was observed. For the strongly alkaline solutions a fall of emf with time over 6 hours was observed which may indicate a greater tendency for absorption of carbon dioxide at this temperature than at 25 °C. B12 solutions were very prone to this effect and were replaced by B13. The study was repeated at 85 °C and results are given for one glass electrode in Table 7. All results for errors refer to values taken after 20 - 30 min of immersion of the glass electrode in each

TABLE 6. Observed emf difference (mV) for hydrogen gas electrodes transferred between solutions at 65 °C

TO	B1	B6	B7	B9	B11	B12	B12Na0	B13	B13Na0	B14
FROM B1	0	347	395	515	626	691	691	720	763	796
B6	-347	0	48	168	279	344	344	373	416	449
B7	-395	-48	0	120	231	299	299	325	371	401
B9	-515	-168	-120	0	111	176	176	205	248	281
B11	-626	-279	-231	-111	0	65	65	94	137	170
B12	-691	-344	-299	-176	-65	0	0	29	72	105
B12Na0	-691	-344	-299	-176	-65	0	0	29	72	105
B13	-720	-373	-325	-205	-94	-29	-29	0	43	76
B13Na0	-763	-416	-371	-248	-137	-72	-72	-43	0	33
B14	-796	-449	-401	-281	-170	-105	-105	-76	-33	0

TABLE 7. Observed emf differences (mV) for hydrogen gas electrodes transferred between solutions at 85 °C

TO	B1	B6	B9	B11	B14
FROM B1	0	348	516	616	804
B6	-348	0	168	268	456
B9	-516	-168	0	100	288
B11	-616	-268	-100	0	188
B12	-702	-354	-186	-86	102
B14	-804	-456	-288	-188	0
pH	1.1	5.8	-	-	12.1

TABLE 8. Errors (mV) for some glass electrodes at 65 °C

Electrode	Manufacturer's description	B1	B9	B11	B13	B13Na0	B14
Q2	0 - 14 pH -5 to 100 °C	0	-	2	5	-	19
K1	0 - 14 pH 10 to 100 °C	-2	1	-	1	22	2
T3	0 - 14 pH 10 to 140 °C	-	-	-	0	19	4
P1	--	0	-5.4	-0.1	-	-	65.3
G1	0 - 12 pH -20 to 70 °C	-1.1	-5.9	-0.1	-	-	14.2
E2	0 - 14 pH 0 to 70 °C	10	-	-1	0	-	27
V2	0 - 11 pH -5 to 80 °C	-1	-	-2	0	-	2
P2	0 - 11 pH -10 to 70 °C	-7	5	-	9	-	56
pH of solution at 65 °C		1.1	-	10.1	12.1	12.4	13.4

TABLE 9. Errors (mV) for two transfers of glass electrodes (G1) between solutions B6 and B1 or B14 at 85 °C

B1	B14
-19.8, -21.8	36.1, 35.2

solution. Table 7 also indicates calculated pH(S) values of the buffers calculated from the Bates-Guggenheim convention. Because of the foreshortening of the pH scale at the higher temperatures, the values are lower than at 25 °C but the coding of the solutions has been retained to avoid confusion.

Glass electrodes for high temperature usage are subjected only to durability tests by the manufacturers. Tables 8 and 9 given the errors for the glass electrodes tested at 65 and 85 °C together with the manufacturers' description of the electrodes' useful ranges. It can be seen from Table 8 that the errors for E2 and P2 are very similar except in the region of pH 14. However, electrode P2 is apparently only intended for use up to pH 11 whilst E2 is stated to be usable to pH 14. Both electrodes were tested below the maximum temperature given by the manufacturer. Of all the electrodes tested, the best performance was from electrode V2, which gave an error of only 2 mV in B14 despite the claim that it is described as a pH 11 electrode. A small error for certain glass compositions is reasonable since in highly alkaline solutions the gel layer of the glass electrode may be dissolved away and this is known to reduce the alkaline error.

The test procedure subjects the electrodes to harsh environments and, despite the claims of the manufacturers that electrodes were usable at high temperatures, several electrodes tested failed due to physical breakdown, i.e. cracking of the glass bulb, or even melting of the plastic insulation of the lead.

Attempts were made to carry out tests up to 130 °C in an autoclave pressurised at 6 p.s.i. nitrogen. Electrodes were transferred by remote handling between dishes with removable lids containing solutions. Two dishes of each solution composition were included, the first serving as an intermediate wash solution. Considerable difficulties were experienced with maintaining the electrical integrity of the high impedance circuit and from failure of the electrode caps and leads to withstand prolonged exposure to high temperatures. Commercially, such electrodes have only their bulbs immersed in high temperature solutions and large temperature gradients must occur down the stem. Considerably more work is necessary before methods could be developed along the lines suggested for temperatures above 85 °C. The high solubility of silver chloride at these temperatures is an additional problem which may be solved by use of silver-silver bromide reference electrodes.

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