CHIMIA

Volumen 21 Fasc. 6 1967 Pag. 209–272

Physikalisch-chemische Methoden und Fragen der Instrumentierung in der chemischen Forschung und Praxis

Im Rahmen des 1. Schweizerischen Treffens für Chemie (17. bis 21. Oktober 1966), das zusammen mit der 3. Internationalen Fachmesse für Laboratoriumstechnik, Meßtechnik und Automatik in der Chemie (ILMAC) vom Schweizerischen Chemiker-Verband in Basel veranstaltet wurde, führte der Verband selber eine Fachtagung über das obengenannte Thema durch. Fünf der sechs an dieser Tagung gehaltenen Vorträge kommen in diesem Fasciculum zum Abdruck.

The Properties and Application of Cation-Responsive Glass Electrodes

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Summary

The comparatively recent development of glass electrodes primarily responsive to cations other than the hydrogen ion has opened up fresh analytical possibilities for the direct electrochemical measurement of sodium, potassium, ammonium, lithium and even divalent cations. Most work has been carried out on Na^+- and K^+- responsive systems, and the paper will describe the response ranges of typical glasses and the interferences to which they are subject. Attention will be given to techniques of usage for obtaining the best results.

Applications have so far mainly been concentrated in the biological sphere, where sodium and potassium measurements are of major importance both in research and routine clinical practice. Here the speed of measurement and opportunity for *in vivo* continuous monitoring are main attractions, particularly for sodium. However, other laboratory applications, e. g. for foods, water and analysis, etc. has been explored.

One industrial application is the continuous automatic determination of micromolar concentrations of sodium in high purity waters. Of interest here are the special techniques which are adopted to obtain stable and reproducible results in this concentration region.

Finally a brief indication will be given of some related new methods of specific ion measurement.

Introduction

Sodium and potassium ion responses by glasses are not newly discovered phenomena, and indeed have been studied for their theoretical interest in relation to *p*H response since the 1930s[1, 2, 3]. However, the recent reorientation of interest and development of useful specific properties is due very largely to the efforts of **Eisenman** and his co-workers, who in a series of publications (see refs. [4, 5] and [6] for summaries) have examined the theoretical aspects of electrode response behaviour. It is inappropriate here to consider the theoretical background defining the glass compositions in terms of their specific ion responses, and the reader is recommended to reviews on the subject, which are available in abridged[7, 8, 9] as well as comprehensive[4, 5, 6] forms. Related work by **Nicolsky**, **Shultz** and their co-workers over several years should also be consulted (summarised in ref.[10]). Attention will be concentrated in this paper on the practical aspects of the electrodes.

Response Characteristics

The data which will be presented here are indicative of the general characteristics which will be found, but variations in specificity of course occur from one type of glass to another and even to some extent between different electrodes of the same composition. This summary of properties should therefore only be taken as an indication to provide the basis for appreciation of the potentialities of the electrodes.

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[1] See M. Dole, *The Glass Electrode*, Wiley, New York 1941, Ch. 7.

[2] B. Lengyel and E. Blum, *Trans. Faraday Soc. 30* (1934) 461.

[3] H. J. C. Tendeloo and A. J. Z. Voorspuy, *Recu. Trav. Chim. Pays-Bas 61* (1942) 531, *62* (1943) 784, 793. See also H. J. C. Tendeloo, A. E. Mans, I. Kateman and F. H. v. d. Voort, *op. cit. 81* (1962) 505.

[4] G. Eisenman, *Biophysic. J. 2* (1962) Part 2, Supplement, p. 259.

[5] G. Eisenman, *Advances in Analytical Chemistry and Instrumentation*, Ed. C. N. Reilley, Interscience, 1965, Vol. 4, p. 213.

[6] G. Eisenman, *Glass Electrodes for Hydrogen and Other Cations*, Ed. G. Eisenman, Marcel Dekker, 1967, Ch. 5 and 7.

[7] G. Mattock, *pH Measurement and Titration*, Heywood, London 1961, p. 130.

[8] A. H. Truesdell, *Inst. Soc. Amer. Proc. 8* (1962) 67.

[9] S. M. Friedman, *Methods of Biochemical Analysis*, Ed. D. Glick, Interscience, 1962, p. 71.

[10] B. P. Nicolsky, M. M. Schultz, A. A. Belijustin and A. A. Lev, *Glass Electrodes for Hydrogen and Other Cations*, Ed. G. Eisenman, Marcel Dekker, 1967, Ch. 7.

Eisenman, Rudin and Casby[11] have presented an empirical equation of Nernst type to describe the mixed potential response of an electrode glass in a solution containing two monovalent cations:

$$E = E^0 + \frac{RT}{F} \ln \left(a_1^{1/n} + k^{1/n} a_2^{1/n}\right)^n,$$

where E^0 is a standard potential, a_1 and a_2 are the activities of the two cations in solution, k and n are empirical constants, and R, T and F have their usual significance. For sodium and potassium ion mixtures, n is unity, so that a definition of the relative response selectivity of a glass to sodium ions in the presence of potassium ions is given by the magnitude of k. From the practical point of view, the interference by ion 2 in the measurement of ion 1 in a measurement involving

$$E = E^0 + \frac{RT}{F} \ln (a_1 + k a_2)$$

is governed by the ratio $k a_2/a_1$. For a given glass composition, for which we shall assume for the present purposes that k is constant, the degree of interference by a_2 is controlled by a_2/a_1. Thus if less than 2% interference is required when $a_2/a_1 = 10^2$ then k must have a value of less than 10^{-4}.

k values can be obtained by observing the responses in two different solutions of known a_1 and a_2 compositions, with solution of the simultaneous equations containing the unknowns k and E^0 (the latter for a practical cell system will also incorporate the reference electrode potential). Alternative solutions of pure 1 and of pure 2 are sometimes used for this, but the author finds that this may give false results, particularly for low values of k. (In passing, it may be noted that aged eletrodes show more stable k values than new electrodes.)[12]

The value of k, which is sometimes termed the selectivity constant, does not define directly the ratio a_2/a_1 above which interference will occur. This is actually defined by $k a_2/a_1$, and for less than 2% interference, for example, a_1 must be at least 100 $k a_2$. It is important therefore to distinguish between the selectivity constant and the more general term of selectivity, which usually implies the ratio of a_2/a_1 above which interference in the measurement of a_1 occurs to greater than a given magnitude. It may be noted that since the potential response to activity is logarithmic, an uncertainty of $\pm$ 0·01 logarithmic unit (analogous to $\pm$ 0·01 pH unit) in the measurement corresponds to an uncertainty of approximately $\pm$ 2% in activity; $\pm$ 0·02 unit $\equiv \pm$ 4·5%, and $\pm$ 0·005 unit $\equiv \pm$1%.

In the following descriptions the response behaviours are shown graphically by plots of theoretical response against experimentally observed behaviour. (In all cases at least two cations are present, because even with an otherwise pure metal ion solution the co-presence of hydrogen ion must always be borne in mind.) The curves shown (except Figure 1b) are based on work carried out with solutions of constant and relatively high ionic strength, where the effects of changing activity coefficients in varying from one cation strength solution to another may be ignored (except possibly at the highest concentrations). The background medium used a large organic cation and showed pH buffer characteristics, so that any cation interference due to the medium would be constant and probably small (because the glasses probably do not respond particularly well to large cations). By preparation of a series of solutions containing differing concentrations of the cations of interest it was found possible to study the response ranges using a conventional pH meter, where a standardisation was carried out on the basis of a given solution having a defined response. Thus in the sodium ion work a 10^{-2}M Na^+ solution was defined as having a pNa = 2·00, and the pH meter was set to pH = 2·00. If the electrode responded theoretically a 10^{-3}M Na^+ solution in contact with the sodium ion-responsive system would then give rise to a reading of 3·00 on the pH meter, equivalent to pNa = 3·00; a 10^{-4}M Na^+ solution would give a reading of 4·00 on the meter, equivalent to pNa = 4·00; and so on.

Sodium Ion-Responsive Glasses

One of the best known of these is NAS 11–18 described by Eisenman *et al.*[11] This is available commercially from Corning Glass Works, and other sodium ion-responsive electrodes are supplied by Electronic Instru-

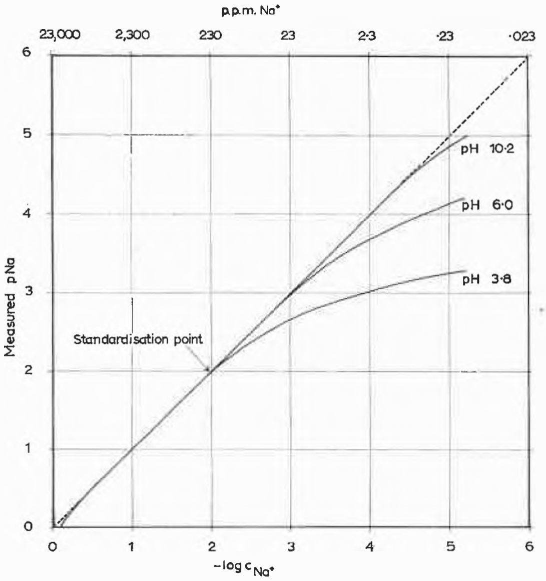

Figure 1a. Typical sodium ion response curves of E.I.L. BH68 and BH104 glasses, showing observed pNa values against $-\log c_{Na^+}$ values for solutions using ethanolamine – HCl buffer medium. System standardised at $\log c_{Na^+} = 2{\cdot}00$

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[11] G. Eisenman, D. O. Rudin and J. U. Casby, *Science 126* (1957) 831.

[12] E. W. Moore and J. W. Ross, *Science 148* (1965) 71.

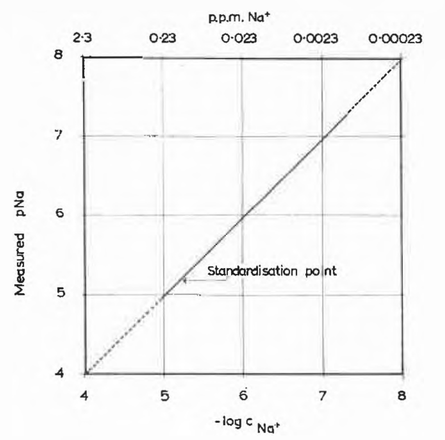

Figure 1b. Response behaviour of BH104 glass in dilute sodium chloride solutions, using saturated ammonia medium, and obtained with the flow-through cell system of the E.I.L. Model 89B (shown in Figure 10). System standardised at 0·1 p.p.m. Na^+

ments Ltd. (U.K.) [BH68 and BH104 glasses][13], Beckman Instruments Inc. (U.S.A.) [type 78178][14] and several European manufacturers.

The response range of E.I.L. BH68 and BH104 glasses is shown in Figure 1.[15] The effect of changing *p*H on the response in a constant sodium concentration solution is shown in Figure 2, where E.I.L. BH 68 and BH104 glasses are compared with NAS 27–4. Bearing in mind that it is the ratio of a_{H^+}/a_{Na^+} that is the important parameter, it can be seen that little *p*H effect is observable below *p*H 7 except at the lowest sodium concentrations. In general it is preferable to maintain $a_{H^+}/a_{Na^+} < 10^{-4}$.[13,14]

The range of response, according to these data, is from approximately M Na^+ to 10^{-5}M Na. In fact this work was not definitive for the dilute solutions, because of background sodium impurities in the medium. Separate studies using pure sodium chloride solutions in an ammonia background have indicated theoretical response even at 10^{-7}M Na^+ (i.e. 0·001 p.p.m.) and possibly weaker, and more recent work discussed below under Plant Applications has confirmed this. Figure 1b illustrates a calibration curve for E.I.L. BH104 glass.

The effect of potassium ions on the sodium ion response of BH 68 and BH104 is shown generally in Figure 3.

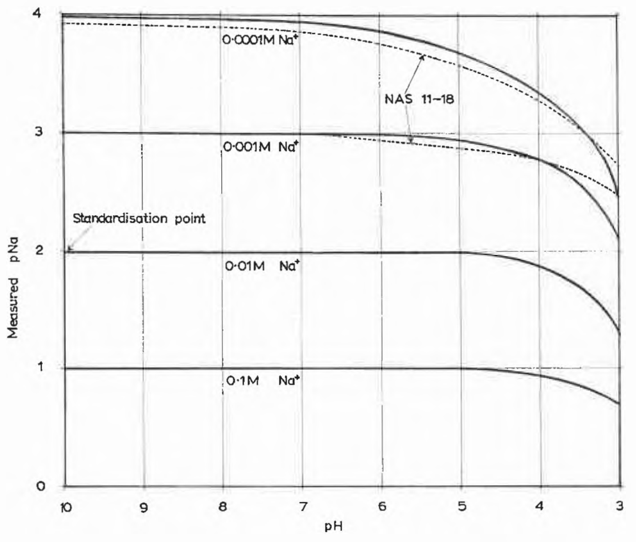

Figure 2. The effect of changing *p*H on apparent *p*Na shown on BH 68 and NAS 11–18 glasses, in solutions having constant values of $-\log c_{Na^+}$ and ethanolamine — HCl background medium. System standardised at $-\log c_{Na^+} = 2{\cdot}00$ at $pH = 10{\cdot}2$

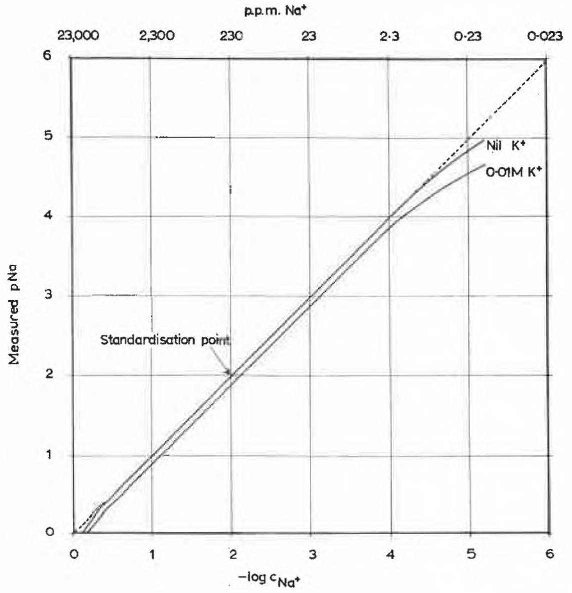

Figure 3. The effect of potassium on observed *p*Na response of E.I.L. BH68 glass, using solutions having ethanolamine — HCl buffer medium at $pH = 10.2$. System standardised at $-\log c_{Na^+} = 2{\cdot}00$ in potassium-free solution

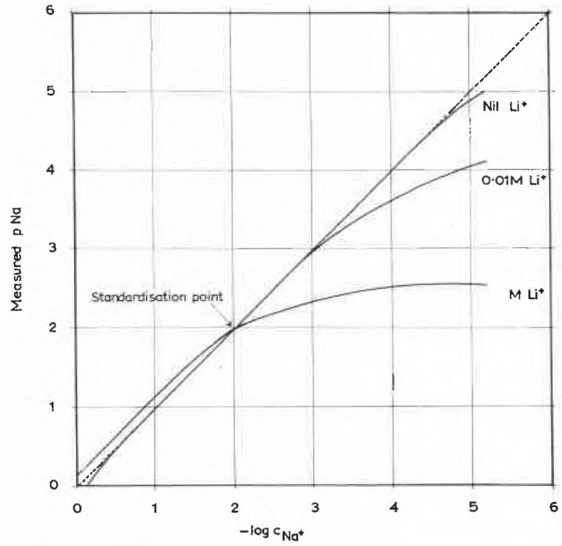

Figure 4. The effect of lithium on observed *p*Na response of BH68 glass, using solutions having ethanolamine — HCl buffer medium at $pH = 10{\cdot}2$. System standardised at $-\log c_{Na^+} = 2{\cdot}00$ in lithium-free solution

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[13] Electronic Instruments Ltd., *Technical Data Sheets 13 and 14.*

[14] Beckman Instruments Inc., Bulletin 7017.

[15] G. MATTOCK, *Analyst 87* (1962) 930.

Although some constant displacement may occur from the values given with pure sodium solutions it has been found[15] that potassium/sodium concentration ratios of up to 100 : 1 for BH 68 and up to 50 : 1 for BH 104 can be tolerated without slope interference beyond the 0·01 *p*Na unit level. These selectivities are better than results obtained by the author with NAS 11–18 glass, for which the equivalent ratio was 10 : 1.

Lithium has a greater effect (Figure 4), only a 10-fold Li^+ excess over Na^+ being tolerable. Alkaline earth metal ions show no effect up to at least 100-fold excess, while anions such as sulphate and phosphate showed no effect (although at phosphate ratios above 50 PO_4^{3-} : 1 Na^+ some deviations occurred which may be attributed to activity coefficient variation).

Potassium Ion-Responsive Glasses

Eisenman *et al.* reported[11] the potassium ion-responsive properties of a glass, termed NAS 27–4 (available from Corning Glass Works), but in the author's hands this was found difficult to fabricate with electrodes. Commercial alternatives are available from Beckman Instruments Inc. (U.S.A. [type 78138][14]) and Electronic Instruments Ltd. (U.K. [type BH 115][13]).

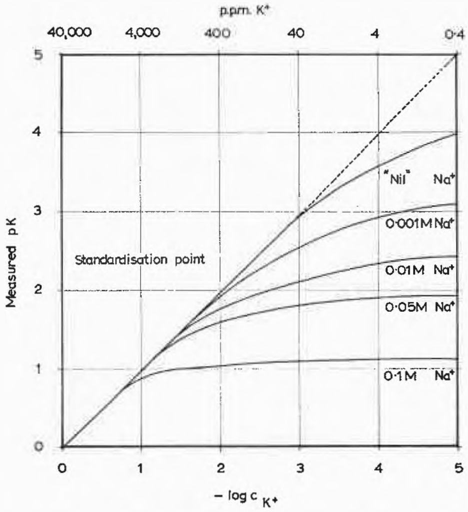

Figure 5. Typical potassium ion response curves of E.I.L. BH 115 glass, showing observed *p*K values against — log c_{K^+} values for solutions using ethanolamine — HCl buffer medium. System standardised at — log c_{K^+} = 2·00. Note that «nil» Na^+ actually represents approximately 0·000 02 M Na^+, present as impurity in the ethanolamine medium

The response range of BH 115[16] is shown in Figure 5, which also includes the effect of various concentrations of sodium. The effective range is down to 10^{-5}M K^+ in the absence of sodium, but the selectivity falls off once the $Na^+ : K^+$ ratio rises above 5 : 1. It should be noted that the «nil» Na curve of Figure 5 actually refers to solutions where the background medium contained about 2×10^{-5}M Na^+ and this may have depressed the response. Also it is quite possible that the ethanolamine medium caused some interference, and consequently these curves may not be entirely definitive. The performance generally is the same with NAS 27–4.

It appears that glasses may improve with ageing, and this is true in the case of Beckman 78137 in its potassium ion response, as reported by Eisenman[17].

The effect of *p*H on BH 115 is shown in Figure 6.

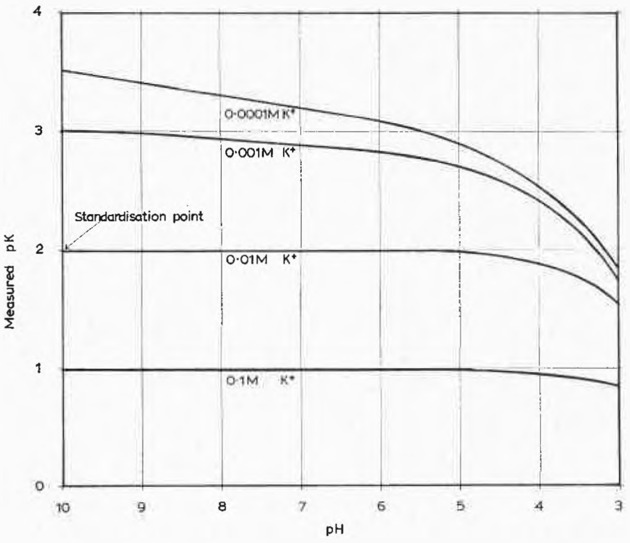

Figure 6. The effect of changing *p*H on apparent *p*K shown by BH 115 glass, in solutions having constant values of — log c_{K^+} and ethanolamine — HCl background medium. System standardised at — log c_{Na^+} = 2·00 at *p*H = 10·2

Ammonium-Responsive Glasses

Ammonium appears to be similar to potassium so far as behaviour with cation-responsive glasses is concerned[14, 15] and certainly BH 115 responds to ammonium ions quantitatively in much the same way as to potassium ions. It is a curious fact that although the degree of sodium ion interference is similar to that for potassium ion response, the presence of sodium in small quantities improves the stability and reproducibility of BH 115 ammonium ion response. Obviously the copresence of potassium and ammonium ions in solution will give rise to mutual interference.

Other Monovalent Cation Responses[18, 19]

Silver. Even *p*H glasses show some slight response to silver ions[20], and BH 68 sodium ion responsive glass shows an even better response to silver than to sodium: Figure 7 illustrates the performance, which is even observable at the low *p*H of 2. Budd[21] has found similarly good silver

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[16] G. Mattock and R. Uncles, *op. cit. 89* (1964) 350.

[17] G. Eisenman, ref. 5, p. 267 and 351.

[18] G. Eisenman, ref. 4, p. 272 and 335.

[19] G. Mattock and R. Uncles, *Analyst 87* (1962) 104.

[20] E. Flater, *Anales Assoc. Quim. Argentina 36* (1948) 117.

[21] A. L. Budd, *J. Electroanal. Chem. 5* (1963) 35.

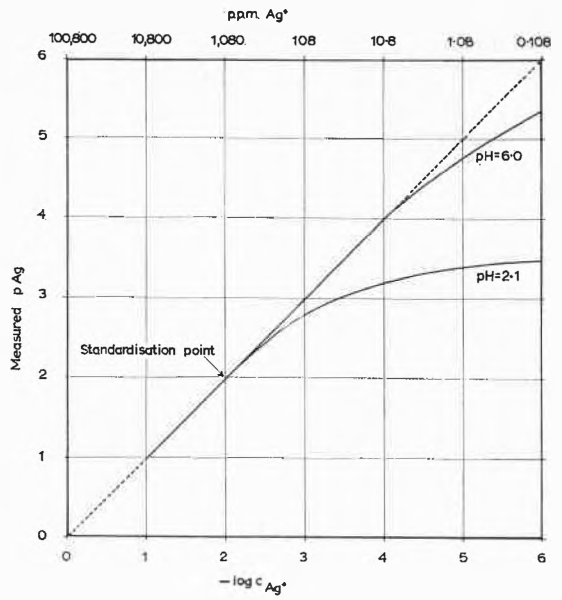

Figure 7. Typical silver ion response curves of BH 68 glass, showing observed pAg values against — log c_{Ag^+} values for solutions using 0·1 M KNO_3 background medium. Systems standardised at — log $c_{Ag^+} = 2{\cdot}00$

responses with both Beckman glasses, 78178 and 78137 and has confirmed that even a 1000-fold excess of Na^+ over Ag^+ shows little effect, while K^+ has no measurable effect.

Lithium. The lithium interference to sodium ion response by BH 68 glass electrodes can be put to use by employing the electrode to respond to lithium ions. Sodium ions of course interfere strongly, but the range M to 10^{-4} Li^+ can be covered in sodium-free solutions (Figure 8).

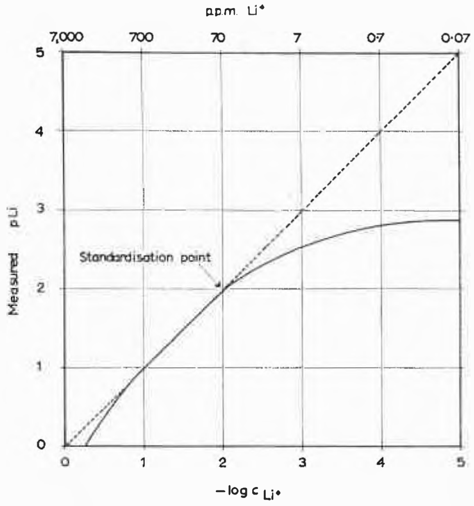

Figure 8. Typical lithium ion response curve of BH 68 glass, showing observed pLi values against — log c_{Li^+} values for solutions using ethanolamine — HCl background medium at $pH = 10{\cdot}2$. System standardised at — log $c_{Li^+} = 2.00$

Thallium. A limited response to thallous ions is shown by BH 68 glass, but the performance is too poor probably to be of other than academic interest.

Divalent Cation-Responsive Glasses

Various attempts have been made to secure a divalent cation response by glasses, and GARRELS, TRUESDELL and their co-workers have recorded[22, 23, 24] some success in the measurement of calcium. The response is not sufficiently specific, however, to be of analytical value in the presence of other alkaline earth metal cations or of alkali metal ions.

It is of incidental interest here to note that a new calcium-responsive electrode, not of a glass type but using a liquid ion exchange system, has been reported by Orion Research Inc. (U.S.A.) and Corning Glass Works (U.S.A.),[25] for which linear response to Ca^{2+} in the range of 10^{-1} to 10^{-4}M Ca^{2+} is claimed, with measurable response between 1 and 10^{-5}M Ca^{2+}, and good toleration towards the presence of 10-fold excesses of sodium and of magnesium over calcium.

Practical Techniques

As with pH electrodes, the technique of using cation-responsive electrodes has a major bearing on the results which can be achieved. It is of even greater importance than in pH measurements, because it is the derived activity or concentration which is of importance rather than the pM value (analogous to pH), and the logarithmic relationship constitutes an inherent limitation on accuracy.

Measuring Cells

The electrodes themselves may take the usual forms developed for pH electrodes, although certain special requirements and in some cases fabrication difficulties have led to special designs, including microelectrodes for *in vivo* biological work.[9, 26, 27, 28]

Reference electrodes for use with the indicator electrodes may be of the usual type, but some care must be exercised in the choice of salt bridge solutions. In most of the work referred to in the previous section the salt bridge solution was simply the background ionic medium, and this formed a simple isolating system between the potassium chloride of the calomel reference electrode and the test solutions. Periodic replacement of the salt bridge solution ensured that potassium did not enter the test solutions as a result of migration through the bridge.

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[22] R.M. GARRELS, M. SATO, M.E. THOMPSON and A.H. TRUESDELL, *Science 135* (1962) 1045.

[23] A.H. TRUESDELL and A.M. POMMER, *Science 142* (1963) 1292.

[24] A.H. TRUESDELL and C.L. CHRIST, *Glass Electrodes for Hydrogen and Other Cations*, Ed. G. EISENMAN, Marcel Dekker, 1967, Ch. 11.

[25] Corning Glass Works, Product Information Sheet, *Corning Calcium Electrode.*

[26] H.D. PORTNOY, *Glass Electrodes for Hydrogen and Other Cations*, Ed. G. EISENMAN, Marcel Dekker, 1967, Ch. 8.

[27] J.A.M. HINKE, *op. cit.*, Ch. 17.

[28] R.N. KHURI, *op. cit.*, Ch. 18.

It is clearly important to prevent ingress into the test solutions of cations which can interfere with the measurement, and barium chloride—or lanthanum chloride—modified calomel electrodes have been suggested[29], since Ba^{2+} and La^{3+} barely interfere with the responses of most of the electrodes. However, the liquid junction potential using these salt bridges is probably large, and may vary significantly from one test solution to another.

Performance

There is a wide discrepancy in the literature on the subject of experimentally achievable reproducibilities.[30] These range for sodium ion-responsive electrodes from ± 2% down to ± 0·2%, and it is valuable to enquire why. The following factors undoubtedly affect performances:

1. The technique used to prepare the glass and to fabricate it into electrodes has a bearing. As with *p*H glasses, the less time used on glass blowing manipulations the better (the temperature of the flame being important), thinner membranes often being superior, and the procedure adopted after blowing is important—the glass should be soaked as soon as possible.
2. The type of storage solution and whether or not the glass is allowed to dry out are significant. Too strong a cation solution strength for storage may be deleterious (0·1 M is a useful maximum), but water should preferably not be employed unless very dilute metal ion concentrations are to be studied. The best storage solution uses the same order of cation concentration as the solutions to be studied.
3. The response range covered and the general solution strength being employed have an important influence. Results are better with the consistent use of an electrode over a narrow concentration range, which probably accounts partially for some of the excellent data reported in clinical work. Linear theoretical response is most easily obtained working over a 2- or 3-decade range.
4. The technique of transfer of the electrode from one solution to another can have a profound effect. If the common practice in *p*H measurement is adopted of rinsing with water between measurements, reproducibilities are very inferior to the use of a transfer technique which involves either wiping dry between solutions, or better through the use of an intermediate wash solution consisting of a portion of the next test solution. Better still is the employment of a flow-through system, where the test solution around the electrode is displaced by the next test solution, without allowing air or other gas to enter the system to cause a phase discontinuity. A suitable simple flow-through arrangement is shown in Figure 9, with which the author has observed marked differences in performance according to whether the electrode was kept in contact with solution all time or whether air was used to displace one solution before another was passed in. (It is interesting to note here that similar though less dramatic effects are observable with *p*H glass electrode systems.)
5. Aged electrodes behave far better than fresh ones, particularly where use has been confined to a relatively narrow concentration range.

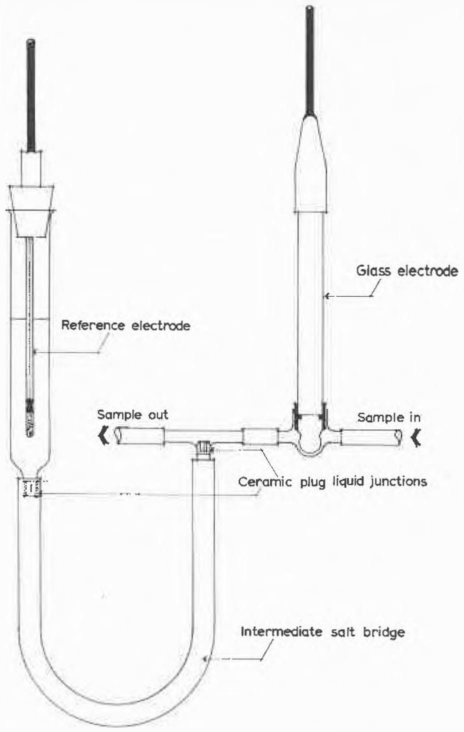

Figure 9. Flow-through cell system for cation measurements, using remote reference electrode with intermiate salt bridge. Note that the salt bridge solution in the reservoir should be at a higher level than the test solution

Factors other than reproducibility are affected by these criteria. Speed of response is certainly dependent on all five factors, and so is stability, for a given type of glass.

Response in Mixed Ion Solutions

The selectivity of a given glass as defined by its selectivity constant *k* may apparently vary according to the concentration regions being studied. This is more apparent with studies over wide concentration ranges and it is sometimes helpful to store the electrode in a mixed ion solution when mixtures are to be studied (*vide* factors 2 and 3 above).

A zero shift effect of as much as 0·1 *p*Na unit may be observed in for example transferring a sodium-ion responsive electrode from a pure sodium solution to one of the same strength but containing some potassium[15]—see Figure 3. However, thereafter no further shift is

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[29] G. Eisenman, personal communication.

[30] See, e. g. ref. [5], p. 351.

usually observed on addition of more potassium. A transient shift may be noted, but the original reading is regained after 2–3 minutes.[31]

Where potassium and sodium determinations are required in a single solution, it is in principle possible to use potassium and sodium ion-responsive glass electrodes to determine the individual ion «activities,» even where substantial interference occurs with one electrode, by solution of a pair of simultaneous equations. Thus

$$E_{Na} = E^0_{Na} + \frac{RT}{F} \ln a_{Na}$$

$$E_K = E^0_K + \frac{RT}{F} \ln (a_K + k a_{Na})$$

where E_{Na} and E_K are experimentally observed values, a_{Na} and a_K are the variables to be determined, k is known from previous studies, and E^0_{Na} and E^0_K are also obtainable from separate measurements with known solution concentrations. FRIEDMAN and BOWERS[32] have devised a computer system for the inline analysis of signals from two such indicator electrodes to give values of a_K and a_{Na}. However the effective use of a simultaneous equation demands that k not be so large as to swamp effective discrimination between different values of a_K at the a_{Na} values obtaining, and that the entire response system be very stable. (It may be noted here again that aged electrodes usually show more stability than new ones.)

Stirring (Flow) Effects

FRIEDMAN and his co-workers noted a streaming effect with their flow-through NAS 11–18 system,[31] and this was also observed by PORTNOY *et al.*[33] The phenomenon is not only seen with Na^+-responsive glasses,[14] but is of greater magnitude with K^+-responsive glasses.[15] PORTNOY *et al.* consider that the variations arising from different flow rates may be traced to the liquid junction.[34] Although this can be a source of error, the author has carried out experiments on capillary measuring systems connected to a reference electrode maintained in a relatively static reservoir, with a recirculating solution, and has observed quite marked flow effects. The rate of stirring of a solution can also affect the observed potential difference between a bulb type sodium or potassium ion-responsive electrode and a commercial reference electrode held in a beaker containing test solution. Substitution of the cation-responsive electrode only by a *p*H glass electrode eliminates the effect, so that it cannot in this case be attributed to the liquid junction.

From the practical point of view, a static system or controlled and preferably low flow rates past the glass electrode should be adopted for measurements.

Applications

A large number of applications has been found for cation-responsive glass electrodes, particularly Na^+-responsive types. Many of these are referenced by EISENMAN[35] and by the author[36] and here it will suffice to indicate only the span of usage.

Biological and Clinical Studies[27, 28, 37–40]

Probably the greatest interest in ion-specific electrodes to date has been shown by biochemists and clinicians, because sodium and to a lesser extent available potassium ion-responsive electrodes offer the possibility of continuous *in vivo* monitoring, as well as rapid *in vitro* measurement. Laboratory measurements can be faster than with a flame photometer, which additionally is not easily adaptable to continuous measurement.

The early *in vivo* work was pioneered by FRIEDMAN and his co-workers (see references [9] and [39] for summaries). HINKE[27] has studied intracellular ion activities using specially constructed microelectrodes, and other studies are summarised by KHURI[28].

In vitro studies have been extensive, particularly of Na^+ levels in blood but also in serum, urine, and cerebrospinal fluid (see references [35, 36] and [38] for reviews).

One recurring feature of many of these investigations is the identification of a small but fairly constant difference in the results compared with those from a flame photometer (see, e.g. references [35] and [36]). It is generally postulated that some sodium ion association is occurring, modifying the free sodium ion level from the total sodium content as given by the flame photometer. However, the point is not wholly proven (see [41]), since it is possible that complicating effects may be occurring at the liquid junction because of the well-known suspension effect which may occur in biological fluids.

Laboratory Analytical Applications[42]

Most of these can be classified as analytical methods for determining sodium and potassium, where advantages over flame photometers are often apparent with certain types of solution. However, studies of micelle

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[31] S.M. FRIEDMAN, J.D. JAMIESON, M. NAKASHIMA and C.L. FRIEDMAN, *Science 130* (1959) 1252.

[32] S.M. FRIEDMAN and F.K. BOWERS, *Anal. Biochem. 5* (1963) 471.

[33] H.D. PORTNOY, L.M. THOMAS and E.S. GURDJIAN, *Talanta 9* (1962) 119.

[34] *Idem, J. Appl. Physiol. 17* (1962) 175.

[35] G. EISENMAN, ref. [5], p. 355.

[36] G. MATTOCK, *Analytical Chemistry 1962* (Proceedings of the Feigl Anniversary Symposium), p. 247.

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formation have been reported[43, 44] and formation constants of complexes have been studied.[45, 46]

Direct electrode measurements offer the attraction of speed in analytical work, provided the results obtained are at an acceptable level of reproducibility. The evidence is that sodium ion-responsive electrodes are in general at least as good as flame photometers and in the analysis of foods, beers, confectionery[36], suspensions[35, 36, 37] and similar systems where the flame photometric method often requires solution pre-treatment or is subject to interference, the electrode method is superior. Even where some inaccuracy results as from sodium interference in potassium ion measurement of beers the simplicity of operation may favour electrode measurement.[36] Natural waters are an obvious choice for quick measurement, and the validity of the results has been well established.[36, 47, 49]

Titration applications have also been reported for the determination of sodium[50] and of potassium[52] as well as studies of the precipitation of potassium, rubidium, caesium, ammonium and silver with calcium tetraphenylboron.[52, 53]

Plant Applications

Sodium ion-responsive electrodes have been used to observe tidal movements in the River Severn in England, to give an indication of periods when relatively salt-free water may be withdrawn for industrial purposes. However, the most recent and interesting application of sodium-ion responsive systems is for the monitoring of extremely low concentrations of sodium in boiler waters. Several years ago the author was concerned in pilot plant studies where Na^+ concentration changes were detected at the 0·002 p.p.m. level, but results were conflicting, and the work was not pursued. More recently, however, Gurney[54] has reported the application of a Beckman electrode for the measurement of Na^+ in the range 0 to 0·01 p.p.m., and has claimed detection at the 0·0001 p.p.m. level.

The main problem in measuring such low concentrations is the fact that *p*H variations can cause swamping interference in these regions, and that in uncontrolled solution environments hysteresis appears to occur. This now appears to have been overcome by Gurney[54] and by Diggens[55]. The latter has incoporated an E.I.L. BH104 glass electrode in an instrument which incorporates a means of stabilising the *p*H and also provides periodic automatic standardisation. The instrument, which is commercially available from Electronic Instruments Ltd. (U.K.) as the Model 89B (see Figure 10), is derived from an earlier continuous cyanide monitor[56] using the same principles. It adjusts and stabilises the *p*H by dubbling ammonia through a sample drawn continuously into the flow type measuring system by means of a peristaltic pump, and can alternatively draw in a standard sample with subsequent automatic re-setting of the electrical zero if any electrode drift has occurred since the previous standardisation. By maintaining this highly controlled environment it has been found possible to monitor over three decades of Na^+ concentration: nominal 0·0001 to 0·001 p.p.m., 0·001 to 0·01 p.p.m., and 0·01 to 0·1 p.p.m. A standard deviation of ± 0·001 p.p.m. has been found in reproducibility tests, corresponding to ± 0·005 p.p.m. at the 95% confidence level. This system has already been successfully applied in pilot trials, particularly in detecting Na^+ breakthrough from ion exchange mixed resin beds, which occurs before silica breakthroughs can be detected. In this application its high sensitivity has permitted extended use of mixed beds for producing very high purity water, which hitherto had been under-run to avoid the possibility of undetected trace breakthrough. It appears[55] from tests on the purest available water that the system can discriminate at the 0·0002 p.p.m. Na^+ level, but the fundamental limitation on further study lies in the fact that even the best ion exchange resin systems may produce water containing this amount of sodium.

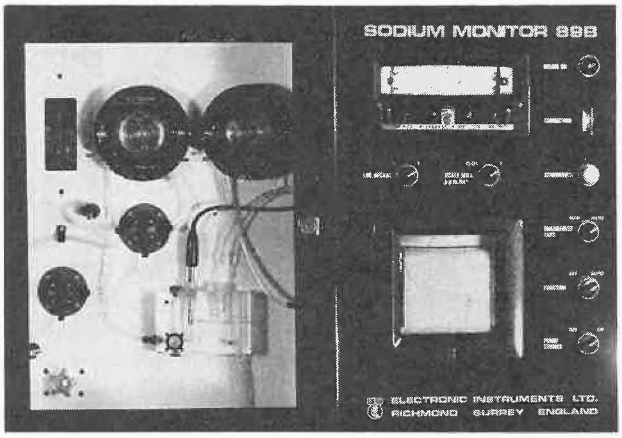

Figure 10. The E.I.L. Model 89B sodium ion monitor, incorporating threee decade response to sodium ion concentration: close-up view of chemical and instrument panels

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Other Methods of Specific Ion Measurement

A final reference can be made to methods of measuring particular ions in solution other than by glass electrodes. Ion exchange resins have been used[25, 57], and other permselective systems based on impregnation of a binding or supporting medium with a suitable salt have been investigated by several workers. **Tendeloo** and his co-workers[58, 59] examined the possibilities of using paraffin and polystyrene membranes impregnated with salts of the cations of interest, but the results were of limited practical usefulness; **Fischer** and **Babcock**[60] also used a paraffin binder. **Gregor** and **Schonhorn**[61] used multilayers of alkaline earth salts of long chain fatty acids held between two halves of a cracked glass slide.

More recently **Pungor** and his co-workers[62, 63] have examined the response properties of sparingly soluble inorganic salts dispersed in silicone rubber membranes for measurement of anions. Silver iodide, for example, has been used for iodide measurements, and barium sulphate for sulphate measurements, although silver chloride was found unsatisfactory for chloride measurements. Strongly basic exchange resins dispersed in silicone rubber were also studied, and measurements of sulphate and chloride made. Sulphates were found to be measurable down to 10^{-6} M, and chloride, down to 10^{-4} M. Phosphate and chloride were found to interfere with sulphate measurement by the barium sulphate system. Cations have also been studied, e.g. nickel using nickel dimethylglyoxime precipitate.[64, 65]

Rechnitz *et al.* have recently examined the iodide-sensitive system and find response down to 10^{-7} M concentrations, with relatively small interference by sulphate, phosphate and chloride anions, and independence of the nature of the cations in dilute solutions.[66] However, the response was found to be rather slow, times of the order of four minutes being necessary to achieve reasonably stable potential values.

Reflecting on the published literature on membrane systems, it would seem to the author that further studies could valuably be made on the resistance of these electrodes to poisoning, e.g. by adsorption. One of the significant practical advantages of glass electrodes is their applicability in a wide of chemical conditions, and for real effectiveness in industrial and biochemical spheres a membrane electrode must be able to tolerate a variety of poisoning agents.

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