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RECOMMENDATIONS FOR THE DETERMINATION OF pH IN SEA WATER AND ESTUARINE WATERS

Prepared for publication by

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Recommendations for the determination of pH in sea water and estuarine waters

The problems of the measurement of the operational pH in sea water and variable ionic strength media estuarine waters are reviewed and methods are recommended by which reproducible values can be obtained.

INTRODUCTION

pH is the most commonly measured chemical parameter in natural waters and knowledge of pH is necessary for the understanding of speciation of trace elements in natural waters which include fresh waters, estuarine waters and sea water. Attention will be directed here to sea water and estuarine waters, since fresh water has been the subject of a recent recommendation (ref. 1). Studies on natural waters constitute some of the few situations where pH is required to have a fundamental meaning, in terms of hydrogen ion activity or concentration. The interpretation of the operational pH measurement raises the fundamental theoretical problem of the immeasurability of a single ion activity. However, before any interpretation can be contemplated, the ability of the measuring system to furnish sufficiently reproducible pH values must be established.

The use of the operational definition of pH (refs. 2,3) assumes that the liquid junction potential remains constant; any deviation from this condition will reduce the certainty of the pH(X) values obtained and make any subsequent interpretation of these data meaningless. Problems associated with the reproducibility of the liquid junction potential constitute the most difficult obstacle in the interpretation of pH. It has been demonstrated (ref. 3) that poor reproducibility of pH data of different glass-reference electrode pairs in estuarine samples was a function principally of the commercial reference electrode and even nominally identical electrodes gave differing results.

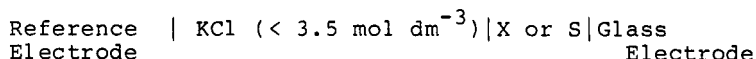
Measurement of pH in sea water has received extensive attention (refs. 4,5). The theoretical difficulties of pH measurements in sea water are increased by the high ionic strength (0.7 mol dm^{-3}) although for some purposes, it is possible to treat sea water as a constant ionic strength medium so the activity coefficients can be taken as invariant. To aid marine pH measurements, synthetic sea water buffers of comparable ionic strength and composition have been developed in an attempt to reduce the residual liquid junction potential between the sample and the calibration solution. The virtues of the various scales available for sea water pH measurements have been critically reviewed recently (refs. 5-7) and will only be outlined here.

pH SCALES

The notional definition of pH in terms of hydrogen ion relative activity

$$\text{pH} = - \lg a_{\text{H}} \quad (1)$$

cannot contribute directly to practical measurements because of the immeasurability of a single ion activity. Instead an operational approach is (ref. 8) adopted of comparison of the sample solution with a standard buffer of assigned pH(S) in the (operational) cell



The value of pH(X) is given by

$$\text{pH}(X) = \text{pH}(S) + \{E(S) - E(X)\}/gT - \{E(JS) - E(JX)\}/gT \quad (2)$$

where $g = (R/F)\ln 10$ and $E(S)$ and $E(X)$ are the cell potential differences in the standard and test solutions respectively, and $E(JS)$ and $E(JX)$ are the liquid junction potentials with standard and test solutions. The two cells have the same temperature throughout, and the same glass and reference electrodes. The operational pH is defined by setting to zero the term involving a change in liquid junction potential when X is replaced by S. The pH(S) values of the IUPAC standard buffers (ref. 9) are assigned by measurements on cells without liquid junction or alternatively (and the difference is insignificant for the present purpose) to a single standard buffer. If the sample and standard buffer differ in ionic strength, as in the case of sea-water and estuarine-water samples, then the change in liquid junction potential (the residual liquid junction potential) manifests itself as an error in the determined pH(X) value and makes any interpretation of the value in terms of hydrogen ion activity or concentration fraught with difficulty. A residual liquid junction potential error of 1 mV is equivalent to an error of 0.017 in pH at 25 °C.

A pH scale with a clearer conceptual significance can be defined (ref. 5,6) in terms of the total hydrogen ion concentration

$$\text{pH(SWS)} = -\lg m_{\text{H}}^{\text{T}} \quad (3)$$

where m_{H}^{T} is the sum of the free and complexed hydrogen ion molalities in the sea water sample.

The pH(SWS) scale is based on synthetic sea water containing sulphate and buffered with 2-amino-2-(hydroxymethyl)-1,3-propanediol [tris(hydroxymethyl)aminomethane (Tris)]. Owing primarily to the formation of the hydrogen sulphate ion, the total hydrogen ion concentration differs from the concentration of free, uncomplexed hydrogen ion. The pH(SWS) of the Tris reference buffers is determined by titration with hydrochloric acid to a final pH of 3. By matching the ionic strength of the saline standards to sea water the residual liquid junction potential is minimised. If sea water rather than pure water is considered as the solvent, then the activity coefficients of components contributing less than 1% of the total ionic strength of the medium will be close to unity. The pH(SWS) scale is therefore equivalent to a hydrogen ion activity scale in the sea water medium.

For estuarine samples the concept has been extended (ref. 10) to cover the salinity range 10 ‰ to 40 ‰ in 5 ‰ intervals and the assigned values for the Tris reference buffers in fluoride-free sea water diluted with distilled water to the appropriate salinity can be summarised (ref. 11) by equation (4)

$$\text{pH(SWS)} = (2559.7 + 4.5 S)/T - 0.5523 - 0.01391 S \quad (4)$$

where S is the salinity in ‰ and T is in Kelvin.

By matching the sample salinity to that of the standard buffer the residual liquid junction potential is minimized. However, this raises the question of how well the whole salinity range can be covered by a small number of buffers. With the pH(SWS) scale, as well as with the IUPAC pH scale, the variation of the residual liquid junction potential contribution, both with reference electrode type and time, constitutes an important factor which mitigates against high reproducibility and repeatability of measurements.

Millero (ref. 12) has recently re-evaluated the data on the dissociation of Tris buffers with special reference to the provision of reliable pK^* values at low salinities. According to this

$$\text{pH(SWS)} = \text{pK}_{\text{T}}^* - (9.73 \times 10^{-5} S - 6.988 \times 10^{-5} S^2) m_{\text{Tris}} \quad (5)$$

where $\text{pK}_{\text{T}}^* = -22.5575 + 3477.5496/T + 3.32867 \ln T$

$$-(2.3755 \times 10^{-2} S - 6.165 \times 10^{-5} S^2)/T + 6.313 S \quad (6)$$

and m_{Tris} is the molality of the Tris buffer. Equation (6) is said to be more reliable than equation (4) at salinities below 20 ‰.

Footnote: ‰ = parts per thousand

A third scale for sea water has been devised based on the free hydrogen ion concentration in synthetic, sulphate-free sea water buffers (ref. 13) but this cannot be determined by simple titration and is evaluated instead from cells without liquid junction. We shall not consider this scale further here except to point out that it can be related to the other two scales (ref. 6,7).

The relations between the pH(IUPAC) and pH(SWS) scales is through the quantity f_{H}' which is a function of the activity coefficient of the hydrogen ion in X and the residual liquid junction potential (ref. 2) and is capable of direct measurement for particular glass-reference electrode pairs as shown in the next Section.

PROCEDURES FOR MEASURING pH OF SEA WATER AND ESTUARINE WATERS

pH measurements in sea water are most commonly made using electrode pairs standardised in standard reference buffers. These buffers retain their popularity largely because certified materials are available. In contrast, saline buffers required for the standardisation of electrode pairs on the pH(SWS) scale have to be prepared individually using a rather tedious procedure. However, measurements relative to standard reference buffers can be subject to systematic errors approaching 0.1 in pH (refs. 3,4) because of variations in the residual liquid junction potential (see equation 2) caused by differences in reference electrode design. To ensure that pH measurements made relative to standard reference buffers are strictly comparable, it is necessary to estimate the variable contribution made by the liquid junction potential. This can be done experimentally by determination of the parameter f_{H}' which may be defined by the equations:

$$\lg f_{\text{H}}' = \lg \gamma_{\text{H}}^{\text{T}} + [E(\text{JS}) - E(\text{JX})]/gT \quad (7)$$

$$= - \lg m_{\text{H}}^{\text{T}} - \text{pH}(\text{X}) \quad (8)$$

The conventional hydrogen ion activity coefficient ($\gamma_{\text{H}}^{\text{T}}$) is characteristic of the sea water medium only, so that differences between f_{H}' values determined for different electrode pairs will provide a direct indication of the systematic errors in pH associated with their use. The f_{H}' value can be determined experimentally by two methods:

a) In the acid titration method (ref. 10) a sea water sample of the appropriate salinity is first adjusted to pH 3 to 4 by addition of strong acid, and the carbon dioxide released is purged off. Subsequent aliquots of acid will then provide known increments of m_{H}^{T} , so that equation (8) can be written as

$$10^{-\text{pH}(\text{X})} = f_{\text{H}}' \cdot m_{\text{H}}^{\text{T}} \quad (9)$$

A plot of the left hand side of equation (9) against m_{H}^{T} gives a straight line of slope f_{H}' .

b) In the buffer method (refs. 3,4), an electrode pair standardised in standard reference buffers is used to determine the pH of a saline buffer of the appropriate salinity. The measured pH of the saline buffer (pH(X)) and the pH assigned on the total hydrogen scale (pH(SWS), equation 3) are then related to give

$$\lg f_{\text{H}}' = \text{pH}(\text{SWS}) - \text{pH}(\text{X}) \quad (10)$$

This is clearly the simplest procedure experimentally, but it does require the preparation of saline buffers according to the procedure outlined by Hansson (ref. 10). Since the salinity of sea water rarely varies by more than $\pm 1\%$, the direct use of saline buffers to measure pH(SWS) is not subject to significant systematic errors due to variations in liquid junction potential. In addition, the electrode response is more rapid when the electrodes are transferred between the buffer and saline samples if saline buffers rather than standard reference buffers are used. The Joint Panel on Oceanographic Tables and Standards (JOPTS) Subcommittee on Carbon Dioxide has consequently recommended that the saline buffer procedure be adopted for sea water measurements, and that the use of IUPAC standard reference buffers for this purpose should be discontinued. For this recommendation to become effective, certified reference materials must become available. In the meantime, all measurements made relative to standard reference buffers should be accompanied by measurements of the f_{H}' values at the appropriate temperature and salinity for the electrode pair employed.

When estuarine waters are measured, the residual liquid junction potential of the electrode pair will contribute significant systematic errors to the measurement whether the electrodes are standardised in standard reference buffers or saline buffers. These errors could in principle be avoided by using a series of saline buffers to cover the salinity range encountered, but in practice this would be unacceptably complicated. For electrodes standardised in standard reference buffers, the systematic errors can be assessed by measuring f_{H}' values over the appropriate salinity range as described above.

If a saline buffer is to be used, a salinity in the middle of the estuarine range (between, say, 15 and 20 ‰) would be appropriate. The systematic errors incurred by the use of this single buffer could then be estimated by measuring the potential difference of the electrode pair in a series of saline buffers spanning the appropriate salinity range. The difference between the pH assigned to a particular buffer by equation (4) (pH(SWS)) and the pH measured by the electrode pair in that buffer relative to the selected standard (pH(SWS)*) is given by (ref. 3)

$$\Delta\text{pH} = \text{pH}(\text{SWS}) - \text{pH}(\text{SWS})^* \quad (11)$$

$$= -\lg [\gamma_{\text{H}}^{\text{T}}(\text{S})/\gamma_{\text{H}}^{\text{T}}(\text{X})] - [E(\text{JS}) - E(\text{JX})]/gT \quad (12)$$

The first term only depends on the composition of the saline buffer and is independent of the electrode pair used in the measurement. The pH values obtained can therefore be used for assessing the systematic errors in the use of a single saline buffer over the whole estuarine salinity range. The measurement of f_{H}' and ΔpH values for pH cells containing a range of conventional reference electrodes (ref. 3) indicates that, although there is good consistency in measurements made with individual electrode pairs (standard deviation < 0.02 in pH), systematic errors approaching 0.1 in pH can be observed between different electrode pairs irrespective of the standard buffers used. Clear differences were observed between various types of commercial electrode, and the f_{H}' and ΔpH values varied with time and between nominally identical commercial electrodes of the same design. The differences in behaviour between various electrode pairs were, in general, more pronounced if the electrodes were standardised in 1:1 phosphate buffer rather than saline buffer, and the time for a steady reading to be reached was often longer in the standard reference buffer. However, the differences between the performance of the electrode pairs in IUPAC standard reference and in saline buffers were small in comparison with the large differences observed between different reference electrodes on both pH scales.

It is clear that thermodynamically useful pH measurements could be obtained with considerably less effort and enhanced reliability if the stability and reproducibility of liquid junction potentials could be increased. Culberson (ref. 5) developed a flow cell for sea-water measurements, which incorporated a renewable free diffusion liquid junction, formed within a vertical capillary tube. This cell permits measurements to be made on small, static sample volumes (5-20 cm³) injected into the cell. Lack of solution agitation does not introduce appreciable errors in these concentrated solutions. Culberson's cell was based on a Beckman micro-blood pH assembly. It initially used a palladium annulus liquid junction (ref. 14) but this caused long equilibration times in sea-water samples after calibration in standard buffers and would be unacceptable for anoxic samples, where redox reactions may occur at the metal junction causing spurious potentials. Subsequent versions of this cell have incorporated a renewable free diffusion liquid junction formed in a capillary tube. Culberson's cell was modified (ref. 3) for estuarine pH measurements at varying ionic strengths. In addition to a significant improvement in reproducibility and a considerable reduction in the systematic errors associated with pH measurements across the salinity range, the flow cell has the additional practical advantages of rapid and reproducible pH response under field conditions where the salinity varies from sample to sample. The cell retains its standardisation for several days to within ± 0.002 in pH in the laboratory and to ± 0.01 in pH in the field.

The practical design and use of the flow cell differs in some details from its use in fresh waters (ref. 1). It is not so important in a high ionic strength medium to have the T-junction close to the glass electrode. Neither has it been found necessary to use a flowing solution. The buffer capacity of sea water is much greater than fresh water and so contamination problems

associated with the glass electrode are reduced. A useful sampling technique (ref. 3) for flow cell measurements was the following: Samples are taken in 25 ml disposable plastic syringes taking care to avoid cavitation and undue gas exchange; any air above the sample is dispelled from the syringe before storage and the syringe closed with a close fitting Luer cap. The sample was applied to the flow cell directly through a three-way stopcock to assist venting any air bubbles to waste. The sample may be left stationary or slowly flowed.

The flow cell was used (ref. 3) to measure the pH of saline buffers on the pH(SWS) scale. Differences were calculated between the values with reference to the 20 ‰ saline buffer and the true values given by equation (4). Much smaller systematic errors were found than when commercial reference electrodes were used. Only at 5 ‰ and 35 ‰ were the errors approaching 0.02 in pH, thus the use of a free diffusion junction significantly reduces the variability of the measurements. The flow cell was found to be capable of producing good quality estuarine water data under field conditions (ref. 3).

RECOMMENDATIONS FOR pH MEASUREMENTS

If precision of ± 0.01 in pH measurements in estuarine water samples is required, it is recommended that:

1. The sample is at a constant, controlled temperature.
2. Electrode pairs should be standardised on either the pH(IUPAC) or pH(SWS) scales but the commercial availability of standard reference materials for the former makes this more convenient in practice for the time being.
3. The electrode pair should be characterised over the appropriate salinity and temperature range to assess the systematic errors associated with variations of liquid junction potential and hydrogen ion activity coefficient. This requires the determination of f_{H^+} or ΔpH values as appropriate, and the conversion factors should be published along with the measured pH(X) or pH(SWS) values.
4. Considerable advantages ensue from using a reference electrode design with renewable liquid junction such as the Culberson cell. By this means a precision of ± 0.01 in pH is obtainable on a routine basis and standardisation is only necessary at the beginning and end of a working day.

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