Pure & Appl. Chem., Vol. 57, No. 6, pp. 877–886, 1985.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

RECOMMENDATIONS FOR THE DETERMINATION OF pH IN LOW IONIC STRENGTH FRESH WATERS

Prepared for publication by

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Recommendations for the determination of pH in low ionic strength fresh waters

The problems of the measurement of the operational pH in low ionic strength media such as fresh waters are reviewed and a method is 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 a prerequisite for the understanding of the distribution of trace elements in their various forms in natural waters. The designation 'natural waters' includes fresh waters, estuarine waters and sea water. Attention will be directed here to fresh waters, since sea water has received considerable attention recently (refs. 1-3). Studies on natural waters constitute some of the few situations where pH is required to have a more fundamental meaning, in terms of hydrogen ion activity or concentration. In the majority of pH measurements, especially in industrial control processes, an arbitrary, but reproducible scale of numbers is all that is required. The interpretation of the operational pH measurement raises a fundamental theoretical difficulty, namely 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. To demonstrate the large effect of an error in observed pH on calculated parameters, the carbonate concentration and the rate of oxidation of Fe(II) in a freshwater sample at different observed pH values are given in Table 1. The 'correct' pH was taken as 7.000 and the percentage error in carbonate concentration and the rate of oxidation for 'observed' pH values of 7.001, 7.010 and 7.100 was calculated. The carbonate concentration is given by (ref. 1)

$$[CO_3^{2-}] = \frac{CA.\ K'_2 / a_H}{1 + 2\ K'_2 / a_H}$$

where K'_2 is the apparent second dissociation constant for carbonic acid ($pK'_2 = 10.28$), and CA is the carbonate alkalinity, chosen as 0.001 equiv dm^{-3}. The rate of oxidation of Fe(II) is given by (ref. 4)

$$\frac{d\,[Fe(II)]}{dt} = k[Fe(II)].[OH^-]^2\ pO_2$$

$$= k[Fe(II)]\ K_W^2\ \gamma_H^2\ pO_2/a_H^2$$

where $k = 2 \times 10^{13}$ min^{-1} atm^{-1} mol^2 dm^{-6};

$pO_2 = 0.2$ atm; $[Fe(II)] = 10^{-4}$ mol dm^{-3} and $\gamma_H = 0.97$.

With pH = - log a_H, the percentage errors are shown in Table I.

The pH of natural waters is often controlled by the carbonate system. In waters with high calcium and bicarbonate content it may be above pH 8 whereas waters subjected to high partial pressure of carbon dioxide, such as ground waters, may be dominated by carbonic acid and have pH as low as 5. For surface waters, the range is pH 6.5 to 8.5. The dissolution of silicate minerals can cause pH to increase to values approaching 10, and this value may be achieved by bicarbonate waters when carbon dioxide is removed by photosynthetic activity. pH values below 4.5 are usually due to the presence of free mineral acids or from oxidation of sulphides by microbially mediated reactions. Fe(III) and Al(III) salts are sometimes responsible for conferring acid properties on a water and organic acids from degraded biological matter may have the same effect (ref. 5).

TABLE 1. Effect of an error in pH on calculated parameters

pH	$[CO_3^{2-}]$ 10^7 mol dm^{-3}	$-\frac{d[Fe(II)]}{dt}$ 10^6 mol dm^{-3} min^{-1}	% error in $[CO_3^{2-}]$	% error in $-\frac{d[Fe(II)]}{dt}$
7.000	5.242	3.84	-	-
7.001	5.255	3.86	0.25	0.47
7.010	5.365	4.02	2.35	4.71
7.100	6.598	6.09	25.9	58.5

FUNDAMENTAL PROBLEMS

The theoretical concepts and difficulties regarding pH and its measurement and interpretation are well documented (ref. 6,7), as are the less than ideal behaviour of glass electrodes and reference electrodes with liquid junction (ref. 8). The glass electrode exhibits errors in its response at low pH (the acid error) and at high pH in the presence of alkali metal ions (the alkaline error), but these deficiencies are unlikely to affect pH measurements in freshwater samples. However, reports of glass electrode errors in very dilute solutions of low buffer capacity and intermediate pH (ref. 9) must be considered relevant for assessing the performance of glass electrodes in freshwaters.

The use of the operational definition of pH (refs. 6,7) 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. Previous work in this connection (ref. 10) has demonstrated 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.

The limitations of the widely employed dip pH measurements in poorly buffered solutions using commercial electrodes can be summarised as:

1). Contamination

The glass electrode has been found to introduce appreciable quantities of contaminants into very dilute, poorly buffered solutions. Insufficient evidence exists to determine exactly the origin of these contaminants. However, two possible explanations can be given: either they arise as a result of surface characteristics of the glass electrode (desorption, dissolution, etc.,) or from insufficient washing of the glass electrode. This latter possibility is thought to be of lesser importance, as carefully conducted studies (refs. 9,11) have shown that an adequate and optimum wash time is 10-15 s, with a solution of composition and temperature similar to the test solution. However, since no attempt was made to remove the superficial washing solution from the electrode surface, carbon dioxide contamination of this solution may occur and lead to errors, but the short exposure of the electrodes to the atmosphere renders this rather unlikely.

2). Stirring Errors

Some dissolution of the glass occurs and so solution agitation is necessary to prevent the resulting contaminants remaining in the vicinity of the glass membrane and changing the measured pH. The solution is usually agitated by stirring. However, this can have several detrimental effects.

a) Stirring frequently produces a "stirring shift", i.e. the potential difference in the stirred solution is not the same as in the stationary solution and this effect is neither repeatable nor reproducible. Superimposed on this potential shift, which may be several mV (ref. 12), are

varying amounts of random "stirring noise". Both of these effects are enhanced at low ionic strengths and detract from the precision of the measurement. Uncertainty exists as to which is the "correct" reading, the stirred or the stationary value. These problems have encouraged some workers, e.g. Galloway and Cosby (ref. 13), to make pH measurements in very dilute solutions on stationary samples. However, this cannot be recommended because of the problems of dissolution of the glass surface. Stirring effects have been referred to as "streaming potential" effects (refs. 13,14) but some doubt exists as to whether this is the true explanation. A streaming potential will arise as a result of a solution of low conductivity flowing through a very narrow capillary, where the solution and the walls of the capillary can have opposite charge. In a dip measurement, a streaming potential could occur due to the dilute sample solution moving within the porous material at the liquid junction, (the diameter of the pores being very small). This explanation would account for the absence of stirring effects with sleeve electrodes and the reduced effects experienced with J-type junctions, where dilution of the salt bridge within the ceramic plug would probably be less than for commercial dip electrodes. An alternative explanation of stirring effects can be obtained by considering the structure of the liquid-liquid interface, as seen by Schlieren photography (ref. 15). Stirring results in a continually changing interfacial area and hence junction geometry and liquid junction potential. Junction geometry will also be affected by leak rate of the bridge solution. The absence of stirring effects in sleeve electrodes observed (ref. 15) could be explained by their generally higher leak rate and thus lower dilution of the salt bridge solution at the liquid junction. (In contrast to this, Midgley and Torrance (ref. 16) observed that their sleeve electrodes exhibited "gross shifts" in potential and were very susceptible to stirring noise).

b) Stirring also perturbs the solution composition by enhancing gaseous exchange across the solution-atmosphere interface. Any loss or gain of dissolved gases, in particular carbon dioxide , is unacceptable in a very poorly buffered solution. Cells designed to minimise gaseous exchange by enclosing the sample may suffer additional problems from desorption or adsorption of ions from the walls of the cell.

3). Restrained liquid junctions

Contamination of the porous restraining material at the liquid junctions of commercial reference electrodes by test and buffer solutions reduces the equitransference of the salt bridge . Except for some sleeve junctions, facilities do not exist for readily renewing the liquid junction and thus removing the contaminents. Dilution of the concentrated salt bridge solution is detrimental to electrode performance as variation in the liquid junction potential may increase as the concentration of the salt bridge decreases (ref. 8). The disadvantages of restrained liquid junctions , that is those that use a physical restraint to prevent the flow of solution, were recognised seventy years ago (ref. 17). Despite these limitations, they have remained popular due to their ease of use and a general lack of understanding of the importance of reference electrodes within the electrochemical cell. The suitability of dip electrodes for precise measurements was also questioned by Guggenheim (ref. 18), who called them "indefinite structure" junctions; he found these junctions gave unstable and irreproducible potentials.

4). Contamination arising from the salt bridge

In the majority of commercial reference electrodes, the denser salt solution overlies the test solution, encouraging convective flow and reducing the ability of the electrode to form a stable liquid junction. High flow rates can produce unacceptible levels of contamination from the salt bridge, especially from sleeve electrodes, with either freshly formed junctions or a poorly fitting sleeve.

5). Circuit disruption

All dip measurements suffer from time lags, due to the making and breaking of the high impedance electrode circuit; this can affect the speed of response of the electrode (ref. 19).

The use of existing commercial reference electrodes would therefore appear to be unsatisfactory for obtaining pH data suitable for subsequent interpretation. More importantly, the low reproducibility of the electrodes makes intercomparisons of pH data collected by different systems meaningless.

MEASUREMENTS IN RELATED MEDIA

The measurement of pH in fresh water has received relatively little attention and no suitable accepted method exists for obtaining high precision data. However, other very dilute, poorly buffered solutions, mostly of industrial interest, have been examined. The recommendations for these pH measurements and pertinent observations will now be discussed, bearing in mind that requirements for freshwater and industrial situations may differ.

Midgley and Torrance have examined the performance of commercial reference (ref. 16) and glass (ref. 20) electrodes in boiler feed waters of very low conductivity. They showed that commercial reference electrodes suffered from poor reproducibility and could cause variations in the potential difference of the cell in flowing solutions. Glass electrodes exhibited (ref. 20) large pH errors in stationary, poorly buffered solutions. Various other workers have (refs. 21,22) indicated that some form of agitation is essential at the glass-solution interface, if reproducible pH data are to be obtained.

Various designs of flow cell have been recommended for use in very dilute solutions (refs. 21-23). However, these have either used very high flow rates, or the cell dimensions were large, requiring large sample volumes, which render these designs unsuitable for laboratory pH measurements on freshwaters. To minimise dilution of the salt bridge solution at the liquid junction, it has been suggested that high leakage rate reference electrodes should be used (ref. 23). This method is also unsuitable for freshwater pH measurements.

In contrast to freshwater measurements, sea water pH measurement has received extensive attention (refs. 14, 1-3). 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 (ref. 3) so the activity coefficients can be taken as invariant. To aid marine pH measurements, sea water buffers of comparable ionic strength and composition have been developed in an attempt to reduce the 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 by Culberson (ref. 2). To avoid many of the difficulties of pH measurements in sea water (gaseous exchange, contamination of the porous material at the liquid junction, etc.,), Culberson (ref. 2) has developed a pH assembly, incorporating a renewable free diffusion liquid junction formed within a vertical capillary tube. This cell permitted measurements to be made on small, static sample volumes (5-20 cm^3) injected into the cell. Lack of solution agitation did 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. 24), but this caused long equilibration times in marine samples after calibration in standard buffers and naturally 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. A similar cell has been used in Newcastle and at Plymouth for estuarine pH measurements at varying ionic strengths (ref. 10). Mattock has described (ref. 25) a similar flow cell, but this used a ceramic plug junction, so many of the problems described above will occur.

MEASUREMENT IN FRESHWATERS

The Culberson cell was adapted to a flowing system (ref. 26) thus preventing the accumulation of contaminants around the glass electrode. This system permitted the liquid junction to be moved closer to the glass electrode to reduce the overall cell resistance, without risking KCl contamination of the sample.

Operation of the Flow cell

The flow cell (ref. 26) is shown in Fig.1. It was mounted in a polyacrylate box which provided physical protection and acted as a water jacket. The micro glass electrode was fitted with a special glass sleeve, mated closely with a corresponding socket. A sharp T-junction was found to be critical to the formation of a reproducible liquid junction and to the fast response of the cell. This was constructed by forming a pin-hole in the wall of a capillary tube using a hot tungsten wire and sealing a second capillary tube around the hole to form a T-junction.

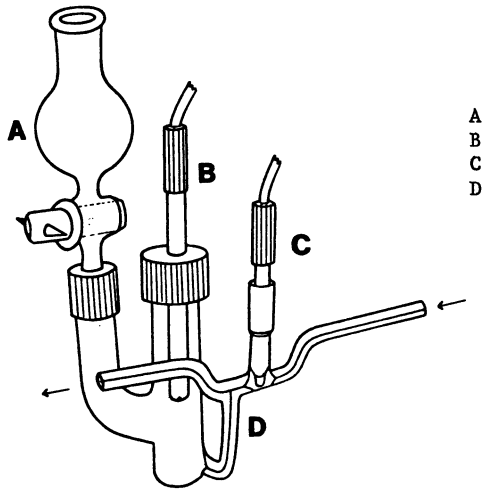
In the previous use of this type of pH assembly by Culberson (ref. 2) and Butler et al. (ref. 10), samples from syringes were injected into the flow cell and hence measurements were made on static solutions. For solutions of very low ionic strength, flowing the solution is a necessity to remove dissolution products and remains of calibration solutions from the surface of the glass electrode. The simplest, and by far the most effective method of obtaining a stable flow was by syphoning directly from the sample bottle. This method was compatible with the requirement that the pH assembly be suitable for field use. For this particular flow cell, no flow dependence was observed in the flow range 1-4 cm min^{-1}. At lower flow rates, drifts in potential were observed. These were attributed to poor solution flushing of the glass electrode.

A fresh liquid junction is readily formed by releasing KCl from the reservoir illustrated in Fig. 1. The liquid junction was clearly visible a few mm below the T-junction, thus maintaining the essential requirement of cylindrical symmetry for this type of junction (ref. 18). The formation of a fresh junction is not always necessary for solutions of similar composition. However, it should be standard practice to reform the junction for each solution, as this process generally disturbed the cell potential difference by a maximum of 1-2 mV for less than 20 s.

To demonstrate the suitability of this flow cell for obtaining high quality pH data for geochemical investigations, the pa_H and pH values of diluted standard reference buffers were determined (Table 2). This shows that excellent agreement is possible between measured pH values and pa_H values from cells without liquid junction.

Comparison of pH measurements made using the flow cell with those using commercially available electrodes showed large discrepancies. A specimen set of results obtained using a combination electrode and a glass-calomel electrode pair both with ceramic plug junctions is shown in Table 3. Identical calibration procedures were adopted for all three systems. Dip measurements were made in enclosed, full beakers at constant but unspecified stirring rates.

The advantages of the flow cell can be summarised as: a). A fresh liquid junction can be readily and reproducibly formed for each solution, greatly reducing the risk of contamination or dilution at the liquid junction. b). The denser salt bridge solution is overlain by the less dense test solution, eliminating natural convective flow and enhancing the formation and maintenance of a stable liquid junction. c). Contamination of the test solution from loss or gain of carbon dioxide is reduced as sample exposure to the atmosphere is negligible. This is important for natural water samples, where pH is dependent on the partial pressure of carbon dioxide. Anoxic samples are particularly sensitive because introduction of oxygen will change



A : KCl reservoir
B : Reference electrode
C : Glass electrode
D : T-Junction

Fig. 1. Modified Flow Cell after Culberson (ref. 2)

TABLE 2. pH values of dilute buffers obtained using the flow cell calibrated on the IUPAC scale at 23 °C

Diluted (1:10) Standard Reference Solution	Molality (mol kg^{-1})	pH	pa_H*
KH Phthalate	0.01	4.124	4.115
1:1 Phosphate	0.0025 + 0.0025	7.077	7.073
1:3:5 Phosphate	0.0008695 + 0.003043	7.610	7.611
Disodium tetraborate	0.005	9.210	9.212

* Using Harned cell without liquid junction and Bates-Guggenheim convention

TABLE 3. Intercomparison of pH values obtained from three electrode systems at 7 °C

Sample		Flow Cell	Radiometer combination electrode (Type GK 2401c)	Russell pH Ltd. Glass/reference (CPR) pair
Dil. (1:10) 1:1 Phosphate		7.13	7.00	7.06
Dil. (1:10) 1:3:5 Phosphate		7.65	7.53	7.53
Fresh water samples from Lake Windermere	1.	7.21	7.00	7.05
	2.	7.22	7.05	7.14
	3.	7.15	7.01	7.06
	4.	7.18	7.01	7.14
	5.	7.09	6.97	7.08
	6.	7.22	7.09	7.17

the solution equilibria. d). Sample contamination from dissolution products of the glass cell and the electrode is reduced with the use of a flowing system. This also permits the liquid junction to be moved closer to the glass electrode, reducing the cell resistance and allowing thermostatting of the liquid junction. This latter is particularly important in obtaining a noise-free potential in very low conductivity solutions at low temperatures. e). Temperature control of the flow cell is simplified by the use of a polyacrylate box which also serves to protect the cell in the field. f). Finally the most important virtue of the flow cell as a pH measuring device is its ability to reproduce pH values of diluted IUPAC buffers in good agreement with those derivable from cells without liquid junction. This is a major step forward, enabling the interpretation of pH to be carried out with greater certainty. It must be emphasized that this study has been restricted to homogeneous solutions, but the effect of particulate or colloidal material on the cell potential difference has been demonstrated (ref. 27). However, the flow cell illustrated in Fig. 1. has been shown to provide reproducible and meaningful results on homogeneous samples.

The superiority of the flow cell over existing commercial dip electrodes has been clearly demonstrated. Large differences (about 0.15 in pH) were observed (Table 3) between pH values of diluted IUPAC buffers and freshwater samples measured with the flow cell and certain commercial glass-reference electrode pairs. Combination electrodes performed particularly poorly and this has been attributed to the extremely low leakage rates and hence poor flushing ability of this design (ref. 28). A second major disadvantage of this type of electrode was highlighted by Schlieren photographs of the combination junction which showed the bridge solution clearly visible and running down the electrode stem and over the pH sensing membrane (ref. 15).

Despite the success of the flow cell approach there are situations where dip-type measurements are necessary or preferable e.g. in titrations. For these purposes a dip-reference electrode incorporating a readily renewable free diffusion liquid junction formed in a capillary, where the liquid junction is protected from stirring effects, has been developed (ref. 28). Like the flow cell it provides pH values for diluted IUPAC buffers, which agree with determinations from cells without liquid junctions.

Instrumentation

A pH meter is required with a discrimination of < 0.003 in pH. Such an instrument is a top-of-the-range research pH meter with digital output. It must meet specifications regarding input currents from high impedance sources (glass electrodes) and the overall instrumental error should not exceed 0.002 in pH (ref. 29).

This type of instrument should be used for measurement of the pH of natural waters even though a reproducibility of 0.01 may be hard to achieve for reasons outlined earlier. Considerable errors can arise (ref. 29) from the use of temperature compensation techniques and rather than use them it is advisable to work in the mV mode of the pH meter. Under such conditions, much simpler instrumentation will suffice., namely, a three and a half digit panel meter (± 199.9 mV) with high impedance matching buffer amplifier, which can be battery powered for field use. Strict attention is necessary to the quality of the high impedance input and socket and the possible ingress of moisture.

Standardisation

The pH meter or alternative instrument should be standardised with IUPAC 1:1 phosphate buffer (ref. 30). For freshwater measurements, the difference between multistandard and single standard assigned values is negligible (refs. 6,7,30). The IUPAC 1:3.5 phosphate buffer should be used for slope checking. In view of the residual liquid junction potential which exists between 0.1 mol kg^{-1} Tris buffer and 1:1 phosphate buffer (3.3 mV) (ref. 15), even for junctions formed in capillary tubes, the use of Tris buffers is not recommended. Some advantages from the point of view of reducing

carry-over may be obtained by the use of diluted IUPAC buffers to which pH values have been assigned (ref. 26) (see Table 2).

Storage of Electrodes

When not in use, glass electrodes should be stored in distilled water, buffer solution or dilute HCl. Reference electrodes and combination electrodes should be stored in KCl solution.

Sample Preparation

The pH of natural waters and, in particular, poorly buffered freshwater samples is not stable but can change with time (ref. 28), because a) the ionic equilibria in solution are temperature dependent, b) the quantities of dissolved gases present change by re-equilibration with the atmosphere, photosynthesis, respiration or microbiological degradation processes, c) reaction occurs with suspended solids which are not in chemical equilibrium with the water. Thus, for natural waters, in-situ pH measurements have been recommended (ref. 31). This is seldom possible and so alternative practical procedures have to be adopted. Samples should be collected in well-washed, darkened, borosilicate glass bottles and not in plastic, metal or soda glass containers. The bottles should be prerinsed with the sample and then completely filled so that when the stopper is replaced it displaces the water in the neck preventing the entrainment of any air. Ideally, the bottle should be maintained at the in-situ temperature of the natural water and pH measured at the same temperature. When this is not possible the measurement should be made at some other temperature and the in-situ pH calculated from the temperature dependence of the carbonate stability constants (ref. 32) The fact that the bottle is sealed preventing gaseous exchange at the air-water interface makes this calculation possible. Poorly buffered waters of high biological productivity should be measured as quickly as possible. Photosynthesis in sealed bottles has been shown to change the pH from 7.8 to 9.3 in two hours (ref. 33). Darkening the bottle encourages respiration which changes the pH from 7.8 to 7.3 in the same time. These represent extreme examples but generally pH measurements on natural water samples should be carried out within hours. More acid waters, where carbonate is not the major buffer, are less prone to biologically induced changes but temperature corrections have to be determined experimentally as they depend on the composition of the water.

Acidic water samples

This report has deliberately focussed attention on the commonest freshwaters which are at near-neutral pH. However, the problems associated with so-called "acid rain" are currently of great concern and so it is worth providing some guidelines for the measurement of pH of such waters. Rainwater is naturally acidic (pH 5) but anthropogenic input of sulphuric and nitric acids can further lower the pH so that it is typically in the range 4.0 - 4.5 with an ionic strength of about 0.2 mmol kg^{-1} (ref. 5). On contacting the earth, the rain water usually gains buffer capacity with a commensurate increase in pH by dissolution of base components in catchment rocks and soils. Only in exceptionally base-poor regions (e.g. Canadian or Scandinavian Shields) is there insufficient buffering so that the surface waters remain acid (<pH 5). These acid waters are neither buffered by the carbonate system nor are they biologically productive. Therefore they are much less prone to pH changes caused by atmospheric exchange or biological processes and so storage prior to measurement can be viable. Rainwater samples can be affected by microbiological processes which can modify the nitrogen species but this is unlikely significantly to affect the pH. Not withstanding these better storage characteristics, it is prudent to perform any pH measurement as soon as possible.

All the fundamental problems associated with measuring pH in low ionic solutions still apply and procedures which advocate performing measurements on quiescent solutions (refs. 13,34) should be avoided. The procedure for measuring pH in acid waters differs in two ways from that advocated for

carbonate-buffered waters at near-neutral pH. It is not possible to predict the temperature dependence and so every effort should be made to preserve the sample at its natural pH. Alternatively, the temperature dependence of the particular water may be estimated by experiment. The standardisation procedure recommended for near-neutral waters is not applicable. In principle, if the liquid junction is unrestrained, it should be possible to use IUPAC buffers. Potassium hydrogen phthalate can be used as the standard and 1:1 phosphate for slope checking (ref. 30). Alternatively, diluted IUPAC buffers (ref. 26) may be used with advantage. Some authors (refs. 13,34) have advocated using strong acids. This is acceptable providing there is no danger of contamination changing the pH of such poorly buffered solutions. Further rigorous experiments are required to validate procedures at these low values of pH and ionic strength.

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