The Determination of pH in Low Ionic Strength Waters 1988

This booklet supplements but does not replace the second part of 'The Measurement of Electrical Conductivity and Laboratory Determination of the Natural, Treated and Waste Waters 1978'

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About This Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in "Analysis of Raw, Potable and Waste Waters". These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has 9 Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sewage Works Control Methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary

1 July 1987

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: "Guide to Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory" issued by the Royal Society of Chemistry, London; "Safety in Biological Laboratories" (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and "The Prevention of Laboratory Acquired Infection", Public Health Laboratory Service Monograph 6, HMSO, London.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

The Determination of pH in Low Ionic Strength Waters 1988

Some General Notes

pH is usually determined either by using an electrode system in which the potential difference observed is a function of the hydrogen ion concentration or by using indicators, substances which exist in differently coloured forms dependent on the hydrogen ion concentration. A booklet has already been issued in this series on the determination of pH in ordinary waters using pH electrodes and a pH meter (1), and analysts are familiar with the use of pH indicators both by solution addition and by use of indicator absorbed onto paper or a similar carrier. However, when determining the pH of waters low in electrical conductivity (<100 μS/cm), such as rain water and many upland waters, problems occur which can cause relatively large errors. The use of indicators or indicator papers is not a satisfactory method of measuring the pH of these waters because they are poorly buffered and contain metals, such as iron, manganese and aluminium, which cause interferences by complexing with the indicator (2).

With electrode-meter systems two problems of measurement arise in particular:

(1) the conductivities of such solutions are very low,

(2) liquid junction potentials may vary significantly.

Adoption of the following procedure will allow a target of 0.2 pH for the total error on a single measurement to be met (Section 2.12).

Electrode Method

1. Introduction

Particular interest is attached to the measurement of pH in low ionic strength waters from upland areas because of the need to assess environmental factors such as acidification and plumbosolvency of waters.

Some users of the SCA method 'The Measurement of Electrical Conductivity and the Laboratory Determination of the pH Value of Natural, Treated and Waste Waters, 1978' have experienced difficulties in measuring the pH of this type of sample. Adoption of the following procedure should improve performance. Laboratory testing has shown that a target of $\leqslant$0.2 pH for the total error on a single measurement can be met (Section 2.12).

2. Performance Characteristics of the Method

2.1	Value determined	pH, which is the logarithm to the base 10 of the reciprocal of the hydrogen ion activity.
2.2	Types of sample	Poorly buffered waters.
2.3	Basis of the method	Measurement of the potential of a cell which is responsive to the hydrogen ion activity and which contains the test solution as electrolyte. The equipment is calibrated using buffer solutions of known pH.
2.4	Range of application	The practical pH range is 0 to 14.
2.5	Calibration Curve	Linear in the pH range 3 to 12.
2.6	Standard deviation	A value of 0.05 pH or less is achievable.
2.7	Limit of detection	Not applicable.
2.8	Sensitivity (slope factor)	The sensitivity is usually close to the value given by the Nernst equation, that is about 59 millivolts per pH at 25°C.
2.9	Bias	None.
2.10	Interferences	Suspended matter and oil can interfere by blocking off the electrode surface. See Sections 4 and 9.
2.11	Time required for analysis	This is a function of the instrument, electrode and sample and is typically up to 5 minutes per sample once the instrument has been set up and standardized.

2.12 *Performance Data*

2.12.1 In a collaborative test in which river and synthetic samples of low conductivity were analysed simultaneously in the same laboratory by different operators, each with his own apparatus, the following results were obtained.

River Sample	A	B	C	D
Electrical conductivity, μS/cm	35.6	35.0	56.3	35.0
Mean pH	5.60	4.79	6.23	4.83
Standard deviation	0.05	0.05	0.07	0.04
Range of within-batch std. devs*	0.02 – 0.06	0.006 – 0.06	0.008 – 0.04	0.004 – 0.05
No. of analysts	9	6	9	6

Synthetic Sample	A	B	C	D
Mean pH	4.41	4.27	4.60	4.60
Standard deviation	0.06	0.14	0.06	0.02
Range of within-batch std. devs*	0.01 – 0.06	0.006 – 0.02	0.00 – 0.08	0.002 – 0.02
No. of analysts	8	6	9	6

*3 or 4 replicates.

A more detailed analysis of the results (3) shows that most analysts met the target of 0.2 pH total error in the laboratory.

2.12.2 In another collaborative exercise in which river and synthetic samples of low conductivity were analysed by separate authorities in their own laboratories, the following results were obtained:

Laboratory		Sample A	Sample B	Synthetic Sample
Forth River Purification Board	Mean	7.33	6.23	6.02
	Std. Dev.	0.01	0.01	0.01
Strathclyde Regional Council Water Dept.	Mean	7.43	6.20	6.07
	Std. Dev.	0.04	0.01	0.02
Mean of eight laboratories	Mean	7.38	6.14	6.04

3. Principle

3.1 The pH of a solution is defined by the equation

$$pH = -\log a_H \quad \ldots(1)$$

where a_H is the activity of hydrogen ions in the solution. Because the hydrogen ion activities cannot be determined experimentally the pH, pH(x), of a solution is determined by measuring the electromotive force (emf, E_x) of a cell containing the test solution, and comparing it with the emf, E_s, of a similar cell in which the test solution is replaced by a standard buffer solution. The cell is of the type:

Reference Electrode	Reference Solution	Salt Bridge	Test or Standard Buffer Solution	Measuring Electrode

$$\text{Then } pH(x) - pH(s) = \frac{(Es - Ex)F}{2.3026\ RT} \quad \ldots(2)$$

where pH(s) is the pH of the standard buffer solution, R is the gas constant, T the absolute temperature and F the Faraday constant.

3.2 The reference electrode is usually a calomel electrode containing concentrated (⩾3M) potassium chloride solution. The measuring electrode is a glass electrode. The essential component of a glass electrode is a pH-sensitive glass membrane, which has the property that a potential difference is developed between its two surfaces when it separates two solutions of different pH. The magnitude of this potential difference is related to the difference in pH between the solutions.

3.3 The term $\frac{2.3026\ RT}{F}$ in equation (2), expressed in millivolts, has the value 59.16 at 25°C. The values at other temperatures are given in Table 1.

Table 1

Variation of Slope Factor with Temperature

Temperature °C	2.3026 RT/F, mV	Acceptable Practical Range*, mV
0	54.20	53.20–55.20
5	55.19	54.19–56.19
10	56.18	55.18–57.18
15	57.17	56.17–58.17
20	58.17	57.17–59.17
25	59.16	58.16–60.16
30	60.15	59.15–61.15

*±2% of theoretical value.

3.4 The emf of the cell is measured with a pH meter, which is a high impedance voltmeter calibrated directly in pH.

3.5 The pH of a solution is a function of temperature, because the potential difference, E, generated between the pair of electrodes which constitute the cell, is given by the equation:

$$E = E_o - 2.3026 \frac{RT}{F} pH$$

3.5.1 E_o is a standard potential and is a function of temperature; because it comprises a number of contributing potentials (reference electrode, junction potential and asymmetry potential) it is also subject to other variations. If the sample solution and the standardizing buffer solutions are at the same temperature, errors due to changes in E_o caused by these other factors are allowed for by the normal standardization of the meter.

3.5.2 The slope factor 2.3026RT/F varies with temperature and for this reason it is desirable that the buffer solution and the samples are at the same temperature. In practice, the observed slope factor may differ from (usually being slightly less than) the theoretical slope. Allowance can usually be made for this with modern pH meters.

3.5.3 The pH of natural water may not be stable. It can change with time due to:

(a) The ionic equilibria in solution being temperature dependent.

(b) Changes in the quantities of dissolved gases present, especially carbon dioxide. This can be a physical loss or gain resulting from unsuitable storage but also because photosynthesis or respiration and oxidative decay of organic matter may proceed even in a sealed bottle.

(c) Reaction with suspended solids which are not in chemical equilibrium with the water.

In some cases the change of pH is so rapid that it is not possible to obtain a stable reading on the pH meter. Vigorous stirring of the sample during measurement may exacerbate these effects. For these reasons many authorities recommend that the pH of natural waters should be measured in situ rather than after transfer of the sample to the laboratory, provided on site measurement gives the required performance.

4. Interferences

4.1 Sediments and precipitates can cause problems by blocking pores or capillaries of the reference electrode or coating the glass electrode surface.

4.2 If oil is present in the sample, eg in a pollution incident, electrodes can become coated and thereby errors may arise. See also Section 9.

5. Hazards

5.1 Calomel electrodes contain mercury (as Hg and Hg_2Cl_2). In the event of a breakage the contents should be disposed of in an approved manner (see Ref. 4 in this series).

5.2 Some commercial buffer solutions contain a mercury (II) salt added as a preservative.

6. Reagents

Glass or polyethylene containers may be used for the storage and conditioning of electrodes.

6.1 Water

For the preparation of standard buffer solutions distilled water which has been freshly boiled or deionised water taken freshly from the column should be used. (Distilled water may be supersaturated with carbon dioxide and have a pH of 4 to 5.) Water used for the preparation of buffer solutions should not have a carbon dioxide concentration greater than that of air-equilibrated water.

6.2 Concentrated Potassium Chloride

The reference electrode should be stored in concentrated potassium chloride solution (eg 4M). This solution can be made up by adding approximately 75 (±1) g of potassium chloride to 250 (±) ml of water and, if necessary, gently warming to aid dissolution.

6.3 Buffer Solutions

6.3.1 Buffer solutions have pH values which are well defined and insensitive to small additions of acid or alkali. A range of buffer solutions of accurately known pH can be prepared in accordance with BS 1647: Pt 2 (5), other formulations are quoted by Mattock (6) and Perrin and Dempsey (7). These publications should be consulted for full details. Suitable reagents for the preparation of standard buffer solutions are available commercially. Although buffer solutions are considered to be stable, it is good practice not to use buffer solutions which are more than one month old.

6.3.2 It is convenient to purchase reagents for standard buffer solutions either in solution, sachet or tablet form.

6.3.3 **pH 4.0 Solution: The Primary Standard**

At 20°C dissolve 10.138±0.001 g of potassium hydrogen phthalate of analytical reagent quality, previously dried at 105°C and cooled and stored in a desiccator, in about 500 ml of water and dilute with water to 1 litre in a calibrated flask. The pH of this solution at various temperatures is given in Table 2, and is defined in BS 1647 Pt. 1 (5).

6.3.4 **pH 4.0 Solution: Low Conductivity AQC Standard**

A low conductivity solution for Analytical Quality Control (AQC) should be included in each batch of samples analysed. A 10^{-4}N solution of hydrochloric acid or sulphuric acid has a pH of 4.00_5 at 20°C (see Table 2) and can be prepared by accurate dilution of volumetric standard acid (available commercially). This solution should be stored in a borosilicate glass container. The variation of pH with temperature is given in the Table 2.

7. Instrumentation

7.1 Electrodes

Most standard pH glass electrodes are suitable for this application, but 'high temperature' and 'micro' electrodes are not recommended. For measuring samples at less than 10°C use of low-resistance glass electrodes is preferable because of improved response times. Most of the problems are associated with the reference electrode and it is recommended that these should be tested before use (Section 13.1). Certain types of glass electrode (eg Ross™ and Thalamid™ electrodes) **must** be used with the corresponding type of reference electrode. Of the commonly used reference electrodes, calomel electrodes are preferred to silver-silver chloride electrodes, because they are less prone to clogging of the liquid junction. Reference electrodes with immobilized or

Table 2

Variation of pH with Temperature

Temperature °C	pH 4 Primary Standard	AQC (pH 4) Low Conductivity Acid Standard	AQC Dilute Buffer Standard (see Section 13.2)
0	4.000	4.00_5	—
5	3.998	4.00_5	7.68
10	3.997	4.00_5	7.67
15	3.998	4.00_5	7.64
20	4.001	4.00_5	7.62
25	4.005	4.00_5	7.61
30	4.011	4.00_5	7.59

gelled filling solutions should not be used. In general, separate glass and reference electrodes have been found to be more reliable than combination electrodes.

It is important to ensure that the level of reference electrode filling solution is well maintained and that there are not air bubbles in the solution. Use of a head of electrolyte above the level of the sample is essential. It may be advantageous to increase this head by connecting an external reservoir of potassium chloride solution. A rate of flow of electrolyte through the junction of 0.1–2.0 ml per day has been found to be satisfactory, but the upper end of the range is to be preferred. Greater or lower rates of flow may not establish adequately reproducible junction conditions. (To estimate the flow rate weigh the tissue-dried electrode, immerse to 1 cm in distilled water for at least 1 hour, dry with a tissue and reweigh.)

Whatever electrode is chosen, performance not only varies between different manufacturers' products but also between batches of the same manufacturer's electrodes. See Section 13.1 and 13.2 for checking on electrode performance. Some new electrodes drift initially and so should be preconditioned according to the manufacturer's instructions.

Care of electrodes

The reference electrode should be stored in concentrated potassium chloride solution. The glass electrode should be stored in a pH 4 or pH 7 buffer solution. Electrodes should never be allowed to become dry. Between individual determinations within a batch of measurements, both electrodes should be left immersed in a sample or standard solution.

Electrodes should not be left in contact with strongly alkaline solutions nor should they be immersed in strongly dehydrating solution (such as chromic acid) for cleaning purposes.

Rejuvenation may be attempted by (a) refilling the reference electrode with fresh KCl filling solution and then leaving the junction to soak in concentrated KCl filling solution for 1 day, (b) soaking the glass electrode 5 times alternately in 0.1N HCl and 0.1N NaOH solutions for 5 minutes. Electrodes should be rinsed well with distilled water before being returned to use.

Regular performance checks should be carried out (see Section 13.1) and poorly performing electrodes should be rejected.

7.2 pH Meter

A pH meter is a high impedance voltmeter (typically greater than 10^{13} ohms) designed to measure the potential difference developed between the glass electrode and the reference electrode and calibrated directly in pH. The meter should be capable of being read to a discrimination of 0.01 pH or better.

8. Sample Collection and Preservation

pH analysis must be carried out under controlled conditions strictly adhering to the recommendations in the following method whether the determination is carried out in

the laboratory or on site. Samples should be collected in borosilicate glass containers. Containers made of soda glass (from which alkali may be leached) or polyethylene (which may be permeable to carbon dioxide) should be avoided. The sample containers and closures should, whenever possible, be washed in the sample being collected. If this is not possible the containers should be washed with distilled or deionized water and dried.

The sample container should be completely filled. In most cases, samples should be stored at ambient temperatures and the pH determined as soon as possible after sample collection. However, if there is the possibility of biological action occurring which might change the pH, the sample should be stored in darkness at 4°C and the temperature brought back to ambient just before pH measurement. Some check must be made on whatever sample collection and storage procedure is adopted.

9. Sample Pretreatment

Samples should be measured as received unless they contain oil or grease which can foul the electrodes. If these materials are present they should be separated using a separating funnel, or by the use of oil-absorbent materials, or by syphoning off a portion of the aqueous phase, or by filtering through a pad of cotton wool, as appropriate. The measurement should then be made on the oil-free aqueous phase.

10. Analytical Procedure

Step	Analytical Procedure	Notes
10.1	Ensure that the instrument and electrode manufacturers' instructions are known and understood.	
10.2	Switch on the pH meter, where necessary set to read pH, and allow the meter to stabilize (note a).	(a) To improve the stability, instruments may be left on permanently. Modern instruments with solid state circuitry require only a short time to stabilize.
10.3	Remove the electrodes from their respective storage solutions, rinse thoroughly with, and immerse in, distilled water (note b).	(b) New electrodes may require conditioning before use; see manufacturer's instructions.
10.4	Open the breather hole on the reference electrode.	
10.5	Measure the temperature of the buffer solution(s) and set the temperature control (note c).	(c) For work of the highest accuracy calibration should be performed with buffers and samples at the same temperature (±2°C) rather than using instrumental temperature correction.
10.6	Wash the electrodes with, and immerse in, pH 7 buffer.	
10.7	Swirl the solution gently about the electrodes and allow the solution to come to rest (note d).	(d) Some analysts use a slow speed magnetic stirrer but this can lead to errors if gases such as carbon dioxide are absorbed by or lost from the solution. Care must also be taken that stirring does not allow the test sample to be affected by acidic or alkaline laboratory atmospheres.
10.8	Set the instrument to read the pH of the buffer solution by adjustment of the appropriate controls (refer to manufacturer's instructions) (notes e and f).	(e) The reading should be recorded when it becomes constant. (f) The exact value of the buffer solution will depend on the temperature of the solution. Refer to buffer solution data.

Step	Analytical Procedure	Notes
10.9	Rinse the electrodes thoroughly with distilled water and pH 4 buffer solution.	(g) If alkaline samples are expected, instead of the pH 4 buffer use one of high pH (eg 9.2).
10.10	Immerse the electrodes in the pH 4 buffer solution and check that the instrument records the correct pH reading. If not, where available, adjust the 'slope' control (notes e, f, g and h).	(h) Calibration should be carried out at least daily and preferably for each batch of analyses.
10.11	Rinse the electrodes thoroughly with distilled water and pH 7 buffer solution. Repeat steps 10.6 and 10.7. If the pH value difference is more than ±0.01 the calibration should be repeated.	
10.12	Rinse the electrodes with and immerse in distilled water to remove any traces of buffer.	
	pH measurement	
10.13	Check the temperature of the sample solution (note c).	
10.14	Wash the electrode thoroughly with sample solution.	
10.15	Immerse the electrodes in the sample solutions, stir or swirl gently for approximately one minute, then stop stirring and record the pH when it has stabilized (notes d, i and j).	(i) If the pH reading does not stabilize it may be a function of the type of sample or may indicate that the pH of the solution is changing. If stabilization is poor it may be necessary to measure the pH after an arbitrary time, say 2 minutes. To minimize stabilization difficulties it is advisable to analyse samples of a similar composition and/or pH range consecutively.
		(j) If the meter is recalibrated it is essential that the electrodes are thoroughly rinsed afterwards to remove all traces of buffer.
10.16	Repeat step 10.15 for other samples. Remember to analyse the AQC solution (note k).	(k) If the pH of the pH 4.00 low conductivity standard is outside the limits 3.95–4.05, repeat the calibration (10.5–10.11). If the error persists, use the low conductivity buffer solution (Section 13.2) as a check on the system in case the pH 4.0 standard is defective: the pH should be within 0.01 of the value in Table 2. If the electrode fails this test either rejuvenate it (Section 7.1) or replace it.
10.17	Replace the cap on the reference electrode and place the electrodes in the appropriate storage solutions (see Section 7.1).	

11. Sources of Errors

11.1 Errors can arise from temperature changes and from changes in equilibria within the sample system. These have been discussed in Section 3.5.

11.2 Errors can arise from deterioration of electrodes or from fouling of electrodes by oils and greases or precipitated materials (see Section 9).

11.3 Stray electrical fields can cause unstable pH indications.

11.4 Excess leakage of reference electrode filling solutions can lead to error.

12. Expression of Results

The pH of a solution is a pure number and has no units. It is a logarithmic function of hydrogen ion activity.

13. Checking the Accuracy of Analytical Results

13.1 Testing Electrodes

A simple test for screening out the worst reference electrodes is given below. It should be applied (a) to new electrodes (b) to electrodes that have not been used for 2 weeks or more and (c) to electrodes in regular use, at intervals of about 4 weeks.

13.1.1 Calibrate the electrodes with pH 7 and pH 4 buffers, as in Section 10.1–10.11 and note the slope factor (mV/pH, % or fraction, as allowed by the pH meter).

13.1.2 Carry out steps 10.12–12.15, using as the 'sample' a 10^{-4}N solution of hydrochloric or sulphuric acid (solutions prepared by dilution of commercial volumetric stock solutions are acceptable). Note the reading in unstirred solution, $pH_{(u)}$.

13.1.3 Stir the solution gently and note the new stable reading, $pH_{(s)}$. If the signal fluctuates, estimate the difference, ΔpH_n, between the maximum and minimum readings.

13.1.4 Calculate the error caused by the residual liquid junction potential.
$\Delta pH_j = pH_{(u)} - 4.005$

13.1.5 Calculate the shift on stirring
$\Delta pH_{stir} = pH_{(s)} - pH_{(u)}$

13.1.6 Compare the results with the ranges defining good and acceptable behaviour in Table 3.

An unacceptable slope factor or residual liquid junction error is reason for rejecting an electrode. The other parameters are indicators of incipient trouble. It is implicit in the test that the electrodes give readings stable to ±0.01 pH within 2 min.

Table 3

Ranges of 'good' and 'acceptable' Performance

Performance Characteristic		Good Range*	Acceptable Range*
Slope factor	mV/pH #	59.2±0.3	58±1
	%	100±0.5	100±1.5
	fraction	1.000±0.005	1.00±0.02
Residual liquid junction error, ΔpH_j		⩽0.03	⩽0.05
Shift on stirring, ΔpH_{stir}		⩽0.005	⩽0.02
Noise, ΔpH_n		⩽0.005	⩽0.02

At 25°C: at other temperatures multiply by (273 + T)/298
* Based on what is achievable with commercially available electrodes (8, 9).

13.2 Routine Analytical Quality Control

The slope factor should be noted on each occasion that particular apparatus is used. These measurements can form the basis of a control chart, although if measurements are not always made at a fixed temperature they must first be 'normalized', eg to 25°C. Variations in slope or a deviation of greater than 1.0 mV or 2% from the theoretical value at the relevant temperature should be regarded as cause for concern. Duplicate determinations should be made on a typical natural water sample in each batch of samples. The difference between these readings should be plotted on a control chart. This provides a check on routine precision for real samples. As a guide to systematic error, determinations should be made on a diluted strong acid of known pH, eg see Section 6.3.4. Another useful low conductivity buffer solution (7, 10) can be prepared from potassium dihydrogen orthophosphate (KH_2PO_4–0.0008659M) and disodium

hydrogen orthosphosphate ($Na_2 HPO_4$–0.003043M). The conductivity of this solution at 25° is approximately 540 μS/cm. The variation of pH with temperature is shown in Table 2.

14. References

(1) *The Measurement of Electrical Conductivity and the Laboratory Determination of the pH Value of Natural Treated and Waste Waters 1978*, HMSO, London, in this series.

(2) Department of the Environment file, W.S. 646/112–(pH measurement) and Report on DoE contract PECD 7/7/174 therein.

(3) Davison W and Gardner M J, *Anal. Chim. Acta*, 1986, **182**, 17.

(4) *Chloride in Water, Sewage and Effluents 1981*, HMSO, London, in this series.

(5) British Standard 1647 Pt 1 and 2, 1984. British Standards Institution, London 1984.

(6) Mattock G, *pH Measurement and Titration*, Heywood, London 1961.

(7) Perrin D D and Dempsey B, *Buffers for pH and Metal Ion Control*, Chapman and Hall, London 1974.

(8) Davison W and Woof C, *Anal. Chem.*, 1985, **57**, 2567.

(9) Midgley D, *Atmos. Environ.*, 1987, **21**, 173.

(10) Covington A K, Whalley P D and Davison W, *Analyst*, 1983, **108**, 1528.

Address for Correspondence

However thoroughly a method may be tested there is always the possibility of a user discovering some hitherto undiscovered problem. Correspondence should be addressed to:

The Secretary
Standing Committee of Analysts
Department of the Environment
43 Marsham Street
Romney House
London SW1P 3PY
United Kingdom

Department of the Environment

Standing Committee of Analysts

Membership Responsible for this Method

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F B Basketter	1	A Lloyd	2
Dr G A Best	1	Dr G H Mansfield	2
R R Birch	2	J C McCullins	1
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