The Measurement of Electrical Conductivity and the Laboratory Determination of the pH Value of Natural, Treated and Waste Waters 1978

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office 90p net

The Measurement of Electrical Conductivity and the Laboratory Determination of the pH Value of Natural, Treated and Waste Waters 1978

Methods for the Examination of Waters and Associated Materials

This volume contains two related methods

Contents

London Her Majesty's Stationery Office

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 a properly equipped laboratory. 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 others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specification 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.

There are numerous handbooks on first aid and laboratory safety. One such publication is 'Code of Practice for Chemical Laboratories' issued by the Royal Institute of Chemistry, London. 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. 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 radiochemical 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 foorwear should be disinfected by appropriate methods if contamination is suspected.

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 the correct protective clothing or 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. If in doubt it is safer to assume that a hazard may exist and take reasonable precautions than to assume that no hazard exists until proved otherwise.

First published 1979

ISBN 0 11 751428 4

About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has 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 individual methods, 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 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 analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst 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 one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine 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 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis
9.0 Radiochemical methods

The actual methods etc 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, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977

Method A Measurement of Electrical Conductivity of Natural, Treated and Waste Waters

1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series.)

1.1	Value determined	The electrical conductivity of the sample. This is often used as a non-specific test for the presence of ionised substances in the sample.
1.2	Type of sample	All natural waters, treated waters, aqueous solutions and effluents.
1.3	Basis of method	The electrical resistance of the sample is determined in a cell of known dimensions.
1.4	Range of application	1 to 100,000 μS/cm, depending on cell construction.
1.5	Standard deviation	This is a function of the instrument used and the nature of the solution. Typically, a relative standard deviation of 1.5% can be readily obtained. Typical performance data is given below (Section 1.11).
1.6	Limit of detection	Depends on cell construction.
1.7	Sensitivity	Function of instrumentation.
1.8	Bias	None.
1.9	Interference	Suspended matter may interfere by mechanically blocking off parts of the electrode system.
1.10	Time required for analysis	After initial setting up and bringing samples to temperature, up to 3 minutes per sample is required.

1.11 Typical performance data

In measurements of the conductivity of synthetic samples carried out by the South West Water Authority using a commercial instrument and a dip-type cell the following results were obtained:[1]

	Standard deviation		
Mean conductivity	Within batch	Between batch	Total
μS/cm	μS/cm	μS/cm	μS/cm
66.7	0.67	0.87	1.10
126.7	0.81	0.75	1.10
257.4	1.75	0.39	1.79
500.9	1.63	0.68	1.76

For the within batch measurements there were 10 degrees of freedom and for the between batch measurements there were 9 degrees of freedom.

In a similar set of measurements on real samples the following results were obtained:

	Standard deviation		
Mean conductivity	Within batch	Between batch	Total
μS/cm	μS/cm	μS/cm	μS/cm
100.8	0.79	2.50	2.62
247.8	1.50	2.58	2.98
251.1	0.98	3.08	3.23
422.3	2.23	2.77	3.55

For the within batch measurements there were 30 degrees of freedom and for the between batch measurements there were 9 degrees of freedom.

2 Principle

2.1 Electrical conductivity is a measure of a solution's ability to conduct electricity. In SI units, the unit of conductivity is the Siemen/metre although, for convenience, most measurements are reported in units of micro Siemens/cm (μS/cm). The unit of μS/cm is equal to the previously used unit of mho/cm.

2.2 The electrical conductivity of a solution depends upon the concentrations of the ions present and temperature of the solution. To a first approximation, the contribution of the conductivity of a solution made by each ion is independent of the presence of other ions and it is possible to regard the conductivity of a solution as being made up from the conductivities of the individual ions present.

Relationship to total dissolved ionizable solids

2.3 Electrical conductivity is often used as a rapid method of estimating the concentration of total dissolved ionizable solids. The relation between this concentration and conductivity will depend upon the nature of the ionized species present and, in general, will vary from one water to another. However, it is usually assumed that for different samples from the same source, conductivity is a measure of total dissolved ionizable solids. For most waters, the factor by which conductivity, in μS/cm, should be multiplied to give the concentration of total dissolved ionizable solids, in mg/l, is between 0.55 and 0.80.

Temperature

2.4 Electrical conductivity varies with temperature and it is necessary to record the temperature at which the measurement was made. In order to facilitate comparison between results, it is usual either to make measurements at a standard temperature, or to correct results obtained at other temperatures to the standard temperature. The variation of conductivity with temperature is complex. When only simple ions are present, the variation with temperature is nearly exponential but, when complex ions are present, shifts in the equilibrium concentrations of the ions present which follow from temperature changes will also contribute to changes in conductivity.

2.5 For most purposes conductivity is measured at 25°C but there are some circumstances in which a measurement at 20°C is needed. Measurement at 25°C is preferred because it is simpler to provide adequate temperature control at a little above the ambient temperature rather than a little below.

2.6 Many instruments include automatic correction of conductivity to a particular temperature but the construction of the instrument assumes a value for the temperature coefficient of variation of conductivity. Such instruments should only be used at temperatures close to the temperature for which they were designed unless it is known that the temperature correction is appropriate to the water under test.

2.7 The temperature coefficient of the conductivity of a water may be determined by measuring the conductivities K_1 and K_2 at two temperatures T_1 and T_2 respectively. The average coefficient of temperature variation of conductivity, α, over the temperature range T_1 to T_2 can then be derived from the following equation (which gives the fractional change of mean conductivity between temperatures T_1 and T_2 per degree Celsius):

$$\alpha = \frac{(K_1 - K_2).\,2}{(K_1 + K_2).\,(T_1 - T_2)}$$

A typical value of α for a freshwater is 0.02 per °C at temperatures near 25°C.

Effect of Polarization

2.8 In practice, it is not possible to measure the conductivity of a water by applying a steady potential difference and measuring the current which passes. This is because the electrodes rapidly become polarized as a result of electrolytic reactions. The difficulty is avoided by applying an alternating potential difference, at a frequency of about 1000 Hz. In this way there is virtually no net electrolytic action and a true reading is obtained.

2.9 While in principle it is possible to construct an apparatus which will permit measurement of conductivity of a water using only the geometrical dimensions of the apparatus and measurements of current and potential difference, this is not done in practice. It is far simpler to calibrate a conductivity cell using solutions of known conductivity—see Section 4.

3 Interferences

Gross suspended matter, oil or grease may cause interference by masking off part of the electrode surface. Removal by settlement or filtration is advisable.

4 Reagents

4.1 Water—deionized or distilled

4.2 Standard Potassium Chloride Solution (0.005 M)

Dissolve 3.728±0.005 g of analytical grade anhydrous potassium chloride, dried for 2 hours at 110±10°C and subsequently stored in a desiccator, in about 200 mls of deionized or distilled water in a beaker, quantitatively transfer to a 1 litre calibrated flask and dilute with deionized or distilled water to the mark. Transfer 50.00±0.05 ml of this solution into a 500 ml calibrated flask and dilute with deionized or distilled water to the mark. The electrical conductivity of this solution, which is 0.005 M in potassium chloride, at 25°C is 718 μS/cm. Table 1 gives alternative concentrations of potassium chloride that can be used as a standard of conductivity[2].

Table 1 Electrical Conductivity of Potassium Chloride Solutions

Concentration of potassium chloride mg/l	Electrical conductivity at 25°C μS/cm
37.28	74
74.56	147
372.8	718
745.6	1413
1492	2767
3728	6668
7456	12900
14920	24820

5 Apparatus

5.1 Conductivity Cells

A conductivity cell usually consists of a cell in which the solution under test is contained in such a way as to cover a pair of rigidly mounted electrodes. Cells are usually constructed of borosilicate glass. The dimensions of the cells and of the electrodes depend upon the values of conductivity expected. Since some poisoning of the electrodes may take place with use, it is essential that the electrodes be kept clean. They should be cleaned according to manufacturer's instructions.

5.2 Most instruments for measuring electrical conductivity consist of a Wheatstone bridge, fed by a low voltage alternating current source. The conductivity cell forms one arm of the bridge. The bridge circuit is arranged so that, at the balance point, the detector indicates either zero or minimum current. Some instruments are designed to give direct reading of conductivity.

5.3 Cell constant

It is usual to calibrate individual cells by reference to solutions of known conductivity. By definition, the conductivity, K, of a solution contained between electrodes of surface area A situated at a distance L apart is given by $K=L/AR$, where R is the measured resistance. If R_o is the measured resistance of a solution of known conductivity K_o, then $K_o=L/AR_o$, or $K_oR_o=L/A$. The value of L/A is the cell constant and it can be used in the equation $K=L/AR$ to convert a measured resistance into the corresponding conductivity. Typical values of cell constants are 0.1 cm^{-1}, for conductivities up to 1,000 μS/cm and 1.0 cm^{-1} for conductivities up to 50,000 μS/cm.

5.4 High frequency instruments measuring conductivity by an inductive procedure are also available. These have the advantage that, as there is no direct contact between sample and electrodes, polarization does not take place.

6 Sample Collection and Preservation

The sample should be collected in a polyethylene bottle and the bottle completely filled and tightly stoppered. Soda glass bottles must not be used. Analysis should be performed as soon as practicable, particularly when there is the possibility of exchange of gases

such as carbon dioxide or ammonia with the atmosphere, or of biological activity. Biological activity can be reduced by storing the samples in the dark at 4°C, however, samples must be brought up to temperature, usually 20°C or 25°C, before conductivity is measured. There is no suitable preservative for conductivity.

7 Analytical Procedure

Step	Analytical Procedure	Notes
7.1	Set the instrument up according to the manufacturer's instructions, using a cell with a suitable constant.	
7.2	Check the cell constant by measuring the electrical conductivity of a standard potassium chloride solution at 25°C (note a).	(a) This should be done after every cleaning at least and preferably before each set of readings.
7.3	Rinse and carefully fill the cell with the sample (note b).	(b) Ensure no air bubbles adhere to the electrodes.
7.4	Measure the temperature of the sample and set the temperature compensator to the sample temperature (notes c, d and e).	(c) If the accuracy is to be maintained to within ±2%, the temperature correction should not extend over more than ±5°C. For more accurate work, the temperature correction should only be used over a correspondingly smaller temperature range. (d) See Section 2.6. (e) For determinations using instruments without temperature compensation, the temperature coefficient must be known to convert the conductivity to the Standard temperature using the formula given in Section 2.7.
7.5	Measure the conductivity of the sample following the instructions supplied with the measuring instrument.	

8 Checking the Accuracy of Analytical Results

(For further information see another publication in this series).

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. As a minimum, however, it is suggested that a solution of known conductivity should be analysed at the same time and in the same way as normal samples (see Sections 4 and 7). The results should then be plotted on a quality control graph in order to facilitate detection of inadequate accuracy and to allow the standard deviation of routine analytical results to be estimated.

9 References

(1) Department of the Environment, file WS/646/113.

(2) R A Robinson and R A Stokes, *Electrolyte Solutions*. Academic Press, New York, 1969.

Method B The Laboratory determination of the pH of natural waters, treated waters, aqueous solutions and effluents by use of an electrode system.

1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series).

1.1	Value determined	pH, which is the logarithm to the base 10 of the reciprocal of the hydrogen ion activity.
1.2	Types of sample	All natural waters, treated waters, aqueous solutions and effluents. The method is not suitable for saline waters or sea water in those cases where an accuracy of better than 0.2pH unit is required.
1.3	Basis of the method	Measurement of the electrochemical 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.
1.4	Range of application	The practical pH range is 0 to 14.
1.5	Calibration curve	Linear in the pH range 2–12 (pH is a logarithmic function).
1.6	Standard deviation	This is a function of the equipment used, the nature of the solution being measured and the analytical technique used. Values in the range 0.1 to 0.005 pH units are quoted by manufacturers. Typical performance data is given below (Section 1.12).
1.7	Limit of Detection	Not applicable.
1.8	Sensitivity	The sensitivity is usually close to the value given by the Nernst equation, that is, about 59 millivolts per pH unit at 25°C.
1.9	Bias	None.
1.10	Interferences	Sodium at pH 10 interferes. Oil, grease and suspended matter can interfere by blocking off the electrode suface. See Section 10.
1.11	Time required for analysis	This is a function of the instrument, of the electrode and of the samples, and is typically up to 2 minutes per sample once the instrument has been set up and standardized.

1.12 Performance data

Tests were carried out by South West Water Authority (August 1976) using a digital pH meter.[1] The pH of buffer solutions were measured daily over a period of ten working days.

pH	Standard deviation		
	Within batch	Between batch	Total
4.0	0.013	0.016	0.021
7.0	0.020	0.020	0.021
9.2	0.014	0.016	0.021

There were 9 degrees of freedom in each estimation of standard deviation.

2 Principle

2.1 The pH of a solution is defined by the equation

$$pH = -\log a_H \qquad \textit{Equation (1)}$$

where a_H is the activity of hydrogen ions in the solution expressed in gram-moles/l. Because the hydrogen ion activities cannot be determined experimentally the pH, $pH_{(x)}$, of a solution is determined by measuring the electromotive force (emf) Ex of a cell containing the test solution, and comparing it with the emf, Es, 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

Then $$pH_{(x)} - pH_{(s)} = \frac{(Es - Ex)F}{2.3026\ RT} \qquad \textit{Equation (2)}$$

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.

2.2 The reference electrode is usually a calomel electrode containing saturated potassium chloride solution. The measuring electrode is a glass electrode. The essential component of a glass electrode is a pH-sensitive glass membrane. This membrane 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.

2.3 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 the following table.

Temperature	2.3026 RT/F millivolts
0	54.20
5	55.19
10	56.18
15	57.17
20	58.17
25	59.16
30	60.15
40	62.13
50	64.12

2.4 The emf of the cell is measured with a pH meter, which is a high impedance volt meter calibrated directly in pH units.

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

$$E = E_0 - \frac{RT}{F} pH$$

2.5.1 E_0 is the standard potential and is a function of temperature; because it comprises a number of contributing potentials (reference electrode, function potential and assymetry potential) it is subject to other variations. If the sample solution and the standardising buffer solutions are at the same temperature, errors due to changes in E_0 caused by these other factors are allowed for by the normal standardization of the meter. A temperature difference of 1°C gives rise to an error of about 0.01 pH unit.

2.5.2 The slope factor RT/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 may differ from (usually slightly less than) the theoretical slope. Allowance can usually be made for this with modern pH meters.

2.5.3 The pH of a 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.

3 Interferences

3.1 Above pH 12 the electrode response may not be linear. In the presence of appreciable concentrations of sodium the response is not linear above pH 10 and there may be damage to the electrode. In subsequent pH determinations the electrode may then give a high response unless it is reconditioned by soaking in dilute hydrochloric acid. See Section 6.

3.2 Oils and greases can coat electrodes and thereby cause errors.

3.3 Sediments and precipitates can cause probelms by blocking pores or capillaries or coating electrode surfaces. See also Section 10.

4 Hazards

There are no special hazards associated with pH measurements other than those likely to be encountered in the handling of solutions which are very acidic, pH<2, or very alkaline, pH>11.

5 Reagents

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

5.1 Water

For the preparation of standard buffer solutions deionized or distilled water which has been freshly boiled should be used. Freshly distilled water may be supersaturated with carbon dioxide and have a pH or 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. This is most simply achieved by boiling freshly distilled water and allowing it to cool. For cleaning the bottles and electrodes and for storage of pH electrodes distilled or deionized water may be used.

5.2 Dilute hydrochloric acid

Dilute hydrochloric acid may be used for the storage and conditioning of electrodes. See manufacturer's instructions for the appropriate strength.

5.3 Buffer Solutions

5.3.1 Buffer solutions are solutions the pH values of which are well defined and these values are not sensitive to small additions of acid or alkali. A range of buffer solutions of accurately known pH can be prepared in accordance with BS 1647:1961[2], other formulations are quoted by Mattock[3]. These pubilcations 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.

5.3.2. For practical purposes it is convenient to purchase reagents for standard buffer solutions either in solution, sachet or tablet form.

5.3.3 *pH* 4.0 *Solution; The primary standard*

Dissolve 10.20±0.01 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 is defined as 4.000 at 15°C. The variation of pH with temperature is as follows:

Temperature °C	pH
0	4.01_1
5	4.00_5
10	4.00_1
15	4.000
20	4.00_1
25	4.00_5
30	4.01_1
40	4.03_1
50	4.06_1
60	4.09_1

6 Instrumentation

6.1 Electrodes

Electrodes for pH measurements are available commercially.

6.1.1 *Reference electrodes*

a. *Mercury-calomel electrode* with saturated, 3.5 M or 0.1 M potassium chloride solution to form a salt bridge. These electrodes are unsuitable at temperatures above 70°C. With some samples, especially those containing sulphides, the use of a double salt bridge is desirable in order to avoid reactions which may lead to precipitation in the calomel cell.

b. *Silver—silver chloride electrode.* This electrode can be used up to 100°C. Potassium chloride saturated with silver chloride is used as the filling solution.

c. Other reference electrodes especially for use at high temperatures (up to 130°C) and high pressures are available[4].

6.1.2 *Measuring Electrodes*

a. *Glass electrodes.* These are almost universally used for pH measurements. Special types are available for temperatures above 60°C and for pH values greater than 10

b. *Combined electrodes.* These are calomel and glass electrodes combined in a single probe and are very conventient to use.

It is important that electrodes are compatible with each other and with the pH meter in use, and that they have suitable connections.

6.1.3. *Care of Electrodes*

New glass electrodes should be prepared for use by soaking in dilute hydrochloric acid according to the manufacturer's instructions.

Electrodes should not be allowed to dry out but should be stored in distilled or deionized water. Electrodes should not be left in contact with strongly alkaline solutions nor should they be immersed in strongly dehydrating solutions (such as chromic acid) for cleaning purposes. It is important to ensure that the level of the reference electrode filling solution is well maintained and that there are no air bubbles in the solution.

6.2 pH meter

A pH meter is a high impedance volt meter designed to measure the potential difference developed between the glass electrode and the reference electrode and which is calibrated directly in pH units.

6.3 Choice of electrode system

Nearly all electrode systems in practical use are purchased from specialist manufacturers rather than constructed in laboratories. Many of the design parameters, such as type of reference electrode and choice of pH sensitive glass, are fixed by the manufacturer, and it only remains for the user to select an electrode system suitable for his own particular needs. Use and maintenance should be in accordance with the manufacturer's instructions.

7 Sample Collection and Preservation

For work of the highest accuracy, the pH of natural waters should be determined *in situ*. If this is not practicable samples may be collected in a borosilicate glass, plastic or metal container. The sample collection vessel should be washed with the sample being collected. Samples may be stored in borosilicate glass or polyethylene containers. The use of soda glass containers should be avoided. The sample containers, including 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 occuring 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. There is a possibility that carbon dioxide may diffuse through some plastic containers. Therefore, samples which have little buffer capacity, for example, from moorland stream or underground waters should be stored in glass containers.

8 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 can 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 appopriate. The measurement is then made on the oil free aqueous phase.

9 Analytical Procedure

Step	Analytical Procedure	Notes
9.1	Make sure that the instrument manufacturer's instructions are known and understood.	
	Calibration	
9.2	Turn on the pH meter and allow it to stabilise. (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 stabilise.
9.3	Check that the electrodes are clean, and ready for use. (note b.)	(b) New electrodes require conditioning before use. (see Section 6.1.)
9.4	If the meter provides this adjustment, zero the meter by switching to the zero setting position and adjusting the instrument to read zero.	
9.5	Where necessary, set the pH meter to read pH.	
9.6	Measure the temperature of the buffer solution(s) and set the temperature control appropriately. (note c.)	(c) This step may be omitted for routine work if the instrument is fitted with an automatic temperature compensation.

Step	Analytical Procedure	Notes
9.7	Select the appropriate pH range for the buffer solution.	
9.8	Wash the electrodes with the buffer solution and then immerse them in the buffer solution.	
9.9	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. It is better to swirl the solution gently about the electrodes, fast stirring of samples can lead to a loss or gain of carbon dioxide and a changing pH.
9.10	Set the instrument to read the pH of the buffer solution by adjustment of the appropriate controls (note e).	(e) The reading should be recorded when it becomes constant; this may take up to three minutes or even longer with solution of high ionic strength.
9.11	Rinse the electrodes with water or with the next buffer to be measured.	
9.12	Immerse the electrodes in a second buffer and check that the instrument records the correct pH reading (notes f and g). If an incorrect reading is obtained, the cause must be discovered and the fault rectified before proceeding. See manufacturer's instructions.	(f) The two buffers should if possible bracket the expected pH of the sample solutions. (g) Calibration should be carried out at least daily and when changing from one instrumental pH range to another.
	pH measurement	
9.13	Check the temperature of the sample solution (note h).	(h) Sample and buffer solutions should have the same temperature to within 2°C.
9.14	Wash the electrode with the sample solution.	
9.15	Immerse the electrodes in the sample solution and record the pH (notes i and j).	(i) If the pH reading does not stabilise, it indicates that the pH of the solution is changing. For some natural waters such as moorland water supplies, it may be necessary to measure the pH after an arbitrary time, usually 1 minute. (j) For the most accurate work the measurement should be immediately preceded by calibration with buffer solutions and immediately followed by a re-calibration to check that no drift has occurred during the measurements on the sample.
9.16	Repeat with other sample solutions. (note k).	(k) If the samples all have similar compositions and pH values then rinsing of the electrodes is unnecessary.

10 Sources of Error

(1) Errors can arise from temperature changes, and from changes of equilibria in the sample system. These have already been discussed in Section 2.

(2) Errors can arise from deterioration of electrodes or from fouling of electrodes by oils and greases or precipitated material. See section 6.3

(3) Stray electrical currents induced by static charges can cause an unstable pH indication.

(4) Leakage of electrode filling solutions can lead to errors.

11 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.

An accuracy of $\pm$ 0.1 pH units is satisfactory for most routine monitoring or description purposes. This accuracy is well within the ability of most commercial instruments but may not be achievable for waters whose pH is unstable.

12 Checking the Accuracy of Analytical Results

(for further information see another publication in this series.)

Once the procedure has been put into routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are available, and they should be used as appropriate. As a minimum, however, it is suggested that a solution of known pH be analysed in exactly the same way as normal samples (see Section 5.4 and steps 9.12 to 9.14). The results should then be plotted on a quality control chart. This will facilitate the detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

13 References

(1) Department of the Environment, file WS/646/112.

(2) British Standard 1647: 1961. British Standards Institution, London, 1961.

(3) G Mattock, pH Measurement and Titration, Heywood and Co Ltd London 1961.

(4) R G Bates, Determination of pH, theory and practice, John Wiley and Sons, New York 1973.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
England

Printed in England for Her Majesty's Stationery Office by Metcalfe Cooper Limited, London
Dd 597631 K24 4/79

Standing Committee of Analysts

Members of the Committee Responsible for these Methods:

Dr G I Barrow	after December 1976*
Mr M Beard	†
Mr J R Borland	until December 1977*
Dr J M Carter	*†
Dr J R P Clarke	†
Dr G W Clayfield	*
Mr B E P Clement	after December 1977*
Dr V G Collins	until January 1977*
Dr J Cope	*
Dr R L Cooper	*
Dr B T Croll	*
Mr T A Dick	*
Mr J W R Dutton	after September 1977*
Mr G M C Eastman	†
Mr K Goodhead	after March 1978*
Mr T R Graham	after January 1977*
Mr E Hodges	*
Mr G J Holland	*
Mr O D Hydes	‡
Mr W M Lewis	*
Mr P J Long	*
Mr J C McCullins	*
Mr B L Milford	†
Mr P Morries	*
Mr D Myles	*
Mr A H Nield	*
Dr R J Otter	until September 1977†
Dr H A Painter	*
Dr S J Patteson	*
Mr A S Pearce	‡
Mr K Petts	†
Mr L R Pittwell	*‡
Dr J E Portmann	*
Mr L D Purdie	*
Mr B D Ravenscroft	*
Prof J P Riley	*
Mr J S Ryan	†
Dr E A Simpson	after September 1977†‡
Mr R Sinar	*
Mr B T Whitham	*
Mr A L Wilson	*
Dr R Wood	until March 1978*

*Main committee member**

Working group member†

Editorial board‡

HER MAJESTY'S STATIONERY OFFICE

Government Bookshops

49 High Holborn, London WC1V 6HB
13a Castle Street, Edinburgh EH2 3AR
41 The Hayes, Cardiff CF1 1JW
Brazennose Street, Manchester M60 8AS
Southey House, Wine Street, Bristol BS1 2BQ
258 Broad Street, Birmingham B1 2HE
80 Chichester Street, Belfast BT1 4JY

Government publications are also available through booksellers

ISBN 0 11 751428 4