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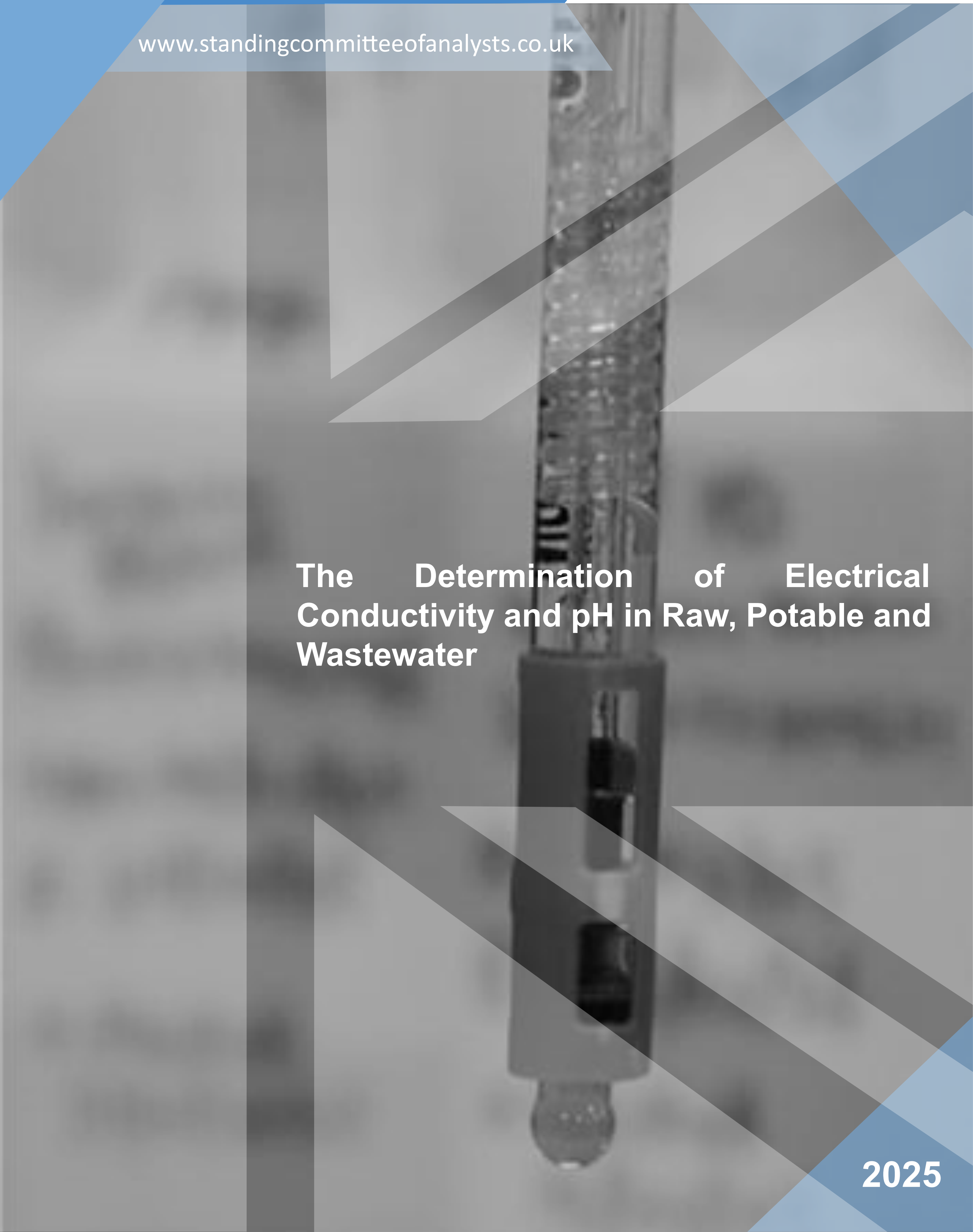

The Determination of Electrical Conductivity and pH in Raw, Potable and Wastewater

2025

The Determination of Conductivity and pH in Raw, Potable and Wastewater

This booklet contains details one manual method for the determination of conductivity, one manual method for the determination of pH and a method for the automated determination of both.

This bluebook updates and replaces:

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

Whilst specific commercial products may be referred to in this document, this does not constitute an endorsement of these products. They serve only as illustrative examples of the types of products available. Equivalent products may be available and it should be understood that the performance of the method might differ when other materials are used and all should be confirmed by validation of the method.

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Contents

About This Series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, wastewater and effluents as well as sewage sludges and biota.

In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of Methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection - often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series “Methods for the Examination of Waters and Associated Materials” and their continuing revision is the responsibility of the Standing Committee of Analysts (SCA) - Established 1972 by the Department of the Environment.

At present, there are several working groups, each responsible for one section or aspect of water quality analysis:

1. General principles of sampling and accuracy of results
2. Microbiological methods
3. Inorganic and physical methods, metals and metalloids
4. Organic methods
5. Biological, biodegradability and inhibition methods
6. Radiochemistry methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will appear on our website – the library for which serves as a record of the bona fide methods developed and produced by the Standing Committee of Analysts.

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Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

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Users should ensure they are aware of the most recent version they seek.

Warning to Users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed, and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc. Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety. Amongst such resources are:

HSE: Information about health and safety at work

RSC: Laboratory best practices

A The Manual Determination of Conductivity in Raw, Potable and Wastewater

A1 Introduction

Conductivity is a measure of a solutions ability to conduct electricity. This is often used as a non-specific test for the presence of ionised substances in a sample. Regardless of the matrix, it is an indicator of change within a water system.

Conductivity measurements are usually reported in µScm^{-1}, a more convenient form of the SI unit Siemens/metre.

After collection the conductivity of samples may change with time for this reason users of this method must establish stability times for their own samples. Factors to consider could include, but is not limited to: sampling arrangements, sample container used and sample storage arrangements.

A2 Performance Characteristics

A2.1	Substances determined	The electrical conductivity of the sample.
A2.2	Type of sample	Raw, potable and wastewater.
A2.3	Basis of method	The electrical resistance of the sample is determined in a cell of known dimensions.
A2.4	Range of application	Appropriate to data range. The method described here is suited to raw and potable waters. Calibration and quality control standards concentration should be appropriate to the ionic concentration of the samples being determined.
A2.5	Standard deviation	See appendices.
A2.6	Limit of detection	See appendices.
A2.7	Bias	See appendices.
A2.8	Interferences	Erroneous data may result by the mechanical blocking of parts of the electrode system by suspended matter, oil or grease.
A2.9	Sample stability	See ISO 5667-3:2024.

A3 Principle

Electrical conductivity is a measure of a solutions ability to conduct electricity. In SI units, the unit of conductivity is the Siemen m^{-1} although, for convenience, most measurements are reported in units of Microsiemens cm^{-1} (μScm^{-1}).

The electrical conductivity of a solution depends on the concentration of the ions present and the temperature of the solution. To a first approximation, the contribution to 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 Ionisable Solids

Electrical conductivity is often used as a rapid method of estimating the concentration of total dissolved ionisable solids. The relation between this concentration and conductivity will depend upon the nature of the ionised species present and, in general, will vary from one water to another.

Temperature

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

Many instruments include automatic temperature compensation but the construction of the instruments assumes an average value for the temperature coefficient of variation of conductivity. For this reason it is advisable to use the temperature compensation only at 20 ± 5 °C.

A4 Hazards

Refer to the manufacturers Safety Data Sheet for full details of the hazards associated with these materials before use. Wear appropriate PPE.

Potassium chloride

No special precautions need to be taken when working with potassium chloride, however it is advisable to wear safety glasses when preparing solutions.

A5 Reagents

Analytical grade reagents or equivalents must, whenever possible, be used. All solutions must be at 20 ± 5 °C

Water must be of Ultra High Quality (UHQ) or equivalent, achieving a conductivity before use of <5 µScm^{-1}.

Calibration Standards

Calibration Standard 3000 µScm^{-1} @ 20 °C

Dissolve 1.8597 ± 0.0005 g of potassium chloride, (previously dried for at least 2 hours but not more than 3 hours at 105 ± 5 °C and allow to cool in a desiccator for 30 ± 10 minutes) in deionised water. Dilute to 1 litre in a volumetric flask. Invert several times and shake in the inverted position to ensure thorough mixing. This must be crosschecked against a traceable standard. This solution is stable for up to a year.

Calibration Standard 1278 µScm^{-1} @ 20 °C

Dissolve 0.7456 ± 0.0005 g of potassium chloride, (previously dried for at least 2 hours but not more than 3 hours at 105 ± 5 °C and allow to cool in a desiccator for 30 ± 10 minutes) in deionised water. Dilute to 1 litre in a volumetric flask. Invert several times and shake in the inverted position to ensure thorough mixing. This must be crosschecked against a traceable standard. This solution is stable for up to one year.

Calibration Standard 300 µScm^{-1} @ 20 °C

Transfer 100 ml ± 0.2 ml of the 3000 µScm^{-1} calibration standard using a volumetric flask and quantitatively transfer into a clean 1 litre volumetric flask. Dilute to the mark with water and stopper the flask. Invert several times and shake to mix thoroughly. Stable for up to one year.

AQC Solutions

These solutions may be prepared from potassium chloride from a different supplier or batch number to that used to prepare the calibration standard. Pre-prepared solutions available from many suppliers may also be used.

Stock Control Solution

Stock standard (0.05M KCl)

Dissolve 3.728 ± 0.005 g (7.456 g for 2 litres) of KCl, dried for at least 2 hours at 105 ± 5 °C but not more than 3 hours, and allowed to cool in a desiccator for 30 ± 10 minutes, in deionised water. Dilute to 1 litre in a volumetric flask and stopper the flask. Invert several times and shake to mix thoroughly. Stable for one month.

Working AQC Solutions

High AQC (0.020M KCl) 2500 μScm^{-1} @ 20 °C

Transfer 400 ml of the 0.05M KCl working stock using a volumetric flask and quantitatively transfer into a clean 1 litre volumetric flask. Dilute to the mark with water and stopper the flask. Invert several times and shake to mix thoroughly. Stable for one month.

Low AQC (0.005M KCl) 650 μScm^{-1} @ 20 °C

Measure 100 ml of the 0.05M KCl working stock using a volumetric flask and quantitatively transfer into a clean 1 litre volumetric flask. Dilute to the mark with water and stopper the flask. Invert several times and shake to mix thoroughly. Stable for one month.

A6 Apparatus

In addition to grade B or better laboratory glassware, the following apparatus will be required.

Conductivity meter

Conductivity electrode

Either the samples must be at 20 °C or the apparatus must compensate for temperature.

A7 Sample Collection, Preservation and Preparation

Samples can be taken in either glass or plastic bottles of suitable size. It is essential that the bottles used are scrupulously clean and free from dust. The sample collection vessel should be washed with the sample being collected. The sample container should be completely filled.

Samples should be analysed as soon as possible after collection, particularly when there is a 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 3 ± 2 °C, however samples must be brought to ambient temperature before analysis. The first aliquot taken from the bottle should be used for this determination.

There is no suitable preservative for conductivity or pH.

Consult ISO 5667-3:2024 for details regarding preservation and handling.

It is important to note that users must establish the stability time of their own samples.

Samples should be measured as received unless they contain oil, grease or gross suspended matter which can affect the electrode. If these materials are present, they can be separated using a separating funnel, by the use of oil absorbent materials, by siphoning off a portion of the aqueous phase, by filtering through a pad of cotton wool or by filtering, as appropriate. The measurement is then made on the oil/gross suspended matter free aqueous phase.

A8 Analytical Procedure

NB. Meter use and displays will vary make to make, always read manufacturer’s instructions.

A8.1 Start Up

A8.1.1 Turn on the conductivity meter.

A8.1.2 Prepare the electrode for use by rinsing the electrode with deionized water and blotting dry with a tissue.

A8.2 Calibration

A8.2.1 Calibrate as shown in manufacturer’s instructions - The display will show a temperature corrected value of the standard that is needed for the calibration (1278 μScm^{-1} @ 20 °C). the standard should be fresh from the bottle and poured in a separate beaker or appropriate containers. Do not allow the probe to come into contact with the container.

A8.2.2 Put the probe in the standard solution, stir gently and press “read”. The display will show “stabilising” and a progress bar as the probe stabilises in the standard.

A8.2.3 Once stabilised the display will show the standard that has just been read and the temperature corrected value.

A8.2.4 Ensure the cell constant is as stated on the probe certificate of conformity and record this in the maintenance records. If the value is outside the accepted tolerance seek the advice.

A8.2.5 Push store to accept the calibration and to go back to measurement mode.

A8.2.6 Check linearity with an appropriate solution.

A8.3 Analysis of samples

A8.3.1 Wash the electrode with the sample solution by filling the beaker, immersing the electrode, swirling and then discarding it.

A8.3.2 Immerse the electrodes in the beaker containing fresh sample and check the temperature of the sample. Record the reading to 1 μScm^{-1}. Results are reported as μScm^{-1}at 20 °C. Standards and samples must fall in the range 20 ± 5 °C as displayed on the meter.

A8.3.3 Repeat steps 8.3.1 and 8.3.2 for all samples and AQC’s in the batch.

A8.3.4 After use the probe should be cleaned and stored according to manufacturer’s instructions.

A9 Interferences

Gross suspended matter, oils and greases can coat the electrodes which may affect performance.

A10 Sources of Error

Gross suspended matter, oils and greases can coat the electrodes which may affect performance.

B The Manual Determination of pH in Raw, Potable and Wastewater

B1 Introduction

pH is the logarithm to the base 10 of the reciprocal of the hydrogen ion activity.

B2 Performance Characteristics

B2.1 Substances determined pH, which is the logarithm to the base 10 of the reciprocal of the hydrogen ion activity.

B2.2 Type of sample Drinking, Raw (Surface and Ground) Waters and wastewaters. The method is not suitable for saline or sea waters of high pH due to sodium error.

B2.3 Basis of method Measurements 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.

B2.4 Range of application
The practical pH is 0 to 14.

B2.5 Calibration Curve
Linear in the pH range 2-12 (pH is a logarithmic function).

B2.6 Standard deviation
See appendices.

B2.7 Limit of detection
Not applicable

B2.8 Sensitivity
The sensitivity is usually close to 59 millivolts per pH unit at 25 °C.

B2.9 Bias
None

B2.10 Interference
Sodium at pH 10 interferes. Oil, grease and suspended matter can interfere by blocking off the electrode surface.

B2.11 Sample Stability
See ISO 5667-3:2024

B3 Principle

The pH of a solution is defined by the equation:

$$pH = -\,log\,[H+]$$

Where H^+ is the activity of hydrogen ions in the solution expressed in gram-moles.litres^{-1}. 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	Reference	:	Salt	:	Test or standard	Measuring
Electrode	Solution	:	Bridge	:	Buffer Solution	Electrode

Then:

$$pH_{(x)} - pH_{(s)} = \frac{(E_S - E_x)F}{2.3026 * RT}$$

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.

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 two solutions.

The term $\frac{2.3026 * RT}{F}$ expressed in millivolts, has the value 59.16 at 25 °C.

The values at other temperatures are given in the following table (JIS Z 8802-2006):

Temperature °C	2.3026 RT/F (millivolts)
0	54.19
5	55.19
10	56.18
15	57.17
20	58.16
25	59.15
30	60.15
40	62.13
50	64.11

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

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:

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

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 asymmetry 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 standardisation of the meter. A temperature difference of 1 °C gives rise to an error of about 0.01 pH unit.

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. The slope is measured daily and must be 95% or better for the method to be accurate. The value is recorded in the maintenance records. Allowance can usually be made for this with modern pH meters.

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.

B4 Hazards

Refer to the manufacturers Safety Data Sheets sheet for full details of the hazards associated with these materials before use. Wear appropriate Personal Protective Equipment.

Potassium di-hydrogen phosphate

Di-sodium hydrogen phosphate

No special precautions need to be taken when working with these salts, however it is advisable to wear safety glasses when preparing solutions.

B5 Reagents

Analytical grade reagents or equivalents must, whenever possible, be used.

Water must be of UHQ quality or equivalent.

Buffer solutions

pH 4, 7 and 10

For convenience, most laboratories prefer to purchase ready-made calibration buffers.

Stock Check Solution

In a 2 litre volumetric flask containing approximately 500 ml of deionised water dissolve 2.356 ± 0.001 g of Potassium di-hydrogen phosphate and 8.640 ± 0.001 g of Di-sodium hydrogen phosphate previously dried at 110-130 °C for at least 2 hours and allowed to cool in a desiccator for 30 ± 10 minutes. Make up to the mark with deionised water. Stopper and invert several times to ensure thorough mixing. This solution is stable for one month.

Working Check Solution pH 7.62

In a 1 litre volumetric flask containing approximately 500 ml of deionised water, add using a glass bulb pipette 100 ml of Stock Check Solution. Make up to the mark with deionised water. Stopper and invert several times to ensure thorough mixing. This solution is stable for one month.

B6 Apparatus

In addition to normal laboratory glassware, the following will be required:

pH meter and electrode

Take advice from manufacture regarding choice, preparation and storage.

B7 Sample Collection, Preservation and Preparation

Samples can be taken in either glass or plastic bottles of suitable size. It is essential that the bottles used are scrupulously clean and free from dust. The sample collection vessel should be washed with the sample being collected. The sample container should be completely filled.

Samples should be analysed as soon as possible after collection, particularly when there is a 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 3 ± 2 °C, however samples must be brought to ambient temperature before analysis. The first aliquot taken from the bottle should be used for this determination.

There is no suitable preservative for conductivity or pH.

Consult ISO 5667-3:2024 for details regarding preservation and handling. It is important to note that users must establish the stability time of their own samples.

Samples should be measured as received unless they contain oil, grease or gross suspended matter which can affect the electrode. If these materials are present, they can be separated using a separating funnel, by the use of oil absorbent materials, by siphoning off a portion of the aqueous phase, by filtering through a pad of cotton wool or by filtering, as appropriate. The measurement is then made on the oil/gross suspended matter free aqueous phase.

B8 Analytical Procedure

B8.1 Turn on the pH meter and allow it to stabilise. To improve stability, instruments may be left on permanently. Modern instruments with solid state circuitry require only a short time to stabilise.

B8.2 Check that the electrodes are clean and ready for use. New electrodes require conditioning before use. See manufacturer’s instructions.

B8.3 Set up and standardise the pH meter in accordance with the instrument operating instructions by adjustment of the appropriate controls. The sample should be gently swirled around the electrodes and then allowed to stand until a steady reading is obtained. Samples should not be vigorously stirred as this can lead to a loss or gain of carbon dioxide and a changing pH. The reading should be recorded when it becomes constant. The meter may have an indicator to show when a stable reading has been reached.

B8.4 Daily calibration is carried out using at least two buffers across range of analysis. This sets the slope of the electrode, which is recorded in the maintenance records. After contact with the buffers the electrode is thoroughly rinsed with deionised water.

B8.5 A daily linearity check at the start and end of pH analysis is carried out. Immediately after calibration (2 point) and at the end of the day's analysis, the linearity check is carried out using pH 7.0 buffer. Record the readings in the maintenance records. Ensure that the result meets the acceptability criteria and act accordingly.

B8.6 Wash the electrode with the sample solution. Fill beaker, immerse electrodes, swirl and discard. Immerse the electrodes in solution and check the temperature of the sample Record pH to 0.01 pH units. Buffers and samples must fall in the range 20 ± 5 °C as displayed on the meter. 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 one minute.

B8.7 Repeat the procedure for all samples and AQC's in the batch. Rinse as in B8.6 for each sample. Samples and calibrants should be analysed at the same temperature.

B9 Interferences

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. Consult manufacturer's instructions for sodium levels and appropriate actions should the electrode be affected.

Gross suspended matter, oils and greases can coat the electrode which may affect performance.

B10 Sources of Error

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

Leakage of electrode filling solutions can lead to errors. See interferences.

C The Determination of Conductivity and pH in Raw, Potable and Wastewater Using an Automated Technique

C1 Introduction

Increasingly pH and conductivity analysis can be automated. This use of an automated technique maximises throughput while still utilising a similar meter as used for manual analysis.

C2 Performance Characteristics

C2.1	Substances determined	Conductivity - measured in μScm-1 pH – which is the logarithm to the base 10 of the reciprocal of the hydrogen ion activity.
C2.2	Type of sample	Raw, potable and waste waters.
C2.3	Basis of method	The electrical resistance of the sample is determined in a cell of known dimensions. Measurements 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.
C2.4	Range of application	Appropriate to data range. The method described here is suited to raw and potable waters. Calibration and quality control standards concentration should be appropriate to the ionic concentration of the samples being determined. The practical pH is 0 to 14.
C2.5	Sensitivity	pH - The sensitivity is usually close to 59 millivolts per pH unit at 25 °C.
C2.6	Standard deviation	See appendices.
C2.7	Limit of detection	See appendices.
C2.8	Bias	See appendices.
C2.9	Sample stability	See ISO 5667-3:2024

C3 Principle

An automated robotic system is designed to perform conductivity and pH measurements on water samples. A typical system comprises of an autosampler that is capable of sampling either from the original sample bottle or a suitable vessel containing a sub sample. The sample is pumped through tubing by peristaltic pumps into flow cells containing conductivity and pH electrodes. The electrodes may also be mounted on a gantry from which they may be lowered into the samples. These electrodes will be connected to an appropriate meter or meters, from which reading may be taken. These meters may be of the same type used to carry out manual determination of colour and turbidity.

For analytical principles see:

Conductivity	A3
pH	B3

Trials should be carried out using samples of known concentrations during method development in order to assign suitable settings within the instrument software. These settings will typically relate to result stability times, the total read time and the number of readings carried out in order to obtain a stable result.

C4 Hazards

Refer to the manufacturers SDS sheet for full details of the hazards associated with these materials before use. Wear appropriate PPE.

Conductivity	A4
pH	B4

C5 Reagents

Conductivity	A5
pH	B5

C6 Apparatus

In addition to normal laboratory glassware, the following will be required.

A robotic system comprising of an autosampler, an appropriate meter or meters, a pH probe and/or a conductivity probe. The system should include a wash function to adequately clean the probes between samples to reduce the risk of carry over.

C7 Sample Collection, Preservation and Preparation

Samples can be taken in either glass or plastic bottles of suitable size. It is essential that the bottles used are scrupulously clean and free from dust. The sample collection vessel should be washed with the sample being collected. The sample container should be completely filled.

Samples should be analysed as soon as possible after collection, particularly when there is a 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 3 ± 2 °C, however samples must be brought to ambient temperature before analysis. The first aliquot taken from the bottle should be used for this determination.

There is no suitable preservative for conductivity or pH.

It is important to note that users must establish the stability time of their own samples.

Consult ISO 5667-3:2024 for details regarding preservation and handling.

Samples should be measured as received unless they contain oil, grease or gross suspended matter which can affect the electrode. If these materials are present, they can be separated using a separating funnel, or by the use of oil absorbent materials, by siphoning off a portion of the aqueous phase, by filtering through a pad of cotton wool, or by filtering, as appropriate. The measurement is then made on the oil/gross suspended matter free aqueous phase.

C8 Analytical Procedure

C8.1 Ensure the Automated Robotic system and associated instruments are switched on. Check that the air supply to the system is working and that the air pressure is correct (if applicable). If a stirring device is used, check that it is working correctly.
Check the pump tubing for any damage and change if necessary.

C8.2 Prepare the calibration standards and place them in the correct containers on the auto sampler.

C8.3 Ensure a calibration is carried out in which the calibration standards are sampled and processed by the Automated Robotic system.

C8.4 Once the calibration is finished, examine the calibration graphs and make a note of any system suitability check values. If any values are outside the quoted tolerances do not proceed with sample analysis. Investigate why the checks are not satisfactory, resolve any problems found and repeat the calibration(s) that failed.

If all of the System Suitability checks are within tolerance levels, commence analysis.

Examples of suitable SSC checks could include for pH, a calibration slope and for conductivity, a cell constant and drift checks for both.

C8.5 If required, prepare a worksheet and racking list to determine the order in which samples will be positioned on the auto sampler.

C8.6 Prepare the AQC standards required and place them in suitable containers on the autosampler along with the samples and blanks (recommended frequency of one in every 20 samples).

C8.7 Some robotic systems are equipped with a barcode reader. If barcodes are used, the sample numbers may be automatically stored in the correct position in the run sequence.

C8.8 The analytical run may be started when all samples and standards are in position. No further operator input is required until the analytical run is complete.

C8.9 When complete, the sample results can be entered onto the laboratory's results database provided that all system suitability checks, calibrations, AQC and blank results are acceptable.

C8.10 All automated systems should be well maintained in order to ensure method performance does not deteriorate. Typically, issues can occur due to restricted sample flow through the system. This can be due to 'flattened' peristaltic pump tubing, the build-up of deposits in the tubing and reduced performance from any motors responsible for pumping sample through the system. A suitable preventative maintenance programme can ensure these issues are rarely encountered. A daily wash with a laboratory cleaning agent can ensure tubing is kept free from any build-up. It is advisable to carry out regular preventative maintenance on any analytical instrumentation in line with the manufacturer's recommendations.

C9 Interferences

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.

Oils and greases coat the electrodes which may affect performance. Gross suspended matter can cause problems by blocking pores or capillaries or coating electrode surfaces.

C10 Sources of Error

Errors can arise from temperature changes, and from changes of equilibria in the sample system.

Errors can arise from the deterioration of electrodes or from fouling of electrodes by oils, greases or precipitated material.

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

Leakage of electrode filling solutions can lead to errors. See interferences.

APPENDIX I – Full Method Performance Data South West Water (SWW) Automated System & Manual Data

pH Automated

		Low Standard	Medium Standard	High Standard	Average Standards	Average Matrices	Surface	Ground	Potable	Bottled
Nominal	pH	4	7	10	-	-	-	-	-	-
Mean	pH	3.96	6.982	9.974	6.972	7.133	7.419	6.48	7.379	7.254
Within Batch SD (S_w)	pH	0.012	0.011	0.012	0.0117	0.055	0.038	0.058	0.062	0.062
Bias	pH units	-0.04	-0.018	-0.026	-0.028	-	-	-	-	-
Degrees of Freedom	-	12	15	19	15	14	16	12	14	15

High Conductivity Automated

		Blank	Low Standard	Medium Standard	High Standard	Average Standards	Average Matrices	Surface	Ground	Final
Nominal	uS/Cm	-	250	1500	4275.455			2500	2500	2500
Mean	uS/Cm	14.92	256.909	1546	4275.455	2026	2642	2663	2666	2614
Within Batch SD (S_w)	uS/Cm	1.193	1.883	8.847	30	13.58	34.72	13.65	67.86	39.02
RSD	%	11.4	1.26	1.06	2.82	1.71	2.37	1.22	2.89	3.21
Recovery	%	-	102.8	103.1	106.1	104.0	98.64	98.78	96.68	99.92
Bias	%	-	2.764	3.067	6.062	3.964	-1.359	-1.217	-3.325	-0.084
Degrees of Freedom	-	16	14	14	12	13	13	10	20	12

pH Manual

		Blank	Low Standard	Medium Standard	High Standard	Average Standards	Average Matrices	Soft Water	Hard Water
Nominal	pH	-	4.01	7.02	10.01				
Mean	pH	-	3.972	7.007	10.013	7.292	7.714	8.174	7.714
Within Batch SD (S_w)	pH	-	0.0189	0.013	0.009	0.019	0.045	0.035	0.045
Bias	%	-	-0.94	-0.19	0.03	-0.37			
Degrees of Freedom	-	-	21	21	21	21			

High Conductivity Manual

		Blank	Low Standard	Medium Standard	High Standard	Average Standards	Average Matrices	Hard Water	Soft Water
Nominal	uS/Cm	-	250	1500	4523	-	-	-	-
Mean	uS/Cm	2.954	257.559	1525	4463.2	2082	86.5135	92.241	80.786
Within Batch SD (S_w)	uS/Cm	1.473	4.112	7.428	49.30	20.28	1.536	0.648	2.424
RSD	%	-	1.77	0.93	3.21	1.97	2.12	1.24	3
Recovery	%	-	103.0	101.7	97.78	100.8	-	-	-
Bias	%	-	3.02	1.67	-2.22	0.82	-	-	-
Degrees of Freedom	-	-	21	21	21	21	-	-	-

APPENDIX II – Average Performance Data Multiple Laboratories

Potable Water pH

		Portsmouth Water		United Utilities		South East Water		SES Water		Thames Water		Scottish Water		Scottish Water		DCWW		DCWW		ALS Wakefield	
		Standards / AQC	treated, surface, ground	Standards / AQC	soft final, hard final, medium final, raw	Standards / AQC	surface, ground, treated	Standards / AQC	raw surface, raw ground, treated	Standards / AQC	tap, ground, raw	Standards / AQC	soft, hard, ground, surface	Standards / AQC	soft, hard, ground, surface	Standards / AQC	soft, medium, ground hard, surface raw	Standards / AQC	soft, medium , ground hard, surface raw	Standards / AQC	soft, medium, hard, raw surface, borehole
Mean	pH units	8.037	7.757	7.280	7.639	7.273	7.830	7.153	8.104	7.221	7.831	6.760	7.430	6.859	7.469	7.011	8.366	7.020	8.071	7.420	7.866
S_w	pH units	0.021	0.046	0.017	0.151	0.005	0.020	0.010	0.019	0.011	0.025	0.018	0.023	0.010	0.058	0.009	0.023	0.007	0.028	0.010	0.015
Bias	pH units	0.005	NA	0.030	NA	0.023	-0.003	0.015	0.058	-0.029	N/A	0.030	N/A	0.043	N/A	0.011	N/A	0.020	N/A	0.028	NA
Degrees of Freedom		16	12	18	20	21	21	10	10	18	15	17	12	14	17	18	15	16	14	16	14
Method Type		Manual		Manual		Automated		Manual		Automated		Manual		Automated		Manual		Automated		Manual	
Date of Testing		Oct-13		Jan-11		Jun-15		Jan-22		2016		Jul-14		Jan-22		Oct-20		Jul-18		Apr-12	

Potable Water Conductivity

		Portsmouth Water		United Utilities		South East Water		SES Water		Thames Water		Thames Water		Scottish Water		Scottish Water		DCWW		DCWW		ALS Wakefield	
		Standards / AQC	treated, surface, ground	Standards / AQC	treated soft, treated ground hard, raw medium surface, raw ground	Standards / AQC	surface, ground, treated	Standards / AQC	raw surface, raw ground, treated	Standards / AQC	tap, ground, raw	Standards / AQC	tap, ground, raw, saline	Standards / AQC	soft, hard, ground, surface	Standards / AQC	soft, hard, ground, surface	Standards / AQC	soft, medium, ground hard, surface raw	Standards / AQC	soft, medium, ground hard, surface raw	Standards / AQC	Soft, medium, hard, raw surface, borehole
Mean	µS/cm @ 20˚C	1123	527	763	387	795	2216	2053	442	685	533	4954	3173	96	161	1304	137	1028	320	1041	250	922	932
S_w	µS/cm @ 20˚C	1.97	2.44	3.05	1.22	2.76	4.80	10.11	2.52	1.53	1.61	1.53	n/a	0.32	0.64	9.32	0.52	1.31	0.66	4.27	0.88	6.55	6.01
RSD	%	0.63	1.11	0.60	2.98	1.35	0.91	1.00	0.97	1.00	1.00	0.30	0.72	0.50	1.00	0.65	0.62	0.54	0.71	0.66	0.90	0.93	0.94
Recovery	%	99.5	N/A	N/A	N/A	100.25	95.7	N/A	95.1	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	99.7	N/A	101	N/A	N/A	96.9
Bias	%	-0.50	N/A	1.61	N/A	-0.02	NA	0.99	NA	-0.14	NA	-0.14	N/A	1.50	N/A	0.23	N/A	-0.32	N/A	1.03	N/A	0.02	3.12
Degrees of Freedom		11	12	22	14	21	21	24	22	11	11	N/A	N/A	14	12	19	18	10	11	13	14	16	16
Method Type		Manual		Automated		Automated		Manual		Automated		Manual		Manual		Automated		Manual		Automated		Manual	
Date of Testing		Apr-15		May-18		Jul-15		Oct-19		2016		2017		Jan-21		Jan-22		Jul-15		Jul-18		May-12	

Wastewater pH

		South East Water		ALS Coventry		ALS Coventry		Environment Agency		ALS Hawarden		ALS Wakefield	
		Standards / AQC	process, treated effluent, treated sewage	Standards / AQC	surface, ground, crude, final, trade	Standards / AQC	ground, crude, final, trade	Standards / AQC	waste water	Standards / AQC	surface, ground, final, crude, trade, landfill leachate, sea water, CRM ERA799, CRM ERA977	Standards / AQC	final, trade, crude
Mean	pH units	7.268	7.457	7.020	8.031	7.037	7.526	7.621	7.307	7.630	8.156	7.053	7.642
S_w	pH units	0.011	0.030	0.018	0.101	0.020	0.081	0.008	0.011	0.070	0.076	0.018	0.051
Bias	pH units	0.0175	N/A	0.020	N/A	0.037	N/A	0.0014	N/A	0.210	0.030	0.053	N/A
Degrees of Freedom		28	22	17	14	15	12	17	10	N/A	N/A	18	13
Method Type		Manual		Automated		Manual		Automated		Automated		Manual	
Date of Testing		Nov-15		Oct-15		Jan-14		Nov-20		Nov-19		Apr-14	

Wastewater Conductivity

		South East Water		ALS Coventry		ALS Coventry		Environment Agency		ALS Hawarden		ALS Wakefield	
		Standards / AQC	surface	Standards / AQC	surface, ground, untreated sewage, treated sewage, trade effluent	Standards / AQC	surface, ground, untreated sewage, treated sewage, trade effluent	Standards / AQC	waste water	Standards / AQC	ground, surface, final, crude, trade, landfill leachate, sea water, CRM ERA01620	Standards / AQC	final, trade, crude
Mean	µS/cm	784	2735	34487	27709	33680	2586	135	1060	1410	12348	4905	7017
S_w	µS/cm	4.9	34.8	108.0	141.0	180.9	13.6	0.1	6.3	N/A	N/A	12.9	82.8
RSD	%	1.84	2.14	0.95	1.04	1.18	1.12	0.35	N/A	3.90	2.44	0.54	1.35
Recovery	%	N/A	94.00	100.4	98.21	99.30	92.59	100.5	N/A	N/A	N/A	100.1	95.88
Bias	%	-1.69	N/A	0.53	-1.79	-0.70	-7.41	0.31	N/A	6.00	0.51	0.06	4.12
Degrees of Freedom		21	21	13	12	15	12	10	13	N/P	N/P	15	17
Method Type		Manual		Automated		Manual		Automated		Automated		Manual	
Date of Testing		Dec-15		Oct-15		Apr-14		Aug-20		Dec-19		May-14	

APPENDIX III - pH Stirring & Refrigeration Data (Portsmouth Water)

Different samples were analysed in duplicate to investigate the effect on pH of using a magnetic stirrer and leaving a sample out for an hour uncovered. To do this, two aliquots of the same samples were poured and left uncovered. One to be analysed immediately without and then with a magnetic stirrer. The second to be analysed an hour later without and then with a magnetic stirrer. All samples were analysed at temperature 18 – 22 ˚C.

			No Stirring (immediate)	Stirring (immediate)	Absolute Stirring Difference (Immediate)	No Stirring (1 hr)	Stirring (1 hr)	Absolute Stirring Difference (1 hr)	Immediate vs 1 hr Unstirred Absolute Difference	Immediate vs 1 hr Stirred Absolute Difference
Sample Date	**Analysis Date**	**Sample Origin**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**
05.06.2023	06.06.2023	RWSOB-B1	7.28	7.29	0.01	7.57	7.52	0.05	0.29	0.23
05.06.2023	06.06.2023	RWSOB-B1	7.28	7.30	0.02	7.46	7.45	0.01	0.18	0.15
05.06.2023	06.06.2023	RWGAM	8.17	8.18	0.01	8.22	8.24	0.02	0.05	0.06
05.06.2023	06.06.2023	RWGAM	8.20	8.20	0.00	8.26	8.30	0.04	0.06	0.10
05.06.2023	06.06.2023	TWITCH	7.49	7.48	0.01	7.70	7.70	0.00	0.21	0.22
05.06.2023	06.06.2023	TWITCH	7.49	7.48	0.01	7.67	7.68	0.01	0.18	0.20
05.06.2023	06.06.2023	ZZFA1	7.40	7.39	0.01	7.60	7.61	0.01	0.20	0.22
05.06.2023	06.06.2023	ZZFA1	7.38	7.33	0.05	7.57	7.59	0.02	0.19	0.26
05.06.2023	06.06.2023	RSLH1	7.11	7.13	0.02	7.45	7.45	0.00	0.34	0.32
05.06.2023	06.06.2023	RSLH1	7.12	7.11	0.01	7.35	7.33	0.02	0.23	0.22
14.07.2023	14.07.2023	RSAPP	7.46	7.42	0.04	7.52	7.53	0.01	0.06	0.11
14.07.2023	14.07.2023	RSAPP	7.45	7.41	0.04	7.52	7.51	0.01	0.07	0.10
14.07.2023	14.07.2023	TWFARL	7.27	7.25	0.02	7.33	7.32	0.01	0.06	0.07
14.07.2023	14.07.2023	TWFARL	7.27	7.25	0.02	7.33	7.32	0.01	0.06	0.07
14.07.2023	14.07.2023	TWITCH	7.49	7.47	0.02	7.51	7.51	0.00	0.02	0.04
14.07.2023	14.07.2023	TWITCH	7.49	7.47	0.02	7.52	7.51	0.01	0.03	0.04
14.07.2023	14.07.2023	RWWAL3	7.31	7.3	0.01	7.34	7.34	0.00	0.03	0.04
14.07.2023	14.07.2023	RWWAL3	7.32	7.29	0.03	7.32	7.32	0.00	0.00	0.03
14.07.2023	14.07.2023	ZZFA3	7.35	7.32	0.03	7.44	7.42	0.02	0.09	0.10
14.07.2023	14.07.2023	ZZFA3	7.33	7.32	0.01	7.43	7.41	0.02	0.10	0.09
18.07.2023	18.07.2023	RWGAM	8.17	8.12	0.05	8.17	8.18	0.01	0.00	0.06
18.07.2023	18.07.2023	RWGAM	8.16	8.12	0.04	8.18	8.18	0.00	0.02	0.06
				Average	0.02		**Average**	0.01	0.11	0.13
				Median	0.02		**Median**	0.01	0.06	0.10
				Max	0.05		**Max**	0.05	0.34	0.32

Testing carried out to check if leaving samples in the fridge for three days in half empty bottle would affect the pH. All samples were analysed at temperature 18 – 22 ˚C. In all cases the pH has been higher when compared with pH tested on day one.

Samples left in the fridge 3 days and retested

			Original No Stirring (immediate)	Original Stirring (immediate)	Absolute Stirring Difference (Immediate)	Refrigerated 3 days No Stirring (immediate)	Refrigerated 3 days Stirring (immediate)	Refrigerated 3 days Stirring Difference (immediate)	Day 1 vs Day 3 Unstirred Absolute Difference	Day 1 vs Day 3 Stirred Absolute Difference
Sample Date	**Reanalysis Date**	**Sample Origin**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**	**pH units**
14.07.2023	17.07.2023	RSAPP	7.46	7.42	0.04	7.54	7.54	0.00	0.08	0.12
14.07.2023	17.07.2023	RSAPP	7.45	7.41	0.04	7.55	7.55	0.00	0.10	0.14
14.07.2023	17.07.2023	TWFARL	7.27	7.25	0.02	7.6	7.6	0.00	0.33	0.35
14.07.2023	17.07.2023	TWFARL	7.27	7.25	0.02	7.61	7.62	0.01	0.34	0.37
14.07.2023	17.07.2023	TWITCH	7.27	7.25	0.02	7.76	7.75	0.01	0.49	0.50
14.07.2023	17.07.2023	TWITCH	7.49	7.47	0.02	7.78	7.76	0.02	0.29	0.29
14.07.2023	17.07.2023	RWWAL3	7.31	7.3	0.01	7.62	7.6	0.02	0.31	0.30
14.07.2023	17.07.2023	RWWAL3	7.32	7.29	0.03	7.64	7.6	0.04	0.32	0.31
14.07.2023	17.07.2023	ZZFA3	7.35	7.32	0.03	7.57	7.56	0.01	0.22	0.24
14.07.2023	17.07.2023	ZZFA3	7.33	7.32	0.01	7.58	7.57	0.01	0.25	0.25
				Average	0.02		**Average**	0.01	0.16	0.18
				Median	0.02		**Median**	0.01	0.11	0.14
				Max	0.05		**Max**	0.05	0.49	0.50

🟧	equals to 0.10 or greater than
🟩	0.09 or under

Members Assisting with these Methods

Without the good will and support given by these individuals and their respective organisations SCA would not be able to continue and produce the highly valued and respected blue book methods.

Chris Pegg	Anglian Water
Emma Thorpe	ALS Laboratories UK Ltd
Paul Colenutt	ALS Laboratories UK Ltd
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Correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts:

secretary@standingcommitteeofanalysts.co.uk

Amendment History

The Determination of Electrical Conductivity and pH in Raw, Potable and Wastewater supersedes the bluebook method of the same name published in 1978 with the following key changes highlighted for your convenience:

Page	Section	Amendment(s)
19	C	New section on automated pH and conductivity analysis.

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