

# Determination of the pH Value of Sludge, Soil, Mud and Sediment; and the Lime Requirement of Soil (Second Edition) 1992

Methods for the Examination of Waters and Associated Methods

This document  
contains 20 pages

# **Determination of the pH Value of Sludge, Soil, Mud and Sediment; and the Lime Requirement of Soil (Second Edition) 1992**

## **Methods for the Examination of Waters and Associated Materials**

This volume contains two related methods with additional notes and references based on experience.

The use of methods given in the first edition, whilst satisfactory for most soils etc give drifting readings with some soils due to the low conductivity of the water in these samples. Similar problems arising with low ionic strength waters resulted in further studies and the publication of a new pH measurement booklet in this series (Ref 3). This present booklet, while not replacing the first edition for pH measurement of those soils for which it is satisfactory, gives additional advice on difficult soil measurements.

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# About This Series

This booklet is part of a series intended to provide recommended methods for determining the quality of water and associated materials. In addition, short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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 is published as a 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.

Although ideally, all methods published should be fully tested, this is not often possible without delay in publication. Furthermore, the limit of detection, range, precision and interference effects applying to instrumental methods can depend on the actual instrument used, as well as on sample type, reagent purity and operator skill, etc. Even methods tested in many laboratories have been known to acquire problems<sup>1</sup>, for example when new products appear (introducing new substances into effluents),<sup>2</sup> when changes in production methods affect reagent quality, or<sup>3</sup> when given methods<sup>4</sup> are used to analyse new types of samples (despite apparent similarity to samples already evaluated). As a guide, the following categories have been given to methods:

- (i) tested, usually in five or more laboratories
  - no grade indicated;
- (ii) tested in one to three or four laboratories
  - Tentative;
- (iii) evaluated, but not fully tested, but publication is urgently required
  - Note;
- (iv) tested and found to be satisfactory by several laboratories, but in the opinion of experts requires a high degree of skill or has some other difficulty such that the method would be replaced if a better method were discovered.
  - Provisional.

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 United 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 and senior technical staff, to decide which method to use for the determination in hand. Whilst the attention of users 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 nine working groups each responsible for one section or aspect of water cycle quality analysis. They are:

- 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 monitoring
- 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, in co-operation with the working group and the main committee. The names of those associated with these methods are listed at the back of this book.

Publication of new or revised methods will be notified to the technical press. A current list of publications may be obtained from the Secretary.

Every effort is made to prevent errors from occurring in the published text. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically. However, should any errors be found, please notify the Secretary.

**Dr D WESTWOOD**

*Secretary*

*5 August 1992*

# 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 and COSHH 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.

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 to be 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: 'Safe Prac-

tices 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 Services 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 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 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.

## Safety while Sampling

Prior consideration must be given, especially when sampling in confined spaces or where access is difficult, to guard against suffocation, drowning, falls, and poisoning or infection by ingestion, inhalation, or skin contact.

## Good Laboratory Practice

The Department of Health issues a booklet entitled: Good Laboratory Practice; the United Kingdom Compliance Programme, 1989. This can be obtained by writing to that Department in London. It deals chiefly with toxicity studies, but much can be applied to analytical chemistry.

# Method A Determination of the pH Value of Sludge, Soil, Mud and Sediment

## A1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Ref 15.)

A1.1	Parameter determined	pH value.			
A1.2	Types of sample	Sludges, soils, muds, sediments and related solids.			
A1.3	Basis of method	Preparation of an aqueous suspension of the solid, followed by potentiometric pH determination.			
A1.4	Range of application	These samples normally have pH values between 4 and 11.			
A1.5	Calibration function	The pH meter scale is linear.			
A1.6	Standard deviation (a)(b)	Type of sample	pH value	Standard deviation (pH units)	Degrees of freedom
A1.6.1		Water pH values:			
		various soils	4.5-7.9	0.02-0.06	45
		raw sludge	5.6-5.7	0.02	18
		liquid digested sludge	7.0-7.1	0.02-0.03	30
		semi solid sludge	7.2	0.04	36
		solid sludge	7.2-11.6	0.04-0.05	9
A1.6.2		Calcium chloride pH values:			
		various soils	3.8-7.4	0.03-0.09	9
A1.7	Limit of detection	Not applicable.			
A1.8	Sensitivity	Theoretically 1 pH unit = 58.17 mV at 20°C but decreases on ageing of electrodes.			
A1.9	Bias	Not known.			
A1.10	Interferences	None known (see section A3).			
A1.11	Time required for analysis	For 8 samples the total analytical and operator times are approximately 60 min and 45 min respectively.			

(a) For soils the standard deviations are between batch standard deviations. These were determined by MAFF (ADAS) Regional Laboratories and the Macaulay Institute for Soil Research (Ref 1).

(b) For sludges the standard deviations are within batch standard deviations. These were determined by the Vales and Chiltern Divisions of Thames Water Authority (Ref 2).

## A2 Principle

The pH value of liquid digested sewage sludge is used to monitor digester performance. The pH value of sludges is generally used to assess the application rate of sludge for

disposal to land. The pH value of soil is characteristic and is also used in the determination of the lime requirement of soil.

A suitable aqueous suspension of the solid is prepared and the pH value of the suspension is determined potentiometrically. For some types of soils, eg horticulture and soil profile samples, it is often useful to determine the pH value of the suspension in 0.01 M calcium chloride solution. The addition of calcium chloride solution gives a pH value which will be independent of the concentration of salts present in the sample.

### A3 Interferences

A3.1 Substances present at their normal concentration in these types of samples do not cause interference. The pH value of suspensions is dependent, to a considerable extent, on the carbon dioxide equilibrium and therefore manipulation after the sampling of liquid sludges and after the preparation of suspensions, should be kept to a minimum. If oil or grease is present in the sample, it should be removed by filtration through a pad of cotton wool prior to carrying out the measurement otherwise a film may form on the surface of the electrodes of the pH meter. Inorganic film-forming substances may also interfere if not removed from the electrodes between determinations.

A3.2 Glass electrodes normally respond to sodium ions at pH values above 9. This may cause errors in the measurement of the pH values of samples such as incinerator ash, lime conditioned sludges and saline soils. In such instances, electrodes constructed of special glass and which have a low sodium ion response should be used.

### A4 Hazards

A4.1 Samples of sewage sludge and of soil rich in sludge are liable to ferment. In consequence the bottles should not be tightly stoppered. Even so they should not be stored in the open laboratory. If samples must be stored, they should be kept at 2-4°C. When handling a stored sample wear gloves, face and eye protection and sufficient body protection to guard against bottles bursting. Use bottle carriers. The gas evolved is usually flammable so all equipment in the vicinity must be flame proof and sources of ignition be absent. Bursting glass bottles can produce micro-organism contaminated shrapnel, plastic bottles can also burst and produce a noisome spray and aerosol. All spillage must be cleaned up. Broken glass should not be handled directly.

A4.2 Sludge and soil can sometimes contain harmful organisms. Scrupulous cleanliness is essential. All cuts should be protected before handling these samples.

A4.3 Care should be taken when handling chloroform.

### A5 Reagents

#### A5.1 Water

For the preparation of standard buffer solutions, distilled water which has been freshly boiled, or deionised water taken freshly from a 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.

#### A5.2 Concentrated potassium chloride

The reference electrode should be stored in concentrated potassium chloride solution (eg 4 M). This solution can be made up by adding approximately  $75 \pm 1$  g of potassium chloride to  $250 \pm 5$  ml. of water and, if necessary, gently warming to aid dissolution.

#### A5.3 Buffer solutions

Standard and buffer solutions of pH values approximately at 4.0, 7.0 and 9.0 are required.

A5.3.1 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 (11), other formulations are quoted by Mattock (12) and Perrin and Dempsey (7). These publications should be consulted for full details. Suitable reagents for the preparation of standard buffer solutions are also



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.

A5.3.2 It is convenient to purchase reagents for standard buffer solutions either in solution, sachet or tablet form.

A5.3.3 pH 4.0 solution: The primary standard

At 20°C dissolve  $10.138 \pm 0.001$  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 1, and is defined in BS 1647 Pt. 1 (11).

A5.3.4 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<sub>5</sub> at 20°C (see Table 1) 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 Table 1.

A5.3.5 Other buffered solutions. See Ref 6.

A5.4  $0.125 \pm 0.005$  M calcium chloride (not always required)

Dissolve about 27.5 g of calcium chloride hexahydrate in about 800 mL of water and dilute to 1 litre in a calibrated flask. Standardize this solution by determining its calcium concentration (see other methods published in this series) and if necessary, adjust the concentration to  $0.125 \pm 0.005$  M calcium chloride by the addition of calcium chloride solution of known strength (approximately 1 M) or water as appropriate.

## A6 Apparatus

A6.1 pH meter (temperature compensated) fitted with a glass electrode and a calomel electrode or a combined glass/calomel electrode. The pH meter should be readable to at least  $\pm 0.05$  pH units. If calomel electrodes cannot be used, use silver electrodes.

A6.2 If the sample readings drift (see section A8.2.2 note f), the following then applies.

A6.2.1 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 A10.1). Certain types of glass electrode (eg Ross<sup>TM</sup> and Thalamid<sup>TM</sup> 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 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 no 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

**Table 1 Variation of pH with Temperature**

Temperature °C	pH 4 Primary Standard	AQC (pH 4) Low Conductivity Acid Standard	AQC Dilute Buffer Standard (see section A10.2)
0	4.000	4.00 <sub>5</sub>	-
5	3.998	4.00 <sub>5</sub>	7.68
10	3.997	4.00 <sub>5</sub>	7.67
15	3.998	4.00 <sub>5</sub>	7.64
20	4.001	4.00 <sub>5</sub>	7.62
25	4.005	4.00 <sub>5</sub>	7.61
30	4.011	4.00 <sub>5</sub>	7.59

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 manufacturer's products but also between batches of the same manufacturer's electrodes. See sections A9 and A10 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 with 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 solutions (such as chromic acid) for cleaning purposes.

Rejuvenation may be attempted by (a) refilling the reference electrode with fresh potassium chloride filling solution and then leaving the junction to soak in concentrated potassium chloride filling solution for 1 day, (b) soaking the glass electrode 5 times alternatively in dilute hydrochloric acid and sodium hydroxide 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 A10.1) and poorly performing electrodes should be rejected.

#### A6.2.2 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 0.05 pH units or better.

#### A6.3 A mechanical shaking apparatus.

### A7 Sample Preservation

Sludge samples may change composition through biological activity and therefore they should be analysed as soon as possible after sampling. Liquid sludge samples will lose carbon dioxide on exposure to air and therefore they must be kept in a closed partially filled polyethylene container until the pH value is determined. In order to avoid loss of carbon dioxide, handling should be minimized. If prolonged storage of sludge samples is unavoidable then either they should be kept in a refrigerator or the biological activity arrested by the use of an appropriate inhibitor. A final solution containing 5-10 ppm of chloroform will be suitable in most circumstances; it should not be used when chlorinated hydrocarbons, etc are also to be determined on the same sample.

## A8 Analytical Procedure

Step	Procedure	Notes
<b>A8.1 Preparation of samples</b>		
<b>Liquid Sludges</b>		
A8.1.1	Generally less than 10% m/v solids. These do not require any preparation (note a).	(a) If visible oil or grease is present it should be removed by filtration through a cotton wool pad prior to step A8.2.1. Use this filtrate at step A8.2.2.
<b>Semi-liquid and solid sludges</b>		
A8.1.2	(Generally more than 10% m/v solids). Determine the dry solids content of the sludge (see Ref 4). Weigh an amount of sample equivalent to a weight of $5.0 \pm 0.1$ g of dry sludge into a 150 mL stoppered conical flask. Add to the flask sufficient water to make the total volume $100 \pm 2$ mL. Stopper the flask and shake until the sample is thoroughly dispersed but in any event for not less than 15 min (notes a, b and c).	(b) It may be necessary to break down the solids in to small pieces prior to shaking. (c) A mechanical shaking apparatus is recommended.
<b>Soils, muds and sediments</b>		
A8.1.3	Weight $10.0 \pm 0.1$ g of the air dried sample, crushed to pass a 2 mm sieve (see sample preparation booklet Ref 5), into a 60 mL wide mouthed, screw capped bottle. Add $25 \pm 1$ mL of water, cap the bottle and shake for $15 \pm 1$ min (note c).	
<b>A8.2 Measurement of pH value</b>		
A8.2.1	Set up the pH meter according to the manufacturer's instructions. Standardise the pH meter using appropriate standard pH buffer solutions (notes d and e).	(d) Use standard buffer solutions of pH value close to that of the sample being tested. (e) Sample solutions, buffer solutions and electrodes should all be at the same temperature (within $\pm 1^\circ\text{C}$ ).
A8.2.2	Rinse the electrodes thoroughly with water. Ensure that the sample is thoroughly dispersed by stirring. Stop the stirrer. Immediately, place the electrodes in the sample. Read the steady pH value from the meter after approximately 30-60 s (notes e and f).	(f) If the pH value continues to vary after 60 s, it is probable that the water is low in ionic strength, measure the pH of the clear supernatant liquid by the method given in Ref 3.
A8.2.3	If a pH value in 0.01 M calcium chloride is required, add $2.0 \pm 0.1$ mL of 0.125 M calcium chloride to the soil suspension (A8.1.3), stir and read the steady pH value from the meter after approximately 30-60 s.	
A8.2.4	Remove the electrodes and rinse thoroughly with water (note g).	(g) Cleaning with acid may be required (see section A6.2.1).
A8.2.5	At the end of the batch of samples clean the electrodes with a soft, wet issue and rinse the electrodes thoroughly with water. (notes g and h).	(h) If silver electrodes are used and there is doubt about their stability, check the electrodes against a buffer solution after every fifth sample, or as experience suggests.

## A9 Sources of Error

A9.1 Errors can arise from temperature changes and from changes in equilibria within the sample system. These have been discussed in section A6.2.1.

A9.2 Errors can arise from deterioration of electrodes or from fouling of electrodes by oils and greases or precipitated materials (see sections A6.2.1, A8.1 note a and A10.1).

A9.3 Stray electrical fields can cause unstable pH indications.

A9.4 Excess leakage of reference electrode filling solutions can lead to error.

A9.5 For interferences see section A3.

## A10 Checking the Accuracy of Analytical Results

Once the methods have 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 sources of inaccuracy 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 typical sample be analysed in duplicate at the same time and in exactly the same way as normal samples. (See section A8). The results should be plotted on a quality control chart which will facilitate detection of inadequate accuracy and will also allow the standard deviation of routine analytical results to be calculated. If there are problems with the method in Ref 3, consider the following points.

### A10.1 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.

A10.1.1 Calibrate the electrodes with pH 7 and pH 4 buffers, as in sections A10.1-A10.11 of Ref 3 and note the slope factor (mV/pH, % or fraction, as allowed by the pH meter).

A10.1.2 Carry out steps A10.12-A12.15 in Ref 3, 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,  $\text{pH}_{(u)}$ .

A10.1.3 Stir the solution gently and note the new stable reading,  $\text{pH}_{(s)}$ . If the signal fluctuates, estimate the difference,  $\Delta\text{pH}_{(n)}$ , between the maximum and minimum readings.

A10.1.4 Calculate the error caused by the residual liquid junction potential.  $\Delta\text{pH}_j = \text{pH}_{(u)} - 4.005$ .

A10.1.5 Calculate the shift on stirring  $\Delta\text{pH}_{\text{stir}} = \text{pH}_{(s)} - \text{pH}_{(u)}$

A10.1.6 Compare the results with the ranges defining good and acceptable behaviour in Table 2.

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  $\pm 0.01$  pH within 2 min.

**Table 2 Ranges of 'good' and 'acceptable' Performance**

Performance Characteristics		Good Range*	Acceptable Range*
Slope factor	mV/pH**	$59.2 \pm 0.3$	$58 \pm 1$
	%	$100 \pm 0.5$	$100 \pm 1.5$
	fraction	$1.000 \pm 0.005$	$1.00 \pm 0.02$
Residual liquid junction error, $\Delta\text{pH}_j$		0.03	0.05
Shift on stirring, $\Delta\text{pH}_{\text{stir}}$		0.005	0.02
Noise, $\Delta\text{pH}_n$		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)

#### A10.2 Routine Analytical Quality Control

The slope factor should be noted on each occasion that the 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 'normalised', 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 Ref 3 section A6.3.4. Another useful low conductivity buffer solution (Refs 7 and 10) can be prepared from potassium dihydrogen orthophosphate ( $\text{KH}_2\text{PO}_4$  - ie 0.0008659 M) and disodium hydrogen orthophosphate ( $\text{Na}_2\text{HPO}_4$  - ie 0.003043 M). The conductivity of this solution at 25° is approximately 540  $\mu\text{S}/\text{cm}$ . The variation of pH with temperature is shown in Table 1.

# Method B Determination of the Lime Requirement of Soil

## B1 Performance

### Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Ref 15).

B1.1	Parameter determined	Lime requirement of soil.		
B1.2	Type of sample	Mineral soil.		
B1.3	Basis of method	The lime requirement of a mineral soil of pH value below 6.5 is calculated from the difference in pH value of a buffer solution alone and of a suspension made by shaking the soil with the buffer solution		
B1.4	Range of application	0.126 kg CaCO <sub>3</sub> /m <sup>2</sup> to 2.52 kg CaCO <sub>3</sub> /m <sup>2</sup> (see also section B6, note f).		
B1.5	Calibration function	Assumed to be linear.		
B1.6	Standard deviation (a)	Lime requirement (kg CaCO <sub>3</sub> /m <sup>2</sup> )	Standard deviation (kg CaCO <sub>3</sub> /m <sup>2</sup> )	Degrees of freedom
		0.00-0.63	0.095	264
		0.63-1.26	0.252	77
		1.26-2.02	0.252	132
B1.7	Sensitivity	0.1 pH unit change of buffer solution. = 0.126 kg CaCO <sub>3</sub> /m <sup>2</sup> for single strength buffer. = 0.252 kg CaCO <sub>3</sub> /m <sup>2</sup> for double strength buffer.		
B1.8	Bias	Not known.		
B1.9	Interferences	None known.		
B1.10	Time required for analysis	For 8 samples the total analytical and operator times are approximately 35 min and 30 min respectively.		

(a) These are between batch standard deviations which were obtained from an inter-laboratory calibration exercise using this method in which 12 MAFF (ADAS) Regional Laboratories took part (Ref 13).

## B2 Principle

The lime requirement of a mineral soil, which is an empirical relationship, is defined as the number of kg of calcium carbonate required to raise the pH value to 6.5 of 1 m<sup>2</sup> of soil, throughout the first 15 cm depth of soil under field conditions. The pH value of the soil is determined by the procedure in Method A Section 8. The lime requirement of a mineral soil of pH value below 6.5 is calculated from the difference in the pH value of a buffer solution alone and of a suspension made by shaking the soil with the buffer solution. The method is based on that recommended by the Ministry of Agriculture, Fisheries and Food (Ref 14). In practice, after the pH value of the soil has been determined, the buffer solution is added to the soil suspension, the mixture is shaken and its pH value determined.

## B3 Interferences

Substances present in soils at their normal concentrations do not cause interference.

## B4 Reagents

B4.1 Buffer solution, double strength

Add 400 ± 1 g of dried, anhydrous calcium acetate, 80.0 ± 0.1 g of 4-nitrophenol and

6.00 ± 0.01 g of light magnesium oxide BP, to approximately 4.5 litres of water (as in section A5.1). Heat the mixture and stir to dissolve, allow to cool and dilute with water to 5 litres. If necessary, stir overnight on a magnetic stirrer to dissolve the last traces of solids. This solution should have a pH value of 7.0 ± 0.1. If necessary, adjust the pH value to within this range by addition of either hydrochloric acid or light magnesium oxide BP.

#### B4.2 Buffer solution, single strength

Add 1 litre of double strength buffer solution to 1 litre of water and mix. This solution should have a pH value of 7.0 ± 0.1. If necessary adjust the pH value to within this range by addition of hydrochloric acid or light magnesium oxide BP.

### B5 Apparatus

B5.1 pH meter fitted with a glass electrode and a calomel electrode. The pH meter should be readable to at least ± 0.05 pH unit.

B5.2 A mechanical shaking apparatus.

### B6 Analytical Procedure

Step	Procedure	Notes
B6.1	Determine the pH value of the soil suspension by the procedure at Method A Section 8. Retain the soil suspension in its bottle.	
	<b>Mineral soils of pH &gt; 6.0.</b>	
B6.2	Add 20 ± 1 mL of single strength buffer solution to 25 ± 1 mL of water and mix. Insert the electrodes and note the pH reading (note a). Adjust the pH meter to read pH 7.00 ± 0.05. Remove the electrodes and rinse them thoroughly with water.	(a) The pH value should be 7.0 ± 0.1. If not, check that the pH meter has been standardised correctly and adjust if necessary. If the pH value is still not 7.0 ± 0.1 then the pH value of the single strength buffer requires adjusting with either hydrochloric acid or light magnesium oxide BP.
B6.3	Add 20 ± 1 mL of single strength buffer solution to the soil suspension. Cap the bottle and shake for 5 mins ± 30 s (note b). Insert the electrodes in the suspension and read the steady pH value, P <sub>1</sub> from the meter (after approximately 30 to 60 s). Remove the electrodes and rinse them thoroughly with water.	(b) A mechanical shaking apparatus is recommended.
B6.3.1	If the pH value P <sub>1</sub> is below 6.0, ignore the result and weigh 10.0 ± 0.1 g sample (A8.1.3) into another 60 mL wide mouthed, screw capped bottle. Add 25 ± 1 mL of water, cap the bottle and shake for 15 ± 1 min. Proceed from step B 6.5.	
	<b>Calculation</b>	
B6.4	Time requirement = $1.26(7.00 - P_1)$ kg CaCO <sub>3</sub> /m <sup>2</sup> (notes c and d)	(c) This calculation assumes that 0.126 kg CaCO <sub>3</sub> /m <sup>2</sup> changes the pH value of the soil from 6.5 to 7.0.  (d) This calculation assumes that under the conditions described a change in pH value of 0.1 of the single strength buffer solution is equivalent to 0.126 kg CaCO <sub>3</sub> /m <sup>2</sup> .

Step	Procedure	Notes
	<b>Mineral soils of pH &lt; 6.0</b>	
B6.5	Add 20 ± 1 ml of double strength buffer solution to 25 ± 1 ml of water and mix. Insert the electrodes and note the pH reading (note a). Adjust the pH meter to read pH 7.00 ± 0.05. Remove the electrodes and rinse them thoroughly with water.	
B6.6	Add 20 ± 1 ml of double strength buffer to the soil suspension. Cap the bottle and shake for 5 min ± 30 s (note b). Insert the electrodes into the stirred suspension and read the steady pH value, P <sub>2</sub> , on the meter (after approximately 30–60 s). Remove the electrodes and rinse thoroughly with water.	
	<b>Calculation</b>	
B6.7	<p>Lime requirement = <math>2.52(7.00 - P_2)</math>            kg CaCO<sub>3</sub>/m<sup>2</sup>            (notes c, e and f).</p>	<p>(e) This calculation assumes that under the conditions described, a change in pH value of 0.1 of the double strength buffer solution is equal to 0.252 kg CaCO<sub>3</sub>/m<sup>2</sup>.</p> <p>(f) 0.126 kg CaCO<sub>3</sub>/m<sup>2</sup> is equivalent to 1.26 tonne CaCO<sub>3</sub>/ha is equivalent to 10 hundredweights CaCO<sub>3</sub>/acre.</p>

## B7 Sources of Error

B7.1 For general sources of error for pH measurements see appropriate booklets in this series, Refs 3 and 6.

B7.2 The calculation of the result is based on an empirical relationship which is dependent on the buffer capacity of the soil; slightly high results will be obtained for soils of low buffer capacity and slightly low results will be obtained for soils of high buffer capacity. These errors are of little practical significance.

## B8 Checking the Accuracy of Analytical Results

Once the methods have 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 sources of inaccuracy 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 typical sample be analysed in duplicate at the same time and in exactly the same way as normal samples (See section B6). The results should be plotted on a quality control chart which will facilitate detection of inadequate accuracy and will also allow the standard deviation of routine analytical results to be calculated.



# References

- (1) Standing Committee of Analysts File WS/646/59 Committee Papers. SCA/8.1/5 and SCA/8.1/6.
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- (3) *The Determination of pH in Low Ionic Strength Waters 1988*. HMSO in this series.
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- (5) *The Sampling and Initial Preparation of Sewage and Waterworks sludges, soils, sediments, plants and contaminated wildlife (2nd Edn.) 1986*. HMSO in this series.
- (6) *The Measurement of Electrical Conductivity Laboratory Determination of the pH Value of Natural, Treated and Waste Waters 1978*. HMSO in this series.
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- (12) Mattock G, *pH Measurement and Titration*, Heywood, London 1961.
- (13) Standing Committee of Analysts File WS/646/59, Committee Paper SCA/8.1/6A.
- (14) Ministry of Agriculture, Fisheries and Food, *Technical Bulletin 27, The Analysis of Agricultural Materials*, HMSO, 1973.
- (15) *General Principles of Sampling and Accuracy of Results 1980*. HMSO in this series.

# Address for correspondence

However well a method is 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  
Department of the Environment (Drinking Water Inspectorate)  
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