

Determination of the pH Value of Sludge, Soil, Mud and Sediment; and Lime Requirement of Soil (1977 version)

Methods for the Examination of Waters and Associated Materials

This volume contains two related methods

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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. 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.

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 has 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 footwear 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 breakages, 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.

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

4 November 1976

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

1 Performance Characteristics of the Method

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

1.1	Parameter determined	pH value.			
1.2	Types of sample	Sludges, soils, muds, sediments and related solids.			
1.3	Basis of method	Preparation of an aqueous suspension of the solid followed by potentiometric pH determination.			
1.4	Range of application	These samples normally have pH values between 4 and 11.			
1.5	Calibration function	pH meter scale is linear.			
1.6	Standard deviation (a) (b)	Type of sample	pH value	Standard deviation (pH units)	Degrees of Freedom
1.6.1		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
1.6.2		Calcium chloride pH values:			
		various soils	3.8- 7.4	0.03-0.09	9
1.7	Limit of detection	Not applicable.			
1.8	Sensitivity	Theoretically 1 pH unit=58.17 mV at 20°C but decreases on ageing of electrodes.			
1.9	Bias	Not known.			
1.10	Interferences	None known (see Section 3).			
1.11	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 and these were determined by MAFF (ADAS) Regional Laboratories and The Macaulay Institute for Soil Research ⁽¹⁾.

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

2 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 0.01M 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.

3 Interferences

3.1 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 will form on the electrodes of the pH meter. Inorganic film-forming substances may also interfere if not removed between determinations.

3.2 Glass electrodes normally respond to sodium ions at pH values above 9.0. 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.

4 Reagents

4.1 Water

Either freshly distilled or deionised water is suitable for preparing aqueous suspensions. It is not necessary to use absolutely carbon dioxide free water.

4.2 0.125±0.005 M calcium chloride

Dissolve about 27.5g 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 its concentration to 0.125±0.005 M calcium chloride by the addition of calcium chloride solution of known strength (approximately 1M) or water as appropriate.

4.3 Standard pH buffer solutions

Standard pH buffer solutions of pH values 4.0, 7.0 and 9.0 approximately are required (see appropriate publication in this series). Tablets or powders are commercially available for the preparation of these solutions.

5 Apparatus

5.1 pH meter (preferably 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 ± 0.05 pH unit.

5.2 A mechanical shaking apparatus.

6 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. 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.

Method B Determination of the Lime Requirement of Soil

1 Performance Characteristics of the Method

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

1.1	Parameter determined	Lime requirement of soil.		
1.2	Type of sample	Mineral soil.		
1.3	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.		
1.4	Range of application	0.126 kg CaCO ₃ /m ² to 2.52 kg CaCO ₃ /m ² (see also Section 6, note f).		
1.5	Calibration function	Assumed to be linear.		
1.6	Standard deviation (a)	Lime requirement (kg CaCO ₃ /m ²)	Standard Deviation (kg CaCO ₃ /m ²)	Degrees of Freedom
		0.00-0.63	0.095	264
		0.63-1.26	0.252	77
		1.26-2.02	0.252	132
1.7	Limit of detection	Not applicable.		
1.8	Sensitivity	0.1 pH unit change of buffer solution =0.126 kg CaCO ₃ /m ² for single strength buffer. =0.252 kg CaCO ₃ /m ² for double strength buffer.		
1.9	Bias	Not known.		
1.10	Interferences	None known.		
1.11	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. ⁽¹⁾

2 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 1m² 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 7. The lime requirement of a mineral solid 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⁽²⁾. 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.

3 Interferences

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

4 Reagents

4.1 Buffer solution, double strength

Add 400±1g of dried, anhydrous calcium acetate, 80.0±0.1g of 4-nitrophenol and 6.00±0.01 g of light magnesium oxide BP, to approximately 4.5 litres of water (as in Section 4.1). Heat the mixture and stir to dissolve the solids, 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.

4.2 Buffer solution, single strength

Add 1 litre of double strength buffer solution to 1 litre 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.

5 Apparatus

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

5.2 A mechanical shaking apparatus.

6 Analytical Procedure

Step	Experimental Procedure	Notes
6.1	Determine the pH value of the soil suspension by the procedure at Method A Section 7. Retain the soil suspension in its bottle. Mineral soils of pH 5.0 to 6.4 inclusive	
6.2	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 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.
6.3	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_1 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.
6.3.1	If the pH value P_1 is below 6.0, ignore the result and weigh 10.0 ± 0.1 g 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 6.5.	
6.4	Lime requirement = $1.26 [(7.00 \pm 0.10) - P_1]$ kg CaCO_3/m^2 (notes c and d) Mineral soils of pH less than 5.0	(c) This calculation assumes that $0.126 \text{ kg CaCO}_3/\text{m}^2$ 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 $0.126 \text{ kg CaCO}_3/\text{m}^2$.
6.5	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 7.00 ± 0.05 . Remove the electrodes and rinse them thoroughly with water.	(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 $0.252 \text{ kg CaCO}_3/\text{m}^2$.
6.6	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_2 , on the meter (after approximately 30–60 s). Remove the electrodes and rinse thoroughly with water.	(f) $0.126 \text{ kg CaCO}_3/\text{m}^2 = 1.26 \text{ tonne CaCO}_3/\text{ha} = 10 \text{ hundredweights CaCO}_3/\text{acre}$.
6.7	Lime requirement = $2.52 [(7.00 \pm 0.05) - P_2]$ kg CaCO_3/m^2 (notes c, e and f).	

7 Sources of Error

7.1 For general sources of error for pH measurements see appropriate booklet in this series.

7.2 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.

8 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 6). 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.

9 References

- (1) Standing Committee of Analysts File WS/646/59, *Committee Paper SCA/8.1/6A*.
- (2) Ministry of Agriculture, Fisheries and Food, *Technical Bulletin 27, The Analysis of Agricultural Materials*, HMSO, 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 Technical Secretary
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
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