Titrimetric Determination of Total and Bicarbonate Alkalinity and Volatile Fatty Acids in Sewage Sludge 1980/89.

Methods for the Examination of Waters and Associated Materials

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Contents

About This Series

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

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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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

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

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

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological 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, under the overall supervision of the appropriate working group and the main committee.

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

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

L R Pittwell
Secretary and Chairman

11 August 1988

Warning to Users

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

Local safety regulations must be observed.

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

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

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

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

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

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

Introduction

The total alkalinity and volatile fatty acids are two of the parameters used to control and monitor sludge digester performance.

The determination of the competent parts of alkalinity in sewage sludge before and after the anaerobic digestion process provides a semi-quantitative measure of the effectiveness of digestion.

The presence of variable concentrations of volatile acids in digested sludge supernatant liquor interferes with the standard analytical procedure for alkalinity[5] normally applied to natural, treated and waste waters. It is difficult to obtain a clear, reproducible titration end-point. For bicarbonate in the absence of acetic acid the titration end-point is at pH 4.5, for acetate in the absence of bicarbonate it is pH 3.3, and for a mixture of bicarbonate and acetate the end-point for titrating lies somewhere between pH 3.3 and 4.5.

For digested sludge supernates, the procedure stated in this booklet is based upon the work of DiLallo and Albertson[1] later tested by Montgomery *et al.*[2] as a rapid method for determining volatile acids and for monitoring sludge digester performance.

For an alternative method of determining volatile fatty acids (see ref. 6).

Titrimetric Determination of Total and Bicarbonate Alkalinity and Volatile Fatty Acids in Sewage Sludge

1. Performance Characteristics of the Methods

Although the analyses are unusually performed as one continuous operation, for convenience the test data is given in two separate sections.

1.1. Total Alkalinity

1.1.1.	Parameter determined	Total alkalinity (see also 1.1.3 below).
1.1.2	Type of sample	Raw and digested sewage sludge.
1.1.3	Basis of method	Electrometric titration to pH 4.0 with standard acid. (If the initial pH is above 8.2, a preliminary titration to this value may be added and 'bicarbonate' alkalinity determined separately from total alkalinity.
1.1.4	Range of application	Up to 400 meq/L. Applicable to samples of pH greater than 4.0.
1.1.5	Calibration function	Linear.

1.1.6 Standard deviation (within batch)

Type of Sample	Total Alkalinity meq/L	Standard Deviation meq/L
digested sludge	68.10	0.44 (a)
digested sludge	49.60	0.36 (b)
	57.2	0.8 (c)

1.1.7	Limit of detection	ca. 1.0 meq/L (d).
1.1.8	Sensitivity	1 mL 0.05 M sulphuric acid = 2 meq/L.
1.1.9	Bias	Not known.
1.1.10	Interferences	See Section 3.
1.1.11	Time required for analysis	For 8 samples the total analytical and operator times are 45 min and 25 min respectively.

1.2 Volatile Fatty Acids

1.2.1	Substances determined	Carboxylic acids and their salts (mainly the volatile fatty acids of chain length C_2-C_6).
1.2.2	Types of sample	Raw and digested sewage sludge.

1.2.3	Basis of method	After completion of the total alkalinity determination the pH is lowered to 3.3, carbon dioxide removed by boiling under reflux and volatile fatty acids determined by electrometric titration from pH 4.0 to 7.0 with standard alkali.
1.2.4	Range of application	Up to about 33 meq/L.
1.2.5	Calibration function	Non-linear.
1.2.6	Standard deviation (c) (within batch)	Acidity meq/L: 27.5 — Within Batch Standard Deviation meq/L: 0.2
1.2.7	Limit of detection	(c) ca. 0.5 meq/L (d).
1.2.8	Sensitivity	1 mL of 0.05 M sodium hydroxide is equivalent to between about 1 meq/L and about 1.25 meq/L dependent on the actual volatile fatty acid concentration.
1.2.9	Bias	Not know.
1.2.10	Interferences	Phosphate causes positive interference (see Section 3).
1.2.11	Time required for analysis	For 8 samples the total analytical and operator times are 80 min and 45 min respectively (excluding the time required to carry out the total alkalinity determination.

(a) Within batch standard deviations determined by Thames Water Authority, Chiltern Division.

(b) Within batch standard deviations determined by Thames Water Authority, Vales Division.

(c) Data from WRC Stevenage Laboratory.

(d) Estimated from the discrimination interval of the burette.

2. Principle

The suspended solids are removed by centrifugation and the total alkalinity is determined on the supernate by electrometric titration with standard acid to pH 4.0. Although the total alkalinity is usually expressed empirically as calcium carbonate, it consists largely of ammonium bicarbonate alkalinity but also includes other carbonates and bicarbonates, salts of volatile acids and ions such as phosphates. For the various ways of expressing alkalinity see ref 5.

If the initial pH value is above 8.2 a preliminary titration to this value enables the 'bicarbonate alkalinity' to be determined separately. If the phosphate concentration is high, part of the bicarbonate alkalinity value will be due to phosphate. The volatile fatty acids are determined by the method of DiLallo and Albertson[1] with modifications suggested by Montgomery *et al.*[2]. Following the completion of the total alkalinity titration, further acid is added to lower the pH to 3.3 and the sample boiled under reflux to remove carbon dioxide. The "volatile fatty acids" value is then determined by back titration to pH 7.0 with standard alkali.

3. Interferences

Substances usually present at their normal concentrations in these types of samples do not cause interference with the total alkalinity determination. Oil or grease can form a film on the pH electrodes and should be removed by filtration through cotton wool prior to carrying out these determinations.

DiLallo and Albertson[1] reported that acetic, propionic and butyric acids at equivalent acetic acid concentrations gave identical titration curves and this was confirmed by Montgomery *et al.*[2] for acetic and butyric acids. Phosphates, similar multiply dissociating ions and non fatty acid ions which on acidification form undissociated acids will cause positive interference under the conditions of the test. These ions are normally present in relatively small amounts and their concentration is unlikely to vary significantly from day-to-day. Since the determination is a routine control test which is looking for a sudden rise in the volatile fatty acids concentration, the effect of these interfering substances is usually unimportant and so is ignored.

4. Reagents

Analytical Grade reagents are suitable.

4.1 Water

Distilled or deionized water is suitable.

4.2 Standard pH Buffer Solutions

Standard Buffer Solutions with pH values of approximately 4.0 and 7.0 (buffers with values of 8.2 and 3.3 would also be useful). See refs 3, 4 and 5 and references therein for formulations.

4.3 Standard Sulphuric Acid Solutions

4.3.1 0.5 M sulphuric acid

Add slowly, with constant stirring, 26.5 ± 0.5 mL of sulphuric acid (d_{20} 1.84) to about 800 mL of water. Cool and dilute with water to 1 litre in a calibrated flask.

Using procedures adapted from ref 5. (for different acids and strengths of solution) standardize against 0.5 M sodium carbonate solution (52.99 ± 0.01g Na_2CO_3/litre). If necessary adjust to the exact concentration by addition of either water or 2 M sulphuric acid prepared and standardized in similar manner. This solution should keep indefinitely.

4.3.2 0.05 M sulphuric acid

Add 50.00 ± 0.02 ml of 0.5 M sulphuric acid (4.3.1) into a 500 mL calibrated flask and dilute with water to the mark. Prepare this solution freshly each week.

4.4 0.05 M sodium hydroxide

Dissolve 2.00 ± 0.01g of sodium hydroxide in about 800 ml of water. Cool and dilute with water to 1 litre in a calibrated flask.

Standardize this solution against potassium hydrogen phthalate. Titrate 25.00 ml of potassium hydrogen phthalate solution (4.5) with 0.05 M sodium hydroxide to a phenolphthalein end point. If necessary, adjust the concentration of the sodium hydroxide solution to exactly 0.05 M by the addition of 2 M sodium hydroxide or water as appropriate. For 2 M sodium hydroxide use forty times the weight of sodium hydroxide given in the procedure above. (See ref 5).

Phenolphthalein solution is reagent A5.9 of ref 5.

4.5 0.05 M potassium hydrogen phthalate

10.211 ± 0.0005g potassium hydrogen phthalate dissolved in water and made up to a litre gives an 0.05 M solution, equivalent to 0.05 M sodium hydroxide.

4.6 Standard acetic acid solution, 1 mL = 10 mg.

Weigh 10.00 ± 0.01g of glacial acetic acid (d_{20} 1.050) in a stoppered glass bottle, transfer quantitatively to a 1 litre calibrated flask and dilute to the mark with water.

5. Apparatus

5.1 pH meter, readable to ± 0.05 pH unit, and fitted with a glass electrode and a calomel electrode or a combined glass/calomel electrode. A stick meter may be used.

5.2 Centrifuge, and centrifuge tubes, 100 ml capacity.

5.3 Magnetic stirrer

6. Sampling and Sample Preservation

For information on sampling see ref 7.

Liquid sludge samples will lose carbon dioxide on exposure to the air and therefore they must be kept in a closed container and the determinations carried out with the minimum of manipulation. **Sludge samples may change composition through biological activity.** They should therefore be analyzed as soon as possible after sampling and in the meantime kept cold but not frozen.

Sludge may ferment and burst stoppered bottles violently; precautions such as gloves, face visor or goggles and covering with a strong cloth should be taken when handling such samples.

7. Analytical Procedure

Step	Procedure	Notes
	Preparation of samples	
7.1	Centrifuge, at a relative centrifugal force of about 2000 G for 10 ± 1 min a sufficient quantity of sludge to produce at least 60 mL of supernate. Do not add any coagulant aids. (Note a).	(a) Some laboratories use 100 ml samples and or different strengths of reagents. Adjust the procedure throughout to accommodate any such local variation. It is recommended that sufficient liquid be obtained to allow for repeat analyses if required.
	Determination of total alkalinity (and if required, bicarbonate alkalinity).	
7.2	Set up the pH meter according to the manufacturer's instructions. Standardize the pH meter using the standard pH buffer solutions of pH 4.0 and 7.0. Rinse the electrodes thoroughly with water.	(b) Use of a magnetic stirrer is recommended. The beaker should not be warmed by the stirrer motor.
7.3	Place 50 ± 1 mL of the supernate from step 7.1 into a 100 ml beaker, insert the electrodes of the pH meter and note the reading. If the initial pH value exceeds 8.2 see step 7.4 before proceeding. Stir constantly (note b). Titrate with 0.5 M sulphuric acid to pH 4.5 and note the amount of acid used (T_1). Continue to titrate with 0.05 M sulphuric acid to pH 4.0 and note the amount of this used (T_2).	(c) The procedure is given as originally drafted with two strengths of standard sulphuric acid used so that a wide range of concentration can be covered in a single determination. Some users may wish to use a single strength chosen to suit the expected sample range. In which case either T_1 or T_2 is zero.
	(Notes c and d).	(d) Retain the sample in the beaker for the volatile fatty acids determination.
7.4	If the initial pH value is greater than 8.2 and determination of bicarbonate alkalinity is required, first titrate to pH 8.2 and note the amount of acid used (T_0). If so desired, T_0 may be compounded of two titrations using both sulphuric acid strengths. In the calculations T_0 is expressed in mL 0.05 M acid. Continue the titration to obtain T_1 and T_2 without rezeroing the burettes, thus obtaining "total" values.	(e) For other sample volumes (v) use a factor of $\frac{50}{v}$. If other strengths of acid are used, express as volumes of 0.05 M acid for this calculation. If values in mg $CaCO_3$/L are required, 1 meq/L is equivalent to 50 mg $CaCO_3$/L. Note that this in no way implies that the sample contains calcium. (See ref 5 and Section 2 above).
	Calculation of the total alkalinity of the sample.	

Step	Procedure	Notes
7.5	For a 50 mL sample (note e) Total alkalinity = $(10T_1 + T_2) \times$ meq/L Bicarbonate alkalinity = $((10T_1 + T_2) - T_0) \times 2$ meq/L	
	Determination of volatile fatty acids.	
7.6	Continue the titration (Step 3) with 0.05 M sulphuric acid to pH 3.3. Then either, for routine control purposes, continue in the same beaker, or if greater accuracy is required, quantitatively transfer with distilled water rinsing to a 100 mL flat bottom flask fitted with a reflux condenser.	
7.7	Boil for 3 ± 0.5 min to remove carbon dioxide. Cool to ambient temperature. If a flask and condenser are used, rinse down the condenser with distilled water, remove the condenser and transfer to a 100 mL beaker.	
7.8	Insert the electrodes of the pH meter (note f) and stir the solution constantly (note b). Slowly titrate with 0.05 M sodium hydroxide to pH 4.0 exactly and note the burette reading. Continue to titrate to pH 7.0 exactly and note the burette reading. Calculate the amount T of 0.05 M sodium hydroxide required to raise the pH from 4.0 to 7.0.	(f) Combined electrodes or a stick pH meter are suitable.
7.9	Remove the electrodes and rinse thoroughly with water.	
7.10	For a 50 ml sample (Step 7.3) the apparent volatile fatty acids concentration, V_A, is equal to T meq/L. Calculate the volatile fatty acids concentration, V from $V = V_A \times F$ meq/L (note g).	(g) See Section 8 for factor F which is obtained from the calibration curve.

8. Preparation of the Calibration Curve for Volatile Fatty Acid Determination

The procedure in this section must be carried out on two independent occasions before application of this method to any samples, and regularly thereafter.

To a series of 100 mL calibrated flasks, pipette 0.00, 1.50, 5.00, 10.00, 15.00 and 20.00 mL of standard acetic acid solution (1 mL = 10 mg) and dilute to the mark with water. These flasks contain respectively 0, 1.67, 4.17, 8.33, 16.67, 25.00 and 33.33 meq/L of acetic acid. Carry out the procedure given in Section 7, steps 7.8 to 7.10 inclusive, on each of these solutions. Plot the apparent volatile fatty acid concentration, V_A (meq/L) against F, where F is the actual volatile fatty acid concentration, V (meq/L), divided by the apparent volatile fatty acid concentration, V_A (meq/L), (ie. $F = V/V_A$). This should result in a smooth curve.

9. Source of Error

The attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. See Section 3 for the effect of interfering substances.

10. Checking the Accuracy of Analytical Results

Once the method has been put into routine operation, many factors may subsequently adversely affect the accuracy of analytical results. It is recommended that experimental tests of the accuracy should be regularly made. As a minimum however, it is suggested that a stable sample or standards of typical range be analysed in duplicate at the same time and in exactly the same way as normal samples. The results should be plotted on a quality control chart which will facilitate the detection of inaccuracy and will also allow the standard deviation of routine analytical results to be estimated.

11. References

(1) DiLallo R and Albertson O E, J Wat. Pollut Cont. Fed. 1961, **33**, 356.

(2) Montgomery H A C, Dymock J F and Thom N S, *Analyst*, 196, **87**, 949.

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

(4) *The Determination of pH in Low Ionic Strength Water 1988*, HMSO in this series.

(5) *The Determination of Alkalinity and Acidity in Water 1981*, HMSO in this series.

(6) *The Determination of Volatile Fatty Acids in Sewage Sludge 1979*. HMSO in this series.

(7) *The Sampling and Initial Preparation of Sewage and Water Works Sludge, Soils, Sediments, Plants and Contaminated Wild Life 1986*. HMSO in this series.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:

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Department of the Environment

Standing Committee of Analysts

Membership responsible for this method

This booklet was originally prepared by a panel of the Sludge and Other Solids Working Group prior to its assimilation into the Working Groups dealing with specific determinands. It had been intended to incorporate these methods in the 1981 Alkalinity and Acidity in Water booklet (Ref 5), but at that time these methods were deemed to be no longer needed. Recently, the test has been revived and a request made that it be issued. Working Group 5 (non-metallic substances) aided by a few co-opted former members has revised it.

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