The Determination of Alkalinity and Acidity in Water 1981

Methods for the Examination of Waters and Associated Materials

This document contains 40 pages

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in Water
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Contents

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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 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. 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. Among such publications are: 'Code of Practice for 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.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or 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.

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. 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.

About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains 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, 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 of 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 nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis*
9.0 Radiochemical methods

*These two working groups are in process of being wound up. Their tasks are being redistributed among the other working groups.

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.

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 for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9TB. 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 the booklet.

TA DICK
Chairman

LR PITTWELL
Secretary

25 September 1981

Note on the Expression of Results

In the water industry, alkalinity, hardness and even acidity are often reported as mg/l $CaCO_3$. This is only a convention and does not imply that either calcium or carbonate are present. As will be explained in the Introduction, both Alkalinity and Acidity can be due to a variety of different substances and care is necessary when interpreting analytical data. Hence the alternative use of other units such as milligrams, moles or equivalents per litre of bicarbonate or carbonate [11]. For Hardness see ref 12.

Introduction

Many natural waters contain ions derived from weak acids or bases, and the hydrolysis of these ions causes the solution to adopt a pH value[1] which differs from that expected for a solution of a strong electrolyte of similar ionic strength. By way of a simple example, the addition of the sodium salt (NaX) of the monoprotic weak acid HX to an otherwise neutral solution will be considered. The salt will fully ionise, but hydrolysis of X^-,

$$X^- + H_2O \rightleftharpoons HX + OH^-,$$
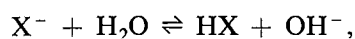
will cause the solution to show a net alkalinity. In this simple example the term alkalinity has a reasonably clear meaning and is effectively the concentration of NaX originally added. It can be determined by titration with strong acid to a pH corresponding to the appropriate equivalence point; this pH is governed mainly by the pK value of HX, but it is also influenced by the ionic strength and by the concentration of HX at the equivalence point. Electroneutrality considerations show that the alkalinity, A, is given by

$$A = [X^-] + ([OH^-] - [H^+])$$

where the [i] terms are for example in mol ℓ^{-1} (or eq. ℓ^{-1}), and $[X^-]$ can be termed the X^- alkalinity.

When, as commonly occurs, the alkalinity derives from the solvolysis of the ions of (the weak, diprotic) carbonic acid, the alkalinity (determined by strong acid titration to the carbonic acid equivalence point) is now

$$A = [HCO_3^-] + 2 \times [CO_3^{2-}] + ([OH^-] - [H^+])$$

where the [i] terms are in mol ℓ^{-1} but each is multiplied by the appropriate factor (2 eq. mol^{-1} for CO_3^{2-}, 1 eq. mol^{-1} for the other terms) so that A has units of eq. ℓ^{-1}. The quantity $[HCO_3^-] + 2 \times [CO_3^{2-}]$ can be termed the carbonate alkalinity and, at very high pH values, may differ significantly from the total alkalinity. The quantities $[HCO_3^-]$ and $[CO_3^{2-}]$ comprise the total (i.e. "free" plus ion-paired) concentrations of these ions. The equivalence point pH for this total alkalinity determination is close to 4.5 and is governed mainly by the pK value for the first ionization of carbonic acid. However, it is somewhat influenced by the ionic strength of the solution and by the total CO_2 content at the equivalence point and for this reason it is necessary in precise work to give consideration to control of possible CO_2 exchange between the solution and the atmosphere during the titration. The empirical selection of pH 4.5 is satisfactory for most routine purposes.

In the event that the carbonate solution contains, additionally, anions derived from acids weaker than carbonic, these will be included in the total alkalinity estimate if the equivalence point is again taken to be pH 4.5, i.e.

$$A = [HCO_3^-] + 2 \times [CO_3^{2-}] + \Sigma[X^-] + ([OH^-] - [H^+])$$

where $\Sigma[X^-]$ is the sum contribution of other weak ions (eg silicate, phosphate, borate, weak organic acid ions) to the alkalinity. When these other ions are absent the individual contributions of HCO_3^-, CO_3^{2-} (and OH^-) to the total alkalinity can be determined (as shown in the first analytical method of this booklet). In the general case that a wide variety of ions other than HCO_3^- and CO_3^{2-} are present it is not usually possible to subdivide the alkalinity between the various species. Table 1 at the end of this introduction gives examples of the alkalinity contribution of various salts of weak acids. It might be noted that it is sometimes useful to titrate to a pH of 8.3 (the HCO_3^- equivalence point). This titration is applicable only when the carbonate ion contributes significantly to the total alkalinity.

Acidity is empirically defined as acidity to pH 4.5 determined by titration with a strong base. Where it is known that part of the acidity present is due to mineral acid a titration of the component acidity to pH 3.7 can provide an indication of the amount of mineral acid present.

Waters with pH values less than 8.3 normally contain dissolved carbon dioxide in addition to that which may be present in combination in the water in the form of bicarbonate. Carbon dioxide is the only acidic component likely to be of significance in public supply and other good quality water. The determination of carbon dioxide is to be included in another booklet in this series[2]. More than trace levels of some ammonium salts in water confer an acid reaction.

In polluted waters and some types of trade effluent, acidity may be due to the presence of strong mineral acids, weak organic acids such as acetic acid and salts which produce an acid reaction by oxidation and/or hydrolysis, eg ferrous and aluminium salts. In some instances it may be appropriate to determine the maximum acidity potential of a sample by means of a pre-oxidation step and a procedure for this is included in the method for determination of acidity described in this booklet. Titrimetric procedures involving the use of colour change indicator for visual detection of the required pH value are generally inappropriate for polluted acidic samples which typically may be coloured or turbid.

Determination of alkalinity or acidity should always be expressed in terms which indicate the particular pH value used in the procedure employed. In the British convention it is customary to express both alkalinity and acidity as milligrams per litre of calcium carbonate. Elsewhere alternative methods of expression of the results for the determinands acidity and alkalinity are used, for example. using units of milli-equivalents per litre.

This booklet provides four methods of analysis, three for alkalinity and one for acidity.

1. The determination of alkalinity over a range most frequently encountered in water samples, ie 20–1000 mg/l as $CaCO_3$.

2. The determination of alkalinity at low levels, ie <20 mg/l as $CaCO_3$.

3. The determination of alkalinity using an air segmented continuous flow automated procedure in the range 20–300 mg/l as $CaCO_3$.

4. The determination of acidity in polluted waters and certain types of trade wastes in the range 20–1000 mg/l as $CaCO_3$.

Each of these methods is empirical and as such it would not be expected that results produced by them would necessarily correspond with results produced by alternative procedures differing in experimental detail.

The following factors had a bearing on the selection of the methods included in this booklet.

Method A   The use of methyl orange in the visual titration of alkalinity dates back to the last century. In method A in this booklet this indicator has been abandoned because it was shown conclusively from performance data examined statistically that errors can occur in the visual detection of the end-point colour change. This was particularly so in artificial light. A mixed indicator is preferred in method A[3].

Method B   Where alkalinity is present at <20 mg/l as $CaCO_3$, it is not practicable because of carbon dioxide interference to determine a stable end-point at pH 4.5. A Gran plot type procedure is used in method B for the determination of alkalinity at such low levels. Methods of this type are further described elsewhere[7, 9, 10].

Method C Although methyl orange was rejected for method A, its use in method C is valid since the detection of a specific end-point is not involved. This automated method using air segmented continuous flow colorimetry has been included to cater for laboratories processing large numbers of samples. Although the alkalinity value determined by this method may not be numerically identical to that obtained using method A, there is typically very good agreement between the two for many raw and potable waters and sewage effluents.

Method D Application of this method is only likely with polluted samples. These are of such diverse type it is not possible to predict the level of precision that might obtain with real samples. The performance data given in the method is derived from synthetic solutions substantially free from extraneous contamination. Because of the likely presence of colour in samples of the type which might be examined by this titrimetric method, only a procedure using an instrumental method for end-point detection is given.

In the following methods, in the interest of brevity, pH value has been referred to simply as pH. Throughout the series of methods results are reported in mg/l (parts per million, expressed as $CaCO_3$). A conversion table showing alternative systems of expressing results is appended.

TABLE 1: Alkalinity—Examples of Contributory Component Alkalinity from Salts of Weak Acids
(As determined in duplicate titrations)

Salt	mg/l	No added $CaCO_3$ Alkalinity (as mg/l $CaCO_3$)	10 mg/l $CaCO_3$ added Alkalinity (as mg/l $CaCO_3$)
Blank	—	0.1 0.1	9.6 9.5
di-Sodium tetra-borate $Na_2B_4O_7$ $10H_2O$	25	6.8 6.8	16.4 16.4
M = 381.36	50	13.9 13.9	24.1 24.0
tri-Sodium citrate $Na_3C_6H_5O_7$ $2H_2O$	25	6.0 6.1	15.1 15.3
M = 294.10	50	11.6 11.9	20.9 20.9
tri-Sodium orthophosphate Na_3PO_4 $12H_2O$	25	7.9 7.7	17.5 17.6
M = 380.13	50	15.4 15.4	25.2 25.4
Sodium silicate 18% m/m Na_2O	25	14.0 13.9	24.0 24.0
36% m/m SiO_2	50	28.1 28.5	38.2 38.1

Salt	pK Value	pH Value of Salt at 10^{-4} g. equiv./l	
		Calculated*	Calculated**
di-Sodium tetra-borate	$pK_{(3)}$ = 13.80	10.00	11.90
tri-Sodium citrate	$pK_{(3)}$ = 6.39	8.19	8.20
tri-Sodium orthophosphate	$pK_{(3)}$ = 12.67	10.00	11.34
Sodium silicate	$pK_{(2)}$ = 11.70	9.99	10.85

* Calculated from $\dfrac{\alpha H}{1 - \alpha H} = \dfrac{K_w}{K_n} \times C$

**Incorrect values calculated from $pH = \frac{1}{2} pK_w + \frac{1}{2} pK + \frac{1}{2} \log_{10} C$. This is the orthodox formula, applicable when C is large compared to α. Not applicable in dilute solutions or when K approximates to K_w.

αH = degree of hydrolysis.

K_w = ionic constant for water = 10^{-14}.

K_n = ultimate dissociation constant.

C = concentration expressed in g. equiv./l.

For Carbonic Acid at 25°C

First dissociation constant $H_2 CO_3 \rightleftharpoons HCO_3^- + H^+$ $K = 4.3 \times 10^{-7}$ pK is 6.37

Second dissociation constant $HCO_3^- \rightleftharpoons CO_3^- + H^+$ $K = 5.61 \times 10^{-11}$ pK is 10.25

Alternative Systems in Common use to Express Alkalinity Values

Milli-equivalents per litre

This is a fundamental scientific unit (often abbreviated as milli-equiv./l, m-equiv./l or m.eq./l.).

$$\left\{ \begin{array}{ll} \text{S.I. system;} & C(\tfrac{1}{2}CaCO_3) = 1 \text{ mol/l (previously 1N)} \\ & C(CaCO_3) \;\; = 1 \text{ mol/l (previously 1M)} \end{array} \right\}$$

In terms of m.eq./l the various forms of alkalinity determined in section 9 are calculated as follows:–

Component alkalinity titratable to pH 8.3

in the range 200 — 1000 mg/l as $CaCO_3 = T_3 \times N_1 \times 10$ m.eq./l

in the range 20 — 200 mg/l as $CaCO_3 = T_3 \times N_2 \times 10$ m.eq./l

Total alkalinity

in the range 200 — 1000 mg/l as $CaCO_3 = (T_4 - T_5) \times N_1 \times 10$ m.eq./l

in the range 20 — 200 mg/l as $CaCO_3 = (T_4 - T_5) \times N_2 \times 10$ m.eq./l

Total alkalinity including that due to suspended matter

in the range 200 — 1000 mg/l as $CaCO_3 = \dfrac{(T_7 - T_6) \times N_1 \times 250.01}{T_7}$ m.eq./l

in the range 20 — 200 mg/l as $CaCO_3 = \dfrac{(T_7 - T_6) \times N_2 \times 250.01}{T_7}$ m.eq./l

TABLE 2: Conversion Table

Alternative Unit for expression of results	Corresponding alkalinity expressed as mg/l $CaCO_3$
1 milli-equivalent	50
1 milli-mole	100
1 part/100,000	10
1 English degree* (= 1 Clarke degree) (1 grain of $CaCO_3$/gallon)	14.29
1 German degree*	17.86
1 French degree*	10
1 U.S. degree*	17.24

* These units are frequently used to express all the various forms of hardness present in waters. (See the appropriate booklet in this series which at present gives results only in terms of mg/l $CaCO_3$).

A

Determination of Alkalinity in Natural, Treated and Waste Waters

A1 Performance Characteristics of the Method

A1.1	Determinand	Alkalinity to pH 8.3 and pH 4.5.
A1.2	Type of Sample	All types of water of pH > 4.5.
A1.3	Basis of method	Titration of the sample with a standard solution of acid, and either visual or instrumental detection of end points at pH 8.3 and pH 4.5.
A1.4	Range of application	20–1000 mg/l as $CaCO_3$. (Method B in this booklet is recommended for 20 mg/l or less.)
A1.5	Standard deviation	a) Total alkalinity by titration to pH 4.5 *i) Using 0.02 N acid.*

Synthetic Solution	Total standard deviation (within laboratory) mg/l as $CaCO_3$			
Nominal Total Alkalinity (mg/l as $CaCO_3$)	Visual Titration		Instrumental Titration	
	Min.	Max.	Min.	Max.
0†	0.05	0.24	0.14	0.46
22.8	0.05	0.57	0.00	0.67
47.7	0.09	0.56	0.09	0.51
96.2	0.23	0.79	0.00	0.60
208	0.29	0.90	0.41	0.80

†boiled and cooled distilled water.

Each value of standard deviation has 9 degrees of freedom.

ii) Using 0.1 N acid**

Synthetic Solution	Total standard deviation (within laboratory) mg/l $CaCO_3$	
Nominal Total Alkalinity (mg/l as $CaCO_3$)	Visual Titration	Instrumental Titration
424	1.1	2.6
636	2.1	3.2
848	2.2	3.7
1060	2.1	3.2

Each value of standard deviation has 9 degrees of freedom.

b) Component alkalinity by titration to pH 8.3*

Synthetic Solution	Total Standard Deviation (within laboratory) (mg/l as $CaCO_3$)			
Nominal Total Alkalinity (mg/l as $CaCO_3$)	Visual Titration		Instrumental Titration	
	Min.	Max.	Min.	Max.
8.6	0.43	1.09	0.40	1.17
21.0	0.52	1.21	0.43	1.27
46.0	0.58	2.19	0.51	1.50
140	1.16	4.04	0.92	3.46

Each value of standard deviation has 9 degrees of freedom.

A1.6	Limit of Detection* (5 Degrees of Freedom) (Note recommendation that range of application is not below 20 mg/l $CaCO_3$.)	Total alkalinity as mg/l $CaCO_3$			
		Visual end point		Instrumental end point	
		Minimum	Maximum	Minimum	Maximum
		0.00	1.73	0.00	3.20

A1.7	Sensitivity	1.0 ml of acid (0.1N) $\equiv$ 50.05 mg/l $CaCO_3$ 1.0 ml of acid (0.02N) $\equiv$ 10.01 mg/l $CaCO_3$
A1.8	Bias	Some possible at lower levels[3]; may also arise from sample instability (see section A7).
A1.9	Interferences	Coloured substances, certain inorganic anions, and organic matter may affect the detection of the titration end point (see section A3 below).
A1.10	Time required for analysis	The total analytical and operator times are the same and for 10 samples equal 1 hour excluding any pre-treatment time.

* These values were obtained from a comparability exercise undertaken by 5 Water Authority laboratories, each carrying out 10 determinations on each of 4 synthetic solutions using both visual and instrumental end point detection.

**These values were obtained from an exercise undertaken by the Thames Water Authority.

A2 Principle

Titration of the samples with standard acid solution and either visual or instrumental detection of end points at pH 8.3 and pH 4.5. Phenolphthalein is used as the visual indicator at pH 8.3 (colour change pink to colourless) and this end point represents the titration of all hydroxide and half the carbonate present. The end point at pH 4.5 is detected visually using bromocresol green-methyl red indicator (colour change greenish blue to grey/pink) and represents the total alkalinity of the sample. The superiority of this mixed indicator compared with methyl orange or methyl orange-xylene cyanol FF has been demonstrated by the statistical evaluation of comparability tests[3].

A3 Interferences

Strongly coloured and/or turbid samples may interfere with the visual detection of the titration end point. Certain oxidizing agents eg free chlorine may bleach the visual indicator and prevent the detection of the end point. (See section A8).

The instrumental titration method is free from the above interferences although difficulties in end-point detection may be experienced in the presence of organic substances. Difficulty in obtaining satisfactory end points by either visual or instrumental titration probably indicates the presence of interfering substances.

Finely divided suspensions of calcium carbonate and magnesium hydroxide, eg in waters softened by a lime-soda process, may be the cause of fading end points in both methods of titration. Such alkaline reactants are not categorized as interfering substances. (See section A8).

A4 Hazards

No particular laboratory hazards are known to be associated with this method.

A5 Reagents

Reagents and chemicals of analytical grade quality shall be used. Water as prepared in section 5.1 shall be used throughout.

A5.1 Demineralized Water, Carbon Dioxide Free

Use demineralized, or distilled water, of pH not less than 6.0.

If the pH of the demineralized water is less than 6.0, immediately before use boil the water for at least 15 minutes in a suitable flask and allow to cool to room temperature whilst keeping the flask closed with a guard tube containing soda-lime.

A5.2 Sodium Carbonate

Immediately before use dry 2 ± 1 g of sodium carbonate, anhydrous, for 60 ± 5 minutes in an electric oven set at $265 \pm 5°C$ and allow to cool in a desiccator.

A5.3 Hydrochloric Acid Solution (0.2N)

Using a graduated pipette fitted with a safety bulb add 9.0 ± 0.1 ml of hydrochloric acid $(d_{20}1.18)$ to a 1000 ml volumetric flask. Dilute to volume with water and mix well.

Standardize this solution as follows using either (a) visual, or (b) instrumental end point detection as appropriate to the titration of samples:–

a)   Visual end point detection

Weigh out accurately 0.1600 ± 0.0050g of sodium carbonate (A5.2) into a 250 ml conical flask and note the weight of sodium carbonate taken.

Add 100 ± 5 ml of water to the flask and swirl to dissolve the carbonate. Add 0.1 ± 0.02 ml of pH 4.5 indicator solution (A6.8) and titrate with hydrochloric acid solution (A5.3) to the disappearance of the greenish-blue colour. Note the titre.

b)   Instrumental and Point Detection

Weigh out accurately 0.1600 ± 0.0050 g of sodium carbonate (A5.2) into a 250 ml beaker and note the weight of sodium carbonate taken.

Add 100 ± 5 ml of water (A5.1) to the beaker and insert a magnetic rotor. Place the beaker on a magnetic stirrer and stir to dissolve the carbonate. Insert electrodes (A6.1) connected to a pH meter. Titrate with hydrochloric acid solution (A5.3) with continuous stirring until the meter reads pH 4.5 ± 0.05. Note the titre.

c)   Blank Determination

Carry out a blank determination using 100 ± 5 ml of water (A5.1) appropriate to the procedure a) or b) used and note the titre.

For both visual and instrumental end-point detection:–

Let the mass of sodium carbonate taken $= M$ g
Let the tiration of sodium carbonate $= T_1$ ml
Let the blank titration $= T_2$ ml

Then the normality (N_1) of the hydrochloric acid solution (A5.3)

$$= \frac{M \times 18.870}{(T_1 - T_2)}$$

A5.4   Hydrochloric acid solution (0.02N)

Pipette 50 ± 0.1 ml of hydrochloric acid solution (A5.3) into a 250 ml calibrated flask. Dilute to volume with water and mix well.

Prepare freshly for use and calculate the normality as follows:–

The normality (N_2) of hydrochloric acid solution (A5.4) = $N_1 \times 0.2$

Alternatively use suitable commercially available standard solutions of hydrochloric acid.

Sulphuric acid solutions of corresponding normality may be used instead of the hydrochloric acid solutions.

A5.5   Buffer Solution pH 4.0[4]

Dissolve 10.20±0.01 g of potassium hydrogen phthalate, previously dried at 105°C for 1 hour, in about 500 ml of water. Transfer the solution to a 1000 ml calibrated flask and dilute to volume with water. The pH of this solution is dependent upon temperature as shown below:

°C	pH
15	4.00
20	4.00
25	4.01

A5.6   Buffer Solution pH 6.9 [4, 5]

Dissolve 3.39±0.01 g of potassium dihydrogen orthophosphate, and 3.55±0.01 g of disodium hydrogen orthophosphate, anhydrous, in about 500 ml of water. Transfer the solution to a 1000 ml calibrated flask and dilute to volume with water. The pH of this solution is dependent upon temperature as shown below:

°C	pH
15	6.90
20	6.88
25	6.87

A5.7   Buffer Solution pH 9.2 [4]

Dissolve 19.07±0.01 g of disodium tetraborate decahydrate, in about 500 ml of water. Transfer the solution to a 1000 ml calibrated flask and dilute to volume with water. The pH of this solution is dependent upon temperature as shown below:

°C	pH
15	9.28
20	9.23
25	9.18

Note: The three buffer solutions (A5.5), (A5.6) and (A5.7) can be replaced by equivalent commercially available buffer solutions.

A5.8   Indicator Solution (pH 4.5)

Dissolve 0.200±0.005 g of bromocresol green and 0.015±0.002 g of methyl red in 100±2 ml of ethanol (95% industrial spirit). The water-soluble, sodium salts of methyl red and bromocresol green are not suitable for preparing this reagent. Store in an amber glass bottle.

If not used within 2 months this solution must be discarded and prepared afresh.

A5.9   Phenolphthalein Indicator Solution

Dissolve 1±0.1 g of phenolphthalein in 100±2 ml of ethanol (95% Industrial spirit) and dilute to 200±4 ml with water. Mix well.

Alternatively dissolve 1±0.1 g of phenolphthalein in 120±2 ml of 2-ethoxyethanol (Cellosolve) and dilute to 200±4 ml with water. Mix well. Loss by evaporation is less with the latter solution and the dropping bottle does not become encrusted.

Immediately before use add sodium hydroxide solution (A5.11) dropwise to either of these solutions to the appearance of a faint permanent pink colour.

A5.10   Sodium Hydroxide Solution (carbonate-free approx. 0.1N)

Dissolve 25±0.5 g of sodium hydroxide pellets, in 25±0.5 ml of water with cooling in a 250 ml conical flask fitted with a cover. Allow to stand until the supernatant liquid is clear.

Using a safety pipette transfer 6.5±0.1 ml of clear solution into a 1000 ml calibrated flask. Dilute to volume with water and mix well.

A5.11   Sodium Hydroxide Solution (approx 0.02N)

Pipette 50±0.1 ml of sodium hydroxide solution (A5.10) into a 250 ml calibrated flask. Dilute to volume with water and mix well.

This solution must be freshly prepared on the day of use. It should be standardized with hydrochloric acid solution (A5.4).

Alternatively use suitable commercially available standard solutions of sodium hydroxide.

A5.12   Sodium Thiosulphate Solution (2.5% m/v)

Dissolve 2.5±0.1 g of sodium thiosulphate pentahydrate in 100±2 ml of water.

This solution must be freshly prepared on the day of use.

A6 Apparatus

A6.1   pH meter and compatible electrode system

Suitable for the measurement of pH to within ±0.05 units over the range pH 3 to pH 10. Where solutions of pH greater than 10 are to be examined a specially selected type of glass electrode is essential.

The electrode system may consist of separate indicating and reference units, or these may be combined within a single assembly.

Each equipment must be used strictly in accordance with the suppliers recommendations.

Immediately before use standardize with buffer solutions (A5.5, A5.6, A5.7).

A6.2   Magnetic Stirrer and Rotor

Suitable to mix 100 ml of solution without splashing. A 25 mm rotor is usually effective.

A7 Sample Collection and Preservation

Preferably using a polyethylene bottle of suitable capacity fill the bottle completely with sample and insert a stopper so that no air remains inside the bottle. If glass containers are used these should be checked to ensure that the glass does not contribute to the alkalinity of the sample.

Ideally samples should be analysed as soon as possible after collection since certain samples may undergo significant changes on storage. However, if storage is unavoidable the samples should be maintained at 4±1°C.

A8 Sample Pretreatment

A8.1   Visual and Instrumental End-point Detection

If necessary remove any turbidity* present by filtering sufficient sample through a suitable filter paper, eg grade GF/C. Immediately determine the alkalinity of the filtrate as described in section A9.

A8.2 Visual End-point Detection

If necessary remove turbidity* as described in section A8.1.

Remove any free chlorine present by adding a sufficient volume of sodium thiosulphate solution (A5.12) usually 1 drop added to 200 ± 5 ml of sample. Carry out the alkalinity determination as described below in section 9 without delay.

* If the suspended matter is alkaline, eg calcium carbonate, it may be desirable to include this alkalinity in the total alkalinity of the water sample. In such circumstances the sample must not be filtered. The total alkalinity should preferably be determined as given below in section A9.16 (visually) or as in section A6.21 (instrumentally) to avoid difficulties due to fading end points, and to ensure that all alkalinity due to suspended matter is included in the determination.

A9 Procedure

Step	Procedure	Notes
	Determination of Component Alkalinity titratable to pH 8.3	
	Visual Method (note a)	(a) This method is not suitable for highly coloured samples; the instrumental method commencing at step A9.4 is recommended.
A9.1	If necessary due to the presence of chlorine or turbidity pretreat the sample as described in section A8	
A9.2	Pipette 100 ± 0.2 ml of sample into a 250 ml conical flask.	
A9.3	Add 0.1 ± 0.05 ml of phenolphthalein indicator solution (A5.9). If a pink colour is obtained titrate hydrochloric acid solution (A5.3) or (A5.4) as appropriate (see note b) to the disappearance of the pink colour and note the titre obtained (T_3 ml).	(b) For samples of component alkalinity titratable to pH 8.3 in the range 200–1000 mg/l as $CaCO_3$ use hydrochloric acid solution (A5.3).
	Otherwise note that the alkalinity titratable with acid to pH 8.3 is zero. In either case retain the solution for use in steps A9.8 and 9.	For the range 20–200 mg/l as $CaCO_3$ use hydrochloric acid solution (A5.4).
A9.4	*Instrumental Method* If necessary due to the presence of turbidity pretreat the sample as described in section A8.	
A9.5	Pipette 100 ± 0.2 ml of sample into a 250 ml beaker.	
A9.6	Place the beaker on a magnetic stirrer and insert a stirring rotor and electrodes (A6.1) connected into a pH meter.	
A9.7	Start the stirrer and if the pH of the sample is greater than 8.3 tirate with hydrochloric acid solution (A5.3) or (A5.4) as appropriate until the meter reads pH 8.3 ± 0.05 (see notes b and c). Note the titre (T_3 ml) otherwise note that the component alkalinity titratable to pH 8.3 is zero. In either case retain the solution for use in step A9.10.	(c) In the vicinity of pH 8.3 add the titrant dropwise and allow at least 30 seconds for the electrodes to attain equilibrium with the solution.
	Determination of Total Alkalinity	
A9.8	*Visual Method* Add 0.1 ± 0.02 ml of pH 4.5 indicator solution (A5.8) to the solution reserved from section A9, step 3.	(d) For samples of total alkalinity in the range 200–1000 mg/l as $CaCO_3$ use hydrochloric acid solution (A5.3).

(contd.)

Step	Procedure	Notes
A9.9	Continue to titrate with hydrochloric acid solution (A5.3) or (A5.4) as appropriate (see note d) to the disappearance of the greenish-blue colour. Note the total titre obtained (T_4 ml).	For the range 20–200 mg/l as $CaCO_3$ use hydrochloric acid solution (A5.4).
	Instrumental Method	
A9.10	Continue to titrate the solution reserved from step A9.7 with hydrochloric acid solution (A5.3) or (A5.4) as appropriate (see note d) until the meter reads pH 4.5 ± 0.05 (see note c). Note the titre (T_4 ml).	(e) In the vicinity of pH 4.5 add the titrant dropwise and allow at least 30 seconds for the electrodes to attain equilibrium with the solution.
	Blank Determination *(visual method)*	
A9.11	Pipette 100 ± 0.2 ml of water into a 250 ml conical flask.	
A9.12	Add 0.1 ± 0.02 ml of pH 4.5 indicator solution (A5.8). Titrate dropwise with the same hydrochloric acid solution used to titrate the sample in step A9.9 to the disappearance of the greenish-blue colour. Note the titre (T_5 ml).	
	Blank Determination *(instrumental method)*	
A9.13	Pipette 100 ± 0.2 ml of water into a 250 ml beaker.	
A9.14	Place the beaker on a magnetic stirrer and insert a stirring rotor and electrodes (A6.1) connected to a pH meter.	
A9.15	Start the stirrer and titrate dropwise with the same hydrochloric acid solution used to titrate the sample in step A9.10 until the meter reads pH 4.5 ± 0.05. Note the titre (T_5 ml).	
	Determination of Total Alkalinity Including that due to Suspended Matter *Visual Method*	
A9.16	Shake the sample and immediately pipette 100.0 ± 0.2 ml into a 250 ml conical flask (see note f).	(f) This method is not suitable for highly coloured samples; the instrumental method commencing at step A9.21 is recommended.
A9.17	Pipette 25.0 ± 0.05 ml of hydrochloric acid solution (A5.3) or (A5.4) as appropriate, into the flask and mix well (see note d).	If the presence of suspended matter makes pipetting difficult or impossible, measure 100 ± 1 ml of sample using a cylinder.
A9.18	Cover the flask with a watch glass and boil the solution gently for 10 mins (see note g).	(g) If the nature of the suspended matter is such that it is not completely soluble in hydrochloric acid, or if acid addition results in coloration, transfer the solution to a 250 ml beaker and use the instrumental method commencing at step A9.24.
A9.19	Cool the flask to room temperature under a stream of cold water.	

Step	Procedure	Notes

A9.20 Add 0.1 ± 0.02 ml of pH 4.5 indicator solution (A5.8) and titrate with sodium hydroxide solution (A5.10) or (A5.11) corresponding to the normality of the acid used (see notes h and i) to the appearance of a greenish-blue colour.

Note the titre (T_6 ml).

(h) Sodium hydroxide solution (A5.10) is suitable for use in the determination of total alkalinity in the range 200–1000 mg/l as $CaCO_3$.

(i) Sodium hydroxide solution (A5.11) is suitable for use in the determination of total alkalinity in the range of 20–200 mg/l as $CaCO_3$.

Instrumental Method

A9.21 Shake the sample and immediately pipette 100.0 ± 0.2 ml into a 250 ml beaker.

A9.22 Pipette 25.0 ± 0.05 ml of hydrochloric acid solution (A5.3) or (A5.4) as appropriate into the beaker (see note d).

A9.23 Cover the beaker with a clockglass and boil the solution gently for 10 minutes.

A9.24 Cool the beaker in a stream of cold water and place on a magnetic stirrer.

A9.25 Insert a stirring rotor and suitable electrodes (A6.1) connected to a pH meter.

A9.26 Start the stirrer and titrate with sodium hydroxide solution (A5.10) or (A5.11) corresponding to the normality of the acid used until the meter reads pH 4.5 ± 0.05 (see note e).

Note the titre (T_6 ml).

Blank Determination (visual method)

A9.27 Repeat steps 16 to 20 using water (A5.1) in the place of the sample and note the titre (T_7 ml).

Blank Determination (instrumental method)

A9.28 Repeat steps A9.21 to 26 using water (A5.1) in the place of the sample.

Note the titre (T_7 ml).

A10 Calculation of Results

Calculate the following alkalinities:–

Component alkalinity titratable to pH 8.3

in the range 200–1000 mg/l as $CaCO_3 = T_3 \times N_1 \times 500.5$

in the range 20–200 mg/l as $CaCO_3 = T_3 \times N_2 \times 500.5$

Total alkalinity

in the range 200–1000 mg/l as $CaCO_3 = (T_4 - T_5) \times N_1 \times 500.5$

in the range 20–200 mg/l as $CaCO_3 = (T_4 - T_5) \times N_2 \times 500.5$

Total alkalinity including that due to suspended matter

in the range 200–1000 mg/l as $CaCO_3 = \dfrac{(T_7 - T_6) \times N_1 \times 12513}{T_7}$

in the range 20–200 mg/l as $CaCO_3 = \dfrac{(T_7 - T_6) \times N_2 \times 12513}{T_7}$

Alkalinity Due to Carbonate, Bicarbonate and Hydroxide

This calculation is only approximate and is only valid when the alkalinity of the sample is due entirely to carbonate, bicarbonate and hydroxide (see substance determined section 1.1).

It is assumed that hydroxide and bicarbonate cannot co-exist and that half the carbonate alkalinity is included by titration to pH 8.3 Other weak acid salts are assumed to be absent.

Let the alkalinity of the sample by titration to pH 8.3 be A mg/l as $CaCO_3$. Let the total alkalinity of the sample by titration to pH 4.5 be B mg/l as $CaCO_3$.

Result of titration	Hydroxide alkalinity as $CaCO_3$	Carbonate alkalinity as $CaCO_3$	Bicarbonate alkalinity as $CaCO_3$
A = 0	0	0	B
A < B/2	0	2A	B — 2A
A = B/2	0	2A	0
A > B/2	2A — B	2(B — A)	0
A = B	B	0	0

(i)   Carbonate alkalinity is present when the alkalinity titratable at pH 8.3 is not zero but is less than the total alkalinity.

(ii) Bicarbonate alkalinity is present if the alkalinity titratable at pH 8.3 is less than half the total alkalinity.

(iii) Hydroxide alkalinity is present if the alkalinity titratable at pH 8.3 is greater than half the total alkalinity.

A11 Sources of Error

See section A3 and note that the interferences listed there are eliminated as shown in section A8. Absorption of atmospheric carbon dioxide during the titration of component alkalinity may be the cause of low results.

B   Determination of Total Alkalinity in Natural, Treated and Waste Waters (Range 0–20 mg/l as CaCO$_3$)

B1 Performance Characteristics of the Method

B1.1	Determinand	Alkalinity to pH 4.5.	
B1.2	Type of sample	All types of water of pH$>$4.5.	
B1.3	Basis of the method	Titration of the sample with a standard solution of acid to successive pH values of 4.5 and 4.2[7] with instrumental pH measurement.	
B1.4	Range of application	0–20 mg/l as CaCO$_3$.	
B1.5	Standard deviation*	Synthetic Solution Nominal Total Alkalinity (mg/l as CaCO$_3$)	Total standard deviation mg/l as CaCO$_3$
		0†	0.09
		2.0	0.19
		5.0	0.22
		8.0	0.18
		13.0	0.29
		18.0	0.29
		†boiled and cooled distilled water. Each value of standard deviation has 9 degrees of freedom.	
B1.6	Limit of Detection	0.47 mg/l as CaCO$_3$ 5 degrees of freedom. *data obtained from a trial undertaken by the Sussex River & Water Division Laboratory, Southern Water Authority.	
B1.7	Sensitivity	1.0 ml of acid (0.02N) $\equiv$ 5.01 mg/l CaCO$_3$.	
B1.8	Bias	No important bias detected.	
B1.9	Interferences	Certain inorganic anions and organic matter may affect the determination of the titration and point (see section B3).	
B1.10	Time required for analysis	6 determinations per hour including standardization of the pH meter.	

B2 Principle

The sample is titrated instrumentally with a standard solution of acid to successive pH values of 4.5 and 4.2 in order to determine the true equivalence point of the titration.

When the alkalinity present is due to carbonate and bicarbonate titration of the sample with acid liberates carbon dioxide. The loss of carbon dioxide from the sample during

titration is extremely variable depending upon the original concentrations of carbonate species present, and upon the titration conditions employed.

At high levels of alkalinity the effect of carbon dioxide at a titration end point of pH 4.5 is not significant. However below about 20 mg/l as $CaCO_3$ the effect of carbon dioxide may be significant and must be minimized. Once the equivalence point of the titration in the vicinity of pH 4.5 has been exceeded a plot of hydrogen ion concentration against volume of standard acid used becomes linear. Extrapolation of this linear section of the graph to zero hydrogen ion concentration determines the equivalence point due to the total alkalinity of the sample. This is shown diagramatically in figure 1.

In practice the two pH values, 4.5, and 4.2, are sufficient to define the linear section of the calibration graph.

B3 Interferences

Difficulties in end-point detection may be experienced in the presence of organic substances. Finely divided suspensions of calcium carbonate and magnesium hydroxide eg in waters softened by a soda-lime process, can contribute alkalinity and may be the cause of fading end-points (see section B8).

B4 Hazards

No particular hazards are known to be associated with this method.

B5 Reagents

Analytical grade reagents and chemicals shall be used. Water as prepared in section B5.1 shall be used throughout.

B5.1 Demineralized Water, Carbon Dioxide Free

Use demineralized, or distilled water, of pH not less than 6.0.

If the pH of the demineralized water is less than 6.0, immediately before use boil the water for at least 15 minutes in a suitable flask and allow to cool to room temperature whilst keeping the flask closed with a guard tube containing soda-lime.

B5.2 Sodium Carbonate

Immediately before use dry 2 ± 1 g of sodium carbonate, anhydrous, for 60 ± 5 minutes in an electric oven set at $265\pm5°C$ and allow to cool in a desiccator.

B5.3 Hydrochloric Acid Solution (0.1N)

Using a graduated pipette fitted with a safety bulb add 9.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) to a 1000 ml calibrated flask. Dilute to volume with water (B5.1) and mix well.

Standardize this solution as follows:—

Weigh out accurately 0.1600 ± 0.0050 g of sodium carbonate into a 250 ml beaker and note the weight of sodium carbonate taken.

Add 100 ± 5 ml of water (B5.1) to the beaker and insert a magnetic rotor. Place the beaker on a magnetic stirrer and stir to dissolve the carbonate. Insert electrodes (B6.1) connected to a pH meter. Titrate with hydrochloric acid solution (B5.3) with continuous stirring until the meter reads pH 4.5 ± 0.05. Note the titre.

Carry out a blank determination by titrating 100 ± 5 ml of water (B5.2) only and note the titre.

Let the mass of sodium carbonate taken $= M$ g
Let the titration of sodium carbonate $= T_1$ ml
Let the blank titration $= T_2$ ml

Then the normality (N_1) of the hydrochloric acid solution

$$= \frac{M \times 18.870}{(T_1 - T_2)}$$

B5.4 Hydrochloric Acid Solution (0.02N

Pipette 50 ± 0.1 ml of hydrochloric acid solution (B5.3) into a 250 ml calibrated flask. Dilute to volume with water (B5.1) and mix well.

Prepare freshly for use and calculate the normality as follows:–

The normality (N_2) of hydrochloric acid solution (B5.4) $= N_1 \times 0.2$.

Alternatively use suitable commercially available standard solutions of hydrochloric acid.

Sulphuric acid solutions of corresponding normality may be used instead of the hydrochloric acid solutions.

B5.5 Buffer Solution pH 4.0[4]

Dissolve 10.20 ± 0.01 g of potassium hydrogen phthalate, previously dried at 105°C for 1 hour, in about 500 ml of water (B5.1). Transfer the solution to a 1000 ml calibrated flask and dilute to volume with water.

The pH of this solution is dependent upon temperature as shown below:

°C	pH
15	4.00
20	4.00
25	4.01

B5.6 Buffer Solution pH 6.9[4, 5]

Dissolve 3.39 ± 0.01 g of potassium dihydrogen orthophosphate, and 3.55 ± 0.01g of disodium, hydrogen orthophosphate, anhydrous, in about 500 ml of water (B5.1). Transfer the solution to a 1000 ml calibrated flask and dilute to volume with water. The pH of this solution is dependent upon temperature as shown below:

°C	pH
15	6.90
20	6.88
25	6.87

Note: The two buffer solutions B5.5 and B5.6 can be replaced by equivalent commercially available buffer solutions.

B6 Apparatus

B6.1 pH Meter and Compatible Electrode System

Suitable for the measurement of pH to within ±0.05 units over the range pH 3 to pH 10.

The electrode system may consist of separate indicating and reference units, or these may be combined within a single assembly.

Each equipment must be used strictly in accordance with the supplier's recommendations.

Immediately before use standardize with buffer solutions (B5.5) and (B5.6).

B6.2 Magnetic Stirrer and Rotor

Suitable to mix 200 ml of solution without splashing. A 25 mm rotor is usually effective.

B7 Sample Collection and Preservation

Preferably using a polyethylene bottle of suitable capacity fill the bottle completely with sample and insert a stopper so that no air remains inside the bottle. If glass containers are used these should be checked to ensure that the glass does not contribute to the alkalinity of the sample.

Ideally, samples should be analysed as soon as possible after collection since certain samples may undergo significant changes on storage. However, if storage is unavoidable the samples should be maintained at $4\pm1°C$.

B8 Sample Pretreatment

If necessary remove any turbidity present by filtering sufficient sample through a suitable filter paper, e.g. grade GF/C. Immediately determine the alkalinity of the filtrate as described in section B9.

However, if the suspended matter is alkaline, it may be desirable to include this alkalinity in the total alkalinity of the water sample. See sections A9.16 onwards of the high range method.

B9 Procedure

Step	Procedure	Notes
B9.1	Preatreatment Stage If necessary filter the sample as described in section B8.	
B9.2	Transfer by cylinder 200 ± 1 ml of sample to a 250 ml beaker.	
B9.3	Place the beaker on a magnetic stirrer and insert a stirring rotor and electrodes (B6.1) connected to a pH meter.	
B9.4	Start the stirrer and using a micro-burette titrate cautiously (see note a) with hydrochloric acid solution (B5.4) until the meter reads pH 4.5 ± 0.05. Note the titre and let this be T_3 ml.	(a) Have the micro-burette tip below the surface of the sample.
B9.5	Continue the titration dropwise until the meter reads pH 4.2 ± 0.05. Note the total titre and let this be T_4 ml.	
B9.6	Calculation (see figure 1) Total alkalinity $= (2T_3 - T_4) \times N_2 \times 250$ mg/l as $CaCO_3$.	
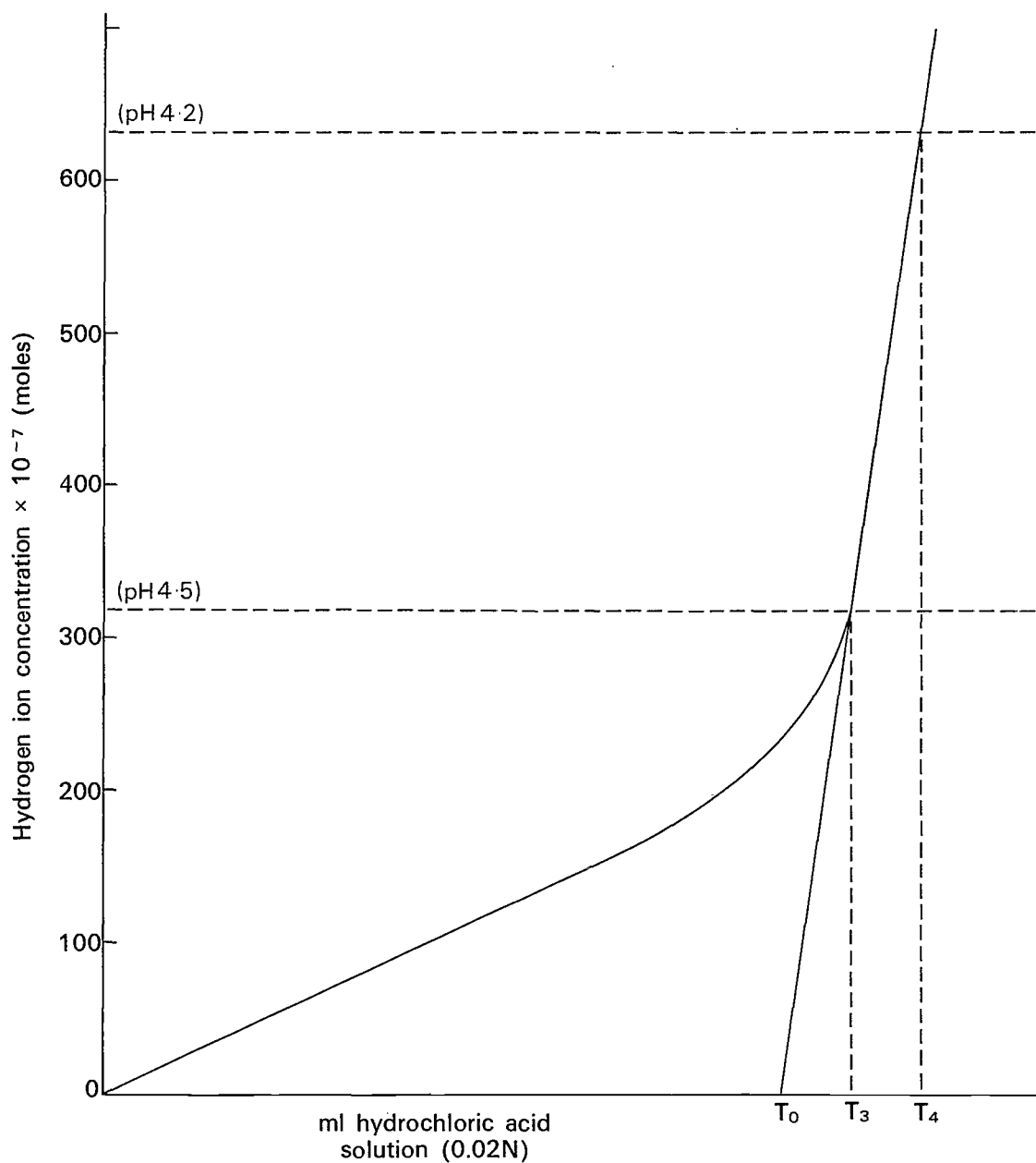
At pH 4.5, hydrogen ion concentration $= 316 \times 10^{-7}$ moles

At pH 4.2, hydrogen ion concentration $= 632 \times 10^{-7}$ moles

T_3 ml $=$ volume of hydrochloric acid solution (0.02N) required to titrate the sample to pH 4.5.

T_4 ml $=$ total volume of hydrochloric acid solution (0.02N) required to titrate the sample to pH 4.2.

T_0 ml $=$ volume of hydrochloric acid solution (0.02N) corresponding to zero hydrogen ion concentration ie the true equivalence point of the titration

Then $T_0 = T_3 - (T_4 - T_3)$

$\qquad = 2T_3 - T_4$

C Continuous Flow Automated Method For the Determination of Alkalinity in Water

C1 Performance Characteristics of the Method

C1.1	Determinand	Methyl Orange Alkalinity in solution, expressed as mg/l $CaCO_3$.
C1.2	Type of sample	Sewage, effluents, raw and potable water.
C1.3	Basis of method	Air segmented continuous flow colorimetry using potassium phthalate buffered Methyl Orange.
C1.4	Ranges of application	20 to 300 mg/l ($CaCO_3$). (Method B is recommended for 20 mg/l or less.)
C1.5	Calibration curves	Linear.

C1.6   Total standard deviation (a)

Sample Type	Total Alkalinity mg/l (as $CaCO_3$)	Total standard deviation (within Laboratory) mg/l (as $CaCO_3$)	
		Min	Max
Sodium Carbonate Solution	48.0	1.64	2.96
Sodium Carbonate Solution	152.0	2.22	3.75
Sodium Carbonate Solution	248.0	3.10	5.70
Borehole Water	96.2	0.83*	3.17*
Sewage Effluent	186.4	1.10*	4.08*

Each value of Standard deviation has 14 degrees of freedom.

* Within batch standard deviations quoted due to sample instability.

C1.7	Limit of detection (a)	1–9 mg/l (each estimate has 10 degrees of freedom.
C1.8	Sensitivity (b)	The optical density change for a 300 mg/l ($CaCO_3$) alkalinity standard in a 15 mm cell at 550 nm is 0.48 optical density units.

C1.9	Bias	No evidence of bias for standard solutions or stable waters with low organic content.
C1.10	Interference	Highly coloured substances and certain oxidizing agents may cause interference by enhancing or bleaching the colour of the methyl orange reagent (see section 3.0).
C1.11	Time required for analysis	Sample rate: 40 per hour Start up time: 30 minutes Shut down time: 15 minutes Sample retention time: 7 minutes

C2 Principle

Basic anions (eg bicarbonate, carbonate and hydroxide) pass from a sample stream through a cellulose acetate dialyser membrane into a reagent stream containing methyl orange pH indicator, buffered with potassium phthalate. The reduction in the red acid component of the indicator is measured as the decrease in absorbance at a wavelength of 550 nm in a 15 mm flow cell.

C3 Interferences

Coloured substances which pass through the dialyser membrane and which absorb light at 550 nm may lead to falsely low results and certain oxidising agents may bleach the methyl orange reagent and cause falsely high results.

At levels normally encountered in potable waters chlorine does not cause significant interference (see table 3).

TABLE 3 (b)

Substance	Concentration mg/l	Effect upon the determination of Alkalinity	
		0.0 mg/l (CaCO$_3$)	150 mg/l (CaCO$_3$)
Sodium Hypochlorite (Cl)	0.20	+1	+2
Sodium Hypochlorite (Cl)	1.00	+1	0
Sodium Hypochlorite (Cl)	5.00	+2	−1

The maximum effects, assuming no interference, are as follows;
   mg/l (CaCO$_3$)±5, 150 mg/l (CaCO$_3$)±4.
(a) Data obtained from an inter-laboratory exercise involving laboratories within Severn Trent Water Authority, Southern Water Authority, Thames Water Authority and Yorkshire Water Authority.

(b) Data obtained by Yorkshire Water Authority.

C4 Hazards

The chromic acid reagent C5.6 is highly corrosive and a powerful oxidizing reagent and should not be allowed to come into contact with organic materials.

The sodium hypochlorite solution C5.7 is also highly corrosive and should not be allowed to mix with acids since this may result in the evolution of chlorine gas.

Both of these reagents should be handled with care and gloves and eye protection worn during their use.

C5 Reagents

Use analytical grade reagents and water as prepared in section C5.1.

C5.1 Demineralized Water, Carbon Dioxide Free

Use demineralized or distilled/deionized water of a pH not less than 6.0. If the pH of the demineralized water is less than 6.0, immediately before use boil the water for at least 15 minutes in a suitable flask and allow to cool to room temperature whilst keeping the flask closed with a guard tube containing soda lime.

C5.2 Buffer Solution pH 3.1

Dissolve 10.20 ± 0.05 g of potassium hydrogen phthalate in 500 ml of water in a 1000 ml volumetric flask. Add 175 ± 1 ml of 0.1N hydrochloric acid (reagent A5.3 Method A), dilute to volume with water and mix well. Stored in a stoppered glass bottle at ambient temperature, this reagent is stable for at least four weeks.

C5.3 Methyl Orange Reagent

Dissolve 0.050 ± 0.001 g of water soluble methyl orange and 25.0 ± 0.5 g of sodium chloride in 750 ml water. Add 5 drops of a neutral non-ionic detergent, dilute to 1000 ml in a calibrated flask and mix well. Stored in an amber glass bottle at ambient temperature this reagent is stable for at least four weeks.

C5.4 Stock Alkalinity Standard (equivalent to 1000 mg/l ($CaCO_3$))

Weigh out 1.059 ± 0.001 g of sodium carbonate previously dried at $265\pm5°C$ for 1–2 hours and cooled in a desicator. Transfer to a 1000 ml calibrated flask, dissolve in water, then make to the mark with water and mix well. Stored in a stoppered glass bottle at 4°C this solution is stable for at least four weeks.

C5.5 Alkalinity Calibrating Standards

Pipette into each of five 100 ml calibrated flasks 5, 10, 20, 25 and 30 ml of Stock Alkalinity Standard C5.4. Dilute to the mark with water and mix well. These solutions contain the equivalent of 50, 100, 200, 250 and 300 mg/l ($CaCO_3$), and can be stored in stoppered glass bottles for up to four weeks.

C5.6 Chromic Acid Reagent

Dissolve 70 ± 5 g of sodium dichromate in 1000 ± 10 ml of sulphuric acid (d_{20} 1.84). Store the reagent in a stoppered glass bottle.

C5.7 Sodium Hypochlorite Solution (10%–14% m/v available chlorine)

Commercial reagent quality solution is suitable.

C6 Apparatus
Figure 2

C6.1 Apparatus for this continuous flow method consists basically of the following:–

Sample presentation unit (sampler).
Multichannel peristaltic pump.
Analytical cartridge (manifold) including pump tubes, mixing coils, dialyser. (See flow diagram.)
Colorimeter, incorporating a flow cell.
Recorder.

Consult the essay review on continuous flow analysis[8] for further information.

C7 Sample Collection and Preservation

Preferably using a polyethylene bottle of suitable capacity fill the bottle completely with sample and insert a stopper so that no air remains inside the bottle. If glass containers are used these should be checked to ensure that the glass does not contribute to the alkalinity of the sample.

Ideally, samples should be analysed as soon as possible after collection since certain samples may undergo significant changes on storage. However, if storage is unavoidable the samples should be maintained at $4\pm1°C$.

Figure 2

Methyl Orange Alkalinity 20 - 300 mg/l (CaCO₃)
Flow Diagram

Peristaltic Pump

Pump Tubes (Flows in ml/minute)

0·32	Air	
0·42	Sample	
0·16	Buffer	
0·32	Air	
0·60	Methyl Orange *	
0·60	Methyl Orange *	
0·80		

Pull Through From Detector Unit

5 Turn Coil

6″ Dialyser

To Waste

10 Turn Coil   10 Turn Coil

12 Turn Coil   12 Turn Coil

To Waste

Flow Cell 15mm
550nm Filter
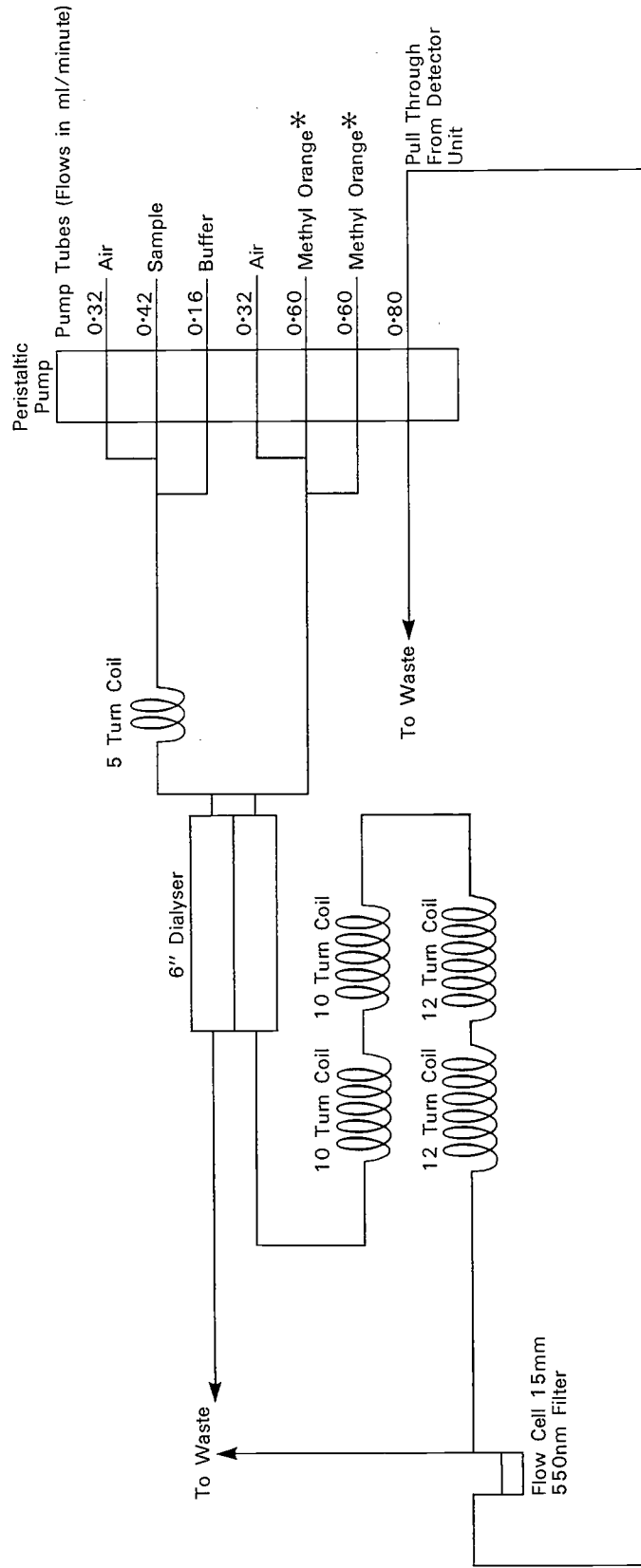
Note: a) 2mm bore glass tubing used for all coils and connections.
b) Mixing coils are 20mm external diameter

60 Sec Sample   (These times may be varied to suit the system)
25 Sec Wash

*Methyl Orange added in two portions to aid bubble pattern

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C8 Procedure

Step	Procedure	Notes

Starting Operation

C8.1 Connect system as shown in Figure 2 (note a).

(a) Follow the manufacturer's general operating instructions, noting that this system operates in the inverse mode. See also reference 8.

C8.2 With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents (note b), start pump and switch on detection and measurement units (note c).

(b) Ensure that there is sufficient of each reagent to avoid 'topping up' during one batch of analysis.

(c) Allow the system to equilibrate for at least 20 minutes and during this period check that the bubble pattern and hydraulic behaviour of the system is satisfactory. If not, eliminate difficulties before proceeding to step C8.3.

Initial Sensitivity Setting

C8.3 When an acceptably smooth baseline trace is obtained at the recorder adjust the response to about 5 percent of full scale (note d).

(d) An elevated setting of the baseline allows for any negative drift that may occur.

C8.4 Insert the sample probe into a portion of the 300 mg/l alkalinity calibration standard (see C5.5) for approximately 2 minutes and then return the probe to the wash position.

C8.5 When a stable response to the standard is obtained (after approximately 7 minutes) adjust the colorimeter to give a response on the recorder of 90 to 95 percent full scale (notes e and f).

(e) A setting 5 to 10 percent below full scale allows for any increase in sensitivity that may occur.

(f) This may be directly possible on some measurements units but others may require range expansion facilities.

Analysis of Samples

C8.6 The sample turntable may be loaded in the following order (note g).

(g) The turntable can be loaded during the initial stabilisation period (steps C8.2 to 4).

The order given is a suggestion. Other loading patterns are discussed in Reference 8.

Position No. on turntable

Position	Description	Notes
1–5	Calibration standards (see C5.5) ascending order	
6–7	Blanks (note h)	(h) Water from the same source as that used to prepare the calibration standards is used for blanks.
8–17	Samples (note i)	(i) A control standard may be included as one of the samples as a check on system control.
18	Calibration standard (note j).	(j) The standard which occupies position No. 4 to check the calibration.
19–20	Blanks	
21–30	Samples	
31	Calibration standard (note j)	

Step	Procedure	Notes
32–33	Blanks	
34–38	Calibration standards in ascending order	

Repeat the sequence 6–38 until all the samples have been processed (note k).	(k) When cross contamination occurs between two samples (visible on the measurement unit trace as incomplete separation of a consecutive sample responses) both samples are re-analysed separated by a blank solution.

C8.7 When a steady baseline is obtained on the measurement unit, re-adjust it to about 5 per cent of full scale if necessary and start the sampling unit.

C8.8 When all the system responses (peaks) due to the processed solutions have appeared on the recorder and a final baseline has been obtained, this unit can be switched off.

Calculation of Results

C8.9 Plot a calibration curve of measurement unit responses (y axis) against concentration (x axis) of standard solutions (note l).	(l) Providing the blank corrected responses of the calibration standard analysed at the end of each group and those at the end of the turntable are all acceptably close to their respective initial blank corrected calibration standard response. If not, refer to reference 8 for a suggested procedure to obtain calibration curves.
C8.10 Using the calibration curve to convert the measurement unit responses (peak heights) into concentrations of alkalinity in the samples (note m).	(m) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes. The results are expressed as mg/l ($CaCO_3$).

Shut Down Procedure

C8.11 Transfer all reagent lines to water and continue pumping for 10 minutes (note n).	(n) After a period of time build up of a residue in the mixing coils may give rise to a very noisy baseline. The manifold should be dismantled and thoroughly cleaned, preferably in an ultra-sonic bath using sodium hypochlorite solution (C5.7). Followed by thorough rinsing in water. Soaking in chromic acid (C5.6) and finally thorough rinsing in water. The manifold may then be rebuilt using a fresh dialyser membrane.

C9 Preparation of Calibration Curve

As indicated in step C8.6, five (at least) calibration standards should be run at the beginning of, and at intervals in, each batch of samples. The concentrations of the standards must be selected having regard for the expected sample alkalinity concentrations and of the manifold configuration in current use. Solutions prepared as detailed C5.5 should be used; intermediate concentrations additional to those given can be prepared if required.

Calibration is carried out as described in Step C8.9.

C10 Sources of Error

A great advantage of continuous flow analysis over manual procedures is that procedural errors inherent in the latter are eradicated; all samples and standards are handled in exactly the same way, providing the apparatus is kept well maintained in

accordance with the makers instructions. Thus, apart from mechanical or hydraulic failures or malfunctions, the greatest sources of error are likely to be those given below.

C10.1   Drifting Calibration Curve

A well maintained system should exhibit little or no drift of either calibration standard response or baseline. However, the presence of blanks and standards in an analytical run provide a means of checking the calibration. Small amounts of drift can be corrected by means of these standards, but large drifts should be investigated further.

C10.2   Inter-sample Carryover

The sample to wash ratio of the sampling device should be optimized, bearing in mind the performance required, at the introduction of this method to a laboratory. However, there may be occasions when carryover is still a problem, mainly when a very high concentration, perhaps above the intended calibration range is followed by a very low concentration. In this circumstance, the two samples concerned must be re-run separated by a water blank.

D   Acidity

Determination of Acidity in Water and Waste Waters

D1 Performance Characteristics of the Method

D1.1	Determinand	Acidity to pH 4.5, Acidity to pH 3.7.
D1.2	Type of sample	Polluted waters and certain trade effluents.
D1.3	Basis of method	Titration of the sample with a standard solution of sodium hydroxide and instrumental (potentiometric) detection of end-point at pH value 4.5 and, if required, at pH value 3.7.
D1.4	Range of application	20–1000 mg/l as $CaCO_3$.
D1.5	Standard deviation	Acidity by titration to pH value 4.5 using 0.02 N sodium hydroxide using Procedure DA (section D9).

Synthetic Solutions Nominal Total Acidity (mg/l as $CaCO_3$)	Total Standard Deviation (within Laboratory) (mg/l as $CaCO_3$)
99.7	3.33
213.3	7.09
509.0	4.98
843.5	9.59

Each value of standard deviation has 5 degrees of freedom.

D1.6	Limit of detection	1.5 mg/l as $CaCO_3$ (10 degrees of freedom). (Method not suitable for samples with acidity less than 20 mg/l as $CaCO_3$.)
D1.7	Sensitivity	1.0 ml of sodium hydroxide (0.1N) = 50.05 mg/l $CaCO_3$. 1.0 ml of sodium hydroxide (0.02N) = 10.01 mg/l $CaCO_3$.
D1.8	Bias	None known except where loss of volatile acids may affect results in the presence of oxidizable acidic metallic salts.
D1.9	Interferences	Oily substances and other organic matter may affect the ease with which the detection of the end point is determined (see section D3).
D1.10	Time required for analysis	The total analytical and operator times are the same and for 10 samples equal 1 hour excluding any pretreatment time (see section D3).

D2 Principle

Titration of the samples with standard sodium hydroxide solution and instrumental detection of the end-point at pH 4.5. An instrumental (potentiometric) procedure is advocated because where acidity is present (other than that due to carbon dioxide) it is

likely to be in a grossly contaminated water sample or trade waste sample. Such samples are frequently coloured and not suitable for titration procedures involving a visual end-point using a colour indicator to show pH change. In some instances it may be known that the acidity present is wholly or substantially due to the presence of mineral acid in which case it may be preferred to use pH 3.7 end-point. It is imperative to report the pH of the end-point used.

Where certain metal salts are present, e.g. those of iron and aluminium, reaction with the alkaline titrant may be relatively slow at room temperature and this can affect electrode response. Moreover, where a sample contains ferrous iron, a reliable measure of the full acidity potential of the sample is obtained only when the ferrous iron is oxidized to ferric. A hot peroxide procedure can be used followed by cooling to ambient temperature before titration. (Procedure B.)

D3 Interferences

Where acidic dissolved gases are present it is appropriate to carry out the titration as soon as possible after collection with avoidance of undue agitation of the sample. In certain heavily polluted waters and trade waste samples there may be contamination present of a type which can interfere with the response of the glass electrode. This may be present as oil or other organic matter and various types of insoluble or sparingly soluble constituents. These contaminants may contribute to the total acidity of the sample and should not be removed in a preliminary processing step. As the end-point is approached time is allowed between addition of titrant for equilibrium to be achieved at the electrode.

D4 Hazards

No particular laboratory hazards are known to occur with this method. Where pipettes are used for the transfer of strong acid or strong alkali solution they should always be of of the safety pipette type.

D5 Reagents

Analytical grade reagents and chemicals to be used. Water as prepared in Section D5.1 to be used in the preparation of reagents.

D5.1 Demineralized or Distilled Water

Distilled or demineralized water of normal grade for analytical purposes. There is no requirement for carbon dioxide-free water in the determination of acidity according to this procedure.

D5.2 Sodium Carbonate

Immediately before use dry 2 ± 1 g of sodium carbonate, anhydrous, for 60 ± 5 minutes in an electric oven set at $265 \pm 5°C$ and allow to cool in a desiccator.

D5.3 Standard Hydrochloric Acid Solution (approx 0.1N)

Using a graduated pipette fitted with a safety bulb add 9.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) to a 1000 ml calibrated flask. Dilute to volume with water and mix well. Alternatively the following solution may be used.

D5.3(a) Standard Sulphuric Acid Solution (approx. 0.1N)

With caution carefully add 3.1 ± 0.1 ml of sulphuric acid (d_{20} 1.84) to 500 ml $\pm$ 50 ml in a 1000 ml calibrated flask. Mix, cool and dilute to volume with water and mix well.

Standardize these solutions using an instrumental (potentiometric) method for neutralization to the desired pH value:

Weigh out accurately 0.1600 ± 0.0050 g of sodium carbonate (D5.2) into a 250 ml beaker and note the weight of sodium carbonate taken. Add 100 ± 5 ml of water to the beaker and insert a magnetic rotor. Place the beaker on a magnetic stirrer and stir to dissolve the carbonate. Insert electrodes (D6.1) connected to a pH meter (D6.1). Titrate with acid solution (D5.3 or D5.3(a)) with continuous stirring until the meter records pH 4.5 ± 0.05. Where it is intended that the acidity of samples will be reported to pH 3.7 this standardization procedure should be operated to the point where the meter reads pH 3.7 ± 0.05. Note the titre.

Carry out a blank determination on 100 ml water as in the foregoing procedure (a) and note the titre.

Let the mass of sodium carbonate taken $\quad = M$ g
Let the titration of sodium carbonate $\quad = T_1$ ml
Let the blank titration $\quad\quad\quad\quad\quad\quad = T_2$ ml

Then the normality (N_1) of the hydrochloric acid solution (D5.3) or sulphuric acid solution (D5.3(a)) is

$$N_1 = \frac{M \times 18.870}{(T_1 - T_2)}$$

D5.4 Standard Hydrochloric Acid Solution (approx. 0.02N)

Pipette 50 ± 0.1 ml of hydrochloric acid solution (D5.3) into a 250 ml calibrated flask. Dilute to volume with water and mix well.

Prepare freshly for use in the standardization of 0.02N sodium hydroxide solution. Calculate the normality (N_2) of hydrochloric acid solution (D5.4) as

$$N_2 = N_1 \times 0.2$$

Alternatively use commercially available standard solutions of acid. Standard acid solution should be stored in glass or polyethylene bottles with well fitting stoppers.

D5.4(a) Standard Sulphuric Acid Solution (approx 0.02N)

Sulphuric acid solution may be used instead of the hydrochloric acid solutions and is required if acidity potential due to salts of iron is to be determined.

Proceed as in D5.4, but use 50 ± 0.1 ml of sulphuric acid solution D5.3(a).

D5.5 Buffer Solution pH 4.0

Dissolve 10.20 ± 0.01 g of potassium hydrogen phthalate, previously dried at 105°C for 1 hour in about 500 ml of water. Transfer the solution to a 1000 ml calibrated flask and dilute to volume with water. The pH of this solution is dependent upon temperature as shown in the table below:

°C	pH
15	4.00
20	4.00
25	4.01

D5.6 Buffer Solution pH 6.9

Dissolve 3.39 ± 0.01 g of potassium dihydrogen orthophosphate, and 3.55 ± 0.01 g of disodium hydrogen orthophosphate anhydrous, analytical reagent grade, in about 500 ml of water. Transfer the solution to a 1000 ml calibrated flask and dilute to volume with water. The pH of this solution is dependent upon temperature as shown in the table below:

°C	pH
15	6.90
20	6.88
25	6.87

Note. The two buffer solutions (D5.5) and (D5.6) can be replaced by equivalent commercially available buffer solutions.

D5.7 Standard Sodium Hydroxide Solution (approx 0.1N)

Dissolve 50 ± 0.5 g of sodium hydroxide pellets in 50 ± 0.5 ml of water with cooling in a 250 ml conical flask fitted with a cover. Allow to stand until the supernatant liquid is clear. Using a safety pipette transfer 6.5 ± 0.1 ml of clear solution into a 1000 ml calibrated flask. Dilute to volume with water and mix well.

Standardize this solution with acid solution (D5.3 or D5.3(a)) using the potentiometric procedure given in section D5.3 for the determination of the selected end-point pH of 4.5 or 3.7.

Normality (N_3) of the sodium hydroxide (D5.7) is:

$$N_3 = \frac{(T_3 - T_2) \times N_1}{V}$$

where T_3 = volume of acid required to neutralize V ml of solution (D5.7) to selected pH. T_2 = volume of acid required to neutralize V ml of water.

Store sodium hydroxide solution in a polyethylene bottle protected from atmospheric carbon dioxide by a soda lime tube or airtight closure.

D5.8 Standard Sodium Hydroxide Solution (approx 0.02N)

Pipette 50 ± 0.1 ml of sodium hydroxide solution (D5.7) into a 250 ml calibrated flask. Dilute to volume with water and mix well.

This solution should be freshly prepared on the day of use and should be standardized with the solution of acid (0.02N) as prepared in (D5.4 or D5.4(a)) using the potentiometric procedure for determination of the selected end-point of pH 4.5 or 3.7.

Normality (N_4) of the dilute (approx. 0.02N) sodium hydroxide solution (D5.8) is:

$$N_4 = \frac{(T_4 - T_2) \times N_2}{V}$$

Where T_4 = volume of acid required to neutralize V ml of solution (D5.8) to selected pH, and
T_2 = volume of acid required to neutralize V ml of water (D5.1) to selected pH.

D5.9 Hydrogen Peroxide Solution, 30% m/v

Store according to directions given by supplier.

D6 Apparatus

D6.1 pH Meter and Compatible Electrode System

The determination of pH value is included in a booklet published in this series.

The meter used should be suitable for the measurement of pH to within ± 0.05 units.

The electrode system may consist of separate indicating and reference units, or these may be combined within a single assembly. All equipment should be used strictly in accordance with the suppliers recommendations. Immediately before use standardize with buffer solutions (D5.5) and (D5.6).

D6.2 Magnetic Stirrer and Rotor

Suitable to mix 100 ml of solution without splashing. A 25 mm rotor is normally appropriate.

D7 Sample Collection and Preservation

Either glass or polyethylene bottles of suitable capacity can be used. Completely fill the bottle with sample and insert stopper so that no air remains inside the bottle.

If it is suspected that the sample contains dissolved acidic gases, it is important that the analysis should be carried out as quickly as possible. Otherwise if necessary store at 4°C and analyse as soon as practicable.

D8 Sample Pretreatment	**D8.1 Treatment in the presence of acidic metallic salts,** eg those of iron, or iron with aluminium. In the presence of more than trace amounts of these metallic salts prior treatment with hydrogen peroxide is advised, although where ferrous salts are present such treatment is deemed essential if the maximum acidity potential of the sample is required. Proceed as described in procedure DB.

D8.2 In this potentiometric titration method for the determination of acidity, it is not advised that other forms of pre-treatment are used.

D9 Procedure

Step	Procedure	Notes

Procedure DA

Method in the Absence of More than Trace Amounts of Acidic Metallic Salts (eg More than 10 mg/l of Iron).

D9.1 Pipette 100 ± 0.1 ml of sample into a 250 ml beaker.

D9.2 Place the beaker on a magnetic stirrer and insert a stirring rotor and electrodes (note a).

(a) Prior to the use of the pH meter the standardization procedure should be carried out (D6.1).

D9.3 Start the stirrer and if the pH of the sample is greater than pH 4.5 the acidity of the sample should be recorded as zero mg/l as $CaCO_3$.

Where the pH is between 4.5 and 3.7 titrate with sodium hydroxide solution (D5.7) or (D5.8) as appropriate until the meter reads pH 4.5 (see notes b and c). Let the titre obtained by T_5 ml (pH 4.5).

(b) If the pH of the sample is lower than pH 3.7 proceed to Step D9.4.

(c) When on adding the titrant the pH closely approaches the chosen pH of the end point, the titrant must be added slowly with intervals of time such that the mixing provision enables equilibrium condition to be reached between the solution under test and the indicating electrode.

D9.4 Where the pH of the sample is less than pH 3.7 mineral acid is likely to be a component of the acid reactants in the sample. In such cases add sodium hydroxide solution (D5.7) or (D5.8) until the meter reads pH value 3.7. Let the titre obtained be T_6 ml (pH 3.7).

Procedure DB

Method of in the Presence of Oxidizable Acidic Metallic Salts
(Note d).

(d) Where volatile acids are present, slight loss of acidity will occur using this method.

D9.5 Pipette or otherwise transfer 100 ± 0.1 ml of sample into a 250 ml beaker.

D9.6 Check that the pH of the sample is below pH 4.0 (note e) and if so remove it from pH meter and add hydrogen peroxide solution (D5.9) in sufficient amount for oxidation of metal salts. 0.25 ml± 0.05 of hydrogen peroxide solution (D5.9) may be appropriate (note f). Boil the treated sample aliquot for 2–5 minutes and then cool to room temperature. Titrate with sodium hydroxide solution 0.02N (D5.8) to pH 4.5. Let the titre obtained be T_7 ml (pH 4.5).

(e) If the pH of the sample is above pH 4.0, but below pH 4.5 proceed to Step D9.7.

(f) Use of hydrogen peroxide in the amount stated with water blank (D5.1) will typically give a solution of pH greater than 4.5 and thus not contribute acidity. This should be checked with each batch of hydrogen peroxide.

Step	Procedure	Notes

D9.7   If pH of sample is above pH 4.0 but below pH 4.5 add 5 ml increments of 0.02N sulphuric acid (D5.4(a)) until pH is below pH 4.0. Let the added volume of 0.02N acid be T_8 ml. Proceed with oxidation with hydrogen peroxide as detailed in Step D9.6. After cooling titrate with sodium hydroxide solution 0.02N (D5.8) to pH value 4.5. Let the titre obtained be T_9 ml (pH 4.5). (Note g).

(g) If acidity to pH 3.7 is to be determined, proceed as in Step D9.8.

Proceed with blank determination as follows. To 100 ml$\pm$1 ml of distilled water add T_8 ml of 0.02N sulphuric acid (D5.4(a)) and 0.25 ml$\pm$0.05 ml of hydroyen peroxide solution. Boil and cool as in Step 6. Titrate with sodium hydroxide solution 0.02N (D5.8) to pH 4.5. Let the titre obtained be T_{10} ml (pH 4.5).

D9.8   If acidity to pH value 3.7 is required proceed as in Steps D9.5 and 6. Let the titre obtained on titrations with 0.02N sodium hydroxide solution to pH 3.7 be T_{11} ml.

D10 Calculation of Results

The end-point used must be included in the expression of results viz.

Acidity to pH ————— — ————— mg/l $CaCO_3$

(a) For titration of acidity where 100 ml of sample used and where titre is T_5ml, T_6ml, T_7ml and T_{11}ml

(i) using 0.02N sodium hydroxide solution acidity as mg/l $CaCO_3$ = titre (ml) $\times$ N_4 $\times$ 500.5

(ii) using 0.10N sodium hydroxide solution acidity as mg/l $CaCO_3$ = titre (ml) $\times$ N_3 $\times$ 500.5

(b) Where pretreatment necessitates acid addition prior to oxidation of acid salts=

Acidity as mg/l $CaCO_3$ = $(T_9 - T_{10}) \times N_4 \times 500.5$

Checking the Accuracy of the Analytical Results

The analyst should establish a control chart procedure suited to the levels and types of alkalinity or acidity encountered in the samples to be analysed.

For most purposes the statistical principles presented in a report published by the Water Research Centre may be adopted[6].

References

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(11) Official Journal of the European Communities L.229 p23. 30.8.80.

(12) *Total Hardness, Calcium Hardness and Magnesium Hardness in Raw and Potable waters by EDTA Titrimetry 1981,* HMSO Methods for the Examination of Waters and Associated Materials.

Department of the Environment/National Water Council

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