

Total Hardness, Calcium Hardness and Magnesium Hardness in Raw and Potable Waters by EDTA Titrimetry 1981

Tentative Methods

Methods for the Examination of Waters and Associated Materials

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This booklet describes methods for the direct determination of total hardness and calcium hardness by titration of samples with standard EDTA solution. An estimate of the magnesium hardness is obtained from the difference between the total hardness and the calcium hardness.

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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 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.

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 radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of 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.

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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, have issued volumes of methods for the analysis of water and sewage culminating in '*Analysis of Raw, Potable and Waste Waters*'. These volumes took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council.

It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

- 1.0 General principles of sampling and accuracy of results
- 2.0 Instrumentation and on-line analysis*
- 3.0 Empirical and physical methods
- 4.0 Metals and metalloids
- 5.0 General non-metallic substances
- 6.0 Organic impurities
- 7.0 Biological methods
- 8.0 Sludge and other solids analysis*
- 9.0 Radiochemical methods.

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

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.

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

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

Note on the Expression of Results

Throughout this booklet, all forms of hardness are expressed as mg/l CaCO_3 . However, this is a convention and is not meant to imply that the actual substance present is calcium carbonate; nor should this be confused with alkalinity which is also often expressed in the same unit. Temporary hardness, precipitated by heating close to the boiling point, is mainly due to the bicarbonates of calcium and magnesium; strontium bicarbonate and magnesium carbonate can also be a cause. Permanent hardness is mainly due to thermally stable soluble salts, chiefly sulphates and chlorides of calcium and magnesium.

Occasionally traces of hardness may be caused by calcium carbonate or by soluble alkali metal double carbonates of calcium and magnesium. Certain other non-alkali metals

with soluble bicarbonates, sulphates etc may also contribute traces of either of the above types of hardness. The commonest of these trace metals, which are removed in the methods described in this booklet, are: manganese, iron, cobalt, nickel, copper, zinc, lead and also barium (bicarbonate only).

For some purposes, results may be expressed in millimoles or milliequivalents per litre of divalent cation. There are also obsolescent units—degrees of hardness:

- 1 English degree of hardness is 1 grain CaCO_3 /gallon (where 1 grain is $\frac{2}{9 \times 7 \frac{1}{8}}$ oz) or 14.28mg/l CaCO_3 .
- 1 French degree of hardness is 10mg/l CaCO_3 .
- 1 German degree of hardness is 10mg/l CaO or 17.9mg/l CaCO_3 .

Method A Total Hardness of Raw and Potable Waters by EDTA Titrimetry Tentative Method (1981 Version)

NOTE: Throughout this method total hardness ^(a) is expressed as mg/l CaCO₃.

A1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Analytical Results 1980, also published in this series).

A1.1	Substance determined	Total hardness (see Section A2).			
A1.2	Type of sample	Raw and potable waters			
A1.3	Basis of the method	Complexometric titration using ethylene diamine tetra-acetic acid (EDTA).			
A1.4	Range of application	Up to 1000 mg/l.			
A1.5	Calibration curve	Not applicable.			
A1.6	Total standard deviation	Concentration (mg/l CaCO ₃)	Total standard deviation (mg/l CaCO ₃)	Sample size (ml)	Degrees of freedom
		5.0 (d)	0.18	100	9 (b)
		32.5 (e)	0.40	100	9 (c)
		100.0 (d)	0.83	50	9 (b)
		297.9 (e)	1.44	25	9 (b)
		350.0 (d)	1.09	25	9 (b)
A1.7	Limit of detection	0.9 mg/l with 4 degrees of freedom ^(b) . (calculated from the within batch standard deviation of a 5 mg/l total hardness solution).			
A1.8	Sensitivity	1 ml of 0.01 M EDTA is equivalent to 1 mg of CaCO ₃ .			
A1.9	Bias	Not known.			
A1.10	Interferences	Certain metal ions interfere (see Section A3).			
A1.11	Time required for analysis	The total analytical and operator times are the same and a typical time for a batch of 10 samples is 1 hour.			

(a) It is important to realise that although this determination is popularly referred to as total hardness content and taken to mean soluble calcium and magnesium compounds any strontium present will be included.

(b) Determined by the Thames Water Authority⁽¹⁾.

(c) Determined by the South West Water Authority⁽²⁾.

(d) Distilled or deionized water spiked with the stated total hardness concentration.

(e) Tap waters.

A2 Principle

A2.1 Total hardness (soluble calcium, magnesium, and strontium) is determined by the complexometric titration of an aliquot of the sample using ethylene diamine tetra-acetic acid (EDTA) in the presence of a suitable indicator.

A2.2 When the indicator Eriochrome Black T is added to a solution containing calcium and magnesium ions at pH 10.0 ± 0.1 the solution will be pink to wine-red in colour depending on the concentration of ions present. On titrating with EDTA the solution will turn blue when sufficient EDTA has been added to complex all the calcium, magnesium and other reactive ions present. It is essential that magnesium ions are present to ensure a satisfactory end point and therefore a small amount of the complexometrically neutral magnesium salt of EDTA is incorporated in the buffer solution.

A3 Interferences

A3.1 Several metal ions interfere with this determination. Some such as copper cause indistinct end points and others such as zinc titrate as total hardness. Various inhibitors have been suggested to minimize these effects and of these sodium sulphide is considered to be the most effective. The effect of various substances on the determination of total hardness, both in the presence and absence of sodium sulphide, is shown in Table 1. This information was obtained by the South West Water Authority⁽³⁾.

A3.2 The method described will work satisfactorily for the vast majority of raw and potable waters encountered. However, there may be a few waters where indistinct end points still occur or where the level of interference is unacceptable. In these cases it is recommended that the total hardness be calculated from the sum of the concentrations of the individual contributing ions (expressed in mg/l CaCO_3) determined by atomic absorption spectrophotometry using other methods in this series⁽⁴⁾⁽⁵⁾.

A4 Hazards

The ammonia buffer solution (see Section A.5.2) and the sodium sulphide solution (see Section A.5.3) are hazardous and gloves and goggles should be worn when preparing and handling these solutions.

A5 Reagents

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated. Analytical reagent grade chemicals are suitable unless otherwise specified.

A5.1 Water

Deionized water or water distilled from an all glass apparatus is suitable.

Table 1

Other substance	Other substance added as	Concentration of other substance (mg/l)	Sodium sulphide	Effect of other substance in mg/l CaCO ₃ at a total hardness concentration of 100 mg/l (c)	
				Effect	Colour change
Copper (as Cu ²⁺)	nitrate	10.0	absent present	— 0	purple – no distinct end point orange/red – blue/grey
Iron (as Fe ³⁺)	chloride	4.0	absent present	+2 +6	pink–blue purple–grey/blue
Lead (as Pb ²⁺)	nitrate	10.0	absent present	0 +2	pink–blue purple–grey/blue
Manganese (as Mn ²⁺)	chloride	0.5	absent present	0 –4	pink–blue pink–blue
Zinc (as Zn ²⁺)	acetate	20.0	absent present	+26 +2	purple–blue pink–blue
		100.0	absent present	+130 +132	purple–blue purple–blue
Phosphate (as PO ₄ ³⁻)	potassium dilydrogen	5.0	absent present	0 0	pink–blue pink–blue

(c) If these other substances did not interfere the effect would be expected (95% confidence) to be between 0.0 ± 4.0 mg/l CaCO₃.

A5.2 Ammonia buffer solution

A5.2.1 This reagent is hazardous (see Section A4) and should be prepared in a fume cupboard. Dissolve 16.9 ± 0.1 g of ammonium chloride in 143 ± 2 ml of ammonia solution (d_{20} 0.880). Add 1.25 ± 0.01 g of magnesium disodium salt of EDTA and dilute with water to 250 ml. The magnesium EDTA salt may not contain exact equivalents of magnesium and EDTA and therefore it is necessary to check each batch of buffer solution, and, if necessary, adjust the solution.

A5.2.2 Dilute 10.0 ± 0.1 ml of standard calcium solution (see Section A.5.6) with water to 100 ml in a calibrated flask. Dilute 10.0 ± 0.1 ml of 0.01M EDTA (see Section A.5.7) with water to 100 ml in a calibrated flask. Add 5.0 ± 0.1 ml of buffer to a 250-ml conical flask and dilute to approximately 100 ml with water. Add one or two drops of Eriochrome Black T indicator solution and mix. The colour should be pure blue without the slightest tinge of red.

(i) If the colour is pure blue, titrate the diluted buffer solution with the diluted calcium standard solution. The buffer is satisfactory if 0.2 ml of this solution produces a reddish tinge after a few seconds. If this is not so continue the titration drop by drop until a faint red tinge is observed. Subtract 0.2 ml from the titre. Multiply the corrected titre by 5 and add this volume of standard calcium solution (1 ml contains 1 mg CaCO₃) to 250 ml of buffer. Dilute a 5.0 ± 0.1 ml portion of the adjusted buffer and recheck as above.

(ii) If the colour has a reddish tinge titrate slowly with the diluted EDTA solution (0.001M) until a pure blue colour is obtained. Multiply the titre by 5 and add this volume of 0.01M EDTA to the 250 ml of buffer solution. Dilute 5.0 ± 0.1 ml of the adjusted buffer solution and recheck as above.

A5.2.3 The buffer solution is stable for up to 1 month when stored in a polyethylene bottle with a tight fitting stopper. The solution should be discarded when 2.0 ± 0.1 ml of buffer added to 50 ± 1 ml of sample fails to produce a pH value of 10.0 ± 0.1 .

A5.2.4 The ammonia buffer is generally considered to provide a better and sharper end point than the alternative odourless buffers. The ammonia buffer should not be used in laboratories where ammonia and alkalinity determinations are regularly carried out. In these circumstances the ethanolamine buffer should be used and analysts should be aware that the performance characteristics quoted in Section A1 may no longer apply. To prepare the buffer add 11.0 ± 0.5 ml of hydrochloric acid (d_{20} 1.18) to approximately 80 ml of water in a 400-ml beaker. Mix and then add slowly with stirring 62 ± 1 ml of ethanolamine (2 amino-ethanol) (d_{20} 1.01). Dissolve 1.0 ± 0.1 g of magnesium disodium EDTA in the mixture and dilute with water to 200 ml. The solution is stable for up to 3 months. This buffer must be checked in the same manner as the ammonia buffer (see Section A.5.2.2).

A5.3 5% m/V Sodium sulphide nonahydrate solution.

This reagent is hazardous (see Section A4). Dissolve 5.0 ± 0.1 g of sodium sulphide nonahydrate or 3.7 ± 0.1 g of sodium sulphide pentahydrate in 100 ± 1 ml of water. This solution rapidly deteriorates and it should be freshly prepared at least monthly. It should be stored in an amber glass bottle with a tightly fitting polyethylene stopper.

A5.4 0.5% m/V Eriochrome Black T indicator solution.

Dissolve 0.50 ± 0.01 g of Eriochrome Black T (sodium 3-hydroxy-4-(1-hydroxy-2-naphthylazo)-7-nitronaphthalene-1-sulphonate) (*CI 14645*) in 75 ± 1 ml of triethanolamine (d_{20} 1.121) (2,2',2'' nitrilotriethanol) and 25 ± 1 ml of ethanol (d_{20} 0.81). Discard this solution when the end point colour change deteriorates.

A5.5 10% V/V Hydrochloric acid

Dilute 10.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) with water to 100 ml in a measuring cylinder.

A5.6 Standard calcium solution 1 ml contains 1 mg CaCO_3 .

Dry some calcium carbonate at $105 \pm 3^\circ\text{C}$ for approximately 1 hour, cool in a desiccator and weigh out 1.000 ± 0.001 g. Transfer the weighed calcium carbonate to a small funnel placed in the neck of a 250-ml conical flask and wash the calcium carbonate into the flask with approximately 50 ml of water. Keeping the funnel in position cautiously add 20 ± 1 ml of 10% V/V hydrochloric acid and warm the flask gently until all the calcium carbonate has dissolved. Cool, transfer quantitatively to a 1-litre calibrated flask and dilute with water to the mark. This solution is stable for at least six months.

A5.7 0.01M Disodium ethylene diamine tetra-acetate dihydrate (EDTA)

A5.7.1 Dry some disodium ethylene diamine tetra-acetate dihydrate at $105 \pm 3^\circ\text{C}$, weigh 3.725 ± 0.001 g, transfer to a small funnel in the neck of a 1-litre calibrated flask and wash the EDTA into the flask with approximately 200 ml of water. Swirl to dissolve and then dilute with water to the mark. Standardize this solution at regular intervals against the standard calcium solution.

A5.7.2 Standardization of the EDTA solution

Pipette 10.0 ml of standard calcium solution into a 250-ml conical flask and dilute with water to approximately 50 ml. Carry out steps A9.2 and A9.3.

Calculate the molarity, M, of the EDTA solution from:—

$$M = \frac{0.01 \times 10}{V}$$

where V is the volume of EDTA used. It is convenient to adjust the molarity of the solution to exactly 0.01 M by addition of the appropriate amount of EDTA or water.

A6 Apparatus Normal laboratory glass and polyethylene ware which has been thoroughly rinsed in distilled or deionized water.

A7 Sample Collection and Preservation The sample should be collected in a clear glass or polyethylene bottle. The bottle should be filled completely with the sample and stoppered so as to leave the minimum of air space. No preservative or acid addition is required. The sample should be analysed as soon as possible after collection.

A8 Sample Pretreatment Total hardness determinations are performed normally only on raw and potable waters. These samples do not require pretreatment except that samples containing gross amounts of particulate matter should be filtered through a 0.45 µm pore size filter as soon as possible after collection. If filtration is carried out there is a risk of removing some hardness.

A9 Analytical Procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
Analysis of samples		
A9.1	Pipette a suitable volume (V_1 ml) of the sample or filtered sample (see Section A8) into a 250-ml conical flask. A suitable volume is up to 100 ml (note a).	(a) Select a sample volume that requires less than 10 ml of EDTA in the titration step. If the sample volume taken is less than 50 ml it should be diluted with water to 50 ml.
A9.2	For each 50 ml of solution add 2.0 ± 0.1 ml of ammonia buffer (note b) and 1.0 ± 0.1 ml of sodium sulphide solution. Add Eriochrome Black T indicator solution dropwise until a pink to wine-red colour is obtained (normally 1 to 3 drops).	(b) The pH of the solution should be 10.0 ± 0.1 (see Section A.5.2.3.)
A9.3	Place the flask against a white background and titrate immediately with the 0.01M EDTA, swirling continuously. As the end-point is approached a blue colour will be observed but a reddish tinge will still be visible. Add the next few drops of EDTA at 5 second intervals until the end point is reached when the last of the reddish tinge disappears and a pure blue colour is left. Record the titre of EDTA (V_2 ml) (note c).	(c) To minimize calcium carbonate precipitation the titration should be completed as soon as possible after the addition of the reagents and certainly within 5 minutes.

Calculation of the result

A9.4 Total hardness as mg/l CaCO_3

$$= \frac{100.09 \times 1000 \times M \times V_2}{V_1}$$

where M=molarity of the EDTA

Blank determination

A9.5 If the result (step 9.4) is less than 10 mg/l CaCO_3 then a blank should be carried out by repeating steps A.9.1 to A.9.3 using water instead of the sample. Record the titre of EDTA (B ml). In the calculation of the result use ($V_2 - B$) instead of V_2 .

A10 Sources of Error

The analytical procedure can be applied to a wide range of raw and potable waters and the attention which it is necessary to pay to sources of error depends on the accuracy required. Each analyst must decide what precautions are appropriate to his particular requirements. The main sources of error in this determination are due to interfering substances titrating as hardness or causing indistinct end points (see Section A3). The effect of possible interfering substances may be determined by analysing samples spiked with total hardness and various concentrations of the potential interfering substances.

A11 Checking the Accuracy of Analytical Results

(For further information see General Principles of Sampling and Accuracy of Results 1980, also published in this series.)

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. However, as a minimum, it is suggested that a solution of known total hardness concentration should be analysed at exactly the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy and will also allow the standard deviation of routine analytical results to be estimated.

A12 References

- (1) Department of the Environment, File WS/646/53, Paper SCA/4.3/H7.
- (2) Department of the Environment, File WS/646/53, Paper SCA/4.3/H6.
- (3) Department of the Environment, File WS/646/53, Paper SCA/4.3/H2.
- (4) *Methods for the Examination of Water and Associated Materials, Calcium in Waters and Sewage Effluents by Atomic Absorption Spectrophotometry, 1977, HMSO.*
- (5) *Methods for the Examination of Water and Associated Materials, Magnesium in Waters and Sewage Effluents by Atomic Absorption Spectrophotometry, 1977, HMSO.*

Method B

Calcium Hardness of Raw and Potable Waters by EDTA Titrimetry Tentative Method (1981 Version)

NOTE: Throughout this method calcium hardness is expressed as mg/l CaCO₃.

B1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Analytical Results 1980, also published in this series.)

B1.1	Substance determined	Calcium hardness (see Section B2).			
B1.2	Type of sample	Raw and potable waters.			
B1.3	Basis of the method	Complexometric titration using ethylene diamine tetra-acetic acid (EDTA).			
B1.4	Range of application	Up to 1000 mg/l.			
B1.5	Calibration	Not applicable.			
B1.6	Total standard deviation (a)	Concentration (mg/l CaCO ₃)	Total standard deviation (mg/l CaCO ₃)	Sample size (ml)	Degrees of freedom
		5.0 (b)	0.24	100	9 (d)
		5.0 (b)	0.45	100	9 (e)
		100.0 (b)	0.71	50	9 (e)
		300.0 (b)	2.59	25	9 (e)
		272.6 (c)	4.69	25	9 (e)
B1.7	Limit of detection	1.37 mg/l with 4 degrees of freedom (d). 2.55 mg/l with 4 degrees of freedom (e). (calculated from the within batch standard deviation of a 5 mg/l calcium hardness solution.)			
B1.8	Sensitivity	1 ml of 0.01M EDTA is equivalent to 1 mg. of CaCO ₃ .			
B1.9	Bias	Not known.			
B1.10	Interferences	Certain metal ions interfere (see Section B3).			
B1.11	Time required for analysis	The total analytical and operator times are the same and a typical time for a batch of 10 samples is 1 hour.			

(a) 5 mg/l magnesium was added during each of these determinations (see Section B2.3).

(b) Distilled or deionized water spiked with the stated calcium hardness concentration.

(c) Tap water.

(d) Determined by the South West Water Authority⁽¹⁾.

(e) Determined by the Thames Water Authority⁽²⁾.

B2 Principle

B2.1 Calcium hardness is determined by the complexometric titration, using ethylene diamine tetra-acetic acid (EDTA) in the presence of a suitable indicator, of an aliquot of the sample in which the magnesium hardness has been precipitated.

B2.2 When EDTA is added to water containing both calcium and magnesium ions it combines first with the calcium ions. If the pH is made sufficiently high (pH 12.0 to 13.0) so that most of the magnesium present is precipitated, and if an indicator is used which combines with calcium only, then the calcium can be determined directly by titration using EDTA.

B2.3 When using the chosen Patton and Reeder indicator it is necessary for some magnesium to be present to obtain a satisfactory end point. The majority of samples will contain sufficient magnesium. However, for those few samples which do not contain sufficient magnesium and for analysing standards and blanks it is necessary to add magnesium. An addition of 5 mg/l magnesium is recommended.

B3 Interferences

B3.1 Several ions interfere with the determination of calcium hardness usually by causing indistinct end points. Various inhibitors have been suggested to minimize these effects and of these sodium sulphide is considered the most effective. The effect of various substances on the determination of calcium hardness in the presence of sodium sulphide is shown in Table B1. This information was obtained by the South West Water Authority⁽³⁾.

B3.2 The method described will work satisfactorily for the vast majority of raw and potable waters encountered. However, there may be a few waters where indistinct end points still occur or where the level of interference is unacceptable. In these cases it is recommended that calcium hardness be determined by atomic absorption spectrophotometry using another method in this series⁽⁴⁾.

B4 Hazards

The sodium sulphide solution (see Section B5.4) is hazardous and gloves and goggles should be worn when preparing and handling the solution.

B5 Reagents

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated. Analytical reagent grade chemicals are suitable unless otherwise specified.

B5.1 Water

Deionized water or water distilled from an all-glass apparatus is suitable.

Table B1

Other substance	Other substance added as	Concentration of other substance (mg/l)	Effect of other substance in mg/l CaCO ₃ at a calcium hardness concentration of 19 mg/l CaCO ₃ (d)	
			Effect	Colour change
Copper (as Cu ²⁺)	nitrate	2.5	0.0	} pink/brown–grey/blue
		5.0	0.0	
		6.0	+ 1.0	} pink/brown–grey/blue (indistinct)
		10.0	+ 1.0	
		20.0	+ 1.0	
Iron (as Fe ³⁺)	chloride	1.0	– 0.5	} pink–blue
		2.0	– 0.5	
		4.0	– 2.0	} dull pink–green/blue (indistinct)
		8.0	– 2.0	
Lead (as Pb ²⁺)	nitrate	2.5	0.0	pink–blue
		5.0	0.0	dull pink–dull blue
		10.0	+10.0	dull pink–grey/blue
Manganese chloride (as Mn ²⁺)		0.5	0.0	pink–blue
		1.0	0.0	pink–pale blue
		2.0	– 1.0	pink–pale blue/green
		10.0	+ 1.0	pale pink–yellow/green
Zinc (as Zn ²⁺)	acetate	5.0	0.0	pink–blue
		10.0	0.0	} pink–blue (end-point drift)
		15.0	+ 1.0	
		20.0	+ 2.0	purple–pale blue (end-point drift)
		50.0	+10.0	purple–dark blue (end-point drift)
Phosphate (as PO ₄ ³⁻)	potassium dihydrogen	5.0	0.0	} pink–blue
		10.0	0.0	
		15.0	0.0	

(d) If the other substances did not interfere the effects would be expected (95% confidence) to be between 0.0 ± 2.0 mg/l CaCO₃.

B5.2 1M Sodium hydroxide (approximately)

Dissolve 4.0 ± 0.1 g of sodium hydroxide pellets in 100 ml of water.

B5.3 Hydrochloric acid.

B5.3.1 10% V/V Hydrochloric acid

As for Method A, Section A5.5.

B5.3.2 0.1M Hydrochloric acid (approximately)

Dilute 9.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

B5.4 5% m/V sodium sulphide nonahydrate solution

As for Method A, Section A5.3.

B5.5 Patton and Reeder indicator

Mix 1.0 ± 0.1 g of Patton and Reeder indicator (3-hydroxy-4-(2-hydroxy-4-sulpho-1-naphthylazo)-2-naphthoic acid) with 100 ± 1 g of dried ($105 \pm 3^\circ\text{C}$) anhydrous sodium sulphate or sodium chloride.

B5.6 Standard calcium solution 1 ml contains 1 mg CaCO_3

As for Method A, Section A5.6.

B5.7 0.01M Disodium ethylene diamine tetra-acetate dihydrate (EDTA)

B5.7.1 As for Method A, Section A5.7.1.

B5.7.2 Standardization of the EDTA solution

Pipette 10.0 ml of the standard calcium solution into a 250-ml conical flask and dilute with water to approximately 50 ml. Add 2.5 ± 0.1 ml of 0.01 % m/V magnesium solution (see Section B5.8) and carry out steps B9.3 and B9.4. Calculate the molarity, M , of the EDTA solution from:—

$$M = \frac{0.01 \times 10}{V}$$

where V (ml) is the volume of EDTA used.

It is convenient to adjust the molarity of the solution to exactly 0.01M by addition of the appropriate amount of EDTA or water.

B5.8 0.01 % m/V Magnesium solution

Dissolve 1.01 ± 0.01 g of oven dried ($105 \pm 3^\circ\text{C}$) magnesium sulphate heptahydrate in water and dilute with water to the mark in a 1-litre calibrated flask.

B6 Apparatus

As for Method A, Section A6.

B7 Sample Collection and Preservation

As for Method A, Section A7.

B8 Sample Pre-treatment

Calcium hardness determinations are performed normally only on raw and potable waters. These samples do not require pre-treatment except that samples containing gross amounts of particulate matter should be filtered through a $0.45 \mu\text{m}$ pore size filter as soon as possible after collection. If filtration is carried out there is a risk of removing calcium salts.

B9 Analytical Procedure

READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of sample	
B9.1	Pipette a suitable volume (V_1 ml) of sample or filtered sample (see Section B8) into a 250-ml conical flask. A suitable volume is up to 100 ml. (Notes a and b)	(a) Select a sample volume that requires less than 10 ml of EDTA in the titration step. If the sample volume taken is less than 50 ml it should be diluted with water to 50 ml. (b) If difficulty is experienced with the end point or if there is known to be no magnesium present in the sample add 2.5 ± 0.1 ml of 0.01 % m/V magnesium solution.

Step	Experimental Procedure	Notes
B9.2	Neutralise any alkalinity in the sample by adding 0.1M hydrochloric acid dropwise from a burette or pipette using litmus paper as the indicator. For each 50 ml of sample or diluted sample add 2.0 ± 0.1 ml of 0.1M hydrochloric acid in excess, boil the solution for 3.0 ± 0.5 minutes and cool to room temperature.	
B9.3	For each 50 ml of sample or diluted sample add 4.0 ± 0.1 ml of 1M sodium hydroxide solution and mix (note c) followed by 2.0 ± 0.1 ml of sodium sulphide solution and mix again. Add 0.10 ± 0.05 g of Patton and Reeder indicator and stir for 60 ± 10 seconds.	(c) The pH should now be 12.0 to 13.0.
B9.4	Place the flask against a white background and titrate immediately with 0.01M EDTA swirling continuously. As the end point is approached a blue coloration will be observed but a reddish tinge will still be visible. Add the last few drops of EDTA at 5 second intervals until the last of the reddish tinge disappears and a pure blue colour is left. Record the titre of EDTA (V_2 ml) (note d).	(d) To minimize calcium carbonate precipitation the titration should be completed as soon as possible after the addition of the reagents and certainly within 5 minutes.

Calculation of the result

B9.5 Calcium hardness as mg/l CaCO_3

$$= \frac{100.09 \times 1000 \times M \times V_2}{V_1}$$

where M = molarity of the EDTA.

Blank determination

B9.6 If the result (step B9.5) is less than 10mg/l CaCO_3 then a blank should be carried out by repeating steps B9.1 to B9.4 using water instead of the sample. (2.5 ± 0.1 ml of 0.01 % m/V magnesium solution will need to be added). Record the titre of EDTA (B ml). In the calculation of the result use ($V_2 - B$) instead of V_2 .

B10 Sources of Error

The analytical procedure can be applied to a wide range of raw and potable waters and the attention which it is necessary to pay to sources of error depends on the accuracy required. Each analyst must decide what precautions are appropriate to his particular requirements. The main source of error in the determination is due to interfering substances causing indistinct end points (see Section B3). The effect of possible interfering substances may be determined by analysing samples spiked with calcium hardness and various concentrations of the potential interfering substances.

B11 Checking the Accuracy of Analytical Results

(For further information see *General Principles of Sampling and Accuracy of Results* 1980, also published in this series.)

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. However, as a minimum, it is suggested that a solution of calcium hardness should be analysed at exactly the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy and will also allow the standard deviation of routine analytical results to be estimated.

B12 References

- (1) Department of the Environment, File WS/646/53, Paper SCA/4.3/H8.
- (2) Department of the Environment, File WS/646/53, Paper SCA/4.3/H9.
- (3) Department of the Environment, File WS/646/53, Paper SCA/4.3/H1.
- (4) *Methods for the Examination of Water and Associated Materials, Calcium in Waters and Sewage Effluents by Atomic Absorption Spectrophotometry, 1977, HMSO.*

Method C Magnesium Hardness of Raw and Potable Waters by EDTA Titrimetry Tentative Method (1981 Version)

C1 Estimation of Magnesium Hardness An estimate of the magnesium hardness (mg/l CaCO₃) may be made by subtracting the calcium hardness (mg/l CaCO₃) determined in Method B from the total hardness (mg/l CaCO₃) determined in Method A. It is stressed that this gives an approximate value of the magnesium hardness firstly because it is based on the subtraction of two other results and secondly because it will include, from the total hardness determination, any strontium present.

C2 Determination of Magnesium Hardness If a direct determination of magnesium hardness is required it is recommended that the magnesium concentration be determined by atomic absorption spectrophotometry using another method in this series⁽¹⁾.

C3 Reference (1) *Methods for the Examination of Water and Associated Materials, Magnesium in Waters and Sewage Effluents by Atomic Absorption Spectrophotometry, 1977, HMSO.*

Address for Correspondence However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this booklet are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
LONDON SW1P 3PY
England

Appendix

Estimation of the Accuracy of Analytical Results using the Total Hardness and Calcium Hardness Methods

1 Introduction

Quantitative investigation of the accuracy achievable when the total hardness and calcium hardness methods are used appears to be limited to work at the South-West and Thames Water Authorities. Before firmly recommending the methods for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of these methods, could estimate the accuracy of its own analytical results and report the findings to the Secretary of the Metals and Metalloids Working Group of the DOE/NWC Standing Committee of Analysts*.

The precision achieved and the effects of any interfering substances that may be present in samples are of particular interest. Any information on these aspects would be useful, but the value of such information would be greatly enhanced if it were obtained to a common plan so that the information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis of results are given in the following sections and it is strongly urged that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible; more complex designs are possible and would give more information.

2 Basis of the Suggested Tests

The limit of detection is governed by the within-batch variability of results at zero determined concentration. The precision of analytical results may depend on the concentration of the total hardness or calcium hardness in the samples analysed and on the type of sample, eg, worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion of each of the following solutions on each of n days, where n is at least 5 and preferably up to 10.

Solution No	Description	Method A Total Hardness	Method B Calcium Hardness
1	Blank †		
2	Another blank †		
3	Standard solution	5 mg/l CaCO ₃	5 mg/l CaCO ₃
4	Standard solution	200 mg/l CaCO ₃	200 mg/l CaCO ₃
5	Typical sample		
6	Same sample spiked with	200 mg/l CaCO ₃	200 mg/l CaCO ₃

† To be regarded as samples having zero determinand concentration and NOT as true blanks.

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section A9, Method A and Section B9, Method B be rigidly followed except that a second TRUE blank should be run with that prescribed in exactly the same manner (ie each of the two true blanks should be titrated in the batch of samples). The six solutions described above should be analysed in random order in with each batch of analyses. Solutions 1 and 4 should be prepared each day exactly as described in the method and on any one day the same batch of water should be used to prepare these four solutions. For solutions 5 and 6 a total of 4 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows:

add with a pipette 1.0 ml of a standard calcium solution (1 ml contains 20 mg CaCO₃ prepared by dissolving 2.00 + 0.01 g of dried calcium carbonate in 40 ± 1 ml of 10% V/V hydrochloric acid and diluting with water to 100 ml) to 100 ml of solution 5.

The total period of the tests may be any convenient time so long as the total hardness or calcium hardness in solution 5 does not change appreciably (up to 2 weeks). The results of the analyses of solutions 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of the spiked total hardness or calcium hardness from 100% may give an indication of the presence of interfering substances.

3 Evaluation of Results

The raw experimental results should be sent to the Department of the Environment for evaluation. However, for those laboratories wishing to make the calculations themselves the details are given below.

3.1 Convert all results to concentrations as described in the method. Deduct the mean response of the first true blank when performing the conversions for solutions 1,3,4,5 and 6 and deduct the mean response for the second true blank when performing the conversion for solution 2.

3.2 For solutions 3,4,5 and 6 calculate the mean concentration of the n results for each solution. For solutions 1 and 2 calculate the overall mean concentration of the 2n results.

3.3 For solutions 3,4,5 and 6 calculate the standard deviation, s, of the n results for each solution from:

$$s = \sqrt{\frac{(X_i - \bar{X})^2}{n-1}}$$

Where X_i = the result from the ith batch

\bar{X} = the mean value of X_i

3.4 Calculate the within-batch standard deviation, s_{wr} , of the results at zero concentration from:

$$s_{wr} = \sqrt{\frac{(X_{1i} - X_{2i})^2}{2n}}$$

Where X_{1i} = the result for solution 1 from the ith batch (see 3.1).

X_{2i} = the result for solution 2 from the ith batch (see 3.1).

Note s_{wr} is not to be confused with the within-batch standard deviation of blank determinations, s_w , from which the limit of detection is often calculated.

3.5 Calculate the mean percentage recovery for total hardness (Method A) or calcium hardness (Method B) from:

$$R = \frac{(1.01 \bar{X}_6 - \bar{X}_5) \times 100}{200}$$

Where \bar{X}_5 = the mean value of the results for solution 5.

\bar{X}_6 = the mean value of the results for solution 6.

3.6 Summarize the results as in the following table:

Solution	No of results	Mean total hardness or calcium hardness concentration (mg/l CaCO ₃)	Standard deviation (mg/l CaCO ₃)	Mean recovery (%)
1 and 2 Blanks	2n=			—
3 Standard				
5mg/l CaCO ₃	n=			—
4 Standard				
200 mg/l CaCO ₃	n=			—
5 sample	n=			—
6 sample +				
200 mg/l CaCO ₃	n=			

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step 3.4 is entered for the row for solutions 1 and 2 and the standard deviations from step 3.3 are entered for solutions 3 to 6.

* Results to be sent to the following:

The Secretary
 The Metals and Metalloids Working Group
 The Standing Committee of Analysts
 The Department of the Environment
 43 Marsham Street
 LONDON SW1P 3PY
 England

Standing Committee of Analysts

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