Boron in Waters, Effluents, Sewage and some Solids, 1980

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £3.20 net

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This booklet contains four methods (Parts B–E), a section of general information (Part A), which see for choice of method, and an appendix on sample pretreatments.

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 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; and 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards.

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.

First published 1981

ISBN 0 11 751583 3

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 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, biologists, 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 nonmetallic 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 occuring 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 9BT. 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

4 December 1980

Part A General Information

Note: Throughout this publication boron is expressed as the element (B).

A1 Comparison of methods

This booklet contains a comprehensive range of methods for the preparation and analysis of all types of sample normally encountered during quality control by the various branches of the water and sewage industries.

A1.1 Boron in waters, effluents and sewage

Boron is almost always present in water as boric acid and/or the tetrahydroxyborate anion, but the amount of the ionized species present depends on the concentration. The equilibrium is affected by the presence of acids or alkalis[2,3]. The methods which follow take these effects into account.

A1.2 Boron in other materials

The determination of boron in some materials, in particular sludges, soils and sediments may necessitate a pretreatment of the sample to get the boron into a soluble form in which it can be measured by one of the methods described. Various pretreatments have been found suitable for different types of sample are described in a series of Appendices (I–IV).

A1.3 Comparison of methods for determining boron in solution

Table 1 compares the methods given in Parts B–E. Parts B and E describe recommended methods based on the colour reaction with curcumin and titration in the presence of mannitol respectively. These methods are based on well established traditional principles, but suffer particularly in that they are time consuming. Parts C and D describe tentative methods based on the colour reaction with azomethine-H. These

Table 1. Comparison of methods for determining boron in solution.

Method	Curcumin	Azomethine-H (automated)	Azomethine-H (manual)	Titration
see part	B	C	D	E
Type of sample	non saline	all	all	all
Range in mg/l	0–5	0–4·5	0–10	1–1000
Limit of detection in mg/l	0·004	0·04	0·04	0·5
Interferences (for details see specific methods).	nitrate, chloride, and high levels of fluoride.	high levels of fluoride.	high levels of fluoride.	slight interference from very high levels of phosphate, fluoride and buffer anions.
Number of analyses achievable per day	15	100	80	6

methods are relatively new, but are simpler and quicker than earlier methods, in particular, Method C should be well suited to those laboratories with the necessary automated analytical facilities who require a method for a large number of samples. These reactions are carried out in aqueous solution, avoiding the use of strong mineral acids. For more detailed information see the performance characteristics and other information given at the beginning of each individual method section.

A2 Common causes of error

The determination of boron is unusually susceptible to errors and therefore requires care and attention to detail in analysis.

A2.1 Losses

Free boric acid and some derivatives may volatilize under certain conditions; unless otherwise specified, care should be taken to avoid the following:

(i) exposure of acid solutions to the air;
(ii) evaporating acid solutions;
(iii) heating alkaline mixtures above 450°C;
(iv) presence of alcohols or other alkylating agents (borate esters are highly volatile);
(v) heating any solid containing boron and fluoride together (boron trifluoride may be formed).

Though unlikely to be present, organoboron compounds are often volatile and hence easily lost to the atmosphere. No details are given herein for their determination, but if the compounds present can be quantitatively decomposed to boric acid or simple hydroxyborates the methods in Parts B–E can be used to complete their determination.

A2.2 Boron contamination

As boron is ubiquitous, serious contamination may occur during trace determinations. The following sources of contamination and remedies should be considered:

(i) Laboratory glassware is usually made from borosilicate glass. Special boron free thermally resistant glass is obtainable; but for routine analysis, old borosilicate glass, well rinsed in hydrochloric acid, may be used for acidic solutions, but should never be used for neutral or alkaline solutions, or for prolonged storage at any pH value. (Borosolicate glassware used previously with alkaline solutions must not be used without very thorough acid rinsing.)
(ii) detergents and soaps used for glassware and labcoats should be boron free, and the use of towels and tissues for drying must be avoided.
(iii) toiletries, talcum powder and cosmetics used by technicians often contain boron and should be avoided or removed, especially prior to accurate trace level determinations.
(iv) water and reagents may contain boron, blanks should be carried out at least in duplicate and agree.

A3 Reagents

Analytical grade reagent chemicals are suitable unless otherwise specified. Distilled and/or deionised water should be used throughout. The presence of boron in the water used for the blank will cause a negative bias when the blank correction is made. The presence of boron in reagent and dilution water will also cause erratic results. The maximum tolerable concentration of boron in such waters is dependent on the concentration range expected in the samples, but should be insignificant for the purpose of the analysis.

A3.0.1 Determination of the Presence of Boron in the Water and Reagents

The following procedure may be used to check the quality of reagents and water used. Measure into three separate boron free beakers quantities of water equal to one sample portion, four sample portions and ten sample portions. Make each portion slightly alkaline by the addition of the same amount of calcium hydroxide to each. Evaporate the four-and-ten-fold portions to the usual sample volume. Adjust the volume with a little extra distilled water if necessary. Carry out a blank determination on each portion of water. If boron is present in the water, the boron found increases in proportion to the amount of water used. Erratic results indicate external boron contamination. Relatively high but constant values indicate impure reagents. A high single volume result with the differences between the single volume result and the four volume and ten volume results approximately in the ratio of one is to three indicates the presence of boron in the distilled water and the reagents.

The following alternative methods have been used to check reagent purity:

(i) Carry out comparative blank determinations using reagent from different batches or suppliers;
(ii) Examine the reagent spectrographically by DC arc emission spectroscopy, using the boron doublet lines at 249.68 and 249.77 nm. For information on a suitable procedure see either Emission spectrophotometric multielement methods of analysis for waters, sediments and other materials of interest to the water industry (1980), issued in this series or standard texts on emission spectroscopy.

A3.1 Hazards

A3.1.1 The curcumin-acetic acid solution (B4.5) must not be pipetted by mouth

A3.1.2 Although azomethine-H has not been reported to be hazardous, little information is available. It should be treated with care and ingestion, and inhalation and skin contact should be avoided.

A3.1.3 The procedure described in Appendix IV should not be used for samples high in organic matter as there is a risk of explosion from such samples. If samples high in organic matter must be so treated see Step 4.1 note b of that Appendix.

A4 Boron standard

Boric acid is a convenient boron standard. To ensure that the material is of stoichiometric composition recrystallization from aqueous solution is advised.

A4.1 Procedure for preparation for recrystallized boric acid

Dissolve about 200 g boric acid in one litre of water by simmering until the crystals have completely dissolved. If necessary add a further small quantity of water to complete solution of the crystals. Cover and cool to room temperature. Filter off the crystals using a hardened filter paper on a buchner funnel and suck as dry as possible. Spread out on filter paper in a tray and dry at room temperature (not above 30°C). For use, dry at room temperature (below 30°C) to constant weight in a desiccator. Do not keep in a desiccator for more than 24 hrs. Store in a tightly stoppered bottle.

A4.2 Standard boron solutions

A4.2.1 Solution A. 1 ml is equivalent to 1000 μg B:

Dissolve 5.719 ± 0.005 g of recrystallized boric acid in water, and dilute with water to 1 litre in a calibrated flask. Store in a polyethylene bottle. This solution is stable for at least one year.

A4.2.2 Solution B. 1 ml is equivalent to 10 μg B:

Dilute 10.00 ± 0.05 ml of Solution A with water to 1 litre in a calibrated flask. Store in a polyethylene bottle. Prepare fresh as required.

A4.2.3 Solution C. 1 ml is equivalent to 1 μg B:

Dilute 10.00 ± 0.05 ml of Solution B with water to 100 ml in a calibrated flask. Store in a polyethylene bottle. Prepare fresh as required.

A5 Samples and sample storage

A5.1 Sample bottles

Preferably, samples should be collected and stored in polyethylene or polypropylene bottles and containers, but soda glass bottles may be used.

Where high accuracy is required, only bottles of proven reliability must be used. Reliability may be ascertained as follows:

Store a standard boron solution in the bottle for a period longer than the normal storage period, then analyse the solution. Clean the bottle in the normal way (using boron free detergent), then store water in it for a similar length of time and analyse the water. The pH of both the standard boron solution and the water should correspond approximately to that of future samples. Reject any bottles that show a significant loss or gain of boron in the two tests. For solid samples boron free containers made from linen, glass or polyethylene are suitable, but paper and cardboard must not be used, as they are a frequent source of boron contamination. Similarly all labels should be on the outside of the bottle as most labelling materials contain boron compounds.

A5.2 Preservation of samples

Samples should be analysed as soon as possible after collection. Sewages and similar samples likely to decompose should be stored in plastic bottles in a refrigerator and analysed within three days. Sample solutions, on standing, may deposit or form a film on the bottle wall (possibly difficult to see) due to the hydrolysis of metal salts, and this deposit may contain boron. Solution of the film or deposit may be possible by rinsing the bottle thoroughly with 1–2 ml of cold 10M hydrochloric acid, washing out the bottle with 5–10 ml portions of boron free water, combining, making up to a suitable volume and analysing separately. Add this extra boron proportionately when calculating the total boron concentration.

A5.3 Sediments

Whether sediments are dissolved or separated and analysed separately, will depend on the problem or control for which the analysis is being made. Care should be taken that no boron is lost by evaporation during drying. If possible, separated sediment samples should be prepared for analysis as speedily as possible prior to long term storage. If sediments are redissolved in the original sample, the method of solution used must be determined by the nature of the sediment itself. Care must be taken not to volatilize any boron compounds. Warming of acidic solutions must be avoided, boric acid is volatile in steam. (See Section A2.1.)

A5.4 Volume correction

Some of the foregoing operations entail increases in volume. If these volume changes cause significant error, the result should be recalculated back to the original sample volume.

A6 Typical boron ranges

Although exceptionally high boron concentrations can occur particularly in trade effluents, the majority of samples are likely to be below the following concentrations:

Sewage	3 mg/l
Drinking Water	0.5 mg/l
River Water	1 mg/l
Sea Water	about 5 mg/l

A7 Analytical quality control

Once a method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Because of the complex relationships between the forms of boron to be determined in water and the wide range of concentrations likely to be encountered, it is beyond the scope of this booklet to present an analytical quality control method that satisfactorily covers all the possible variables. Therefore, the analyst must follow the guidelines and statistical practices set out in standard texts such as that published by the Water Research Centre[1] and select control procedures appropriate to his chosen analytical procedure.

As a minimum, however, it is suggested that a standard solution of boron of suitable concentration should be analysed at 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.

A8 Testing for interference effects

Interference effects may cause either high or low results. If it is desired to know whether a substance can cause interference, a series of experiments should be carried out similar to those for analytical quality control but using solutions containing known amounts of the suspected interferent, at and above its expected concentration in the samples to be analysed.

A8.1 Removal if necessary of fluoroborate, perborate and other interfering anions

There are several apparently divergent statements in the literature about fluoride interference. Samples of fluoroborates (or conversely mixtures of borates and fluoride) do eventually give equilibrium mixtures, but the reaction is slow and dependent on temperature and pH. Some anion exchange resins can separate acidified samples of fluoride, fluoborate, borate and other anions. Although the treatment used is very dependent on circumstances, free boric acid is almost unionized and most interfering anions such as fluoride and nitrate can be removed by absorption onto a boron selective resin (Amberlite IRA 743 is suitable), the boric acid being eluted off the column with 10% sulphuric acid, which also regenerates the column. Sequential elution is sometimes possible using conventional anion exchange resins and a procedure is included in Part C (steps 7.1 and 7.2) which can be adapted to other methods. The analyst is therefore advised to determine whether for analytical problem in hand fluoroborate will for practical purposes be hydrolysed and be determined as borate, or whether separation and determination by some other means is advisable. See also Refs 4 and 5. Perborate, which is present in washing powders, decomposes readily to borate.

A9 References

(1) Cheeseman RV and Wilson AL, *Water Research Centre Technical Report TR66*. Water Research Centre, Medmenham 1978.

(2) Waggott A, *Water Research*, **3**, 749–765, 1969. Pergamon Press.

(3) Nies NP, *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Edn, Vol 3, 608–652. J Wiley and Sons. Chichester.

(4) Strelow FWE, *Anal Chem*, **32**, 1185–8, 1960.

(5) Kraus A and Nelson F, Paper 837, *International Conference on the Peaceful Uses of Atomic Energy*, Vol VIII, Geneva 1955.

Part B Curcumin Method

B1 Performance characteristics of the method

(Sample aliquots as in Section B9)

B1.1	Substance determined	Boron.		
B1.2	Type of sample	All liquid samples except those high in halides, provided pretreatment is adequate, and solutions from the pretreatment given in the appendices.		
B1.3	Basis of method	Reaction with curcumin under anhydrous conditions to form a coloured complex known as rosocyanine whose concentration is measured spectrophotometrically.		
B1.4	Range of application (a)	0 to 5 mg/l (see section B9).		
B1.5	Calibration curve (a)	Linear to 5 µgB in the sample aliquot (see section B8).		
B1.6	Total Standard deviation (a) (c)	Type of sample	Boron concentration (mg/l)	Total Standard Deviation (mg/l)
		Tap water	0.15	0.002 (b)
B1.7	Limit of detection (a)	0.004 mg/l (b)		
B1.8	Sensitivity (a)	5 µgB gives an absorbance of approximately 1.4 units.		
B1.9	Bias (a) (c)	None – apart from interferences.		
B1.10	Interferences (a)	Nitrate; high concentrations of halide (eg sea water), fluoride and fluoroborate (see sections B.3 and A8.1).		
B1.11	Time required for analysis (a)	15 samples per day.		

(a) These data were obtained by Borax Research Ltd.
(b) With approximately fourteen degrees of freedom.
(c) A synthetic unknown sample containing among other things 0.24 mg/l Boron was analysed by 30 laboratories using a method similar to this, with a total standard deviation of 0.05 mg/l and a relative error (bias) of 0% (2).

B2 Principle

B2.1 The method described is based on that of Hayes and Metcalfe[1] and experimental work carried out by Borax Research Ltd.

B2.2 Boric acid reacts quantitatively with curcumin under anhydrous conditions in a sulphuric acid-acetic acid medium to produce the boron-curcumin complex rosocyanine which is coloured red. The rosocyanine is considered to be formed via protonation of the curcumin by acid which then reacts with boric acid to form the complex. Excess curcumin in its protonated form is also coloured red. This is indistinguishable from rosocyanine until the reaction mixture is diluted with alcohol, whereupon the excess protonated curcumin reverts to its normal yellow form dissolving together with rosocyanine to produce an orange to red solution.

B3 Interferences

There is no detailed information concerning the effect of interfering substances on the method. Inorganic salts in general do not interfere since they are precipitated on dilution of the reaction mixture by the alcohol, and subsequently filtered off. The effect of some other substances on the determination of boron by the curcumin method is shown in Table 2. The data were obtained by Borax Research Ltd.

Table 2. Effects of Other Substances on the Method.

Other substance	Amount of other substance added (µg)	Effect in µgB of other substance at boron levels of 5 µg
Nitrate as NO_3*	5	−0.6
	50	−0.4
	500	−3.4
Fluoride as F^-*	5	+0.1
	50	+0.1
	500	−3.9
Fluoroborate as BF_4*	5	−0.1
	50	−0.3
	500	−3.6
Sodium chloride as NaCl	30,000	−0.9

* Added as potassium salts.
95% confidence limits at 5 µg Boron are approximately ±0.1 µg.

B4 Reagents

Analytical reagent grade chemicals are suitable.

B4.1 Water (see section A.3)

B4.2 Calcium hydroxide, saturated solution

Shake an excess of calcium hydroxide with water in a polyethylene bottle, allow to settle and use the clear supernatant liquid.

B4.3 Litmus paper – red

B4.4 0.5% m/V Mannitol solution

Dissolve 0.50±0.005 g of neutral mannitol in water and dilute to 100 ml in a measuring cylinder. Store the solution in a polyethylene bottle; it is stable for at least 1 week.

B4.5 0.125 m/V Curcumin reagent

Dissolve 0.125±0.005 g of curcumin in 100±0.5 ml glacial acetic acid by gently warming. Store the solution in a polyethylene bottle; it is stable for at least 3 months.

B4.6 Sulphuric acid-acetic acid

Add slowly with stirring 50±0.5 ml of sulphuric acid (d_{20} 1.84) to 50±0.5 ml of glacial acetic acid. Cool and store the solution in a polyethylene bottle.

B4.7 Standard boron solution

See Section A4.2.3 Solution C, 1 ml is equivalent to 1.0 µgB.

B4.8 Industrial methylated spirit 74° over proof

B5 Apparatus

B5.1 Silica crucibles 50 mm × 50 mm of 50 ml nominal capacity, or
Silica evaporating basins 110 mm × 50 mm deep nominal capacity 150 ml.

B5.2 Water bath or steam bath

B5.3 Muffle furnace for ignitions up to 550°C

B5.4 A spectrophotometer for use at 550 nm capable of accepting 10 mm cells and capable of measurements up to an optical density of 2.0 is suitable.

B6 Sample collection and preservation

See section A.5.

B7 Analytical Procedure

READ THE HAZARDS SECTION A3.1 BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
	Analysis of samples	
	Pretreatment stage (note a)	
B7.1	Place an aliquot of sample solution (Vml) (note b, c) containing up to 5 μgB into a silica crucible or basin and dilute to 50±1 ml with water.	(a) Start here for determination of boron when it is known that this pretreatment is suitable otherwise use the solution prepared by a procedure given in appendices. (b) See section 9 for suitable volumes. (c) The sample solution is either the original sample or the pretreated solution from appendices.
B7.2	Add a minute piece of red litmus paper, add 5±0.1 ml saturated aqueous calcium hydroxide solution, swirl to mix (note d) add 0.5±0.05 ml mannitol solution and evaporate to dryness on a water bath.	(d) The sample must be alkaline at this stage.
B7.3	Place the crucible in a cold muffle furnace and gradually heat to 550±10°C and maintain at 550±10°C for 15 min±5 min. Remove from the furnace and allow to cool to room temperature.	
	Colorimetric stage	
B7.4	Add 1.5±0.05 ml of curcumin reagent (note e) swirl to mix, and allow to stand for 10±2 min, swirling the contents occasionally.	(e) The reagent should be run down the internal sides of the crucible from the tip of the pipette during the addition. (See A3.1.1.)
B7.5	Add 1.5±0.05 ml sulphuric acid – acetic acid reagent (note e), swirl to mix, and allow to stand at room temperature for 20±5 min.	
B7.6	Transfer the mixture to a clean, dry 50 ml calibrated flask (note f). Dilute the mixture with industrial methylated spirit, stopper the flask and mix the contents.	(f) Use a jet of industrial methylated spirit from a polyethylene 'squeeze type' wash bottle and a small filter funnel to ensure quantitative transfer.
B7.7	Filter through a prewashed hardened ashless filter paper capable of removing particles over about 5 μm (note g).	(g) Samples and standards may alternatively be stood overnight and the clear supernatant measured.
B7.8	Meanwhile set up the spectrophotometer (see section B5.4) according to the manufacturers instructions. Adjust the zero of the instrument with industrial methylated spirits in the reference cell. Measure the absorbance of the filtered solution at 555 nm using 10 mm cells (note h). Recheck the instrument zero. Let the absorbance of the sample be A_s.	(h) Matched cells should be used.

Step	Procedure	Notes
	Blank determination	
B7.9	A blank must be included with each batch of determinations using the same batch of reagents as for samples at the same time as samples. Water (note i) is used in place of the sample and is processed in exactly the same way as the sample. Let the absorbance of the blank be A_b.	(i) The blank may be water if no other pretreatment was required for the sample, or the blank solution from a previous pretreatment described in the appendices.
	Calculation of Results	
B7.10	The absorbance due to boron in the sample is given by $A_p = A_s - A_b$ Determine the mass M (in μgB) of boron in the sample from the value of A_p and the calibration curve (see section B8).	
B7.11	Calculate the boron concentration C in the original sample (in mg B/l). from C = M/V (note j).	(j) A multiplication factor will also be required if the sample was diluted before analysis, or the volume changed during one of the pretreatments described in the Appendix.

B8 Preparation of the calibration curve

The procedure given in this section must be carried out with each batch of samples. Any significant departure from linearity or variation in the 0.00 value indicates the technique is suspect at some stage.

To a series of 50-ml capacity silica crucibles add 0.00, 1.00, 2.00, 3.00, 4.00 and 5.00 ml of standard boron solution C. The crucibles now contain 0.00, 1.0, 2.0, 3.0, 4.0, 5.0 μgB. Subject the solutions to the procedure given in section B7 steps 2 to 9. Plot the results for $(A_s - A_b)$ against μgB. The calibration curve is linear to at least 5 μgB.

B9 Concentration range of the method

Suitable aliquots of sample to be used can be estimated from Table 3.

Table 3.

Expected concentration	Aliquot to be used
(mg B/l)	(ml)
<0.2	25.0
0.2–0.5	10.0
0.5–1	5.0
1–2	2.5
2–5	1.0

When higher concentrations of boron are likely to be encountered, it is recommended that the samples are diluted to an appropriate concentration, the appropriate multiplication factor being used in the calculation.

B10 References

(1) Hayes MR and Metcalfe J, *Analyst*, 1962, **87**, 956–969.
(2) *Standard Methods for the Examination of Water and Waste Water*, 14th edition. 1975, APHA Washington DC.

Part C Azomethine-H Continuous Method

C1 Performance characteristics of the method

C1.1	Substance determined	Boron in solution.
C1.2	Type of sample	Fresh and saline waters, crude and treated industrial sewage effluents.
C1.3	Basis of method	A continuous automatic analyser is used to treat the sample with azomethine-H to form a coloured complex whose concentration is measured absorptiometrically.
C1.4	Range of application (a)	Up to 4.5 mg/l.
C1.5	Calibration curve (a)	Linear to 4.0 mg/l, curving slightly above this. (The gradient at 4.5 mg/l is 98% of that below 4.0 mg/l.)
C1.6	Total standard deviation (a)	See table below
C1.7	Limit of detection (a)	0.04 mg/l.
C1.8	Sensitivity (a)	Dependent on many factors but typically 1 mg/l gives an absorbance of about 0.12.
C1.9	Bias (a)	No significant bias has been observed with a range of samples including sea water, peaty streams, sewage effluent and trade wastes from malting and detergent manufacture. Slight positive bias has been noticed with a petrochemical plant effluent (see C3.3).
C1.10	Interferences (a)	See section C3.
C1.11	Time required for analyses	The total analytical time for 10 and 40 samples is approximately 2 and 4 hours. These times include correction for colour which may not be necessary.

C1.6 Total standard deviation (a)

Type of Sample	Boron concentration (mg/l)	Total standard deviation (mg/l)
Deionized water	0.0	0.016
Standard solution	0.5	0.02
Standard solution	4.0	0.04
River waters (b)	0.1–0.2	0.02
Sewage effluents (b)	0.5–1.0	0.02

(a) These data were obtained by the Forth River Purification Board, Edinburgh laboratory, with 9 degrees of freedom. Almost identical data has recently been obtained from 3 other laboratories (see Section C5).
(b) Numerous samples within the range given.

C2 Principle

The method described is based on that of Shanina *et al*[2], and the automated method of Edwards[1]. Azomethine-H, which is the condensation product of H-acid

8-aminonaphth-l-ol-3,6-disulphonic acid and salicylaldehyde, reacts in aqueous solution with dissolved forms of boron at a pH of about 5. A yellow complex is formed the absorbance of which is measured at 420 nm and is related to the boron concentration by means of a calibration curve. Possible interfering cations are masked by the use of ethylenediaminetetraacetic acid.

C3 Interferences

C3.1 Colour. If coloured waters are analysed, the background colour correction procedure steps C8.5 to C8.7 and C8.10 should be used. 100 Hazen units of colour gives a reading equivalent to 0.16 mg/l Boron.

C3.2 Chromium VI, iron II and III, aluminium, calcium, nitrite, fluoride, carbonate and hydrogen-carbonate can interfere. Table 4 lists the concentrations of these substances at which interference is just detectable and at which (with 95% confidence it reaches a coefficient of variation of 5% in addition to the within batch standard deviation. In other words, when the error for 1 mg/l Boron becomes ± 0.028 mg/l and $\pm$ 0.078 mg/l respectively.

C3.3 The substances listed in Table 5 cause no detectable interference (at 95% confidence) at concentrations at least up to that listed.

C3.4 Variation in sample pH of between the values of pH2 and pH13 did not produce interference. A 10% positive error was found with a petrochemical plant effluent.

Table 4. Summary of known interferences.

Interfering species	Concentration at which interference is just detectable for a 1 mg/1B sample mg/l	Concentration at which interference reaches $\pm$5% for a 1 mg/1B sample mg/l
Chromium (VI)	5	10
Iron (II)	200	300
Iron (III)	10	25
Aluminium	ca100	100
Calcium	500	3000
Nitrite	20 (as N)	50 (as N)
Hydrogen Carbonate	200	1000
Carbonate	500	1000
Fluoride	500	

All data with at least 3 degrees of freedom.

Table 5. Substances for which no interference was detected.

Substance tested	Highest concentration tested (mg/l)	Substance tested	Highest concentration tested (mg/l)
Sodium	10,000	Silica	1,000 (as SiO_2)
Potassium	10,000	Nitrate	1,000 (as N)
Magnesium	10,000	Orthophosphate	1,000 (as P)
Chromium III	1,000	Sulphide	100
Manganese	1,000	Sulphate	10,000
Nickel	1,000	Chloride	10,000
Copper II	1,000		
Zinc	1,000	Ammonia	1,000 (as N)
Cadmium	100	Anionic detergent	1,000
Lead II	100	Nonionic detergent	1,000

All data with at least 3 degrees of freedom.

C4 Reagents

Analytical-reagent grade chemicals are suitable. If not available, use the purest reagent grade material.

C4.1 Water

See section A3.

C4.2 10% m/V. Potassium hydroxide solution

Dissolve 10±0.1 g of potassium hydroxide in water and dilute to 100 ml in a measuring cylinder. Store in a polyethylene bottle.

C4.3 Polyoxyethylene lauryl ether

Dissolve 1±0.5 g Polyoxyethylene lauryl ether (Brij 35 or similar) in water and dilute to 100 ml in a measuring cylinder. Store in a glass bottle.

C4.4 Buffer solution

Dilute 500±2 ml of glacial acetic acid to 750±2 ml with water. Add 10.0±0.1 g of disodium ethylenediaminetetraacetate dihydrate and 300±1 g ammonium acetate and warm to dissolve. Adjust to pH 5.2±0.1 with acetic acid or ammonia solution (d_{20} 0.88) if necessary. Add 1.0±0.2 ml of Brij concentrate. Store in a polyethylene bottle.

C4.5 Azomethine-H reagent

Dissolve 900±10 mg of azomethine-H (see D4.2) and 2.0±0.1 g of ascorbic acid in 70±1 ml of water while heating gently (not exceeding 70°C), and dilute with water to 100±0.5 ml. Add 100±0.5 ml of buffer solution and mix thoroughly. Store in a glass bottle. The reagent is stable for 2 days only.

C4.6 Background correction reagent

Mix 100±1 ml of buffer solution with 100±1 ml water. Store in a polyethylene bottle.

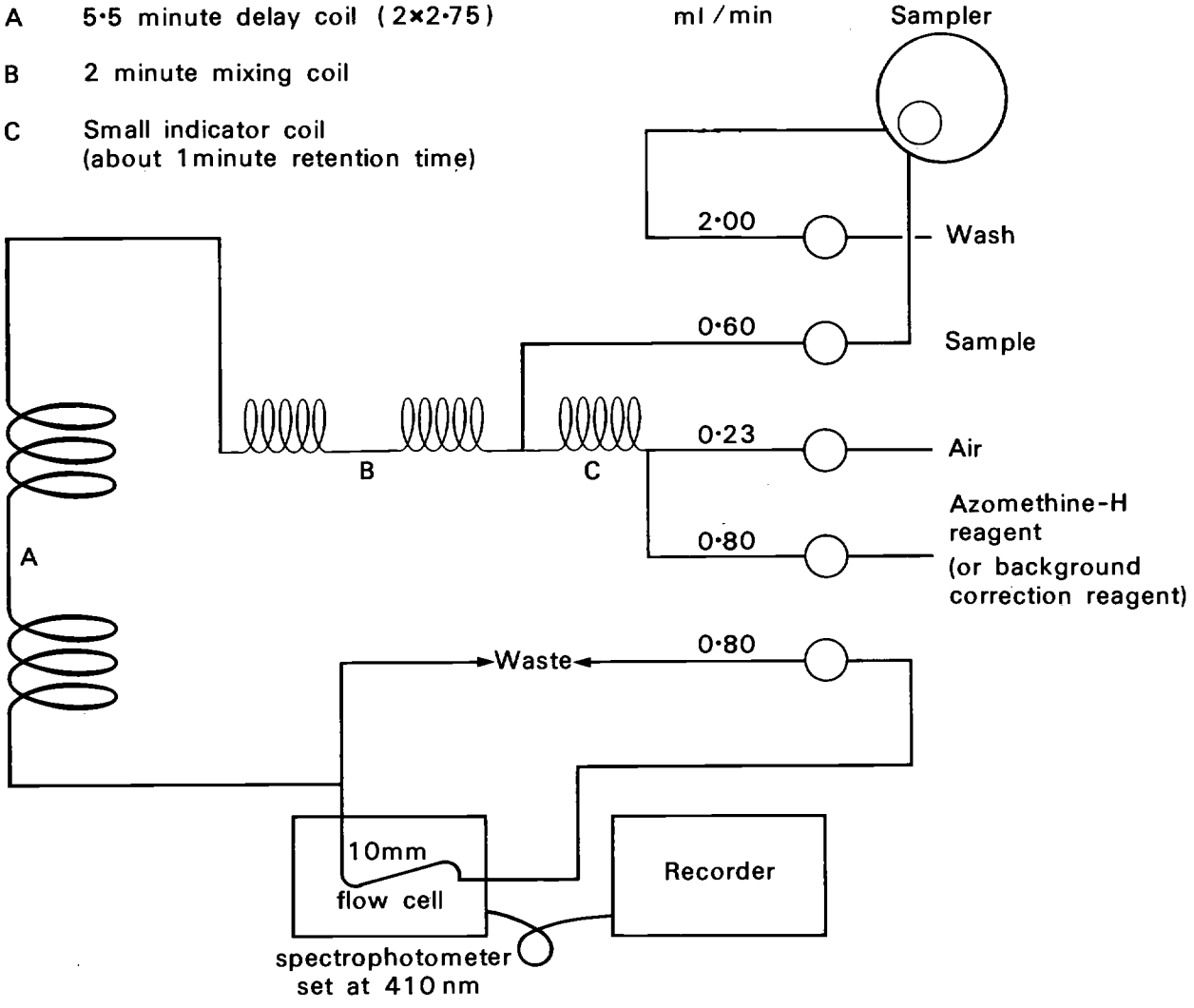

Fig.1 A TYPICAL MANIFOLD ARRANGEMENT

C4.7 4 mg/l Standard boron solution. 1 ml is equivalent to 4μgB.

Dilute 4.00±0.01 ml of standard boron solution A (Section A4.2.1) with water to 1 litre in a calibrated flask. Store in a polyethylene bottle. Prepare freshly as required. Standard solutions containing 1, 2 and 3 mg/l boron may also be required, these may be prepared by diluting 25, 50 and 75 ml respectively of this 4 mg/l standard with water to 100 ml. Other concentrations can be obtained in similar manner.

C5 Apparatus

The apparatus consists basically of a sampler (with a sample cam of 30/hr with a 2:1 sample to wash ratio), proportioning pump, a manifold or analytical cartridge, colorimeter with a 10-mm tubular flow cell (410 nm filters), and a recorder. Follow manufacturers instructions if available. Fig 1 shows the system used for obtaining the test data. A constant temperature heating bath (baths at 37°C and 40°C have been evaluated) improves the performance data by about 10%. The debubbler before the measuring cell is not shown in the figure. See also the essay review on Air Segmented Continuous Flow Analysis.

C6 Sample collection and preservation

Filter samples immediately after collection through a rapid filtering glass fibre filter capable of retaining particles of about 1 μm size. Store the filtered samples in completely filled polyethylene bottles at about 4°C until required for analysis. See also section A5.

C7 Sample pretreatment

No pretreatment is required for the analysis of raw waters (fresh and saline) or for crude or treated sewage and most industrial effluents.

C8 Analytical Procedure

Step	Procedure	Notes
	Analysis of samples	
C8.1	Connect the system as shown in Fig 1 (note a). Switch on the colorimeter and recorder and allow to warm up.	(a) Follow the manufacturers general operating instructions (see also ref 1 and Section C10).
C8.2	With the reagent lines in the appropriate reagent solutions (note b) and the sampler probe in the sampler wash water, switch on the pump and pump for 15 min.	(b) The reagent line is placed in the azomethine-H reagent solution for this stage (the background correction reagent is not used).
C8.3	Meanwhile load the sample turntable with standard solutions, blanks and samples (notes c and d) and make preliminary adjustments to the colorimeter (note e).	(c) The following order has been found to be satisfactory Cup No — Contains 1–3 — 4 mg/lB standard 4–5 — Water 6 — 1 mg/lB standard 7 — 2 mg/lB standard 8 — 4 mg/lB standard 9–10 — Water 11–21 — Samples 22–23 — Water The sequence 8–23 can be repeated until all the samples have been positioned. End with a repeat of 8–10. (d) If the system used does not produce a linear response over the concentration range used, include extra standard solutions to obtain the curve. (e) A suitable setting will give 80% full scale deflection for a 4 mg/lB standard. It will normally be known from experience but on the first occasion a preliminary run to step 8.4 will be necessary.

Step	Procedure	Notes
C8.4	Switch on the recorder drive and adjust the colorimeter to a stable base line. Start the sampler and when the first 4 ppm standard peak appears adjust scale expansion to give a peak to correspond to 80% full scale deflection. Allow sampling and analysis to proceed until the peaks corresponding to all the samples have appeared. Switch off the recorder drive.	
	Compensation for sample colour (note f)	(f) Steps C8.5 to C8.7 may be omitted if the analyst, due to his experience judges it to be unnecessary.
C8.5	Transfer the reagent line (note g) to water for a few seconds and then place it in the background correction reagent and pump for 15 min.	(g) The reagent line is washed and placed in the background correction reagent for this stage (the azomethine-H reagent solution is not used).
C8.6	Meanwhile load the sample positions on the turntable with samples requiring colour correction (see note c and h).	(h) If the samples are almost colourless or all similar in colour include at intervals a short series such as the following: two water samples, a standard with added azomethine-H, two water samples, two different standards with added azomethine-H and two water samples. This series will provide a read out scale for location of other samples.
C8.7	Switch on the recorder drive and adjust the colorimeter to a stable base line, but do not adjust the scale expansion. Allow sampling and re-analysis to proceed until the peaks corresponding to all samples have appeared. Switch off the recorder drive.	
	Shut down procedure	
C8.8	Transfer all reagent lines to water and pump for at least 15 min.	
	Stop the pump and turn off all the system (note a).	
	Calculation of Results	
C8.9	Plot a calibration curve of recorder response for the standard solutions against mg/lB (note i and j).	(i) Air blips may be observed at the beginning and end of each peak, these should be ignored and measurement made using the flat central plateau of each peak. Appearance of such blips is attributed to aging reagents. If such blips are large enough to cause problems prepare fresh reagents.
	Using the calibration curve convert the recorder response obtained at step 4 for each sample to boron concentration C_G in mg/lB (note i and k).	
	Using the same calibration curve convert the recorder response obtained at step 7 for each sample to apparent boron concentration C_A in mg/l boron.	
		(j) Provided the response is linear up to 4.0 mg/lB, the preparation of a calibration curve may be omitted if the analyst, due to his experience judges it to be unnecessary.
		(k) Alternatively a factor may be used if the analyst is satisfied that the system is stable and linear.
C8.10	Correction needed for background colour Calculate the actual boron concentration C (in mg/l) from $C_B = C_G - C_A$ (note l).	(l) A multiplication factor may be required if the samples were diluted prior to analysis.

Step	Procedure	Notes
C8.11	When background colour correction is not necessary Calculate the actual boron concentration C_B (in mg/l) from $C_B = C_G$ (note l).	

C9 Concentration range for the method

The method is employed to determine boron within the range 0–4 mg/l B. On many instruments, the response is linear to 4 mg/l and almost linear to 5 mg/l. The method may, however, be used over the extended range of 0–10 mg/l, but this will involve the construction of a calibration curve to allow for non-linearity at the higher concentrations; 80% of linear response being observed at 10 mg/l. It is recommended that samples containing greater than 4 mg/l, be diluted to below 4 mg/l, the appropriate multiplication factor being used in the calculation.

C9.1 Preparation of a calibration curve and calibration standards for higher concentrations

C9.1.1 Preparation of standards from 0–10 mg/lB

Carry out the procedure given in Section C4.7 but change the volume of standard boron solution A (Section A4.2.1). Measure out as many ml of solution A4.2.1 as mg/lB required in the standard and make up to the 1 litre mark with water.

C9.1.2 Preparation of Calibration Curve

Proceed as in Section C8 as far as the end of the first paragraph of step C8.9; but load the sample turntable cups with a progressive series followed by a random arrangement of standard solutions of from 0–10 mg/lB content instead of the samples indicated in step C8.3 note c.

C10 Sources of error

The analytical method can be applied to a wide range of samples and the attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. The following sub-sections describe the main sources of error and how they can be minimized. Each analyst must decide which precautions are appropriate to his particular requirements. If during an analysis, a standard sample is not within three standard deviations of the expected result, investigate the cause. If the standard concentration itself is not at fault, discard the whole series and repeat the analyses once the fault has been located.

C10.1 Contamination

The problems of contamination discussed in Section A are generally applicable to this method.

C10.2 Correction for Colour Samples

As described previously, colour is a recognised source of error which is adequately corrected for by the procedure described. In general, however, if the colour of the sample is less than 100 Hazen units for each 1 mg/l of boron present then no background correction stage will be required.

C10.3 Air blips

'Blips' may occur at the beginning and end of a peak due to changes in reagent concentration in sections containing sampler-introduced air. These can usually be ignored but if a very high 'standard calibration' setting has been required then blips will interfere with the ability to accurately measure the peak height. If such interference does occur, then it is almost certainly because the azomethine-H concentration in the reagent has fallen too low, due to age, and fresh reagent should be prepared and the samples re-run.

C10.4 Interfering substances

See Section C3.

C11 References

(1) Edwards RA, *Analyst*, 1980, **105**, pp. 139–146.
(2) Shanina TM, Cel'man NE, Mikhailovskaya VS, *J Anal Chem USSR* (Translated Edition), 1967, **22**, pp. 663.
(3) *Air Segmented Continuous Flow Analysis*, 1979. HMSO London.

Part D Azomethine-H Method

D1 Performance characteristics of the method

(Sample aliquots as in Section D9).

D1.1	Substance determined	Boron in solution.		
D1.2	Type of sample	Raw, potable and saline waters, sewage effluents and solutions from the pretreatment given in the appendices.		
D1.3	Basis of method	Reaction with azomethine-H to form a coloured complex whose concentration is measured spectrophotometrically.		
D1.4	Range of application (a)	Up to 10 mg/l (This range may be extended by dilution).		
D1.5	Calibration curve (a)	Linear to at least 10 µg Boron.		
D1.6	Total standard deviation (a)	Type of Sample	Boron concentration (mg/l)	Total Standard deviation (mg/l)
		Standard solution (b)	0.00	0.0085
		,,	0.20	0.017
		,,	1.0	0.032
D1.7	Limit of detection (a)	0.04 mg/l.		
D1.8	Sensitivity (a)	10.0 µg boron gives an absorbance of approximately 0.30 units.		
D1.9	Typical blank values (a)	0.20–0.24 absorbance units.		
D1.10	Bias (a)	None known apart from interference effects.		
D1.11	Interferences (a)	No significant interferences have been detected in potable waters (see section D.3).		
D1.12	Time required for analysis (a)	For 10 samples:- operator time 30 mins. Total analytical time 60 mins.		

(a) These data were obtained by Yorkshire Water Authority, South Eastern Division with at least ten degrees of freedom.
(b) Distilled water spiked with the stated boron concentration, as boric acid.

D2 Principle

The method described is based on that of Shanina[1] modified by later workers[2-4]. Azomethine-H which is the condensation product of H-acid (8-aminonaphth-l-ol-3,6-disulphonic acid) and salicylaldehyde reacts in aqueous solution with dissolved forms of boron at a pH of about 5. A yellow complex is formed the absorbance of which is measured spectrophotometrically at 420 nm and is related to the boron concentration by means of a calibration curve. Possible interfering cations are masked by the use of ethylenediaminetetraacetic acid.

D3 Interferences

There is little detailed information concerning the effect of interfering substances on the method. Generally, no important interference problems are expected with unpolluted saline and fresh waters; but the effect of interferences should be considered particularly in polluted samples. Information that may be relevant is given in the following sections.

D3.1 No significant interference was detected in potable water samples containing up to at least the following concentrations:

Nitrate	20 mg/l (N)
Aluminium	10 mg/l (Al)
Copper	10 mg/l (Cu)
Ferric Iron	10 mg/l (Fe)
Manganese	10 mg/l (Mn)
Zinc	10 mg/l (Zn)

Data obtained by Yorkshire Water Authority, South Eastern Division.

D3.2 Beryllium interferes by forming a similarly coloured compound with azomethine-H. 1 mg/l beryllium is equivalent to 0.06 mg/l boron.

D3.3 The effect of some other substances on the determination of boron by this azomethine-H method is shown in Table 6. The data were obtained by Borax Research Ltd.

D3.4 Operating temperatures above 20°C may cause fading of the coloured complex, even whilst samples are being read. No such problems have been encountered at ambient temperatures below 20°C. This information was obtained by Borax Research Ltd.

Table 6. Effect of Other Substances on the Method.

Other substance	Amount of other substance added (mg)	Resultant Total Boron content µg	Effect in µgB of the other substance at boron levels of 5 µg
Nitrate*	5		+0.3
	50		+0.3
	500		+0.3
	5000		+0.3
Fluoride*	5		+0.3
	50		+0.3
	500		+0.3
Nitrate+fluoride*	5000+5000		+0.3
Fluoroborate as (BF_4)*	5	5.06	+0.3**
	50	11.2	−0.8**
	500	67	−33.0**
Sodium chloride as NaCl	30,000		+0.3

* Added as potassium salts.

** These figures will vary with conditions and time delay between solution preparation and measurement and are only given as a guide.

95% confidence limits at 5 µg Boron are approximately ±0.3 µg.

D3.4 The effect of some other substances on the determination of boron by an automatic azomethine-H method is shown in Part C Tables 4 and 5. The effects are expected to be similar for this manual method.

D3.5 Fluoride may interfere when present under the right conditions and in sufficient amounts relative to boron to form considerable fluoroborate ion. See Section A8.1. The boric acid (H_3BO_3) content of a mixture can be separated from fluoroborates, see Section A8.1, and determined by this method. An alternative procedure must be used for the determination of the fluoroborates, see the essay review on the use of Ion Chromatography in Water Analysis also published in this series. There is evidence that some types

of highly coloured organic matter may interfere in a complex manner. Analysts should check this, and if necessary use an appropriate pretreatment procedure to remove this interference.

D4 Reagents

Analytical reagent grade chemicals are suitable. If not available, use the purest reagent grade material.

D4.1 Water see section A3.

D4.2 Azomethine-H Preparation

Dissolve 18±0.1 g of H-acid (8-aminonaphth-l-ol-3,6-disulphonic acid monosodium salt) in 1 litre of water with gentle heating, neutralize to pH 7±0.5 with potassium hydroxide solution and filter if necessary. Add hydrochloric acid dropwise to give a pH value of 1.5±0.1. While still warm, add 20 ml salicylaldehyde and shake vigorously for one hour while heating gently all the time. Do not exceed 40°C. It is important not to exceed this time or temperature otherwise salicylaldehyde will be lost by evaporation. Cool and allow the azomethine-H to settle overnight (preferably for 16 hours). Centrifuge and discard the supernatant liquid; slurry the residue with ethanol and filter through a rapid filtering glass-fibre filter-paper capable of retaining particles of about 1 μm diameter. Dry at 105°C for three hours and store in a desiccator until ethanol free. The resulting produce is bright orange and stable if kept in a desiccator or tightly capped bottle. The yield of azomethine-H should be approximately 18 g.

D4.3 Azomethine-H reagent solution

Dissolve with warming 1.0±0.1 g azomethine-H and 2.0±0.1 g ascorbic acid in about 70 ml water. Transfer to 100-ml calibrated flask, cool and dilute to the mark with water. Allow the solution to stand for 90 minutes before using. Stored in a glass bottle, the solution is stable for 1–2 days but when solid matter begins to separate the solution must be discarded.

D4.3.1 Alternatively, the directly prepared solution which follows may be used; but, as the final solution is not exactly identical with that above, comparison tests should be made. The same reagent solution should be used for both sample and standard analyses.
Add 2.0±0.05 g of H-acid to 200±5 ml of cold water and add 1.2±0.05 ml of salicylaldehyde and stir until a clear bright yellow solution is obtained (this takes about 30 minutes at room temperature). Add 2.5±0.05 g of ascorbic acid and stir until dissolved. Filter through an ashless hardened rapid filtering filter paper and make up to 500±10 ml with water.

D4.4 Buffer solution

Dissolve 3.0±0.1 g of disodium ethylenediaminetetraacetate in 150±1 ml water. Add 125±1 ml of glacial acetic acid and dissolve 250±1 g of ammonium acetate in the resulting mixture by stirring and gentle heating. Store in a glass or plastic bottle.

An alternative buffer solution which has been used when large amounts of heavy metals are present is 12.5±0.05 g tetra sodium ethylenediaminetetraacetate, 5.0±0.05 g disodium nitrilotriacetate and 250±1 g ammonium acetate dissolved in 150±1 ml of water and the pH adjusted to 6.3 with glacial acetic acid. The test data given in Section D1.6 do not apply, but similar test data have been obtained. (Make only sufficient solution for the day's need).

D4.5 Standard boron solution

See Section A4.2.3 Solution C, 1 ml is equivalent to 1.0 μgB.

D5 Apparatus

D5.1 25 ml polypropylene graduated flasks

D5.2 A spectrophotometer for use at 420 nm capable of accepting 10-mm cells is suitable.

D6 Sample collection and preservation

See Section A5.

Step	Procedure	Notes
	Analysis of sample (note a)	
D7.1	Transfer a suitable volume V (not exceeding 15 ml) of the sample to a 25-ml polypropylene calibrated flask (note b). If necessary, add sufficient water to produce a volume of 15±0.5 ml.	(a) The sample may be the original or a pretreated sample. If the sample pH is outside the range 5.5–8.5 adjust to pH 7. (b) See Section D9 for suitable sample volume.
D7.2	Add 5.0±0.05 ml azomethine-H reagent solution. Mix by swirling.	
D7.3	Add 4.0±0.1 ml buffer solution. Mix by swirling.	
D7.4	Make up to volume with water. Mix and stand the flask in a water bath at not warmer than 20°C for 20±2 mins (note c).	(c) Fading of the colour may occur at above 20°C.
D7.5	Meanwhile set up the spectrophotometer (see Section D5.2) according to the manufacturers instructions. Adjust the zero of the instrument with water in the reference cell. Measure the absorbance of the solution at 420 nm using 10 mm cells against water in the reference cell (note d). Recheck the instrument zero. Let the absorbance of the sample be A_s.	(d) Matched cells should be used.
	Blank determination	
D7.6	A blank must be included with each batch of determinations using the same batch of reagents as for samples. Carry out steps D7.2 to D7.5 using 15 ml water in place of the sample (note e). Let the absorbance of the blank be A_b.	(e) The blank may be water if no other pretreatment was required for the sample or the blank solution from a previous pretreatment described in the appendices.
	Compensation for sample colour and turbidity (note f)	
D7.7	Treat a separate portion of V ml of the sample exactly the same way as described in step 7.1. Omit step 7.2 and continue exactly as described in steps 7.3 to 7.5. Let the absorbance obtained be A_c.	(f) This step may be omitted if the analyst, due to his experience, judges it to be unnecessary.
	Calculation of Results	
D7.8	The absorbance due to boron in the sample is given by $A_r = A_s - A_b$ or when a correction for colour/ turbidity is made. $A_r = A_s - A_b - A_c$. Determine the mass M (in μgB) of boron in the sample, from the value of A_r and the calibration curve (see Section D8).	
D7.9	Calculate the boron concentration C in the original sample (in mg B/l) from $C = M/V$ (note g).	(g) A multiplication factor may be required if the sample was diluted before analysis or arising out of manipulations during pretreatment stages.

D8 Preparation of the calibration curve

As both solid azomethine-H and its solutions are of variable stability depending on the temperatures to which they have been exposed, and this affects the intensity of the colour formed with boron, the calibration curve should be checked each day the method is used. Samples and standards should be analysed together. A new curve should be drawn if reagent D4.3.1 is used instead of reagent D4.3, and vice versa.

To a series of 25-ml polypropylene calibrated flasks, add 0.00, 2.00, 4.00, 6.00, 8.00, 10.00 ml respectively of standard boron solution. The flasks now contain 0.0, 2.0, 4.0, 6.0, 8.0, 10.0 μgB respectively. Subject the solutions to the procedure given in Section D7 steps 7.1 to 7.6. Plot the results for $A_s - A_b$) against μgB. The calibration curve is linear and passes through the origin.

D9 Concentration range of the method

Suitable sample aliquot volumes (step D7.1) are as follows:

Expected Concentration mg/l Boron	Aliquot taken ml
<0.5	15
0.5–1.0	10
1.0–2.0	5
2–5	2
5–10	1

When higher concentrations of boron are expected, it is recommended that large aliquots of the samples be diluted quantitatively to bring the diluted sample into one of the above ranges. The results obtained must then be multiplied by the appropriate dilution factor.

D10 References

(1) Shanina TM, Cel'man NE, Mikhailovskaya VS. *J Anal Chem USSR* (Translated Edition), 1967, **22,** pp. 663.

(2) John MK et al, *Analytical letters,* 1975, **8,** 559–568.

(3) Schucker GD et al, *Analytical Chemica Acta,* 1975, **75,** 95–100.

(4) Basson WD et alia, *Analyst,* 1969, **94,** 1135–1141.

Part E Mannitol—Titration Method

E1 Performance characteristics of the method

(Sample aliquots as detailed in Step E7.1 note a)

E1.1	Substance determined	Boron in solution.	
E1.2	Type of sample	Raw water, sewage and trade effluents, and solutions from the pretreatment given in the appendices.	
E1.3	Basis of method	Boric acid in the presence of mannitol is titrated with a standard alkali solution.	
E1.4	Range of application (a)	Up to 1000 mg/l Boron.	
E1.5	Total standard deviation (b)	Boron concentration (mg/l)	Total standard deviation (mg/l)
	Type of sample		
	Trade effluent	0.5	0.3
	Trade effluent plus boron	20	0.3
	Trade effluent plus boron	200	1.0
E1.6	Limit of detection (a)	0.5 mg/l.	
E1.7	Sensitivity (a)	1.00 ml sodium hydroxide 0.05M is equivalent to 540.6 μgB.	
E1.8	Bias (a)	None apart from interference effects.	
E1.9	Interferences	See Section E3.	
E1.10	Time required for analysis (a)	Operator time, one sample per column per hour. Total time 6 samples per ion exchange column per day.	

(a) These data were obtained at English China Clays, Central Laboratories, and Borax Research Ltd with at least ten degrees of freedom.

(b) These data were obtained at English China Clays, Central Laboratories with at least ten degrees of freedom for each value. Similar data were obtained by Borax Research Ltd.

E2 Principle

Following treatment with an ion exchange resin to remove possible interfering cations, the solution is neutralized to pH 7.0. Mannitol is added to promote ionization of boric acid followed by titration with a standard alkali solution to pH 7.0.

The mannitol-boric acid complex titrates as a monoacid provided the solution is saturated with mannitol[1,2].

E3 Interferences

Substances which could be expected to precipitate as hydroxides during the titration must be removed by ion exchange. Titration of small amounts (about 20 mg/l) of Boron in the presence of large amounts (about 200 mg/l) of Fluoride gives a negative bias (about 5%). Titration of boric acid in the presence of large amounts of phosphate reduces the precision, with a tendency to positive bias.

E4 Reagents

Analytical reagent grade chemicals are suitable.

E4.1 Water must be carbon dioxide free (see also Section A3).

E4.2 2M Hydrochloric acid

Add 170±5 ml of hydrochloric acid (d_{20} 1.18) to approximately 500 ml of water in a 1 litre cylinder, mix, allow to cool and dilute with water to 1 litre.

E4.3 2M Sodium hydroxide

Dissolve 80±0.2 g of sodium hydroxide pellets in 500 ml of water, cool and dilute with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

E4.4 Mannitol (neutral).

E4.5 Boric acid recrystallized (see Section A4.1).

E4.6 0.05M Sodium hydroxide (carbonate free).

Transfer 10.0±0.1 g of sodium hydroxide pellets to a 50-ml polypropylene test tube and dissolve in 10.0±0.1 ml of water. Stopper and allow to stand overnight. Withdraw 3.0 ml of the supernatant liquid and dilute with carbon dioxide free water to 1 litre in a measuring cylinder. Store in a polyethylene bottle. Protect from absorption of carbon dioxide from the air. This solution should be standardized against recrystallized boric acid before use.

Weigh out approximately 0.1 g of recrystallized boric acid, weighed to the nearest 0.0001 g and record the weight M(g). Transfer this boric acid to a 250-ml polyethylene beaker, add 100±5 mls of carbon dioxide free water then place on a magnetic stirrer to dissolve the crystals. With the aid of a pH meter titrate with sodium hydroxide 0.05M to pH 7.0±0.01. Add 15±0.1 g of mannitol then titrate with sodium hydroxide 0.05M back to the original pH of 7.0±0.01. Record the volume V(ml) used during this final step.

E4.7 Strongly acidic cation exchange resin.

E5 Apparatus

E5.1 Polyethylene beakers, 250-ml.

E5.2 Magnetic stirrer.

E5.3 pH meter with glass electrode and calomel reference electrode.

E5.4 A column made from polyethylene tube 500 mm length and 12 mm diameter containing a resin bed 300 mm long of a strongly acidic cation exchange resin in the hydrogen form.

E6 Sample collection and preservation

See Section A5.

E7 Analytical procedure

Step	Procedure	Notes
	Analysis of sample	
E7.1	Transfer a suitable volume of the sample (Aml) (see note a) to a prepared column containing a suitable cation exchange resin (for anions see note b). The resins chosen will be dependent on the ions to be removed. (See note b, and trade catalogues.) Allow to pass through the resin bed at the rate of 3 to 4 ml/minute into a 250-ml polyethylene beaker.	(a) For samples containing up to 100 mg/l Boron use 100 ml. For samples containing 100–1000 mg/l Boron use 25 ml.

Step	Procedure	Notes
E7.2	Rinse the column with 2×25 ml of water, combine the rinsings with the eluate in a beaker of suitable size containing a magnetic stirrer bar.	(b) If there is doubt as to the suitability of the resin, test with a standard borate solution which should not be absorbed, then test with solutions of those ions that need to be removed which should be absorbed. Anions can be removed by an analagous procedure (see Section A8.1). A similar test of resin suitability should be made.
E7.3	Using a pH meter, adjust the solution to pH 3.0 ± 0.1 by addition of either hydrochloric acid (2M) or sodium hydroxide solution (2M or 0.05M). Use a magnetic stirrer to assist mixing (note c).	(c) Steps E7.3 and E7.4 may be omitted if large amounts of carbon dioxide are not present in in the test solution.
E7.4	Warm the solution to 30–40°C, then displace carbon dioxide, either (i) By placing under a moderate vacuum, or (ii) By passing carbon dioxide free nitrogen or air through the solution.	
E7.5	Add 0.05M sodium hydroxide solution by dropwise addition to bring the sample pH to 7.0 ± 0.01.	
E7.6	Add 15 ± 0.1 g mannitol then titrate with 0.05M sodium hydroxide back to pH 7.0 ± 0.01. Let the volume of sodium hydroxide (0.05M) used in this step be V_s ml.	
	Blank determination	
E7.7	A blank must be run with each batch of determinations using the same batch of reagents as for the samples. Water (note d) is used in place of the sample and is processed in exactly the same way as the sample. Let the titration obtained in the final step of the blank determination be V_b ml.	(d) The blank water may be distilled water if no other pretreatment was required for the sample or the blank solution from a previous pretreatment described in the appendices.
	Calculation	
E7.8	(See also B7.11 note j.) Calculate boron content of sample as follows: $$\text{Boron content (mg/l)} = \frac{(V_s - V_b)\times M\times 174.97\times 1000}{A\times V}$$ where V_s = volume of sample titration in ml (E7.6). V_b = volume of blank titration in ml (E7.7). V = ml of 0.05M sodium hydroxide solution (E4.6). M = g of boric acid (E4.6). A = volume of sample aliquot in ml (E7.1).	

E8 References

(1) Kremer H, *Anal Chem.* 1955, **27,** 144.

(2) Jeffrey PG, *Chemical Methods of Rock Analysis.* Pergamon, 1970.

Appendix I

Sample Pretreatments—

Introduction

I1 Many samples (eg raw and potable waters, and some effluents), containing little organic matter and interfering species require no pretreatment other than those given in the respective methods.

I2 Some samples (eg sludge), high in organic matter or coloured will require pretreatment to destroy the organic matter and bring the suspended matter into a form suitable for measurement. A suitable pretreatment is described in Appendix III.

I3 The pretreatment discussed in 2 and described in Appendix III destroys organic matter and ensures that most, if not all, of any boron compounds are brought into solution. If only those in solution or those that are extractable are of interest the sample should be submitted to one of the preliminary treatments described in Appendix II before any pretreatment is made.

I4 Although the pretreatment discussed in 2 and described in Appendix III will bring most boron compounds into solution some resistant borosilicates and similar minerals may not be included. If it is necessary to include these, this may be achieved by carrying out the pretreatment described in Appendix IV. This pretreatment is particularly suitable for soils and sediments.

I5 When the boron is in solution it is necessary to consider possible interferences.

If high levels of nitrate are expected to cause interference with the chosen method (B or E), the sample can be freed of nitrate, by including the optional step 3.3 in the pretreatment described in Appendix III.

If high levels of cations are expected to cause interference with the chosen method, the the sample can be freed of cations by including the ion exchange steps E7.1 and E7.2 described in method E.

Appendix II

Preparation of an extract for the determination of water-soluble boron in soils, sediments and sewage sludges

II.1 Principle

The portion of the total boron content in a dried sample[1] which is available to plants can be assessed by extraction with boiling water[2,4,5]. Soluble or extractable boron in the sample is present both as water soluble and adsorbed borate, which can subsequently be determined in the extract by a suitable method.

II.2 Sample preparation

Dry soil and sediment samples at 30°C in a gentle current of air.

Sludge and other similar materials are liable to lose boron on drying so preferably wet sludge is used and, if required, the dry weight is obtained on a separate sample.

To determine the dry weight, measure out an appropriate known amount of wet sludge on to a preweighed tray, spreading it to form a shallow layer. This sludge is then dried to constant weight at a temperature of not greater than 110°C. As appropriate, weight or volume may be used for the initial measurement of wet sludge onto the tray. The boron results are calculated accordingly. (Methods of reporting the boron content of sludge vary. Weight of boron per weight of dry or of wet sludge or per volume of wet sludge are all used.)

This procedure which is empirical is used for the control of sludge application to agricultural land.

If instead of the above empirical value a true total extractable boron is determined (see Section 4), a note should accompany the result to indicate that it is not the empirical agricultural figure but a total extractable value.

II.3 Analytical procedure

Step	Procedure	Notes
II3.1	Either transfer an appropriate weight of solid sample (note a) to a 250-ml flask and add 80±1 ml water. Or transfer 80±1 ml liquid sludge to a 250-ml flask.	(a) Use 40±0.1 g soil or sediment or 2.0±0.1 g dried sludge.
II3.2	Attach a 14-cm cold finger condenser and heat the flask. Allow the water to boil for an appropriate period (note b) and immediately filter through a prewashed filter paper capable of retaining 5 µm particles, under vacuum if necessary. Retain the filtered extract for the determination of boron. The filtration should be as rapid as possible and should be terminated when the volume of filtrate is sufficient for subsequent analysis (note c).	(b) 5 minutes (±15 seconds) for soil or sediment. 10 minutes (±30 seconds) for liquid or dried sludges. The reflux time is critical and the commencement of boiling can be judged from the time when steam begins to condense on the condenser. (c) Do not allow the sample to stand and cool prior to or during filtration as this will lead to re-adsorption of boron by the solids.

II.4 Determination of Total Extractable Boron

Occasionally a true total extractable boron value is required. Carry out the above experimental procedure, but filter as completely as possible, using vacuum to speed filtration. Return the solid to the extraction flask as completely as possible and repeat the extraction using a fresh 80±1 ml of water. Repeat this procedure as often as necessary, analysing each extract until the additional boron extracted is too small to be significant. Sum the successive boron extraction values to arrive at the total extractable boron.

Appendix III

Pretreatment for boron determinations in the presence of organic matter and nitrate

III.1 Reagents

Water (see Part A Section 3).

III1.1 Saturated calcium hydroxide solution

Shake an excess of calcium hydroxide with distilled water in a polythene bottle, allow to settle and use the clear supernatant liquid.

III1.2 Litmus paper—red.

III1.3 Devarda's alloy, ground to pass a 300 BSS mesh sieve.

III1.4 1% Hydrochloric acid.

Dilute 10 ± 1 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

III.2 Apparatus

100 ml Platinum or glazed silica crucibles.
Polyethylene 100 ml beakers, filter funnels and stirring rods.
A temperature controlled muffle furnace preferably with a silica lining.

III.3 Analytical Procedure

Step	Procedure	Notes
III3.1	Transfer 50.0 ± 0.5 ml of liquid sample or 1.00 ± 0.001 g of ground, dried solid material to a crucible.	
III3.2	Add a minute piece of red litmus paper, add 5.0 ± 0.1 ml of saturated calcium hydroxide swirl to mix (note a) and evaporate to dryness on a water bath. Ash the residue (note b) overnight in a muffle furnace at 450 ± 10°C.	(a) The sample must be alkaline at this stage. If not add extra saturated calcium hydroxide until the sample is alkaline. (b) Raise the temperature slowly to 450°C while a gentle current of air is being drawn through the furnace.
	Nitrate removal step (note c)	
III3.3	Cool and add 10 ± 1 ml of water and 0.10 ± 0.01 g Devarda's alloy (if nitrate is high more Devarda's alloy may be required). Evaporate to dryness on a water bath.	(c) This step may be omitted if nitrate removal is not required.
III3.4	Cool and add 10.0 ± 0.5 ml of 1% hydrochloric acid, break up the ash with a polyethylene rod, stir gently and filter through a prewashed hardened ashless filter paper retaining particles over about 20 μm in size contained in a polyethylene funnel. Wash the residue with two 5 ± 1 ml portions of water. Combine the filtrate and the washings, in a 50-ml calibrated flask, make up to volume. If required, proceed with ion exchange separation in Steps C7.1 and 2.	
	Blank determination	
III3.5	Duplicate blanks must be run with each set of determinations using the same batches of reagents and types of containers as for samples.	

Appendix IV

Pretreatment for boron determinations in the presence of resistant borosolicates and similar materials

IV.1 Application

This pretreatment is particularly suitable for total boron determinations in many soils and sediments[3].

IV.2 Reagents

IV2.1 Water (see Part A Section 3).

IV2.2 Sodium peroxide (do not use wet reagent).

IV2.3 Approximately 6M Hydrochloric acid

With stirring add 600±10 ml hydrochloric acid (d_{20} 1.18) to about 350 ml of water. Make up to 1 litre in a measuring cylinder with water.

IV.3 Apparatus

IV3.1 An agate pestle and mortar

IV3.2 A BSS 100 mesh sieve

IV3.3 25-ml Platinum or nickel crucibles

IV3.4 A temperature controlled muffle furnace preferably with a silica lining.

IV3.5 100 ml polyethylene beakers with lids.

IV.4 Analytical Procedure

Step	Procedure (note a)	Notes
IV4.1	Transfer 0.500±0.001 g of sample, ground to pass a 100 mesh sieve, to a small agate mortar (notes b and c).	(a) Samples MUST CONTAIN NOT MORE THAN TRACES OF ORGANIC MATTER. Always carry out a test ignition of a very small sample behind a safety screen prior to preparing the analytical sample. If the reaction is at all violent see note b below.
		(b) If it is essential to analyse a sample high in organic matter containing resistant boron compounds and mechanical separation is not practical, make the sample alkaline with calcium hydroxide solution and ignite in air at as low a temperature as possible until the organic matter is burnt off. Then cool the crucible and carry out this procedure.
IV4.2	Weigh 2.0±0.1 g of sodium peroxide then transfer approximately 1.5 g to the mortar, rub sample and peroxide together with pestle to produce an intimate mixture (notes c and d).	(c) If only a small amount of organic matter is present modify the procedure in steps IV4.2 and IV4.3 as follows: Quickly grind the 2 g of sodium peroxide in the mortar, and transfer this also to the crucible. Mix intimately using a metal spatula. Then fuse as detailed at the end of step IV4.3.
		(d) This step must not be delayed to avoid moisture pickup.

Step	Procedure	Notes
IV4.3	Transfer the contents of the mortar to a small crucible. Add the remaining sodium peroxide (step IV4.2) to the mortar, and use it to rub the mortar clean of any residual sample, also transfering this too to the crucible. Cover the crucible and place in a muffle furnace at 480°C ± 10°C for 10 minutes, then remove and allow to cool (notes c and d).	
IV4.4	Place the crucible and lid on its side in a 100-ml polyethylene beaker, add 20 ml of water and cover with a polyethylene lid. When the sinter has dissolved, rinse and remove crucible and lid. Add 6M hydrochloric acid slowly until the extract is acidified (note e). Dilute to 50 ml. Proceed with ion exchange separation if required (note f).	(e) Approximately 9.0 ml of 6M hydrochloric acid is required. (f) The extract should be free from mineral grains and should not require filtering.
	Blank determination	
IV4.5	Duplicate blanks must be run with each set of determinations using the same batches of reagents and types of containers as for samples.	

References

(1) *The Sampling and Initial Preparation of Sewage and Waterworks Sludges, Soils, Sediments and Plant Materials prior to Analysis*, 1977, London HMSO.

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