Oxidised Nitrogen in Waters 1981

Methods for the Examination of Waters and Associated Materials

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

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

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 inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General 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.

T A DICK
Chairman

L R PITTWELL
Secretary

4 December 1980

A. General Information

A1 Introduction to the Methods

A1.1 The term "total oxidized nitrogen" (often abbreviated as TON) is always understood to mean the total concentration, in compatible units, of nitrate and nitrite, since these two ions provide the greatest contribution to TON in most waters.

Other forms of "oxidized nitrogen" — chiefly hydroxylamine — have occasionally been detected in some waters, thus making the definition "total oxidized nitrogen" as defined above not strictly appropriate in such cases. Hydroxylamine is not detected by any of the methods in this booklet except Method B. See a separate method in this series of publications for specific hydroxylamine determination.

In reporting oxidized nitrogen concentrations, whether of nitrate, nitrite or TON, the customary UK practice is to refer to the concentration in terms of the element, N. This practice is used throughout this booklet and thus satisfies the requirement of compatibility mentioned above.

A1.2 Since no one method has performance characteristics making it suitable for application to all types of sample, several methods are recommended in order to give full coverage of the requirement to determine oxidized nitrogen at various stages of the water cycle. They fall into three groups:

A1.2.1 **Methods for total oxidized nitrogen (TON)**
Method B uses reduction with Devarda's alloy of nitrate and nitrite to ammonia for subsequent determination. This long-established method is particularly useful for TON determination on a sample portion already used for the determination of ammonia using distillation. Methods C and D are continuous flow methods, both based on the reduction of nitrate to nitrite for subsequent colorimetric determination. Method C uses a cupric ion/hydrazine solution for reduction, while method D, designed for seawater analysis uses a heterogeneous system with metallic cadmium as the reducing agent.

A1.2.2 **Methods for nitrate**
Method E, using visible spectrophotometry, is applicable to a wide range of samples and has good sensitivity. Method F, using direct UV spectrophotometric measurement of nitrate absorption, is simple and precise, but is restricted, by interference from organic matter, to samples of low organic content or of nitrate concentration sufficiently high to allow dilution to reduce the interference. Method G, using an ion-selective electrode, may suffer from inferior precision and accuracy but with care can be applied to the analysis of raw and potable waters.

Methods B to D can also be used for the determination of nitrate in samples whose nitrite concentration is considered to be negligible in relation to the nitrate concentration or in samples in which the concentration of nitrite has previously been determined, thus allowing its subtraction from the total oxidized nitrogen concentration. This latter approach may result in poorer precision than direct determination of nitrate alone.

Determination of nitrate by use of total oxidized nitrogen methods finds extensive use. For this reason, Table 1 shows a comparison of all six methods, B to G, in terms of their ability to determine nitrate. From this table, and the performance characteristics sections of the methods themselves, the analyst can select the most appropriate method for the sample types requiring analysis.

A1.2.3 **Methods for nitrite**
Method H is a spectrophotometric method for application to nitrite determination in raw, potable and some waste waters. A continuous flow version of this method is described as part of method C. Method J describes the determination of nitrite at the relatively high levels encountered in some industrial effluents and process waters.

Table 1 Comparison of Methods for Total Oxidized Nitrogen and Nitrate

	B	C	D	E	F	G
Method	Reduction/Distillation (Devarda's Alloy)	Continuous Flow (Copper/ Hydrazine)	Continous Flow (Cadmium)	Visible Spectrophotometry (Sulphosalicylic Acid)	UV Spectrophotometry (Direct measurement)	Ion-Selective Electrode
Type of Sample	All, except saline	All, except saline	Saline	All, except saline	Non-saline, low in organic matter	Raw and Potabble
Tested Range (a) mg/1 NO_3 as N	12–40	0.02–36	0.0175–0.56	0.2–10	0.1–9.0	1–50 (log-linear response)
Upper Range Limit (b)	10 mg in sample aliquot	40 mg/1 without prior dilution	0.7 mg/1 without prior dilution	5 μg in sample aliquot	80 μg in sample aliquot	1000 mg/l
Maximum Concentration measurable using Maximum Sample Aliquot	30 mg/l	40 mg/l	0.7 mg/l	0.2 mg/l	2 mg/l	1000 mg/l
Maximum Sample Aliquot ml	350	–	–	25	40	–
Limit of Detection mg/l	0.2	0.01–0.26	0.0084	0.003-0.013	0.03	0.05–0.5
Time Required for Analysis (c) Samples per hour	1	Up to 60	Up to 20	Up to 6	10	Up to 20
Comments	Can be performed after determination of ammonia (on the same sample portion by distillation. TOTAL OXIDIZED N METHOD	TOTAL OXIDIZED N METHOD	TOTAL OXIDIZED N METHOD Low level range only.	METHOD FOR NITRATE ALONE	Interference from organic matter restricts sample applicability. Ideal for underground waters and as a general sorting test. METHOD FOR NITRATE ONLY	Relatively poor precision. For use as a sorting test for rapid monitoring. METHOD FOR NITRATE ONLY

(a) Tested range – The range of concentrations for which standard deviation data has been obtained.
(b) Upper Range Limit – limit to which the method is known to give linear response.
(c) Total analytical time.

A2 Standard Solutions and Reagents common to the methods

Analytical Grade reagents should be used whenever possible.

A2.1 **Water**

Distilled deionized water is recommended for use in all solutions and reagents throughout these methods, except where otherwise noted. Its nitrate concentration must be low in relation to samples, otherwise bias may result.

A2.2 **Stock Standard nitrate solution. 1 ml contains 1mg NO_3^- as N** (not for method F).

NOTE: The concentration of nitrate here, and in all subsequent references, is given in terms of the element, N.

Dissolve 7.220 ± 0.005g of potassium nitrate (dried at 105° for at least two hours) in about 800 ml of water in a 1 litre calibrated flask. Add 1.0 ± 0.1 ml of the preservative solution (Section A2.5). Make up to volume with water and store the solution in a stoppered glass bottle. This solution is stable for at least three months.

A2.3 **Standard nitrate solution. 1 ml contains 100 µg N.** (not for method F).

Pipette 100 ml of stock solution A2.2 into a 1 litre calibrated flask. Add 1.0 ± 0.1 ml of preservative solution (Section A2.5). Make up to volume with water and store in a stoppered glass bottle. This solution is stable for at least three months.

A2.4 **Working Standard nitrate solutions** (Not for method F).

The following table details the preparation of working standard solutions which may be required for calibration of methods. Use pipettes and calibrated flasks for all dilutions. Add preservative solution (Section A2.5) at a concentration of 0.1% V/V to all standards, and store them in stoppered glass bottles for up to three months.

Standard Solution	Volume for Dilution to 1000 ml ml	Nitrate concentration of working standard mg/l
A2.2	40	40
..	30	30
..	20	20
..	15	15
..	10	10
..	8	8
A2.3	50	5
..	40	4
..	20	2
..	10	1
..	5	0.5

A2.5 **Preservation solution**

Dissolve 0.1 ± 0.01g of phenylmercuric acetate in 20 ± 2 ml of methanol. Dilute to 100 ml with water in a measuring cylinder. Store in a stoppered glass bottle.

Note: This reagent is toxic and should be handled accordingly in its neat form. But when added at the specified concentration to standards and samples the hazard is reduced, although the presence of mercury in such solutions must not be overlooked.

A2.6 **Stock Standard Nitrite solution. 1 ml contains 100 µg N**

Dissolve 0.4922 ± 0.0002g of sodium nitrite (dried at 105°C for at least two hours) in about 800 ml of water in a 1 litre calibrated flask. Make up to volume with water and store the solution in an amber glass bottle. This solution is stable for at least one month.

A2.7 **Standard nitrite solution. 1 ml contains 1 µg N**

Pipette 10 ml of stock solution A2.6 into a 1 litre calibrated flask. Make up to volume with water. Prepare this solution freshly as required.

A3 Sample Collection, Storage and Preservation

A3.1 Nitrite may undergo either reduction or oxidation with some rapidity in certain types of sample. It may also be formed either by reduction of nitrate or oxidation of ammonia. Stringent precautions are necessary when nitrite is to be determined, when nitrite is present in significant concentrations or when nitrate alone is to be determined in the presence of a significant concentration of nitrite.

Samples should be collected in glass bottles and must be analysed as soon as possible after collection. Tests should be carried out on each particular sample type to determine the maximum acceptable delay between sampling and analysis. No reliable preservation method is known.

When the nitrite concentration is insignificant, samples may be collected in glass or hard polyethylene bottles and should be analysed as soon as possible. When delays in analysis are inevitable, storage at 4°C may improve stability. Allow the samples to warm to room temperature before analysis. Preservation may be affected by addition of sufficient of the preservative solution (Section A2.5) to give an overall concentration of 0.1% V/V*. Tests have shown that the nitrate concentration of raw and potable water is thus stabilised for at least four weeks. However, tests should be carried out to verify the stability of other types of sample.

* If the samples are to be analysed using method F, this form of preservation may be unacceptable because of the interference arising, as exemplified in Part F3. However, addition of exactly equivalent amounts of the preservation solution to all standards and samples will allow correction of the interference, although with an increase in the limit of detection.

Method B For the Determination of Total Oxidized Nitrogen using Devarda's Alloy Tentative Method

B1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Ref 15)

B1.1	Substances determined:	Nitrate + nitrite
B1.2	Type of Sample:	Raw, potable & waste water
B1.3	Basis of method:	Reduction of nitrite and nitrate to ammonia by Devarda's alloy under alkaline conditions. Distillation and subsequent determination of ammonia by titration.
B1.4	Range of application:	Up to 10 mg of oxidized nitrogen in the sample aliquot taken. Using the full sample volume, this is equivalent to 28 mg/l. See also Section B9.
B1.5	Standard deviation (a):	

Sample Type	Total Standard Deviation	Degrees of Freedom
Solution of Potassium Nitrate, 40 mg/l (250 ml sample).	0.27 mg/l	3
Final Sewage Effluent 12 mg/l (250 ml sample).	0.10 mg/l	11

B1.6	Limit of Detection (a):	0.2 mg/l (4 degrees of freedom).
B1.7	Sensitivity:	Using a 100 ml sample 1.0 ml of 0.02M hydrochloric acid is equivalent to 2.8 mg/lN.
B1.8	Bias:	Not known. Sample instability may be a potential source of bias.
B1.9	Interference:	Certain amides such as urea may be slowly hydrolysed during the distillation to yield ammonia. See Section B3.
B1.10	Time required for analysis:	about 1 hour.

(a) based on information supplied by the North West Water Authority.

B2 Principle

The sample is neutralized and then made alkaline with magnesium oxide. Free and saline ammonia are removed by distillation; Devarda's alloy is then added and the distillation continued, the ammonia resulting from the reduction of oxidized nitrogen (nitrate plus nitrite) being absorbed in boric acid solution and titrated with standard acid.

B3 Interferences

Certain amides, including urea at levels greater than 10 mg in the sample aliquot, may be slowly hydrolysed to produce ammonia in small amounts during the reduction and distillation stage of the method.

B4 Hazards

There are no special hazards in this method. Normal laboratory safety precautions should be observed.

B5 Reagents

Analytical grade reagents should be used whenever possible.

B5.1 **Amonia — free water** (to be used throughout this method).

There are two methods for preparing such water:

Preparation

Method A: Pass distilled water through a bed of strongly-acidic cation exchange resin (in the hydrogen form). Collect the eluate and store in a glass-stoppered bottle containing about 10 g/l of the same ion exchange resin.

Method B: Acidify distilled water with 0.1 ml/l of sulphuric acid (d_{20} 1.84) and redistil in an all-glass apparatus previously deemed to be free from ammonia (see step B7.1). Discard the first 50 ml of distillate, then collect and store the rest of the distillate as described in method A above.

B5.2 **Standard 0.02M hydrochloric acid**

Prepare and standardize this reagent according to standard analytical procedures. Let the exact concentration be C moles per litre. Store in a glass or polyethylene container.

B5.3 **0.05% m/V Methyl red indicator solution**

Dissolve 0.5 ± 0.1g of methyl red in about 900 ml of water and dilute with water to 1 litre in a measuring cylinder. Store in a glass or polyethylene container.

B5.4 **0.15% m/V Methylene blue solution**

Dissolve 1.5 ± 0.1g of methylene blue in about 900 ml of water and dilute with water to 1 litre in a measuring cylinder. Store in a glass or polyethylene container.

B5.5 **Indicating Boric acid solution**

Dissolve 20 ± 1g of boric acid in about 900 ml of warm water. Cool to room temperature. Add 10 ± 1 ml of methyl red and 2.0 ± 0.2 ml of methylene blue solution and dilute to 1 litre in a measuring cylinder. Store in a glass or polyethylene container. One drop of 0.1M sodium hydroxide solution added to 20 ml of this solution should be sufficient to change the colour from purple to green: if this is not, discard the solution and prepare freshly.

B5.6 **0.05% m/V Bromothymol blue Indicator solution**

Dissolve 0.5 ± 0.02g of bromothymol blue in about 900 ml of water and dilute with water to 1 litre in a measuring cylinder. Store in a glass or polyethylene container.

B5.7 **2% V/V Hydrochloric Acid solution**

Dilute 20 ± 1 ml of hydrocholoric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder. Store in a glass or polyethylene container.

B5.8 **4% m/V Sodium Hydroxide solution**

Dissolve 40 ± 2g of sodium hydroxide pellets in about 800 ml of water. Cool to room temperature and dilute with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

B5.9 **Light Magnesium oxide,** carbonate-free

Ignite magnesium oxide at 500°C to remove carbonates.

B5.10 **Devarda's Alloy powder.**

B5.11 **Antibumping granules.**

B5.12 **Antifoaming agent.**

Chips of paraffin wax are suitable.

B5.13 **Nessler's reagent**

a. Dissolve 35 ± 1g of potassium iodide and 12.5 ± 0.5g of mercuric chloride in about 700 ml of water. Gradually add a saturated solution of mercuric chloride with stirring until a slight permanent red precipitate is formed (about 40–50 ml of the saturated solution should be required).

b. Carefully dissolve 120 ± 2g of sodium hydroxide pellets in 150 ± 10 ml of water and cool to room temperature.

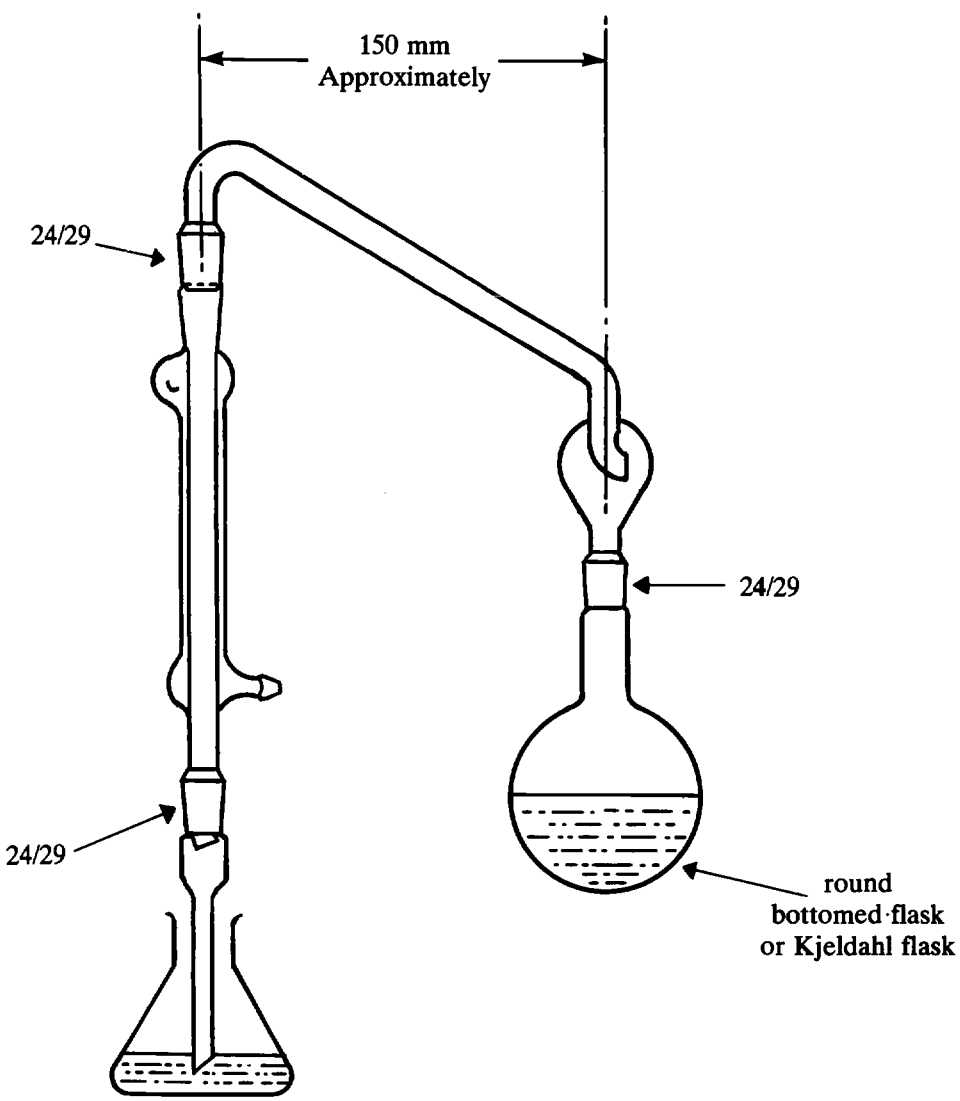


Fig 1 Distillation apparatus

Figure courtesy of the British Standards Institution

Combine the two solutions, (a) and (b) and cool to room temperature. Add a further 1.0 ± 0.1 ml of saturated mercuric chloride solution and mix thoroughly. Dilute the combined solution with water to 1 litre in a measuring cylinder. Store in the dark in a rubber stoppered glass bottle. Allow the reagent to stand, for settlement, for at least a week before use.

NOTE: THIS REAGENT IS TOXIC. All residues containing it from operations described in the methods must be collected and subjected to mercury recovery procedure (1) before final disposal.

B6 Apparatus

In addition to normal laboratory apparatus, distillation apparatus is required which incorporates an 800–1000 ml capacity distillation flask attached to an anti-splash head and a vertical condenser arranged so that its outlet can be submerged in absorbent solution. See Figure 1.

B7. Analytical Procedure

Step	Procedure	Notes
	Checking the apparatus (note a)	
B7.1	Add about 350 ml of water to the distillation flask. Add a few anti-bumping granules and assemble the distillation apparatus as shown in Figure 1.	(a) These steps should be carried out whenever the apparatus has been out of use for more than a few days, and whenever the preceding sample analysed in it has shown a nitrogen concentration high (in the analysts judgement) in comparison to the concentrations usually determined.
B7.2	Commence distillation and after a few ml of distillate have been discharged, collect 50 ml of the distillate in one of a matched pair of 50 ml Nessler cylinders. Into the other cylinder place 50 ml of water.	
B7.3	Add to the cylinder containing the distillate 2.0 ± 0.2 ml of Nessler's reagent.	
B7.4	After about 10 minutes compare the two cylinders visually. No difference in colour should be apparent; a yellowish colour in the Nessler reagent-treated cylinder indicates the presence of ammonia in the distillate at a concentration of 0.01 mg/l or greater.	
B7.5	Continue to collect and test portions of the distillate until adequate freedom from ammonia is indicated.	
B7.6	Empty the flask but do not rinse it. The apparatus is now ready for the analysis of samples.	
	Analysis of samples	
B7.7	Place an aliquot, V ml, of sample, containing not more than 10 mg TON and with a maximum volume of 350 ml, in the distillation flask.	
B7.8	Add a few drops of bromothymol blue indicator. If a yellow colour is obtained add sodium hydroxide solution (B5.8) until the colour just changes to blue. If a blue colour is first obtained, add hydrochloric acid solution (B5.7) until the colour just changes to yellow. If necessary, adjust the volume of the flask contents to about 350 ml with water.	

Step	Procedure	Notes
B7.9	Add 0.25 ± 0.05g of light magnesium oxide B5.9 to the distillation flask and immediately attach the flask to the distillation apparatus (note b).	(b) Anti-foaming agent may be necessary with certain waste waters or sewages.
B7.10	Heat the flask so that distillation proceeds at a rate of about 10 ml/min. Distil a total volume of 200 ± 20 ml. Collect the distillate in a 350 ml receiving flask (notes c and d).	(c) Collect the distillate (via a submerged condenser tip) into a receiving flask containing 50 ± 5 ml of indicating boric acid if ammonia is to be determined. Reserve the distillate for the determination of ammonia by titration. See reference 2. (d) Discard the distillate if ammonia is not to be determined.
B7.11	Replace the receiving flask by a second flask containing 50 ± 5 ml of indicating boric acid. Submerge the condenser tip in the solution.	
B7.12	After allowing the contents of the distillation flask to cool to room temperature, detach the flask and adjust the volume of the contents to about 350 ml with water.	
B7.13	Add 1.0 ± 0.1g of Devarda's alloy powder to the distillation flask and immediately re-attach the flask to the distillation apparatus.	
B7.14	Heat the flask so that distillation proceeds at a rate of about 10 ml/min. Distil a total volume of 200 ± 20 ml.	
B7.15	Having collected 200 ± 20 ml of distillate, titrate with standard 0.02M hydrochloric acid to a purple end point (note e). Record the volume, A ml, of standard acid used.	(e) Titration to the purple colour may also be carried out during the course of the distillation. The end point is reached when continued distillation causes no further reversion to the green colour of the indicator. Titration in this manner ensures the collection of all ammonia without necessarily collecting 200 ml of distillate, and may also reveal prolonged evolution of ammonia due to gradual hydrolysis of interfering amides.
	Analysis of Blank	(f) If ammonia is also to be determined (see note d) a blank value obtained from steps B7.7 to B7.10 will also be required (see note c).
B7.16	Carry 350 ml of water through steps B7.7 to B7.15. Record the volume, B ml, of standard acid used (note f).	
	Calculation of Result	

B7.17 $$\text{TON mg/lN} = \frac{A-B}{V} \times 14.01 \times 1000 \times C$$

where

V = volume in ml of sample used (step B7.7)

A = volume of 0.02M hydrochloric acid used for sample titration

B = volume of 0.02M hydrochloric acid used for blank titration

C = exact concentration, in moles per litre, of standard hydrochloric acid.

B8 Calibration

B8.1 The basis of this method is that the Devarda's alloy brings about quantitative reduction of nitrate and nitrite to ammonia. It is, therefore, vital to check periodically that this is so. The check can be made by (i) carrying a standard solution of nitrate through the procedure, (ii) checking recovery of nitrate from a spiked sample. The nitrate concentrations used in these checks should be selected so as to be typical of those commonly determined in samples.

If quantitative reduction is not being achieved, then either the extent of reduction must be carefully evaulated so that a correction factor can be applied, or the Devarda's alloy must be discarded in favour of a fresh batch.

It is recommended that reduction be checked at least on every occasion that a new batch of Devarda's alloy is used, and preferably at regular intervals during its use, particularly if the number of analyses is small with a consequent low rate of reagent consumption.

B8.2 This method relies upon the correct preparation and standardization of the 0.02M hydrochloric acid for its calibration.

B9 Change in Concentration Range of the Method

The method permits the determination of up to 28 mg/l using the full sample volume of 350 ml. Smaller sample aliquots can be taken in order to extend considerably the concentration range of the method. The analyst should check the precision of whatever variation is used.

B10 Sources of Error

B10.1 This method is open to the usual possible errors of any titration procedure. The analyst must take whatever precautions are appropriate to the particular analytical requirements.

B10.2 Care should be taken to avoid losses of ammonia during distillation. If there is any question of such losses occurring, carry a standard ammoniacal nitrogen solution through the procedure and check recovery.

B10.3 Interfering substances. See Section B3.

B11 Use of Other Methods for Ammonia Determination

Any of the other recommended methods of ammonia determination (2) (ie potentiometric, spectrophotometric, continuous flow) may be used as an alternative to the titration method given above. The performance characteristics in Section B1 will no longer apply, and 2% V/V hydrochloric acid (Reagent B5.7) must be substituted for the indicating boric acid at step B7.11. The calculation of results will also need to be modified.

Method C

Continuous flow methods for the determination of total oxidized nitrogen or nitrite
Tentative Methods

C1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Reference 15)

C1.1	Substances determined:	Nitrate + nitrite, or nitrite alone.
C1.2	Type of Sample:	Raw, potable & waste waters.
C1.3	Basis of methods:	Continuous flow colorimetry for the determination of nitrite with the addition of a copper/hydrazine reducing reagent for reduction of nitrate to nitrite.
C1.4	Ranges of application: (See Section C9)	Total oxidized nitrogen up to 40 mg/l. Nitrite up to 1.0 mg/l.
C1.5	Calibration curves:	Linear.

C1.6 Total Standard deviation (a):

C1.6.1 Nitrate + Nitrite

Calibration Range	Sample Type	Concentration mg/l	Standard Deviation mg/l N	
Up to 10 mg/l N	Standard Solution	1.0	0.01 −0.06	(b)
Up to 10 mg/l N	Standard Solution	9.0	0.08 −0.22	(b)
Up to 10 mg/l N	River Water	7.8	0.08 −0.13	(c)
Up to 40 mg/l N	Standard Solution	36.0	0.48	(d)
Up to 40 mg/l N	River Water	20.7	0.35	(d)

C1.6.2 Nitrite

Calibration Range	Sample Type	Concentration mg/l	Standard Deviation mg/l	
Up to 0.2 mg/l N	Standard Solution	0.02	0.008 −0.0020	(c)
Up to 0.2 mg/l N	Standard Solution	0.145	0.0031	(d)
Up to 1.0 mg/l N	River Water	0.1	0.0052−0.0093	(b)
Up to 1.0 mg/l N	Standard Solution	0.9	0.0055−0.026	(b)
Up to 1.0 mg/l N	River Water	0.53	0.0050−0.0073	(c)

C1.7 Limit of Detection (a):

C1.7.1 Nitrate + Nitrite:	0.05–0.26 mg/l (b) (Calibration range up to 10 mg/l).
C1.7.2 Nitrite:	0.01–0.05 mg/l (e) (Calibration range up to 1 mg/l).

C1.8 Sensitivity:	
C1.8.1 Nitrate + nitrite:	40 mg/l gives an absorbance of about 1.5 units.
C1.8.2 Nitrite:	1 mg/l gives an absorbance of about 0.80 units.
C1.9 Bias (a):	Average inter-laboratory bias – 0.03 mg/l on analysing river water with a nitrate + nitrite concentration of 5.22 mg/l (b). (Calibration range up to 10 mg/l). Average inter-laboratory bias + 0.014 mg/l N on analysing river water with a nitrite concentration of 0.537 mg/l (b). (Calibration range up to 1 mg/l). Sample instability may be a potential source of bias.
C1.10 Interference:	No serious interferences are known. See Section C3.
C1.11 Time required for analysis:	Preparation and shutdown time about 40 minutes. Sampling rate dependent on the wash characteristics of the system, but may be up to 60 samples per hour.

Notes:

(a) All data taken from results (13) of the Harmonised Monitoring Scheme of the Department of the Environment, generated by use of automated methods essentially the same as described in this method and calibrated in the range indicated. Each estimate of standard deviation has between 9 and 18 degrees of freedom, as have the limit of detection estimates.
(b) Four laboratories' results.
(c) Two laboratories' results.
(d) Single laboratory's results.
(e) Three laboratories' results.

C2 Principle

The method provides for the automated determination of nitrate + nitrite in discrete samples by means of continuous flow analysis (3). The essential features of the apparatus are given in Section C6.

Nitrate is reduced to nitrite by hydrazine under alkaline conditions, using cupric ion as a catalyst. The total nitrite is then treated with sulphanilamide and N–1–naphthylethylenediamine dihydrochloride under acidic conditions to form a characteristic pink azo-dye.

Nitrite alone can be determined by omission of reduction. See Section C6.2.

C3 Interferences

The effect of commonly-occurring constituents of raw, potable and waste water on the determination of nitrate + nitrite (calibration range up to 20 mg/l) is shown in Table 1. No data are given for the determination of nitrite alone. See Table 1 in Part H3, which provides a guide to interference effects for this method.

C4 Hazards

N-l-naphthylethylenediamine dihydrochloride and hydrazine sulphate should both be regarded as special hazards. Skin contact with the solids and reagents incorporating them should be avoided.

Normal laboratory precautions should be observed when handling the other reagents.

The precautions given in the essay review on air segmented continuous flow analysis (3) should be observed.

Table 1 (a)

Other Substance (Expressed in terms of substance in brackets)	Concentration of other substance mg/l	Effect in mg/l N of other substance at a nitrate concentration of 0.0 mg/l NO_3^- as N	10.0 mg/l NO_3^- as N
Sodium chloride (Cl^-)	2500	0.00	+0.1
Sodium bicarbonate (HCO_3^-)	1000	−0.02	+0.2
Sodium sulphate ($SO_4^=$)	1000	0.00	−0.2
Sodium orthophosphate ($PO_4^=$)	100	0.00	−0.2
Sodium silicate (SiO_2)	100	+0.01	−0.1
Calcium chloride (Ca)	1000	0.00	−0.2
Magnesium acetate (Mg)	100	0.00	−0.2
Iron (III) sulphate (Fe)	10	−0.04	−0.1
Manganese (II) sulphate (Mn)	10	+0.03	0.0
Zinc sulphate (Zn)	10	0.00	−0.1
Copper sulphate (Cu)	10	−0.01	−0.3
Lead acetate (Pb)	10	−0.05	0.0
Aluminium sulphate (Al)	10	+0.02	+0.1
Potassium Fluoride (F^-)	10	0.00	−0.1
Ammonium chloride (NH_3 as N)	100	0.00	+0.2
Potassium cyanide (CN^-)	10	0.00	−0.1
Urea ($CO(NH_2)_2$)	10	0.00	−0.2

If the other substances did not interfere, the effects would be expected (95% confidence) to lie between:

± 0.08 at 0.00 mg/l N

± 0.06 at 10.0 mg/l N

(a) These data were obtained by Thames Water Authority, Directorate of Scientific Services, New River Head Laboratories.

C5 Reagents

Analytical grade reagents should be used whenever possible. See Part A2.1 regarding water.

C5.1 **0.2M Sodium hydroxide solution**

Dissolve 8.0 ± 0.1g of sodium hydroxide pellets in about 900 ml of water and dilute to 1 litre with water in a measuring cylinder. Add 1.0 ± 0.1 ml of a suitable wetting agent (C5.5). Store in a stoppered polyethylene bottle.

C5.2 **Stock copper sulphate solution**

Dissolve 1.2 ± 0.1g of cupric sulphate pentahydrate in about 80 ml of water in a 100 ml calibrated flask. Make up to volume with water. This solution is stable for at least six months.

C5.3 **Hydrazine-copper reagent**

Dissolve 1.50 ± 0.01g of hydrazine sulphate in about 800 ml of water. Add 1.50 ± 0.01 ml of the stock copper sulphate solution and make up to 1 litre with water in a calibrated flask. Store the reagent in a clear glass bottle. The reagent is stable for at least one week.

Note: Read Section C11 regarding the optimization of this reagent.

C5.4 **Sulphanilamide reagent**

To about 750 ml of water add 100 ± 1 ml of orthophosphoric acid (d_{20} 1.68) and mix. Add 0.500 ± 0.005g of N–1–naphthylethylene diamine dihydrochloride and 10.0 ± 0.1g of sulphanilamide and completely dissolve. Dilute to 1 litre with water in a measuring cylinder and store the reagent in an amber glass bottle, avoid unnecessary exposure to the atmosphere. This reagent is stable for up to one week.

C5.5 **Selection of wetting agent**

The presence of a wetting agent in the system is desirable in order to promote smooth hydraulic flow. A non-ionic surfactant of the polyoxyethylene alcohol type or the alkyl-phenoxypolyethoxy ethanol type will be found suitable.

C6 Apparatus

C6.1 Apparatus for this continuous flow method consists basically of the following:
Sample presentation unit (sampler).
Multichannel peristaltic pump.
Analytical cartridge (manifold) including pump tubes, mixing coils and dialyser unit.
Colorimeter, incorporating a flow cell of between 10 mm and 50 mm path length.
Recorder. (Measurement unit).
Consult the essay review on air segmented continuous flow analysis (3) for further information.

C6.2 The design of the analytical manifold for nitrate + nitrite determination is shown in Figure 2, and that for nitrite determination is shown in Figure 3. Note that the analytical manifold in Figure 2 can readily be adapted to conform to Figure 3, thus facilitating change over between determinations.

C7 Analytical Procedure

Step	Procedure	Notes
	Starting Operation	
C7.1	Connect the system as shown in Figure 2 (nitrate + nitrite determination) or Figure 3 (nitrite determination) (notes a and b).	(a) Follow the manufacturer's general operating instructions. (b) For further information, see reference (3).
C7.2	With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents (note c), start the pump and switch on detection and measurement units (note d).	(c) Ensure that there is sufficient of each reagent to avoid 'topping up' during one batch of analyses. (d) Allow the system to equilibrate for at least 20 minutes and during this period check that the bubble pattern and hydraulic behaviour of the system is satisfactory. If not, eliminate difficulties before proceding to step C7.3.
	Initial Sensitivity Setting	
C7.3	When an acceptably smooth baseline trace is given at the measurement unit, adjust the baseline response to about 5 per cent of full scale (note e) with the zero control and then transfer the sample probe into a C_M standard solution (note f).	(e) An elevated setting of the baseline allows for any negative drift that may occur. (f) C_M is the greatest concentration that the calibration is intended to cover.
C7.4	When there is a positive stable response at the measurement unit due to the colour produced from the C_M standard solution (note g), adjust this response with the scale expansion control to read between 90 and 95 per cent of full scale (notes h and i)	(g) The sample probe need remain only in the C_M standard solution for sufficient time to give a steady reading. (h) A setting 5 to 10 per cent below full scale allows for any increase in sensitivity that may occur. (i) This may be directly possible on some measurement units but others may require range expansion facilities.

Step	Procedure	Notes
C7.5	Return the sample probe to rest in the wash position (note j).	(j) First remove any traces of standard solution from the outside of the sample probe.

Analysis of Samples

C7.6 Load the sample turntable in the following order (notes k and l).

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

(l) The order given is a suggestion. Other loading patterns may be used.

Position No on turntable	Solution
1–5	Calibration standards in ascending order, see Section C8.
6–7	Blank (note m).
8–17	Samples.
18	Calibration standard (note n).
19–20	Blank (note m).
21–30	Samples.
31	Calibration standard (note n).
32–33	Blank (note m).
34–38	Calibration standards in ascending order.

(m) Water from the same source as that used to prepare the calibration standards.

(n) The standard which occupies position No 4 to check the calibration.

Repeat the sequence 6–38 until all the samples have been processed (note p).

(p) When cross contamination occurs between two samples (visible on the measurement unit trace as incomplete separation of consecutive sample responses) both samples are re-analysed, separated by a blank solution.

C7.7 When a steady baseline is obtained on the measurement unit, re-adjust it to about 5 per cent of full scale if necessary and start the sampling unit.

C7.8 When all the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained this unit can be switched off.

Calculation of Results

C7.9 Plot a calibration curve of measurement unit responses (y axis) against concentration (x axis) of standard solutions (note q).

(q) Providing the blank corrected responses of the calibration standard analysed at the end of each group and those at the end of the turntable are all acceptably close to their respective initial blank corrected calibration standard response. If not, refer to reference (3) for suggested procedure to obtain calibration curves.

Step	Procedure	Notes
C7.10	Using the calibration curve(s) (Section C8) convert the measurement unit responses due to the samples into concentrations in the samples (note r).	(r) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes. The results are expressed as mg/l, total oxidized nitrogen or nitrite as appropriate.
	Shut-down Procedure	
C7.11	Transfer all reagent lines to water and pump for at least 15 minutes.	

C8 Preparation of Calibration Curve

C8.1 As indicated in step C7.6, five (at least) calibration standards should be run at the beginning of, and at intervals in, each batch of samples. The concentrations of the standards must be selected having regard for the expected sample concentrations, and of the manifold configuration in current use.

C8.2 For calibration of total oxidized nitrogen determinations, standard nitrate solutions, prepared as described in Part A2.4, should be used.

C8.3 For calibration for nitrite determinations, working standard solutions should be prepared freshly for each occasion by dilution of the standard nitrite solution (Part A2.7) as follows:

Into a series of 50 ml calibrated flasks pipette the following volumes of working standard solutions A2.7:

2.5, 5.0, 10.0, 20.0, 30.0, 40.0 ml.

Dilute to volume with water and mix. These flasks now contain solutions of 0.05, 0.1, 0.2, 0.4, 0.6 and 0.8 mg/l NO^-_2 as N respectively.

C9 Changes in concentration range of the methods

Any calibration range up to a maximum of 40 mg/l (nitrate + nitrite) or 1 mg/l (nitrite) may be used, to suit the anticipated concentration range of the samples. The calibration range is set as described in steps C7.4 to C7.6. Data in sections C1.6, C1.7, C1.9 and C3 were obtained using the specified calibration ranges. The analyst should determine standard deviation, limit of detection and bias data for other calibration ranges that may be routinely used.

C10 Sources of Error

C10.1 A great advantage of continuous flow analysis over manual procedures is that procedural variability inherent in the latter is eradicated; all samples and standards are handled in exactly the same way, providing the apparatus is kept well maintained in accordance with the makers instructions. Thus, apart from mechanical or hydraulic failures or malfunctions, the greatest sources of error are likely to be those given below.

C10.2 **Interfering substances.** (See Section C3)

The method is free from interferences caused by commonly occurring components of natural fresh waters. However, vigilance should be exercised. Whenever an unusual component or an unusually high concentration of some other component is known to be present in a sample, either recovery experiments should be carried out, or the result should be checked by another method in this series. Particular attention should be paid to samples with extreme concentrations of acidity or alkalinity, since these may interfere with the reduction step. This step may also be affected by high concentrations of organic complexing agents which may complex the copper in the reduction reagent.

C10.3 **Drifting calibration curve**

A well maintained system should exhibit little or no drift of either calibration standard response or baseline. However, the presence of blanks and standards in an analytical run (Step C7.6) provides a means of checking the calibration. Small amounts of drift can be corrected by means of these standards, but large drifts should be investigated further.

C10.4 **Inter-sample carryover**

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

C11 Optimisation of the Reduction of Nitrate to Nitrite

C11.1 The concentration of hydrazine sulphate given in Section C5.3 is a typical value; the optimum concentration may vary from batch to batch of the solid reagent. Whenever a new batch is used, the following optimisation procedure should be adopted.

C11.2 Prepare the following solutions:

C11.2.1 *Stock hydrazine sulphate solution*

Dissolve 5.0g hydrazine sulphate in about 900 ml of water and dilute to 1 litre with water in a calibrated flask.

C11.2.2 *Hydrazine sulphate solutions 1.0 to 2.0g (all ± 0.01g) hydrazine sulphate per litre.* To a series of eleven 100 ml calibrated flasks add from a burette respectively 20, 22, 24, 26, 28, 30, 32, 34, 36, 38 and 40 ml (all ± 0.05 ml) of the stock hydrazine sulphate solution. Make up each flask to volume with water. These flasks now contain 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 and 2.0 g/l hydrazine sulphate.

C11.2.3 *Copper sulphate solution*

Dilute 0.750 ± 0.005 ml of the stock copper sulphate solution C5.2 to 1 litre with water in a calibrated flask.

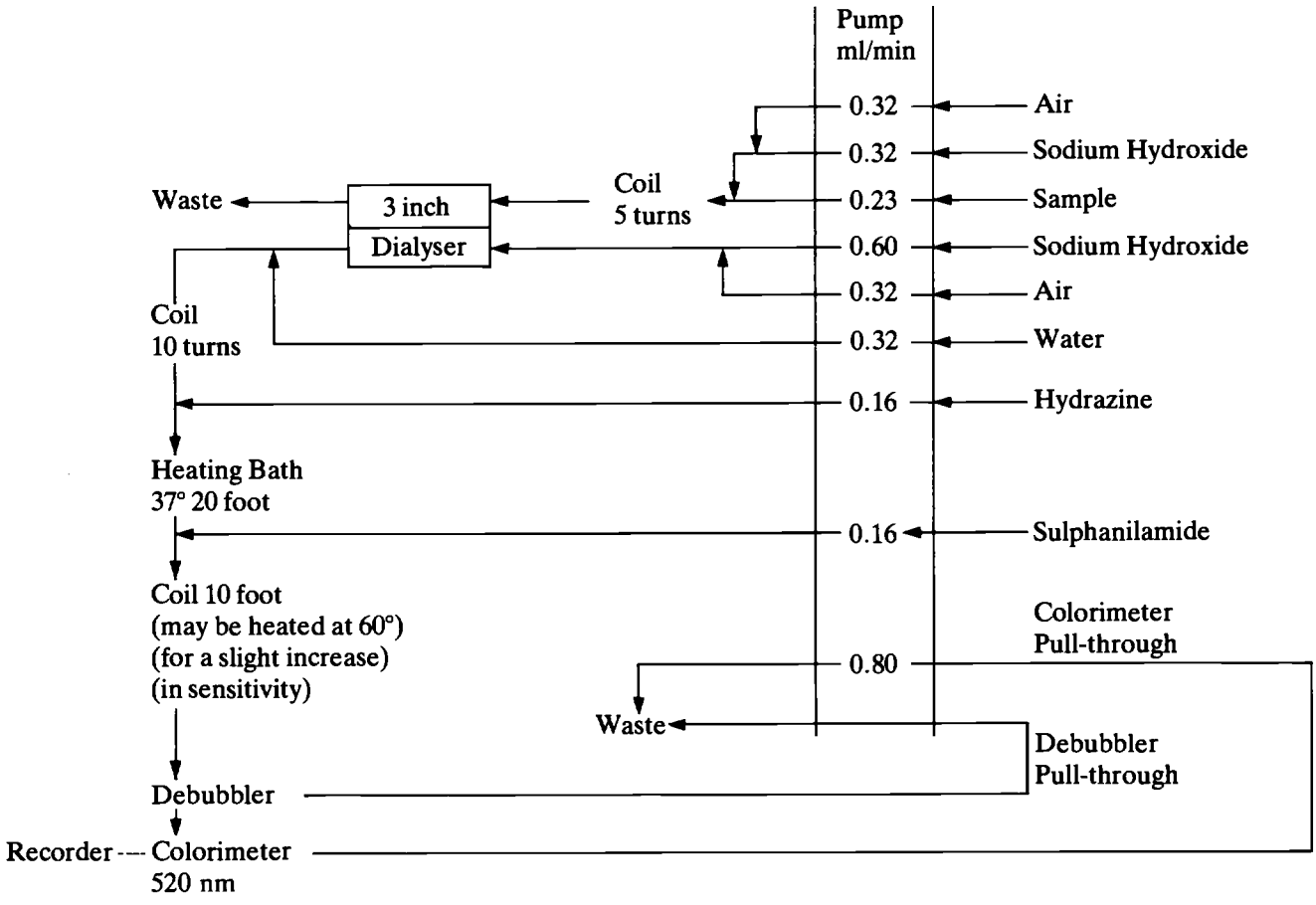
C11.3 (Refer to Figure 2)

Follow the Analytical Procedure from Step C7.1, but modify the analytical manifold arrangement by placing the sample line in a 40 mg/l *nitrite* standard solution and the water line (0.32 ml/min) in the copper sulphate solution C11.2.3, and connect the hydrazine/copper line (0.16 ml/min) to the sample presentation unit. At Step C7.3 adjust the baseline to about 50 per cent of full scale and omit the rest of that step and the whole of Step C7.4. At step C7.6, load the turntable with the hydrazine sulphate solutions (C11.2.2) in ascending order of concentration. Omit step C7.7.

C11.4 When the peaks have been recorded, place the sample line in a 40 mg/l *nitrate* solution, and after about 20 minutes re-present the hydrazine sulphate solutions. Leave the colorimeter controls unaltered.

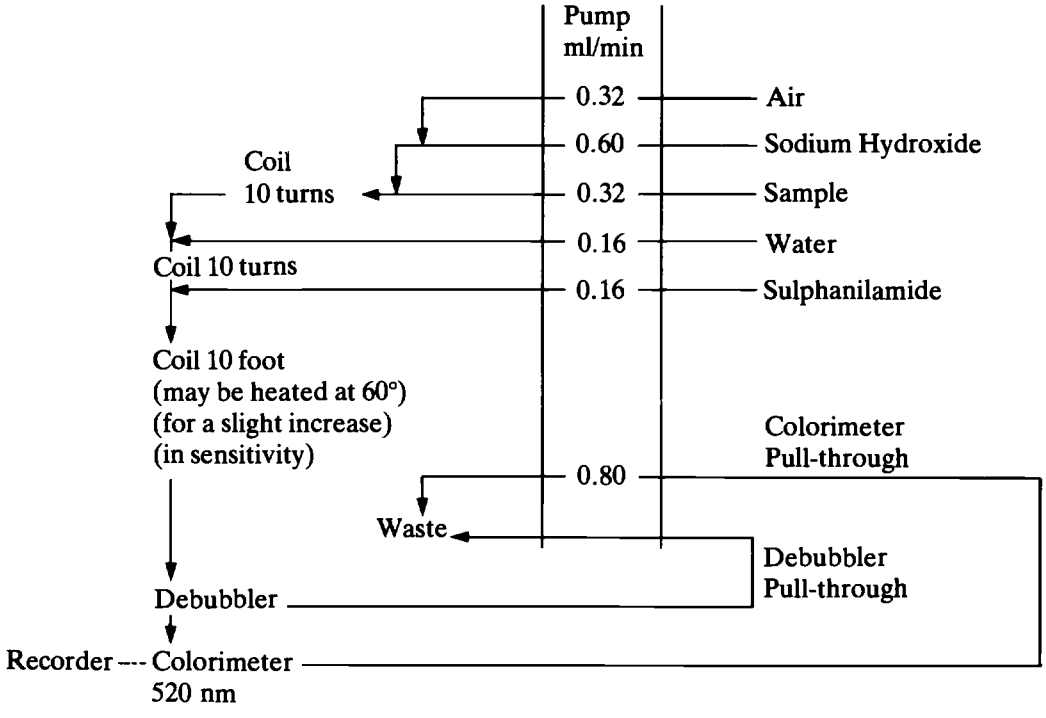
C11.5 After the second batch of peaks have been recorded, shot down the system (Step C7.11) and rearrange the analytical manifold to be in accordance with Figure 2.

C11.6 Compare the results obtained from Steps C11.3 and C11.4. The correct hydrazine sulphate concentration is that which gives maximum response for nitrate, but this must correspond with the response obtained with nitrite at the level of hydrazine sulphate, ie there should be no loss of nitrite response at the optimum value.



All coils 2 mm bore, 20 mm mean diameter

Figure 2 Analytical Manifold for Automated Analysis of Nitrate and Nitrite at up to 40 mg/l



All coils 2 mm bore, 20 mm mean diameter

Figure 3 Analytical Manifold for Automated Analysis of Nitrite at up to 1 mg/l

Method D Continuous Flow Methods for the Determination of Total Oxidized Nitrogen or Nitrite in Sea Water Tentative Methods

D1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Reference 15)

D1.1 Substances determined:	Nitrate + nitrite, or nitrite alone.
D1.2 Type of Sample:	Sea water.
D1.3 Basis of methods:	Continuous flow colorimetry for the determination of nitrite, with the use of mixing coil containing a copperised cadmium wire for the reduction of nitrate to nitrite.
D1.4 Ranges of application:	TON up to 700 µg/l nitrite up to 70 µg/l.
D1.5 Calibration graphs:	linear to 700 µg/l for TON determination linear to 140 µg/l for nitrite determination.

D1.6 Within-batch Standard Deviation (a):

	Concentration µg/l	Standard Deviation µg/l
TON determination on seawater samples with 15 mm flow cell	17.5	0.28 (b)
	140	1.5 (b)
	35	0.96 (c)
	280	1.1 (c)
	70	0.7 (d)
	560	0.96 (d)
Nitrite determination on seawater samples with 50 mm flow cell	3.5	0.056 (e)
	7	0.07 (e)
	35	0.07 (b)
	28	0.042 (b)
	35	0.25 (c)
	70	0.042 (c)

D1.7 Limit of Detection (a):	TON: 1.3 µg/l Nitrite: 0.26 µg/l.
D1.8 Sensitivity (a):	TON: 70 µg/l = 0.2 Absorbance Units (15 mm flow cell) Nitrite: 14 µg/l = 0.15 Absorbance Units (50 mm flow cell).
D1.9 Bias (a):	Not known. Sample instability may be a potential source of bias.
D1.10 Interference:	None expected from commonly occurring constituents of fresh or saline waters.

D1.11	Time required for analysis:	Preparation and shutdown time about 40 minutes. Sampling rate may be up to 20 per hour (nitrate + nitrite) or up to 40 per hour (nitrite). See Section D5.3.

Notes:

(a) Data from the Ministry of Agriculture, Fisheries and Food laboratory at Lowestoft, with 19 degrees of freedom in all cases. Apparatus incorporating a Technicon Auto Analyser II colorimeter was used to obtain the data on standard deviation and was operated in the absorbance ranges identified by the following notes:

(b) absorbance range 0.5 absorbance units
(c) " " 1.0 " "
(d) " " 2.0 " "
(e) " " 0.2 --- ---

D2 Principle

The method provides for the automated determination of nitrate + nitrite in discrete samples by means of continuous flow analysis. The essential features of the apparatus are given in Section D5. Nitrate is reduced to nitrite by passing of the sample-containing stream through tube containing copperized cadmium wire in which reduction takes place (4). The total nitrite is then treated with sulphanilamide and N–1–naphthylethylene diamine dihydrochloride under acidic conditions to form a pink azodye. Nitrite alone can be determined by omitting the reduction coil.

Cadmium reduction is the preferred method for affecting the nitrate to nitrite reduction in seawater. This method may also be used for the analysis of freshwater containing low levels of oxidized nitrogen.

D3 Hazards

D3.1 Cadmium and its salts are toxic. Rubber gloves should be worn when handling cadmium wire.

D3.2 N–1–naphthylethylene diamine dihydrochloride should be regarded as a special hazard, and skin contact with it, and reagents incorporating it, should be avoided.

D4 Reagents

Analytical grade reagents should be used whenever possible. See Part A2.1 regarding water.

D4.1 **2% m/V Copper sulphate solution.**

Dissolve 20 ± 2g of cupric sulphate ($CuSO_45H_2O$) in about 800 ml of water and then dilute with water to 1 litre in a measuring cylinder. This solution is stable for at least six months. Store in a glass-stoppered bottle.

D4.2 **Hydrochloric Acid solution, approximiately 1M.**

Cautiously dilute 89 ± 1 ml of concentrated hydrochloric acid (d_{20} 1.18) to 1 litre with water in a measuring cylinder. Store in a glass or polyethylene container.

D4.3 **35% m/V Stock ammonium chloride solution (saturated).**

Dissolve 350 ± 10g of ammonium chloride in about 800 ml of water and dilute to 1 litre with water in a measuring cylinder. Store in a glass or polyethylene container.

D4.4 **approximately 12% m/V Working ammonium chloride solution.**

Dilute 20 ± 0.1 ml of the stock ammonium chloride solution to 60 ml with water in a measuring cylinder. Store in a glass or polyethylene container.

D4.5 **approximately 0.7% m/V Working ammonium chloride solution**

Dilute 2.00 ± 0.01 ml of the stock ammonium chloride solution to 100 ml with water in a measuring cylinder. Store in a glass or polyethylene container.

D4.6 **Reductor coil preparation**

Measure and cut off 1 metre of 1 mm diameter cadmium wire. Measure and cut off 110 cm of Tygon or polyethylene tubing 1.5 mm internal diameter. Insert the cadmium wire into the tubing leaving 5 cm space at each end of the tubing. Using a 20 ml plastic syringe pass 10 ml of 1M hydrochloric acid through the tube followed by 10 ml of water. Then inject 10 ml of 2% copper sulphate solution followed by at least two 10 ml washes of water to remove any sediment of deposited copper. Then inject 10 ml of 0.7% w/v ammonium chloride solution through the tube and wind into a coil around a former of approximately 25 mm diameter. To regenerate, pump reagents as above through the coiled tube using the spare port of the 4-way chromatography valve (see figure 4 below). Note that this reductor coil must not be allowed to dry.

D4.7 **1% m/v Sulphanilamide.** *Stock solution.*

Dissolve 5.0 ± 0.1g of sulphanilamide in a mixture of 50 ml of hydrochloric acid (d_{20} 1.18) and about 300 ml of water. Dilute to 500 ml with distilled water in a measuring cylinder. Store in a glass or polyethylene container.

D4.8 **0.17% m/v Sulphanilamide.** *Working solution.*

Dilute 10 ± 0.1 ml of the stock solution to 60 ml with distilled water in a measuring cylinder. Store in a glass bottle.

D4.9 **0.1% m/v N–l–naphthylethylene diamine dihydrochloride** *Stock solution.*

Dissolve 0.50 ± 0.01g of N-l-naphthylethylene diamine dihydrochloride in about 400 ml of water and dilute to 500 ml in a measuring cylinder. Store the reagent in an amber glass bottle. Renew the solution when a brown colour develops.

D4.10 **0.017% m/V N-l-naphthylethylene diamine dihydrochloride.** *Working solution.*

Dilute 10 ± 0.1 ml of the stock solution to 60 ml with water in a measuring cylinder. Prepare this solution freshly on each occasion. Store in an amber glass bottle.

D4.11 **Synthetic seawater**

Dissolve 31.0 ± 0.2g of sodium chloride, 10.0 ± 0.1g of magnesium sulphate heptahydrate and 0.050 ± 0.001g of sodium bicarbonate in about 800 ml of water and dilute to 1 litre in a measuring cylinder. Store in a glass or polyethylene container.

D4.12 **Standard Nitrate Solution.** 1 ml contains 1 μg N.

Pipette 10 mls of standard nitrate solution (Part A2.3) (1 ml contains 100 ug) into a l litre calibrated flask. Make up to volume with synthetic seawater. Prepare this solution freshly as required.

D4.13 **Working standard nitrate solutions**

The following table details the preparation of working standard solutions, from which may be selected those necessary for a particular calibration range. Use pipettes and calibrated flasks for all dilutions. Synthetic seawater must be used for dilution in all cases. Prepare these solutions freshly as required.

Volume of standard solution D4.12 for dilution to 100 ml ml	Nitrate concentration of working standard μg/l
75	750
50	500
40	400
30	300
25	250
10	100
5	50
1	10

D4.14 **Standard nitrite solution,** 1 ml contains 10 μg N.

Pipette 50 ml of stock standard nitrite solution (Part A2.6) (1 ml contains 100 μg) into a 500 ml calibrated flask. Make up to volume with synthetic seawater. Store in an amber glass bottle. This solution is stable for at least one month.

D4.15 **Standard nitrite solution.** 1 ml contains 0.1 .305 μg N

Pipette 10 ml of standard nitrite solution D4.14 (1 ml contains 10 μg) into a 1 litre calibrated flask. Make up to volume with synthetic seawater. Prepare this solution freshly as required.

D4.16 **Working standard nitrite solutions**

Follow the instructions given in D4.13, but substituting the standard nitrite solution D4.15 (1 ml contains 0.1 μg N). The concentrations of the resulting standards will be one tenth of those in the table, ie in the range 0.075 to 0.001 mg/l (75 to 1 μg/l).

D5 Apparatus

D5.1 Apparatus for this continuous flow method consists basically of the following:
Sample presentation unit (sampler)
Multichannel peristaltic pump
Analytical cartridge (manifold) including pump tubes and mixing coils
Colorimeter, incorporating flow cells of 15 mm and 50 mm
Recorder.

Consult the Essay Review on air segmented continuous flow analysis (3) for further information.

The design of the manifold is shown in Figure 4.

D5.2 In addition to the above basic requirements, the following are specifically required:

D5.2.1 A liquid chromatography-type 4 way valve to by-pass the reducing coil for determination of nitrite.

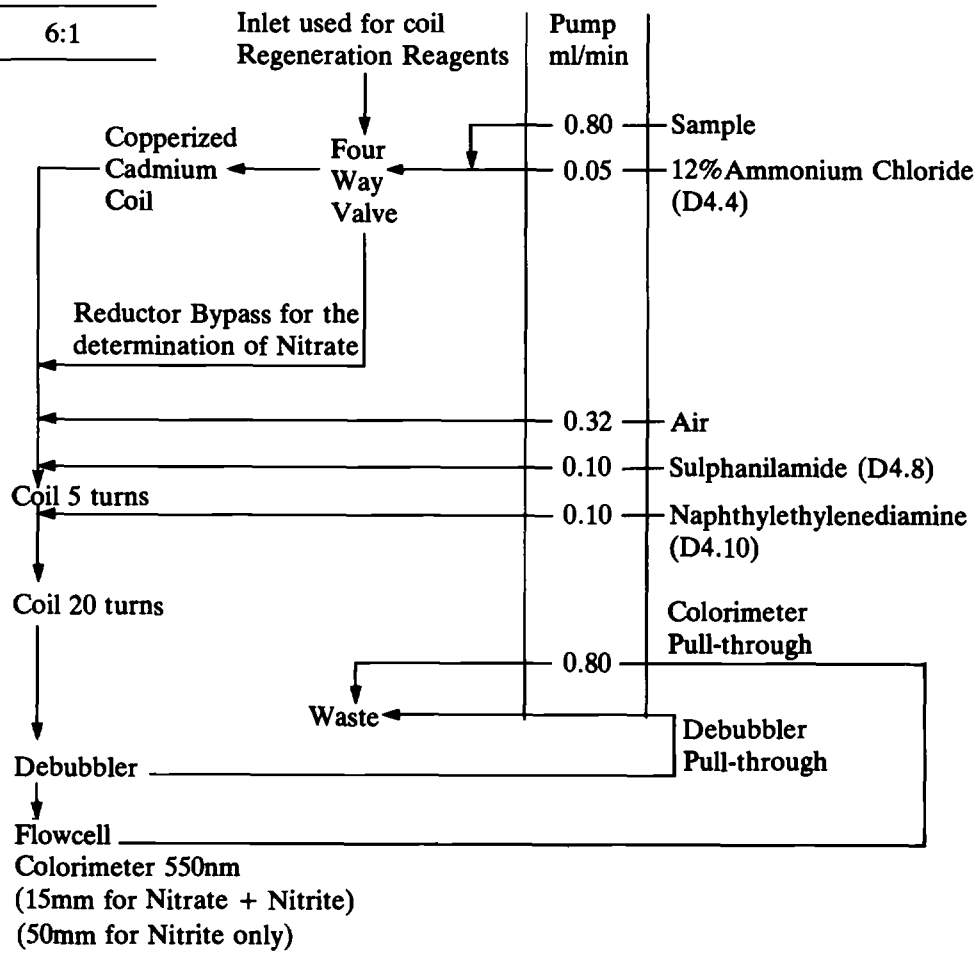
D5.2.2 A copperised cadmium reducing coil. See Section D4.6. Never let this coil run dry.

D5.3 The sample presentation unit should be operated at a sample wash ratio of 15:1 and at up to 20 samples per hour for the determination of nitrate + nitrite. For the determination of nitrite the sample wash ratio is 6:1 and the sampling rate up to 40 samples per hour.

D6 Sample preparation

Filter samples through glass fibre filters type GF. C and store in glass bottles. Keep cool and in the dark. Nitrocellulose membrane filters must not be used. 4 ml polystyrene sample cups must be washed with approximately 1M hydrochloric acid before use.

Determinand	Sample Rate per hour	Sample/Wash Ratio
Nitrate + Nitrite	20	15:1
Nitrite	40	6:1



All coils 2mm bore, 20mm mean diameter

Figure 4 Analytical Manifold for Automated Analysis of Nitrate plus Nitrite or Nitrite only

D7 Analytical Procedure

Step	Procedure	Notes
	Starting Operation	
D7.1	Connect as shown in Figure 4 (notes a and b).	(a) Follow the manufacturer's general operating instructions. (b) See reference (3).
D7.2	With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents (note c) start pump and switch on detection and measurement units (note d).	(c) Ensure that there is sufficient of each reagent to avoid 'topping up' during one batch of analysis. (d) Allow the system to equilibrate for at least 20 minutes and during this period check that the bubble pattern and hydraulic behaviour of the system is satisfactory. If not, eliminate difficulties before proceeding to step D7.3.
D7.3	Set the colorimeter control to suit the concentration range of the samples if the instrument has the facility to attenuate the absorbance range (note e).	(e) See notes to Section D1 and the data in Section D1.6 for illustration of appropriate absorbance ranges.

Step	Procedure	Notes
	Initial Sensitivity Setting	
D7.4	When an acceptably smooth baseline trace is given at the measurement unit adjust the baseline response to about 5 per cent of full scale (note f) with the zero control, and then transfer the sample probe into a C_M standard solution (note g).	(f) An elevated setting of the baseline allows for any negative drift that may occur. (g) C_M is the greatest concentration that the calibration is intended to cover.
D7.5	When there is a postive stable response at the measurement unit due to the colour produced from the C_M standard solution (note h) adjust this response to read between 90 and 95 per cent of full scale (notes i and j).	(h) The sample probe need remain only in the C_M standard solution for sufficient time to give a steady reading. (i) A setting 5 to 10 per cent below full scale allows for any increase in sensitivity that may occur. (j) This may be directly possible on some measurement units but others may require range expansion facilities.
D7.6	Return the sample probe to rest in the wash position (note k).	(k) First remove any traces of standard solution from the outside of the sample probe.
	Analysis of Samples	
D7.7	Load the sample turntable in the following order (notes l and m).	(l) The turntable can be loaded during the initial stabilization period (steps 2 to 4). (m) The order given is a suggestion. Other loading patterns may be used (3).

Position No on turntable	Solution
1–5	Calibration standards in ascending order, see Section D8.
6–9	Blank (note n).
10–17	Samples.
18	Calibration standard (note p).
19–22	Blank (note n).
23–30	Samples.
31	Calibration standard (note p).
32–35	Blank (note n).
36–40	Calibration standards in ascending order.

(n) This must be synthetic seawater (Reagent D4.11) from the same batch as that used to prepare the calibration standards.

(p) The standard which occupies position No 4 to check the calibration.

Repeat the sequence 6–40 until all the samples have been processed (note q).

(q) When cross contamination occurs between two samples (visible on the measurement unit trace as incomplete separation of consecutive sample responses) both samples are reanalysed, separated by a blank solution.

D7.8 When a steady baseline is obtained on the measurement unit, re-adjust it to about 5 per cent of full scale if necessary and start the sampling unit (note r).

(r) See Section D5.3.

Step	Procedure	Notes
D7.9	When all the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained, this unit can be switched off.	
	Calculation of Results	
D7.10	Plot a calibration curve of measurement unit responses (y axis) against concentration (x axis) of standard solutions (note s).	(s) Providing the blank corrected responses of the calibration standard analysed at the end of each group and those at the end of the turntable are all acceptably close to their respective initial blank corrected calibration standard response. If not, refer to reference (3) (Part L) for suggested procedure to obtain calibration curves.
D7.11	Using the calibration curve(s) convert the measurement unit responses due to the samples into concentrations in the samples (note t).	(t) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes. The results are expressed as mg/l, total oxidized nitrogen or nitrite as appropriate.
	Shut-down Procedure	
D7.12	Isolate the Cd/Cu reductor and continue to pass ammonium chloride solution through it (note u). Immerse the reagent lines in water and continue pumping for a further 20 minutes. Then turn off the pump and release the pressure in the pump tubes. Carry out any necessary maintenance in preparation for the next run.	(u) The reductor coil must never be allowed to become dry. Isolate it to retain liquid when pressure on the pump tube is released.

D8 Preparation of Calibration Curve

D8.1 As indicated in step D7.7, five (at least) calibration standards should be run at the beginning of, and at intervals in, each batch of samples. The concentrations of the standards must be selected having regard for the expected sample concentrations.

D8.2 For calibration for total oxidized nitrogen determinations, working standard nitrate solutions, selected from those described in Section D4.13, should be used.

D8.3 For calibration for nitrite determinations, working standard nitrite solutions, selected from those described in Section D4.16, should be used. Note that the manifold must be configured correctly, bypassing the reductor coil. See Section D5.

D9 Separate determination of nitrite

With the manifold configured correctly, bypassing the reductor column, the analytical procedure is identical with that described in Section D7.

D10 Checking efficiency of reduction

Comparison of response (using the same colorimeter setting) for nitrate and nitrite standards of the same concentration should show agreement to within 10%. If this is not the case a new reductor column should be prepared. Reductor column lifetime will depend on frequency of use and sample type.

D11 Sources of Error

Refer to Part C10. The same remarks broadly apply to this method.

D12 Cadmium Disposal and Recovery

1 Cadmium compounds are notifiable wastes and must not be disposed on to land without consent. Limitations can also be applied to its discharge to rivers and sewers. Recovery should therefore be considered.

2 Recovery methods for cadmium are dependent on the concentration present, the other substances present and the amount of waste to be treated. The following information may be useful.

2.1 Cadmium can be almost completely precipitated as sulphide. The method given for mercury removal in either the method for Chemical Oxygen Demand (1) or Chloride (17) in this series could be used, but other methods are available.

2.2 Cadmium can be absorbed by ion exchange resins.

2.3 Cadmium can be removed by electrodeposition (18, 19).

2.4 Cadmium can be deposited as metal by cementation over zinc granules.

3 Which ever method is used some concentration and or purification may be necessary prior to acceptance by the metal recovery trade. Cadmium waste is usually accepted as sulphide, oxide, or metal of reasonable purity. For further information consult the dealers who are listed in trade indexes such as the latest edition of Kompass (16), or ask the Cadmium Association, London.

METHOD E The Spectrophotometric Determination of Nitrate Tentative Method

E1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Reference 15)

E1.1 Substance determined:	Nitrate ion.
E1.2 Type of Sample:	Raw, Potable and Waste Water.
E1.3 Basis of Method:	Nitrate reacts with sulphosalicylic acid to form a yellow compound whose concentration is measured spectrophotometrically.
E1.4 Range of application:	Up to 0.2 mg/l in the maximum sample volume of 25 ml. The range can be extended upwards by taking a smaller sample volume.
E1.5 Calibration Curve:	Linear to at least 0.2 mg/l (with the maximum sample volume of 25 ml.)

E1.6 Total Standard Deviation (a):

Sample Type	Concetration mg/l	Sample Volume ml	Total Standard Deviation mg/l
Standard Solution	0.00	25	0.001–0.005
Standard Solution	0.20	25	0.005–0.011
River Water	4.40	1.0	0.07–0.48
Spiked River Water	9.18	0.5	0.16–0.98
Spiked River Water	10.0	0.5	0.06–0.12

E1.7 Limit of Detection (a):	0.003–0.013 mg/l
E1.8 Sensitivity (a):	0.2 mg/l gives an absorbance of about 0.68 units in 40mm cells, using the maximum sample volume of 25ml.
E1.9 Bias (a):	Average inter-laboratory bias on stable river water samples containing no interfering substances was less than 1%, in most cases not significant, but biases as high as +11% and −14% have been observed in individual laboratories. Sample instability may be a potential source of bias.
E1.10 Interference:	See Section E3.
E1.11 Time required for analysis:	1–3 hours to analyse 6 samples (total time).

(a) These data were obtained from two interlaboratory exercises in which four laboratories participated. 9 degrees of freedom for all estimates of standard deviation.

E2 Principle

Sulphosalicylic acid, formed by addition to the sample of sodium salicylate and sulphuric acid, reacts with nitrate to give a product which, upon treatment with alkali, gives a stable yellow colour whose absorbance at 415 nm is proportional to nitrate concentration (5). Ethylenediaminetetra-acetic acid is added with the alkali to prevent precipitation in hard water samples. Sodium azide is added when necessary to overcome nitrite interference.

E3 Interferences

(b) The effect of commonly-occurring constituents of raw, potable and waste water is shown in Table 1. The main interferents are chloride, orthophosphate, magnesium and manganese (II).

Tests have shown that the method will tolerate a sample colour of up to 150 Hazen units providing the sample blank correction procedure (Step E7.11) is observed.

Table 1

Other Substance (Expressed in terms of substance in brackets)	Amount of other substance in a 25 ml sample aliquot µg	Effect in ug N of other substance at a nitrate amount, in the 25 ml sample aliquot, of	
		0.00 µg N µg	5.00 µg N µg
Sodium chloride (Cl^-)	10,000	+0.03	−0.73
..	2,000	+0.01	−0.16
Sodium bicarbonate (HCO_3^-)	10,000	−0.02	−0.52
..	2,000	−0.03	−0.18
Sodium sulphate ($SO_4^{=}$)	10,000	+0.04	+0.16
Sodium orthophosphate ($PO_4^{\equiv}$)	1,000	+0.30	−0.73
..	100	+0.11	+0.17
Sodium silicate (SiO_2)	250	+0.15	+0.30
Calcium chloride (Ca)	5,000	+0.23	+0.38
..	2,500	+0.02	−0.14
Magnesium acetate (Mg)	5,000	+0.14	+0.29
..	2,500	−0.05	+0.12
Iron (III) sulphate (Fe)	20	+0.08	−0.02
Manganese (II) sulphate (Mn)	20	+0.92	+0.99
..	5	+0.05	+0.13
Zinc sulphate (Zn)	20	−0.02	+0.07
Copper sulphate (Cu)	20	+0.03	+0.19
Lead acetate (Pb)	20	+0.02	+0.07
Aluminium sulphate (Al)	20	0.00	−0.02
Potassium Fluoride (F^-)	20	−0.07	−0.06
Ammonium chloride (NH_3 as N)	500	−0.12	−0.17
Potassium cyanide (CN)	20	+0.15	+0.01
Urea ($CO(NH_2)_2$)	50	+0.04	+0.13

If the other substance did not interfere, the effects would be expected (95%) confidence) to lie between

± 0.16 at 0.00 µg N
± 0.20 at 5.00 µg N

(b) Data in this section were compiled by ICI (Organics Division), the Central Electricity Research Laboratories, and by Thames Water Authority, New River Head laboratories.

E4 Hazards

The usual precautions must be observed when handling concentrated sulphuric acid and strong sodium hydroxide solutions, and sodium azide in both solid and solution form. Solutions containing azide should not be flushed to drain without first being decomposed. An excess of sodium nitrite solution will suffice.

E5 Reagents

Use analytical grade reagents whenever possible. See Part A2.1 regarding water.

E5.1 **Sulphuric acid,** d_{20} 1.84.

E5.2 **Glacial Acetic Acid,** d_{20} 1.28.

E5.3 **20% m/V sodium hydroxide/5% m/V EDTA solution**

Cautiously dissolve 200 ± 2g of sodium hydroxide pellets in about 800 ml of water. Add 50 ± 0.5g of ethylene diamine tetracetic acid disodium salt and dissolve. Cool to room temperature and make up to 1 litre with water in a measuring cylinder. Store in a polyethylene bottle.

E5.4 **0.5% m/V sodium azide solution**

Carefully dissolve 5.0 ± 0.5g of sodium azide in about 900 ml of water and dilute to 1 litre with water in a measuring cylinder. Store in a glass bottle labelled "POISON".

E5.5 **1% m/V Sodium salicylate solution**

Dissolve 1 ± 0.1g of sodium salicylate in 100 ± 1 ml of water. Store in a glass or polyethylene bottle. Prepare this solution freshly on each day of operation.

E6 Apparatus

E6.1 Any colorimeter or visible spectrophotometer equipped with 40 mm cells may be used.

E6.2 A water bath and a series of small (about 25 ml) capacity evaporating dishes are required. If the dishes are new, or not in regular use, they should first be thoroughly rinsed with water. Blank determinations (Step E7.10) should then be carried out in each dish. The results should give, from their standard deviation, a limit of detection comparable to that quoted in Section E1.7.

E7 Analytical Procedure

Step	Procedure	Notes
	Analysis of samples	
E7.1	Take an aliquot, V ml, of sample (note a) of between 0.5 ml and 25 ml, such that the aliquot contains between 1 and 5 μg NO_3 as N. Place in a small evaporating dish (note b).	(a) Samples with pH>8 should be neutralised with acetic acid. (b) See Section E6.2
E7.2	Add 0.5 ± 0.005 ml of sodium azide solution (note c).	(c) The addition of sodium azide can be omitted when the concentration of nitrite is known to be insignificant (in the analysts judgement) in comparison to the nitrate concentration.
E7.3	Add 0.2 ± 0.002 ml of glacial acetic acid. Wait for at least five minutes.	
E7.4	Evaporate the mixture to dryness on a boiling water bath.	
E7.5	Add 1 ± 0.01 ml of sodium salicylate solution, mix well and evaporate the mixture to dryness. Remove from the water bath and allow to cool to room temperature.	

Step	Procedure	Notes
E7.6	Add 1 ± 0.01 ml of sulphuric acid and dissolve the residue by gentle agitation. Stand for ten minutes.	
E7.7	Add 10 ± 1 ml of water followed by 10 ± 0.1 ml of sodium hydroxide/EDTA solution.	
E7.8	Transfer the mixture to a 25 ml calibrated flask. Rinse the basin contents into the flask but do not make up to volume. Place the flask in a water bath at 20 ± 0.5°C for 10 ± 2 minutes. Then remove the flask and make up to volume with water.	
E7.9	Measure the absorbance of the solution at 415 nm in 40 mm cells against distilled water as reference (notes d and e). Let the absorbance be A_s units.	(d) Do not interchange the reference and sample cells, unless they have been shown to be an optically matched pair. (e) Tests of standard solutions indicate that their absorbance values remain constant over 24 hours.
	Blank determination	
E7.10	Take 5 ± 0.05 ml of water and carry it through steps E7.1 to E7.9. Let the absorbance (step E7.9) be A_B units.	
	Correction for Coloured Samples (Note f).	(f) This correction must be applied at the analyst's discretion. Typically it will be required when the colour of the sample exceeds 20 Hazen units if the maximum sample volume is to be used.
E7.11	Take the same sample aliquot as used in step E7.1 and carry it through steps E7.1 to E7.9, but omitting the addition of sodium salicylate at step E7.5. Let the absorbance be A_c units.	
	Calculation of Results	
E7.12	Calculate the absorbance due to nitrate on the sample, A_r, from $A_r = A_S - A_B - A_C$ Determine the mass of nitrate, M μg expressed as nitrogen, from A_r and the calibration curve (Section E8). Nitrate concentration of the sample $= \frac{M}{V}$ mg/l where V is the sample volume taken in step E7.1	

E8 Preparation of Calibration Curve

(To be performed with each new batch of reagents).

E8.1 Prepare a working standard nitrate solution of 1 mg/l, as described in Part A2.4. To a series of clean, dry evaporating basins add, from a burette, 1, 2, 3, 4 and 5 ml of this standard solution respectively, corresponding to 1, 2, 3, 4 and 5 μg of nitrate (N) in the respective basins.

E8.2 Carry each basin through the analytical procedure, step E7.2 to E7.9, together with a blank determination.

E8.3 Subtract the absorbance of the blank solution from the absorbances of each of the standard solutions and plot a calibration graph of absorbance against mass of nitrate, μg N. This should be linear through the origin.

E9 Change in Concentration Range of the Method

The method permits the determination of up to 0.2 mg/l using the full sample volume of 25 ml. Smaller sample aliquots may be taken in order to extend considerably the concentration range of the method: examples of this extension and its precision are to be found in Section E1.6, but the analyst should check the precision of whatever variation is used.

E10 Sources of Error

The main sources of error in this method are potential interferences, which are discussed in Section E3.

Method F The Determination of Nitrate by Direct Ultra-Violet Spectrophotometry Tentative Method

F1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Reference 15)

F1.1	Substance determined:	Nitrate ion.
F1.2	Type of Sample:	Non-saline waters low in organic matter and certain waste waters with high levels of nitrate.
F1.3	Basis of Method:	Ultra-Violet spectrophotometry.
F1.4	Range of application:	Using a 40 ml sample up to 2.0 mg/l, which can be extended upwards by taking a smaller sample volume.
F1.5	Calibration Curve:	Linear at least to 2.0 mg/l as N, using a 40 ml sample.

F1.6 Total Standard Deviation (a):

Type of Sample	Sample Size ml	Concentration mg/l	Total Standard Deviation mg/l
Drinking water A	40	0.098	0.013
River water	40	0.60	0.009
Potassium nitrate solution	40	1.00	0.005
Drinking water B	40	1.60	0.017
Borehole water	4	9.0	0.108

9 degrees of freedom in each case

F1.7	Limit of detection:	0.03 mg/litre as N (9 degrees of freedom) for samples containing no interfering substances, but may be much higher if interfering substances are present (see Sections F3 and F10).
F1.8	Sensitivity (a):	1 mg/l nitrate N gives an absorbance of approximately 0.44, using 40 ml of sample.
F1.9	Bias:	Not known. Sample instability may be a potential source of bias.
F1.10	Interferences (a):	Organic matter, bromide, iodide, iron (III) and chromate are the most serious interferences. See Section F3.
F1.11	Time required for analysis (a)	10 samples per hour (analytical and operator time).

(a) Information supplied by North West Water Authority. Each estimate of standard deviation has 9 degrees of freedom.

F2 Principle

The nitrate ion has a strong absorption band in the far ultra-violet with a peak at 202 nm and in the absence of other substances which absorb in this region of the spectrum, nitrate can be determined rapidly by direct measurement of its ultra-violet absorbance.

F3 Interferences

F3.1 Scattering of light by undissolved particles is a greater source of error in the ultra-violet than in the visible region of the spectrum. Suspended matter or turbidity must, therefore, be removed and the method must not be used on samples which cannot be filtered to give a clear and bright filtrate.

F3.2 Many dissolved substances which may occur in water absorb radiation at the lower end of the ultra-violet range and this is the main restriction on the use of the method. The nitrite ion absorbs over a similar wavelength range to nitrate, but is removed by the addition of sulphamic acid. Carbonate and hydroxyl ions interfere, but are easily eliminated by acidification. The sulphuric-sulphamic acid reagent will prevent interference by carbonate and/or hydroxyl ions up to 2000 mg/l (calculated as calcium carbonate, $CaCO_3$) and up to 6.4 mg/l of nitrite nitrogen.

F3.3 The effects caused by certain other substances likely to cause interference are shown in Table II.

Table II (c)

Other Substance (Expressed in terms of substance in brackets)	Concentration of other substance (mg/l) in a 40 ml sample portion	Effect in mg/l N of other substance at a nitrate concentration of		
		0.000 mg/l	0.100 mg/l	2.000 mg/l
sodium chloride (Cl^-)	4000	+0.033	+0.020	+0.007
potassium bromide (Br^-)	0.8	+0.053	+0.039	+0.053
potassium iodide (I^-)	0.7	+0.084	+0.060	+0.093
iron (III) chloride (Fe)	0.3	+0.070	+0.041	+0.103
.. ..	1.0	+0.194	+0.184	+0.174
ammonium ferrous sulphate (Fe)	20	+0.033	+0.050	+0.026
potassium dichromate (Cr)	0.1	+0.020	+0.006	−0.006
manganese (II) sulphate (Mn)	100	+0.022	+0.033	+0.004
sodium nitrite (N)	5	+0.072	+0.020	+0.078
sodium carbonate (Na_2CO_3)	2000	+0.024	+0.015	+0.021
Manoxol OT (as the substance)	5	+0.007	+0.002	+0.001
Preservation solution (note a)	0.1 (note b)	+0.209	+0.169	+0.162

If the other substances did not interfere, the effects would be expected (95% confidence) to lie between:

± 0.016 at 0.000 mg/l N ± 0.020 at 0.100 mg/l N ± 0.087 at 2.000 mg/l N

(a) As described in Part A2.5

(b) 0.1 ml in a 40 ml sample portion. This corresponds to 2.5 times the dose recommended in Part A3.1

(c) These data were obtained by Thames Water Authority, Directorate of Scientific Services, New River Head Laboratories

F3.4 Dissolved organic matter, mainly humic substances, is the most frequent cause of interference, but dissolved iron (especially ferric iron) and other heavy metals and hexavalent chromium may interfere. Chloride and bromide ions show absorption in the ultra-violet in the region of 200 nm and below, and other ions show a steeply-rising absorption with decreasing wavelength as the wavelength approaches 200 nm which is the lower limit of the wavelength range of ultra-violet spectrophotometers. The choice of 210 nm as the wavelength for the measurement of nitrate concentration is made so as to be close to the peak maximum and to minimize interference by chloride. Use of the maximum absorbance wavelength of 202 nm would increase this interference. Even so the method is not suitable for most saline waters largely because of interference by bromide ions.

F3.5 A correction for ultra-violet absorbing substances other than nitrate is made by measuring the absorbance of samples at two wavelengths, 210 and 275 nm. At concentrations suitable for measuring at 210 nm the nitrate ion has no significant absorbance at the higher wavelength. Subtraction of the absorbance at 275 nm multiplied by an appropriate factor from the gross absorbance at 210 nm gives a corrected absorbance from which the nitrate concentration is calculated (6) (7) (8). An average correction factor of 4.0 for organic matter in potable water sources in the UK has been recommended, but this must be confirmed or a more appropriate factor for each source of water determined by comparison with the nitrate determined by some other method.

The value of this factor may vary between 2 and 5 for potable waters. If the absorbance at 275 nm exceeds 10 per cent of that at 210 nm the result is of doubtful value and the method should not be used. For potable waters this situation is likely to occur with waters from upland reservoirs which are low in nitrate and high in organic matter derived from peat.

F3.6 An additional check on the validity of the result can be obtained by comparing the shape of the absorption curve of the sample between 200 and 240 nm with that of a standard solution of potassium nitrate. The curves should be generally similar and show a point of maximum slope at the same wavelength, otherwise the validity of the result is in doubt. This comparision should be made, both initially and from time to time, on samples from sources which have a pronounced absorbance at 275 nm.

F4 Hazards

F4.1 Ultra-violet light is damaging to the eyes and can produce skin burns on prolonged exposure. Care should be taken to ensure that there is no light leak from the apparatus.

F4.2 Normal precautions must be observed when handling concentrated sulphuric acid.

F5 Reagents

Analytical grade reagents should be used whenever possible.

F5.1 **Distilled water** (to be used throughout this method)

Water obtained by distillation in an all-glass apparatus and stored in glass containers should be used throughout this method. De-ionized water is not suitable owing to the presence of traces of ultra-violet absorbing organic matter derived from the ion-exchange resins. See Section F11.

F5.2 **5% V/V Sulphuric acid**

Add slowly and cautiously with stirring 25 ± 0.5 ml of sulphuric acid (d_{20}1.84) to about 250 ml of distilled water in a 1-litre beaker or flask standing in cold water. Allow to cool to room temperature and dilute to 500 ml with water in a measuring cylinder. Store in a glass stoppered bottle.

F5.3 **Sulphuric Acid/Sulphamic Acid Reagent**

Dissolve 5.0 + 0.1g of sulphamic acid in 500 + 10 ml of sulphuric acid 5% V/V (F5.2). This solution is stable for at least 2 months. Store in glass stoppered bottle.

F5.4 **Stock standard nitrate solution.** 1 ml contains 100 μg N

Dissolve 0.722 + 0.001g of potassium nitrate (dried at 105° for at least two hours) in about 800 ml of water and make up to 1 litre with water in a calibrated flask. Store the solution in a stoppered glass bottle. This solution is stable for two weeks.

F5.5 **Working standard nitrate solution** 2 mg/l

Pipette 20 ml of the stock standard nitrate solution (F5.4) into a 1 litre calibrated flask and make up to volume with water. Prepare this solution freshly.

F6 Apparatus

F6.1 General

Glass vessels should be used for all reagents, standards and samples. They must be scrupulously clean preferably by treatment with concentrated sulphuric acid and thorough rinsing with tap water followed by distilled water.

F6.2 **Ultra-violet/Visible spectrophotometer**

An instrument capable of reading absorbances at wavelengths down to 200 nm.

F6.3 **10 mm Silica cells** (reserved for this method, see step F7.1).

F6.4 **Glass fibre filterpapers** retaining particles over about 1 μm diameter.

F7 Analytical Procedure

Step	Procedure	Notes
	Check of matching and cleaning cells (note A).	
F7.1	Fill both sample and reference cells with distilled water, and measure the absorbance difference at 210 nm (note b). This should not exceed 0.02 absorbance units (note c). Reserve the cells solely for this method and always use the same cell for the reference solution.	(a) Carry out this check on the cells before beginning the analysis of any sample. (b) If the absorbance reading is negative reverse the cells. (c) Clean the cells as directed in Section F6.1 if the absorbance difference is unacceptable. Discard the cells if repeated cleaning is not effective.
	Determination of Reagent/Cell Blank	
F7.2	Add 1 ± 0.1 ml of sulphuric acid/sulphamic acid reagent to a 50 ml calibrated flask. Dilute to volume with distilled water, mix well, and record the absorbances, B_{210} and B_{275}, of this blank at 210 and 275 nm against distilled water in the reference cell. If the absorbance at either wavelength exceeds 0.05 absorbance units discard the reagent and prepare a fresh reagent solution.	
	Analysis of Samples (note d)	(d) Samples with negligible turbidity or suspended matter need not be filtered. Omit steps F7.3 and F7.4 and start at step F7.5.
F7.3	Assemble a 7 cm glass fibre filter paper in a suitable holder, wash with at least 100 ml distilled water. Read the absorbance of the final washing at 210 nm. When corrected for any difference in absorbance between the cells this must not exceed 0.02 absorbance units. If this figure is exceeded continue washing with distilled water or reject the filter paper (note e).	(e) Each filter paper used must be pre-washed. The absorbance check on the washing need only be one per paper for each batch of samples.
F7.4	Filter the sample through the 7 cm glass fibre paper prepared as in step F7.3. Reject the first 20 ml of filtrate. The filtrate must be clear and bright.	
F7.5	Measure by pipette a volume, Vml, of sample containing not more than 80 μg nitrate nitrogen, into a 50 ml calibrated flask. Add 1 ± 0.1 ml of sulphuric acid/sulphamic acid reagent. Dilute to volume with distilled water and mix well.	

Step	Procedure	Notes
F7.6	Measure the absorbance at 210 and 275 nm against distilled water in the reference cell. If the sample absorbance at 275 nm exceeds 10 per cent of the absorbance at 210 nm the result will be unacceptable and another method will have to be used.	
F7.7	**Calculation of Result** Calculate the corrected absorbance of the sample, A_C, at 210 nm as follows: $A_C = (A_{210} - B_{210}) - F(A_{275} - B_{275})$ where A_{210} = Absorbance reading of sample at 210 nm. B_{210} = Absorbance reading of reagent/cell blank at 210 nm. A_{275} = Absorbance reading of sample at 275 nm (note f). B_{275} = Absorbance reading of reagent/cell blank at 275 nm. F = Correction factor, which is normally 4 but must be determined for each source of water (note F).	(f) See Section F3.5
F7.8	Determine the mass of nitrate (as N), M μg, in the sample from A_c and the calibration curve.	
F7.9	Nitrate concentration of the sample = $\frac{M}{V}$ mg/l	

F8 Preparation of Calibration curve.

(To be carried out with each batch of analyses).

F8.1 Measure by pipette the volumes in the table below of dilute standard nitrate solution 2 mg/l (F5.4) and transfer to a series of 50 ml calibrated flask.

Volume of Standard Nitrate Solution ml	μq Nitrate (N)
5	10
10	20
15	30
25	50
40	80

F8.2 To each flask add 1 ± 0.1 ml of sulphuric acid/sulphamic acid reagent (F5.3). Dilute to volume with distilled water and mix well.

F8.3 Measure the absorbances at 210nm against distilled water in the reference cell and USING THE SAME CELL AS THAT USED FOR THE REAGENT/CELL BLANK.

F8.4 Subtract the reagent/cell blank absorbance reading at 210nm from these absorbance readings and plot the corrected readings against the amounts of nitrate nitrogen in micrograms.

F9 Change in Concentration Range of the Method.

The method permits the determination of up to 2 mg/l using the full sample volume of 40 ml. Smaller sample aliquots may be taken in order to extend considerably the concentration range of the method; examples of this extension and its precision are to be found in F1.6, but the analyst should check the precision of whatever variation is used.

F10 Sources of Error

F10.1 The main cause of errors with the direct UV spectrophotometric method for nitrate is the ubiquitous nature of water-soluble UV-absorbing substances. All apparatus with which samples and standards come into contact in any way must be kept scrupulously clean and preferably not used for other purposes. Experience has shown that the use of the cells for other purposes may increase the absorbance of the cell at low UV wavelengths and that the contaminating substance cannot be removed by normal methods of cleaning. It is, therefore, necessary to check the absorbance matching of the cells before commencing the analysis of each batch of samples.

F10.2 The nitrate is calculated from a measurement near the lower limit of the wavelength range of most UV spectrophotometers and any deficiency in maintenance and adjustment of the spectrophotometer is likely to cause errors. Hence the requirement to recalibrate the method with each batch (Section F8.1).

F10.3 Interfering substances. See Section F3.

F10.4 Quality of distilled water. See Section F5.1. For a method of checking distilled water quality see Section F11.

F11 Distilled Water Quality

De-ionised water is not suitable for use with this method due to the presence of traces of UV-absorbing substances derived from the ion-exchange resins as well as organic matter in the original water before passage through the de-ionizer. It may be advisable to check that the distilled water used is sufficiently free from UV absorbing material and the following method is suggested.

F11.1 Place 500 ± 20 ml distilled water in a clean all glass distillation apparatus.

F11.2 Distil 200 ± 10 ml and retain this distillate separately.

F11.3 Distil a further 50 ± 10 ml and retain this portion of distillate.

F11.4 Continue the distillation until a total of 400 ± 20 ml has been distilled.

F11.5 With the distillate from step F11.3 in the reference cell measure the absorbance at 210 nm of the residue in the distillation flask from step F11.4

F11.6 Repeat step F11.5 using distillate from step F11.2 (the forerunnings) instead of the residue.

F11.7 When corrected for the cell difference, absorbance measurements on the residue and forerunnings of a satisfactory distilled water do not differ more than 0.005 absorbance units. If the absorbance difference exceeds this, repeat the test. If the second test confirms the previous result, the laboratory supply of distilled water must be redistilled until it complies with these requirements.

Method G The Determination of Nitrate using a Nitrate-Selective Electrode Tentative Method

G1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Reference 15)

G1.1 Substance determined: Nitrate ion.

G1.2 Type of Sample: Raw and potable waters.

G1.3 Basis of Method: Samples are treated with a reagent to make uniform their ionic strenth and pH value. The nitrate concentration is measured potentiometrically in the treated sample by means of a nitrate-selective electrode, using either a calibration curve or by a standard addition procedure. (See Section G7).

G1.4 Range of application: 1–1000 mg/l.

G1.5 Calibration Curve: Log-Linear over the range of application.

G1.6 Total Standard Deviation (a):

Procedure 1 (see Section G7)

Sample Type	Concentration mg/l	Standard Deviation mg/l	Degrees of Freedom
Synthetic Solution	1.00	0.020–0.177	9
Synthetic Solution	50.0	0.59 –5.5	9
Potable Water	6.5	0.13 –0.58	9
Spiked River Water	21.5	0.52 –1.8	9

Procedure 2 (See Section G7)

Sample Type	Concentration mg/l	Standard Deviation mg/l	Degrees of Freedom
Synthetic Solution	1.00	0.043–0.283	9
Synthetic Solution	50.0	0.98 –8.1	9
Potable Water	6.7	0.08 –0.76	9
Spiked River Water	21.9	0.32 –1.8	9

G1.7 Limit of detection: (Defined as the limit of Nernstian Response under the conditions of the method) — Dependent upon electrode type. Typically the lower limit of Nernstian response is in the range 0.05 to 0.5 mg/l

G1.8 Sensitivity: — The potential of the electrode changes by approximately 60 mV per decadic change of nitrate concentration, in accordance with the Nernst equation.

G1.9 Bias (a):
Procedure 1 (See Section G7)

Sample Type	Concentration mg/l	Bias Range %
Synthetic Solution	1.00	−1 to + 32
.. ..	50.0	0 to + 7
Potable Water	6.5	+1 to + 22
Spiked River Water	21.5	−2 to + 20
Procedure 2 (See Section G7)		
Synthetic Solution	1.0	−1 to + 11
.. ..	50.0	−2 to + 13
Potable Water	6.7	+3 to + 18
Spiked River Water	21.9	−1 to + 9

G1.10 Interference: A range of anions interfere. See Section G3.

G1.11 Time Required for Analysis: 15 minutes for electrode calibration and analysis of a single sample. 5 minutes for subsequent samples.

(a) Data from interlaboratory exercises, in which four laboratories participated. Samples were analysed in duplicate on each of five separate days.

G2 Principle

G2.1 The sample is treated with a reagent to make uniform the ionic strength and pH value. The nitrate-selective electrode adopts a potential, with respect to a reference electrode, which is proportional to the logarithm of the activity of nitrate ions in the treated sample. Because the ionic strengths in both standards and treated samples are similar, the sensed activity is read directly as a concentration from the calibration curve, or calculated from known addition results.

The reagent specified is selected as compatible with all known commercial nitrate electrodes. Other formulations, such as those based on borax, are satisfactory for some electrodes but less satisfactory for others.

G2.2 Two analytical procedures are given. One relies upon the preparation of a calibration curve from which the concentration of samples is read off; this is referred to as procedure 1. Procedure 2 is a known addition procedure, making use of the electrode's pre-determined sensitivity factor, or "slope".

Procedure 2 may have advantages when electrode drift is a problem (Sections G10.4 and G10.5).

Other alternative procedures, such as the Gran's Plot method involving multiple standard additions, are given in references (9) and (10).

G2.3 Results from interlaboratory exercises have confirmed there to be a wide variation in accuracy and precision with this method (G1.6 and G1.9). This method therefore must be regarded as suitable only for rough sorting analysis until the analyst has satisfied himself that higher precision and accuracy are obtainable in his laboratory.

G3 Interferences

G3.1 The method is only suitable for samples giving pH values in the range 3 to 10 after addition of the buffer solution (Section G5.4); strongly acid or alkaline samples must first be neutralised prior to buffer addition.

G3.2 Nitrate-selective electrodes suffer interference from several commonly-occurring anions. The exact extent of interference varies between electrodes. However, manufacturers usually quote selectivity coefficients (expressed on a molar

basis) from which the likely extent of interference can be calculated using the formula

$$E = \frac{100\ \Sigma_i\ K_i\ X_i^{\frac{1}{Z_i}}}{C}$$

where K_i is the selectivity coefficient for the interfering anion, i;

X_i is the concentration, in moles per litre, of the interfering anion, i;
Z_i is the valency of the anion, i;
C is the concentration, in moles per litre, of nitrate in the sample;
E is the percentage apparent increase in the measured nitrate concentration caused by the interfering anions.

The following table gives typical selectivity coefficients for a range of anions, together with computed concentrations which would cause an apparent 1 mg/l increase in the measured nitrate concentration when present singly in a 10 mg/l nitrate solution:

Anion	Valency	Selectivity Coefficient	Concentration of Anion (in mg/l) to give apparent 1 mg/l increase on 10 mg/l nitrate
Chloride	1	5×10^{-3}	51
Bicarbonate	1	3×10^{-4}	1450 (as HCO_3^-)
Nitrite	1	5×10^{-2}	2 (as N)
Fluoride	1	7×10^{-4}	194
Iodide	1	10	.09
Bromide	1	10^{-1}	5.7
Carbonate	2	2×10^{-4}	358 (as $CO_3^=$)
Cyanide	1	10^{-2}	19 (as CN)
Sulphate	2	6×10^{-4}	331

G3.3 The buffer solution (Section G5.4) may be modified as described in sections G10.2 and G10.3 to overcome interference from nitrite or chloride. The buffer solution already contains sufficient sulphuric acid to overcome interference from the concentrations of bicarbonate and carbonate usually found in raw and potable waters.

G3.4 Certain types of electrode may be affected by organic matter, including detergents. With one type of electrode sodium dodecyl sulphate and dioctyl sodium sulphosuccinate gave K_i values of respectively 12 and 4.

Analysis of samples containing detergents may therefore be inadvisable. Detergent traces resulting from cleaning of apparatus may also cause difficulties.

G4 Hazards

There are no special hazards with this method. Normal laboratory safety precautions must be observed.

G5 Reagents

Analytical grade reagents should be used whenever possible. See Part A2.1 regarding water.

G5.1 **Sulphamic acid, H_2NSO_3H.**

G5.2 Silver sulphate, Ag_2SO_4.

G5.3 **Approximately 1M sulphuric acid**

Carefully add 56 ± 1 ml of concentrated sulphuric acid (d_{20} 1.84) to about 900 ml water and dilute to 1 litre in a measuring cylinder. Store in a glass stoppered bottle.

G5.4 **Buffer Solution,** *approximately 1M potassium dihydrogen orthophosphate/ 0.05M sulphuric acid.*

Add 50 ± 1 ml of 1M sulphuric acid to about 800 ml of water and mix thoroughly.

Then dissolve 136 ± 1g of potassium dihydrogen orthophosphate in the mixture. Dilute the whole to 1 litre with water in a measuring cylinder. This solution is stable for at least three months. Store in a glass-stoppered bottle.

G5.5 **Standard Nitrate solution,** *1 ml contains 5 mg NO_3 as N* (for procedure 2 only)

Prepare this solution in the same way as described in part A2.2 but using 36.09 ± 0.05g of potassium nitrate. This solution is stable for at least three months. Store in a glass stoppered bottle.

G6 Apparatus

G6.1 Nitrate-selective electrode. Several types of electrode are commercially available: attention should be paid to the selectivity and response range of the electrodes in choosing one for use.

G6.2 **Reference electrode.** The correct selection and maintenance of the reference electrode is of great importance. The electrode should have preferably a sleeve-type liquid junction, or a large frit-type liquid junction. Follow the manufacturer's instructions concerning the choice of bridge solution, but avoid those solutions containing nitrate ions; a potassium chloride solution of concentrations between 3 and 4M is generally satisfactory for chloride-based reference electrode systems (eg calomel electrodes). This bridge solution should be renewed at least once a week. The reference electrode must be repaired or renewed at the first sign of any deterioration in performance. The potential of the electrode should, in the absence of temperature effects, remain steady to ± 0.01 mV. If the flow rate of the liquid junction exceeds 0.1 ml/5 cm head/day, it is preferable to use a mercury/mercurous sulphate/1M sodium sulphate reference electrode to avoid contamination of the nitrate electrode with chloride ions.

G6.3 **pH/millivoltmeter.**

The meter should have one high impedance input ($>10^{10}$ ohm) and be precise to ± 0.2 mV or less. The precision of the method is to a large extent dependent on the precision of the potential measurements. A meter with a direct reading concentration scale may be used.

G6.4 **Magnetic stirrer.** *with PTFE or polypropylene-coated stirring bars.*

G7 Analytical Procedures

Note that two distinct procedures are given in this section. See sections G2.2 and G2.3

Step	Procedure	Notes
	Procedure 1 — Graphical or Direct Reading Method	
G7.1	Pipette 50 ml of sample into a dry 100 ml beaker and add by pipette 2 ml of buffer solution. (Notes a, b and c).	(a) Strongly acid or alkaline samples must first be neutralized. See Section G3.1. (b) The sample temperature must be within 1°C of the temperature at which calibration is carried out (G10.4). (c) Refer to Section G10 for sample pre-treatment procedures when nitrite and/or chloride interference is likely.
G7.2	Stir the solution by means of the magnetic stirrer. The stirring rate should be brisk, but not sufficient to create a large vortex (note d).	(d) To avoid possible heating of the sample by the stirrer motor, a thin sheet of insulating material may be placed under the beaker.

Step	Procedure	Notes
G7.3	Immerse the tips of the electrodes (previously connected to the meter, with the nitrate electrode connected to the high-impedance input) in the solution, taking care not to trap air bubbles on the electrode tips.	
G7.4	Measure and record the potential E_1 mV, between the electrodes when it has become constant to within 0.1 mV in 30 seconds (note e).	(e) The electrodes should be removed from the solution as soon as possible after taking a measurement (step G7.5) in order to minimize possible contamination of the nitrate electrode from interfering ions present in either the sample itself or the reference electrode bridge solution.
G7.5	Remove the electrodes from the solution, rinse them with water and blot with tissue paper, taking care not to damage the nitrate electrode membrane.	
G7.6	Repeat steps G7.1 to G7.5 for each sample in turn (note f).	(f) The time required for electrode equilibration will be reduced, and possible hysteresis effects will be avoided if, wherever possible, samples are analysed in ascending order of concentration.
	Calculation of Results	
G7.7	Determine the nitrate concentration from the potential, E_1 mV, and the calibration curve (Section G8). Report the results as mg/l (note g).	(g) Direct readout of concentration is available with some meters. See Section G8.4.
	Electrode Storage	
G7.8	Between batches of samples, store the nitrate-selective electrode in a standard solution within the normal concentration range of the samples. The reference electrode should be stored in water contained in a separate vessel.	
	Procedure 2 — Known Addition method	
G7.9	Proceed as in steps G7.1 to G7.4. Immediately upon completion of step G7.4 (but ignoring note e) inject, by micro-pipette, 0.2 ml of a 5000 mg/l nitrate standard solution (G5.5). Measure and record the new potential, E_2mV, when it has become constant to within 0.1 mV in 30 seconds (note e applies at this point).	
G7.10	Repeat step G7.9 for each sample in turn.	
	Calculation of Results	
G7.11	Determine the electrode's "slope factor", S, in mV per decadic change in concentration as detailed in G8.3 (note h).	(h) As an alternative, carry a 10 mg/l standard solution through step G7.9. Let the two potentials be E_3 and E_4. Then: $S = 2.096\,(E_3 - E_4)$
G7.12	Nitrate concentration of the sample = $\dfrac{20}{\left[1.004 \times \text{antilog}\left(\dfrac{E_1 - E}{S}\right)^2\right] - 1}$ mg/l	

Step	Procedure	Notes
	Electrode Storage	
G7.13	All as described in G7.8.	

G8 Preparation of Calibration Curve

(To be carried out with each batch of samples see also Section G10.4).

G8.1 Prepare three working standard nitrate solutions which encompass the expected range of sample nitrate concentrations, using Part A2.4.

G8.2 Proceed as in steps G7.1 to G7.4 for the three solutions, using the lowest concentration first. Note the temperature at the time of calibration.

G8.3 Plot a graph of the measured potentials, in mV, for the three solutions against the logarithm to base 10 of the concentration, in mg/l, of the solutions. The graph should be linear. The slope of the graph, S, should be evaluated in units of mV per decadic change of concentration, and should fall in the range 58.5 ± 2 for normal laboratory temperatures (ie 15–25°C). If this is not so, refer to the electrode's instruction manual.

G8.4 Some meters have the facility for giving a direct readout of concentration when used with ion-selective electrodes. Calibration is usually effected using three standard solutions, selected and prepared as given in G8.1. The meter's handbook should be consulted for full details.

G9 Changes in the Concentration Range of the Method

G9.1 This method has been tested in the range 1 to 50 mg/l. The calibration, however, is linear considerably above this range and, with suitable calibration standards to verify linearity, the method can be used for concentrations of up to 1000 mg/l.

G9.2 The method may also be used for concentrations below 1 mg/l, but in this case several closely-spaced standard solutions will be required for adequate definition of the calibration, which may become non-linear. In addition, at such low levels interferences from other ions may be difficult to overcome.

G10 Sources of Error

G10.1 As exemplified in Section G1, this method is prone to poor precision. A number of factors may combine to produce poor precision, and these are discussed in the following sections. Overall, it is particularly important with this method to work in a careful, reproducible fashion, the details of which can only be fully established by individual experience.

G10.2 **Nitrite interference**

If the samples contain sufficient nitrite to interfere (see section G3.2), add 0.1g of sulphamic acid to each 50 ml portion at step G7.1 of the procedure. Ensure dissolution is complete before continuing the procedure.

G10.3 **Chloride interference**

If the samples contain sufficient chloride to interfere (see section G3.2) modify the buffer composition by first diluting it ten-fold and then adding silver sulphate to give a concentration in the diluted buffer solution of 3 ± 0.1 g/l.

For Procedure 1, the experimental procedure and calculation of results remains the same, save that 25 ml of sample or standard and 25 ml of the modified buffer solution are used. However, note that a reference electrode bridge solution containing no chloride must be used, thus requiring a change to a mercury/mercurous sulphate reference electrode system.

For Procedure 2, the experimental procedure is modified as for Procedure 1. The calculation remains the same, but if the alternative method of determining S described

in note h is used the formula for S becomes:

$$S = 1.431\ (E_3 - E_4)$$

If the extra sample dilution necessary for this procedure is undesirable because the nitrate-nitrogen concentrations in the samples are low, it may be preferable to substitute the more expensive silver fluoride for the silver sulphate. In this case, the original buffer (G5.4) is used as in the original procedure (G7) and a volume of 0.014M silver fluoride solution is added to both standards and test portions. The volume is $H \times 10^{-2}$ ml, where H is the maximum concentration of chloride in the samples in mg/l.

G10.4 **Calibration Drift**

Providing the temperature of samples and standards are controlled to be within 1°C of each other, the slope of the calibration curve should remain constant throughout an analytical batch. However, the actual potentials given by the calibration standards may drift from their initial values. To guard against errors resulting from such drift the calibration should be checked with one of the calibration standards every 30 minutes, or after every 10 determinations, whichever is the sooner. In the event of drift being discovered, recalibration should be carried out immediately. Two other remedies are suggested in the following subsections.

G10.5 Drift may often result from improper maintenance of either of the electrodes. Always maintain and store the electrodes in accordance with the maker's instructions and with the additional information given in this method.

A well-maintained electrode system may drift because of an effect from a sample component. In this circumstance, the known Addition procedure (Procedure 2) is to be preferred.

G10.6 **Surface active material**

Complex effects arise with certain types of nitrate-selective electrode from the presence of organic matter, particularly anionic detergents at concentrations of above 1 mg/l as Manoxol OT. Attention must be paid to this possibility whenever samples containing these concentrations are to be analysed. In extreme cases it may not be possible to employ this method on such samples.

Method H For the Spectrophotometric Determination of Nitrite

H1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Reference 15)

H1.1	Substance determined:	Nitrite ion.
H1.2	Type of Sample:	Sewage effluents, raw and potable waters.
H1.3	Basis of Method:	Nitrite ions react with a reagent containing sulphanilamide and N–1–naphthylethylene diamine in dilute phosphoric acid. An azo-dye is formed and its concentration is determined spectrophotometrically.
H1.4	Range of application:	Up to 0.25 mg/l using the maximum sample volume of 40 ml. The range can be extended upwards by taking a smaller sample volume.
H1.5	Calibration Curve:	Linear to at least 0.25 mg/l (with the maximum sample volume of 40 ml).

H1.6 Total Standard Deviation[+]:

Sample Type Spiked with Sodium Nitrite	Sample Volume (ml)	Cell Size (mm)	Nitrite (N) (mg/l)	Total Standard Deviation (mg/l) (14 degrees of freedom)
Distilled water	40	40	0.000	0.0001 – 0.0003
.. ..	40	40	0.040	0.0002 – 0.0018
.. ..	10	10	0.40	0.003 – 0.009
.. ..	5	10	1.60	0.007 – 0.040
Sewage effluent	5	10	1.01	0.004 – 0.021
Sea water	40	10	0.20	0.001 – 0.003
River water	25	10	0.30	0.002 – 0.012

H1.7	Limit of detection[+]:	0.0001 to 0.002 mg/l.
H1.8	Sensitivity:	(1) 2.5 μg nitrite (N) = 0.66 absorbance units at 540 nm, 40 mm cell. (2) 10 μg nitrite (N) = 0.67 absorbance optical density units at 540 nm, 10 mm cell
H1.9	Bias[+]:	Inter-laboratory bias on stable samples containing no interfering substances was less than 1% and in most cases not significant. Sample instability may be a potential source of bias.

H1.10	Interferences:	Amines, oxidizing agents, chloramines, thiosulphate, hexametaphosphate, acids, alkalies and ferric iron may interfere (see Section H3). Compensation for colour and turbidity can be made (see H7.6).
H1.11	Time required for analysis+:	1–2 hr to analyse 20 samples.

+ This data was obtained from an interlaboratory exercise in which 5 laboratories participated.

H2 Principle

The method is based on the diazotization of sulphanilamide by nitrite in the presence of phosphoric acid, at pH 1.9, and the subsequent formation of an azo-dye with N-l-napthylethylenediamine (11)(12). The absorbance of this dye is measured at about 540 nm and is related to the nitrite concentration by means of a calibration curve.

H3 Interferences

The effect of other substances on the determination is shown in Table III

Table III (a)

Other substance (expressed in terms of substance in brackets)	Amount of other substance in a 40 ml sample aliquot µg	Effect in µg N of other substance at a nitrite amount, in the 40 ml sample aliquot, of		
		0.00 µg N	1.00 µg N	10.0 µg N
Magensium Acetate (Mg)	1,000	0.00	0.00	−0.07
Potassium Chloride (K)	100	0.00	0.00	−0.07
	1,000	0.00	−0.03	−0.13
Sodium Chloride (Na)	100	0.00	0.00	−0.02
	1,000	0.00	−0.01	−0.13
Sodium Bicarbonate ($CaCO_3$)	5,000	0.00	+0.03	+0.01
(b) *($NaHCO_3$)	*8,400			
	10,000	0.00	+0.03	+0.06
	*16,800			
Potassium Nitrate (N)	1,000	0.00	0.00	−0.06
Ammonium Chloride (N)	100	0.00	−0.01	−0.03
Cadmium Chloride (Cd)	10	+0.01	−0.03	−0.03
	100	0.00	−0.03	−0.03
Zinc Acetate (Zn)	10	0.00	+0.03	−0.09
	100	0.00	−0.04	0.00
Manganese Chloride (Mn)	10	0.00	+0.03	−0.07
	100	0.00	+0.04	−0.03
Ferric Chloride (Fe)	10	0.00	+0.04	−0.03
	100	0.00	−0.06	−0.51
Cupric Acetate (Cu)	10	−0.03	+0.03	−0.03
	100	−0.06	−0.06	−0.07
Aluminium Sulphate (Al)	100	0.00	0.00	−0.03
Sodium Silicate (SiO_2)	100	0.00	0.00	—
Urea ($CO(NH_2)_2$)	100	0.00	+0.04	−0.09
Hydroxylammonium Chloride ($HONH_3Cl$)	100	0.00	0.00	−0.01
Calgon (Sodium Hexametaphosphate)	50	0.00	−0.53	−0.10
$(NaPO_3)_6$	500	0.00	−0.80	−8.10
Sodium Thiosulphate ($S_2O_3^{=}$)	100	0.00	−0.03	−0.82
	1,000	0.00	0.00	−0.77

Other substance (expressed in terms of substance in brackets)	Amount of other substance in a 40 ml sample aliquot µg	Effect in µg N of other substance at a nitrite amount, in the 40 ml sample aliquot, of		
		0.00 µg N	1.00 µg N	10.0 µg N
Free Chlorine (Cl)	2	0.00	−0.22	−0.25
	20	−0.01	−1.01	−2.81
Chloramines (Cl)	2	0.00	−0.06	−0.07
	20	−0.01	−0.30	−2.78

If the other substances did not interfere, the effects would be expected (95% confidence) to be between:

± 0.02 at 0.00 µg N ± 0.08 at 1.00 µg N ± 0.14 at 10.0 µg N

(a) These data were obtained by Yorkshire Water Authority, SE Division

(b) $NaHCO_3$ values were amounts added, $CaCO_3$ values are the conventional alkalinity equivalent values.

H4 Hazards

N-1-napthylethylenediamine dihydrochloride should be regarded as a special hazard. Skin contact with the solid and solution containing it should be avoided.
Normal precautions to avoid skin contact and/or ingestion should be taken in the handling of all the other reagents.

H5 Reagents

Analytical grade reagents should be used whenever possible. See Part A2.1 regarding water.

H5.1 **Sulphanilamide reagent**

Dissolve 40.0 ± 0.5g of sulphanilamide in a mixture of 100 ± 1 ml of orthophosphoric acid (87% m/V) and 500 ± 50 ml water contained in a beaker. Dissolve 2.0 ± 0.2g of N-1-naphthylethylenediamine dihydrochloride in the resulting solution. Transfer to a 1 litre calibrated flask and make to volume with water. Mix well and store in a stoppered amber glass bottle. The reagent is stable for 1 month when stored at 4°C and brought to room temperature immediately prior to use.

H5.2 **10% V/V Orthophosphoric acid solution**

Add 25.0 ± 0.2 ml of orthophosphoric acid (87% m/V) to 150 ± 25 ml water. Mix and cool to 20 ± 2°C. Transfer the solution to a 250 ml calibrated flask and make to volume with water. Stored in an amber bottle, the reagent is stable for 1 month.

H6 Apparatus

H6.1 General

All glassware should be cleared using 10% (V/V) hydrochloric acid followed by thorough rinsing with water.

H6.2 **Spectrophotometer**

A spectrophotometer capable of operating at 540 nm and of accommodating 10 mm and 40 mm pathlength cells.

Alternatively an absorptiometer with a filter having a transmittance maximum at about 540 nm can be used, but a reduction of sensitivity and precision may result.

Step	Procedure	Notes
	Analysis of Samples	
H7.1	Pipette up to 40 ml of sample (containing up to 10 μg nitrite nitrogen) into a 50 ml calibrated flask. Let the volume of sample taken be Vml. Add water (if necessary) to give a total volume of 40 ± 2 ml (note a).	(a) This step is important, for too low a pH value may otherwise result during diazotization.
H7.2	Add 1.00 ± 0.05 ml of sulphanilamide reagent. Mix immediately by swirling.	
H7.3	Dilute with water to the mark. Mix and allow to stand (note b).	(b) The pH value must be 1.9 ± 0.1 at this stage. See sections H10.1 and H10.2.
H7.4	Prepare a blank by treating 40 ± 2 ml of water as described in step H7.2 and H7.3.	
H7.5	Measure the absorbance of the sample and blank solutions against water in the reference cell using a spectrophotometer at a wavelength of 540 nm (notes c and d) between 30 minutes and 120 minutes after step H7.3. Let the absorbance of the sample solution by A_s and that of the blank solution A_b (note e).	(c) The wavelength of the absorbance maximum should be checked for each individual instrument. This wavelength should be used for all subsequent measurements. (d) Do not interchange the reference and sample cells unless they have been shown to be an optically matched pair. (e) Over the range 10°C–25°C the effect of temperature on the time for full colour development is given in the following table:

Development Time (Mins)	Percent colour development		
	10°C	18°C	25°C
15	95	96	96
30	96	99	100
60	100	100	100

The blank value increases with increasing temperature and blanks and samples should not differ by more than 2°C.

Compensation for colour and/or turbidity in the sample

H7.6 If such interference is suspected, treat a duplicate sample as in step H7.1. Then add 1.00 ± 0.05 ml of 10% V/V phosphoric acid and continue as described under H7.3 to H7.5. Let the absorbance obtained be Ac.

Calculation of results

H7.7 Calculate the absorbance, A_r, due to nitrite in the sample from:
$A_r = A_s - A_b$
or when a correction for colour and turbidity (step H7.6) has been made:
$A_r = A_s - A_b = A_c$.

H7.8 Determine the mass of nitrite (as N), M μg in the sample from A_r and the calibration curve.

H7.9 Nitrite concentration in the sample

$$= \frac{M}{V} \text{ mg/l}$$

H8 Preparation of Calibration Curve

(To be carried out for each batch of new reagents)

H8.1 Into a series of 50 ml graduated flasks add (by means of a 10 ml micro burette) the volumes of nitrite solution (Part A2.7) shown in the table below.

ml of Solution A2.7	μg Nitrite (N)	Cell size (mm)
0.00	0.00 (Blank)	10 & 40
0.50	0.50	40
1.00	1.00	10 & 40
1.50	1.50	40
2.00	2.00	40
2.50	2.50	10 & 40
5.00	5.00	10
7.50	7.50	10
10.00	10.00	10

H8.2 Add water to give a volume of 40 ± 2 ml in each flask.

H8.3 Continue as under procedure steps H7.2 to H7.5.

H8.4 Subtract the absorbance of the blank solution from the absorbances obtained for all other standards. For each cell size plot the corrected absorbances against the μg of nitrite (N) added. The calibration curve is normally linear and passes through the origin.

H9 Change in Concentration Range of the Method

The method permits the determination of up to 0.250 mg/l using the full sample volume of 40 ml. Smaller sample aliquots may be taken in order to extend considerably the concentration range of the method; examples of this extension and its precision are to be found in Section H1.6, but the analyst should check the precision of whatever variation is used.

H10 Sources of Error

H10.1 If the alkalinity of the sample is high, such that a pH value of 1.9 ± 0.1 is not attained at stage H7.3 additional 10% V/V phosphoric acid should be added prior to step H7.2. The method will tolerate an alkalinity of at least 250 mg/l as $CaCO_3$ when 40 ml of sample is used.

H10.2 In the unlikely event that the acidity of the sample be high, prior neutralization with sodium hydroxide solution may be necessary in order to comply with step H7.3.

H10.3 **Interfering substances** — see Section H3.

Method J The Determination of Nitrite by Titration Tentative Method

J1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see Reference 15)

J1.1	Substance determined:	Nitrite.
J1.2	Type of Sample:	Effluents and polluted water.
J1.3	Basis of Method:	Addition of a known excess of sulphanilic acid and back titration with sodium nitrite solution.
J1.4	Range of application:	Up to 100 mg/l using the maximum sample volume of 400 ml.

J1.5 Standard Deviation (within batch) for standard solutions (a)

Nitrite Concentration mg/l	Standard Deviation mg/l	Degrees of of Freedom
6.9	0.372	7
13.8	0.313	5
20.7	0.350	4
37.6	0.313	5
34.5	0.313	5
51.75	0.375	3
69.0	0.313	5

J1.6	Limit of detection:	2 mg/l
J1.7	Bias:	None detected. Sample instability may be a potential source of bias.
J1.8	Interferences:	Aromatic amines may interfere
J1.9	Time required for analysis:	About 30 minutes per sample.

(a) Data from ICI Organics Division, Blackley.

J2 Principle

The nitrite in a measured volume of sample is reacted under acid conditions, in the presence of sodium bromide as catalyst with a known excess of sulphanilic acid. The reaction temperature must be kept below 15°. The unreacted sulphanilic acid is titrated with standard sodium nitrite solution with either visual or electrometric end point detection.

J3 Interferences

The only likely interferences are from aromatic amines.

J4 Hazards

Normal precautions to avoid skin contact and/or ingestion should be taken on the handling of all the reagents.

J5 Reagents

Analytical grade reagents should be used whenever possible. See Part A2.1 regarding water.

J5.1 1M sodium carbonate solution

Dissolve 106 ± 1g of sodium carbonate in about 900 ml of water and dilute to 1 litre in a measuring cylinder. Store in a glass or polyethylene bottle.

J5.2 Sulphanilic acid solution

Dissolve 86.6 ± 0.1g of sulphanilic acid (dried at 105°C for at least two hours) by boiling with about 400 ml of water and sufficient 1M sodium carbonate solution (J5.1) to make the solution faintly alkaline to brilliant yellow indicator paper. Filter the hot solution, cool, and transfer to a 1 litre calibrated flask. Dilute to 1 litre with water and mix well. Store in an amber glass bottle.

J5.3 Standard 0.5M sodium hydroxide solution

Dissolve 20.00 ± 0.05g of sodium hydroxide stick in about 800 ml of water. Allow the solution to cool to room temperature, then dilute to 1 litre with water in a calibrated flask. Standardize the solution by normal alkalimetric procedures. Store in a screw-capped polyethylene bottle.

J5.4 0.5% m/V phenolphthalein indicator solution

Dissolve 0.5g of phenolphthalein in 50 ± 1 ml of water and 50 ± 1 ml of industrial methylated spirits Store in a glass bottle.

J5.5 Hydrochloric acid d_{20} 1.18.

J5.6 Starch iodide indicator paper.

J5.7 Sodium bromide.

J5.8 10% V/V nitric acid solution

Dilute 100 ± 1 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder. Store in a glass or polyethylene bottle.

J5.9 0.5M sodium nitrite solution

Dissolve 34.5 ± 0.5g of sodium nitrite in water contained in a 1 litre calibrated flask, make up to volume with water and mix well. Standardize the solution as follows:

Weigh about 4g (the exact weight is not required) of sulphanilic acid into a 1 litre beaker; dissolve by boiling in 250 to 300 ml of water. Cool and titrate immediately with standard 0.5M sodium hydroxide using 0.3 ml of 0.5% phenolphthalein solution as indicator. Record the volume, A_S ml, of standard sodium hydroxide solution used in the titration.

Dilute the neutralized solution to 800 ml with water and cool to a maximum temperature 15°C. Add 25 ml of hydrochloric acid, and titrate immediately with the sodium nitrite solution to be standardized. Add the titrant in a steady stream, with gentle stirring, to within 1.0 ml of the necessary amount calculated from the alkali titration and finish the titration by adding the nitrite solution 0.1 ml at a time until an immediate faint blue colour is obtained on spotting a drop of the titrated solution on starch-iodide paper five minutes after the last addition of nitrite. Record the volume, B_S ml, of sodium nitrite solution used in the titration.

Carry out a blank titration on 800 ml water, 25 ml of hydrochloric acid J5.5 and the same amount of 0.5M sodium hydroxide, A_s ml, that was required to neutralize the

sulphanilic acid. Record the volume, C_S ml, of sodium nitrite solution used in this blank titration.

Note that addition of sodium bromide as catalyst is not necessary in this standardization procedure.

Factor, F, of the sodium nitrite solution $= \frac{A_S}{B_S - C_S}$

J5.10 **0.1M sodium nitrite solution**

Pipette 50 ml of a standardized 0.5M sodium nitrite solution J5.9 into a 250 ml calibrated flask. Make the volume up with water and mix. Prepare this reagent freshly each day. (Note, the factor F (J5.9) also applies to this solution).

J6 Apparatus

J6.1 Only normal laboratory apparatus is required for the method when visual end point detection is used. Electrometric end point detection requires additional apparatus as follows:

Two 50 mm^2 platinum foil electrodes.

Magnetic stirrer and plastic covered stirrer bar.

A 1.5 volt dc power source (eg 1.5 volt dry battery)

Potentiometer.

Galvanometer: A taut suspension mirror instrument with high resistance coil, preferably fitted with a variable shunt.

J7 Analytical Procedure

Step	Procedure	Notes
	Visual End Point Detection	
J7.1	Transfer a measured volume, Vml, of the sample (note a) to a 600 ml beaker. Dilute to 400 ml, if necessary. Add 10.00 ± 0.05 ml sulphanilic acid solution and 5.0 ± 0.1g of sodium bromide (note b). Stir to dissolve.	(a) The volume must not exceed 400 ml, and must not contain more than 40 mg nitrite nitrogen. (b) Sodium bromide is added to catalyse the diazotisation reaction when analysing samples. It can be omitted in standardization procedures. See Section J5.9.
J7.2	Cool the solution to below 15°C and add 10.0 ± 0.1 ml of hydrochloric acid. Stir to mix (note c)	(c) The solution must be stirred gently to avoid stirring air into it.
J7.3	Titrate the solution with 0.1M sodium nitrite (J5.10). The end point is reached when an immediate blue colour is still obtained when a drop of the titrated solution is spotted onto starch iodide paper 5 minutes after the last addition of titrant. (Notes d and e). Note the volume of titrant added. A ml.	(d) The 5 minutes standing at the end point is to allow completion of the diazotisation reaction. (e) The titrant should be added in 0.1 ml increments at the time.
J7.4	Carry out a blank titration under the same conditions, using 400 ml of water instead of sample.	
J7.5	Note the volume of titrant added. B ml.	
	Electrometric End Point Detection	
J7.6	Proceed as in Step J7.1 but limit V to 150 ml. Cool the solution to 15°C.	

J7.7 Immerse the electrodes in the solution, positioned so they are 15 mm apart. (Note f). Apply a potential of 50 mV across them. Balance the galvanometer.

J7.8 Add 10.0 ± 1 ml of hydrochloric acid (J5.5). Stir magnetically to mix (note g).

J7.9 Titrate the solution with 0.1M sodium nitrite solution (J5.10), making slow additions while stirring magnetically. The end point is reached when a permanent galvanometer deflection is observed indicating depolarization of the electrodes. Note the volume of titrant, A ml.

J7.10 Carry out a blank titration under the same conditions, using 150 ml of water in place of the sample. Note the volume of titrant, B ml.

Calculation of Results

J7.11 Nitrite concentration in the sample

$$= \frac{(B - A) \times 1400 \times F \text{ mg/l}}{V}$$

where: A = volume, in ml, of 0.1M sodium nitrite required in the sample titration.

B = volume, in ml, of 0.1M sodium nitrite required in the blank titration.

V = volume, in ml, of sample taken for the test.

F = factor for 0.5M sodium nitrite solution (J5.9).

(f) The electrodes should be cleaned before use by immersion in boiling 10% V/V nitric acid solution.

(g) The solution must be stirred gently to avoid air entrainment.

J8 Calibration

Calibration is effected by the standardization of the sodium nitrite solution as described in Section J5.9.

J9 Sources of Error

J9.1 The method is subject to the usual possible errors of any titration procedure. The analyst must take whatever precautions are appropriate to the particular analytical requirements.

J9.2 Visual detection of the end-point may be difficult in some samples. The use of the electrometric method will avoid this difficulty.

K Checking the Accuracy of Analytical Results

Once the methods have been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of a nitrate or nitrite such as potassium nitrate or sodium nitrite of suitable concentration 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. For more detailed information on the types of test available and the interpretation of their results, standards texts — such as those published by the Water Research Centre (14) and by the DOE/NWC Standing Committee of Analysts (15) — should be consulted.

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Estimation of the Accuracy of Analytical Results using the Tentative Methods in this Booklet

Before firmly recommending the tentative 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 any of these methods could estimate the accuracy of its own analytical results and report the findings to the Technical Secretary of the General Non-Metallic Substances Working Group* of the DOE/NWC Standing Committee of Analysts, together with full details of the precise method used.

The precision achieved is of particular interest. The value of this information would be greatly enhanced if it were obtained at the same determinand concentrations as those for which some information has already been gained, as set out in the Performance Characteristics sections of these methods.

Similar information at other determinand concentrations, and for sample types other than those already studied, would also be of great assistance. Detailed specifications for the tests to be carried out are beyond the scope of this booklet, but standard texts — such as those published by the Water Research Centre (14) and by the DOE/NWC Standing Committee of Analysts (15) — provide guidelines from which precision tests may be designed. The same texts also provide guidelines for interference and recovery tests and any information on these matters would be gratefully received.

* Results should be sent to:
The Secretary
The General Non-Metallic Substances Working Group
The Standing Committee Analysts
The Department of the Environment
2 Marsham Street
London
SW1P 3EB
England

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The British Standards Institution provided figure 1. As the SCA panel which produced this booklet is also the BSI sub-committee for the same determinands, the consequent exchange of ideas with both BSI and ISO TC 147 SC2 WG1 is gratefully acknowledged. However, though often similar to methods being considered by ISO, the methods are not identical.

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Address for Correspondence

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

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The Standing Committee of Analysts
The Department of the Environment
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