Ammonia in Waters 1981

Methods for the Examination of Waters and Associated Materials

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Contents

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Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

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

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or 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 occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by t' Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9TB. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

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

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

A General Information

A1 Introduction to the Methods

Most waters contain ammonium salts ("saline ammonia") and free ammonia in equilibrium with each other:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

This equilibrium is extremely dependent on pH – with high pH favouring the formation of free ammonia – and, to a lesser extent, on temperature, pressure and ionic concentration (or salinity) of the water.

The total concentration of the two species, more usually termed the "ammoniacal nitrogen" or "total ammonia" concentration, is generally understood to be the determinand in methods for the determination of "ammonia" in water, and is so in all the methods given in this booklet. Where it is required, differentiation between the two species can be made from the total ammonia concentration using published information. See references 1 and 2.

In reporting ammonia concentrations, the customary United Kingdom practice is to refer to the concentration in terms of the element, N. This practice is used throughout this booklet.

Six methods for the determination of ammonia are given, with the intention of providing one or more methods for application to any type of sample. Table A1 gives a comparison between the methods which, in conjunction with the Performance Characteristics sections of the methods themselves, should enable the analyst to select the most appropriate method for a particular sample type.

The manual spectrophotometric methods for ammonia (Parts D and E) are based on the well known reaction in which monochloramine, formed by reaction of ammonia and hypochlorite reacts with a phenol to form an indophenol blue compound. However, a method using salicylate gave performance characteristics similar to those obtained with a method using phenol itself, and the added advantages of great reagent stability and more pleasant handling characteristics. It is the preferred method for all except saline samples. (See also Sections D2 and F2).

Because the high concentration of magnesium normally present in seawater would be partially precipitated at the high pH value required for stable colour formation in the salicylate-based method, a phenol-based method, with a lower operating pH value, is preferred for the analysis of seawater samples. This is described in Part E. However, the salicylate chemistry can be modified in order to deal with some seawaters and estuary waters by increasing the concentration of the sodium citrate added as a complexing agent. See Section F3.2.

The specifications for the automated ammonia methods (Parts F and G) reflect the foregoing considerations. However, separate chemistries, based on salicylate and on phenol and designated S and P Chemistries respectively, are provided in Part F. See Section F2.

A2 Sample Collection and Preservation

These instructions are common to all methods.

A2.1 Samples can be collected in either glass or polyethylene containers. They should be analysed as soon as possible after sampling, but if this should not be possible, storage at 4°C is recommended in order to minimize ammonia concentration changes.

A2.2 Where delays in analysis are inevitable, and as an alternative to refrigeration, the sample may be brought to pH2 with hydrochloric acid (d_{20} 1.18). The sample must be neutralized immediately prior to analysis with concentrated sodium hydroxide solution known to be free from ammonia. Differentiation between the forms of ammonia present in the preserved sample is not possible following such pretreatment.

This method was effective in preserving the concentration of a sewage effluent at 0.8 mg/l for at least four weeks. (Information from Thames Water Authority).

A2.3 Samples containing suspended matter should be allowed to settle prior to analysis, or preferably filtered through a glass fibre or membrane filter. However, note that ammonia can be absorbed during filtration. The filter medium must first be checked in this respect.

Alternatively, and particularly for highly coloured and/or turbid samples, the distillation procedure given in Part B should be followed for preliminary separation of ammonia, recognising that ammonia associated with particulate matter may thus be recovered.

A2.4 Samples containing free chlorine should be dechlorinated at the time of sampling by the addition of a small crystal of sodium thiosulphate.

Table A1 Comparison of Methods

Method	Titration	Potentiometric Probe	Spectrophotometry (Salicylate/DIC)	Spectrophotometry (Phenol/DIC)	Continuous Flow (Both chemistries)	Continuous Flow (Phenol/DIC)
Part	B	C	D	E	F	G
Type of Sample	All, except saline	All	All, except saline	Saline	All, except saline	Saline
Tested Range mg/l (a)	Up to 40	Up to 50	Up to 5.0	Up to 0.62	Up to 40	Up to 0.140
Upper Range Limit (b)	10 mg in sample aliquot	100 mg/l	0.04 mg in sample aliquot	0.05 mg in sample aliquot	50 mg/l without prior dilution	1 mg/l without prior dilution
Maximum Concentration using Maximum Sample Aliquot	30 mg/l	100 mg/l	1 mg/l	1 mg/l	50 mg/l	1 mg/l
Maximum sample Aliquot ml	350	—	40	50	—	—
Limit of Detection mg/l	0.2	<0.5	0.003–0.008	0.006	0.009	0.0013
Time Required for Analysis (c)	30 minutes per sample	About 3 minutes per sample, dependant upon concentration	1-2 hours for 9 samples	3 hours for 30 samples	Up to 60 samples per hour	Up to 40 samples per hour
Comments	Best suited to polluted waters. Potential interference from volatile bases	Relatively poor precision. For use as a sorting test or for continuous monitoring	All these methods offer good precision and high sensitivity.			

(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 for the stated number of samples. Note that these times are intended only as a guide.

A3 Standard Solutions and Reagents Common to the methods

A3.1 Ammonia free water

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 Part B6.1 to B6.5). Discard the first 50 ml of distillate, then collect and store the rest of the distillate as described in method A above. Do not go to dryness nor allow solid to form on the walls of the distillation flask.

Testing:
Carry 500 ml of the water under test through the distillation procedure, steps B6.1 to B6.12 but omitting the addition of 350 ml of water in step B6.9. Collect only 100 ml of distillate in a 100 ml calibrated flask and determine ammonia concentration in the

distillate by whichever method is to be used for analysis of samples. The concentration in the water under test is given by 0.2Z mg/l where Z is the result in mg/l. If, in the analysts judgement, this concentration is significant, an appropriate correction should be applied. Preferably, ammonia should not be detected at all in the distillate.

A3.2 **Low-ammonia seawater**

In order to avoid problems with differing refractive indices and ionic strength between blanks and samples in determinations on saline waters, seawater known to be low in ammonia should be used. This may most reliably be obtained far from land, or in coastal waters known to be free of sewage effluent. Test this seawater as described in Section A3.1 to establish its ammonia concentration.

A3.3 **Stock Standard Ammonia Solution A.** 1 ml contains 1 mg NH_3 as N

Dissolve 3.819 ± 0.005 g of ammonium chloride (dried at 105°C for at least two hours) in about 800 ml of ammonia-free water (Section A3.1). Dilute to 1000 ml with ammonia free water in a calibrated flask. Store the solution in a stoppered glass bottle for not more than one week.

A3.4 **Standard Ammonia solution B.** 1 ml contains 10 μg NH_3 as N

Pipette 10 ml of stock standard solution A3.3 into a 1000 ml calibrated flask. Make up to volume with ammonia-free water (Section A3.1) and mix. Store the solution in a stoppered glass bottle for not more than one week.

A3.5 **Standard Ammonia Solutions C**

The following table A2 details the preparation of working standard solutions which may be required for calibration of methods. Use pipettes and calibrated flasks for all dilutions, and store the solutions in stoppered glass bottles for not more than two days.

Table A2 Preparation of Standard Ammonia Solutions (A3.5)

Standard Solution	Volume for dilution to 1000 ml ml	Ammonia Concentration of resulting solution mg/l
A3.3	50	50
A3.3	40	40
A3.3	30	30
A3.3	20	20
A3.3	10	10
A3.3	5	5
A3.3	2.5	2.5
A3.4	100	1
A3.4	80	0.8
A3.4	60	0.6
A3.4	50	0.5
A3.4	40	0.4
A3.4	20	0.2
A3.4	10	0.1
A3.4	5	0.05

A3.6 **Standard Ammonia solutions for seawater analysis**

Standard solutions should be prepared from the stock standard ammonia solution A3.3 as described in sections A3.4 and A3.5 but using low-ammonia seawater (section A3.2) instead of ammonia-free water for dilution.

A3.7 **Cleaning Solution**

Dissolve 100 ± 2 g of potassium hydroxide in 100 ± 2 ml of water. Cool the solution and add 900 ± 50 ml of industrial methylated spirits. Store in a polyethylene bottle. THIS REAGENT IS TOXIC.

A4 General Remarks on Apparatus

All apparatus coming into contact with samples of standards in these methods should be free from ammonia. This is particularly important in the determination of low concentrations. Except where alternative methods are stated, all such apparatus should be cleaned using cleaning solution (section A3.7), thoroughly rinsed in ammonia free water (A3.1), and thereafter reserved solely for ammonia determinations.

B Tentative Method for the Determination of Ammonia by Titration

B1 Performance Characteristics of the Method

B1.1	Substance determined:	ammonia and ammonium ion.
B1.2	Type of Sample:	raw, potable and waste waters.
B1.3	Basis of Method:	after neutralization, the sample is made alkaline by the addition of magnesium oxide. The ammonia is distilled into indicating boric acid and titrated with standardized hydrochloric acid.
B1.4	Range of application	0.07 – 10 mg ammonia in the sample aliquot taken.
B1.5	Calibration graph:	Not applicable.

B1.6 Total Standard Deviation (a):

Sample Type	Volume of Sample ml	Concentration (mg/l)	Standard Deviation mg/l	Degrees of Freedom
Standard Solution	250	4	0.23	10
Standard Solution	250	40	0.56	11
Settled Sewage	100	35	0.70	16
Sewage Effluent	250	1.8	0.16	11

B1.7	Limit of Detection (a):	0.2 mg/l (4 degrees of freedom) using 250 ml sample.
B1.8	Sensitivity:	1.0 ml of 0.02 M hydrochloric acid is equivalent to 2.8 mg/l, using a 100 ml sample.
B1.9	Bias	No information apart from that arising from the presence of interfering species.
B1.10	Interferences:	Volatile amines. Amides such as urea may be hydrolysed to yield ammonia. See Section B3.
B1.11	Time Required for Analysis:	30 minutes (total analytical and operator time)

(a.) These data were obtained by the North West Water Authority.

B2 Principle

The pH value of the sample is first adjusted to be within the range 6.0 to 7.4. Magnesium oxide is then added to provide mildly alkaline conditions, and the liberated ammonia is distilled into indicating boric acid solution for subsequent titration with standard hydrochloric acid.

For work at low concentrations of ammonia, distillation may instead be into dilute hydrochloric acid for subsequent determination by the spectrophotometric method (Part D) or the Continuous Flow method (Part F).

B3 Interferences

Volatile amines, including hydrazine, will distil concurrently with the ammonia and will thus interfere by consuming the titrant acid.

Certain amides, such as urea, may be slowly hydrolysed to produce ammonia. Up to 10 mg of urea can be tolerated in the Sample aliquot.

B4 Reagents

Analytical grade reagents should be used whenever possible. All water used in this method must be ammonia-free (Part A3.1).

B4.1 **Standard 0.02 M Hydrochloric acid**

Prepare and standardize this reagent according to standard analytical procedures reference 3. Let the exact concentration be C moles per litre.

B4.2 **0.05% m/V Methyl red indicator solution**

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

B4.3 **0.15% m/V Methylene blue solution**

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

B4.4 **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 solution and 2.0 ± 0.2 ml of methylene blue solution. Dilute to 1 litre with water 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 reagent should be sufficient to change the colour from purple to green; if this is not so, discard the solution and prepare freshly.

B4.5 **0.05% m/V Bromothymol blue Indicator solution**

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

B4.6 **1% V/V Hydrochloric acid solution**

Dilute 10 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder. Store in a glass or polyethylene bottle.

B4.7 **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 to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

B4.8 **Light Magnesium oxide,** carbonate-free

Ignite magnesium oxide at 500°C to remove carbonates.

B4.9 **Antibumping granules**

B4.10 **Antifoaming agent**

Chips of paraffin wax are suitable.

B4.11 **Nessler's reagent**

NOTE: THIS REAGENT IS TOXIC. All residues containing it from operations described in the methods must be collected and subjected to a mercury recovery procedure (4) before final disposal.

Solution 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).

Solution B

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

Combine the 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.

* The solubility of mercuric chloride varies widely with temperature from about 30 g/l at 0° to about 610 g/l at 100°. It is about 50–80 g/l at room temperature.

B5 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.

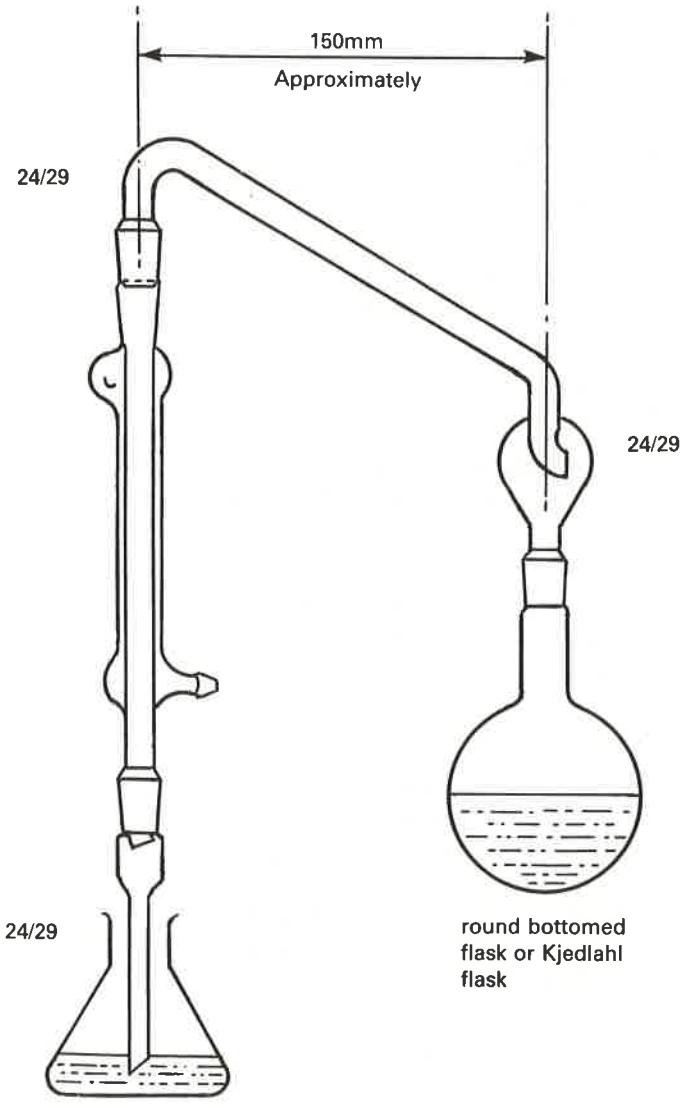


Fig 1 Distillation apparatus for ammonia determination

Diagram Courtesy of the British Standards Institution

B6 Analytical Procedure

Step	Procedure	Notes
	Checking the apparatus (note a)	
B6.1	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 an ammonia concentration high (in the analyst's judgement) in comparison to the concentrations usually determined. For determinations at low levels, some analysts prefer to carry out these steps on all apparatus before each determination.
B6.2	Commence distillation and after a few milli-litres 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.	
B6.3	Add to the cylinder containing the distillate 2.0 ± 0.2 ml of Nessler's reagent.	
B6.4	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.	
B6.5	Continue to collect and test portions of the distillate until adequate freedom (in the analyst's judgement) from ammonia is indicated.	
B6.6	Empty the flask, but do not rinse it. The apparatus is now ready for the distillation of samples.	
	Distillation of Samples	
B6.7	Measure 50 ± 5 ml of Indicating boric acid solution into the receiving flask (note b). Position the flask so that the condenser tip is submerged in the acid.	b. Hydrochloric acid must be substituted if the spectrophotometric methods are to be used. See Section B9.
B6.8	Transfer a volume, V ml, of the sample to the distillation flask. The volume should not exceed 350 ml and should contain not more than 10 mg NH_3 as N.	
B6.9	Add a few drops of bromothymol blue indicator. If a yellow colour is obtained, add sodium hydroxide solution (B4.7) until the colour just changes to blue. If a blue colour is first obtained, add hydrochloric acid solution (B4.6) until the colour just changes to yellow. Then, if necessary, adjust the volume of the flask contents to about 350 ml with water.	
B6.10	Add 0.25 ± 0.05g light magnesium oxide to the distillation flask and immediately attach the flask to the distillation apparatus (note c)	c. Anti-foaming agent may be necessary with certain waste waters or sewages.

Step	Procedure	Notes
B6.11	Heat the flask so that distillation proceeds at a rate of about 10 ml/min. Distil a total volume of 200 ± 20 ml. Lower the receiver flask to prevent the contents being drawn into the condenser when heat is removed.	
B6.12	Having collected 200 ± 20 ml of distillate, titrate with standard 0.02M hydrochloric acid to a purple end point (note d). Record the volume, A ml, of standard acid used.	d. 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.
	Blank determination	
B6.13	Carry out a blank distillation using 350 ml of water instead of the sample. Record the volume of 0.02M hydrochloric acid used (B ml).	
	Calculation of Result	
B6.14	Ammonia mg/l NH_3 as N $= \frac{A-B \times 14.01 \times 1000 \times C}{V}$ where V = volume of sample used; 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.	

B7 Calibration

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

B8 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.

B9 Spectrophotometric Determination of Ammonia

Following the Analytical Procedure in Section B7 through to step B7.12, but substituting hydrochloric acid (B4.6) for the Indicating boric acid at step B6.7. Having collected 200 ± 20 ml of distillate, make up to 500 ml with water in a calibrated flask. Determine the ammonia concentration of this solution by either the manual spectrophotometric method (Part D) or the continuous flow method (Part F). Let the ammonia concentration thus determined by Z mg/l.

Then ammonia in the sample is calculated from

$$\frac{500Z \text{ mg/l}}{V}$$

Where V in the volume in ml of sample taken for distillation (step B6.8).

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 Ammonia present in distilled water will cause errors. Carefully observe the procedure given in Section A3.1 to ensure freedom from this error.

B10.3 Care should be taken to avoid losses of ammonia during distillation. If there is any question of such losses occurring, carry a standard ammonia solution through the procedure and check recovery.

B10.4 Interfering substances. See Section B3.

C Tentative Method for the Determination of Ammonia Using an Ammonia Potentiometric Probe

C1 Performance Characteristics of the Method

C1.1	Substance determined:	ammonia and ammomium ion.
C1.2	Type of Sample:	Saline and non-saline waters, effluents and sewage.
C1.3	Basis of Method:	Reaction with alkaline reagent to form ammonia whose concentration is measured potentiometrically.
C1.4	Range of application:	0.5 to 50 mg/l (Concentrations below 0.5 mg/l and above 50 mg/l can be measured by slight modification. See section C8).
C1.5	Calibration graph:	Linear (when plotted on semi-logarithmic paper)

C1.6 Total Standard Deviation (a):

Type of sample	Ammonia concentration mg/l	Total Standard deviation (mg/l)
Standard solution (b)	0.5	0.01 (c)
(b)	2	0.05 (c)
(b)	25	0.02–1.2(d)
Sea water (spiked)	0.5	0.01 (e)
River water	3	0.05–0.4(d)
Sewage effluent	3	0.04–0.5(d)
Sea water (spiked)	5	0.1 (e)
Sewage effluent	8	0.06–0.5(d)
Sea water (spiked)	50	1.3 (e)

C1.7	Limit of Detection:	About 0.2 mg/l. See Section C8. (Defined as the limit of Nernstian response under the conditions of the method)
C1.8	Sensitivity:	About 59mV per decadic change of ammonia concentration.
C1.9	Bias:	Sample instability, high ionic strength, and the presence of interferences may give rise to biased results.
C1.10	Interferences	Volatile amines and organic substances which readily form ammonia or volatile amines under alkaline conditions are positive interferences (see Section C3).
C1.11	Time required for analysis	30 minutes for calibration and analysis of a single sample, 3 minutes for subsequent samples.

(a) Each estimate has approximately 9 degrees of freedom.
(b) Solution of ammonium chloride in distilled water.
(c) These data were obtained at the Central Electricity Research Laboratories.
(d) The range of estimates from 3 laboratories in the North West Water Authority is given.
(e) These data were obtained at the MAFF Fisheries Laboratory.

C2 Principle

The sample is treated with an alkaline buffer solution to liberate ammonia and sequester metals which might otherwise complex with ammonia. The ammonia diffuses through a gas permeable membrane of an electrode altering the pH value of its internal solution. This change in pH value is sensed by a pH electrode. The concentration of ammonia is obtained using either a pH/millivoltmeter and graph paper, or a selective ion meter. See References 5, 6 and 7 for general information on this type of method.

C3 Interferences

C3.1 There is little detailed information concerning the effect of interfering substances on the method. Generally, no important interference problems are likely with unpolluted saline and fresh waters; but the effect of interferences should be particularly considered in polluted samples. The most likely sources of interferences are discussed in the following sections.

C3.2 The response of the electrode is affected by transfer of water vapour through the membrane if there is an osmotic pressure difference across the membrane. For waters whose total concentration of dissolved species is less than 0.1M the error should not be appreciable.
For sea water samples separate standard, alkaline buffer and internal filling solutions are recommended, so errors will not be appreciable.
For other samples the error could be appreciable, but it might be possible either to dilute the samples until the total concentration of dissolved species is less than 0.1M or to modify the standard, alkaline buffer and internal filling solutions to minimize the osmotic pressure differences.

C3.3 The effect of some other nitrogen containing substances on the determination of ammonia by the electrode method is shown in table C1.

Table C1

Other substances	Concentration in mg/l of other substance	Effect in mg/l of the other substance at ammonia concentration of 1 mg/l
Hydrazine (as N_2H_4)	4	+ 0.06
Cyclohexylamine	1	+ 0.03
Morpholine	10	+ 0.03
Octadecylamine	0.4	+ 0.14
Urea	11	less than + 0.01

C3.4 Surface active agents and some organic solvents reduce the life time of the electrodes membrane. High concentrations of these substances may result in electrode failure.

C4. Hazards

There are no special hazards with this method other than those associated with the preparation and handling of very alkaline solutions.

C5. Reagents

Analytical grade reagents should be used whenever possible.

C5.1 Alkaline buffer solution

Dissolve 40 ± 0.2g of sodium hydroxide and 37.2 ± 0.2g of ethylenediaminetetraacetic acid disodium salt in about 900 ml of water and dilute with water to 1 litre in a measuring cylinder. Store the solution in a polyethylene bottle. See also Section C8.3.1.

C5.2 Electrode storage solution (0.1M ammonium chloride solution)

Dissolve 5.4 ± 0.1g of ammonium chloride in about 900 ml of water and dilute with water to 1 litre in a measuring cylinder. Store the solution in a glass bottle.

C5.3 **Sea water buffer solution**

Dissolve 16 ± 0.2g of sodium hydroxide and 400 ± 4g of trisodium citrate dihydrate in about 900 ml of water and dilute with water to 1 litre in a measure cylinder. Store the solution in a polyethylene bottle. See also Section C8.3.1.

C5.4 **Electrode internal filling solution for sea water analysis**

Dissolve 3.94 ± 0.02g of ammonium chloride in about 90 ml of water and dilute with water to 100 ml in a calibrated flask. Dissolve 0.1 ± 0.01g of silver nitrate in 100 ± 10 ml of water and add 0.1 ± 0.01 ml of this solution to the flask containing the ammonium chloride solution. Shake the flask and allow the precipitate to settle before use of the supernatant liquid.

C6 Apparatus

C6.1 **Electrode**

An ammonia gas sensing electrode incorporating an internal reference electrode and a diffusion type membrane is required. Suitable electrodes are commercially available. Internal filling solutions for fresh water applications are supplied by the manufacturer. For sea water applications the electrode should be modified by use of the electrode internal filling solution for sea water samples (section C5.4) in place of that supplied with the electrode.

C6.2 **Meter**

Either a pH/millivoltmeter, precise to ± 0.2 mV or a selective ion meter is required. Suitable meters are commercially available.

C6.3 **Magnetic stirrer** with a thin sheet of insulating material eg cork, to prevent heat transfer.

C6.4 **PTFE or polypropylene coated stirring bars.**

C6.5 **Conical flasks**

100 ml conical flasks capable of accepting the electrode are preferred to minimize ammonia losses. The flasks should be clean and dry.

C7 Analytical Procedure

Step	Procedure	Notes
	Preparation	
C7.1	Make sure that the instrument manufacturer's instructions are known and understood.	
C7.2	Ensure that the standard solutions and samples will be at the same temperature when analysed (note a).	a. The temperature of the samples needs to be within 1°C of the temperature of the standard solutions. The temperature should be 20 ± 5°C.
C7.3	Switch on the meter and allow it to stabilize. Set the meter to read in mV (note b).	b. When using a meter giving a direct concentration reading refer to the manufacturer's instructions.
C7.4	Thoroughly rinse the electrode with ammonia-free water (Part A3.1) (note c).	c. Rinse with low-ammonia sea-water (Part A3.2) when analysing sea water samples.

Step	Procedure	Notes
	Calibration	
C7.5	Pipette 50 ml of a 0.5 mg/l standard solution (note d) to a 100 ml conical flask.	d. For sea water analysis use the sea water standard solutions (Part A3.6).
C7.6	Inserting a stirring bar, place the flask on the stirrer and stir gently to mix. Immerse the tip of the electrode in the solution, taking care not to trap air bubbles on the end. While still stirring gently, pipette 5 ml of alkaline buffer solution (notes e and f) into the solution. When the meter reading has become constant to within ± 0.1mV over 30 seconds, record the observed potential. Remove the electrode rinse with water and gently wipe dry with a tissue. Let the observed potential of the 0.5 mg/l standard solution be P_a.mV.	e. For sea water analysis pipette 10 ml of sea water buffer solution (Reagent C5.3) in place of the 5 ml alkaline buffer solution. f. Stirring should be gently and the alkaline buffer solution should be added just prior to the measurement since ammonia may be lost to the atmosphere from stirred alkaline solution. The pH value of the solution must be 11.5 at this stage (pH indicator paper may be used to check).
C7.7	Pipette 50 ml of a 5 mg/l standard solution (note d) into a 100 ml conical flask and proceed as described in step C7.6. Let the observed potential of the 5 mg/l standard solution be P_b.mV (note g).	g. $P_b - P_a$ should be 58.5 ± 2mV
C7.8	Pipette 50 ml of a 50 mg/l standard solution (note d) into a 100-ml concial flask and proceed as described in step C7.6. Let the observed potential of the 50 mg/l standard solution be P_cmV (note h).	h. $P_c - P_b$ should be 58.5 ± 2mV
	Analysis of samples	
C7.9	Measure 50.0 ± 0.1 ml of sample (note i) into a 100 ml conical flask and proceed as described in step C7.6. Let the observed potential of the sample be P_s.	i. If the samples are known to be of similar ammonia concentration, rinsing of the electrode between measurements in unnecessary.
C7.10	Repeat step C7.9 for other samples to be determined (note i). The calibration steps C7.5 to C7.8 should be repeated when appropriate (note j).	j. The analyst must judge the frequency necessary to ensure that the accuracy required is maintained. (See Section 9.4).
	Termination	
C7.11	Immerse the electrode in about 50 ml of the electrode storage solution, or in about 50 ml of sea water internal filling solution when the electrode filling solution has been used for the electrode.	
C7.12	Switch off the stirrer, and follow the manufacturer's instructions for shut-down of the meter.	
	Calculation of results (note k)	
C7.13	Using semi logarithmic graph paper prepare a calibration curve for the standard solutions by plotting the concentrations in mg/l of the log axis against the corresponding observed potential (P_a,P_b,P_c mV on the linear axis.)	k. These steps do not apply when a meter giving a direct concentration reading is used. Refer instead to the manufacturer's instructions.
C7.14	Determine the concentrations C (in mg/l) of ammonia in the sample, from the value of P_s and the calibration curve.	

C8 Concentration range of the method

C8.1 This method has been fully tested in the range 0.5 to 50 mg/l. There is considerable evidence to suggest that it can be used up to 1,000 mg/l (see section C8.2) and down to 0.01 mg/l (see section C8.3).

C8.2 The upper limit of calibration (on semi-log paper) is at least 1,000 mg/l and, with appropriate calibration standards to verify the linearity, the method can be used for samples containing up to 1,000 mg/l. However, continued use at high concentrations is inadvisable. Dilution of samples to below 50 mg/l is to be preferred, and is easily achieved by prior dilution of the sample.

C8.3 The calibration (on semi log paper) is linear down to about 0.2 mg/l. Below this level it becomes curved. Nevertheless it is possible to make valid determination down to 0.01 mg/l or less. For work at low concentrations, the following points will require attention:–

C8.3.1 *Removal of traces of ammonia from the buffer solutions*

(Reagents C5.1 or C5.3). This can be done at the time of their preparation by boiling the solution for about 20 minutes before cooling and making up to 1 litre. Solutions already prepared may similarly be boiled, but adjust the volume after boiling to the initial volume.

C8.2.3 *Careful characterization of the calibration curve*

Use several calibration standards with closely-spaced concentrations.

C8.3.3 *Allowance for slower electrode response times*

Several minutes may be required for equilibration.

C8.4 **Total Standard Deviation of determinations of low concentrations:–**

Sample	Ammonia Concentration mg/l	Total Standard Deviation (a) mg/l
Standard solution (b)	0.05	0.006(c)
Standard solution (b)	0.10	0.005(c)
Sea Water	0.003	0.0002(d)
Sea Water	0.05	0.002(d)

(a) Each estimate has approximately 9 degrees of freedom
(b) Solution of ammonium chloride in distilled water
(c) These data were obtained at the Central Electricity Research Laboratories
(d) These data were obtained at the MAFF Fisheries Laboratory

C9 Sources of error

C9.1 The analytical procedure can be applied to a wide range of waters and the attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. The following sub-sections describe the main sources of error. Each analyst must decide which precautions are appropriate to his particular requirements.

C9.2 **Interfering substances**
See section C3.

C9.3 Ammonia may be slowly lost from alkaline solution. However, provided measurements are made rapidly (yet consistent with allowing equilibrium to be achieved) this error should be negligible. Calibration standards must always be freshly treated; on no account attempt to reuse calibration standard solutions which have previously been made alkaline.

C9.4 **Calibration drift**

Providing the temperatures of samples and standard solutions are controlled within 1°C of each other the slope of the calibration curve should remain constant. However, the actual potentials given by calibration standard solutions may drift from their initial values. To reduce errors resulting from such drift the calibration should be checked at least every 3 hours or after every 20 determinations, whichever is the sooner.

C9.5 **Reducing errors**

The use of automated systems incorporating thermostatic control such as that described in reference 8 may enable higher precision, accuracy and sample throughout to be achieved.

D Method for the Spectrophotometric Determination of Ammonia in Water

D1 Performance Characteristics of the Method

D1.1	Substance determined:	ammonia and ammonium ion.
D1.2	Type of Sample:	Sewage, effluents, raw and potable waters.
D1.3	Basis of Method:	Ammonia reacts with hypochlorite and salicylate ions in solution in the presence of sodium nitroprusside. A coloured compound is formed and its concentration is determined spectrophotometrically.
D1.4	Range of application:	Up to 1 mg/l, using the maximum sample volume of 40 ml. The range can be extended upwards by taking a smaller sample volume.
D1.5	Calibration curve:	Linear up to at least 1 mg/l (with the maximum sample volume of 40 ml).

D1.6 Total Standard Deviation:

Sample Type	Concentration mg/l	Cell Path Length† mm	Standard Deviation	Degrees of Freedom
Standard Solution	0.150	40	0.003(a)	14
Standard Solution	1.00	10	0.015-0.038(b)	9
Standard Solution	5.00	10	0.09 (a)	14
Well Water	0.217	40	0.004-0.010(b)	9
Sewage Effluent	0.877	10	0.009-0.027(b)	9

† All sample portions were 40 ml, except for the 5.00 mg/l standard solution for which it was 5 ml.

D1.7	Limit of Detection (b):	0.003-0.008 mg/l (9 degrees of freedom)
D1.8	Sensitivity (a):	0.2 mg/l gives an absorbance of approximately 0.7 units (using 40 mm cells); 0.75 mg/l gives an absorbance of approximately 0.65 units (using 10 mm cells). In both cases, the maximum, 40 ml sample size was used.
D1.9	Typical Blank Value (a):	Approximately 0.06 absorbance units (40 mm cell).
D1.10	Bias:	None, apart from the presence of interfering substances.
D1.11	Interferences:	See Section D3.
D1.12	Time Required for Analysis (b):	2.5 to 3 hours total analytical time for 9 samples. 1.5 to 2 hours operator time.

(a) Data obtained by Yorkshire Water Authority (one laboratory)
(b) Data from an interlaboratory exercise involving five participants.

D2 Principle

Ammonia reacts with hypochlorite ions, generated in situ by the alkaline hydrolysis of sodium dichloroisocyanurate, and with sodium salicylate at about pH 12.6 in the presence of sodium nitroprusside to form a coloured compound (thought to be related to indophenol blue). The compound is blue, but appears green against the yellow colour of the reagent blank. The absorbance of the compound is measured spectrophotometrically and related to the ammonia concentration in the sample by means of a calibration curve. Sodium citrate is used to mask possible interfering cations. See also references 9, 10 and 11.

D3 Interferences

The effect of other substances on the determination of ammonia by this method is shown in Table D1. The data were obtained by Thames Water Authority.

Table D1 Interference Effects

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 an ammonia concentration (N) of		
		0.000 mg/l	0.200 mg/l	0.500 mg/l
Sodium Chloride (Cl^-)	1000	+ 0.002	+ 0.013	+ 0.033
Sodium Bicarbonate (HCO^-_3)	1000	+ 0.002	+ 0.002	− 0.025
Sodium Orthophosphate ($PO_4^=$)	100	0.000	− 0.001	− 0.015
Sodium Sulphate ($SO_4^=$)	500	0.000	+ 0.001	−
Potassium Fluoride (F^-)	5	+ 0.002	− 0.001	−
Potassium Nitrate (N)	50	+ 0.006	+ 0.002	−
Sodium Silicate (SiO_2)	50	0.003	0.000	−
Sodium Thiosulphate ($S_2O_3^=$)	10	− 0.001	− 0.007	−
Potassium Cyanide (CN^-)	5	+ 0.002	+ 0.019	+ 0.016
Calcium Chloride (Ca)	500	0.000	+ 0.013	− 0.001
Magnesium Acetate (Mg)	50	+ 0.004	− 0.009	+ 0.002
Iron (III) Sulphate (Fe)	10	+ 0.001	+ 0.003	−
Aluminium Sulphate (Al)	5	0.000	+ 0.008	−
Copper Sulphate (Cu)	5	+ 0.003	+ 0.011	−
Zinc Sulphate (Zn)	5	+ 0.003	+ 0.006	−
Lead Acetate (Pb)	10	+ 0.001	+ 0.016	+ 0.011
Aniline ($C_6H_5NH_2$)	1	+ 0.040	+ 0.040	−
Ethanolamine ($C_2H_4OH\ NH_2$)	1	+ 0.164	+ 0.114	−

If the other substances did not interfere, the effect would be expected (95% confidence) to lie between:
0.003 mg/l at 0.000 mg/l N
0.014 mg/l at 0.200 mg/l N
0.021 mg/l at 0.500 mg/l N

D4 Hazards

Normal precautions to avoid skin contact and/or ingestion should be taken in the handling of all reagents.
The sodium dichloroisocyanurate solution and particularly the solid reagent should not be allowed to come into contact with acid since this would result in the evolution of highly toxic chlorine gas.

D5 Reagents

(Analytical grade reagents should be used whenever possible. All water used in this method must be ammonia-free (Part A3.1)).

D5.1 Salicylate Reagent

Dissolve 130 ± 1 g of sodium salicylate and 130 ± 1 g of tri-sodium citrate in about 950 ml of water contained in a 1000 ml calibrated flask. Then add 0.970 ± 0.005 g of sodium nitroprusside (ensure that the pH value is not greater than 8.0 before making this addition). Swirl to dissolve the solid and then make the volume up to the mark with water. Stored in an amber glass bottle, this reagent is stable for at least two weeks.

D5.2 **Sodium dichloroisocyanurate reagent (DIC)**

Dissolve 32.0 ± 0.1g of sodium hydroxide in 500 ± 50 ml of water. Cool the solution to room temperature and add 2.00 ± 0.02 of sodium dichloroisocyanurate (dichloro-s-triazine 2, 4, 6 (1H, 3H, 5H) – trione sodium salt) to the solution. When solution is complete, transfer to a 1000 ml calibrated flask. Make up to volume with water and mix well. Stored in amber glass bottle at 4°C this reagent is stable for at least two weeks.

D6 Apparatus (In addition to normal laboratory apparatus).

D6.1 **A spectrophotometer** capable of operating at a wavelength of 655 nm and equipped with 10 mm and 40 mm pathlength cells is required. Alternatively, an absorptiometer with a filter having a transmittance maximum at about 655 mm can be used, but a reduction in sensitivity and precision of determination may result.

D6.2 **A waterbath** capable of operating at 25 ± 0.2°C is preferred, but is not essential. See Section D7, note (c).

D7 Analytical Procedure

Step	Procedure	Notes
	Analysis of Samples	
D7.1	Pipette up to 40 ml of sample (Volume Vml) into a 50 ml calibrated flask and make up to 40 ± 0.5 ml with water (if necessary). (Note a).	a. It is essential that aliquots less than 40 ml are diluted prior to adding the reagents.
D7.2	Add 4.00 ± 0.05 ml of Salicylate reagent and mix well.	
D7.3	Add 4.00 ± 0.05 ml of DIC reagent and mix well.	
D7.4	Dilute with water to the mark, mix well (note b) and develop the colour in a water bath at 25.0 ± 0.2°C (note c).	b. At this stage the pH value of the solution should be 12.6 ± 0.1. c. Other temperatures between 20°C and 30°C may be used but all calibrations and determinations should be carried out at the same temperature (within ± 0.2°C). The final absorbance decreases by 1.1% per °C when the colour development temperature is increased from 20°C to 30°C.
D7.5	Remove the flask from the water bath after 30–60 minutes and measure the absorbance of the solution at 655 ± 2 nm (note d) in a cell of appropriate pathlength against water in the reference cell. Let the absorbance be A_s.	d. The wavelength of maximum absorbance should be checked for each individual instrument. This wavelength should be used for all subsequent measurements.
	Blank	
D7.6	Prepare a blank by treating 40 ± 0.5 ml of water as described under steps D7.2 to D7.5. Let the absorbance of the blank be A_b.	
	Compensation for colour and for turbidity in the sample	
D7.7	If such interference is suspected, use the distillation method, Part B (see Section B9) and take up to 40 ml of the distillate for step D7.1.	

Step	Procedure	Notes
	Calculation of Results	
D7.8	Calculate the absorbance due to ammonia in the sample, A_r from $A_r = A_s - A_b$ Determine the mass of ammonia, M μg (expressed as nitrogen) in the sample, from A_r and the Calibration curve. Ammonia concentration in the sample $= \frac{M}{V}$ mg/l NH_3 as N. where V = volume of sample taken in step D7.1.	

D8 Preparation of Calibration Curve (to be performed with each new batch of reagents)

D8.1 Dilute 100 ml of standard solution B. (Part A3.4) to 1000 ml with water in a calibrated flask. Then add, using a burette, volumes of the diluted solution to a series of 50 ml calibrated flasks, as shown in the table D2 below:-

Table D2

Volume of Solution (ml)	Mass of N (μg)	Pathlength of Cell (mm)
0.0	0	10 & 40
2.0	2	40
4.0	4	40
6.0	6	40
8.0	8	40
10.0	10	10
20.0	20	10
30.0	30	10
40.0	40	10

D8.2 Add water to each flask to give a volume of 40 ± 0.5 ml.

D8.3 Continue as under Procedure, steps D7.2 to D7.5.

D8.4 Subtract the absorbance of the blank solution from the absorbances for all the other standards and plot calibration curves for each cell size. These are normally linear and pass through the origin.

D9 Change in Concentration Range of the Method

The method permits the determination of up to 1 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 D1.6, but the analyst should check the precision of whatever variation is used.

D10 Sources of Error

The analytical procedure can be applied to a wide range of waters and the attention which it is necessary to pay to sources of error depends upon the accuracy required. The two main sources of error in this method are colour and turbidity, overcome by use of preliminary distillation (Part B), and the interfering substances given in Section D3.

E Tentative Method for the Spectrophotometric Determination of Ammonia in Seawater

E1 Performance Characteristics of the Method

E1.1	Substance determined:	Ammonia and ammonium ions.
E1.2	Type of Sample:	Sea water and estuarine water.
E1.3	Basis of Method:	Ammonia reacts with hypochlorite and phenate ions in solution in the presence of potassium ferrocyanide. A blue coloured complex is formed and its concentration is determined spectrophotometrically.
E1.4	Range of application:	Up to 1 mg/l, using the maximum sample volume of 50 ml and a 10 mm path-length cell. The range can be extended upwards by taking a smaller sample volume.
E1.5	Calibration curve:	Linear to at least 1 mg/l (with the maximum sample volume of 50 ml).
E1.6	Standard Deviation (a):	See table below.
E1.7	Limit of Detection (a):	0.006 mg/l (9 degrees of freedom).
E1.8	Sensitivity (a):	5 μg ammonia N = 1.0 absorbance units at 640 nm 100 mm cells.
E1.9	Bias (a):	None, apart from the presence of interfering substances
E1.10	Interferences:	No significant error when the multiple standard addition method of calibration described is applied. This is essential for polluted water, as if not applied, primary, secondary and tertiary amines and nitrite would interfere seriously leading to low results. Significant interference is not normally encountered in the analysis of open ocean water.
E1.11	Time required for analysis (a):	About 3 hours to analyse 30 samples.

Sample Type	Concentration mg/l	Standard Deviation mg/l	Degrees of freedom
Open sea water	0.060	0.0018†	9
Estuary water (Humber)	0.061	0.0011†	9
Heavily polluted sea water (from fish rearing)	0.62	0.0304*	48

† Within-batch standard deviation. 100 mm path-length cell.
* Total standard deviation. 10 mm path-length cell.

(a) Data from MAFF, Fisheries Laboratory.

E2 Principle

(References 12, 14–18)

Ammonia reacts with hypochlorite ions, generated in situ by the alkaline hydrolysis of sodium dichloroisocyanurate, and with phenol at about pH 10.5 in the presence of potassium ferrocyanide to form a coloured compound (thought to be related to indophenol blue). The absorbance of the compound is measured spectrophotometrically and related to the ammonia concentration in the sample by use of internal standards or a calibration curve. Sodium citrate is added to prevent precipitation of magnesium hydroxide. Choice of controlled temperature – just above ambient (30°C) – and activation of the required reaction by UV irradiation gives high sensitivity and minimal interference in a short reaction time.

E3 Interferences

The methyl and ethyl primary, secondary and tertiary amines and nitrite are known to interfere, so reducing the response to ammonia of the indophenol blue reaction. The multiple standard addition method of calibration compensates for this effect. Interference testing is carried out by making identical standard ammonia additions to pure seawater alongside "polluted" samples. Parallel lines of the same slope indicate absence of interference of this type. Urea and the common natural amino acids are believed not to interfere if the specified temperatures and pH values are adhered to; at higher temperature or pH value they are hydrolysed to ammonia and so included in the result. See also reference 12.

E4 Hazards

E4.1 *The Ultra-violet lamp* used on this method emits radiation harmful to the eyes. Wear UV-absorbing glasses or goggles when looking at the illuminated lamp.

E4.2 *Phenol* is toxic by skin absorption. Gloves and eye protection should be worn when handling it.

E4.3 The *sodium dichloroisocyanurate* solutions and particularly the solid reagent should not be allowed to come into contact with acid since this would result in the evolution of highly toxic chlorine gas.

E5 Reagents

Analytical grade reagents should be used whenever possible. All water used in this method must be ammonia-free (Part A3.1).

E5.1 Phenol reagent

Dissolve 25 ± 0.1 g of phenol (pure white, crystalline) in about 200 ml of ethanol and dilute to 250 ml with ethanol in a calibrated flask. Transfer to an amber glass bottle. Prepare this reagent freshly every day.

E5.2 Chlorinating reagent

Solution A

Dissolve 10.0 ± 0.1 g of sodium hydroxide stick in 100 ± 10 ml of water. Cool the solution to room temperature. Add 2.00 ± 0.02 g of sodium dichloroisocyanurate (dichloro-S-triazine 2, 4, 6 (1H, 3H, 5H) – trione sodium salt) to the solution and dissolve.

Solution B

Dissolve 22.0 ± 0.1 g of sodium hydroxide stick in 800 ± 50 ml of water. Add 400 ± 5 g of tri-sodium citrate and dissolve. Boil the solution for about 15 minutes to remove ammonia. Allow to cool to room temperature. Combine the two solutions A and B, and make up to 1 litre with water in a calibrated flask. Prepare this reagent freshly for each occasion.

E5.3 Catalyst Reagent

Dissolve 1.25 ± 0.10 g of potassium ferrocyanide in about 200 ml of water and make up to 250 ml in a calibrated flask. Prepare freshly each day, and keep in an amber glass bottle.

E6 Apparatus

The following items, in addition to normal laboratory apparatus, are required:-

E6.1 **A spectrophotometer** capable of operating at 640 nm with 10 mm, 40 mm and preferably 100 mm path length cells.

E6.2 **A thermostatically-controlled hot plate with reflecting surface,** set at 30 ± 1°C.

E6.3 **An array of one or two 365 nm UV lamps** set in above the hot plate to give uniform irradiation, each having two 8″ 15W tube type elements before a reflector and safety glass. (Most types of sun-tan lamps will suffice). See Section E4.1.

E6.4 **A micropipette** capable of dispensing 0.250 ± 0.002 ml volumes of solution.

E6.5 **150 ml conical pyrex flasks** fitted with pyrex stoppers.

E7 Analytical Procedure

Step	Procedure	Notes
	Analysis of Samples	
E7.1	Pipette 50 ml of the sample (note a) into each of four dry 150 ml conical flasks (Section E6.5).	a. The ammonia concentration must not exceed 1 mg/l
E7.2	Add standard ammonia solution, prepared as in part A3.5, such that 0.25, 0.50 and 0.75 ml when added to the sample aliquot will be respectively approximately 0.5, 1 and 1.5 times the expected sample ammonia concentration. Use the micropipette (Section E6.4) for making 0.25, 0.50 and 0.75 ml additions to the 2nd, 3rd and 4th flasks, respectively.	
E7.3	Using the micropipette, (Section E6.4) add to the 1st, 2nd, 3rd and 4th flasks respectively 1.00, 0.75, 0.50 and 0.25 ml of low ammonia sea water (Part 3.2) in order to bring the flask contents to 51 ml in each case.	
E7.4	Add to each flask 2.00 ± 0.02 ml of phenol reagent, and mix well.	
E7.5	Add to each flask 2.00 ± 0.02 ml of chlorinating reagent, and mix well.	
E7.6	Add to each flask 2.00 ± 0.02 ml of catalyst reagent, and mix well. Stopper the flasks.	
E7.7	Place the flasks on the hot plate, (Section E6.2) set at 30 ± 1°C and direct the beams from the UV lamps, (Section E6.3) onto the flasks. Leave the colour to develop for at least 30 minutes (Note b).	b. All four flasks containing a particular sample must be carried through this step together.
E7.8	Measure the absorbance of each solution at 640 nm in cells or cuvettes of appropriate path length (notes c and d) against low-ammonia sea water in the reference cell. Let the absorbances be A_{s1}, A_{s2}, A_{s3}, and A_{s4}.	c. The wavelength of maximum absorbance should first be checked for each instrument, and should be used in all subsequent measurements. d. The cell or cuvette path length should be such that the absorbance for all four solutions lies within the range 0.01 to 1.2 units.

Step	Procedure	Notes
	Blank	
E7.9	Prepare a blank solution by carrying a single 51 ml portion of low ammonia sea water (Part A3.2) through steps E7.4 to E7.8, with step E7.8 being carried out together with the sample. Let the absorbance, measured in cells or cuvettes of the same path length as used for the samples, be A_B.	
	Calculation of Results	
E7.10	For each of the four flasks calculate the absorbances due to ammonia, A_{rl-4}, by subtracting A_B from A_{sl-4}.	
E7.11	Plot a four-point graph of A_{rl-4} against added ammonia, in μg. (note e). Extrapolate the line through the four points to zero absorbance and hence read off the sample ammonia concentration, M μg. The ammonia concentration in the sample = $\frac{M}{50}$ mg/l.	e. Correct the amount added by multiplying by 0.98, to take account of the slight dilution resulting from step E7.3.

E8 Change in Concentration Range of the Method

The concentration range of the method extends to 1 mg/l. Samples with greater concentrations may be analysed by first diluting to 250 ml with low ammonia seawater (Part A3.2) and then taking a 50 ml aliquot of that solution through the analytical procedure, beginning at step E7.1. The result is calculated as follows:-

$$\text{ammonia concentration in the sample} = \frac{5M}{V} \text{ mg/l}$$

where V = volume of sample diluted to 250 ml
M = mass of ammonia in μg (step E7.11)

F Tentative Method for the Continuous Flow Determination of Ammonia

F1 Performance Characteristics of the Method

F1.1	Substance determined:	Ammonia and ammonium ions.
F1.2	Type of Sample:	Sewage, effluents, raw and potable water.
F1.3	Basis of Method:	Continuous flow colorimetry, using reactions described in Section F2.
F1.4	Range of application:	Fa: Up to 50 mg/l, with dialysis Fb: Up to 1 mg/l, without dialysis Fc: Up to 0.5 mg/l, without dialysis (a) Fd: Up to 5 mg/l, without dialysis
F1.5	Calibration curve:	Linear
F1.6	Total Standard Deviation (b):	

Sample Type	Concentration mg/l	Range(c)	Chemistry(d)	Standard Deviation mg/l	Degrees of Freedom
Standard Solution	0.1	Fc	S	0.007	9
Standard Solution	0.4	Fc	S	0.038	9
Standard Solution	1.0	Fd	S	0.025	19
Standard Solution	5.0	Fd	S	0.053	19
Standard Solution	5.0	Fa	S	0.11	9
Standard Solution	40.0	Fa	S	0.16	9
Spiked Potable Water	0.2	Fc	S	0.011	9
River Water	1.43	Fd	S	0.099	19
Sewage Effluent	29.1	Fa	S	0.26	9
Polluted River Water	11.2	Fa	S	0.13	9
Standard Solution	0.1	Fb	P	0.01	19
Standard Solution	1.0	Fb	P	0.02	19
Standard Solution	4.0	Fa	P	0.19	19
Standard Solution	50.0	Fa	P	0.42	19
River Water	0.27	Fb	P	0.01	19
Sewage Effluent	20	Fa	S	0.025	19

F1.7	Limit of Detection (b):	Range Fa, chemistry P: 0.5 mg/l Range Fb, chemistry P: 0.01 mg/l Range Fc, chemistry S: 0.009 mg/l Range Fd, chemistry S: 0.03 mg/l.
F1.8	Bias:	None, apart from the presence of interfering species.
F1.9	Interferences:	See Section F3.
F1.10	Time Required for Analysis:	The automated systems described are capable of operating at up to 60 determinations per hour. Set-up time and wash-through time may amount to 30 and 20 minutes (total) respectively.

Notes:
(a) An adaptation for the range 0-0.2 mg/l in sea water is mentioned in Section F3.2, but the test data here do not apply.
(b) Data obtained by Yorkshire Water Authority and Thames Water Authority
(c) See Section F1.4
(d) See Section F2 and F5.

F2 Principle

Ammonia in the sample reacts with hypochlorite ions to form monochloramine. This reacts with a phenolic compound in the presence of sodium nitroprusside to form a blue, indophenol-type compound which is measured colorimetrically. All reactions are carried out automatically using continuous flow techniques.

Two distinct chemistries are presented for this method. In one, designated throughout this method as chemistry P, the phenolic compound is phenol itself, and sodium hypochlorite is used as the source of hypochlorite ions. In the other, designated S, the phenolic compound is salicylate ion, with hypochlorite generated in situ by alkaline hydrolysis of sodium dichloroisocyanurate.

Sodium hypochlorite solution is considerably less stable than dichloroisocyanurate solution (See Section F5.4P and F5.10S), but since it has been part of the extensively used P chemistry for a number of years, its specification has been retained. It could also serve as an alternative in the S chemistry if dichloroisocyanurate is not available.

See Part A1 regarding the relative merits of S and P chemistries.

The two chemistries involve quite separate reagents and manifolds. This is made clear in Sections F5 and F6. A common feature of both manifolds is the inclusion of a dialyser for use in the analysis of samples, containing high levels of ammonia, which may be turbid. The dialyser is bypassed for the determination of low levels of ammonia.

F3 Interferences

F3.1 The effect of some other substances on the determination of ammonia, range Fc, chemistry S, is given in table F2. The effect of certain combinations of other substances, as indicated by brackets, on the determination of ammonia, range Fb, chemistry P, is given in table F3; more detailed information on the effects of individual substances on chemistry P is lacking.

F3.2 Magnesium interferes in both S and P chemistries, by forming a precipitate of magnesium hydroxide at the high pH values (>12) required for full colour development. For this reason, complexing agents are employed; trisodium citrate for the S chemistry, and sodium citrate plus disodium ethylenediamine tetracetic acid for the P chemistry.

At the concentrations of complexing agents specified, both methods will tolerate magnesium at concentrations normally encountered in most non-saline waters. With the methods prescribed here, the various chemistries will tolerate the maximum magnesium concentrations given in table F1 below.

The tolerance of both chemistries to magnesium can be increased, to deal with partially saline (eg estuarine) waters, by increasing the concentration of tri-sodium citrate in the reagents (up to the limit of solubility, which is 390 g/l). Beyond that limit, a reduction in operating pH value to about pH 10 is necessary. This requires the use of a P-type chemistry, as described in Part G, for satisfactory operation.

Table F1 Amounts of Magnesium tolerated in mg/l†

Range	P Chemistry tri sodium citrate as text	S Chemistry concentration	S Chemistry 120 g/l tri sodium citrate	S Chemistry 180 g/l tri sodium citrate
Fa	1500	1500		
Fb	500	750	1500	
Fc and Fd	—	500*	—	1500

* If a trisodium citrate concentration of 100 g/l is used, with a salicylate rate of 0.42 ml/min and a sample rate of 0.23 ml/min and a 50 mm flow cell path length, the range becomes 0-0.2 mg/l ammonia and estuarine and sea waters can be analysed, but the test data above does not apply.
Note, if the citrate concentration or other conditions are changed, it is necessary to recalibrate the method under the new conditions.
† Yorkshire Water Authority information.

Table F2 Interference data for S Chemistry

Other substance (Expressed in terms of substance in brackets)	Concentration of other substance mg/l	Effect in mg/l N of other substance at an ammonia concentration (N) of	
		0.000 mg/l mg/l	0.400 mg/l mg/l
Sodium chloride (Cl^-)	2500	0.000	− 0.010
Sodium bicarbonate (HCO^-_3)	1000	+ 0.010	+ 0.030
Sodium sulphate ($SO_4^=$)	1000	− 0.005	+ 0.040
Sodium orthophosphate ($PO_4^=$)	100	0.000	+ 0.020
Sodium silicate (SiO_2)	100	− 0.005	–
Sodium nitrate (N)	100	0.000	+ 0.040
Sodium nitrite (N)	10	− 0.015	− 0.030
Potassium Fluoride (F^-)	10	− 0.005	− 0.030
Potassium cyanide (CN^-)	10	0.000	− 0.030
Calcium chloride (Ca)	1000	+ 0.005	+ 0.040
Magnesium acetate (Mg)	100	0.000	− 0.015
Iron (III) sulphate (Fe)	10	+ 0.070	+ 0.145
Iron (III) sulphate (Fe)	2	+ 0.020	+ 0.035
Manganese (II) sulphate (Mn)	10	+ 0.015	+ 0.040
Zinc sulphate (Zn)	10	0.000	+ 0.030
Copper sulphate (Cu)	10	+ 0.015	+ 0.020
Lead acetate (Pb)	10	− 0.005	+ 0.005
Aluminium sulphate (A1)	10	− 0.005	+ 0.025
Urea ($CO(NH_2)_2$)	10	0.000	+ 0.020
Ethanolamine (C_2H_4-OH-NH)	1	+ 0.030	+ 0.050
Triethylamine ($(C_2H_5)_3N$)	1	0.000	+ 0.020

If the other substances did not interfere, the effect would be expected (95% confidence) to lie between:
± 0.015 mg/l at 0.000 mg/l N
± 0.045 mg/l at 0.400 mg/l N

Table F3 Interference data for P Chemistry

Other Substances	Concentration of other substances mg/l	Effect in mg/l N of the combination of other substances at an ammonia concentration of 1.000 mg/l N
Calcium	200	+ 0.100
Magnesium	150	
Calcium	200	+ 0.177
Magnesium	150	
Iron (III)	20	
Copper	1.5	
Nickel	1.0	
Cadmium	0.5	
Aluminium	1.0	
Lead	2.0	
Manganese	2.0	
Zinc	15	
Chloride	2000	− 0.049
Nitrate (as N)	25	
Nitrite (as N)	10	
Sulphate	200	
Fluoride	10	

Table F3 Interference data for P Chemistry *(Contd.)*

Other Substances	Concentration of other substances mg/l	Effect in mg/l N of the combination of other substances at an ammonia concentration of 1.000 mg/l N
Anionic Detergent (as Manoxol OT)	10	− 0.101
Phenol	3	
Cyanide	0.1	
Thiocyanate	10	
Bicarbonate (as HCO_3^-)	800	
Triethylamine	10	+ 0.008

If the combinations of other substances did not interfere, the effect would be expected (95% confidence) to lie between ± 0.074 mg/l N.

F4 Hazards

F4.1 The precautions given in reference 13 should be observed.

F4.2 *Phenol* is toxic by skin absorption. Gloves and eye protection should be worn when handling it, or any reagent or effluent from chemistry P containing it.

F4.3 *Sodium dichloroisocyanurate and sodium hypochlorite* must not be allowed to come into contact with acid because highly toxic chlorine gas will be produced.

F5 Reagents

Analytical grade reagents should be used whenever possible. All water used in this method must be ammonia-free (Part A3.1).
Note: All reagents exclusively for one or other of the separate chemistries, P and S, are identified with a suffixed P or S as appropriate. See also Section F2.

F5.1 **Sodium hydroxide solution**

Dissolve 40 ± 1 g of sodium hydroxide pellets in 800 ml water, cool and dilute to 1000 ml with water in a measuring cylinder.

F5.2P **EDTA Reagent 1** (See also section F5.12)
Dissolve 10.0 ± 0.5 g of disodium ethylene diamine tetra-acetic acid and 10.0 ± 0.5 g of trisodium citrate in approx 200 ml of water. Dilute to 1 litre with water in a calibrated flask. Adjust the pH value to 12.5 with sodium hydroxide solution (reagent F5.1). The reagent is stable for at least two weeks. Store in a plastic container.

F5.3P **EDTA Reagent 2** (See also section F5.12)
Dissolve 10.0 ± 0.5 g of disodium ethylenediamine tetraacetic acid and 10.0 ± 0.5g of trisodium citrate in approx 200 ml of water. Dilute to 1 litre with water in a calibrated flask. Adjust the pH value to within 10.5-11.0 with the sodium hydroxide solution (reagent F5.1). Finally, add 20.0 ± 0.5 ml of acetone. The reagent is stable for at least two weeks. Store in a plastic container.

F5.4P **Sodium hypochlorite solution,** 2.5 – 3.5% w/v available chlorine
Dilute 250 ± 10 ml of sodium hypochlorite solution (10–14% w/v available chlorine, filter if necessary) to 1 litre with water in a graduated cylinder. Store in an amber glass bottle. Prepare this solution freshly each time the method is used.

Note that other commercially available sodium hypochlorite solutions, which may be more stable, may be preferable to the relatively unstable 10–14% grade, providing that an available chlorine concentration of at least 2.5% w/v is obtainable for the working solution.

F5.5P **Alkaline phenate reagent**

Dissolve 36.0 ± 0.5 g of sodium hydroxide pellets in about 400 ml of water. Add slowly with stirring 80.0 ± 0.5 g of phenol (pure white, crystalline) OR 100 ± 1 ml of liquid phenol (80% w/v in water, commercially available). Allow to cool, and dilute to 1 litre with water in a calibrated flask. Mix well. Store in an amber glass bottle and keep at a temperature of between 1 and 5°C when not in use. Allow to warm completely to room temperature before use. This reagent is stable for up to 5 days; discard it before that time if a pink colour develops.

F5.6P **Sodium nitroprusside reagent**

Dissolve 1.0 ± 0.1 g of sodium nitroprusside in approx 400 ml of water. Dilute to 1 litre with water in a calibrated flask and mix well. Store in an amber glass bottle. The life of this solution is variable and depends on storage conditions. As a guide, solutions older than two weeks should not be used, nor those which have darkened or precipitated.

F5.7 **10% V/V Hydrochloric acid solution**

Dilute 100 ± 10 ml of hydrochloric acid (d_{20} 1.18) to 1 litre with water in a measuring cylinder.

F5.8S **Citrate reagent** (See also Section F5.12)

Dissolve 40.0 ± 0.5 g of trisodium citrate in about 950 ml of water. Dilute to 1 litre with water in a measuring cylinder. Store the solution in a glass or plastic bottle. This reagent is stable for at least three weeks.

F5.9S **Salicylate reagent**

Dissolve 34.0 ± 0.5 g of sodium salicylate in about 950 ml of water contained in a 1 litre calibrated flask. Then add 0.400 ± 0.005 g of sodium nitroprusside (ensure that the pH value is not greater than 8.0 units before making this addition). Swirl to dissolve the solid and then make up to volume with water. Stored in an amber glass bottle, this reagent is stable for at least two months.

F5.10S **Sodium dichloroisocyanurate reagent (D.I.C)**

Dissolve 10.0 ± 0.1 g of sodium hydroxide stick in 500 ± 5 ml of water. Cool the solution to room temperature and then add 0.800 ± 0.08 g of sodium dichloroisocyanurate (dichloro-s-triazine 2, 4, 6 (1H, 3H, 5H) – trione sodium salt) to the solution. When dissolution is complete, transfer the solution to a 1 litre calibrated flask. Make up to volume with water and mix well. Stored in an amber glass bottle at 4°C, this reagent is stable for at least two weeks.

F5.11S **Salicylate/Citrate mixed reagent** (for range (c) Section F1.4))

Dissolve 34.0 ± 0.5 g of sodium salicylate and 40.0 ± 0.5 g of trisodium citrate in about 950 ml of water contained in a 1 litre calibrated flask. Then add 0.400 ± 0.005 g of sodium nitroprusside. Swirl to dissolve the solid and then make up to volume with water. Stored in an amber glass bottle, this reagent is stable for at least two weeks. (see also Section F5.12)

F5.12 **Wetting agent**

The inclusion of a wetting agent in reagents in order to promote smooth flow in the system is optional. If used, the wetting agent should be any proprietary detergent of the alkyl benzene sulphonate type and should be added to give a concentration of 0.1% V/V in reagents F5.2P, F5.3P, F5.8S and F5.11S.

F6 Apparatus

F6.1 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.
Recorder

Consult the essay review (13) on continuous flow analysis for further information.

F6.2 The design of the manifold depends on the chemistry adopted. Figure 2 shows that for S chemistry operating in ranges Fa or Fb (section F1.4) changing ranges simply requires reversal of the sample stream and the water stream. Figure 4 shows the corresponding manifold for P chemistry.

Figure 3 shows the S chemistry manifold for ranges Fc and Fd. This is essentially a slight modification of figure 2 and permits greater sensitivity because of the larger sample flow-rate. It is the preferred configuration for the analysis of potable waters.

F6.3 S chemistry requires the use of *colorimeter filters* giving maximum transmission at 650 nm; with a flow cell path length of 15 mm. P chemistry uses 630 nm filters, again with 15 mm (minimum) flowcell pathlength.

F6.4 For the analysis of low levels of ammonia the design of both systems can be improved by drawing air used for segmentation through dilute hydrochloric acid (reagent F5.7) in order to absorb any atmospheric ammonia. Contamination can be reduced by capping filled sample cups with thin aluminium foil which will be pierced as the sampling probe descends. File the probe end to an angle of 45° to ensure it pierces the foil. A plastic dust cover on the turntable will guard against the sample cup being picked up by the probe on its return.

F7 Analytical Procedure

Step	Procedure	Notes
	Starting Operation	
F7.1	Connect the system as shown in Figures 2, 3 or 4 as appropriate (notes a and b).	a. Follow the manufacturer's general operating instructions. b. See reference 13.
F7.2	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 F7.3.
	Initial Sensitivity Setting	
F7.3	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.

Step	Procedure	Notes
F7.4	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 in the C_M standard solution only 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.
F7.5	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	
F7.6	Load the sample turntable in the following order (notes k and l).	k. The turntable can be loaded during the initial stabilization period (steps F7.2 to F7.4). l. Other loading patterns may be used.

Position no on turntable	*Solution*
1–5	Calibration standards in ascending order (see section F8).
6–7	Blank (note m).
8–17	Samples (note n).
18	Calibration standard (note o)
19–20	Blank (note m).
21–30	Samples (note n).
31	Calibration standard (note o).
32–33	Blank (note m)
34–38	Calibration standards in ascending order.

m. Water.
n. A control standard should occupy one of the sample positions as a check of system control.
o. 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 reanalysed separated by a blank solution.
F7.7	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.	
F7.8	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 (note p).	
	Calculation of Results	
F7.9	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 13 for suggested procedures to obtain calibration curves.

Step	Procedure	Notes
F7.10	Using the calibration curve(s) convert the measurement unit responses due to the samples into concentrations of ammonia 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.
	Shut-down Procedure for P Chemistry	
F7.11	Transfer all reagent lines except the nitroprusside line to water, place the nitroprusside reagent line in 10% V/V hydrochloric acid solution (note s), and continue pumping for 10 minutes.	s. Staining and eventual residue build-up may occur in the final mixing coil(s) after prolonged pumping of reagents through the sample treatment area of the system. This is thought to be caused by the formation of brown ferrocyanides and/or hydroxides or both from the slow reaction of nitroprusside and alkali. Unless removed, this residue could cause an irregular liquid flow through the system which may result in erratic traces on the measurement unit read-out. This stain is removed by the hydrochloric acid which is pumped through the system.
F7.12	Place all lines back in water for 5 minutes and finally switch off pump, detection and measurement units.	
	Shut-down Procedure for S Chemistry	
F7.13	Transfer all reagent lines to water and pump for at least 15 minutes (note t).	t. No staining of any coils should result when this chemistry is used.

F8 Preparation of Calibration Curve

As indicated in step F7.6, 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 ammonia concentrations and of the manifold configuration in current use. Working standard ammonia solutions prepared as detailed in Part A3.5 should be used: intermediate concentrations additional to those given can be prepared if required.

Calibration is carried out as described in step F7.9.

F9 Changes in Concentration Range of the Method

Changes between the three ranges of application given in section F1.4 are effected by simple modifications in pump tube connections, as indicated in figures 2, 3 and 4 and in section F6.2.

Within those three ranges there is scope for further change by using a restricted range of calibration standards and adjusting the sensitivity to give full scale response as indicated in step F7.4. Such modifications, and the performance verification of them, must be made at the analysts discretion.

F10 Sources of Error

F10.1 A great advantage of continuous flow analysis over manual procedures is that procedural errors inherent in the latter are eradicated; all samples and standards are handled in exactly the same way, providing the apparatus is kept well maintained in accordance with the makers instructions. Thus, apart from mechanical or hydraulic failures or malfunctions, the greatest sources of error are likely to be those given below.

F10.2 **Interfering substances** (see section F3)
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 unusually high concentration is present, either recovery experiments should be carried out, or the results should be checked by another method in this series. Particular attention should be paid to samples with extreme concentrations of acidity or alkalinity.

The presence of certain amino compounds, such as are encountered in treated cooling waters or in other special types of industrial effluent, may cause severe interference.

F10.3 **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 provide a means of checking the calibration. Small amounts of drift can be corrected by means of these standards, but large drifts should be investigated further.

F10.4 **Inter-sample carryover**

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

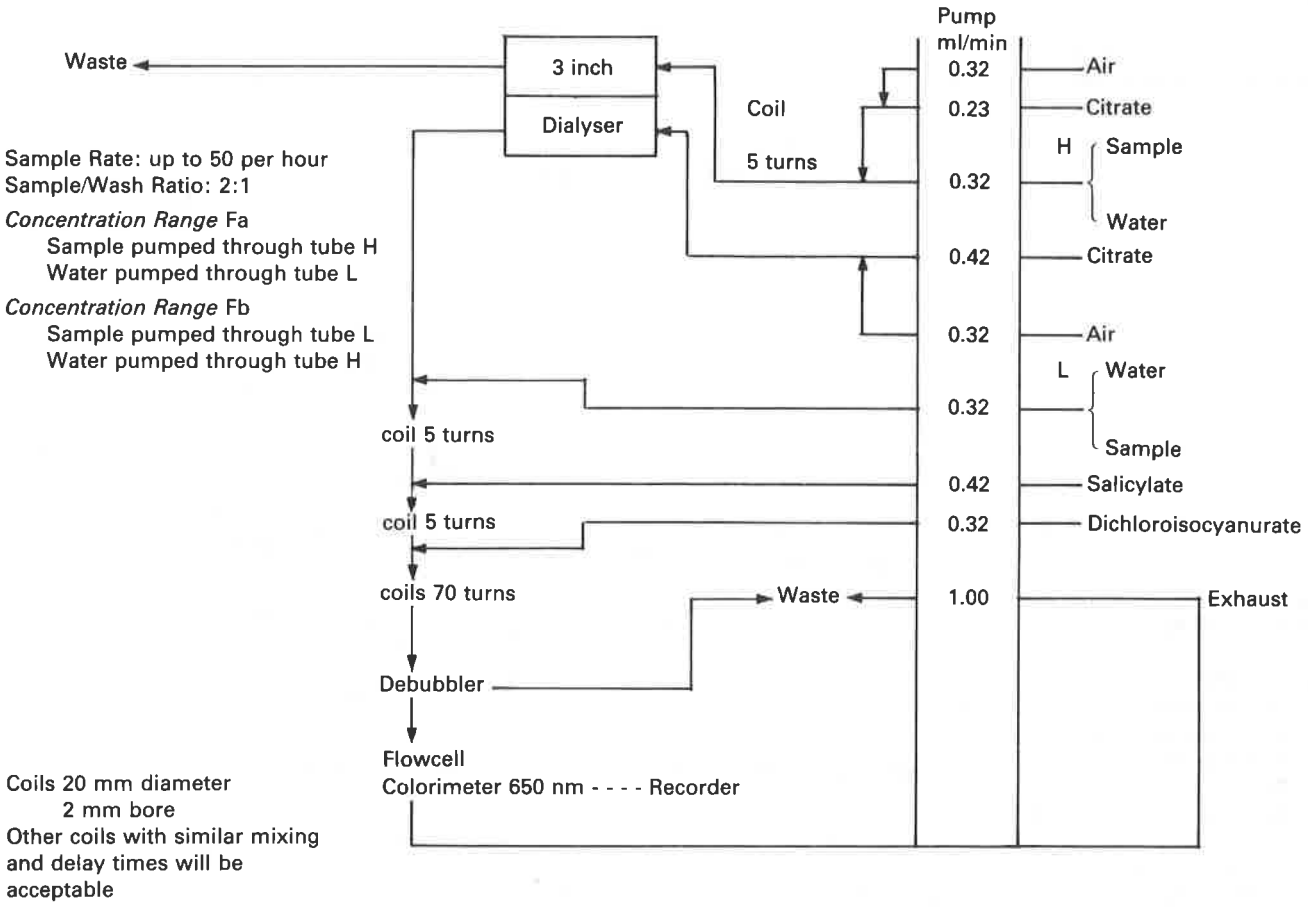
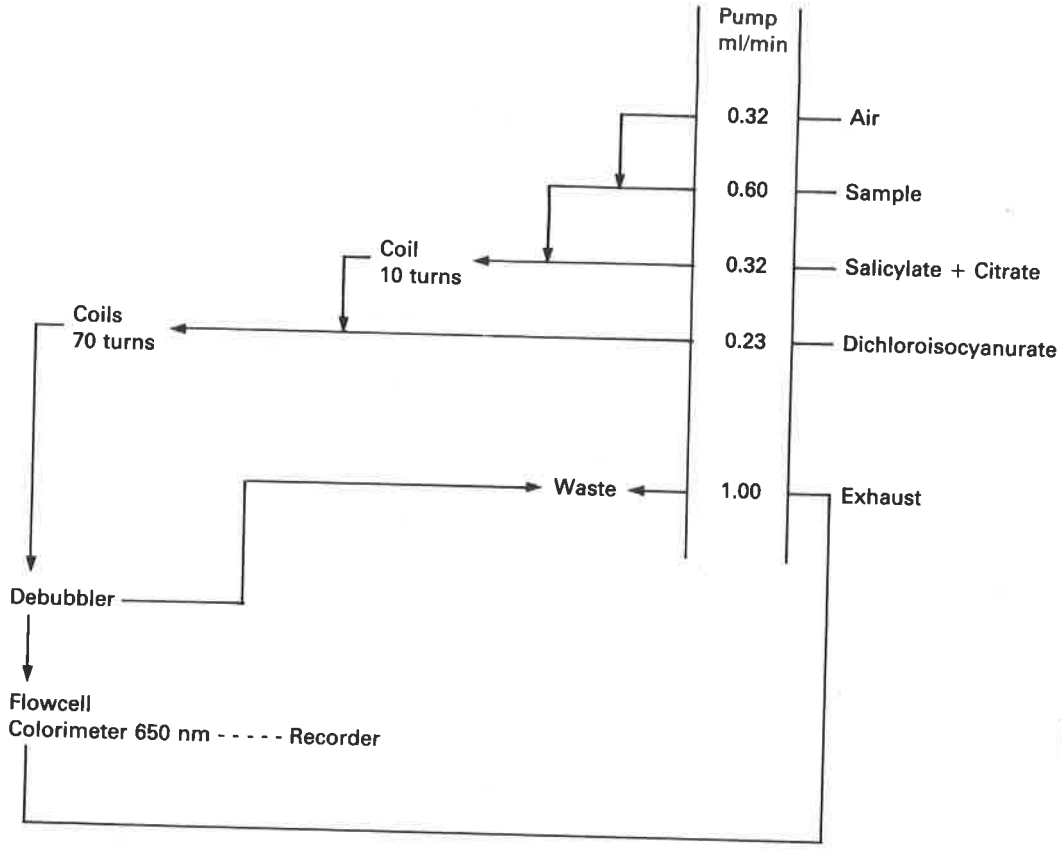


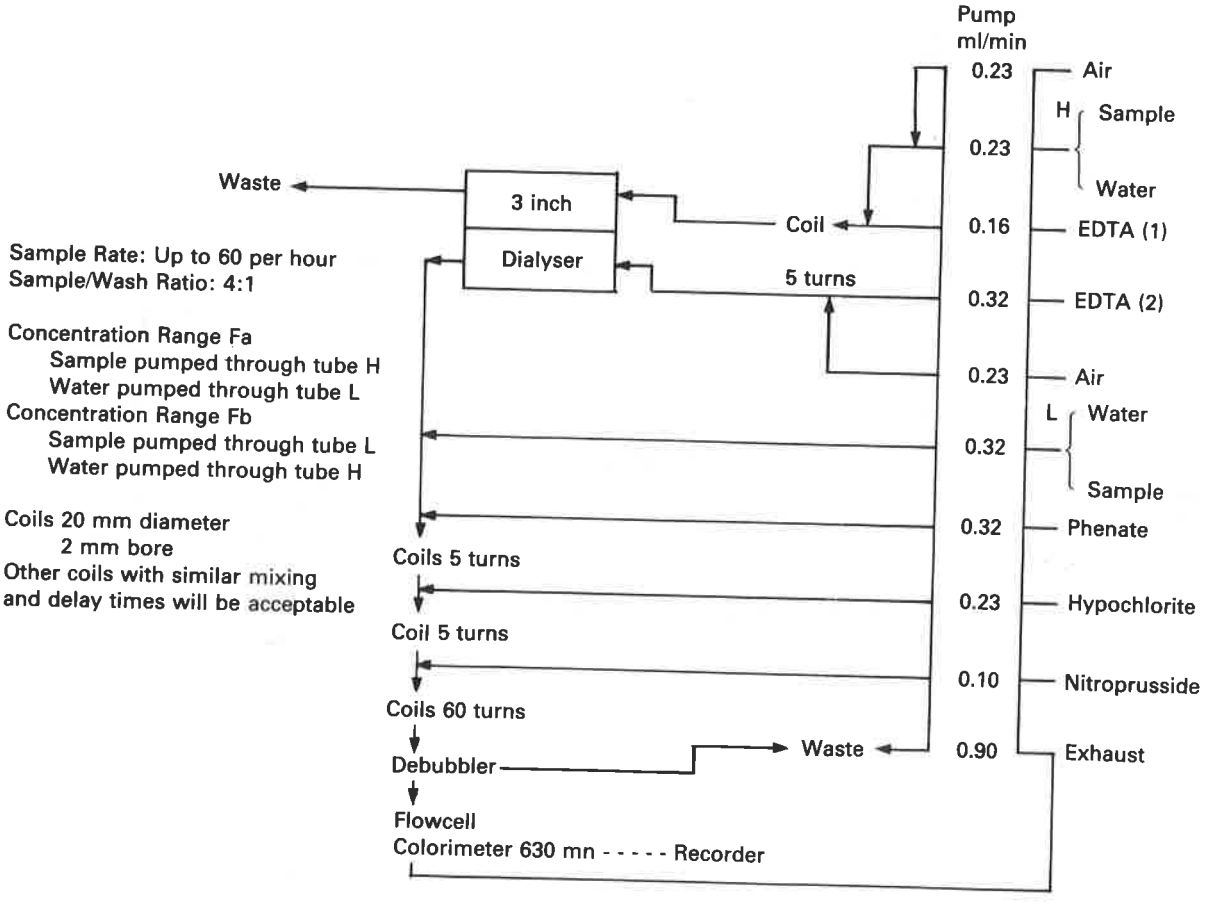
Figure 2 Manifold for S Chemistry (Ranges Fa and Fb)
Automated Determination of Ammonia

Sample Rate: Up to 50 per hour
Sample/Wash Ratio: 2:1



Coils 20 mm diameter
2 mm bore
Other coils with similar mixing
and delay times will be acceptable

Figure 3 Manifold for S Chemistry (Ranges Fc and Fd)
Automated Determination of Ammonia



Sample Rate: Up to 60 per hour
Sample/Wash Ratio: 4:1

Concentration Range Fa
Sample pumped through tube H
Water pumped through tube L
Concentration Range Fb
Sample pumped through tube L
Water pumped through tube H

Coils 20 mm diameter
2 mm bore
Other coils with similar mixing
and delay times will be acceptable

Figure 4 Manifold for P Chemistry (Ranges Fa and Fb)
Automated Determination of Ammonia

G Method for the Continuous Flow Determination of Ammonia in Sea Water

G1 Performance Characteristics of the Method

G1.1	Substance determined.	Ammonia and ammonium ion.
G1.2	Type of sample.	Sea water and estuarine water.
G1.3	Basis of method	Continuous flow colorimetry, using reactions described in Section G2.
G1.4	Range of application.	Up to 0.14 mg/l
G1.5	Calibration curve.	Linear to at least 0.2 mg/l.
G1.6	Total standard deviation.	

(a) Concentration mg/l	Standard Deviation	Degrees of Freedom
0.013	0.001	9
0.057	0.002	9
0.140	0.001	9
0.165	0.005	9

G1.7	Limit of detection.	(a) 0.0038 mg/l.
G1.8	Sensitivity.	(a) 0.07 mg/l gives an absorbance of approximately 0.2 units.
G1.9	Bias	

(a) Concentration mg/l	Max Possible bias. %
0.057	+ 6.7
0.165	+ 4.4

G1.10	Interference	(a) Methyl and ethyl primary, secondary and tertiary amines and nitrite reduce the response of the reaction. See section G3.
G1.11	Time required for analysis.	The automated system described is capable of operating at up to 40 determinations per hour. Set-up time and wash-through time may amount to 70 and 20 minutes respectively.

(a) Data obtained by Humber Estuary Committee.

G2 Principle

Ammonia reacts with hypochlorite ions, generated in situ by the alkaline hydrolysis of sodium dichloriscocyanurate, and with phenol in the presence of potasium ferrocyanide to form a blue indophenol type compound, which is measured colorimetrically. All reactions are carried out automatically using continuous flow techniques.

The reaction stream is heated to 30° after adding the reagents and is irradiated with long wavelength, low power UV light for 16 minutes before measuring the absorbance. (UV irradiation activates the indophenol reaction without hydrolysing amino acids and related compounds). Reference 12, 13, 19 and 20. The procedure given in Section 8 is based on current MAFF Fisheries Laboratory practice.

G3 Interference

Methyl and ethyl primary, secondary and tertiary amines, and nitrite reduce the response of the reaction. If these substances are present at concentrations greater than 1 mg N/1, multiple standard addition is necessary to overcome this interference (see Section G9.2 and reference 12).
Urea and common natural amino acids do not interfere.

G4 Hazards

Normal precautions to avoid skin contact and/or ingestion should be taken in the handling of all reagents.
The sodium dichloroisocyanurate solution and particularly the solid reagent should not be allowed to come into contact with acid since this would result in the evolution of highly toxic chlorine gas.
Phenol is toxic by skin absorption. Gloves and eye protection should be worn when handling it, or any reagent or effluent containing it.
The protective screen must be in place at all times when UV light is being used.

G5 Reagents

All water used in this method should be of low ammonia content (see A3.1)
Analytical reagent grade chemicals should be used unless otherwise recommended.

G5.1 37% V/V Ethanol Solution

Dilute 37 ± 1 ml of ethanol to 100 ± 1 ml with water in a measuring cylinder.
Prepare the reagent freshly each day.

G5.2 Ethanol – Phenol Solution

Dissolve 3.9 ± 0.05 g of phenol (re-distilled if necessary) in 100 ± 1 ml of 37% v/v ethanol solution (G.5.1).
Prepare the reagent freshly each day.

G5.3 6% m/V Sodium Hydroxide Solution

Dissolve 6 ± 0.1 g of sodium hydroxide pellets in about 80 ml of water. Cool to room temperature and dilute to 100 ± 1 ml in a measuring cylinder. Prepare the reagent freshly each day.

G5.4 39% m/V Sodium Citrate Solution

Dissolve 390 ± 2 g of trisodium citrate dihydrate in about 900 ml of water and dilute to 1000 ± 5 ml in a measuring cylinder. The solution is stable for at least 3 weeks.
Store in a glass or plastic bottle.

G5.5 Chlorinating reagent

Solution A

Dissolve 0.39 ± 0.02g of sodium dichloroisocyanurate in 33 ± 1 ml of 6% m/V sodium hydroxide solution.

Solution B

Place 200 ± 2 ml of 39% m/V sodium citrate solution and 67 ± 1 ml of 6% m/V sodium hydroxide solution in a 500 ml conical flask and boil on a hot plate for at least 15 minutes. Allow to cool to room temperature and adjust the volume to 250 ± 15 ml with water.
Combine the two solutions A and B in a measuring cylinder and dilute, if necessary to 300 ± 5 ml with water. Prepare this reagent freshly each day.

G5.6 **Catalyst solution**

Dissolve 0.194 ± 0.002 g of potassium ferrocyanide trihydrate ($K_4Fe(CN)_6.3H_2O$) in about 80 ml of water and dilute to 100 ± 1 ml in a measuring cylinder.
Prepare this solution freshly each day.

G5.7 **10% V/V Hydrochloric Acid solution**

Dilute 10 ± 1 ml of hydrochloric acid (d_{20} 1.18) to 100 ± 1 ml in a measuring cylinder. Store in a glass bottle.

G5.8 **Standard ammonia solution. 1 ml contains 14 μg as N.**

Pipette 14 ± 0.05 ml of stock standard solution A3.3 into a 100 ml calibrated flask. Make up to volume with low-ammonia sea-water (Section A3.2) of similar salinity to that of the samples under examination.

G6 Apparatus

G6.1 **Apparatus for this continuous flow method consists basically of the following:-**

Sample presentation unit (sampler) with 2 selectable wash receptacles, for ammonia-free water (A3.1) and low ammonia sea water (A3.2) respectively.
Multichannel peristaltic pump.
Analytical cartridge (manifold) including pump tubes and mixing coils.
Colorimeter, incorporating a flow cell.
Recorder.
Consult the essay review (13) on continuous flow analysis in this series for further information.

G6.2 The design of the manifold is as in Figure 5.

G6.3 **Two 200 mm 15W, 365 nm UV lamps,** with reflectors, are mounted in the cover of the analytical cartridge position about 2 cm above the last series of mixing coils downstream of the heating bath. Aluminium foil is placed under the coils to act as reflector.

G6.4 **Heating bath** to raise the temperature of the sample to 30°C.

G6.5 **Colorimetry interference filters,** giving maximum transmissions at 640 nm, are used with a flow cell of 50 mm path length.
Cells with optically flat end plates are preferred to the round ended cells normally used in autoanalysers, to minimize the refractive index effect.

G6.6 Air used for segmentation must be drawn through dilute hydrochloric acid solution (G5.7) in order to absorb any atmospheric ammonia.

G6.7 The 4 ml polystyrene sample cups must be washed with dilute hydrochloric acid solution (G5.7), rinsed, and drained immediately before use. The filled cups should be protected from atmospheric contamination by capping with thin aluminium foil, which will be pierced as the sampling probe descends. File the probe end to an angle of 45° to ensure it pierces the foil. A plastic dust cover on the turntable will guard against the sample cap being picked up by the probe on its return.

G7 Sampling and Sample Storage

G7.1 Filter samples, on collection, through a glass fibre filter, rejecting the first few ml of filtrate. Analyse the filtrate with the minimum delay. If immediate examination is not possible, store the filtrate in glass bottles. See Section A2. If, in order to prevent biological action, samples are frozen, special freezer bottles must be used.

G8 Analytical Procedure

Step	Procedure	Notes
G8.1	Connect system as shown in Figure 5 (notes a and b).	(a) Follow the manufacturer's general operating instructions.
G8.2	Place the sample probe and reagent lines in ammonia-free water (A3.1). Start the pump and switch on the detection and measurement units (note c).	(b) See Essay Review (13) on Continuous analysis in this series.
		(c) Ensure that there is sufficient of each reagent to avoid 'topping up' during one batch of analysis.
G8.3	Allow the system to equilibrate for at least 30 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 4.	
	Set the baseline as required on the chart recorder.	
	Initial Sensitivity Setting	
G8.4	Introduce reagents in to the pipelines, after 10 minutes transfer the sample probe into low ammonia sea water of the same salinity within ± 1°/00 salinity as the samples. Run the system for 10 minutes (note d)	(d) The method is correct for both high and low ammonia levels with variable salinity as occurs especially in estuarine tidal cycles. The procedure distinguishes between reagent blank and "refraction" absorbance which is a function of salinity. A "refraction" absorbance/salinity calibration curve can be constructed using pure low-ammonia seawater of varying salinity including the low-ammonia deionized water baseline (G8.3). Addition of reagents to the low-ammonia seawater of appropriate salinity gives the colour blank by difference. The ammonia colour response calibration curve is obtained by adding known amounts of ammonia to the low-ammonia seawater wash medium of appropriate salinity.
G8.5	When an acceptably smooth baseline trace is given at the measurement unit, transfer the sample probe into a C_M standard solution (note e) and adjust the baseline response to about 5 per cent of full scale (note f).	(e) C_M is the greatest concentration that the calibration is intended to cover. This standard solution is prepared as described in Part A3.6.
		(f) An elevated setting of the baseline allows for any negative drift that may occur.
G8.6	When there is positive stable response at the measurement unit due to the colour produced from the C_M standard solution (note g), adjust this response to read between 90 and 95 per cent of full scale (note h).	(g) The sample probe need remain only in the C_M standard solution for sufficient time to give a steady reading.
		(h) A setting of 5 to 10 per cent below full scale allows for any increase in sensitivity that may occur.
G8.7	Return the sample probe to rest in the wash solution (note i).	(i) First remove any traces of standard solution from the outside of the sample probe.
	Analysis of Samples	
G8.8	For each batch of samples of similar salinity 'spiked' standards are recorded at the beginning, end and intermittently during the run. Load the sample turntable in the following order (note j).	(j) The turntable can be loaded during the initial stabilization period (steps G8.2 to G8.4).

Step	Procedure			Notes
	Group (Section G10)	*Position on Turntable*	*Solution*	
	(1)	1–4	Low ammonia sea water.	
	(2)	5–8	'Spiked' low ammonia sea water.	
	(3)	9–28	Samples (notes k and l)	
	(4)	29–32	Low ammonia sea water.	(k) A 'spiked' standard (Section G9.2) should occupy one of the sample positions as a check on system control.
	(5)	33–36	'Spiked' low ammonia sea water.	(l) When cross contamination occurs between two samples (visible on the measurement unit trace as incomplete separation of consecutive sample responses) re-examine both samples, separating with a low ammonia sea water solution.
	Shut down procedure			
G8.9	Transfer all the lines to ammonia-free water (A3.1) and continue pumping for at least 15 minutes and finally shut off pump, detection and measurement units.			
	Maintenance			
G8.10	If cleaning becomes necessary due to dirty samples, faulty operation, or as a routine after some months, pump dilute hydrochloric acid solution (reagent G5.7) through the sample line for 5 minutes. Follow immediately, by ammonia-free water (A3.1) pumped for at least 15 minutes.			

G9 Calibration

G9.1 For sea water, calibration is carried out by addition of known amounts of ammonia to low ammonia sea water (A3.2) of similar salinity to the samples. Interference is not normally encountered with water from the open sea. If the salinity of the sample differs by more than 1°/00 from the low ammonia sea water used to prepare the standards proceed by standard addition as in G9.2.

G9.2 **Standard Addition Procedure**

For estuarine water, test for interferences by addition of standard ammonia spikes to the sample. If interference is found, replace the standard prepared with low ammonia sea water by a portion of sample spiked with known amounts of ammonia. Calculate the result for each sample from the appropriate 'spike' concentration used for the standard addition.
Typical calibration 'spiked' solutions are prepared as follows:-

For Sea Water

Dilute 1.0 ml standard ammonia solution (G5.8) to 100 ml in a calibrated flask with low ammonia sea water.

For estuarine water

Dilute 1.0 ml standard ammonia solution (G5.8) to 100 ml in a calibrated flask with the sample under examination.

G10 Calculation of Results

Construct a base line on the recorder chart, using the values obtained in Step G8.8 Groups (1) and (4) and measure all peak heights from this line. Measure the peak height of the sample (step G8.8 Group (3)) and the 'spiked' calibration standard or 'spiked' sample if the standard addition method has been used. (Step G8.8 Groups (2) and (5)).

G10.1 Using calibration standards in low ammonia sea-water
Calculate the ammonia content of the samples by direct proportion from

$$\frac{a}{b_1} \times C_1 \text{ mg/litre}$$

where a is the peak height in mm of the sample.
b_1 is the peak height of mm of the calibration standard.
and C_1 is the concentration of ammonia (N) in mg/l in the calibration standard (G9.2).

G10.2 Using standard addition with 'spiked' samples:-
Calculate the ammonia content from:

$$\frac{a}{b_2 - a} \times C_2 \text{mg/litre}$$

where b_2 is the peak height in mm of the spiked sample and C_2 is the 'spike' concentration of ammonia (N) expressed as mg/l in the spiked sample.

G11 Extension of the Range of the Method

To cover polluted sea water and water from fish-rearing establishments, the range of the method can be extended up to about 1.0 mg/l by substituting a 10 mm path-length flow cell instead of the 50 mm cell stated in G6.5. The linearity of the method in this higher concentration range should be confirmed.

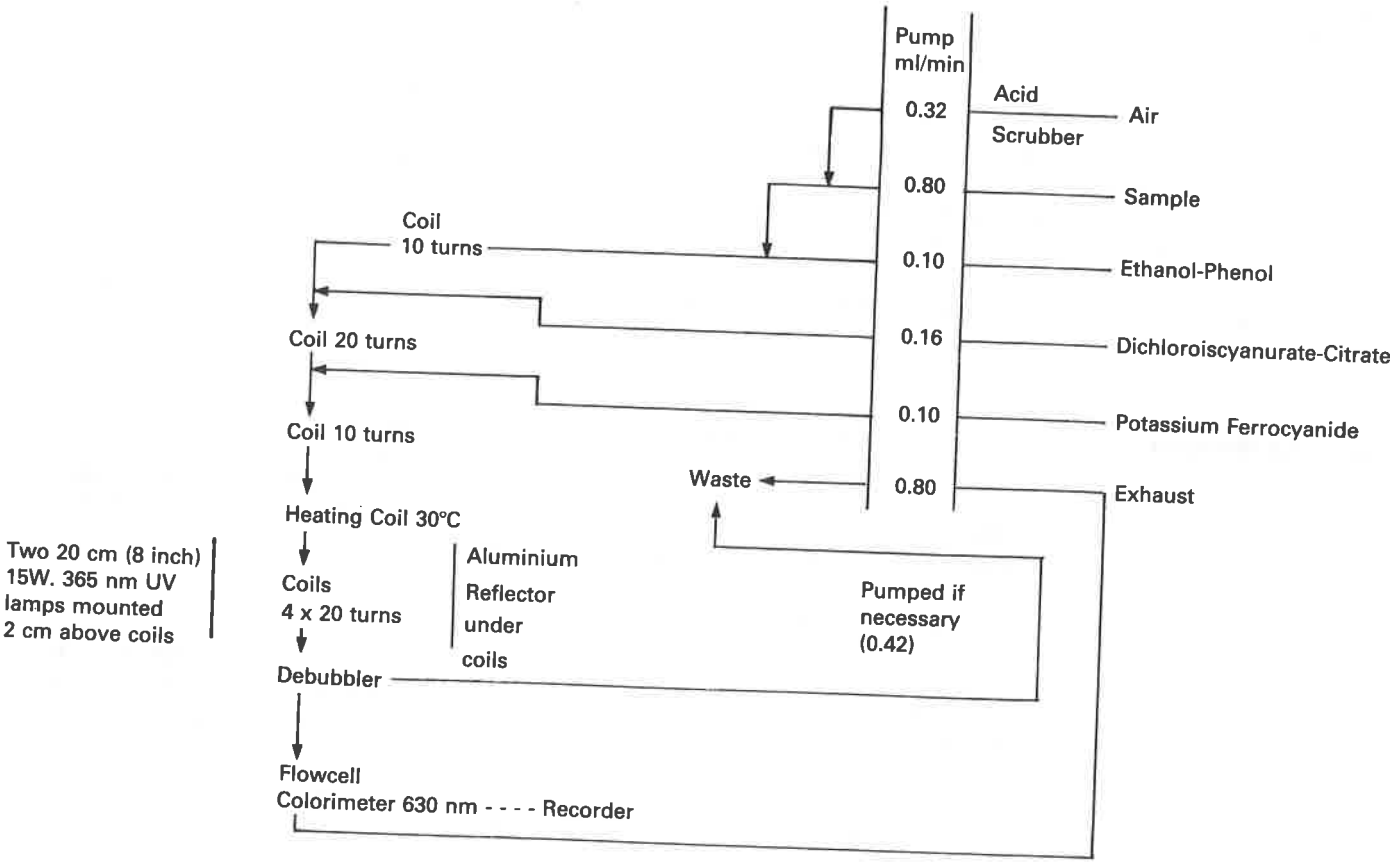


Figure 5 Manifold for Sea Water
Automated Determination of Ammonia

H 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 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 ammonia 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 (21) and by the DOE/NWC Standing Committee of Analysts (22) – should be consulted.

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Appendix

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 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 determined 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 determined concentrations, and in 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 (21) and by the DOE/NWC Standing Committee of Analysts (22) – 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.

* The Secretary
Standing Committee of Analysts
General Non-Metallic Substances Working Group
Department of the Environment
43 Marsham Street
London
SW1P 3PY

Address for Correspondence

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

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The Standing Committee of Analysts
The Department of the Environment
43 Marsham Street
LONDON SW1P 3PY
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