Flow Injection Analysis
An Essay Review and Analytical Methods
1990

Methods for the Examination of Waters and Associated Materials

HMSO

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Methods for the Examination of Waters and Associated Materials

The Detailed Analytical Methods are for:

Ammonia
Oxidized Nitrogen
Nitrite
Orthophosphate
Chloride
Silicate
Sulphate
Hardness, and
Alkalinity

Others are possible, but details are not given.

London: HMSO

First Published 1991

ISBN 0 11 752339 9

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Contents

About This Series

This booklet is part of a series intended to provide recommended methods for determining the quality of water and associated materials. In addition short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

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 These volumes inevitably took some years to prepare so that they were often partially out of date before they appeared in print.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 is published as a series of booklets on single or related topics; 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 or requirement for that particular method.

Although ideally, all methods published should be fully tested, this is not often possible without delay in publication. Furthermore, the limit of detection, range, precision and interference effects applying to instrumental methods can depend on the actual instrument used, as well as on sample type, reagent purity, operator skill, etc. Even methods tested in many laboratories have been known to acquire problems when a new domestic product appeared (introducing a new substance into effluents), changes in production methods altered reagent quality, or the method was used to analyse a new type of sample (despite apparent similarity to samples already evaluated). As a guide, the following categories have been given to methods:
tested, usually in five or more laboratories
— no grade indicated;
tested in one to three or four laboratories
— Tentative;
evaluated, but not fully tested, but publication is urgently required
— Note;
tested and found to be satisfactory by several laboratories, but in the opinion of experts requires a high degree of skill or has some other difficulty such that the method would be replaced if a better method were discovered..
— Provisional.

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 technical staff, to decide which of these methods to use for the determination in hand. Whilst the attention of users 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 a committee of the Department of the Environment set up in 1972. Currently it has nine Working Groups each responsible for one section or aspects of water cycle quality analysis. They are:

1.0 General Principles of Sampling and Accuracy of Results
2.0 Microbiological Methods
3.0 Empirical and Physical Methods
4.0 Metals and Metalloids
5.0 General Nonmetallic Substances
6.0 Organic Impurities
7.0 Biological Monitoring
8.0 Sewage Works Control Methods
9.0 Radiochemical Methods.

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the 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.

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 and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. 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 that booklet.

L R PITTWELL
Chairman & Secretary

1 February 1990

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 the due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or workplace, or subsequently for maintenance of waste disposal workers. 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. 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.

The best safeguard is a through 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. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. 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.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Safe practices in 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 Services Monograph 6, HMSO, London.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect tratment 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 inury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient, give information on the nature of the injury especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Safety while Sampling

Prior consideration must be given, especially when sampling in confined spaces or where access is difficult, to guard against suffocation, drowning, falls, and poisoning or infection by ingestion, inhalation, or skin contact.

Good Laboratory Practice

The Department of Health issues a booklet entitled: Good Laboratory Practice; the United Kingdom Compliance Programme, 1989.
This can be obtained by writing to that Department in London. It deals chiefly with toxicity studies, but much can be applied to analytical chemistry.

Foreword

In another booklet[1] in this series a review is made of discrete automated methods of analysis including Robots. That booklet also includes the second edition of the air-segmented continuous flow booklet. The third related concept of automatic analysis, Flow Injection Analysis (FIA) is reviewed here.

This booklet contains:

(a) The applicability of FIA to water analysis.

(b) Descriptions of the component parts of an FIA system with diagrams of examples where appropriate.

(c) Fundamental concepts of FIA.

(d) Appendices of an analytical procedure and details of methods for those determinands known to be used.

1 Introduction

Flow injection techniques evolved from continous flow analysers which were initially given major prominence in the early 1960s with the introduction of commercially available air segmented analysis systems[1][2]. Ever improving automation and data handling capability provides the need for more rapid analysis with greater numbers of samples being handled by single systems and fewer analysts.

Both this and some practical problems experienced with air segmented continuous flow analysis (CFA), as perceived at least by some workers, encouraged a number of researchers to continue to seek alternative ways of providing continuous flow analysis.

By the mid-seventies work by various groups throughout the world quite independent of one another, but on parallel lines, evolved the system now known as 'Flow Injection Analysis' (FIA). By general agreement major responsibility for the promotion of the technique has been attributed to Ruzicka and Hansen[3].

FIA differs from earlier air segmented systems in that the sample is injected directly into a moving stream without the addition of air. The sample-reagent zone mixes and reacts as it moves downstream towards the detector, the degree of dispersion is controlled by a variety of factors, their impact being specific to the analytical system in use. It is the control of this dispersion which is at the heart of the technique and coupled with short, highly reproducible retention times separates FIA from other CFA and provides the potential for sampling rates up to 200 per hour.

Predominantly FIA has been applied to colorimetric methods using well established chemistries also found on both air segmented and discrete analysis systems. Such analysis can be simple involving no more than the addition of the sample to the moving reagent/carrier stream or involve dialysis; solvent extraction; multiple reagent addition as intermediate steps.

Improved sensitivity can be achieved from a stopped flow technique, on line pre-treatment etc, but at the expense of sampling rate. FIA can also be applied to other detection systems eg ion selective electrodes or as a means of sample introduction to Atomic Absorption Spectrophotometry (AAS).

Simple and easy to use requiring minimal operator training, and needing little maintenance, FIA allows fast changeover from one chemistry to another and easy method development or modification when required.

It is a valuable additional technique for those laboratories requiring to use continuous flow analysis systems with a high degree of automation.

2 Application in the Water Industry

Flow injection analysis (FIA) is finding increased use in the Water Industry. Analytical laboratories which had previously used air-segmented continuous flow automatic analysis (CFA) to determine parameters associated with the aquatic environment, have introduced the concept of FIA into their working practices, not to replace CFA but to complement it. When there are small batch sizes of samples requiring numerous determinands to be measured, FIA might be a preferred technique. For low-level concentration work where speed of analysis is essential to off-set air-borne contamination again FIA is of value. The concept of FIA lends itself quite readily to the on-line monitoring of a water course.

Table 1 gives a list of some of the determinations most frequently carried out to which an FIA technique can be applied.

Table 1 Some determinands frequently analysed in the Water Industry to which FIA has been applied.

Ammonia	Sulphate	Aluminium
Oxidized Nitrogen	Hardness	Iron
Nitrite	Alkalinity	Boron
Orthophosphate	pH	COD
Chloride	Conductivity	Cyanide
Silicate	Fluoride	Surfactants

This table reflects what is known to be achievable and is not regarded as an exhaustive list of determinands which can be measured using the FIA technique. The contents of the table are also referred to in another publication in this series, Discrete and Air Segmented Automated Methods of Analysis including Robots. An Essay Review (Second Edition) 1988.[1]

An appendix of this booklet gives information on some individual methods which are in use.

3 Equipment

A flow injection analyser consists of four major components. A propelling system to transport the carrier stream to the detector. An injection system to introduce the liquid sample into the carrier stream. A reaction zone to introduce reactants and achieve the appropriate mixing in the moving stream, and finally a detector to continuously monitor the flowing stream. See Fig. 1.

3.1 Propelling Systems

In transporting the stream to the detector the propelling system must be constant and reproducible to achieve a constant dispersion and residence time. There are in general four types of propelling systems; the peristaltic pump, the displacement (piston) pump, gas pressure systems, and, constant head devices.

3.1.1 Peristaltic Pumps

The peristaltic pump is the most popular of the systems available; it normally has several channels, the commonest carrying up to five pump tubes. The pumping rate is changed by using colour coded pump tubes of different internal diameters. The tubes are also supplied in various materials so that organic, acidic and basic solutions can be pumped. The delivery rate of the pump tube will change with time, but as this is a slow change it will not normally affect analytical results providing regular recalibration of the method is carried out. The peristaltic pumping action tends to give pulsed streams, but this has effectively been overcome by rotating the pump head at a high rate and by having closely spaced rollers. The roller contact with the tubes can be many times per second. (See Fig 2).

A minor problem associated with peristaltic pumps is that they generate static electricity which may affect measurements by ion selective electrodes, this can be overcome by short circuiting the inlet and outlet of each tube.

3.1.2 Displacement Pumps

Displacement pumps have not been widely used for flow injection analysis despite the high precision in volume delivery and reproducible timing, since they are designed as single channel units which makes them expensive when compared to peristaltic pumps. Their action can produce high pressures up to several hundred atmospheres.

The displacement pump also produces a pulsed stream, especially single-piston pumps, and dampers and restrictors are required to obtain a pulse free flow.

3.1.3 Gas Pressure Systems

A pressure regulated inert gas is used to pressurise the reagent and carrier containers, the flow on each stream is controlled by a ball/screw restrictor valve. The resulting flow is pulse free along with no generated electrical interference.

The main problems with these systems are regulating the flows on each stream and the possible bubble formation from the different solubility of the gas in the various reagents. (See Fig 3).

3.1.4 Constant Head Devices

Gravity fed reagent and carrier streams give pulse free systems, but require large reservoirs of solutions so that only small differences in the hydrostatic pressure are observed.

3.2 Injection Systems

The requirements of the injection system are that a highly reproducible sample volume is injected as a well defined zone into the carrier stream with minimum disturbance of the carrier flow. The requirement of precision is particularly important as the physical dispersion coefficient (see section 5) obtained can be critically dependent on the volume injected, with small changes in the volume producing large changes in peak height.

Although the use of a considerable variety of devices has been reported in the research literature, it is not possible to achieve the ideal performance necessary for the valve to exert no influence on the dispersion and precision. Early FIA valves were constructed so as to have an external sample loop which could be readily changed and a by-pass line so that the carrier stream continued to flow while the valve was in transition between the 'fill' and 'inject' positions. The latter design feature has not appeared in commercially available equipment which has to a large extent standardised on the six-port rotary injection valve.

This is a low pressure valve with an external loop. The carrier stream flow is stopped during the movement of the valve rotor and thus the speed with which the valve is actuated affects the dispersion. These valves can be mechanically actuated either by an electric motor or pneumatically, in which case the gas pressure is controlled by a solenoid valve.

Similar performance may be obtained from commercially available 8-port slider valves which may be configured with either one or two sample loops. Mechanical actuators are also available for these types of valve.

Recently more complex valves have appeared for FIA purposes in which the movement of one rotor causes the simultaneous injection of two solutions into two parallel carrier streams, thus facilitating the merging zone configuration. See Figs 4 and 5.

3.3 Reaction Zone

3.3.1 Tubing

The simplest type of manifold consists of a single length of tubing. In order to achieve the appropriate degree of mixing from the interdispersion of merging streams, in a reasonable time scale and without undue carry-over between successive injections, the tubing is constructed from a non-wettable plastic, often polytetrafluoroethylene (PTFE), and has a bore of about 0.5 mm. Tubing of this sort is inexpensive, readily available and easily flanged for making low dead-volume connections. This type of connection, although inexpensive, can be a source of imprecision if connections have to be repeatedly made and broken. There are various other devices available of which the type utilising friction fit end-ferrules enabling the tube ends to be accurately lined up gives better precision.

As a typical manifold may contain several metres of flexible tubing it is convenient to coil the tubing. This also promotes mixing as a secondary flow pattern (a circulation from the centre to the wall) is produced, although this is not significant unless the tubing is tightly coiled. Other physical contortions, such as knitting* have been used to promote mixing. Poor precision will result from tubing that is allowed to change its configuration during the routine operation of the FIA system.

**Knitting:*
Knitting is the term used to fix the lengths of tubing in shapes, other than the normal coil, to promote mixing.

3.3.2 Mixing

Multi-line manifolds, in which reagents are added at downstream confluence points, have been proposed for many determinations. As the conditions are such that laminar flow is obtained it is quite difficult to achieve efficient mixing at confluence points and therefore the geometry of such confluence is configured to promote mixing as, for example, with the 60 degree confluence with the outflow on the angle bisector.

3.3.3 Treatment

Devices such as the packed-bed reactor, a small column of inert glass beads, and its practical lowest limit, the single bead-string reactor* are often incorporated downstream of the confluence point to promote mixing.

A wide variety of chemical manipulations have been carried out in FIA manifolds. In addition to the basic homogeneous single phase reactions, liquid-liquid extractions may be performed by merging an immiscible liquid stream. Under these conditions, segmentation of the streams occur and as one of them will wet the tube wall, (the organic solvent in the case of an organic liquid/water/PTFE tubing system), extraction of components will occur. On-line phase separation may be achieved by a variety of means, the simplest of which is to use gravity at a vertical T-piece. The direction of the flow of organic liquid may be assisted by the inclusion of a PTFE whisker†. Membrane separators, again made of PTFE have also been used and recently tubular membranes (as typified by the Gortex material) have been shown to be effective. Membranes of this sort are also permeable to gases and allow gas liquid separation. The acceptor stream can be gaseous as in hydride generation for AAS or Inductively Coupled Plasma Optical Emission Spectrophotometry (ICP-OES), or liquid as in the transfer of carbon dioxide in the determination of carbonate/hydrogen carbonate on the acidification of the sample zone. Dialysis membranes have also been incorporated into FIA manifolds.

The packed bed reactors, described above for the promotion of mixing, could contain chemically active functions. Thus on-line reductions may be achieved with, for example cadmium reactors, as can preconcentration and matrix removal with ion exchange resins, possibly incorporating chelating functions.

3.4 Detectors

The requirements for the detector are those normally associated with analytical instrmentation in general, namely high sensitivity rapid response, low noise, good stability, wide dynamic range and it should make a minimum contribution to the dispersion effect. This may be quite difficult to achieve in practice as it necessitates the use of low volumes and an absence of sharp bends or changes in diameter of the reaction tubing. In general, detectors designed for use in High Performance Liquid Chromatography (HPLC) and Ion Chromatography (IC) will be suitable for flow injection purposes.

3.4.1 Colorimetric methods

The most widely used detectors are those for measuring molecular absorption in solution, ie measuring the absorbance of light (radiant energy) by a coloured solution. Other approaches relative to molecular activity which are finding increased use are molecular chemiluminescence, bioluminescence, or fluorescence.

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*A single bead-string reactor consists of a PTFE tube which is packed with glass beads whose diameter is 60–80 per cent of the tube diameter.

†*Whisker:*
Whiskers is the general term for the PTFE or hydrophobic paper used in T shaped continuous phase separators. The organic phase is separated by its adhesion to these hydrophobic materials.

3.4.2 Electrochemical methods

Electrochemical methods have also been used to a considerable extent, the most popular being potentiometry and amperometry. Because these detectors respond to the concentration in the fluid immediately adjacent to the sensing surface it is important that flow cells are designed so that the concentration in the centre of the zone is sensed. Thus this area has seen more development than solution spectrophotometry in terms of the design of cells specifically for flow injection work, though a similar programme of development is evident for the molecular luminescence spectrometries.

3.4.3 AAS/ICP-OES methods

A considerable number of publications have appeared describing the use of atomic spectrometric methods, the majority of which concern AAS, but there is an increasing minority concerned with ICP. Most of the publications describe the interfacing between the reaction zone and the spectrometer as the simple connection of the distal end of the tubing to the outside of the nebuliser.

Two samples of published work[4,5] are cited in the References section of the booklet but numerous others are to be found in text books on the subject of FIA, eg References 3 and 6.

4 Data Acquisition

FIA, like all continuous flow analysers, monitors the response by the detection/measurement system to the changing concentrations of a determinand or its chemical derivative with time.

Information is therefore available as a continuum of data points which can be:

(a) displayed as an analogue signal on a potentiometric recorder from which manual calculations can be made.

(b) fed into a microprocessor or computer system programmed to provide individual sample results in the required format.

Common practice is to compare the responses from samples with those obtained from a series of standards which have been analysed in the same way under identical conditions and from which an appropriate calibration can be obtained.

The continuum of information can be used in three different ways best described from the pictorial presentation obtained from the analogue signal, but equally valid from electronic digital systems.

(i) Peak height—Using this procedure and having established a base line or zero determinand response, calibration and sample values are obtained from an identification of the maximum signal relative to the base line produced by each standard or sample on its passage through the detector/measurement system.

Peak height measurements can however be limited by high determinand concentration depleting the reagents to generate a non-linear response. A similar effect can also arise consequent of other chemical reactions occurring during the analytical procedure.

It is however, not essential that peak maximum is used as the reference point of the measurement; any point on the rising or falling profiles can be chosen.

Peak height is the most commonly used technique particularly when data can only be obtained in the analogue form. The precision and accuracy achieved will be affected by the speed of response of the detector to the changes in the flowing stream and extent to which the profiles from such changes have reproducible symmetry.

(ii) Peak area—Having established the base-line or zero determinand response, the area relative to that base line and enclosed by values produced as each standard or sample passes through the detector/measurement system is obtained. Comparisons are then made as in (i).

The calculation can be carried out manually from the analogue signal, but more usually is microprocessor controlled or provided by computer software.

Peak area is more dependent upon the flow rate than peak height and suffers the same linearity problems. It offers little advantage and is less commonly used.

(iii) Peak-width—Least used and relevant only when the chemistry involved reaches a precise reproducible and identifiable event ie a given redox potential in titrations. Values can then be obtained under constant conditions by the measurement of the peak width on the analogue output or microprocessor/computer simulation in the digital mode. It is not necessary for the signal to have a linear relationship with concentration.

The choice of procedures to be adopted for a particular analysis can be at the analyst's discretion, but will be determined by:

(1) the application involved

(2) the equipment to be used—all commercially available equipment provide peak height; peak area and peak width are not always available

(3) accuracy and precision required from the results.

5 Fundamental Concepts

5.1 Dispersion

During the residence period in the flow system the injected and carrier fliuds mix. The extent of this mixing is controlled by the fluid flow patterns in the reaction zone. Most flow injection (FI) analyses are based on the detection of species produced from the reaction between components of the injected solution and components of the carrier stream(s) and thus some mixing is necessary. As the extent of mixing increases, method sensitivity and sampling frequency decrease, so the development of an FIA procedure involves the design of an appropriate degree of mixing.

Flow injection reaction zones can be classified into two broad design types (see section 3.3), single-line and multi-line. These differ in that in the former, a significant contribution to the mixing normally comes from the inter-dispersion of sample and reagent due to the flow patterns in the open tubing, whereas in the latter a significant amount of mixing is due to stream merging at confluence points.

The shape of the reaction product profile which is recorded is a combination of physical dispersion and chemical reaction effects. The physical and chemical conditions usually employed in FIA give rise to chromatography-type peaks rather than to autoanalyser-type peaks.

5.2 Quantifying Dispersion

In FIA the extent of the dispersion is usually expressed in terms of peak height. This may be contrasted with chromatography practice, in which peak separation is of prime importance, and thus the extent of dispersion is expressed in terms of peak width. The ratio of the injected concentration, C_o, of a given component to that corresponding to any point on the dispersed concentration gradient, C_g, is known as the dispersion coefficient, D_g. Thus each peak is characterised by an infinite number of D_g values ranging from infinity at the beginning of the peak, falling to a minimum at the peak maximum and rising to infinity again at the end of the peak.

The value of the dispersion coefficient at the peak maximum is normally used as a single parameter to characterise the extent of mixing in any particular FI system and is simply given the symbol D. Typically it is measured as the ratio of the detector response to the undiluted injected solution to that at the maximum of the FI peak. A test compound to which the detector responds linearly is chosen; for example, in the case of spectrophotometric detection, solutions of potassium permanganate or dyes may be used. In practical terms, the dispersion coefficient is the ratio of concentrations, before and after the dispersion processes have occurred, in the element of fluid that yields the analytical read-out.

Values of D may be conveniently classified as 'reduced' (<1), 'limited' (1–3), 'medium' (3–10) and 'large' (>10).

5.3 Factors Controlling Dispersion

The overall peak profile is made up of the concentration gradients generated by the flow characteristics of the fluid in the particular reaction zone together with a contribution from diffusion along concentration gradients. Several different hydrodynamic regimes occur in FI reaction zones in common use.

5.3.1 Laminar Flow and Diffusion

Tube diameters and flow-rates commonly used are such that laminar flow would be expected in the absence of any other effects. This produces a parabolic velocity profile between the stream-line in the centre of the tube, which is flowing at twice the average linear velocity, and the stream-lines at the tube walls, which are stationary (see b, Fig 6). The resultant peak shape is sharp rise followed by an infinitely long tail (see b, Fig 7). The effects of this process are offset by molecular diffusion across the concentration gradients so generated. As diffusion in liquids is a relatively slow process, it only makes a significant contribution when long residence times are involved. A diffusion dominated peak is Gaussian in shape (see e, Fig 7).

5.3.2 Other Flow Patterns

There are usually no sustained periods of turbulent flow. It may occur during the injection process if a valve is used that diverts the carrier through a loop by some stream switching mechanism during which neither the valve is by-passed nor the pump stopped. Turbulence might be expected immediately downstream from confluence points at which the streams merge at right or obtuse angles. Regions of tortuous flow occur through packed beds and single bead strings. The effect is to make peaks more symmetrical.

Some reaction zones are deliberately designed with mixing chambers. These produce exponential peaks. Sudden increases in tube diameter can produce a similar effect from the resulting eddy currents. This is often observed with solution spectrophotometric cells, particularly those of volumes greater than 8 μl.

Tight coiling (or other similar contortion) of the tubing produces a circulatory flow from the tube walls to the centre. This reduces the peak width. Although FI tubing is often coiled for convenience of construction, the coil radius is not usually small enough for this effect to be significant.

5.3.3 General Guidelines

The effects described above may be summarised as a collection of 'rules' concerning dispersion coefficient. These are:

(a) D increases with increasing tube length

(b) D increases with increasing tube diameter

(c) D increases with increasing average flow rate (this is a rather gross generalisation as there are many reaction zones in use for which D is largely independent of the average flow rate and there are situations in which D increases as the average flow rate decreases)

(d) D increases with increasing detector volume

(e) D increases with increasing molecular diffusion coefficient (the effect is only observed for large differences in this parameter).

(f) D decreases with increasing volume injected (this is the single most powerful method of changing D)

(g) D decreases with the use of packed beds and bead strings

(h) D decreases with increasing tortuosity of tubing (eg tight coiling)

(i) D decreases with increasing temperature (again this is a rather gross simplification as the effect observed depends on the variation in diffusion coefficient and viscosity with temperature).

5.4 Illustrating Dispersion

It is difficult to provide accurate diagrams of the dispersion process in FIA because of the dimensions of the tubing used, the magnitude of the injected volume and the high linear flow rates. If the sample volume is 50 μl and the internal diameter of the tubing is 0.5 mm, the sample occupies a length of about 250 mm. If a longitudinal cross section of the tubing is represented by a scale drawing in which 1 cm represents 0.5 mm (a typical tube diameter), then the length of the initial sample zone at time, $t=0$ would be 500 cm.

Drawing the shape of the dispersing sample zone at $t>0$ also presents problems. Under conditions of laminar flow (see section 5.3.1 above), the centre stream-line is moving at 170 mm s^{-1} for a bulk flow of 1 ml min^{-1}.

Thus on the scale selected, the centre of the profile is displaced 340 cm for every second of elapsed time. It should be borne in mind that most text-book illustrations of dispersion in FIA show atypically small volumes and concentration contours representing only the first few milliseconds of laminar flow. Diagrams illustrating different stages in the dispersion process are given in Fig 6. The corresponding concentration profiles are shown in Fig 7.

5.5 Predicting Values of D

The only way at present to assemble a reaction zone with a desired D value is to use the guidelines above together with previous experience and measurements of the effect of changing some parameters on the observed value of D. This is particularly true for manifolds designed for gas diffusion, solvent extraction, dialysis or precipitation where the manifold may be designed for preconcentration.

Although it is possible to write equations for most of the hydrodynamic regimes described above when considered individually, it is not possible to produce useful equations for any given reaction zone which incorporates several different types of flow. Most practical reaction zones fall into this category. Attempts have been made to derive equations empirically[7] and to devise simple models for the overall flow effects[8]. This latter approach appears the more promising.

5.6 Precision of Flow Injection Measurements

The precision of flow injection measurements depends on the precision of physical dispersion and of chemical reaction. The precision of D depends on the precision of the factors outlined earlier (section 5.3). The most important of these are the fluid flow patterns and the volume injected and thus high precision will only be obtained if good quality pumps and valves are employed.

The use of high precision moving parts means that each element of the injected fluid is in the manifold for a reproducible time and, as the fluid dymanics ensure reproducible mixing with reagents, the extent of chemical reaction observed is also reproducible and thus high precision is obtained.

Product profiles may differ substantially from the physically dispersed reactant profile, depending on the relative concentrations of the reactants in the fluid elements and the reaction kinetics.

6. Safety

Safety is of paramount importance in the laboratory; an environment in which the risk of serious injury can be high if safe working practices are not observed.

Users of Flow Injection Analysis Equipment must be aware of and follow the Safety Code of Practice applicable to the laboratory in which they work.

This should include:

(1) Wearing of laboratory coats and safety spectacles at all times whilst working in the laboratory.

(2) Ensure, before use, that every piece of electrical equipment has been fitted with an approved electrical plug carrying the appropriate fuse and that such equipment has been tested by an authorised person to verify that it is safe to use.

(3) All manufacturer's instructions or, in their absence, working instructions written by an authorised person, are followed.

(4) All chemicals used in any analysis should be clearly identified. The hazards associated with their use and any specific handling instructions must be clearly understood.

(5) Clean glassware to be used, not cracked or chipped such that it presents a hazard to users or adjacent personnel.

It should only be used for the purpose described in the analytical method and for which it was designed.

(6) Any system malfunction should be reported and checked by an authorised person before continuing with the analysis.

Specific chemical hazards are highlighted in the individual methods where appropriate. **COSHH REGULATIONS MUST BE OBSERVED**[9].

References

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2. Skeggs, L T., *Am. J Clin. Pathol.*, 1957, **28**, 311.
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4. Tyson, J F., *Analyst*, 1985, **110**, 419.
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7. Gomez-Nieto, M A., Luque de Castro, M D, Martin, A and Valcarcel, M., *Talanta*, 1985, **32**, 319.
8. Stone, D C and Tyson, J F., *Analyst*, 1987, **112**, 515.
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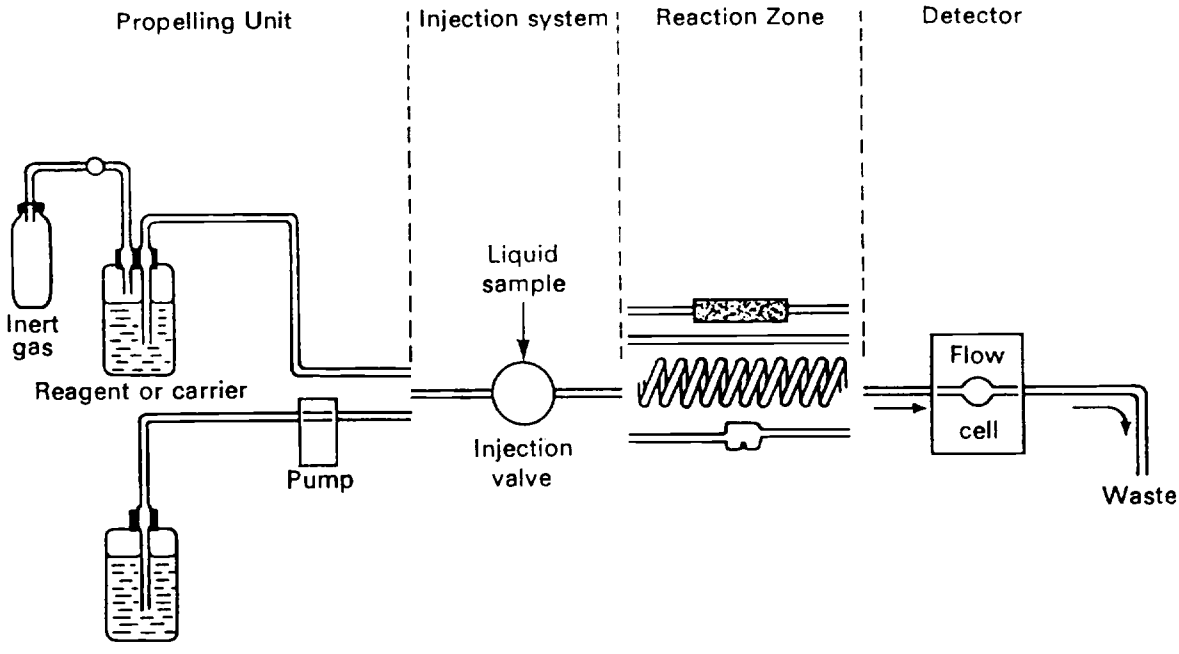
Figure 1 General arrangement of an FIA system



Various alternatives are shown at each section.

Figure 2 Schematic diagram of a peristaltic pump

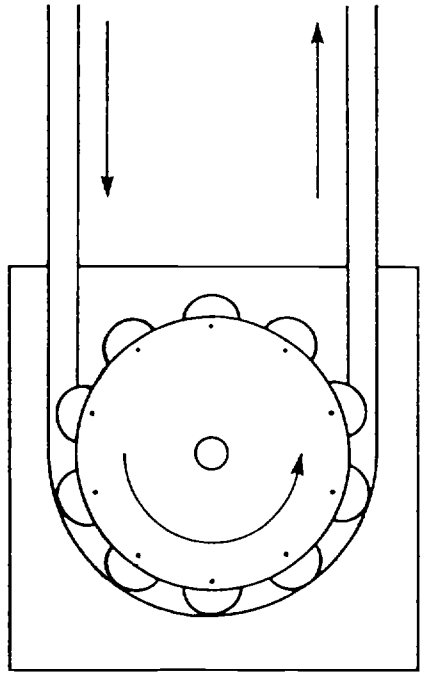


Figure 3 Pressure-based propelling system

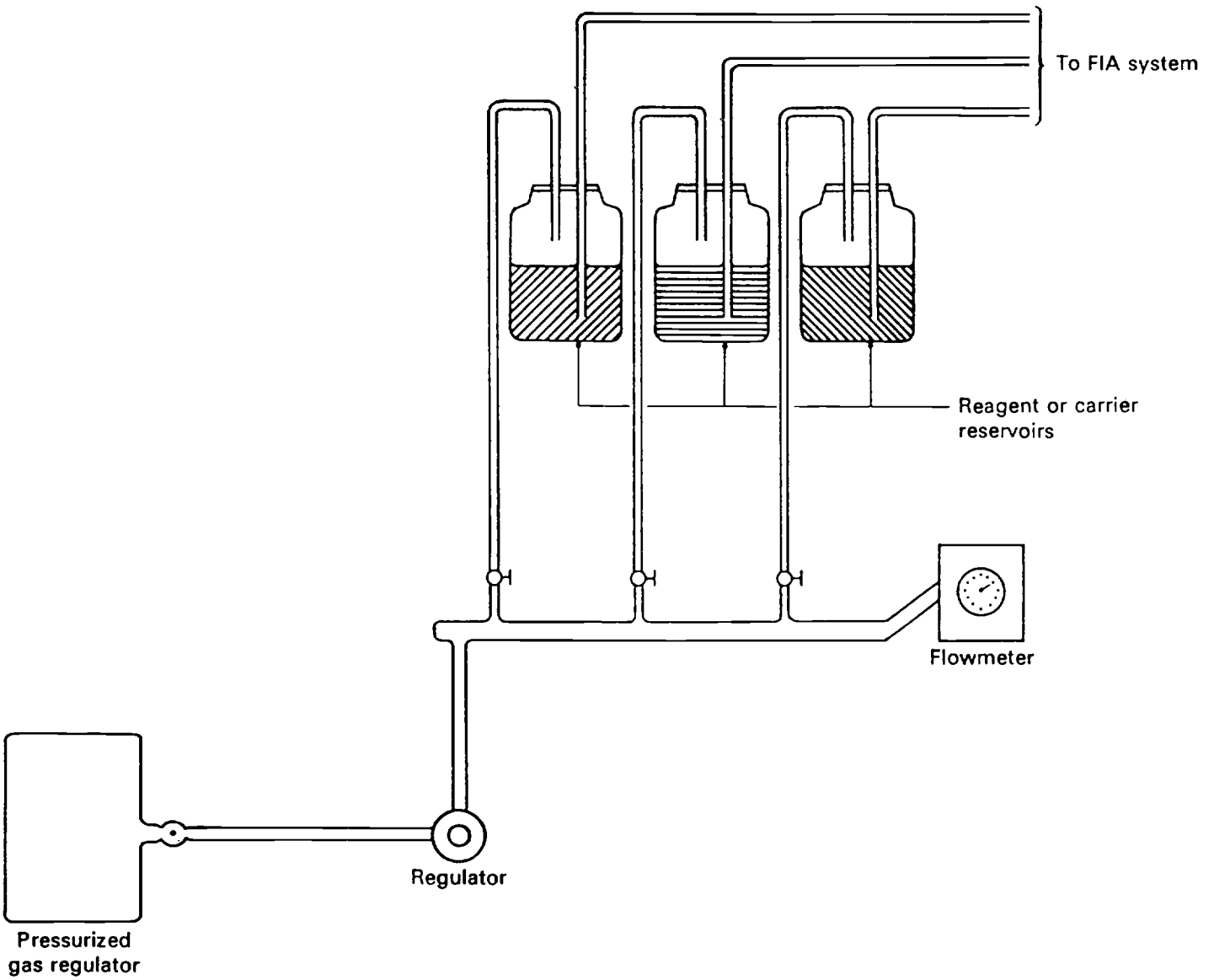


Figure 4 Rotary injection valve

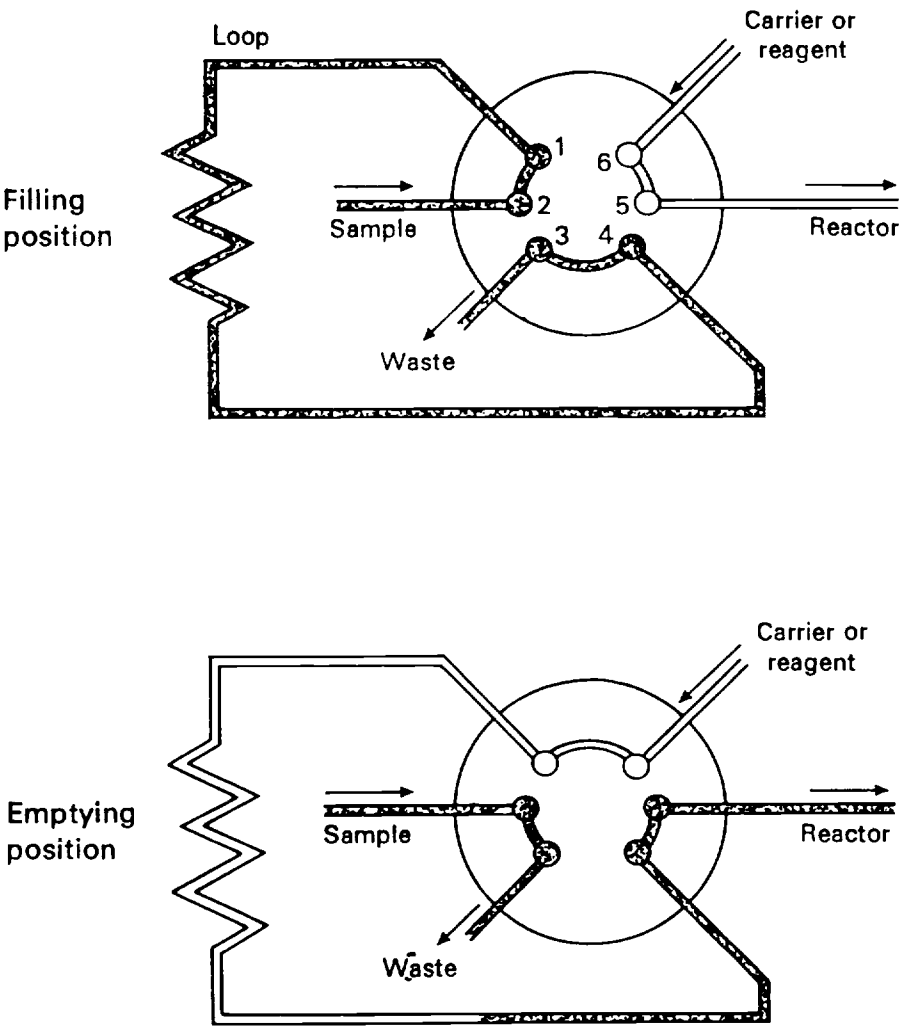
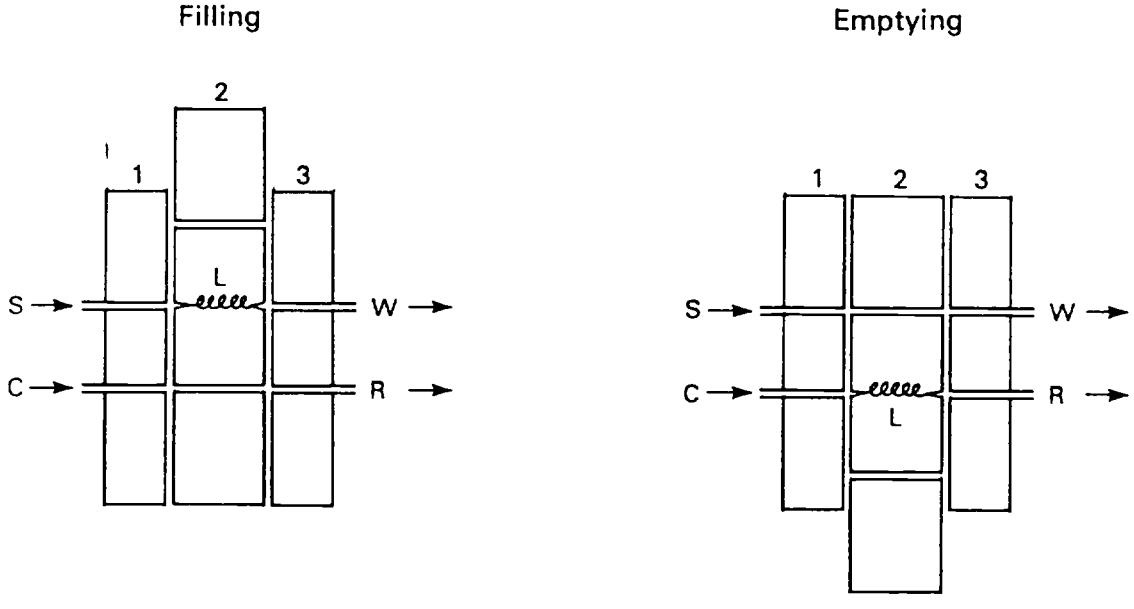
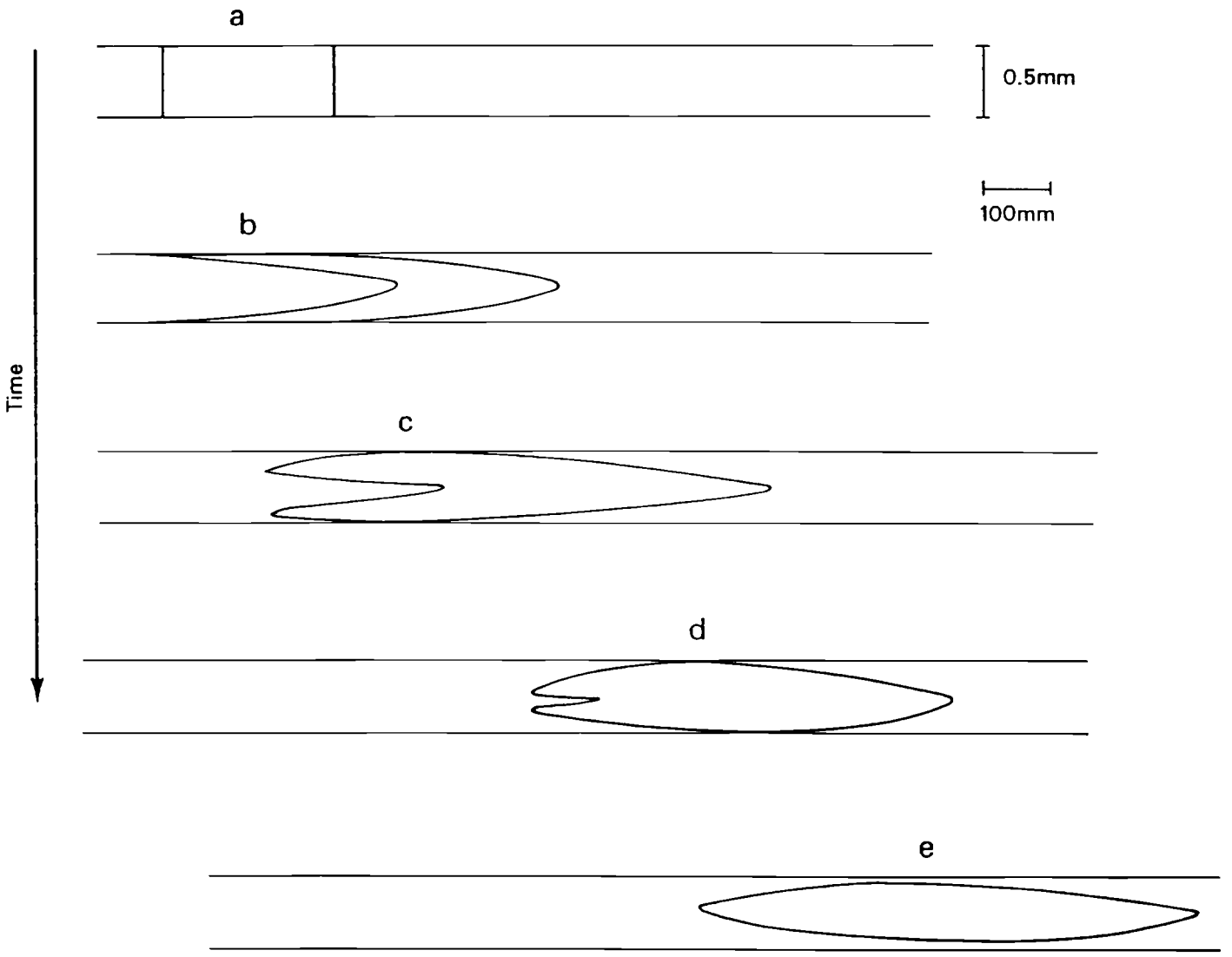


Figure 5 Sliding injection valve



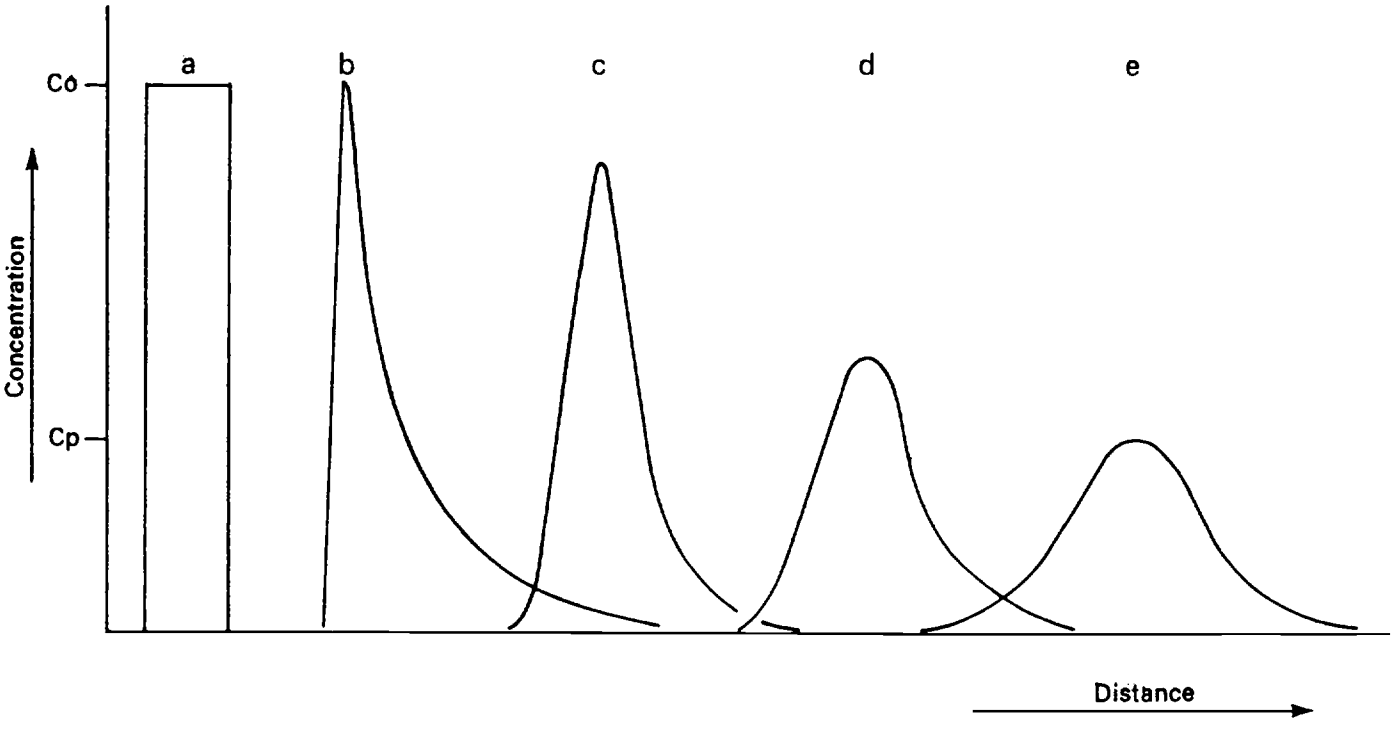
S Sample
C Carrier
W Waste
L Sample loop
R Reactor

Figure 6 Representation of concentration contours at stages in the dispersion process



a. At the instant of injection (t=0) of 50μL into a 0.5mm i.d. tube
b. After 1 s of laminar flow
c. and d. Combination of laminar flow and diffusion (only radial diffusion makes a significant contribution)
e. As for c. and d. but with significant contribution from diffusion
Note the difference in longitudinal and axial scales

Figure 7 Concentration - distance profiles along the centre stream-line for the four stages of dispersion shown in Figure 6



The concentration represented is that obtained by averaging over a small volume. The profiles also give an indication of the shape of the response-time peaks obtained with a detector which views a small radial region. Detectors which view axially distort the profiles considerably. For peak e, the dispersion coefficient D, is given by Co/Cp where Co is the injected concentration and Cp is the concentration at the peak maximum.

Appendices

Foreword to the Appendices

The analytical methods detailed in the appendices are known to be in use in one or more water utility laboratories. The systems used are either those which are available commercially or those which are produced as hybrid systems by the individual. FIA systems are classed as being modular in design and a DIY system is attainable.

Where computerised data handling is used to process raw analytical detector responses from the FIA system, the analyst should ensure that the results are correct. If possible, periodic checks by comparison to manual interpretation should be made.

The analyst should be aware that any modifications to the chemistries described here might result in changes in the performance data obtained. The limit of detection quoted for each method was calculated as 4.65 multiplied by the standard deviation value of the lowest calibration standard used.

Water

The water used to prepare reagents and standard solutions and to provide a blank or baseline response should contain a negligible concentration of the determinand(s) of interest when compared to the lowest standard solution of that determinand under examination. Distilled or deionised water is suitable for the purpose.

Sample Collection, Preservation and Storage

Samples are collected in suitable bottles filled to overflowing ensuring that the bottle, cap, lid or cover is made of material that will not interfere with the determinand(s) under test. Bottles themselves might require a pretreatment, eg with acid, to prevent adsorption of the determinand by glass. Samples should be analysed as soon as possible after collection. Storage at 4°C may improve stability. Alternatively, the addition of a preserving agent might be suitable for an individual determinand.

Reagents and Standards

Analytical grade chemicals are used to prepare reagent and standards unless stated in the individual method.

Apparatus

Apparatus for the flow injection methods consists basically of the following:

A propelling system to transport the carrier stream to the detector	eg peristaltic or piston pump
An injection system to introduce the sample or standard solution	eg syringe or autosampler, used in conjunction with a valve
A reaction zone	ie to introduce reagents and for mixing
A detector	ie to continuously monitor the flowing stream

Appendix 1: Analytical Procedure for the Methods in Appendix 2

If a commercially available system is to be used, the manufacturer's operating instructions should be used explicitly. In their absence, the procedure shown here should be considered.

If the same FIA reaction zone and detector are to be used for a second chemistry, it is important to ensure that all traces of the first chemistry are removed. This can be achieved by pumping a suitable cleaning solution, eg dilute acid or detergent, through the analytical system for, say, 10 minutes followed by pumping distilled water for at least the same time.

Step	Procedure	Notes
Starting Operation		
1.	Connect the propelling, injection and transport and reaction systems together as appropriate to the chemistry. (notes a, b and c)	(a) See appendix for specific determinand chemistries. (b) For commercially available systems follow manufacturer instructions. (c) The injection system may be linked to an auto-sampler for large batches of samples.
2.	Place all reagent, carrier and sample stream lines in water, start the propelling system and switch on the detection and measurement units. (note d)	(d) Allow the system to equilibrate for a time at least equivalent to the particular determinand response time. During this time operate the injection system manually or automatically (refer to note c above) and check that the hydraulic behaviour is satisfactory and no leaks occur. Eliminate difficulties before proceeding to step A1.3
3.	Place the reagent and carrier lines in their respective reservoirs. (notes e and f)	(e) Allow the system to restabilise before proceeding to step 4. (f) Where degassing of reagents is required, eg for elevated temperature chemistries, the procedure of bubbling helium through each reagent for 10 mins is recommended. However, reagents subjected to vacuum or ultrasound may be suitable alternatives for degassing.
Initial Sensitivity Setting		
4.	When an acceptably smooth baseline trace is given at the measurement unit (note g), adjust the baseline response to about 5 per cent of full scale (note h) with the zero control, and set chart speed (note i).	(g) ie no excessive pulsing or intermittent 'spiking' caused by a gas bubble in the detector flow cell or passing rapidly through the flow cell respectively. (h) An elevated setting of the baseline allows for any negative drift that may occur. (i) A chart speed of 1 cm/min is suitable except for responses around the baseline where 2 cm min^{-1} may be more appropriate.

Step	Procedure	Notes
5.	Load the sample loop manually or automatically (note j)	(j) As stated in the particular determinand chemistry (see Appendix). Use a smooth, rapid action if injection is by syringe. The quantity of sample volume used should always be greater than the nominal volume of the sample loop, the excess volume being discharged to waste.
6.	When there is a positive response at the measurement unit due to the reaction product produced from the C_M standard solution, (note k) adjust this response with the scale expansion facility to read between 90 and 95 per cent of full scale. (note l) or as appropriate	(k) Where C_M is the maximum concentration that the calibration is intended to cover. (l) A setting 5 to 10 per cent below full scale allows for any increase in sensitivity that may occur.
7.	Repeat steps 5 and 6 at least twice more. (note m)	(m) Allows final adjustment of sensitivity and a check on repeatability to be made.
Production of Calibration Curve		
8.	Employ the same loading technique, to that used for the C_M standard solution for a series of standard solutions (note n) to produce a series of responses on the measurement unit.	(n) A typical series might be $0.2C_M$, $0.4C_M$, $0.6C_M$, $0.8C_M$ and $1.0C_M$ and usually injected in ascending order of concentration.
9.	A calibration curve is obtained of measurement unit responses (MUR) (y axis) against concentration (x axis) of standard solutions. (note o)	(o) The calibration should be checked at frequent intervals during the analysis of samples, the frequency being dependent on the number of samples in the analysis batch. MUR should relate to a common arbitrary zero.
Analysis of Samples		
10.	Employ the same loading technique for samples as for standard solutions. (see step 8) (note p)	(p) The system response is sufficiently fast to permit a return to baseline on the measurement unit after each single injection.
11.	Analytical quality control (AQC) solutions should be subjected to the same treatment as samples. (note q)	(q) For quality control purposes.
12.	When all the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained this unit can be switched off.	
Calculation of Results		
13.	Utilise the calibration curve generated at step 9 (note r) to convert the measurement unit responses due to the samples into concentration of determinand in the samples. (note s)	(r) Providing that the calibration check standard responses after relating them to the common arbitrary zero are acceptably close to their respective initial calibration standard response. (s) The measure unit responses of the samples are first related to the common arbitrary zero.
Shut Down Procedure		
14.	Transfer all reagent lines to water and pump water through the tubing of the system for at least 10 mins. Switch off all moving parts.	

Appendix 2: Analytical Methods

Method A. Ammonia

B. Oxidised Nitrogen

C. Nitrite

D. Orthophosphate

E. Chloride

F. Silicate

G. Sulphate

H. Hardness

I. Alkalinity

Method A. For the Determination of Ammonia

Throughout the method the ammonia concentration is expressed as mg N L^{-1}

A.1 Performance Characteristics of the Method

A1.1	Substance determined	Ammonia and ammonium ions
A1.2	Type of sample	(a) Raw and potable waters; (b) Raw, potable and wastewater.
A1.3	Basis of methods	The sample is injected into a flowing stream and (a) merges with reagents to provide a coloured product whose concentration is measured spectrophotometrically; (b) ammonia diffuses across a PTFE membrane into an indicator recipient stream whose change in absorption is measured spectrophotometrically.
A1.4	Ranges of application	(a) up to 2.5 mg N L^{-1} (b) up to 25 mg N L^{-1}
A1.5	Calibration curves	Lagrange curve correction applied.
A1.6	Standard Deviation (between batch)	See table below
A1.7	Limit of detection	(a) 0.06 mg N L^{-1} (b) 0.8 mg N L^{-1}
A1.8	Recovery	>98 per cent
A1.9	Interference	Refer to Table D1 in 'Ammonia in Water, 1981', note (ii). Amines could interfere in this method (b).
A1.10	Time required for analysis	Up to 70 results per hour.

Solution	Concn. (mg N L^{-1})	Std Deviation (mg N L^{-1})	Deg. of F.
(a) Standard	0.6	0.029	23
Standard	2.4	0.077	23
(b) Standard	5.0	0.168	23
Standard	20.0	0.275	23

Notes: (i) The standard deviation and limit of detection data quoted in the above table were obtained by the National Rivers Authority, Nottingham Environmental Laboratory.
(ii) Ammonia in Waters 1981. Methods for the Examination of Waters and Associated Materials.

A2 Principles

(a) Ammonia in the sample reacts with hypochlorite ions to form monochloramine. This reacts with a phenolic compound in the presence of the sodium nitroprusside to form a blue, indophenol-type compound whose concentration is measured spectrophotometrically at 655 nm.

The phenolic compound is salicylate ion, with hypochlorite generated in situ by alkaline hydrolysis of sodium dichloroisocyanurate.

(b) The pH of the sample is elevated to at least pH 11 by sodium hydroxide and the ammonia present is released as gaseous ammonia which diffuses across a PTFE membrane into a buffered indicator stream. The change in absorption is measured spectrophotometrically at 592 nm.

A3 Hazards

Sodium dichloroisocyanurate must not be allowed to come into contact with acid because highly toxic chlorine gas will be produced.

Normal laboratory precautions should be observed with regards to safety. The reader should read section 6 in the main text of this document before proceeding with this method.

A.4 Reagents and Standards

Method (a)

A4.1 Salicylate reagent

Dissolve 130 ± 1 g of sodium salicylate in about 950 mL of water. Add 130 ± 1 g of tri-sodium citrate and dissolve, followed by 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 make up to $1{,}000 \pm 10$ mL with water, mix well. Stored in an amber glass bottle at 4°C, this reagent is stable for at least two weeks.

A4.2 Sodium dicholoroisocyanurate reagent (DIC)

Dissolve 32.0 ± 0.1 g of sodium hydroxide in 500 mL of water. Cool the solution to room temperature and 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. Make up to $1{,}000 \pm 10$ mL with water and mix well. Stored in an amber glass bottle at 4°C this reagent is stable for at least two weeks.

A4.3 Stock Standard Ammonia Solution; 1,000 mg N L^{-1}

Dissolve 3.819 ± 0.005 g of ammonium chloride (dried at 105°C for at least two hours) in about 800 mL of water. Quantitatively transfer this solution to a 1-litre calibrated flask, make up to the mark with water and mix well. This solution is stable for at least one month.

A4.4 Working (Intermediate) Standard Ammonia Solution; 10 mg N L^{-1}

To a 1-litre calibrated flask add 10 ± 0.01 mL of stock standard solution (A4.3) dilute to the mark with water and mix well. This solution should be prepared weekly.

A4.5 Calibration Standard Ammonia Solutions (Range (a))

To a series of 100 mL calibrated flasks add 30, 20, 15, 5 and 2 ± 0.01 mL of Intermediate standard solution (A4.4). Make up to the mark with water and mix well. These solutions should be prepared daily.

Method (b)

A4.6 Sodium Hydroxide Solution

Dissolve 10.0 ± 0.2 g of sodium hydroxide in about 500 mL of water. Cool and dilute to $1{,}000 \pm 10$ mL with water and mix well. This solution is stable for at least two weeks.

A4.7 Indicator buffer solution

Dissolve 0.035 ± 0.002 g of phenol red powder and 0.20 ± 0.01 g of ammonium chloride in about 950 mL of water. Adjust the pH of this solution such that it gives an absorbance of 0.25 ± 0.01 when measured at 540 nm in a 10 mm cell with reference to water. Dilute the prepared solution to $1{,}000 \pm 10$ ml with water and mix well.

A4.8 Working (Intermediate) Standard Ammonia Solution; 100 mg N L^{-1}

To a 1-litre calibrated flask add 100 ± 0.1 mL of stock standard solution (A4.3) dilute to the mark with water and mix well. This solution should be prepared weekly.

A4.9 Calibration Standard Ammonia Solutions (Range (b))

To a series of 100 mL calibrated flasks add 40, 30, 20, 10, and 5 ± 0.01 mL of intermediate standard solution (A4.8). Make up to the mark with water and mix well. These solutions should be prepared daily.

A5 Flow Diagram

See Diagram A for Ammonia determination.
A(i) for up to 2.5 mg N L^{-1}
A(ii) for up to 25 mg N L^{-1}

Method B. For the Determination of Oxidized Nitrogen

Throughout the method the oxidized nitrogen concentration is expressed as mg N L^{-1}

B1 Performance Characteristics of the Method

B1.1	Substance determined	Nitrate and nitrate ions collectively as oxidised nitrogen
B1.2	Types of sample	Raw, waste and potable waters
B1.3	Basis of method	The sample is injected into a flowing stream which merges with reagents. The resulting coloured product (see PRINCIPLE section) has its concentration measured spectrophotometrically
B1.4	Range of application	Up to 20 mg N l^{-1}
B1.5	Calibration Curve	Linear

B1.6 Standard deviation (between batch)

Standard Solution (mg N l^{-1})	Standard Deviation (mg N l^{-1})	Deg of F
(a) 4.0	0.08	23
(b) 16.0	0.15	23

B1.7	Limit of Detection	0.12 mg N L^{-1}
B1.8	Recovery	>94 per cent
B1.9	Interferences	Phosphate above 5 mg P L^{-1} can suppress reduction.
B1.10	Time required for analysis	Up to 70 results per hour.

Notes: The standard deviation and limit of detection figures quoted in the above table were obtained by the National Rivers Authority, Nottingham Environmental Laboratory.

B2 Principle

Nitrate is reduced to nitrite using copperised cadmium filings. The nitrite produced, together with any nitrite present in the sample, is then diazotised with sulphanilamide and coupled with N-(1-naphthyl)-ethylene diamine. The resulting azo dye is measured spectrophotometrically at a wavelength of 520 nm.

B3 Hazards

N-1-naphthylethylene diamine dihydrochloride should be regarded as a special hazard. Skin contact with the solid and the reagent incorporating it should be avoided.

Cadmium is highly toxic; wear gloves when handling material. Normal laboratory precautions should be observed with regards to safety. The reader should read section 6 in the main text of this document before proceeding with this method.

B4 Reagents and Standards

B4.1 Ammonium Chloride Solution

Dissolve 10.7 ± 0.1 g of ammonium chloride in about 500 mL of water. Dilute to 1,000 ± 10 mL with water and mix well. Stored in a glass bottle this reagent is stable for at least 1 month.

B4.2 Sulphanilamide reagent

Carefully add 50 ± 0.5 mL of hydrochloric acid (d_{20}1.18) to about 500 mL of water. Add 10.0 ± 0.1 g of sulphanilamide and swirl to dissolve. Dilute to 1,000 ± 10 mL with water and mix well. Store the reagent in an amber glass bottle, avoiding unnecessary exposure to the atmosphere. This reagent is stable for up to one week.

During the preparation of this reagent ultrasonic degassing must not be used.

B4.3 N-1-naphthylethylene diamine reagent

Dissolve 1.0 ± 0.01 g of N-(1-naphthyl)-ethylene diamine dihydrochloride in about 500 mL of water. Dilute to 1,000 ± 10 mL and mix well. This solution is stable for at least one month when stored in an amber glass bottle.

B4.4 Stock Standard Nitrate Solution; 1,000 mg N l^{-1}

Dissolve 7.215 ± 0.005 g of potassium nitrate (previously dried at 105°C for 2 hours) in about 800 mL of water. Quantitatively transfer this solution to a 1-litre calibrated flask, make up to the mark with water and mix well. This solution is stable for at least one month.

B4.5 Working (Intermediate) Standard Nitrate Solution; 100 mg N L^{-1}

To a 1-litre calibrated flask add 100 ± 0.1 mL of stock standard solution (B4.4) dilute to the mark with water and mix well. This solution should be prepared weekly.

B4.6 Calibration Standard Solutions

To a series of 100 mL calibrated flasks add 20, 15, 10, 5 and 2, ±0.01 mL of intermediate standard solution (B4.5). Make up to the mark with water and mix well. These solutions should be prepared daily.

B4.7 Preparation of the Cadmium Reduction Column

B4.7.1 Cadmium granules 0.2–2.0 mm

B4.7.2 1 per cent Copper Sulphate Solution:

Dissolve 1.0 ± 0.001 g of copper sulphate pentahydrate, $CuSO_4$, $5H_2O$, in 1,000 ± 10 mL of water and mix well.

B.4.7.3 0.5 M Hydrochloric Acid solution:

Carefully add 42.0 ± 0.5 mL of hydrochloric acid (d_{20}1.18) to 500 mL of water. Dilute to 1,000 ± 10 ml of water and mix well.

B4.7.4 Procedure

Swirl 5–10 g of the cadmium granules (B4.7.1.) with 50 mL of the hydrochloric acid solution (B4.7.3) and allow to settle for 2 min. Decant off the supernatant acid solution and rinse the granules twice with water. Add to the rinsed cadmium granules 50 mL of copper sulphate solution (4.7.2) and swirl the mixture. Discard the liquid and rinse the granules three times with ammonium chloride solution (B4.1).

Do not allow the prepared granules to become dry.

B5 Flow diagram

See Diagram B for Oxidised Nitrogen determination.

Method C. For the Determination of Nitrite

Throughout the method the nitrite concentration is expressed as mg N L^{-1}

C1 Performance Characteristics of the Method

C1.1	Substance determined	Nitrite ion
C1.2	Type of sample	Raw and potable waters
C1.3	Basis of method	The sample is injected into a flowing stream which merges with reagents. The resulting coloured product (see PRINCIPLE section) has its concentration measured spectrophotometrically
C1.4	Ranges of application	(a) up to 1.0 mg N L^{-1} (b) up to 0.1 mg N L^{-1}
C1.5	Calibration Curves	Linear

C1.6 Standard deviation (between batch)

Solution	Concn.[n]	Standard Deviation (mg N L^{-1})	Deg. of F.
(a) Standard	0.8	0.005	19
	0.2	0.003	19
(b) Standard	0.05	0.002	19
Tap Water	0.011	0.005	19

C1.7	Limit of Detection	(a) 0.014 mg N L^{-1} (b) 0.009 mg N L^{-1}
C1.8	Recovery	(a) Not available (b) 97 per cent
C1.9	Interferences	No serious interferences are known
C1.10	Time required for analysis	Up to 80 results per hour

Notes: The standard deviation and limit of detection figures quoted in the above table were obtained by Thames Water Utilities New River Head Laboratory, London.

C2 Principle

The nitrite in solution is treated with sulphanilamide and N-1-Naphthylethylene diamine dihydrochloride under acidic conditions to form a characteristic pink azo-dye whose concentration is measured spectrophotometrically at a wavelength of 520 nm;

C3 Hazards

N-1-Naphthylethylene diamine dihydrochloride should be regarded as a special hazard. Skin contact with the solid and the reagent incorporating it should be avoided.

Normal laboratory precautions should be observed with regards to safety. The reader should read section 6 of the main text of this document before proceeding with this method.

C4 Reagents and Standards

C4.1 Sulphanilamide reagent

To about 750 mL of water add 100 ± 1 mL of orthophosphoric acid (d_{20}1.68, LOW IN NITRITE grade) and mix. Add 0.500 ± 0.005 g of N-1-naphthylethylene diamine dihydrochloride and 10.0 ± 0.1 g of sulphanilamide and completely dissolve. Dilute to 1 litre with water in a calibrated flask and mix well. Store the reagent in an amber glass bottle, avoiding unnecessary exposure to the atmosphere. This reagent is stable for up to one week. During the preparation of this reagent ultrasonic degassing must not be used.

C4.2 Stock Standard Nitrite Solution; 100 mg N L^{-1}

Dissolve 0.4922 ± 0.002 g of sodium nitrite (dried at 105°C for at least 2 hours) in about 800 ml of water. Quantitatively transfer this solution to a 1-litre calibrated flask, make up to the mark with water and mix well. Store the solution in an amber glass bottle. This solution is stable for at least one month.

C4.3 Working (Intermediate) Standard Solution A; 10 mg N L^{-1}

To a 100 ml calibrated flask add 10 ± 0.01 mL of stock standard solution (C4.2) dilute to the mark with water and mix well. This solution should be prepared weekly.

C4.4 Calibration Standard Solutions (Range (a))

To a series of 100 mL calibrated flasks add 10, 8, 6, 4 and 2 ± 0.01 mL of intermediate standard solution A (C4.3). Dilute to the mark with water and mix well. These solutions should be prepared daily.

C4.5 Working (Intermediate) Standard Solution B; 1 mg N L^{-1}

To a 100 mL calibrated flask add 10 ± 0.01 mL of intermediate standard solution A (C4.3), dilute to the mark with water and mix well. This solution should be prepared daily.

C4.6 Calibration Standard Solution (Range (b))

Repeat section C4.4 substituting intermediate standard B (C4.5) for intermediate standard A (C4.3)

C5 Flow Diagram

See Diagram C for Nitrite determination.

(a) Up to 1 mg N L^{-1}
(b) Up to 0.1 mg N L^{-1}

Method D. For the Determination of Phosphate

Throughout the method the phosphate concentration is expressed as mg P L^{-1}

D1 Performance Characteristics of the Method

D1.1	Substance determined	Reactive phosphorus (see PRINCIPLE section)
D1.2	Type of sample	Raw and potable waters
D1.3	Basis of method	The sample is injected into a flowing stream which merges with reagents. The resulting coloured product (see PRINCIPLE section) has it concentration measured spectrophotometrically
D1.4	Range of application	Up to 2.5 mg P L^{-1}
D1.5	Calibration Curve	Linear

D1.6 Standard deviation (within batch)

Solution	Concn. (mg P L^{-1})	Standard Deviation (mg P L^{-1})	Deg. of F.
Tapwater	1.14	0.015	9
Spiked tap water	2.069	0.023	9

D1.7	Limit of Detection	0.07 mg P L^{-1}
D1.8	Recovery	>97 per cent
D1.9	Interferences	Refer to 'Phosphorus in Water, 1981'
D1.10	Time required for analysis	Up to 80 results per hour

Notes: (i) The standard deviation and limit of detection figures quoted in the above table were obtained by Thames Water Utilities, New River Head Laboratory, London.
(ii) Phosphorus in Waters, Effluents and Sewages 1980. Methods for the Examination of Waters and Associated Materials.

D2 Principle

Orthophosphate ions react with a solution containing molybdic acid, ascorbic acid, trivalent antimony ions and hydrogen ions, to form a 12-molybdophosphoric acid, which is reduced in situ to a blue heteropoly compound (phosphomolybdenum blue) in which antimony is incorporated. The concentration of the phosphomolybdenum blue compound is measured spectrophotometrically at a wavelength of 660 nm.

The acid conditions used may cause partial hydrolysis of condensed phosphates, and/or some of the more labile organic phosphates, if present. For this reason, the determinand is referred to as reactive phosphorus instead of orthophosphate.

D3 Hazards

Antimony potassium tartrate is toxic and care must be taken not to inhale or ingest the compound. Skin contact with the solid or reagent incorporating it should be avoided.

Normal laboratory precautions should be observed with regards to safety. The reader should read Section 6 in the main text of this document before proceeding with this method.

D4 Reagents and Standards

D4.1 Stock Phosphate Reagent

Cautiously add with stirring 140 ± 5 mL of sulphuric acid (d_{20}1.84) to about 750 mL of water in a 2-litre beaker surrounded by cold water.Allow to cool and mix well. Add 0.300 ± 0.001 g of antimony potassium tartrate and 13.4 ± 0.1 g of ammonium molybdate, and allow to dissolve. Quantitatively transfer this solution to a 1-litre calibrated flask, make up to the mark with water and mix well. This solution is stable for at least one month.

D4.2 Working Phosphate Reagent

Add 100 ± 5 mL of stock phosphate reagent (D4.1) to about 500 mL of water in a 1-litre calibrated flask. Add 13.00 ± 0.01 g of ascorbic acid and 1.0 ± 0.2 mL of a phosphorous-free detergent, eg Teepol, as a wetting agent. When completely dissolved, make up to the mark with water and mix well. This reagent is prepared daily and should be discarded if it turns blue.

D4.3 Stock Standard Phosphate Solution; 500 mg P L^{-1}

Dissolve 2.1950 ± 0.005 g of potassium dihydrogen orthophosphate (previously dried at 105 ± 5°C for 1 hour and stored in a dessicator) in about 750 mL of water. Quantitatively transfer the solution to a 1-litre calibrated flask, make up to the mark with water and mix well. This solution is stable for at least three weeks.

D4.4 Working (Intermediate) Standard Phosphate Solution; 25 mg P L^{-1}

To a 100 mL calibrated flask add 5 ± 0.01 mL of stock standard solution (D4.3) dilute to the mark with water and mix well. This solution should be prepared weekly.

D4.5 Calibration Standard Solutions

To a series of 100 mL calibrated flasks add 10, 8, 6, 4, and 2 ± 0.01 mL of intermediate standard solution (D4.4), dilute to the mark with water and mix well. These solutions should be prepared daily.

D5 Flow Diagram

See Diagram D for Phosphate determination.

Method E. For the Determination of Chloride

Throughout the method the chloride concentration is expressed as mg Cl L^{-1}

E1 Performance Characteristics of the Method

E1.1	Substance determined	Chloride ion
E1.2	Type of sample	Raw, waste and potable waters
E1.3	Basis of method	The sample is injected into a flowing stream which emerges with reagents. The resulting coloured product (see PRINCIPLE section) has its concentration measured spectrophotometrically
E1.4	Range of application	Up to 300 mg CL L^{-1}
E1.5	Calibration Curves	Linear

E1.6 Standard deviation (between batch)

Standard Solution (mg Cl L^{-1})	Standard Deviation (mg Cl L^{-1})	Deg. of F
(a) 60	1.3	23
(b) 240	8.0	23

E1.7	Limit of Detection	3 mg Cl L^{-1}
E1.8	Recovery	>98 per cent
E1.9	Interference	Refer to section D3 in 'Chloride in Water, 1981' (note (ii))
E1.10	Time required for analysis	Up to 90 results per hour

Notes: (i) The standard deviation and limit of detection figures quoted in the above table were obtained by the National Rivers Authority Nottingham Laboratory.

(ii) Chloride in Waters, Sewage and Effluents 1981. Methods for the Examination of Waters and Associated Materials.

E2 Principle

Chloride forms mercury (II) chloride by reaction with mercury (II) thiocyanate. The liberated thiocyanate reacts with the ferric nitrate present to produce coloured ferric thiocyanate whose concentration is measured spectrophotometrically at a wavelength of 463 nm.

The concentration of ferric thiocyanate is proportional to the chloride concentration.

E3 Hazards

Mercury salts and methanol are toxic, and nitric acid is corrosive. Gloves and eye protection should be worn. Normal laboratory precautions should be observed with regards to safety. The reader should read Section 6 in the main text of this document before proceeding with this method.

E4 Reagents and Standards

E4.1 Stock Mercury (II) Thiocyanate Solution

Dissolve 4.17 ± 0.01 g of mercury (II) thiocyanate in about 500 mL of methanol. Dilute to $1{,}000 \pm 10$ mL with methanol and mix well. Stored in an amber glass bottle this reagent is stable for at least one month.

E4.2 Stock Iron (III) Nitrate Solution

Dissolve 2 ± 0.5 g of iron (III) nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$, in about 500 mL of water. Carefully add 21.0 ± 0.2 mL of nitric acid (d_{20}1.42). Dilute to $1{,}000 \pm 10$ ml with water and mix well. Stored in an amber glass bottle this reagent is stable for at least one month.

E4.3 Mixed Reagent

To 150 ± 0.5 mL of stock mercury (II) thiocyanate solution (E4.1) add 150 ± 0.5 mL of stock iron (III) nitrate solution (E4.2) and mix. Dilute this solution to $1{,}000 \pm 10$ mL with water and mix well. Stored in an amber glass bottle this reagent is stable for at least two weeks.

E4.4 Stock Standard Chloride Solution; 1,000 mg Cl L^{-1}

Dissolve 1.648 ± 0.001 g of sodium chloride (previously dried at 105°C for two hours) in about 800 mL of water. Quantitatively transfer this solution to a 1-litre calibrated flask and make up to the mark with water and mix well. The solution is stable for at least one month.

E4.5 Calibration Standard Solutions

To a series of 100 mL calibrated flasks add 30, 20, 15, 10 and 5 ± 0.01 mL of the stock standard solution (E4.4), dilute to the mark with water and mix well. These solutions should be prepared daily.

E5 Flow Diagram

See Diagram E for Chloride determination.

Method F For the Determination of Silicate

Throughout the method the silicate concentration is expressed as mg SiO_2/L^{-1}

F1 Performance Characteristics of the Method

F1.1	Substance determined	Reactive silica
F1.2	Type of sample	Raw and potable waters
F1.3	Basis of method	The sample is injected into a flowing stream which merges with reagents. The resulting coloured product (see PRINCIPLE section) has its concentration measured spectrophotometrically
F1.4	Range of application	Up to 21.4 mg SiO_2 L^{-1} ($\equiv$ 10 mg Si L^{-1})
F1.5	Calibration Curve	Linear

F1.6 Standard deviation (between batch)

Standard Solution (mg SiO_2 L^{-1})	Standard Deviation (mg SiO_2 L^{-1})	Deg of F.
10.7	0.17	19
4.2	0.14	19

F1.7	Limit of Detection	0.5 mg SiO_2 L
F1.8	Recovery	>99 per cent
F1.9	Interference	If the pH of the sample falls outside the range 2 to >10 units and is heavily buffered, the silico-molybdate complex may not be formed under the conditions of this method. Neutralisation of the sample may be effective in eliminating this source of interference. Phosphate may interfere slightly (note (ii))
F1.10	Time required for analysis	Up to 80 results per hour.

Notes: (i) The standard deviation and limit of detection figures quoted in the above table were produced by Thames Water Utilities at their New River Head Laboratory, London.
(ii) Silicon in Waters and Effluents 1980. HMSO.

F2 Principle

Silicates in solution react with molybdate to form a silicomolybdate complex. This complex is reduced by ascorbic acid to molybdenum blue. Interference by phosphate can be overcome by the addition of tartaric acid. The resultant compound is measured spectrophotometrically at 660 nm.

F3 Hazards

Care must be taken when handling acids. Eye protection and gloves must be worn.

Normal laboratory precautions should be observed with regards to safety. The reader should read Section 6 in the main text of this document before proceeding with this method.

F4 Reagent and Standards

F4.1 Molybdate Reagent

Carefully add 10.0 ± 0.1 mL of sulphuric acid (d_{20}1.84) to about 800 mL of water. Mix well and cool. Dissolve 10.0 ± 0.05 g of ammonium molybdate in this acid solution and dilute to 1,000 ± 10 mL of water. Store in a plastic container.

F4.2 Tartaric acid reagent

Dissolve 50.0 ± 0.5 g of tartaric acid in about 800 mL of water and dilute to 1,000 ± 10 mL with water. Store in a plastic container.

F4.3 Ascorbic acid solution

Dissolve 20.0 ± 0.25 g of ascorbic acid in about 800 mL of water. Add 50 ± 1 mL of acetone and mix. To this add 0.50 ± 0.05 g of sodium dodecyl sulphate (wetting agent), dissolve and dilute to 1,000 ± 10 mL with water.

F4.4 Stock Silicate Standard Solution; 2,139 mg SiO_2 L^{-1} (≡ 1,000 mg Si L^{-1})

Weigh 1.000 g ± 0.001 g of finely powdered silica, spectrophotometric grade, into a clean platinum crucible, add 5.0 ± 0.1 g of anhydrous sodium carbonate and mix intimately with a thin nickel spatula, cover the crucible with a platinum lid. Heat the crucible to red heat until the mixture begins to fuse, careful control of the heating will be required to avoid losses due to the spitting as the melt bubbles. When the bubbling has subsided, heat the crucible strongly until a clear transparent melt is obtained. Allow the crucible to cool, place it on its side in a 250 mL polyethylene beaker and place the lid in the beaker. Add 150 ± 10 mL of boiling water to the beaker and place it on a steam bath until the melt has dissolved. After rinsing the crucible and lid, remove from the beaker and cool the solution. Quantitatively transfer the contents of the beaker with washings to a 1-litre calibrated flask and make up to the mark with water and mix well. Transfer the solution to a clean, dry polyethylene bottle for storage. The solution is stable for at least one year.

Stock silicate standard solutions are commercially available. Alternatively, see Phosphorus and Silicon in Waters, Effluents and Sludges 1990 Sections E5.8.1 and G2.3.1.

F4.5 Working (Intermediate) Standard Silica Solution; 213.9 mg SiO_2 L^{-1} (≡ 100 mg Si L^{-1})

To a 100 mL calibrated flask add 10 ± 0.01 mL of stock standard solution (F4.4), dilute to the mark with water and mix well. This solution should be prepared weekly.

F4.6 Calibration Standard Solutions

To a series of 100 mL calibrated flasks add 10, 8, 6, 4, and 2 ± 0.01 mL of intermediate standard solution (F4.5), dilute to the mark with water and mix well. These solutions should be prepared daily.

F5 Flow Diagram

See Diagram F for Silicate determination.

Method G For the Determination of Sulphate

Throughout the method the sulphate concentration is expressed as mg SO_4^{2-} L^{-1}

G1 Performance Characteristics of the Method

G1.1	Substance determined	Sulphate ion
G1.2	Type of sample	Raw and potable waters
G1.3	Basis of method	The sample is injected into a flowing stream which merges with reagents. The resulting turbidity (see PRINCIPLE section) has its concentration measured spectrophotometrically
G1.4	Range of application (ii)	Up to 200 mg SO_4 L^{-1}. Instrument dependent, see G1.7 and G6.
G1.5	Calibration Curves	Non linear

G1.6 Standard deviation (i)

Solution	Concentration mg SO_4 L^{-1}	Total Std. Dev mg SO_4 L^{-1}	Def of F
Potable Water	18.9	0.37	5
River Water	104.3	1.15	7

G1.7	Limit of Detection (ii)	Instrument dependent below 10 mg SO_4 L^{-1}. Users should determine the limit of detection (to a relative accuracy of 10%) and, if needed, the limit of reliable detectability, using their own instrument. It is suggested that if concentrations of below 5 mg SO_4 L^{-1} need to be determined, either a larger sample injection or sample preconcentration be used depending on the instrument design (see Section G6)
G1.8	Recovery	No data available
G1.9	Interferences	Main interfering substances are bicarbonate and carbonate/alkalinity, and chlorine. For further information of interferences see the sulphate booklet in this series, note (iii)
G1.10	Time required for analysis	Up to 70 results per hour.

Notes:
(i) Data obtained by the former Anglian Water, Regional Standards Laboratory, Cambridge.
(ii) Data obtained by the former Anglian Water, Regional Standards Laboratory and Thames Water Utilities New River Head Laboratory
(iii) Sulphate in Waters, Effluents and Solids (2nd Edition) 1988, HMSO, in this series.

G2 Principle

Sulphate reacts with barium chloride to form a suspension of barium sulphate which is stabilised by gelatin and thymol: hydrochloric acid is present to prevent the precipitation of barium carbonate, phosphate and sulphite. The turbidity is measured spectrophotometrically at 540 mm.

G3 Hazards

Barium chloride is a Schedule 1 poison and should be handled with care. Eye protection should be worn and a fume cupboard used when handling.

Normal laboratory precautions should be observed with regards to safety. The reader should read Section 6 in the main text of this document before proceeding with this method.

G4 Reagents and Standards

Standard Laboratory Reagent (SLR) grade barium chloride and thymol, and technical grade gelatin powder have been satisfactorily used.

G4.1 0.01 M Hydrochloric acid solution

Carefully add 0.9 ± 0.02 ml of hydrochloric acid (d_{20} 1.18) to about 800 mL of water; make up to $1{,}000 \pm$ mL with water.

G4.2 Barium chloride reagent

This reagent should be prepared strictly in accordance with the procedure shown below because the degree of suspension of barium sulphate is controlled by several factors and can depend on the mode of preparation of the reagent.

Dissolve 0.20 ± 0.02 g of thymol crystals in about 500 mL of 0.01 M hydrochloric acid (G4.1) with stirring, at a temperature of 80 ± 10°C. Cool the resulting solution to 40 ± 5°C and then dilute to $1{,}000 \pm 10$ mL with 0.01 M hydrochloric acid solution and mix well. Slowly add 4.0 ± 0.1 g of powdered gelatine. Once it has dissolved add 20.0 ± 0.1 g of barium chloride dihydrate and continue stirring until all has dissolved. Filter the resulting solution through GF/C filter paper under slight vacuum.

This reagent is usually stable for up to 3 months, but discard if the sensitivity starts to deteriorate.

G4.3 Stock Standard Sulphate Solution; 1,000 mg SO_4 L^{-1}

Dissolve 1.479 ± 0.001 g of anhydrous sodium sulphate (dried for 3 hrs at 105°C) in above 500 mL of water. Quantitatively transfer this solution to a 1-litre calibrated flask, make up to the mark with water and mix well. Store this solution in an amber glass bottle and keep cool. The solution is stable for several months.

G4.4 Calibration Standard Solutions

To a series of 100 ml calibrated flasks add 20, 15, 10, 5, 2, 1 ± 0.01 mL of stock standard solution (G4.3), dilute to the mark with water and mix well. These solutions should be prepared daily.

G5 Flow Diagram

See Diagram G for Sulphate determination.

G6 Change in Concentration Range of Method

Lower or higher concentrations of sulphate may be determined by varying the sample loop volume; up to 150 μL/0.8 mm id, 30 cm length has been satisfactorily used for low sulphate concentrations (2.5 mg SO_4 L^{-1}) but no detailed performance data are available. The analyst should verify the performance of any modified system.

Method H For the Determination of Total Hardness

Throughout the method the hardness concentration is expressed as mg $CaCO_3$ L^{-1}

H1 Performance Characteristics of the Method

H1.1	Substance determined	Total hardness
H1.2	Type of sample	Raw and potable waters
H1.3	Basis of method	The sample is injected into a flowing stream which merges with reagents. The resulting coloured product (see PRINCIPLE section) has its concentration measured spectrophotometrically
H1.4	Range of application (i)	200–400 mg $CaCO_3$ L^{-1}
H1.5	Calibration Curve	Linear in this application range

H1.6 Standard deviation (i) (between batch)

Standard Solution (mg $CaCO_3$ L^{-1})	Standard Deviation (mg $CaCO_3$ L^{-1})	Deg. of F
300	7	19

H1.7	Limit of Detection (i)(ii)	200 mg $CaCO_3$ L^{-1} (an arbitrary minimum reporting level)
H1.8	Recovery	No available data
H1.9	Interference	Not tested
H1.10	Time required for analysis	Up to 80 results per hour

Notes: (i) The standard deviation and limit of detection figures quoted in the above table were produced by Thames Water Utilities, New River Head Laboratory, London.

(ii) The range of application can be lowered by changing the end-point of the calmagite reagent (see Section H4.5.1).

H2 Principle

The calcium ions in the sample forms a more stable Ca-EDTA complex, releasing magnesium ions to form a red complex with calmagite (1-(1-hydroxy-4-methyl-2-phenylax)-2-naphthol-4-sulphonic acid). Any magnesium hardness will be determined directly but as calcium.

Although other metals form complexes with calmagite, these absorb light at different wavelengths to that of calcium.

H3 Hazards

Normal laboratory precautions should be observed with regards to safety. The reader should read Section 6 in the main text of this document before proceeding with this method.

H4 Reagents and Standards

H4.1 pH 10.0 Buffer

Dissolve 3.59 ± 0.05 g of sodium hydroxide and 6.18 ± 0.02 g of boric acid in 800 mL of deionised water and dilute to 1 litre, in a grade A calibrated flask. Adjust the pH to 10.0 ± 0.1 with 1 M sodium hydroxide or 1 M hydrochloric acid.

H4.2 Stock Calmagite Solution

Dissolve 1.5 ± 0.05 g of calmagite in approximately 800 mL of deionised water and stir for one and a half hours. Dilute to 1 litre and filter the solution through a rapid filter paper. The solution should be prepared as required.

H4.3 Stock Magnesium Chloride Solution

Dissolve 0.25 ± 0.02 g of magnesium chloride in 200 mL of pH 10 buffer and dilute to 250 mL with buffer.

H4.4 Stock Ethylenediamine tetraacetic acid disodium salt (EDTA)

Dissolve 2.16 ± 0.02 g of EDTA in approximately 200 mL of pH buffer and dilute to 250 mL in a grade A calibrated flask with buffer.

H4.5 Working Calmagite Reagent

Mix 100 ± 1 mL of stock EDTA solution (H4.4) with 100 ± 1 mL of stock magnesium solution (H4.3). Add to this mixed solution 780 ± 10 mL of buffer solution (H4.1) and mix well. To this solution add 20 ± 0.5 mL of stock calmagite reagent (H4.2). Finally add extra EDTA solution (H4.4) at the rate of 1 mL at a time while stirring until the colour is 'royal blue (blue with just a hint of red)'.

H4.5.1 Pump the working calmagite reagent (H4.5) through the system and set the baseline (blank) to 10 per cent of the full-scale detector response. Inject a 200 mg $CaCO_3$ L^{-1} standard solution and record the strength of the detector response. Add 1 mL of EDTA solution (H4.4) to the working calmagite reagent (H4.5), mix well and pump this solution through the system. Reset the baseline and repeat the injection of the 200 mg $CaCO_3$ L^{-1} standard solution. The optimum end-point of the reagent is achieved when the 200 mg $CaCO_3$ L^{-1} standard solution has a detector response of 10–15 per cent of its full-scale deflection. If the standard solution has a response of less than 10 per cent the addition of magnesium chloride solution (H4.3) will bring the response back to the optimum end-point. The final solution should be stored in a glass bottle and kept for not more than 1 week.

H4.6 Stock Standard Hardness Solution; 4,000 mg $CaCO_3$ L^{-1}

Weigh 4.000 ± 0.005 g of $CaCO_3$ previously dried in an oven at 105 ± 5°C for 1 hour, cooled and store in a dessicator. Using mili-q water dilute to approximately 600 mL. Carefully add between 10 and 20 mLs of hydrochloric acid (sufficient to dissolve the calcium carbonate), and mix. Adjust the pH of the standard solution to pH 6.5 using the pH 10 buffer and transfer to a 1-litre calibrated flask ensuring all containers and pH electrodes are thoroughly washed into the flask and dilute to the mark with water.

H4.7 Calibration Standard Solutions

To a series of 100 ml calibrated flasks add 10, 9, 8, 7, 6, and 5 ± 0.01 mL of stock standard solution (H4.6), dilute to the mark with water and mix well. These solutions should be prepared weekly.

H5 Flow Diagram

See Diagram H for Total Hardness determination.

Method I For the Determination of Alkalinity

Throughout the method the alkalinity concentration is expressed as mg $CaCO_3L^{-1}$ (see page 9 of Alkalinity booklet HMSO for alternative ways of expressing alkalinity)

I 1 Performance Characteristics of the Method

I1.1	Substance determined	Alkalinity (methyl orange)
I1.2	Type of sample	Raw and potable waters
I1.3	Basis of method	The sample is injected into a flowing stream which merges with reagents. The resulting coloured product (see PRINCIPLE section) is measured spectrophotometrically
I1.4	Range of application	Up to 300 mg $CaCO_3L^{-1}$ or 366 mg L^{-1} HCO_3^- or 180 mg L^{-1} CO_3^{2-} or 6 m eq. L^{-1}
I1.5	Calibration Curve	Linear

I1.6 Standard deviation (within batch)

Standard Solution (mg $CaCO_3$/L)	Standard Deviation (mg $CaCO_3$/L)	Deg of F
150	1.41	9
15	0.79	9
Tap water 228	0.94	9

I1.7	Limit of Detection	6.5 mg $CaCO_3$/L or 7.9 mg L^{-1} HCO_3^- or 3.9 mg L^{-1} CO_3^{2-} or 0.13 m eq. L^{-1}
I1.8	Recovery	No available data
I1.9	Interferences	Highly coloured substances and certain oxidising may cause interference by enhancing or bleaching the colour of the methyl orange reagent.
I1.10	Time required for analysis	Up to 80 results per hour

Notes: The standard deviation and limit of detection figures quoted in the above table were obtained by Thames Water Utilities, New River Head Laboratory, London.

I 2 Principle

Basic anions (bicarbonate, carbonate and hydroxide) in the sample react with the buffered methyl orange. The reduction in the red acid component is measured as a decrease in the absorbance at a wavelength of 560 nm.

I 3 Hazards

Normal laboratory precautions should be observed with regards to safety. The reader should read Section 6 in the main text of this document before proceeding with this method.

I 4 Reagent and Standards

I 4.1 Methyl orange reagent

Dissolve 0.0425 ± 0.0002 g of methyl orange in about 750 mL of water. Add to this solution 2.55 ± 0.02 g of potassium hydrogen phthalate and stir until dissolved. Finally, cautiously add 0.36 ± 0.01 mL of hydrochloric acid (d_{20}1.18) and dilute the whole to $1{,}000 \pm 10$ mL with water and mix well. This solution is stable for at least one month.

I 4.2 Stock Standard Alkalinity Solution: 3,000 mg $CaCO_3$ L^{-1}

Dissolve 3.18 ± 0.01 g of sodium carbonate (previously dried at 265 ± 5°C for 2 hrs and cooled in a dessicator) in about 800 mL of water. Quantitatively transfer this solution to a 1-litre calibrated flask, make up to the mark with water and mix well. This solution is stable for at least 1 month if stored in a stoppered glass bottle at 4°C.

I 4.3 Calibration Standard Solutions

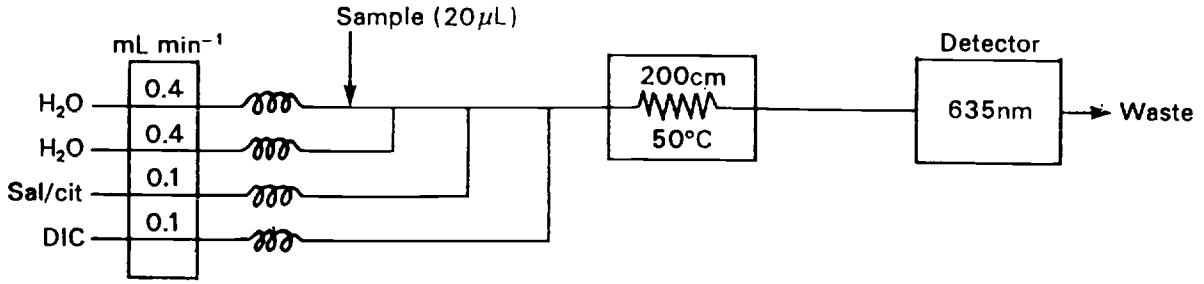
To a series of 100 mL calibrated flasks add 10, 8, 6, 4 and 2·0.01 mL of stock standard solution (I4.2), dilute to the mark with water and mix well. These solutions should be prepared daily.

I 5 Flow Diagram

See Diagram I for Alkalinity determination.

Diagram A Ammonia

(a)



(b)

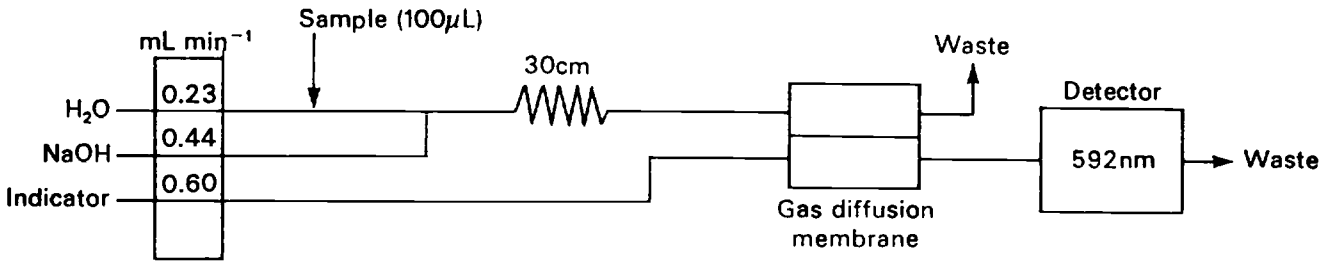


Diagram B Oxidised nitrogen

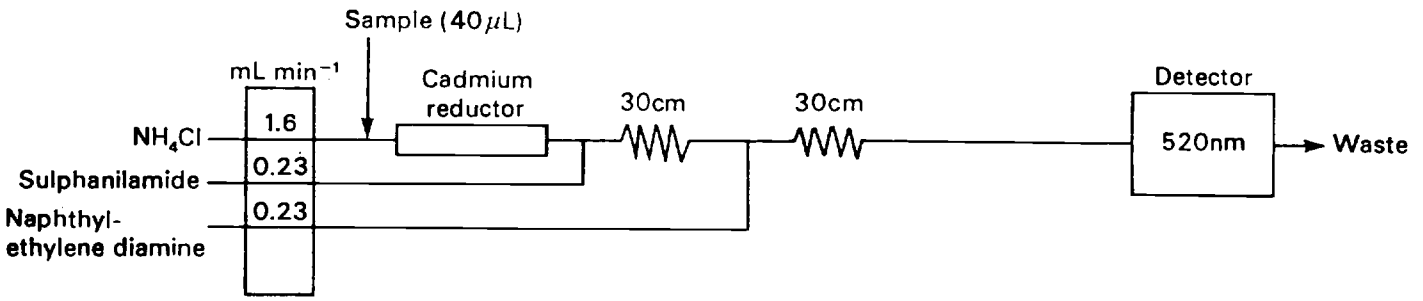


Diagram C Nitrite

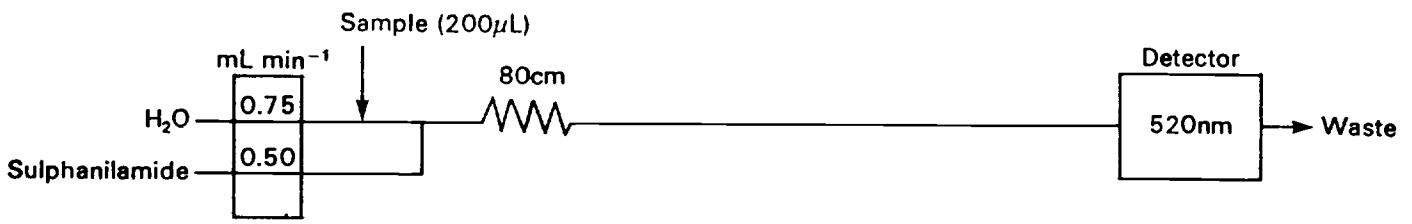


Diagram D Phosphate

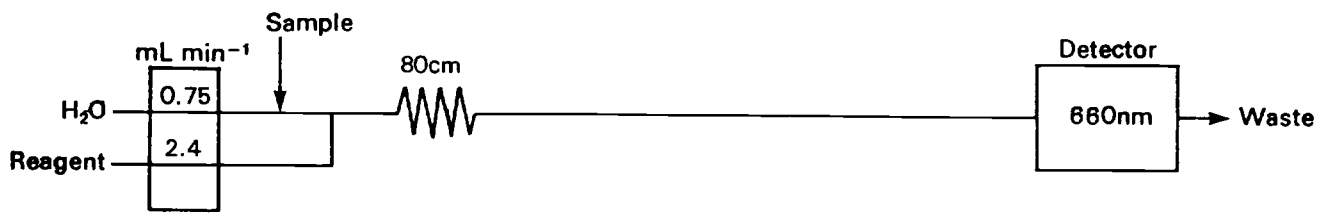


Diagram E Chloride

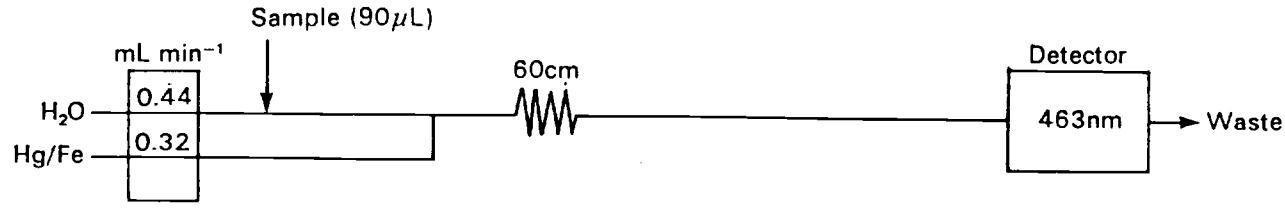


Diagram F Silicate

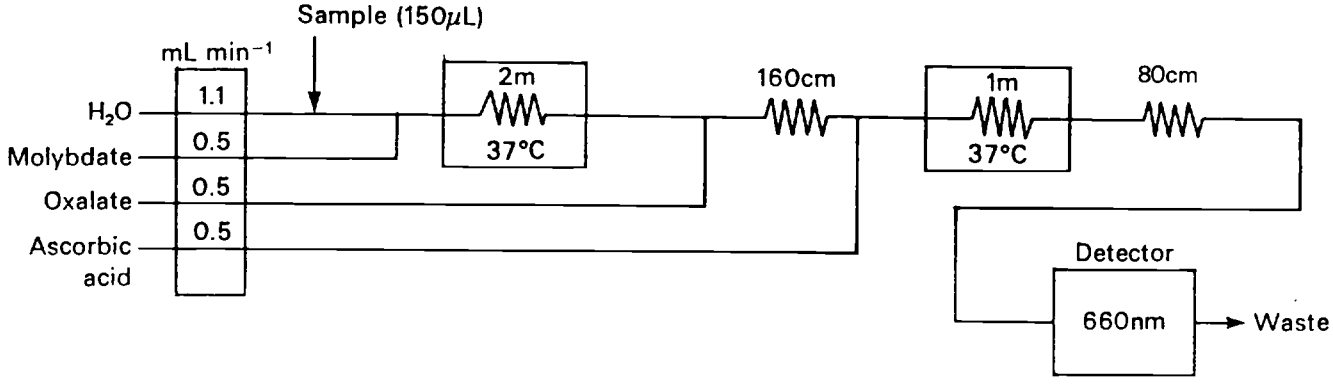


Diagram G Sulphate

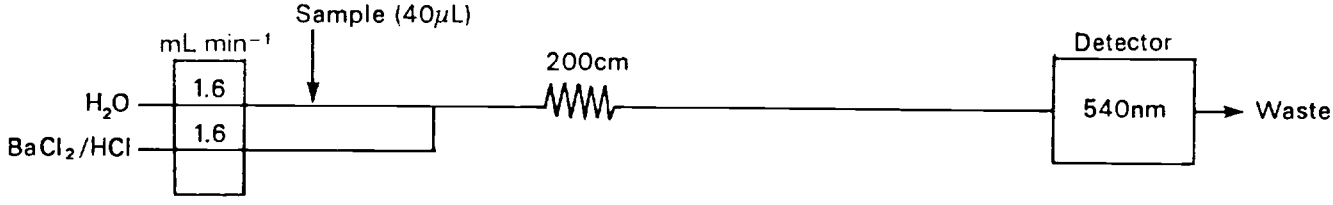


Diagram H Hardness

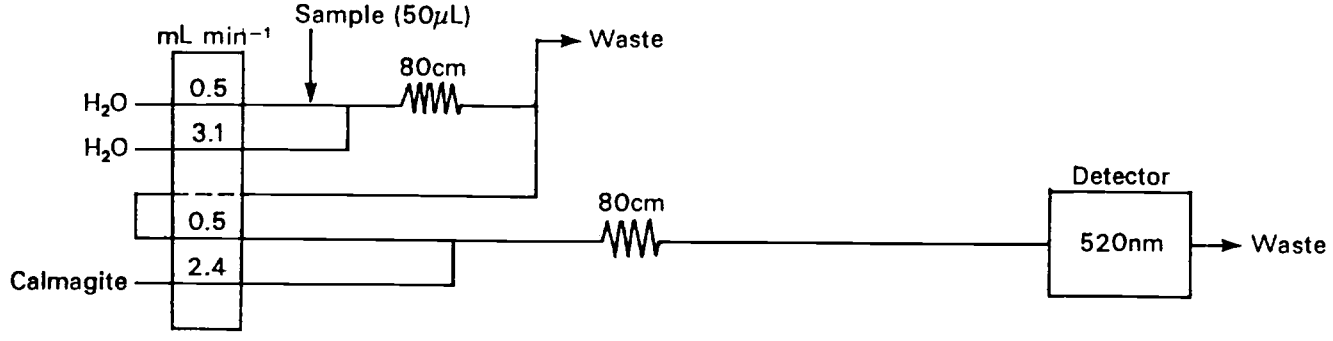
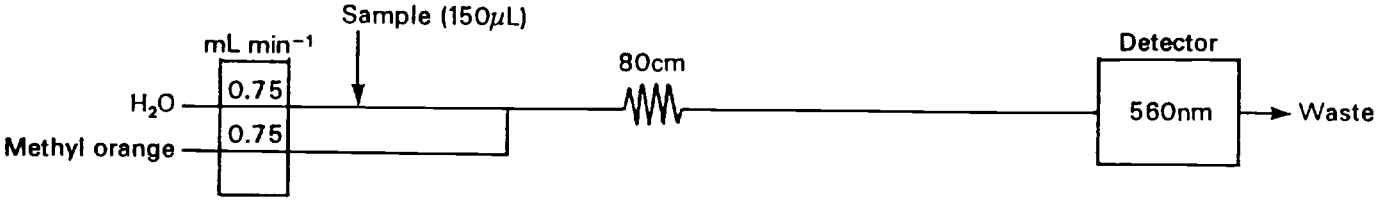


Diagram I Alkalinity



Address for Correspondence

However thoroughly a method may be tested there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:—

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The Standing Committee of Analysts
Department of the Environment (Drinking Water Inspectorate)
Romney House
43 Marsham Street
LONDON
SW1P 3PY

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Dd292740 1/91 C8 G443 10170

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