Total Nitrogen and Total Phosphorus in Sewage Sludge 1985

Methods for the Examination of Waters and Associated Materials

London: Her Majesty's Stationery Office

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London Her Majesty's Stationery Office

Warning to users

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

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

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. Known or suspected poisoning cases are usually sent to the nearest hospital having special equipment. To ensure admission to the correct hospital at once, always state whether poisoning is likely when calling an ambulance or arranging for an admission to hospital.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. 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.

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About this series

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

The preparation of this series and its continuous revision is the responsiblity 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 seven Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No. 5.

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
Secretary

31 October 1983

General Introduction

This booklet describes methods for the determination of "total nitrogen" and "total phosphorus" in complex heterogeneous samples of sewage sludge resulting from waste water treatment processes used within the Water Industry.

"Total nitrogen" for the purposes of this booklet is defined as that which is contributed by free ammonia, inorganic ammonium compounds and those types of organic nitrogen compounds that are converted to ammonium sulphate by the digestion procedures given in the booklet.

"Total phosphorus" comprises orthophosphate, and both condensed inorganic phosphates (hydrolysable phosphate) and organo-phosphorus compounds which are converted to orthophosphate by the digestion procedures. Methods given in another booklet in the series[1] may possibly be applied to the separate determination of individual phosphorus species.

Because sewage sludge is applied to agricultural land as a fertilizer there is a need to monitor application rates and to assess the retention and/or availability of nitrogen and phosphorus by the analysis of soils and sediments; and to assess the uptake of nitrogen and phosphorus by plant material by the analysis of the plant material. Thus soil, sediment and plant material analysis falls within the scope of this booklet and is discussed in Section 0.4. However, for the reasons given in that section it is not possible for the booklet to include analytical methods specifically for those materials.

The sampling of heterogeneous materials needs special consideration by the analyst and these considerations are discussed in Section A. It is impossible to give a universally applicable method of preparation, but instead technically sound courses of action are recommended and the reader is referred to authoritative texts.

Having obtained a sample the next stage is to prepare that sample for analysis. Again the booklet cannot be specific because of variations in the size, texture and homogeneity of samples. The recommended procedure is to homogenise the bulk sample and to take a representative portion of the homogenised sample for digestion by one of the techniques outlined in Section 0.1.

Although liquid samples are normally taken for analysis it is recognised practice to report results on a dry weight basis as g determinand/kg sample. Consequently the total solids content of the homogenised sample used for analysis must be determined.

0.1 Digestion Procedures

Of the three digestion procedures described in this booklet (summarised as Table 1) that in Section B is the most rigorous and is likely to give the most complete recovery of nitrogen, particularly from heterocyclic compounds. The analyst is advised if using the digestion procedures in Sections C or D to ensure that the recovery by nitrogen is acceptable for the purpose of the analysis.

Table 1

Procedure Catalyst/Reagent	Section B Mercury/ Potassium Sulphate	Section C Copper/Sodium sulphate	Section D Hydrogen Peroxide
Sulphuric acid volume	10 ml	10 ml	2 ml
Sludge wet dry	5–10 g 0.25–0.50 g	– 0.5 g	2 g –
Range of application	Up to 80 g N/kg; up to 12 g P/kg	Up to 50 g N/kg; up to 30 g P/kg	Up to 50 g N/kg; up to 30 g P/kg
Limit of detection	0.8 g N/kg; 0.8 g P/kg	1.0 g N/kg; 1.0 g P/kg	3.0 g N/kg; 2.0 g P/kg
Apparatus	300 ml Kjeldahl flask / 250 ml tube Gas or electric heat / Block digester	75 ml tube Block digester	100 ml tube Block digester
Mode of operation	Manual reference method	Semi-automatic**	Semi-automatic**
Comments	Mercury must be recovered from residues.*	Easier disposal of residues than Section B method	Digest is free from added metals.
Scale of use	Small numbers of samples	Large numbers of samples/Large numbers of samples	Large numbers of samples

*If a manual method is required for routine use it may be possible to replace mercury in the catalyst mixture by copper, provided that the sulphate/sulphuric acid ratio specified in Section B is maintained. (Note: longer digestion times may be required if copper is used as the catalyst.) The analyst, however, must ensure that no significant loss of performance results from this change of metal catalyst. Copper and selenium have been widely used, either separately or together. Catalysts containing *toxic* selenium are reported to give shorter clearing times than other catalysts but the recovery of nitrogen may be low. The use of selenium is not recommended. Titanium used as its dioxide is finding increased use as a catalyst for digestion procedures of this type.

**Used in conjunction with the air-segmented continuous flow determination of ammonia and orthophosphate given in Section E of this booklet.

0.2 Analysis of Digest Solutions

0.2.1 Nitrogen Content

Following Section B method the solution obtained is distilled under alkaline conditions and the liberated ammonia absorbed in boric acid to be titrated with standard acid (Section B10.11).

Following Sections C and D methods the nitrogen content of the resulting solution is determined using the automatic spectrophotometric procedure given in Section E.

0.2.2 Phosphorus Content

The phosphorus content of digest solutions is determined spectrophotometrically using the phosphomolybdenum blue procedure in either manual or automated form as appropriate to the number of samples handled. (See Sections B10 (step 23) and E.)

0.3 Interchangeability of Procedures outlined in Sections 0.1 and 0.2

Many combinations of digestion technique and the subsequent analysis of the digest solution are possible.

All performance characteristics given in this booklet were obtained with the stated combinations. However, an analyst wishing to use procedures in a different combination from those given in this booklet should ensure that a satisfactory performance can be obtained. Problems may arise, e.g. a small scale digestion method may not be compatible with a titrimetric finish for nitrogen. Also the appearance of a turbidity can interfere in the colorimetric determination of phosphorus which might be the case with a digest solution from the mercury catalysed procedure if the digest solution is not diluted sufficiently before using the phosphomolybdenum blue method.

0.4 Applicability to Soil Sediment and Plant Material Analysis

Particularly with regard to soil analysis agriculturalists are mainly interested in the nitrogen and phosphorus contents actually available to the growing plant. Since soil conditions, method of cultivation, type of plant etc., vary so widely it is beyond the scope of the booklet to provide suitable methods for all cases. However, such methods are available from MAFF[2] and WRc[3] and readers are strongly recommended to discuss their particular analytical requirements with ADAS and/or WRc. Due attention must be paid to methods of obtaining representative samples of soil sediment and plant material.

Methods given in this booklet for total nitrogen and total phosphorus in sewage sludge may be capable of application to solids, sediments and plant material. However, it is the responsibility of the analyst concerned to ensure that meaningful results are obtained if the methods are applied as such.

Notes

1 Throughout this booklet nitrogen is expressed as the element (N) and phosphorus as the element (P). Determinands are expressd as g/kg of sample on a dried solids basis.

2 The determination of total nitrogen and total phosphorus in sewage sludge involves conversion to ammonia and orthophosphate in solution respectively with subsequent determination of these two parameters. Consequently the performance characteristics table for each method (Sections B1, D1) states concentrations of nitrogen as mg N/l and phosphorus as mg P/l. However, as Note 1 above shows, the concentration of determinand is expressed as g/kg of sample on a dried solids basis and therefore, also appearing in the performance characteristics table is the equivalent g/kg value of the mg/l value based on the assumption that the total solids content is 5.0% merely to exemplify how the g/kg value is obtained. If variations of sample mass and/or total solids content prevail, they of course, will be referred to in the final determinand concentration.

A The Initial Preparation of Sewage Sludges for Analysis

A1 Introduction

The biological treatment of sewage and other organic wastes produces a wide range of sludges which can be broadly classified into the following groups; primary, secondary, digested and dewatered – each with its own special characteristics.

Sampling of the bulk material is discussed in detail in Part A of another publication in this series[4] where the importance of a valid sampling technique is emphasised. Since any bulk sample itself may be extremely heterogeneous it is also essential that following receipt of the sample in the laboratory any sub-samples derived from the laboratory samples should accurately represent the orginal material otherwise the analytical results will be of limited value[5].

The initial preparation of soils, sediments, and plant materials is reviewed in Part B of the previously mentioned publication[4]. However, the preparation of sewage sludges specifically is not covered.

The possible loss of ammonia particularly from digested or lime treated sludges during preparation poses special problems. Since nitrogen may be present as free ammonia, ammonium compounds, or as organically bound nitrogen the analyst should establish from the user the exact analytical requirements or the use to which the data is to be put. If the Total Nitrogen content is required it is recommended that analysis is carried out on the wet sample as received.

For operational purposes the "free" (readily available) ammonia content may be determined on a portion of the natural or induced filtrate whilst the mainly organically bound usually termed "slow release" nitrogen may be determined using dried, ground material. These latter determinations are empirical and it is possible that a small but variable portion of the "free" ammonia may be retained in the sample after oven drying at 105°C.

The agricultural value of the nitrogen present in sewage sludge depends on the form in which it is present together with the type of plant and time of year. "Free" ammonia is considered to be immediately 'available' to pasture or plants although it may be rapidly lost by leaching, whilst organic nitrogen is released more slowly over a longer period measured in years. Empirically based calculations are used to derive information for the farmer from the analytical data[6].

Nutrient levels are normally expressed on a dry matter basis, therefore the analyst will need to determine the dry matter content in addition to nitrogen and phosphorus levels, either on the sample as received, or, providing any loss of volatile elements is acceptable to the user, the determination of nitrogen and phosphorus may be made on a previously dried and ground sample.

A2 Sampling and Sample Preservation

A2.1 Safety (See also Section A4.1)

The normal personal protection used with this type of material is advised e.g. hand and face protection. The latter may include the use of a suitable breathing mask on occasions.

A2.2 Sampling

Using a suitable procedure[4,5,6] and with due consideration of the comments given in Section A1, obtain typically about 1 kg (1 litre) of representative sample in a wide necked screw capped plastic bottle. The operator must ensure that the sample taken is representative of the bulk material from which it was obtained.

A2.3 Sample preservation

Preferably samples should be processed in preparation for analysis immediately upon receipt in the laboratory, but if storage is unavoidable place the samples in the dark at 4°C to minimise changes in compostion.

A3 Sample Pretreatment

The sample received in the laboratory will usually contain moisture, and any attempt to dry the sample prior to analysis may result in some loss of nitrogen particularly a loss of free ammonia from digested or lime treated sludges. Therefore, whenever total nitrogen is to be determined, a sub-sample for analysis must always be prepared using either of the methods to homogenise wet sludge (Sections A4.3.1 and A4.3.2) as appropriate, depending upon the water content, mobility and texture of the sample. The solids contents on drying at 105°C must be determined using a separate portion of the homogenised sample.

A4 Wet Preparation of Samples for Analysis

A4.1 Hazards

It is important to follow normal good hygiene precautions since sewage sludge may contain pathogens and other toxic substances. All sample preparation procedures given in this booklet should be carried out in laboratories equipped with very efficient fume extraction and air-ventilation systems.

Preferably the homogeniser should be of a sealed type to prevent the escape of aerosols, and if possible the homogeniser should be operated inside a well ventilated fume cupboard.

A4.2 Apparatus

Homogeniser, sealed type, preferably capable of accommodating 1 litre of sample. Also, it is preferable that the design of homogeniser allows no loss of nitrogen during the homogenisation of the sample.

A4.3 Procedure

A4.3.1 Highly mobile (liquid) samples

Homogenise the entire representative sample (Section A2) typically 1 litre. Reserve one portion for use in one of the digestion procedures given in Sections B, C or D, and take a second portion for the determination of total solids content as given in Section A5.

A4.3.2 Less mobile samples

Table 400–500 g of the representative sample (Section A2) and weigh to within ± 1 g. Let this mass be W_1. Add a suitable volume of distilled or deionised water, mix thoroughly and treat the mixture in the homogeniser. Weigh the total mass of homogenised mixture obtained to within ± 1 g and let this be W_2.

Reserve one portion of this mixture for use in either one of the digestion procedures given in Sections B, C or D, and take a second portion for the determination of total solids content as given in Section A5. Let this value be B%.

The original total solids content of the sample (Section A5) = A%

where $A = \frac{W_2 \times B}{W_1}$

A5 Determination of Total Solids Content on drying the Sample at 105°C

A5.1 Hazards

Normal laboratory safety precautions must be observed and the determination is preferably carried out inside a well ventilated fume cupboard.

A5.2 Apparatus

A5.2.1 Steam bath or infra-red lamp

A5.2.2 Oven capable of maintaining a temperature of 105±2°C. (An oven of the forced ventilation type may make the use of a water bath unnecessary.)

A5.2.3 Sample drying dish. A shallow glass, silica or porcelain dish of capacity approximately 100 ml.

A5.3 Procedure

Step	Procedure	Notes
A5.3.1	Place a suitable dish (A5.2.3) inside an oven at 105±2°C for about 1 hour.	
A5.3.2	Allow to cool to room temperature in a desiccator and weigh to within ± 0.005 g.	
A5.3.3	Repeat steps A5.3.1 and A5.3.2 until a constant mass is attained (note a).	a) Constant mass is attained when the mass after successive drying and weighing cycles differs by not more than 5 mg of the apparent dry mass.
A5.3.4	Add between 10 g and 50 g of homogeneous sample (note b) to the tared dish. Reweigh the dish to within ± 0.005 g. Let the mass of sample taken be W_3 g.	b) The sample will have been prepared as given in Section A4.3.1/2.
A5.3.5	Place the dish on a steam bath and evaporate the sample almost to dryness (note c).	c) Alternatively evaporate the sample to dryness using either i) a forced ventilation oven at 105±2°C or ii) an infra-red lamp taking care to avoid charring of the solids.
A5.3.6	Transfer the dish to an oven at 105±2°C and heat at this temperature for 1.0±0.1 h (note d).	d) If an oven has been used to carry out step A5.3.5 the dish remains in the oven for this further period of 1.0±0.1 h.
A5.3.7	Allow the dish to cool in a desiccator and weigh to within ± 0.005 g.	
A5.3.8	Repeat steps A5.3.6 and A5.3.7 until a constant mass is attained (note a). Let the constant mass of dry sample solids obtained be W_4 g.	
	Calculation	
A5.3.9	The total solids content of the sample on drying at 105°C $= \frac{100 W_4}{W_3}$ %	

A6 Dry Preparation of Samples for Analysis

Changes in sample composition may take place during the drying procedure, e.g. a loss of free ammonia. The analyst must consider whether or not possible changes in sample composition during the drying procedure will have a significant effect upon the analytical results obtained in comparison with the analytical results obtained after using the wet preparation methods of section A4.

As discussed in the introduction (Section A1) this method may be satisfactory to obtain an empirical determination of organic nitrogen content, provided that the user of the analytical data is made aware of the possible limitations of the dry preparation procedure of samples for analysis.

A6.1 Hazards

Normal laboratory safety precautions must be observed. The laboratory must be well ventilated and fitted with fume extractors.

Problems may arise from dust generated during the sample grinding procedure and preferably such operations should be carried out inside a well ventilated fume cupboard.

Grinding mills should be operated with extreme care in accordance with safety procedures given by the manufacturer.

A6.2 Apparatus

The materials of construction of mills, sieves, drying trays and of other apparatus used in contact with the sample must not give rise to contamination problems.

A6.2.1 Grinding mill

e.g. a laboratory scale hammer mill.

A6.2.2 Aluminium dishes

Commercially available shallow disposable type, nominal capacity 1500 ml.

A6.2.3 Sieve

1 mm aperture.
(Note: Suitable sieves are possibly incorporated within the hammer mill.)

A6.2.4 Brush

Suitable, e.g. a 1" paint brush, for use in the transfer of ground samples from grinding mill receivers to storage containers.

A6.3 Procedure

Step	Procedure	Notes
A6.3.1	Weigh an aluminium dish to within ± 0.1 g.	
A6.3.2	Transfer the entire sample typically 500–1000 g, to the dish (note a) and reweigh to within ± 0.1 g. Let the mass of sample taken be W_5 g.	a) For the purpose of determining nitrogen and phosphorus in dried sludge it is not necessary to know the dried solids content of the original sample as received. However, since dried solids content is a useful characteristic of the original sample it is conveniently determined, thereby avoiding sub-sampling problems, by drying the entire sample quantitatively as given in this procedure.
A6.3.5	Return the dish to the oven for periods of 2 hours until a constant mass is obtained (note b). Let the constant mass of dry sample solids be W_6 g.	b) Constant mass is attained when the mass after successive drying and weighing cycles differs by not more than 1% of the apparent dry mass. If required the total solids content of the sample on drying at 105°C $= \frac{W_6 \times 100}{W_5}$ %
A6.3.6	Grind the total dried material (typically 10–50 g) in a mill to pass a 1 mm aperture sieve (note c).	c) If a bag is used to receive ground material it should be turned inside out and shaken and brushed between samples to remove adhering particles.

A6.4 Sources of Error

Frequent cleaning of grinding mills must be carried out to prevent the cross-contamination of samples.

B Manual Determination of Total Nitrogen and Total Phosphorus Contents in Sewage Sludge (Mercury Catalysed, Flask Digestion Method)

B1 Performance Characteristics of the Method

B1.1	Substance determined	Total nitrogen and total phosphorus
B1.2	Type of sample	Sewage sludge;
B1.3	Basis of the method	Rigorous acid digestion of the sample in the presence of mercury catalyst to convert nitrogen compounds present (but see Section B2) to ammonium sulphate; distillation of the digest under alkaline conditions and titration of the liberated ammonia. By processes of oxidation and hydrolysis all types of phosphorus present are converted to orthophosphate which is determined using the phosphomolybdenum blue method.
B1.4	Range of Application	1) Nitrogen: up to 80.0 g N/kg 2) Phosphorus: up to 12 g P/kg
B1.5	Calibration Curve	1) Nitrogen: not applicable 2) Phosphorus: linear to 0.4 mg P/l digest solution = 12 g P/kg
B1.6	Standard Deviation	1) Nitrogen

Sample	N content mg/l	Total standard deviation mg/l	Degrees of freedom
Nicotinic acid solutions	10 (d)	0.2	8 (a)
	100	1.7	10 (a)
	200	10.3	23 (b)
	400	9.2	23 (b)
	g/kg	g/kg	
Sewage sludge, wet (2.5 g)	1.73	0.08	12 (a)
Sewage sludge, dry (0.5 g)	35.3	1.1	29 (b)

2) Phosphorus

Sample	P content mg/l	Total standard deviation mg/l	Degrees of freedom
Dequest 2010 Solution (c)	100 (c)	9.7	23 (b)
	200	8.0	23 (b)
	g/kg	g/kg	
Dried ground sludge (10.5 g)	29.4	1.1	29 (b)

B1.7	Limit of detection	1) Nitrogen: 0.8 g N/kg; 25 degrees of freedom (b) 2) Phosphorus: 0.8 g P/kg; 20 degrees of freedom (b)

B1.8 Sensitivity	(a) Nitrogen: 1.0 ml of 0.02M hydrochloric acid solution is equivalent to 0.28 mg of nitrogen equivalent to 2.2 g N/kg of sample (b) Phosphorus: 25 ml of test solution (see Section B10 step 24) containing 0.4 mg P/l gives an absorbance change of approximately 0.6 absorbance units using a 40 mm cell at a wavelength of 882 nm.
B1.9 Bias	a) Nitrogen: No information apart from that arising from the presence of interfering species. b) Phosphorus
B1.10 Interferences	a) Nitrogen: See Section B3.1. b) Phosphorus: See Section B3.2.
B1.11 Time required for analysis	Nitrogen and Phosphorus

	Time (hours) for 6 determinations			
	Flasks		Tubes/heating block	
	Operator	Total	Operator	Total
Sample digestion	1.5	2.5	1.5	4.0
Complete analysis	3.25	5.0	3.25	6.25

Note: When using a heating block the digestion times will be of a similar order even if the number of digestions is increased to 20.

a) Data obtained by the North West Water Authority, Burnley Laboratory, using flask digestion.
b) Data obtained by the Anglian Water Authority, Bedford Sewage Division, Cotton Valley Laboratory, using tube digestion in a heated metal block. Hydrogen peroxide was added as an anti-foaming agent during the initial stages of the digestions of sewage sludge. (See Section B10.5, note d.)
c) Dequest 2010. A Monsanto Company phosphonic acid product – 1-disodium, hydroxyethylidene-1,1-diphosphonic acid. To prepare a 100 mg P/l solution dissolve 0.55 g Dequest 2010 (60% active as the phosphonic acid as supplied) in a litre of water (see Section B6.1).
d) To prepare a 10 mg N/l solution dissolve 0.879 g nicotinic acid (dried at 105°C) in a litre of water (see Section B6.1).

B2 Principle

By digestion of the sample in the presence of sulphuric acid, potassium sulphate and mercuric oxide as catalyst, organo-nitrogen groups, with certain exceptions, are converted to ammonium sulphate together with any free ammonia and ammonium nitrogen present.

Potassium sulphate is included in the digestion mixture in sufficient amount relative to sulphuric acid, to raise the boiling point to 365 ± 10°C. This temperature is sufficiently high to ensure complete conversion of organic nitrogen to ammonium ion but not so high as to cause loss of ammonia by volatilisation.[7,8,9]

The ammonium nitrogen produced is in fact complexed by the mercury used to catalyse sample digestion.

Phosphorus present as orthophosphate remains unchanged by these digestion conditions. All other forms of phosphorus are converted to orthophosphate by oxidation and/or hydrolysis. Thus the orthophosphate content of the digest represents the total phosphorus present in the original sample.

The digest solution is diluted to specified volume and suitable volumes of this solution are taken to allow the determination of nitrogen and phosphorus from a single digestion of sample.

To determine nitrogen the digest solution is treated with sodium thiosulphate to decompose the mercury ammonia complex and is then made strongly alkaline. Ammonia thus liberated is distilled from this solution, absorbed in boric acid and titrated with standard mineral acid solution.

Orthophosphate is determined by treating the digest solution with a solution containing molybdic acid, ascorbic acid, trivalent antimony ions and hydrogen ions, to form a 12-molybdophosphoric acid compound that is reduced in situ to a blue heteropoly compound (phosphomolybdenum blue) in which antimony is incorporated.

The digestion fails to determine nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitroso, oxime, semi-carbazone and nitrile. The introduction of a reduction stage prior to digestion increases the scope of the method. Treatment with hydriodic acid has been used for this purpose[8].

B3 Interferences

B3.1 Nitrogen determination

B3.1.1 Halides

Halides e.g. possibly arising from industrial wastes and sludge conditioners may interfere as a result of the loss of mercury catalyst by volatilisation as mercury halide and consequent incomplete conversion of organic nitrogen to ammonia.

B3.1.2 Nitrate/Nitrite

The presence of nitrate and/or nitrite may lead to erratic results but this interference is ill-defined. At the levels of nitrate/nitrite generally encountered in sewage sludge it is unlikely that any important interference will occur.

B3.2 Phosphorus determination

B3.2.1 Arsenic

Arsenic present as arsenate, or oxidised to arsenate during the digestion of the sample, will cause serious interference. The extent of interference is time dependent because the colour of the arsenomolybdate complex develops only slowly. As a guide 0.025 mg/l of arsenate (as As(V)) in the "test" solution, Section B10 step 24, may give a response equivalent to about 0.015 mg/l of phosphorus (as P) when using a 30 ml test solution volume[1].

B3.2.2 Silicon

The method will tolerate 10 mg/l of silicon as SiO_2[1]. High silicon/phosphorus ratios in samples where the phosphorus level is low may cause significant errors. However since the highly acid conditions of the digestion procedure tend to dehydrate any silicates present to form insoluble silica, interference from silica does not appear to be a serious problem, except that any turbidity due to silica may interfere with the spectrophotometric measurement of the phosphorus complex.

B3.2.3 Chromium (VI)

Chromium (VI) is reported to interfere at the 1 mg/l level[1]. This would be equivalent to 0.2% m/m of chromium (as Cr) on a dried sample solids basis. However, after digestion any chromium present is most likely to be in the chromium (III) form.

B3.2.4 Mercury–ammonia complex

The mercury ammonia complex formed during the digestion procedure will interfere in the colorimetric determination of phosphorus if the procedure given in section B10 steps 24 to 31 is not strictly followed.

B4 Elimination of Interferences

There is no single treatment that will systematically deal with all interference problems. There are however certain processes that will have a selective effect and the analyst must use discretion in their application.

B4.1 Determination of total nitrogen

B4.1.1 Halides

After sample has been added to the digestion vessel as given in Section B10 omit the addition of catalyst in step B10.2 until steps B10.3 to B10.5 have been carried out. If necessary extend the heating period of step B10.5 to ensure that the bulk of the halide present is removed. Cool the vessel, add 6.8 ± 0.1 g of catalyst mixture and proceed as given in step B10.6.

B4.2 Determination of total phosphorus

B4.2.1 Arsenate

Treat the digest solution with metabisulphite/thiosulphate reagent to reduce arsenate to arsenite prior to the addition of reagent B6.4.5. Full details of the procedure are given in another booklet in this series[1].

B4.2.2 Silica

Possible interference due to a turbidity caused by the presence of insoluble silica in the digest solution is usually avoided by the necessary high dilution of the digest solution prior to the phosphorus determination. Insoluble silica may be removed by filtration if necessary.

B5 Hazards

B5.1 It is important to follow normal good hygiene precautions since sewage sludge may contain pathogens and other toxic substances.

B5.2 Concentrated sulphuric acid should only be added to samples inside a fume cupboard since toxic volatile substances such as hydrogen cyanide or hydrogen sulphide may be evolved from some samples on acidifying.

B5.3 During the digestion of the sample sulphur trioxide will be evolved. Therefore the digestion procedure must be carried out inside a well ventilated fume cupboard and the flasks containing hot concentrated sulphuric acid must be shielded from the operator who should wear protective clothing, gloves and a full face shield. Alternatively, the digestion apparatus may incorporate equipment to prevent the escape of harmful reaction products into the laboratory atmosphere and/or render the reaction products harmless, e.g. neutralised, before discharge to the laboratory's main drainage system.

The distillation step following digestion requires the use of hot concentrated sodium hydroxide solution and a full face shield should be worn.

B5.4 Mercury, the catalyst, is toxic; consequently digest solutions must not be pipetted by mouth. All residues obtained from any of the procedures given in Section B10 should be treated as described in Section B14 of this booklet.

B5.5 Hydrogen peroxide is a vigorous oxidising agent and must be handled with care.

B5.6 Antimonyl potassium tartrate and ammonium molybdate are toxic reagents and solutions containing them must not be pipetted by mouth.

B6 Reagents and Standards

Analytical reagent grade materials should be used except where otherwise stated. Calibrated glassware should meet the recognised criteria for accuracy.

B6.1 Water

The water used for blank determinations, for preparing digest solutions, reagent and standard solutions and for dilution purposes, should have nitrogen and phosphorus contents that are negligible compared with the smallest concentrations to be determined in the samples. Distilled or deionised water is usually suitable.

B6.2 Digestion reagents

B6.2.1 Sulphuric acid

(d_{20}1.84)

B6.2.2 Potassium sulphate/mercuric oxide — catalyst

Mix by grinding together 138±2 g of potassium sulphate and 2±0.1 g of mercuric oxide. Alternatively use equivalent commercially available catalyst tablets. Whichever is used, the catalyst mix should be kept in a container labelled "HIGHLY TOXIC" which is stored in a locked outer receptacle when not in use.

B6.2.3 30% m/v Hydrogen peroxide solution

B6.2.4 Anti-bumping granules

e.g. pumice stone, 1 mm mesh

B6.3 Total nitrogen determination reagents

B6.3.1 Sodium hydroxide – sodium thiosulphate reagent

Cautiously dissolve 400±10 g of sodium hydroxide pellets and 25±1 g of sodium thiosulphate in about 800 ml of water. Cool and dilute to 1000±10 ml with water. Mix well and store in a polyethylene bottle. This reagent is stable for at least one month.

B6.3.2 0.05% m/v Methyl red indicator solution

Dissolve 0.5±0.1 g of methyl red, water soluble grade, in about 900 ml of water and dilute with water to 1000±10 ml. Mix well and store in a glass or polyethylene container. This reagent is stable for at least six months.

B6.3.3 0.15% m/v Methylene blue solution

Dissolve 1.5±0.1 g of methylene blue in about 900 ml of water and dilute with water to 1000±10 ml. Mix well and store in a glass or polyethylene container. This reagent is stable for at least one month.

B6.3.4 Indicating boric acid solution

Dissolve 20±1 g of boric acid in about 900 ml of warm water. Cool to room temperature. Add 10±1 ml of methyl red solution (B6.3.2) and 2.0±0.2 ml of methylene blue solution (B6.3.3) and dilute to 1000±10 ml. Mix well and store in a glass or polyethylene container. 0.1 ml of 0.01M sodium hydroxide solution added to 20 ml of this solution should be sufficient to change the colour from purple to green; if not, discard the indicating boric acid solution and prepare freshly. This solution is stable for at least three months.

B6.3.5 0.02M Hydrochloric acid soution

Prepare and standardise this solution according to standard analytical procedures. Adjust the concentration to exactly 0.02M. Maintain a check of the strength of this hydrochloric acid solution whilst in use. Alternatively an 0.02M solution of sulphamic acid may be used.

B6.4 Total phosphorus determination reagents

B6.4.1 4% m/v Ammonium molybdate

Dissolve 20±0.2 g of finely ground ammonium molybdate, $(NH_4)_6Mo_7O_{24}4H_2O$, in water and dilute with water to 500±10 ml. Mix well and store in a polyethylene bottle. This solution is stable for at least one month.

B6.4.2 0.28% m/v Antimonyl potassium tartrate

Dissolve 0.28±0.01 g of antimonyl potassium tartrate in water, warming if necessary, and dilute with water to 100±1 ml. Store in a borosilicate bottle in a refrigerator. Prepare freshly each week.

B6.4.3 1.76% m/v Ascorbic acid

Dissolve 2.64±0.02 g of ascorbic acid in 150±2 ml water. This solution should be prepared just before use.

B6.4.4 14% v/v Sulphuric acid

Add slowly and cautiously, with stirring, 140±2 ml of sulphuric acid $ld_{20}1.84$) to 800±10 ml of water in a 2-litre beaker immersed in cold water. Allow to cool and dilute with water to 1000±10 ml. Store in a glass bottle. This reagent is stable for at least six months.

B6.4.5 Mixed reagent

A quantity suitable for 50 determinations may be prepared by mixing together, in the order given, 250±2 ml of 14% v/v sulphuric acid (B6.4.4), 75±1 ml of 4% m/v ammonium molybdate (B6.4.1), 150±2 ml 1.76% m/v ascorbic acid (B6.4.3) and 25±0.5 ml of 0.28 m/v antimonyl potassium tartrate (B6.4.2), mixing after each addition. This reagent should be prepared freshly as required. Any unused reagent is discarded.

B6.4.6 1.0M Sodium hydroxide solution

Cautiously dissolve 20±1 g of sodium hydroxide pellets in about 400 ml of water. Cool and dilute with water to 500±10 ml. Store in a polyethylene bottle. With normal precautions, this reagent should be stable for at least six months.

B6.4.7 0.5M Sulphuric acid solution

Cautiously add 20±0.5 ml of 14% m/v sulphuric acid (B6.4.4) to 100±10 ml of water. This reagent is stable for at least six months.

B6.4.8 0.5% m/v Phenolphthalein indicator solution

(Required as an indicator of neutralisation if samples need to be neutralised.) Dissolve 0.5±0.01 g of phenophthalein in 60±1 ml industrial methylated spirit. Add 40±1 ml water. Mix well and store in a glass bottle. This solution is stable for at least 3 months.

B6.5 Phosphate stock standard solution

1 ml is equivalent to 100 μg P.

Dissolve 0.4394±0.0005 g of anhydrous potassium dihydrogen orthophosphate in water. Quantitatively transfer this solution to a 1-litre calibrated flask and make up to the mark with water. Store in a borosilicate glass bottle in a refrigerator at 4°C. This solution is stable for at least 3 months.

B6.6 Phosphate working standard solution

1 ml equivalent to 1 μg P.

Dilute 10.00 ml of the stock standard solution (B6.5) to 1 litre with water in a calibrated flask and mix. This solution is prepared freshly as required; any excess remaining is discarded.

B6.7 Phosphate calibration standard solutions

To each of a series of 50 ml calibrated flasks add 0.00, 1.00, 2.00, 5.00, 10.00 and 15.00 ml of working standard solution (B6.6). The flasks now contain 0.0, 1.0, 2.0, 5.0, 10.0 and 15.0 μg P respectively. Dilute each solution to about 40 ml with water and subject the solutions to the procedure given in Section B10 steps 28–29. Plot the results for (Ys–Yb) against μg P (B10:34–B10:35). The calibration curve is linear to at least 15 μg P.

B7 Apparatus

B7.1 Digestion vessels

Kjeldahl digestion flasks, 300 ml capacity. Alternatively digestion tubes, 250 ml capacity, may be used with a heating block.

B7.2 Heating device for digestion vessels

Kjeldahl digestion flasks may be heated singly over a Bunsen flame or by some form of electric heating. It is usually convenient to carry out several digestions simultaneously and the flasks may be mounted on a suitable rack heated either by gas or by electricity.

Whilst the heating device must be capable of producing the digestion conditions given in Section B10, the surface of the flask above the level of the liquid contents must not be subjected to overheating.

Digestion tubes are most conveniently heated using a compatible heating block (see Appendix), provided that the digestion conditions chosen offer a closely similar precision and accuracy of result to the flask method or which is acceptable to the operator.

B7.3 Distillation apparatus for nitrogen determination

Assemble as given in Figure 1 from the following commercially available components:

Round-bottomed flask, capacity 500 ml. The neck should be fitted with a PTFE sleeve to prevent possible seizure with the condenser due to contact with the alkaline reagent introduced in Section B10, step 15.
Condenser
Splash head
Delivery adaptor
Conical "receiver" flask, capacity 250 ml.

Commercially available distillation (usually steam distillation as depicted in Fig. 2) units may be used if the operator is satisfied that no loss of ammonia occurs during the distillation procedure. Apparatus performance may be checked by using solutions containing known amounts of ammonium chloride in the place of digest solutions.

B7.4 Apparatus for phosphorus determination

B7.4.1 Spectrophotometer

A spectrophotometer for use at 882 nm capable of accepting 40 mm cells is suitable. If this wavelength is not obtainable a wavelength of 725 nm may be used with approximately 70% of the sensitivity at 882 nm.

A filter photometer fitted with a suitable red filter may be used but a loss of sensitivity will occur and the results will be less reliable.

B7.4.2 40 mm path-length optically matched cells

Both sample and reference cells should be kept scrupulously clean. The same cells should be used for sample and reference cells respectively. They should always be placed in the same position in the holder with the same face towards the light source.

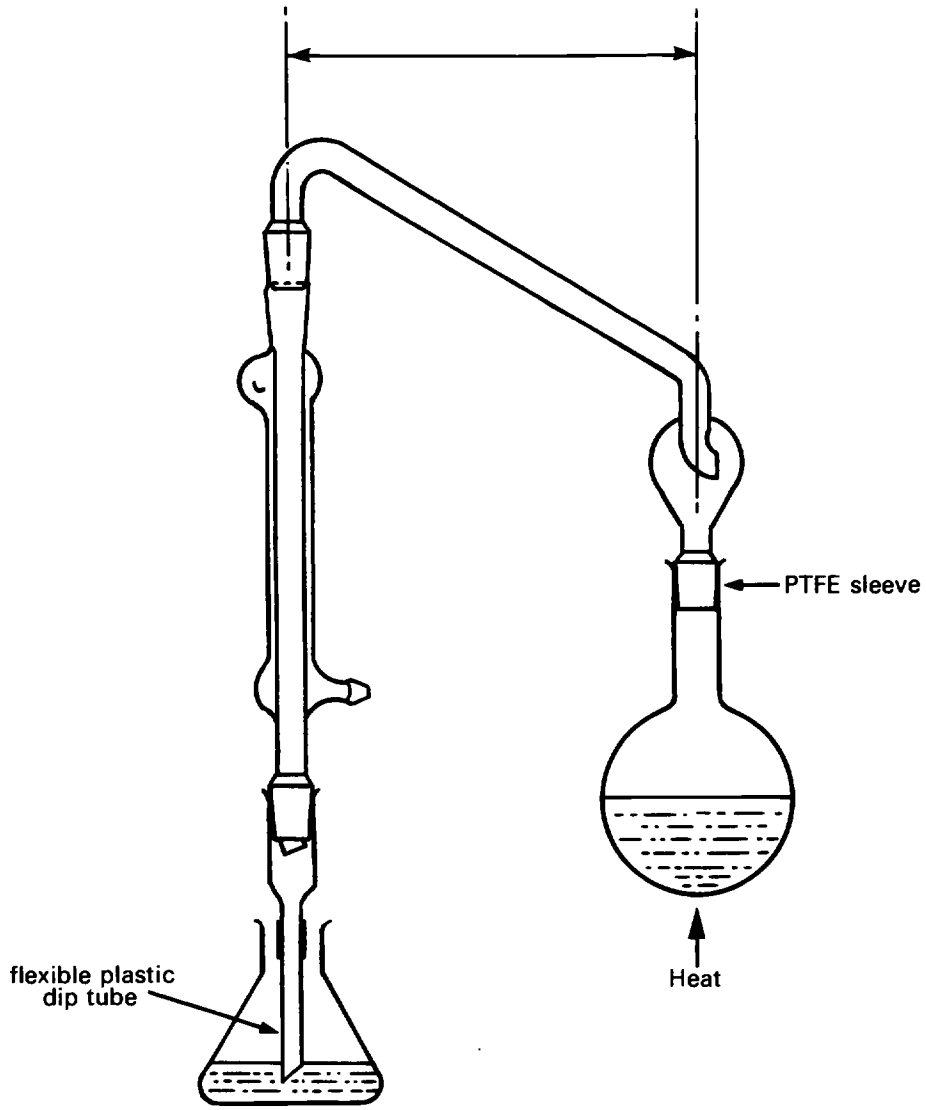

Figure 1 Distillation apparatus

B8 Sample Collection and Preservation See Section A2.

B9 Sample Pretreatment See Section A3.

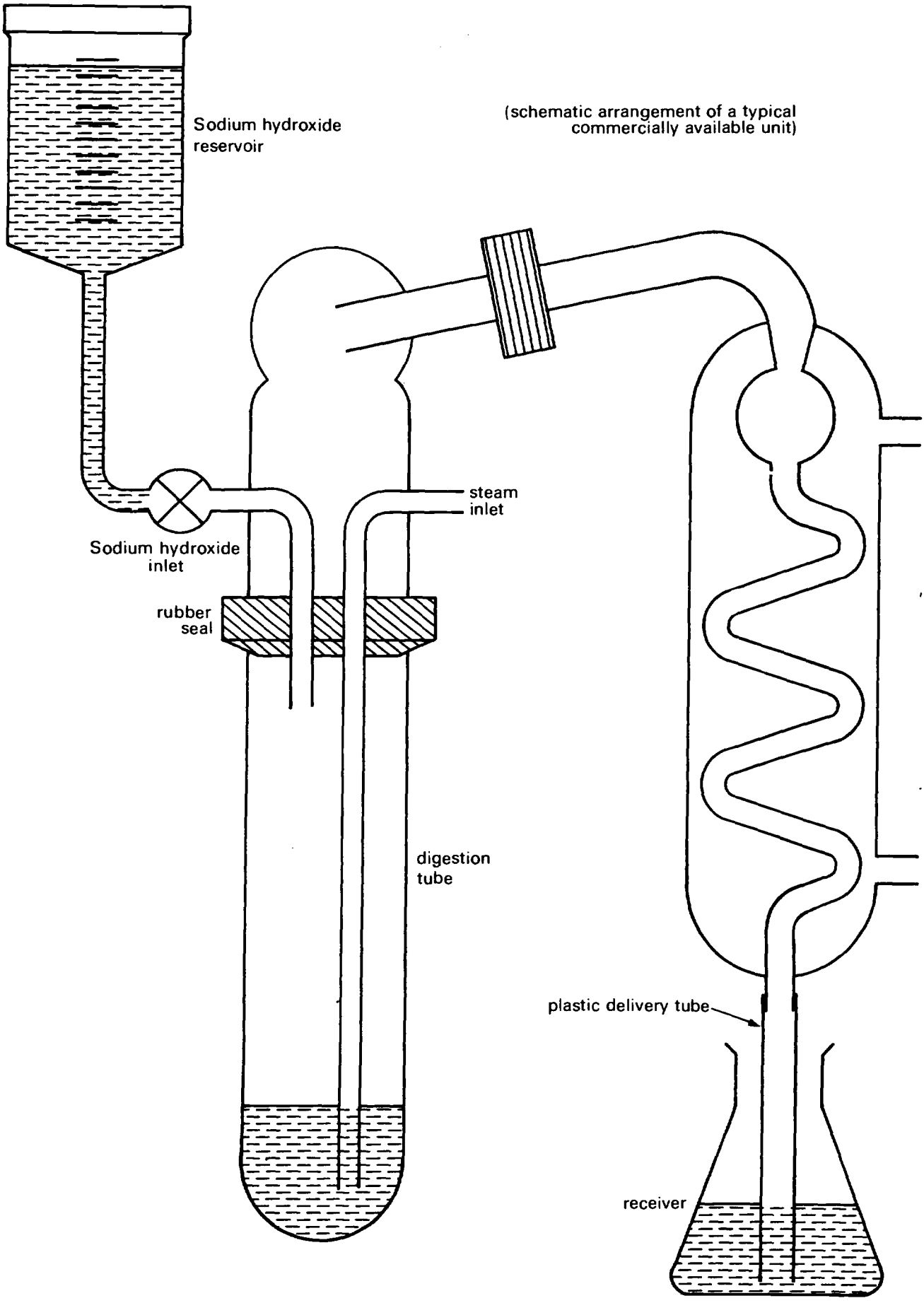

Figure 2 Steam distillation apparatus

B10 Analytical Procedure

Read Hazards, Section B5, before starting this procedure

Step	Procedure	Notes
	Digestion Procedure	
B10.1	Transfer a known amount of homogenised sample (note a) to a 300 ml Kjeldahl digestion flask (note b). Let the mass of sample taken be Mg.	a) For wet (homogenised) sludge: take a weight which on a dried solids basis falls between 0.25–0.50 g as dried sludge, e.g. up to 5% dried solids allows a weight of wet (homogenised sludge) between 5–10 g to be taken. For dried sludge: weight falls between 0.25–0.5 g. Do not exceed a weight of 0.5 g dried sludge or its equivalent weight of wet sludge. Incomplete digestion of the sample may result.
B10.2	Add 6.8±0.1 g of catalyst mixture (B6.2.2) and 2–3 anti-bumping granules (B6.2.4).	b) Digestion tubes of similar capacity may be used as an alternative to flasks.
B10.3	Cautiously add 10±0.5 ml of sulphuric acid (B6.2.1) whilst gently swirling the digestion vessel.	
B10.4	Stand the flask on a digestion rack inside a fume cupboard (note c).	c) Digestion tubes may be inserted into a suitable heating block.
B10.5	Heat the digestion vessel gently to evaporate any water present and until any foaming ceases (note d).	d) In the early stages of wet sludge digestion foaming and bumping may cause problems. The addition of 5.0±0.5 ml of hydrogen peroxide (B6.2.3) may serve to minimise such problems. The operator must however ensure that this procedure does not affect the validity of the result obtained.
B10.6	Heat the digestion vessel more strongly to sustain brisk boiling (note e). The sulphuric acid should reflux strongly up to about halfway along the neck of the digestion vessel. White fumes of sulphur trioxide will be visible above the clear reflux area (note f).	e) Avoid overheating the upper sections of digestion flasks or tubes. f) Strong heating is needed to achieve decomposition of refractory nitrogen compounds. Cooling by fume extraction systems and draughts could reduce the digestion temperature and therefore should be prevented. Confirmation of correct digestion conditions may be shown by the recovery of nitrogen from nicotinic acid control standards and the recovery of phosphorus from organic phosphorus compounds e.g. Dequest 2010 (see Sections B1.6 and B15).
B10.7	When the contents of the digestion vessel have become clear or no more than a pale straw colour (note g), continue to reflux as in step B10.6 for 60±10 min (note h).	g) The digestion mixture chars initially and usually becomes a clear, pale straw or colourless solution within about 30 minutes. h) Any silica present in the sample may cause turbidity and certain metals may contribute colours.

Step	Procedure	Notes
B10.8	Allow the solution to cool to 40±5°C and cautiously add 40±5 ml of water whilst swirling the flask (note i).	i) Water is added to prevent crystallisation of the digestion solution. Any crystals that appear may be dissolved by gentle warming and further dilution of the solution with water.
B10.9	Transfer the solution quantitatively to a 500 ml calibrated flask and dilute to volume with water. Mix well. Use this solution for the determination of total nitrogen content as given in steps B10.11 to B10.21 and for the determination of phosphorus as given in steps B10.23 to B10.29 (note j).	j) Any insoluble material present which might cause interference with either the measurement of ammonia [B10.11 to B10.20] or the measurement of phosphate [B10.23 to B10.29] is allowed to settle out before proceeding further into the respective analytical measurements.
B10.10	**Blank Digestion Procedure** (note k)	
	Carry out steps B10.1 to B10.9 as given above, replacing a known amount of homogenised sample (B10.1) by a suitable volume of water (B6.1). Reserve this solution for use as given in steps B10.21 and B10.31.	k) Blank values are normally insignificant and determination is only required infrequently at the discretion of the analyst depending on the relevance of blank values in relation to nitrogen and phosphorus values being found in sludges.
	Distillation Procedure for total nitrogen determination	
B10.11	Assemble the distillation apparatus as shown in figure 1. If contamination is suspected clean thoroughly before use e.g. by rinsing or by purging with steam.	
B10.12	Transfer 250±5 ml of sample digest solution obtained as given in step B10.9 to the distillation flask, together with a few anti-bumping granules (B6.2.4).	
B10.13	Add 50±5 ml of indicating boric acid solution (B6.3.4) to the receiver flask.	
B10.14	Reassemble the apparatus (note l).	l) Ensure that the tip of the delivery adaptor is below the surface of the indicating boric acid solution.
B10.15	Add 20±1 ml of sodium hydroxide/sodium thiosulphate reagent (B6.3.1) to the distillation flask and quickly reassemble the apparatus.	
B10.16	Heat the flask with a Bunsen burner so that distillation proceeds at about 10 ml/minutes (notes m and n).	m) Use commercially available units according to the manufacturer's instructions. The appearance of a black precipitate of mercuric sulphide signifies that the correct distillation conditions have been achieved.
B10.17	Collect about 120 ml of distillate then lower the receiver so that the delivery adaptor is above the surface of the solution.	n) The receiving boric acid solution becomes green during the course of the distillation.
B10.18	Continue to collect a further 30 ml of distillate.	

Step	Procedure	Notes
B10.19	Stop the distillation and rinse the delivery adaptor with about 5 ml of water.	
B10.20	Titrate the solution in the receiver flask with 0.02M hydrochloric acid solution (B6.3.5) to the appearance of a permanent grey-purple colour. Note the titre and let this be T_1 ml.	
	Blank Distillation (note k)	
B10.21	Transfer 250 ± 5 ml of blank digest solution obtained as given in step 10.10 to the distillation flask and proceed as given in steps B10.13 to B10.20. Let this titre be T_2 ml.	
B10.22	**Calculation**	

If the digestion procedure was carried out using a wet homogenised sample prepared as given in Section A4.3.1, total nitrogen content

$$= \frac{(T_1-T_2) \times 0.28 \times 200}{M \times A} \text{ g/kg}$$

and if prepared as given in Section A4.3.2,

$$= \frac{(T_1-T_2) \times 0.28 \times 200}{M \times B} \text{ g/kg}$$

If the digestion procedure was carried out using dried sample obtained as given in Section A6, total nitrogen content (note o)

$$= \frac{(T_1-T_2) \times 0.28 \times 200}{M} \text{ g/kg}$$

T_1 = sample titre (ml 0.02M hydrochloric acid solution)
T_2 = blank titre (ml 0.02M hydrochloric acid solution)
M = mass of sample taken (g)
A = dried solids content of sample as received (%m/m)
B = dried solids content of samples after homogenisation in the presence of added water as given in section A4.3.2
0.28 = mg of nitrogen equivalent to 1.0 ml of hydrochloric acid solution (0.02M)
200 = factor relating M and A to the volume of digest solution taken in the distillation step
2 = factor relating M to the volume of digest solution used in the distillation step.

o) A possible loss of nitrogen may have taken place during the drying procedure, consequently the analyst must interpret this result with caution (see Sections A1 and A6).

Step	Procedure	Notes
	Determination of total phosphorus	
B10.23	Transfer 25.0±0.05 ml of sample digest solution (B10.9) to a 100 ml calibrated flask. Dilute to volume with water and mix well to obtain the "test" solution.	
B10.24	Transfer a known volume of "test solution" (B10.23) not exceeding 30 ml to a 50 ml calibrated flask. Let this volume be V±0.05 ml (note p). (See also B11)	p) Alternative procedure to steps B10.24 to B10.27 – transfer V ml of "test" solution to a 100 ml beaker. Insert pH electrodes and add sufficient sodium hydroxide solution to raise the pH of the solution to 3.0 units. Quantitatively transfer this solution to a 50 ml calibrated flask ensuring that V ml plus rinsings do not exceed 40 ml and proceed as given in step 10.28.
B10.25	Add 2 drops of phenolphthalein indicator solution (B6.4.8).	
B10.26	Add 1.0M sodium hydroxide solution (B6.4.6) dropwise just to the appearance of a pink colour.	
B10.27	Add by 0.05 ml aliquots the 0.5M sulphuric acid solution (B6.4.7) sufficient to discharge the pink colour then dilute the solution with water to 40±1 ml. Mix well.	
B10.28	Add 8.0±0.2 ml of mixed reagent (B6.4.5) (note q), dilute to volume with water and mix well.	q) An automated pipette is suitable for dispensing this reagent.
B10.29	After at least 10 minutes and not more than 30 minutes measure the absorbance of the solution (B10.28) in a 40 mm pathlength cell at a wavelength of 882 nm. Let the absorbance = Y_s (note r).	r) The exact wavelength of maximum absorption must be checked for each instrument and used throughout the procedure. This maximum should be checked at regular intervals and after each service. If 882 nm is not obtainable on the instrument use instead 725 nm (B7.4.1).
	Blank determination (note j)	
B10.30	Transfer 25.0±0.05 ml of blank digest solution (B10.10) to a 100 ml calibrated flask. Dilute to volume with water and mix well to obtain a blank reference solution.	
B10.31	Transfer V±0.05 ml of the blank reference solution (B10.30) (note s) to a 50 ml calibrated flask.	s) V ml corresponds to the volume of dilute sample digest solution taken at step B10.24.
B10.32	Proceed as given in steps B10.25 to B10.29. Let the absorbance = Y_b.	
	Compensation for colour and turbidity (note t)	t) Omit this step when the colour or turbidity of a dilute sample digest solution is not contributing an appreciable fraction of the total absorbance.

Step	Procedure	Notes

B10.33 Process V ml of dilute sample digest solution (B10.24) as given in steps 10.25 to 10.29 except that 4±0.1 ml of 14% v/v sulphuric acid solution (B6.4.4) is used in place of reagent (B6.4.5) in step B10.28. Let this absorbance = Y_c.

Calculation of Results

B10.34 The absorbance (Y_p) due to phosphorus in the processed solution is given by

$$Y_p = Y_s - Y_b$$

or when a correction for colour and turbidity is made (B10.33)

$$Y_p = Y_s - Y_b - Y_c$$

B10.35 Determine the mass C (in g P) of phosphorus in the processed solution from the value of Y_p and the calibration curve or single point calibration (see Section B6.7).

B10.36 If the digestion procedure was carried out using a wet homogenised sample prepared as given in Section A4.3.1, total phosphorus content

$$= \frac{C \times 200}{M \times V \times A} \text{ g/kg}$$

and if prepared as given in Section A4.3.2,

$$= \frac{C \times 200}{M \times V \times B} \text{ g/kg}$$

If the digestion procedure was carried out using dried samples obtained as given in Section A6, total phosphorus content

$$= \frac{C \times 2}{M \times V} \text{ g/kg}$$

where

C = g P in the processed solution (B10.35)
M = mass of sample taken (g)
V = volume of test solution taken (ml) (B10.24)
A = dried solids content of sample as received (% m/m)
B = dried solids content of sample after homogenisation in the presence of added water as given in Section A4.3.2
2 and 200 = factors arising from the use of diluted aliquots of sample digest solution.

B11 Concentration Range of the Method for Total Phosphorus

Suitable aliquots of dilute sample digest to be used (B10.24) may be estimated from the following table:

Expected concentration (as P) g/kg dry sample	mg/l of digest solution (B10.9)	Volume of test solution to be used V ml (step B10.24)
1.2	0.6	30.0
1.2 – 4.0	0.6 – 2.0	20.0
4.0 – 8.0	2.0 – 4.0	10.00
8.0 – 16.0	4.0 – 8.0	5.00
16.0 – 32.0	8.0 – 20.0	2.00
32.0 – 120.0	20.0 – 60.0	1.00

B12 Extension of the Range of the Method

B12.1 Total nitrogen

If required the range of the method can be extended to higher concentrations of nitrogen by the use of stronger standard hydrochloric acid solution for the titration of ammonia in the distillate. Alternatively smaller volumes of digest solution may be distilled. In either case appropriate modifications to the calculation of results will be necessary.

If lower concentrations of ammonia need to be determined suitable volumes of digest solution may be analysed colorimetrically using the continuous flow procedure given in Section E of this booklet, or possibly by using the manual version of the method given in another booklet[10] of this series of methods provided that the digest solution is first neutralised. Note that at all concentrations of nitrogen it is possible to use colorimetry instead of distillation/titrimetry to determine the ammonia content of the digest solution.

B12.2 Total Phosphorus

The upper limit of the range of the method may be extended by greater dilution of the sample digest solution prior to the colorimetric steps. A more limited extension may be achieved by using the procedure given in section B10 steps B10.25 to B10.31 except that the absorbance is measured at 725 nm instead of 882 nm.

It is not possible to extend the lower limit of the method for the reasons given in section B13.6 regarding turbidity.

B13 Sources of Error

B13.1 The Sampling of the Original Material

The problems of obtaining representative samples of complex, labile, heterogenous materials such as sludges, slurries, soils and sediments, are discussed in Section A. The analyst must regard these problems as possible sources of error.

B13.2 Sub-sampling preparation for analysis

The necessary sub-sampling of the initial representative sample taken must also be recognised as a potential source of error.

Statistical techniques may show that relatively large sub-samples are required in order to obtain meaningful analytical results within defined confidence limits. In the context of this booklet, the available analytical procedure, particularly the digestion step, places a tight constraint upon such ideal techniques. For practical reasons the mass of wet sub-sample analysed by the procedure given in Section B10 does not exceed 10 g. This amount may fall well below that ideally required from the original larger bulk of complex material and therefore the analyst must exercise close controls upon sampling and sub-sampling procedures. Particular care must be taken in respect of factors such as the selection of the initial sample, possible mechanical loss of consitutents during sub-sampling operations and possible changes in composition during storage.

B13.3 Digestion Procedure

Sample foaming and spattering, particularly in the initial steps of the digestion procedure can lead to errors. Close control of digestion temperature and of the duration of the digestion is also necessary to avoid errors, particularly in the determination of total nitrogen (see Section B2). The continued "digestion" period (step B10.7) after the digest has cleared is an essential part of the process to ensure complete recovery of nitrogen, particularly that present as part of a heterocyclic system. However over-prolonged digestion may lead to falsely low results.

Excessive heating of the digestion flask or tube above the liquid level may lead to the loss of nitrogen from the digest.

B13.4 Distillation Procedure for Total nitrogen

The distillation rate and time of distillation must be closely controlled otherwise a complete recovery of evolved ammonia may not be obtained.

B13.5 Ammonia content of water used for blank determinations

The blank titre should not exceed 0.3 ml of 0.02M hydrochloric acid solution (B6.3.5). If it does exceed this value check the preparation of the indicator boric acid solution (B6.3.4). The water used for the determination of nitrogen may need to be prepared by distillation under acid conditions and/or in the presence of potassium permanganate. If a high value persists then all the reagents and working conditions should be critically examined.

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* In the publication in this series "Ammonia in Waters, 1981" information is given (Section A3) on the preparation of ammonia-free water.

B13.6 Total Phosphorus Determination

Before carrying out the colorimetric determination of phosphorus the digest solution obtained as given in Section B10, step 9 must be diluted with water for the following reasons:

1. It must be diluted with water prior to neutralisation otherwise the addition of alkali may cause the precipitation of any mercury–ammonia complex present. The resulting turbidity may interfere with the colorimetric determination of phosphorus present.

2. The digest solution must also be diluted with water to avoid the precipitation of the mercurous salt formed by the reducing action of the ascorbic acid present in mixed reagent (B6.4.5). Again the resulting turbidity may interfere with the colorimetric determination of the phosphorus present.

B13.7 Phosphorus content of water used for blank determinations

The reagent blank, although small, is not insignificant for the most accurate work, and should not exceed 0.02 absorbance units. If it does exceed this value the water should be redistilled. If a high value persists then the reagents and working conditions should be critically examined.

B14 Disposal of Mercury-Containing Residues from the Distillation Flask

In order to avoid risks to the environment, e.g. sewage treatment works and watercourses, and to recover some of the cost of expensive reagents, the following procedure is recommended.

As the residual contents of the distillation flask are strongly alkaline and may be hot, a safety vizor and gloves must be worn during the operation when the flask is dismantled from the distillation apparatus. This procedure and the decantation of the supernatant liquid should be carried out under a fume extraction hood.

B14.1 Procedure

Cool the residual contents of the distillation flask and transfer to a suitable container e.g. a 2.5 litre glass bottle (a Winchester quart bottle). Allow the precipitate of

mercuric sulphide to settle. The supernatant alkaline liquor should be oxidised or diluted 500 to 1 with water before disposal.

MERCURIC SULPHIDE IS A NOTIFIABLE WASTE AND MUST NOT BE DISPOSED TO LAND WITHOUT CONSENT. Precious metal refiners may accept mercuric sulphide for recovery. For information on mercury recovery for reuse if no repurchaser is available see Ref 13 in this series.

B15 Checking the Accuracy of the Analytical Result

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of analytical results. It is recommended that experimental tests to check sources of inaccuracy should be made regularly. Many types of test are possible and should be used as appropriate.

As a minimum control, it is suggested that a standard solution of nicotinic acid (pyridine-β-carboxylic acid) e.g. 10 mg N/l (i.e. 100 ml of a solution containing 0.879 g nicotinic acid/litre) and a standard solution of an organic-phosphorus compound, e.g. "Dequest 2010" of suitable concentration [see footnote (c) of Section B1] should be analysed at the same time and in exactly the same way as normal samples. The results obtained may then be evaluated by control chart techniques such as those recommended[12].

Note that nicotinic acid does not char easily. It may be necessary for complete recovery of nitrogen to add a small amount of a nitrogen-free organic substance that does char easily to create the reducing conditions necessary at the beginning of a digestion process[9]. Sucrose (about 0.1 g) or washed filter paper may be suitable. When digesting nicotinic acid it is particularly important to reflux the digest mixture as given in steps B10.6 and B10.7[7,8,9].

C Semi-Automated Determination of Total Nitrogen and Total Phosphorus in Dried Sewage Sludge (Copper Catalysed, Multiple Tube, Block Digestion Method followed by Air Segmented Continuous Flow Colorimetry)

C1 Performance Characteristics of the Method

C1.1	Substances determined	Total nitrogen and total phosphorus.
C1.2	Type of sample	Sewage sludge.
C1.3	Basis of method	Digestion of the sample with concentrated sulphuric acid in the presence of sodium sulphate and copper catalyst to convert nitrogen compounds present (see Section B2) to ammonium sulphate. At the same time, by processes of oxidation and hydrolysis, all types of phosphorus present are converted to orthophosphate. The ammonia and orthophosphate contents of the digest solution are determined by continuous flow colorimetry to enable the total nitrogen and phosphorus contents of the sample to be calculated.
C1.4	Range of application	1) Nitrogen up to 50 g N/kg (i.e. 1 to 50 mg N/l in digest solution) 2) Phosphorus up to 30 g P/kg (i.e. 1 to 30 mg P/l in digest solution)
C1.5	Calibration curves	1) Nitrogen: linear to 50 g N/kg (i.e. linear to 50 mg N/l in digest solution) 2) Phosphorus: linear to 30 g P/kg (i.e. linear to 30 mg P/l in digest solution)
C1.6	Total standard deviation (17 degrees of freedom)	1) Nitrogen N content g N/kg — Total standard deviation g N/kg Dried ground sludge — 29.1 — 0.4 2) Phosphorus P content g P/kg — Total standard deviation g P/kg Dried ground sludge — 20.0 — 0.3
C1.7	Limit of detection	1) Nitrogen 3.0 g N/kg sample (= 3.0 mg N/l digest solution) 2) Phosphorus 2.0 g P/kg sample (= 2.0 mg P/l digest solution)

C1.8	Sensitivity	1) Nitrogen: a digest solution containing 50 mg N/l gives an absorbance change of approximately 0.22 absorbance units using a 15 mm path-length cell. 2) Phosphorus: a digest solution containing 30 mg P/l gives an absorbance change of approximately 0.6 absorbance units using a 15 mm path-length cell.
C1.9	Time required for analysis	For 40 samples simultaneously in a heating block

Procedure	Total time (h)	Operator time (h)
Digestion	6	2
Total (and analysis)	8	3

The data presented in the above table were obtained jointly by the Severn Trent Water Authority (Coalport Analytical Laboratory) and the Yorkshire Water Authority (Sheffield Laboratory). The analysis of the digest solutions were carried out using method E of this booklet.

The limit of detection figures were obtained visually from the recorder traces in mg N/l and mg P/l respectively from Section E methodologies and converted into g N/kg and g P/kg accordingly.

C2 Principle

C2.1 Digestion of the sample

A representative homogeneous portion of dried sample, ground to pass 1 mm, is digested for 2.75 h with concentrated sulphuric acid and a catalyst mixture of copper and sodium sulphates under reflux conditions in a programme controlled heated aluminium block (see Appendix). When cool the digestate is diluted to volume with water, mixed well, and retained for subsequent analysis (Section C2.2).

C2.2 Analysis of digest solution

The ammonia and orthophosphate contents of the digest solution are determined using the automated procedures given in section E and then related to the total nitrogen and total phosphorus contents of the original sample.

C3 Interferences

See Sections B3.1.2 and B3.2.1 to B3.2.3.

C4 Hazards

It is important to follow normal good hygiene precautions since sewage sludge may contain pathogens and other toxic substances.

The digestion involves the heating of concentrated sulphuric acid and during the digestion sulphur trioxide will be evolved.

The procedures therefore must be carried out inside a fume cupboard fitted with an efficient extraction system. Alternatively, the digestion unit may incorporate equipment to prevent the escape of harmful reaction products into the laboratory atmosphere and/or render the reaction products harmless, e.g. neutralised before discharge to the laboratory's main drainage system.

C5 Reagents

Analytical reagent grade chemicals are used except where stated otherwise.

C5.1 Water

The water used for blank determinations and for preparing digest solutions should have ammonia and phosphate contents that are negligible compared with the smallest concentrations to be determined in the samples. Distilled or deionised water is usually suitable.

C5.2 Digestion reagents

C5.2.1 Sulphuric acid (d_{20}1.84)

C5.2.2 Pumice stone, granular, 8 to 20 mesh, as anti-bumping granules.

C5.2.3 Digestion catalyst mixture. Mix together 600±5 g of sodium sulphate, anhydrous, and 18±0.2 g of copper sulphate, pentahydrate.

C5.3 Reagents for the automatic analysis of digest solutions

See Section E3.

C6 Apparatus

C6.1 Digestion

C6.1.1 A heating block suitably drilled to accommodate 40 digestion tubes, and which can be thermostatically controlled at a temperature sufficient to maintain the digest mixture at the boil under reflux conditions (see Appendix).

C6.1.2 Digestion tubes, calibrated (75 ml).

C6.1.3 Stand for digestion tubes.

C6.1.4 Fume cupboard fitted with an efficient extraction system capable of safely removing heavy toxic fumes that are generated during digestion. Also refer to Section C4.

C6.1.5 Nitrogen and phosphorus-free paper squares of sufficient dimensions to enclose the sample, may be suitable for the weighing and transfer to the digestion tube (C6.1.2) of some types of sample.

C6.2 Analysis of digest solutions

Air-segmented continuous flow apparatus assembled as given in Section E6.

C7 Sample Collection and Preservation

As given in Section A2.

C8 Sample Pretreatment

As given in Section A6 or alternatively as given in Section A4.

C9 Analytical Procedure

Read Hazards, Section C4, before starting this procedure

Step	Procedure	Notes
C9.1	Weigh 0.5±0.005 g of dried, ground sample into a digestion tube (notes a and b). Let this weight be M_2 g.	a) Alternatively, the sample may be weighed into a tared paper square (C6.1.5). The paper is "fluted" into quarters to avoid loss of sample on the balance pan during weighing; fold paper so that the sample is completely enclosed when transferring the whole to a digestion tube.

C9.2 Add 1.0±0.05 g of catalyst mixture and 15–20 granules of pumice stone.

C9.3 Cautiously add 10.0±0.5 ml of sulphuric acid (d_{20}1.84) (note c) with swirling to mix the contents.

C9.4 Insert the tube into the heating block (note d).

C9.5 Cautiously heat the tube at 200°C to evaporate the water present.

C9.6 Increase the thermostat setting of the block to increase the temperature of the tube contents to boil under reflux and maintain this temperature for 2.75 h (note e).

C9.7 Switch off the heating block and when fumes cease to evolve from the tubes remove the tubes from the block (note f).

C9.8 Allow the tube to cool for a further 10 minutes then with continuous swirling add about 30 ml of water to the contents of the tube (note g).

C9.9 Cool the tube to room temperature. Quantitatively transfer the contents to a 500 ml calibrated flask and dilute to volume with water. Mix well and retain the solution for analysis by the procedures given in Section E (note h).

C9.10 Blank digestion procedure

Add 1.0±0.05 of catalyst mixture and 15–20 granules of pumice stone to a digestion tube. Carry out steps C9.3 to C9.9 to obtain a blank digest solution. Retain this solution for analysis by the procedures given in Section E.

C9.11 Calculation of result (note i)

Let the nitrogen content of the digest solution corrected for any blank value = C mg/l, and the phosphorus content, similarly, = D mg/l. Thus the total nitrogen content of the sample

$$= \frac{C \times 0.5}{M_2} \text{ g/kg}$$

and the total phosphorus content of the sample

$$= \frac{D \times 0.5}{M_2} \text{ g/kg}$$

where M_2 = mass, in grams, of the dried ground sample taken (C9.1).

b) Repeat steps C9.1–C9.4 inclusive for the number of samples to be processed as one batch.

c) The acid may be delivered using a dispenser.

d) After note (b) above, if a single extraction hood is used for the maximum number of digestion tube spaces available in the heating block and this maximum number exceeds the number of samples in the batch, make up to the maximum with blank digestions containing reagents only (C9.10).

e) During this time sulphuric acid should reflux from the sides of the tubes from a height 15–25 mm above the top of the heating block.

f) Usually 15 minutes after the end of the digestion programme.

g) The tube should be held pointing away from the operator.

h) The solution may be stored at room temperature in a polyethylene bottle for at least 2 weeks without significant loss of determinands. Any insoluble material which might cause interference with either the measurement of ammonia or phosphate [Section E] is allowed to settle out before proceeding further into the respective analytical measurements.

i) This calculation is carried out after a mg/l value for N and P is obtained from the analytical procedures given in Section E.

C10 Sources of Error

C10.1 See Section E8.

C10.2 The introduction of a "standard" sample, as an indication that the analytical technique of a combination of digestion and analysis of digest solution is operating within acceptable limits of precision and accuracy, is a satisfactory arrangement. However, it is difficult to produce a standard sample of sewage sludge. The method detailed in Section B is considered the reference method because of the rigorous digestion conditions evolved. The method here in Section C may have its limitations to digest heterocyclic compounds if present even when the sample is digested for 2.75 h (see Section C9, step 6) but checks can be made of the performance of the method to analyse samples of sludge on a routine basis. One suggested approach is for the analyst to undertake repeat measurements of a bulk sample of dried, homogeneous sludge using the reference method in Section B and use the results to check the performance of Method C. Other approaches using reference materials could be used. The National Bureau of Standards, US Department of Commerce, issues reference materials such as Orchard leaves, Bovine liver, Spinach and Tomato leaves each with a Certificate of Analysis.

D Semi-Automated Determination of Total Nitrogen and Total Phosphorus in "Wet" Sewage Sludge (Hydrogen Peroxide, Multiple Tube, Block Digestion Method followed by Air-Segmented Continuous Flow Colorimetry)

D1 Performance Characteristics of the Method

D1.1 Substances determined	Total nitrogen and total phosphorus.
D1.2 Type of sample	Sewage sludge.
D1.3 Basis of method	Digestion of the sample with concentrated sulphuric acid and 50% m/v hydrogen peroxide (see Section C1.3 for conversion details). After dilution of the digest, ammonia and orthophosphate are determined by air segmented continuous flow colorimetry as given in Section E.
D1.4 Range of application	1) Nitrogen: up to 50 g N/kg (i.e. 1–50 g N/l in digest solution) 2) Phosphorus: up to 30 g P/kg (i.e. 1–30 mg P/l in digest solution)
D1.5 Calibration curves	1) Nitrogen: linear to 50 g N/kg (i.e. linear to 50 mg N/l in digest solution) 2) Phosphorus: linear to 30 g P/kg (i.e. linear to 30 mg P/l in digest solution)
D1.6 Total standard deviation (19 degrees of freedom)	1) Nitrogen

	N content g N/kg	Total standard deviation g N/kg
Sludge A	36.7	0.74
Sludge B	22.0	0.26

2) Phosphorus

	P content g P/kg	Total standard deviation g P/kg
Sludge A	13.0	0.39
Sludge B	3.95	0.7

D1.7 Limit of detection	1) Nitrogen: 3 g N/kg (= 3 mg N/l of digest solution) 2) Phosphorus = 2 g P/kg (= 2 mg P/l of digest solution)
D1.8 Sensitivity	1) Nitrogen: a digest solution containing 50 mg N/l gives an absorbance change of approximately 0.22 absorbance units using a 15 mm path-length cell. 2) Phosphorus: a digest solution containing 30 mg P/l gives an absorbance change of approximately 0.6 absorbance units using a 15 mm path-length cell.

D1.9 Time required for analysis

Procedure	Total time (h)	Operator time (h)
Digestion	2	1
Complete analysis	4	2

The limit of detection figures were obtained visually from the recorder traces in mg N/l and mg P/l respectively from Section E methodologies and converted to g N/kg and g P/kg accordingly.

The performance data were obtained by Yorkshire Water Authority (Analytical Laboratory, Doncaster) and the following applies. The data for sewage sludge are based on a sludge of dried solids content of 5% m/m. The values for total standard deviation are derived from mg/l of nitrogen and mg/l of phosphorus obtained from the analytical procedures given in Section E. Also, all other mg/l values stated are derived from Section E procedures.

D2 Principle

D2.1 Digestion of the sample

A representative homogeneous portion of the sample is digested with concentrated sulphuric acid in a programme controlled heated aluminium block (see Appendix) using 50% hydrogen peroxide to complete the destruction of the organic matter. When cool the digestate is diluted to volume with water, mixed well and retained for subsequent analysis (D2.2).

D2.2 Analysis of digest solution

The ammonia and orthophosphate contents of the digest solution are determined using the automated procedures given in section E and then related to the total nitrogen and total phosphorus contents of the original sample.

D3 Interferences

See Sections B3.1.2 and B3.2.1 to B3.2.3.

D4 Hazards

It is important to follow normal good hygiene precautions since sewage sludge may contain pathogens and other toxic substances.

The digestion involves the heating of concentrated sulphuric acid and 50% hydrogen peroxide, both of which cause burns if brought into contact with skin. Any spillages of hydrogen peroxide must be washed away with copious volumes of water. During the digestion sulphur trioxide will be evolved. The procedure, therefore, must be carried out inside a fume cupboard fitted with an efficient extraction system.

D5 Reagents

Analytical reagent grade chemicals are used unless stated otherwise.

D5.1 Water

The water used for blank determinations and for preparing digest solutions should have ammonia and phosphate contents that are negligible compared with the smallest concentrations to be determined in the samples. Distilled or deionised water is usually suitable.

D5.2 Digestion reagents

D5.2.1 Sulphuric acid (d_{20}1.84)

D5.2.2 Pumice stone, Granular, 8 to 20 mesh, as anti-bumping granules.

D5.2.3 Hydrogen peroxide 50% m/m (d_{20}1.18).

Each new batch of this reagent should be checked to ensure it gives an acceptable blank in the total phosphorus determination. (Some batches of this reagent contain significant amounts of phosphorus).

D5.3 Reagents for the automatic analysis of digest solutions

See Section E3.

D6 Apparatus

D6.1 General

All glassware must be thoroughly cleaned and rinsed before use. To remove phosphate residues wash with sulphuric acid (D5.2.1) and rinse well with water.

D6.2 Heating device

Use a programme controlled heated metal block digester to accommodate straight sided digestion tubes of 100 ml capacity (see Appendix).

D6.3 Analysis of digest solutions

Air-segmented continuous flow apparatus assembled as given in Section E6.

D7 Sample Collection and Preservation

As given in Section A2.

D8 Sample Pretreatment

As given in Section A4.

D9 Analytical Procedure

Read Hazards section D4 before starting this procedure.

Step	Procedure	Notes
D9.1	Weigh 2.00±0.01 g of the sample of homogenised wet sludge and transfer to a digestion tube. Let the mass of sample be M_3 g (notes a and b).	a) Use not more than 10 ml of water to effect quantitative transfer. It is an obvious advantage to weigh the sludge directly into the tared digestion tube.
D9.2	Add 2.0±0.1 ml of sulphuric acid (D5.2.1) and two anti-bumping granules (D5.2.2) to the tube.	b) Repeat steps D9.1–D9.3 inclusive for the number of samples to be processed as one batch.
D9.3	Insert the tube into the heating block.	
D9.4	Cautiously heat the tube at 200°C to evaporate the water present (note c).	c) Refer to Appendix.
D9.5	Increase the thermostat setting of the block to increase the temperature of the tube contents to boil under reflux (note c).	
D9.6	Remove the tube from the heating block and allow to cool to a temperature at which the hydrogen peroxide (D5.2.3) can be safely added without excessive foaming (note d).	d) After 3 min is normally adequate.
D9.7	Carefully add 1±0.1 ml of the hydrogen peroxide (D5.2.3) to the tube, allowing it to run down the side of the tube. Mix by gentle swirling.	
D9.8	Replace the tube in the block and reheat until all traces of water have disappeared and the solution is again boiling under reflux.	
D9.9	Repeat steps D9.6 to D9.8 until 8 ml of the hydrogen peroxide have been added (note e).	e) The volume of hydrogen peroxide might be reduced if recoveries with the reduced volume are satisfactory to the analyst.

Step	Procedure	Notes
D9.10	Remove the tube from the heating block and allow to cool (note f).	f) Ensure that all reaction fumes have ceased to evolve before removing the tube.
D9.11	Cautiously add about 30±5 ml of water to the digest, replace the tube in the block and bring the contents back to boiling. As soon as the solution boils, remove the tube from the block and cool to room temperature.	
D9.12	Quantitatively transfer the contents of the tube to a 100-ml graduated flask and dilute to volume with water (note g). Mix well and retain the solution for analysis by the procedures given in Section E (note h).	g) If graduated digestion tubes have been used, make up to the 100 ml mark with deionised water. h) The solution may be stored at room temperature in a polyethylene bottle for at least 2 weeks without significant loss of determinands. Any insoluble material present which might cause interference with either the measurement of ammonia or phosphate [Section E] is allowed to settle out before proceeding further into the respective analytical measurement.
D9.13	**Blank digestion procedure** Add 10±2 ml of water (D5.1) followed by 2.0±0.1 ml of sulphuric acid (D5.2.1) and two anti-bumping granules (D5.2.2) to the tube. Carry out steps D9.3 to D9.12 to obtain a blank digest solution retained for the analysis by the procedures given in Section E.	
D9.14	**Calculation of result** (note i) Let the nitrogen content of the digest solution corrected for blank value = E mg/l and the phosphorus content similarly, = F mg/l. Thus the total nitrogen content of the sample $= \frac{E \times 10}{M_3 \times A}$ g/kg (note j) and the total phosphorus content of the sample $= \frac{F \times 10}{M_3 \times A}$ g/kg (note j) Alternatively, the total nitrogen content of the sample $= \frac{E \times 10}{M_3 \times B}$ g/kg (note k) and the total phosphorus content of the sample $= \frac{F \times 10}{M_3 \times B}$ g/kg (note k) In all equations above, 10 = factor relating M_3 and A or B to the 100 ml volume of digest solution obtained (D9.12).	i) This calculation is carried out after a mg/l value for N and P is obtained from the analytical procedures given in Section E. j) When using a wet homogenised sample as prepared by the procedure given in Section A4.3.1, where A in the equation = solids content of sample as received (% m/m) k) When using the preparation of sample procedure given in Section A.4.3.2, where B = the dried solids content of the sample after homogenisation in the presence of added water (% m/m).

D10 Sources of Error

D10.1 See Section E8.

D10.2 The introduction of a "standard" sample, as an indication that the analytical technique of a combination of digestion and analysis of digest solution is operating within the acceptance limits of precision and accuracy, is a satisfactory arrangement. However, it is difficult to produce a standard sample of sewage sludge. The method detailed in Section B is considered the reference method because of the rigorous digestion conditions evolved. The method here in Section D may have its limitations to digest heterocyclic compounds if present but checks can be made (see Section C10.2).

E

Air-Segmented Continuous Flow Colorimetric Analysis of Digest Solutions for Ammonia and Orthophosphate

Note: Except where modified to accommodate the relatively high acidity of the digest solution the ammonia method is similar to the S chemistry of method F of the 'Ammonia in Waters 1981' booklet in this series[10].

E1 Performance Characteristics of the Method

E1.1	Substances determined	Ammonia and orthophosphate
E1.2	Type of sample	Digest solutions from the digestion of sewage sludge from either Section C or Section D procedures.
E1.3	Basis of the methods	See Section E2, "Principle".
E1.4	Range of application	1) Ammonia: up to 50 mg N/l 2) Orthophosphate: up to 30 mg P/l
E1.5	Calibration curves	1) Ammonia: linear to 50 mg N/l 2) Orthophosphate: linear to 30 mg P/l
E1.6	Total standard deviation (19 degrees of freedom)	1) Ammonia: Standard solution mg N/l — Total standard deviation mg N/l 20 — 0.3 30 — 0.3 40 — 0.5 2) Orthophosphate Standard solution mg P/l — Total standard deviation mg P/l 20 — 0.2 25 — 0.2
E1.7	Limit of detection	1) Ammonia: 3 mg N/l 2) Orthophosphate: 2 mg P/l
E1.8	Sensitivity	1) Ammonia: A digest solution containing 50 mg N/l gives an absorbance change of approximately 0.22 absorbance units using a 15 mm path-length cell. 2) Orthophosphate: A digest solution containing 30 mg P/l gives an absorbance change of approximately 0.6 absorbance units using a 15 mm path-length cell.
E1.9	Time required for analysis	For 40 sample digest solutions the analysis time is approx. 2 h, 1 h of which is operator time.

The data presented in the above table were obtained jointly by the Severn Trent Water Authority (Coalport Analytical Laboratory) and the Yorkshire Water Authority (Doncaster Laboratory). The limit of detection values were obtained visually from the recorder traces.

E2 Principle

The solution containing ammonium and orthophosphate ions resulting from the digestion of nitrogen and phosphorus compounds present in the original sample is analysed automatically by the technique of air-segmented continuous flow colorimetry.

One chemistry determines ammonia (and hence total nitrogen in the original sample) by forming an indophenol blue type compound using the reaction between ammonia, hypochlorite and salicylate[10].

The second chemistry determines orthophosphate (and hence total phosphorus in the original sample) by the reaction of orthophosphate with molybdic acid, ascorbic acid, trivalent antimony ions and hydrogen ions, to form a 12-molybdophosphoric acid compound that is reduced in-situ to a blue heteropoly compound (phosphomolybdenum blue) in which antimony is incorporated.

E3 Interferences

See Sections B3.1.2 and B3.2.1 to B3.2.3.

E4 Hazards

The precautions given in the essay review on continuous flow analysis[11] should be observed.

Normal laboratory safety precautions must be observed. Concentrated sulphuric acid (d_{20} 1.84) must be handled cautiously; ammonium molybdate and antimony potassium tartrate are toxic, and solutions containing them, as well as other reagent solutions, must not be pipetted by mouth.

E5 Reagents and Standards

Analytical reagent grade chemicals are used except where stated otherwise.

E5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have ammonia and phosphate contents that are negligible compared with the smallest concentrations to be determined in the samples. Distilled or deionised is usually suitable.

E5.2 Ammonia determination reagents

E5.2.1 Citrate reagent 1

Dissolve 40 ± 0.5 g trisodium citrate and 34 ± 0.1 g of sodium hydroxide in about 800 ml of water in a 1-litre beaker. Dilute to 1000 ± 10 ml with water and mix well.

Stored in a glass or plastic bottle this reagent is stable for at least 3 weeks.

E5.2.2 Citrate reagent 2

Dissolve 400 ± 0.5 g of trisodium citrate in about 950 ml of water. Dilute to 1000 ± 10 ml with water and mix well. Stored in a glass or plastic bottle this reagent is stable for at least 3 weeks.

E5.2.3 Salicylate reagent

Dissolve 34.0 ± 0.5 g of sodium salicylate in about 950 ml of water in a 1-litre calibrated flask. Add 0.400 ± 0.005 g of sodium nitroprusside (ensure that the pH value of the salicylate solution is not greater than 8.0 before making this addition). Swirl to dissolve the solid and dilute to volume with water and mix well. Stored in an amber glass bottle this reagent is stable for at least 2 weeks.

E5.2.4 Sodium dichloroisocyanurate reagent

Dissolve 10.00 ± 0.05 g of sodium hydroxide in 500 ± 50 ml of water. Cool the solution to room temperature and add 0.800 ± 0.008 g of sodium dichloroisocyanurate

(dichloro-s-triazine 2,4,6(1H,3H,5H) trione sodium salt). When dissolution is complete, quantitatively transfer the solution to a 1-litre calibrated flask, dilute to volume with water and mix well. Stored in an amber glass bottle between 1–5°C, this reagent is stable for at least 2 weeks.

E5.2.5 10% v/v Sulphuric acid

Cautiously add with stirring 100±1 ml sulphuric acid (d_{20} 1.84) to about 800 ml of water in a 2-litre beaker immersed in cold water. Allow to cool and dilute with water to 1000±10 ml. Stored in a glass or plastic bottle this solution is stable for at least 3 months.

E5.2.6 1.5% v/v Sulphuric acid solution

Cautiously add with stirring 15±0.5 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water in a 2-litre beaker immersed in cold water. Allow to cool and dilute with water to 1000±10 ml. Stored in a glass or plastic bottle this solution is stable for at least 3 months.

E5.2.7 Ammonia stock standard solution, 1 ml = 1 mg N

Dry about 5 g of ammonium chloride for 1 hour at 105°C and allow to cool in a desiccator. Dissolve 3.819±0.001 g of the dry ammonium chloride in about 800 ml of water. Quantitatively transfer the solution to a 1-litre calibrated flask and make up to the mark with water. Mix well. This solution is stable for at least 4 weeks.

E5.2.8 Ammonia working standard solution, 1 ml = 0.1 mg N* (see Section E5.4)

Add 20±0.05 ml of ammonia stock standard solution (E5.2.7) to a 200 ml calibrated flask, dilute to volume with water and mix well. This solution is stable for at least 4 weeks.

E5.2.9 Ammonia calibration standard solutions* (see Section E5.4)

Add 15±0.5 ml of 10% v/v sulphuric acid solution (E4.2.5) to each of six 100 ml calibrated flasks. Add 5.00, 10.00, 20.00, 30.00, 40.00, and 50.00 ml of ammonia working standard solution (E5.2.8) into the series of flasks and dilute to volume with water. Mix well. These solutions contain ammonia at concentrations of 5.0, 10.0, 20.0, 30.0, 40.0 and 50.0 mg N/l respectively. These calibration standard solutions are stable for at least one week.

E5.3 Phosphate determination reagents

E5.3.1 10% v/v Sulphuric acid surfactant solution

Add 0.5±0.05 ml of a phosphorus free surfactant to about 800 ml of water in a 2-litre beaker immersed in cold water. Cautiously add with stirring 100±5 ml of sulphuric acid (d_{20} 184). Allow to cool and dilute with water to 1000±10 ml and mix well. Stored in a glass or plastic bottle this solution is stable for at least 3 weeks.

E.5.3.2 1.5% v/v Sulphuric acid solution

Refer to Section E5.2.6.

E5.3.3 Ammonium molybdate reagent

Cautiously add with stirring 62±1 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water in a 2-litre beaker immersed in cold water. When cool add 10.0±0.1 g ammonium molybdate and dissolve. Then add 0.5±0.05 g of antimony potassium tartrate and dissolve. Dilute this solution with water to 1000±10 ml and mix well. Stored in a dark bottle this solution is stable for at least 3 weeks.

E5.3.4 Ascorbic acid reagent

Dissolve 17.6±0.1 g of ascorbic acid in about 700 ml of water in a 1-litre calibrated flask. Add 50±1 ml of acetone and make up to 1-litre with water and mix well. Stored in an amber glass bottle at between 1–5°C this solution is stable for at least 3 weeks. A sufficient amount should be taken out daily and allowed to come to room temperature before use.

E5.3.5 Phosphate stock standard solution, 1 ml = 1 mg P.

Dry about 6 g of potassium dihydrogen phosphate at 105°C for 1 hour. Allow to cool in a desiccator. Dissolve 4.390±0.001 g of the dry potassium dihydrogen phosphate in about 300 ml of water. Quantitatively transfer the solution to a 1-litre calibrated flask and make up to the mark with water. Mix well. This solution is stable for at least 4 weeks.

E5.3.6 Phosphate working standard solution, 1 ml = 0.05 mg P* (see Section E5.4)

Add 10.0±0.01 ml of phosphate stock standard solution (E5.3.5) to a 200 ml calibrated flask, dilute to volume with water and mix well. This solution may be stored in a refrigerator at 1–5°C for at least one week.

E5.3.7 Phosphate calibration standard solutions* (see Section E5.4)

Add 15±0.05 ml of 10% v/v sulphuric acid solution (E4.2.5) to each of six 100 ml calibrated flasks. Add 5.00, 10.00, 20.00, 30.00, 40.00 and 50.00 ml of phosphate working standard solution (E5.3.6) into the series of flasks, dilute to volume with water and mix well. These solutions contain phosphate at concentrations of 2.5, 5.0, 10.0, 15.0, 20.0 and 25.0 mg P/l respectively. These calibration standard solutions are stable for at least one week.

E5.4 Combined standard solutions

If the determination of the ammonia and phosphate contents of the digest solutions from either method, section C or section D, are undertaken simultaneously, the following combined standard solutions can be used to replace the individual ammonia and phosphate standard solutions marked with an asterisk (*) in sub-sections E5.2 and E5.3.

E5.4.1 Combined working standard solution, 1 ml = 0.1 mg N and 0.05 mg P

Add 20.00±0.05 ml of ammonia stock standard solution (E5.2.7) and 10.00±0.05 ml of phosphate stock standard solution (E5.3.5) to a 200 ml calibrated flask, dilute to volume with water and mix well. This solution may be stored in a refrigerator at 1–5°C for at least one week.

E5.4.2 Combined calibration standard solutions for the simultaneous determination of ammonia and phosphate

Add 15±0.05 ml of 10% v/v sulphuric acid solution (E4.2.5) to each of six 100 ml calibrated flasks. Add 5.00, 10.00, 20.00, 30.00, 40.00 and 50.00 ml of combined working standard solution (E5.4.1) to the series of flasks and dilute to volume with water. Mix well.

These solutions, which are prepared fresh daily, contain ammonia and phosphate at the concentrations shown in the table below:

Arbitrary Flask No.	1	2	3	4	5	6
Ammonia mg N/l	5.0	10.0	20.0	30.0	40.0	50.0
Phosphate mg P/l	2.5	5.0	10.0	15.0	20.0	25.0

E6 Apparatus

E6.1 The following apparatus which is set out in Figures 3 (ammonia) or 4 (phosphate) is required:

Sample presentation unit (sampler).

Multichannel peristaltic pump.

Analytical cartridges, incorporating pump tubes, mixing coils and/or delay coils and dialyser unit.

Detectors (colorimeters or spectrophotometers), which each house a flow-through cell of path length 15 mm

Read-out (measurement) unit (recorder or printer).

Consult the essay review[11] on continuous flow analysis for further information.

E6.2 With reference to Section E4.4 and the simultaneous determination of ammonia and phosphate, the component parts of the above apparatus are easily brought together to produce a dual channel system with a net saving of a sampler, pump and possibly a read-out unit (recorder).

E7 Analytical Procedure Applicable to both Ammonia and Orthophosphate as Individual Determinations

Step	Procedure	Notes
	Starting operating	
E7.1	Connect the system as shown in Figures 3 (ammonia) or 4 (phosphate) as appropriate (notes a and b).	a) Follow the manufacturer's general operating instructions. b) See reference 11.
E7.2	With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents (note c). Start pump and switch on detector and measurement unit (note d).	c) Ensure that there is sufficient of each reagent to avoid 'topping up' during one batch of analysis. d) Allow the system to equilibrate for at least 20 minutes and during this period check that the bubble pattern and hydraulic behaviour of the system is satisfactory. If not eliminate difficulties before proceeding to step E7.3.
	Initial Sensitivity Setting	
E7.3	When an acceptably smooth baseline trace is given on the measurement unit, adjust the baseline response to about 5 per cent of full scale (note e) and then transfer the sample probe into a C_M standard solution (note f).	e) An elevated setting of the baseline allows for any negative drift that may occur. f) C_M is the greatest concentration that the calibration is intended to cover.
E7.4	When there is a positive stable response at the measurement unit due to the colour produced from the C_M standard solution (note g), adjust this response to read between 90 and 95 per cent of full scale (notes h and i).	g) The sample probe need only remain in the C_M standard solution for sufficient time to give a stable reading. h) A setting 5 to 10 per cent below full scale allows for any increase in sensitivity that may occur. i) This may be directly possible on some measurement units but others may require range expansion facilities.
E7.5	Return the sample probe to rest in the wash position (note j).	j) First remove any traces of C_M standard solution from the outside of the sample probe.

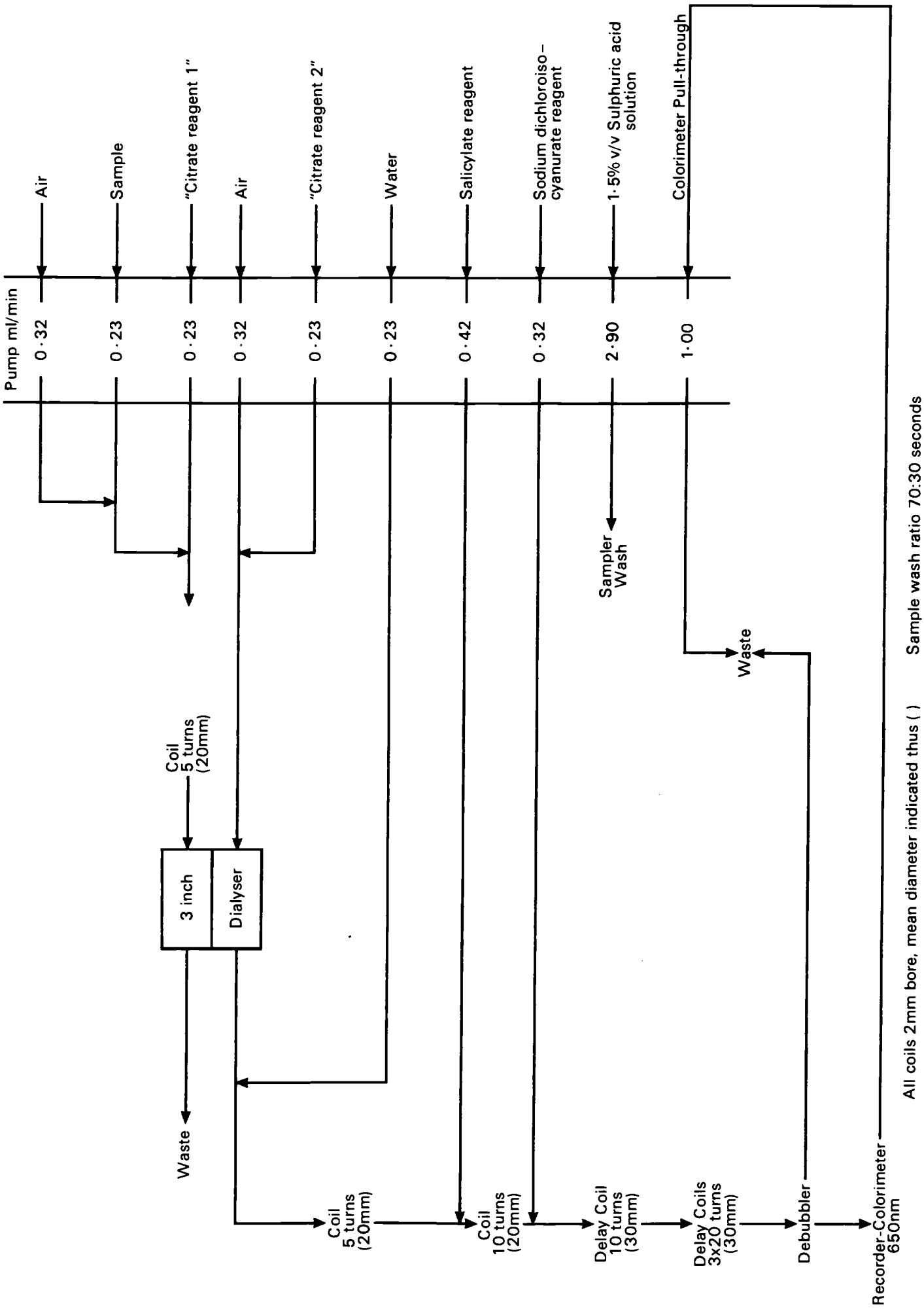

Figure 3 Automated ammonia line (flow) diagram

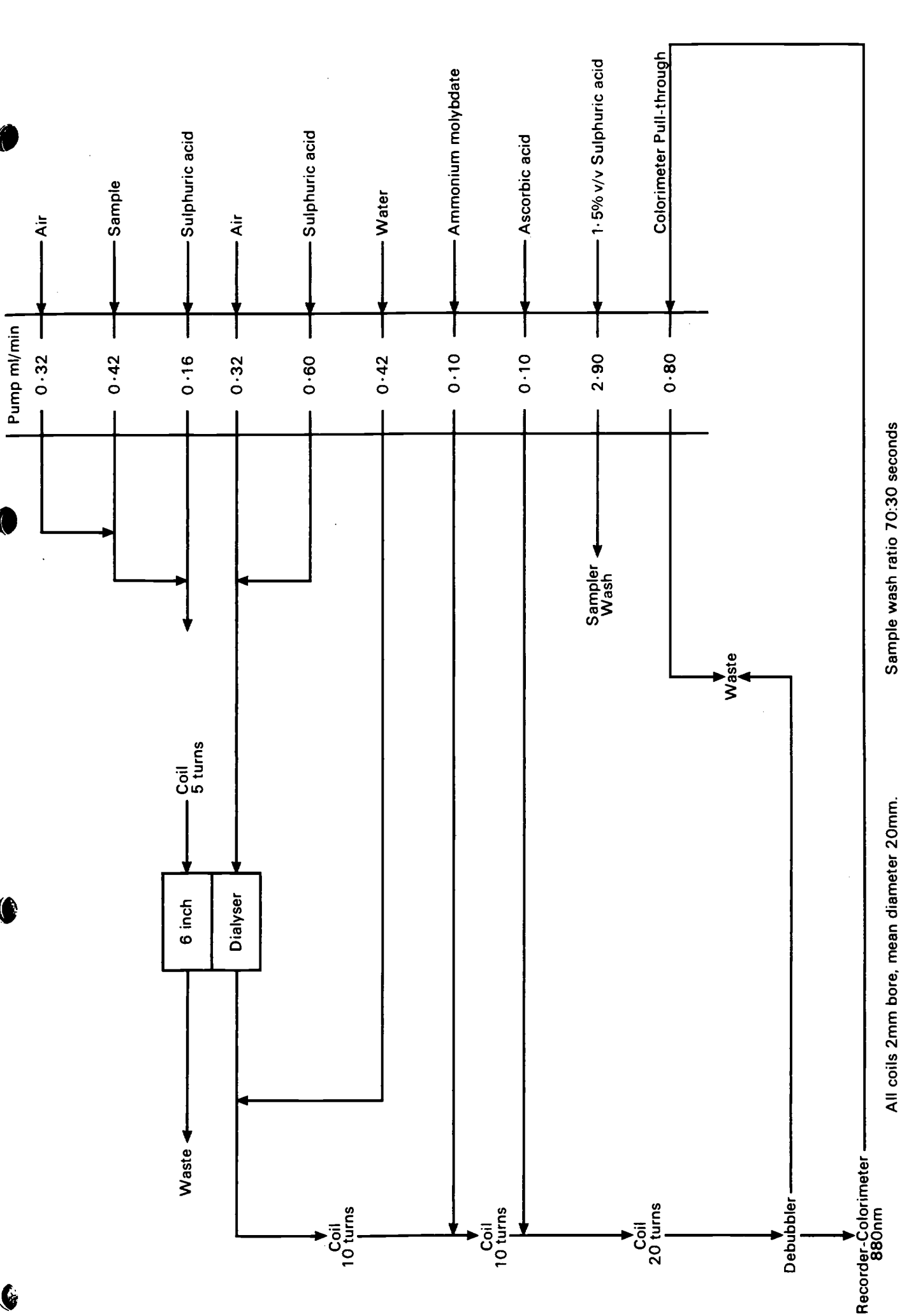

Figure 4 Automated phosphate line (flow) diagram

Step	Procedure	Notes
	Analysis of Samples	
E7.6	Load the sample turntable in the following order (notes k and l). **Position No on turntable/Solution** 1–6 Calibration standards in ascending order 7–8 Blank (note m) 9–18 Samples (note n) 19 Calibration standard (note o) 20–21 Blank (note m) 22–31 Samples (note n) 32 Calibration standard (note o) 33–34 Blank (note m) 35 Calibration standard (note o)	k) The turntable can be loaded during the initial stabilization period (steps E7.2 to E7.4). l) The order given is in current use. Alternative arrangements of solution on the turntable are discussed in Reference 9. m) Blank digest solution n) A control standard should occupy one of the sample positions as a check of system control (see Section E9). o) The standard which occupies position No. 5 to check the calibration.
	Repeat the sequence 7–21 until all the samples have been processed (notes p and q).	p) If cross contamination occurs between two samples (visible on the measurement units trace as incomplete separation of consecutive sample responses) both samples are reanalysed, perhaps in reverse order, separated by a blank solution.
E7.7	When a steady baseline is obtained on the measurement unit (after step E7.5) re-adjust the baseline to about 5 per cent of full scale if necessary and start the sampling unit.	q) The complete calibration may be checked at the end of the analytical batch if necessary.
E7.8	When all the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained, this unit can be switched off.	
	Calculation of Results	
E7.9	Plot a calibration curve of measurement unit responses (y axis) against concentration of standard solutions (x axis) (note r).	r) Providing the blank corrected responses of the calibration standard analysed at the end of each group of samples and those at the end of the turn-table (if used) are all acceptably close to their respective blank corrected initial calibration standard response. If not, refer to reference 9 for suggested procedures to obtain calibration curves. Note: Providing the linearity of calibration is acceptable to the analyst, a single point calibration might suffice.
E7.10	Using the calibration curve(s) or single point calibration convert the measurement unit responses due to the samples into concentrations of ammonia or orthophosphate in the samples (note s).	s) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes. The ammonia results are expressed as mg N/l and for orthophosphate as mg P/l.
	Shut-down Procedure	
E7.11	Transfer all reagent lines to water and continue to pump for at least 15 minutes. Switch off pump and detection unit(s).	

E8 Sources of Error

Refer to Reference 11.

E9 Checking the Accuracy of the Analytical Result

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution is analysed at the same time and in exactly the same way as normal samples. This standard solution, whose concentration is 90 per cent of the highest concentration that the calibration is intended to cover, is termed the quality control standard [see Section E7.6 (note n)]. It is prepared from a different stock standard solution to that used for preparing the calibration standards, but which has been stored under identical conditions.

The measured concentration of the quality control standard solution should then be plotted on a quality control chart which will facilitate detection of inadequate results, and will also allow the standard deviation of routine analytical results to be estimated.

Further information on accuracy of results can be found in Reference 12.

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Appendix The Use of Block Digesters

1 Introduction

Block digesters are finding increasing use in the analytical laboratory to digest samples and convert determinands of interest to a more determinable form. The most common reasons for the increase are that traditional digestion techniques tend to (i) consume much operator time, (ii) use a large area of bench space for multiple digestions and (iii) be hazardous. A block digester approach tends to reduce these three aspects of a digestion procedure. Also, it is claimed that experimental conditions are more controlled with the use of block digesters, resulting in an increase in precision and accuracy of data.

There are numerous factors relating to the use of block digesters, and, before describing them it is appropriate to define what is meant by the term BLOCK DIGESTER.

2 Description of a Block Digester

A block digester is a solid block of metal (usually aluminium) which is so drilled to hold securely a number of straight-sided, round-bottomed glass tubes in which the digestion of the samples takes place. The block is capable of being heated to high temperatures and is equipped with a heat supply which may be thermostatically controlled and time-programmed.

3 Related Factors

3.1 Block digesters of various sizes and different number of drilled holes are commercially available. The limiting factors are the required diameter of the holes and the proviso that the solid fraction of the block surrounding each hole is uniform, capable of retaining uniform heat to ensure that digestion of the sample is complete, independent of the position in the block. Drilled holes on the perimeter of the block tend not to conform with the proviso. This non-conformity is discussed in Section 3.5.

The wide choice of block digester in terms of the number of holes and hence the number of samples that can be digested simultaneously, would suggest that the purchase of a block digester does not need to be justified by the number of samples to be handled, as automation usually has to be. Currently, 6, 12, 16, 20, 24, 35, 36 and 40-hold block digesters are known to be in use and there seems no reason why an appropriate solid block of metal should not be purchased and drilled according to individual requirements.

3.2 Most sizes of heating block, as purchased, may either be secured to the surrounding case or be removable. Blocks of the latter type may be interchangeable. There are potential advantages with both arrangements of design and the operator must decide which design is best for his particular application and required accuracy of result. The following design features of both types of block digester are given for the guidance of the potential user.

3.2.1 Secured heating block

The disadvantages are obvious, but a distinct advantage is an increased guarantee that heat is uniformly distributed throughout the block. With a secured heating block, a minimum air-space between block and the case containing the heating elements is assured. In some designs the heating element(s) protrude into the lower quarter of the block. An experiment to determine the temperature variation across a secured heating block has been described[1]. The block measured (in inches) approximately 11 × 8 × 7.5 high and contained 40 drilled holes. A thermocouple was suspended in an empty digestion tube in each of the 40 holes in sequence for a fixed period of time.

A mean temperature value of 355°C was recorded with a standard deviation at that temperature of 1°C. A temperature profile of the experiment is given in Fig. 5. Two temperature zones were obtained at 353°C and 355°C. Only four hole positions were at variance as shown. This variance, however, did not affect the precision of result.

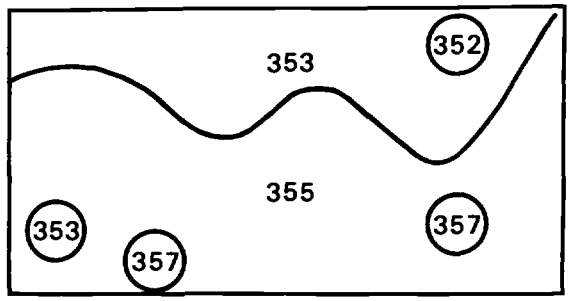

Figure 5 Diagram of measured temperature values (°C)

3.2.2 Removable heating block

Advantages

Subject to constant dimensions of the surrounding heater cases obtained from one manufacturer, the following options (a) to (f) may all be applicable to a block digester design which allows for the block to be removed from the heater case.

(a) One block may be replaced by another of identical dimensions.
(b) With identical dimensions of block, a 6-holed block for example may be interchanged with a 12-holed block.
(c) A single block may be replaced by two or more blocks whose combined dimensions are the same as the single block which they are replacing.
(d) Two or more blocks can have different numbers of drilled holes per block.
(e) Two or more blocks can have the same number of drilled holes but with different diameters.
(f) An undrilled block may be used to complete the total block volume available within the heater case.

Disadvantages

The possibility of not being able to secure a uniform distribution of heat across the whole volume of the available block space may result from any of the following.

(a) The air-space between a single block and the heater case must be sufficient to enable ease of removal of the block and may lead to excessive heat losses.
(b) If one block is replaced by two or more smaller blocks, the additional air-spaces may result in further heat losses.
(c) The temperature profile across the total block volume within the heater case may be affected by the precision of manufacture of the blocks, particularly if two or more small blocks are used in one heater case. Where multiple blocks are used it may prove troublesome if, before routine use, block temperatures are not measured at all possible configurations within the heater case and if the blocks are not then coded with regard to configuration to give desired temperatures.
(d) Temperature monitoring itself may prove more troublesome with the removable block design of block digester where multiple blocks are used. Each block should have its own provision for emplacement of a thermometer or other temperature measuring device.

3.3 Thermostat Control and Programming

These controls are either located on the front panel of the heater case or they are incorporated in a separate control unit.

In general block digesters with only a manual thermostat control have the control mechanism and the temperature display on the front panel of the heater case.

Block digesters which have, in addition, temperature programmable facilities, usually have all the electronics incorporated into a separate control unit.

Both arrangements have their merits but it is essential that electronics should always be protected from potential liquid spillages.

3.4 Confirming the Temperature of the Block

Some temperature adjustment controls have a temperature display whereas others are simply numbered. Even with temperature displays there appears to be no guarantee that the actual temperature of the block is the temperature set by the operator. Initial checks for all block digesters should be made to confirm temperature dial settings or to assess the deviation from the setting. The following procedure for measuring the temperature of the block is suggested.

3.4.1 Procedure for measuring the temperature of the block

1. Select a temperature setting or number on the display.
2. Fill each drilled hole with fine, dry sand.
3. Switch on the heating block.
4. Place a thermometer (or calibrated thermocouple) into the centre of the sand at the mid-depth of a drilled hole in a central position on the block. Keep the thermometer upright.
5. Leave thermometer in-situ until the temperature is observed not to change by more than one degree (or unit) in one minute.
6. Confirm step 5 for a further one minute and record temperature.
7. Repeat steps 4 to 6 for each drilled hole.
8. Repeat steps 1 to 7 for other temperature or numbered settings on the display.

The above procedure may be inconvenient and more precise than is required. Two modifications are offered as possible suitable alternatives:

(a) At stage 2 in the above procedure read: "Place an appropriate digestion tube into each drilled hole."
At stage 4 in the above procedure read: "Place the thermometer into the tube and hold in an upright position such that the bulb of the thermometer is just above the base of the tube."

(b) At stage 2 repeat (a) above.
At stage 4 read: "Place a thermocouple between the tube and the side of the drilled hole such that the tip rests between mid-depth and base of the drilled hole."

Having ascertained the relationship between measured temperature and temperature control setting by either of the previously listed procedures or any other chosen procedure, it is then convenient to refer to the temperature control setting to identify the operating temperature.

3.4.2 Procedure for measuring digest temperatures

The fit of the tube to the block and the height of the liquid in the tube may all cause minor variations in the actual digestion temperature. For some digestions this may affect the accuracy and precision of the results. If it is necessary to check this, run a set of typical digestions (not required for analysis) and measure the temperature of each with a pre-checked thermometer or sheathed thermocouple, being careful to immerse to the same depth in each tube. If the block contains anomalous holes only check positions being used.

3.5 Digestions at the Perimeter of the Block

On occasions, the operator may observe that there is a reduction in the volume of liquid in the digestion tubes placed in the central holes of the block, as compared with volumes in tubes in holes at its perimeter. The operator should then ascertain whether the reduction of liquid (reagents) results in an incomplete digestion of the sample(s).

Ideally, this check is achieved by simultaneously digesting one standard sample at each drilled hole position and calculating any deviation in determinand concentration(s) relative to the position in the block. An exercise in which twelve samples of a solid material were each digested in duplicate in a 40-holed block digester, one in the centre and the other on the perimeter of the block, is detailed in Ref. 1. The results of the exercise indicated that digestion was complete, independent of the position in the block.

3.6 Selection of Digestion Tubes

The following points are considered important for the selection of the glass tube used for digestion.

(a) The glass itself must be durable, resistant to high temperatures, have a low coefficient of expansion and of a thickness which allows a rapid transfer of heat to the solution contained within.
(b) Tubes are normally straight-sided and round-bottomed. They should fit snugly into the drilled hole yet must be easily removable.
(c) Invariably, the digested sample is subsequently analysed as a solution. Calibrated digestion tubes are an advantage in the preparation of this solution.
(d) The overall height of the tube is also important. The level of the liquid in the digestion tube should not protrude above the top of the heating block and the remaining height should be such that the air space above the level of the liquid is sufficient for satisfactory reflux of the liquid without loss.
(e) Enquiries to suppliers of digestion tubes regarding guarantees of tolerances of manufacture have revealed a reluctance to supply such a guarantee. To some extent this attitude is understandable but naturally it makes the user's life more difficult. However, a few glass-blowing companies will guarantee tolerance for their manufacture, but it is emphasised that the potential user of the tubes should produce the specification of dimensions and liaise closely with the manufacturer. An increased precision of manufacture is usually associated with increased costs, although, with small, local companies, on a tube to tube basis compared to the tubes offered by the manufacturer of the block digester, the price is usually lower even with the "increase". Screw-capped culture tubes, bought in bulk, have been used for small-scale block digestion. It is worth bringing to the attention of potential purchasers that experience has shown as high as 20% rejection on the grounds of inappropriate dimensions.

3.7 Safety Precautions

3.7.1 Removal of toxic fumes

The digestion procedures may result in the generation of toxic fumes. The need for an efficient extraction system to remove the fumes cannot be over emphasised. The operator should consider a custom-built extraction hood which is conveniently seated on top of a collection of digestion tubes in the block. The extraction hood may then be connected at its distal end to a suitable fume removal unit. Advice on extraction systems of this type is usually available from manufacturers.

3.7.2 Safety screens

It is highly recommended that a safety screen is placed between block digester and operator.

Tube failure and spillage

Digestion tubes may crack, or the control mechanism may malfunction and the temperature of the block increase unexpectedly. There is great danger to the operator if digestion reagents come into contact with a heated block. Switch off at the mains before touching the block at all or attempting to remove undamaged tubes. After such an event, the electronics should be thoroughly inspected by a qualified electrician for damage. The drilled holes should be thoroughly cleaned with copious amounts of water or very dilute alkali solution using pads of tissue paper soaked in water or dilute alkali.

Bibliography

Notes for the use of Block Digesters in chemical analysis. K W Petts, Water Research Centre Laboratory Record No. 264-S, 1984.

Address for Correspondence

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

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

Department of the Environment

Standing Committee of Analysts

Membership aiding with this Method

This method took a long time in preparation and testing. It was one of the methods proposed right at the start. After 1975 it was in the care of Panel 8.1, but subsequently moved to Panel 5.3 when Working Group 8 (Sludge Methods) was dissolved and then to Panel 5.1. Hence the number of people concerned with its preparation is large. As most of the panel and working group members were actively concerned, no distinction is made between the various panels and working groups. Main Committee members listed are those serving at times when that Committee was consulted.

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