Formaldehyde, Methanol and Related Compounds in Raw, Waste and Potable Waters, 1982 Tentative Methods

Methods for the Examination of Waters and Associated Materials

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Formaldehyde, Methanol and Related Compounds, in Raw, Waste and Potable Waters, 1982 Tentative Methods

Methods for the Examination of Waters and Associated Materials

This booklet contains an introduction and six methods:

A. The Manual Determination of Free Formaldehyde
B. The Manual Determination of Total Formaldehyde
C. The Automated Determination of Free Formaldehyde
D. The Automated Determination of Total Formaldehyde
E. The Automated Determination of Methanol
F. The Determination of Methanol by Gas Chromatography

Contents

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Warning to users

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

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

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

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

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About this series

This booklet is part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users — the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst 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 responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has 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 nonmetallic 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, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series 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 the booklet.

T A DICK
Chairman

L R PITTWELL
Secretary

3 February 1983

Manual and Automated Methods for the Determination of Formaldehyde, Methanol and Related Compounds

1. Introduction

1.1 Determinands

Formaldehyde may be present in raw, waste and potable waters in various forms. The simplest form to be found is *free (monomeric) formaldehyde* and it is this type of formaldehyde which is likely to be toxic*. However, other forms of formaldehyde may produce free formaldehyde under certain conditions and it is therefore desirable to detect their presence. These other forms of formaldehyde are categorised into the following groups:

(a) formaldehyde which is adsorbed onto particles
(b) para (polymeric) formaldehyde
(c) formaldehyde that has combined with other compounds to produce definite identifiable substances eg. *hexamine,* which may be in solution or adsorbed onto particles.
(d) formaldehyde that has combined with for example proteins which may then remain in solution or be adsorbed onto other particles.

Also, free formaldehyde is an oxidation product of methanol.

1.2 Analytical Procedures

Six analytical methods, three manual and three automated, are presented in the booklet.

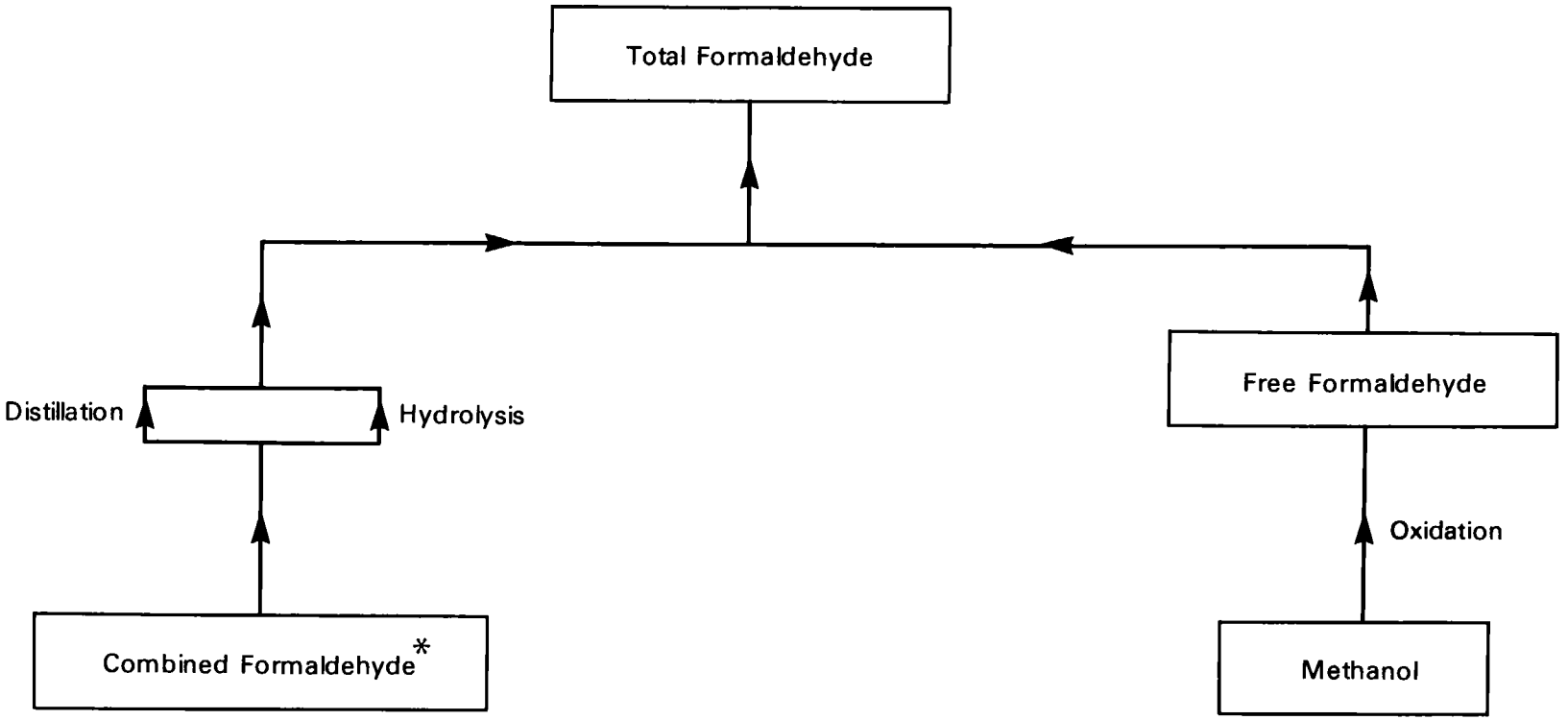
	Method	Determinand	Range of concentration (mg/l)	Basis
A.	Manual	Free formaldehyde	0–2	Spectrophotometry
B.	Manual	Total formaldehyde	0–10	Distillation and spectrophotometry
C.	Automated	Free formaldehyde	0–25	Spectrophotometry
D.	Automated	Total formaldehyde	(i) 0–25	Direct hydrolysis and spectrophotometry
			(ii) 0–5	Distillation and spectrophotometry
E.	Automated	Methanol	0–20	Oxidation and spectrophotometry
F.	Manual	Methanol	0–50	Gas chromatography with flame ionization detection

*Toxicity review 2, FORMALDEHYDE. R J Fielder et al, Health and Safety Executive, Occupational Health and Hygiene Laboratories, London.

Methods A–E are related since in each procedure free formaldehyde is finally determined spectrophotometrically from its reaction with acetylacetone in the presence of an excess of an ammonium salt to form the yellow compound, 3,5-diacetyl-l,4-dihydrolutidine (Ref. 1). The relationship between formaldehyde, methanol and hexamine can be shown by a line diagram (Fig. 1). However, the pretreatment required to produce free formaldehyde differs between the methods and this difference is discussed in the ensuring section.

The determination of methanol by gas chromatography (method F) is considered separately.

Figure 1 LINE DIAGRAM OF THE RELATIONSHIP BETWEEN FORMALDEHYDE, METHANOL AND HEXAMINE



*The term "combined formaldehyde" is used to represent those forms of formaldehyde, including hexamine, which produce free formaldehyde under certain conditions.

1.2.1 Spectrophotometric methods

1.2.1.1. Manual

Method A. Determination of free formaldehyde

Only with clear and colourless water samples can the method be directly applied without pretreatment. The method is unsuitable for raw and waste waters because of their possible turbidity and colour. The analyst may wish to consider the use of manual dialysis for these latter samples but an alternative approach to compensate for turbidity and colour is to substitute the colour-producing reagent with an acid solution† and re-analyse the samples. The free formaldehyde content of the samples is then obtained by difference.

Method B. Determination of "hexamine"

This method employs acid-distillation to convert hexamine to free formaldehyde. Therefore, the analyst must consider the possibility of the compounds previously categorized as groups (a), (b) and (d) producing free formaldehyde under the stated conditions of the distillation procedure. Free formaldehyde itself will also contribute to the value of the "hexamine" concentration obtained. It is for these reasons that this method and the automated "hexamine" (method D) have been designated "The Determination of Total Formaldehyde".

1.2.1.2. Automated

Method C. Determination of free formaldehyde

Turbidity and colour are removed from the sample by dialysis. Therefore, the method is suitable for raw and waste waters. In addition, those forms of formaldehyde categorized as group (a) will be removed by dialysis and it is highly probable that group (d) compounds will also be removed at the dialysis stage because of the inability of the large protein molecules to diffuse through the dialyser membrane. Paraformaldehyde, $(HCHO)_n$ (group (b)) may or may not be removed by dialysis depending on the value of 'n'.

Hexamine (group (c)) shows a positive response [100 mg hexamine/1 = 8.5 mg formaldehyde/1]. Therefore, if significant quantities of hexamine are present it is preferable to correct for interference by using free and total formaldehyde (method D) data in the following formula:

$$F = (F_f - 0.0659F_t) \times 1.07$$

where F = the true free formaldehyde value,

F_f = the observed free formaldehyde value,

and F_t = the observed total formaldehyde (hexamine and free formaldehyde) value.

Method D. Determinaton of total formaldehyde

Formaldehyde in a combined form is less toxic than free formaldehyde but if subjected to sewage treatment on admixture with domestic sewage, the combined forms of formaldehyde may be broken down to free formaldehyde. A differentiation between free formaldehyde and combined forms of formaldehyde is thus required.

A value of the formaldehyde concentration by the total formaldehyde method will include the free formaldehyde concentration originally present. Total free formaldehyde is therefore determined and two procedures (i) hydrolysis and (ii) distillation are offered to convert combined forms of formaldehyde to free formaldehyde.

Method E. Determination of methanol

A value of the methanol concentration obtained by this method may include the free formaldehyde concentration originally present. Also, it is reported that hexamine in a concentration of 5.0 mg/l gives a response equivalent to 4.65 mg methanol/l. These factors must be taken into consideration before the methanol result is reported.

1.2.2. Gas chromatography method

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† Dissolve 150 ± 1 g of ammonium acetate in about 800 ml of water. Add 3.0 ± 0.1 ml of glacial acetic acid and dilute to 1-litre with water. Mix well.

The method for the determination of the concentration of methanol is based on gas liquid chromatography. Samples are injected directly onto the chromatographic column and methanol is detected by means of a flame ionization detector system.

Other substances may exhibit similar separation characteristics to methanol on the column in use. Confirmation of identity is therefore necessary on a second column exhibiting different separation characteristics.

1.3. Recommendation for Routine Analysis

It is recommended that to obtain as complete as possible a sample assay, the sample should be subjected to three analyses, namely the determination of total formaldehyde, free formaldehyde and methanol.

2. Sample Collection and Preservation

Samples should be collected in glass containers which have been cleaned with a proprietory cleaning agent that does not interfere with the analysis, thoroughly rinsed with water and air dried between 60–80°C. Screw caps made from a formaldehyde-based resin should not be used.

No special preservation techniques are employed. However, samples should be analysed as soon as possible after collection or within 24 hours after collection, if stored in a refrigerator between 1° and 5°C.

Samples may lose the determinand of interest to the atmosphere by volatilization. Therefore, they should be stored in full, tightly-stoppered containers in those cases where it is safe to do so.

3. Checking the Accuracy of Analytical Results

(for further information see another publication in this series*)

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 minumum, 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. 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.

4. Sources of Error

The attention which it is necessary in a laboratory to pay sources of error depends on the accuracy required of the analytical results. The following sub-sections summarise the main sources of error:

4.1. Contamination

The technique and working conditions should be critically examined and any contamination eliminated or minimized.

4.2. Interfering Substances

See relevant section in each method of the booklet. Also, as noted in the introduction to the collection of methods; free formaldehyde, combined formaldehyde (including hexamine) and methanol are inter-related. Consequently each substance may interfere with the others. It is for this reason that the sample should be subjected to all three analyses as recommended to obtain as complete a sample assay as possible.

4.3. Calibration Standards

The linearity of the calibration curves is given in the performance characteristics tables. However, the slope of the calibration curve may vary dependent on the type of equipment used or it may alter daily on the same equipment. Therefore, a calibration curve should be produced for each batch of samples as described in the relevant sections of the procedures.

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*"General Principles of Sampling and Accuracy of Results, 1980", also published in this Series ISBN/011/751491/8

A. A Manual Method for the Determination of Free Formaldehyde using Spectrophotometry

A1. Performance Characteristics of the Method*

A1.1	Substance determined	Free formaldehyde		
A1.2	Type of sample	Raw, waste and potable waters		
A1.3	Basis of method	Free formaldehyde reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, diacetyldihydrolutidine, whose concentration is measured spectrophotometrically		
A1.4	Range of application	Up to 2.0 mg/l		
A1.5	Calibration curve	Linear		
A1.6	Standard deviation (within batch) (5 degrees of freedom)		Formaldehyde concentration (mg/l)	Standard deviation (mg/l)
		Standards	0.5	0.02
			2.0	0.02
		Samples		
		Sewage effluent	0.5	0.02
		Trade waste	1.45	0.03
A1.7	Limit of detection* (5 degrees of freedom)	0.1 mg/l		
A1.8	Bias	Less than 10% as indicated by recovery data from 'spiked' samples (see Table 1)		
A1.9	Interferences	See Section 3		
A1.10	Sensitivity	A 2.0 mg formaldehyde/l standard solution gives an absorbance change of approximately 0.23 absorbance units using a 20 mm cell		
A1.11	Time required for analysis	8 samples/hour all of which is operator time		

*The information given in the above table was produced by the Anglian Water Authority.

Table 1. Recovery of free formaldehyde from 'spiked' samples (single determinations)

Sample	Initial concentration of free formaldehyde (mg/l)	Concentration of free formaldehyde added (mg/l)	Concentration of free formaldehyde found (mg/l)	% recovery of added formaldehyde
Sewage effluent	0.5	0.5	1.0	100
Trade effluent	1.45	0.5	1.9	90

A2. Principle

The method is based on the work of Nash([1]). Formaldehyde reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, 3,5-diacetyl-1,4-dihydrolutidine, the concentration of which is measured spectrophotometrically at a wavelength of 430 nm.

A3. Interferences

At the concentration levels of formaldehyde examined by the method, a solution containing 100 mg/l of the following appears not to interfere:

acetone, methanol, formic acid, chloroform, phenol, nitrate, nitrite, ammonia, chloride, sulphate, potassium hydrogen phthalate, Di-n-butyl phthalate, benzaldehyde, acetaldehyde, chloral, glucose and ninhydrin.

Only with clear and colourless water samples can the method be directly applied without pretreatment. The method is unsuitable for raw and waste waters showing significant turbidity or colour. The analyst may wish to consider the use of manual dialysis for these samples but an alternative approach to compensate for turbidity and colour is to substitute the colour-producing reagent with an acid solution (See Section A5.12) and re-analyse the samples. The free formaldehyde content of the samples is then obtained by difference.

As the colour development conditions are mildly acidic, hexamine yields some formaldehyde within this period which therefore reacts as free formaldehyde.

If the presence of significant quantities of hexamine is suspected, correction for its interference may be made by using the concentration of formaldehyde determined by both this method and by the manual total formaldehyde procedure (Method B.) in the following formula:

$$F = \frac{F_f - x F_t}{1 - x}$$

where F = true free formaldehyde value
F_f = observed free formaldehyde value obtained by this method
F_t = observed total formaldehyde value obtained by method B
x = the proportion of hexamine breaking down to free formaldehyde in this method, which is:

$$\frac{\text{observed free formaldehyde from hexamine standard}}{\text{mg/l of hexamine standard} \times 1.29}$$

(1 mg hexamine/l gives a theoretical response equivalent to 1.29 mg free formaldehyde/l).

A4. Hazards

Sulphuric acid, sodium hydroxide, acetylacetone and acetic acid are corrosive. Eye protection and gloves should be worn when handling chemicals, and any spillages should be washed away with copious quantities of water.

A5. Reagents and Standards

Analytical reagent grade chemicals are used except where stated otherwise. Calibrated glassware should meet the recognized criteria for accuracy.

A5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have a formaldehyde content which is negligible compared with the smallest concentration of formaldehyde to be determined in the samples.

Distilled or deionized water will usually be suitable.

A5.2 0.5M Sulphuric acid solution

Cautiously add with stirring 27 ± 0.5 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water. Cool, make up to 1 litre with water in a calibrated flask and mix. Store in a glass stoppered bottle. This solution is stable for at least 3 months.

Standardize this acid solution against the 1.0M sodium hydroxide solution (Section A5.3).

A5.3 1.0M Sodium hydroxide solution

Dissolve 40 ± 0.5 g of sodium hydroxide pellets in about 600 ml of water. Cool, make up to 1 litre with water in a calibrated flask and mix. Store in polyethylene stoppered bottles. This solution is stable for at least 1 month providing it is protected against attack by atmospheric carbon dioxide.

Standardize this alkali solution against a primary standard eg. potassium hydrogen phthalate, sulphamic acid.

A5.4 Sodium sulphite Solution

Dissolve 125 ± 1 g of anhydrous sodium sulphite in about 600 ml of water and make up to 1.0 ± 0.01 litre with water. Store in a glass stoppered bottle. This solution is prepared fresh as required.

A5.5 Thymolphthalein indicator solution

Dissolve 1.0 ± 0.02 g of thymolphthalein in 1.0 ± 0.01 litre of ethanol. Store in a glass stoppered bottle. This solution is stable indefinitely subject to evaporation losses of the ethanol.

A5.6 Acetylacetone solution

Dissolve 150 ± 1 g of ammonium acetate in about 800 ml of water, add 3.0 ± 0.1 ml of glacial acetic acid and 2.0 ± 0.1 ml of acetylacetone with stirring, make up to 1 litre with water in a calibrated flask and mix. This solution is stable for at least one week when stored in an amber-coloured glass stoppered bottle in a refrigerator between 1° and 5°C.

A5.7 Formaldehyde stock standard solution, 1 ml ≙ 20 mg formaldehyde

Weight 6.0 ± 0.1 g of formaldehyde solution (40 per cent m/v) and quantitatively transfer to a 100 ml calibrated flask. Add 10 ± 0.1 ml of 0.5M sulphuric acid solution. After 10 ± 0.1 min, add 10 ± 0.1 ml of 1M sodium hydroxide solution and dilute to the calibration mark with water. Standardize this stock solution by transferring 25 ± 0.1 ml into a flask and neutralizing to thymolphthalein indicator. Transfer 25 ± 0.1 ml of sodium sulphite solution into a second flask and neutralize to thymolphthalein indicator. Quantitatively add the neutral sodium sulphite solution to the neutral formaldehyde solution and titrate with 0.5M sulphuric acid solution.

1 ml of 0.5M sulphuric acid ≙ 30.03 mg of formaldehyde.

A5.8 Formaldehyde intermediate solution, 1 ml ≙ 0.2 mg formaldehyde

Note: It is more convenient to make set dilutions of the standardized stock solution and plot the calibration curve to suit eg. if the stock solution was 20.2 mg/l, the intermediate solution will be 0.202 mg/l.

Dilute 10.0 ± 0.1 ml of the stock standard solution (A5.7) to 1 litre with water. This solution is stable for at least one month.

A5.9 Formaldehyde working standard solution, 1 ml ≙ 0.002 mg formaldehyde

Dilute 1.0 ± 0.01 ml of the Intermediate Standard to 100 ml with water. This solution should be prepared fresh on the day of use.

A5.10 Hexamine stock standard solution, 1 ml = 1.0 mg hexamine

Weight 1.00 ± 0.01 g Hexamine. Dissolve in water, transfer quantitatively to a 1-litre calibrated flask, and dilute to the calibration mark with water.

A5.11 Hexamine interference standard solution, 1 ml = 0.01 mg hexamine

From the stock standard solution (A5.10) prepared a solution in water so that 1000 ml = 10 mg hexamine. This solution is prepared fresh daily.

A5.12 Acid reagent substitute

Prepare this reagent as in A5.6 but omit the acetylacetone.

A6. Apparatus

50 ml calibrated glass tubes with stoppers
Two matched 20 mm cells
A spectrophotometer or colorimeter for use at a wavelength of 430 nm
A water bath at 60°C ± 2°C
An ice-water bath.

A7. Analytical Procedure

Read Section A4 on hazards before starting this procedure

Step	Analytical Procedure	Notes
	Starting Operation	
A7.1	Switch on water bath	
	Calibration	
A7.2	Add 5.0, 10.0, 15.0, 20.0 and 25.0 ml aliquots of the working standard (A5.9) into each of five calibrated tubes	
A7.3	Add 25.0 ± 0.1 ml acetylacetone reagent to each, and to a 'blank' tube	
A7.4	Make each tube up to the 50 ml mark with water and mix (Note a)	(a) These solutions now contain 0.2, 0.4, 0.6, 0.8 and 1.0 mg formaldehyde/l, providing that 1 ml of the working standard = 0.002 mg formaldehyde
A7.5	Place the tubes in the water bath at 60 ± 2°C for 10 ± 1 min (note b)	(b) The stoppers should be rested lightly in the mouths of the tubes to prevent excessive loss of volume by evaporation
A7.6	Cool the contents of the tube rapidly by placing the tubes in an ice-water bath for a minimum time of 3 minutes	
A7.7	Transfer a portion of each of the coloured solutions in turn to a 20 mm cell (note c) and measure the absorbance of the solution against the 'blank' solution contained in the second cell using the spectrophotometer at a wavelength of 430 mm (note c)	(c) Rinse the 20 mm cell at least once with the solution under test and refer to manufacturers instructions for use of the spectrophotometer
A7.8	Prepare a calibration curve by plotting the absorbance values against concentration of the formaldehyde standard solutions (note a)	
	Analysis of Samples	
A7.9	Add 25.0 ± 0.1 ml of sample into a calibrated tube (note d)	(d) A smaller volume may be used if the concentration of formaldehyde is expected to exceed 2.0 mg/l, but the volume must be made up to 25 ml before proceeding with step A7.10.
A7.10	Add 25.0 ± 0.1 ml of acetylacetone reagent to the tube and mix	
A7.11	Follow steps A7.5 to A7.7 inclusive	

Step	Analytical Procedure	Notes
	Calculation of Results	
A7.12	Using the calibration curve, convert the absorbance of the sample solution into concentration of free formaldehyde in the solution ('C' mg/l). The concentration of free formaldehyde in the original sample (Z mg/l) is then obtained by the equation, $Z = \frac{C \times 50}{y}$ where y = the sample volume taken (normally 25 ml), (note e)	(e) The results are expressed as mg HCHO/litre
	Correction for hexamine concentration	
A7.13	Add 25 ± 0.1 ml of a 10 mg hexamine/l standard solution (A5.11) to a calibrated tube	
A7.14	Follow steps A7.3 to A7.7 inclusive	
A7.15	Convert any absorbance of the solution into apparent concentration of free formaldehyde using the calibration curve obtained at step A7.8. The value of 'x' (note f) is then calculated.	(f) $F = \frac{F_f - xF_t}{1 - x}$ (see Section A3 of this method)
	Obtaining the true free formaldehyde concentration	
A7.16	A total formaldehyde determination on the sample is carried out using method B of this booklet and the true free formaldehyde concentration in the sample is obtained, by relating the concentration values of formaldehyde given at steps A7.12, A7.15 and here, in the equation $F = \frac{F_f - xF_t}{1 - x}$ (see Section A3 of this method)	

B. A Manual Method for the Determination of Total Formaldehyde using Spectrophotometry

B1. Performance Characteristics of the Method*

B1.1	Substance determined	Total formaldehyde ie. free formaldehyde and combined forms of formaldehyde which includes hexamine
B1.2	Type of sample	Raw, waste and potable waters
B1.3	Basis of method	Formaldehyde in a combined state (eg. hexamine) is converted to free formaldehyde when distilled under acidic conditions. The total free formaldehyde in solution reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound diacetyldihydrolutidine whose concentration is measured spectrophotometrically.
B1.4	Range of application	Up to 10 mg total formaldehyde/l (≡ 7.75 mg hexamine/l)
B1.5	Calibration curve	Linear up to 5 mg/l
B1.6	Standard deviation (within batch) (5 degrees of freedom)	

	Formaldehyde concentration (mg/l)	Standard deviation (mg/l)
Standards	1.0	0.01
	10.0	0.50
Samples		
Sewage effluent	3.9	0.33
Trade waste	8.5	0.47

B1.7	Limit of detection (5 degrees of freedom)	0.9 mg/l
B1.8	Bias	Less than 10% as indicated by recovery data from 'spiked' samples (see Table 2)
B1.9	Interferences	See Section B3
B1.10	Sensitivity	A 10.0 mg formaldehyde/l standard solution gives an absorbance change of approximately 0.23 absorbance units using a 20 mm flow-cell
B1.11	Time required for analysis	4 samples per hour all of which is operator time

*The information given in the above table was produced by the Anglian Water Authority.

Table 2. **Recovery of total formaldehyde from 'spiked' samples (single determinations)**

Sample	Initial concentration as total formaldehyde (mg/l)	Concentration of total formaldehyde added (mg/l)	Concentration as total formaldehyde found (mg/l)	% recovery of added total formaldehyde
Sewage effluent	3.9	1.0	4.9	100
Trade effluent	8.5	1.0	9.4	90

B2. Principle

The method is based on the work of Nash([1]). Formaldehyde reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, 3,5-diacetyl-1,4-dihydrolutidine, the concentration of which is measured spectrophotometrically at a wavelength of 430 nm. Combined forms of formaldehyde are released into solution under acidic conditions and then reacted with acetylacetone as above.

B3. Interferences

At the concentration levels of formaldehyde examined by the method a solution containing 100 mg/l of any one of the following appears not to interfere:

acetone, methanol, formic acid, chloroform, phenol, nitrate, nitrite, ammonia, chloride, sulphate, potassium hydrogen phthalate, Di-n-butyl phthalate, benzaldehyde, acetaldehyde, chloral, glucose, and ninhydrin.

If the method is used to determine the concentration of formaldehyde in a combined state (eg. hexamine), any free formaldehyde present in the sample is considered as an interferent. Therefore, the concentration of free formaldehyde should be determined using method A and the concentration of formaldehyde in a combined state calculated as follows:

$$F_c = F_t - F_f$$

where F_c = the concentration of formaldehyde in a combined state
F_t = the concentration of total formaldehyde obtained by this method
F_f = the concentration of free formaldehyde obtained by method A.

B4. Hazards

Sulphuric acid, sodium hydroxide, acetylacetone and acetic acid are corrosive. Eye protection and gloves should be worn when handling chemicals, any any spillages should be washed away with copious quantities of water.

B5. Reagents and Standards

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

B5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have a formaldehyde content which is negligible compared with the smallest concentration of formaldehyde to be determined in the samples. Distilled or deionized water will usually be suitable.

B5.2 0.5M Sulphuric acid solution

Cautiously add with stirring 27 ± 0.5 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water. Cool, make up to 1 litre with water in a calibrated flask and mix. Store in a glass stoppered bottle. This solution is stable for at least 3 months.

Standardize this acid solution against the 1.0M sodium hydroxide solution (Section B5.4).

B5.3 4.5M Sulphuric acid solution

Cautiously add with stirring 243 ml ± 5 ml of sulphuric acid (d_{20} 1.84) to about 700 ml of water. Cool, make up to 1 litre with water in a calibrated flask and mix. This reagent is stable for at least 3 months.

B5.4 1.0M Sodium hydroxide solution

Dissolve 40 ± 0.5 g of sodium hydroxide pellets in about 600 ml of water. Cool, make up to 1 litre with water in a calibrated flask and mix. Store in a polyethylene stoppered bottle. This solution is stable for at least 1 month providing it is protected against attack by atmospheric carbon dioxide.

Standardize this alkali solution against a primary standard eg. potassium hydrogen phthalate, sulphamic acid.

B5.5 Sodium sulphite solution

Dissolve 125 ± 1 g of anhydrous sodium sulphite in about 600 ml of water and make up to 1.0 ± 0.01 litre with water. Store in a glass stoppered bottle. This solution is prepared fresh as required.

B5.6 Thymolphthalein indicator solution

Dissolve 1.0 ± 0.02 g of thymolphthalein in 1.0 ± 0.01 litre of ethanol. Store in a glass stoppered bottle. This solution is stable indefinitely subject to evaporation losses of the ethanol.

B5.7 Acetylacetone solution

Dissolve 150 ± 1 g of ammonium acetate in about 800 ml of water, add 3.0 ± 0.1 ml of glacial acetic acid and 2.0 ± 0.1 ml of acetylacetone with stirring, make up to 1 litre with water in a calibrated flask and mix. This solution is stable for at least one week when stored in an amber-coloured glass stoppered bottle in a refrigerator between 1° and 5°C.

B5.8 Formaldehyde stock standard solution, 1 ml ≙ 20 mg formaldehyde

Weight 6.0 ± 0.1 g of formaldehyde solution (40 per cent w/v) and quantitatively transfer to a 100 ml calibrated flask. Add 10 ± 0.1 ml of 0.5M sulphuric acid solution. After 10 ± 0.1 minutes add 10 ± 0.1 ml of 1M sodium hydroxide solution and dilute to the calibration mark with water. Standardize this stock solution by transferring 25 ± 0.1 ml into a flask and neutralizing to thymolphthalein indicator. Transfer 25 ± 0.1 ml of sodium sulphite solution into a second flask and neutralise to thymolphthalein indicator. Quantitatively add the neutral sodium sulphite solution to the neutral formaldehyde solution and titrate with 0.5M sulphuric acid solution.

1 ml of 0.5M sulphuric acid = 30.03 mg of formaldehyde.

B5.9 Formaldehyde intermediate standard solution, 1 ml ≙ 0.2 mg formaldehyde

Note: It is more convenient to make set dilutions of the standardized stock solution and plot the calibration curve to suit eg. if the stock solution was 20,200 mg/l, the intermediate solution will be 202 mg/l.

Dilute 5.0 ± 0.01 ml of the Intermediate Standard (B 5.9) to 100 ml with water in a calibrated flask and mix. This solution should be prepared fresh on the day of use.

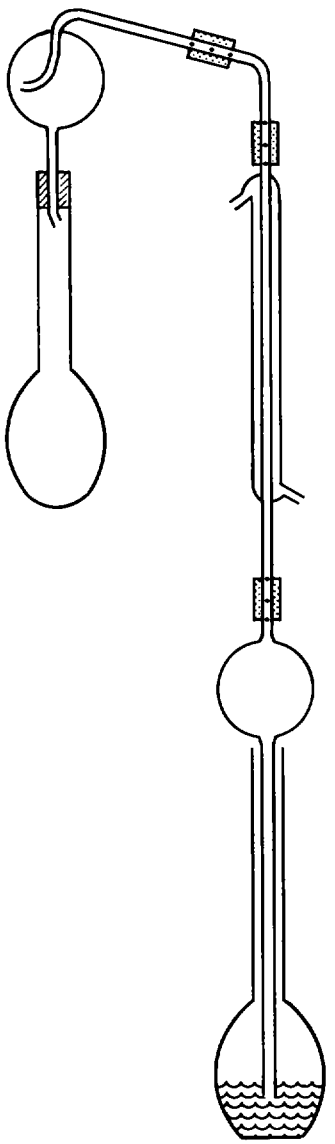
B5.10 Formaldehyde working standard solution, 1 ml ≙ 0.01 mg formaldehyde

Dilute 5.0 ± 0.01 ml of the Intermediate Standard (B5.9) to 100 ml with water in a calibrated flask and mix. This solution should be prepared fresh on the day of use.

B6. Apparatus

50 ml calibrated glass tubes with stoppers
Two matched 20 mm cells
A spectrophotometer or colorimeter for use at a wavelength of 430 nm
A water bath at 60°C ± 2°C
An ice-water bath
Glass distillation apparatus consisting of the following which is set up as shown in Figure 2
Kjeldahl flask (minimum capacity 100 ml)
Liebig condenser
Safety delivery tube
Calibrated flask 250 ml
Antibumping granules
A controlled electric heating mantel, (a small bunsen flame may be used, but is less desirable)
It is convenient to use a bank of six distillation units with the condensers connected in series.

Figure 2 DISTILLATION APPARATUS



Long neck
(a volumetric flask may be used)

B7. Analytical Procedure

Read Section B4 on hazards before starting this procedure

Step	Analytical Procedure	Notes
	Starting Operation	
B7.1	Switch on water bath	
	Calibration	
B7.2	Add 10.0, 20.0, 30.0, 40.0 and 50.0 ± 0.1 ml aliquots of the working standard (5.10) into each of five Kjeldahl flasks and make up to 50 ml with water where necessary (Note a).	(a) Equivalent to 2.0, 4.0, 6.0, 8.0 and 10.0 mg/l formaldehyde, provided that the working standard is 1 ml = 0.01 mg
B7.3	Add 50 ml of water to another Kjeldahl flask to act as a 'blank' solution.	
B7.4	Add 10.0 ± 0.1 ml 4.5M sulphuric acid (B5.3) to each flask, 0.3 g anti bumping granules, and mix.	
B7.5	Connect the flasks to the distillation units. See Figure 2.	
B7.6	Add 50 ml of water to a 250 ml calibrated receiving flask (Note b)	(b) The distal end of the safety delivery tubes should be positioned just below the surface of this water
B7.7	Distil approximately 40 ml of the solution(s) over a gentle heat until the appearance of white fumes of sulphuric acid (Note c).	(c) 15–20 minutes dependent on degree of heat
B7.8	Switch off heat	
B7.9	Withdraw the receiving flask from the delivery tube	
B7.10	Make each receiving flask up to the 250 ml mark with water and mix well (Note d)	(d) These solutions now contain 0.4, 0.8, 1.2, 1.6 and 2.0 mg of formaldehyde/l
B7.11	Add 25 ± 0.1 ml of the diluted distillates (B7.10) to 5 calibrated tubes	
B7.12	Add 25 ± 0.1 ml of acetylacetone reagent to each tube and to a 'blank' tube containing 25 ± 0.1 ml of water and mix well (note e)	(e) These solutions now contain 0.2, 0.4, 0.6, 0.8 and 0.1 mg of formaldehyde/l
B7.13	Place the tubes in the water bath at 60 ± 2°C for 10± 1 min (Note f)	(f) The stoppers should be rested lightly in the mouths of the tubes to prevent excessive loss of volume by evaporation
B7.14	Cool the contents of the tubes rapidly by placing the tubes in an ice-water bath for a minimum time of 3 min.	
B7.15	Transfer a portion of each of the coloured solutions in turn to a 20 mm cell and measure the absorbance of the solution against the 'blank' solution contained in the second cell using the spectrophotometer at a wavelength of 430 nm (note g)	(g) Rinse the 20 mm cell at least once with the solution under test and refer to manufacturers instructions for use of the spectrophotometer
B7.16	Prepare a calibration curve by plotting the absorbance values against concentration of the formaldehyde standard solutions	

Step	Analytical Procedure	Notes
	Analysis of samples	
B7.17	Add 50 ± 0.1 ml of sample into a Kjeldahl flask (note h)	(h) A smaller volume may be used if the concentration of formaldehyde is expected to exceed 10 mg/1, but the volume should be made up to 50 ml with water before proceeding to step B7.18.
B7.18	Follow steps B7.4 to B7.15 inclusive	
	Calculation of Results	
B7.19	Using the calibration curve (B7.16) convert the absorbance of the sample solution into concentration of total formaldehyde in the solution ('C' mg/l)	
	The concentration of total formaldehyde in the original sample (Z mg/l) is then obtained by the equation $Z = \frac{C \times 500}{y}$ mg/l	
	Where y = the sample volume taken (normally 50 ml) (note i)	(i) the results are expressed as mg HCHO/litre

C. A Method for the Determination of Free Formaldehyde using Air Segmented Continuous Flow Spectrophotometry

C1. Performance Characteristics of Method*

C1.1	Substance determined	Free formaldehyde		
C1.2	Type of sample	Raw, waste and potable waters		
C1.3	Basis of method	Free formaldehyde reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, diacetyldihydrolutidine, whose concentration is measured spectrophotometrically		
C1.4	Range of application	Up to 25.0 mg/l		
C1.5	Calibration curve	Linear		
C1.6	Standard deviation (within batch) (9 degrees of freedom)		Formaldehyde concentration (mg/l)	Standard deviation (mg/l)
		Standards		
			1.0	0.03
			25.0	0.21
		Samples		
		Sewage	19.2	0.24
		Sewage effluent	4.3	0.07
C1.7	Limit of detection† (9 degrees of freedom)	0.15 to 0.3 mg/l		
C1.8	Bias	Less than 10% as indicated by recovery data from 'spiked' samples (see Table 3)		
C1.9	Interferences	See Section C3		
C1.10	Sensitivity	A 25.0 mg formaldehyde/l standard solution gives an absorbance change of approximately 0.7 absorbance units using a 15 mm flowcell		
C1.11	Time required for analysis	Sampling rate 30 h^{-1}; response time 16 min. Operator time approx 1 h for 30 samples		

*The information given in the above table was produced by the Water Research Centre Stevenage Laboratory).

†The instrument baseline was too steady to estimate a limit of detection from the analysis of blanks. The figures in the table are derived from:

i) The minimum discrimination interval of the recorder trace (1.0% of full scale deflection, 100% = 25 mg/l).

ii) The variability of the low standard or sample.

These figures may be upper estimates.

Table 3. Recovery of free formaldehyde from 'spiked' samples (single determinations)

Sample	Initial concentration of free formaldehyde (mg/l)	Concentration of free formaldehyde added (mg/l)	Concentration of free formaldehyde found (mg/l)	% recovery of added formaldehyde
Sewage	9.0	5.0	13.7	94
Sewage effluent	0.8	10.0	10.3	100

C2. Principle

The method is based on the work of Nash[1], which has been automated by Musselwhite and Petts[2]. Formaldehyde reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, 3,5-diacetyl-1,4-dihydrolutidine, the concentration of which is measured spectrophotometrically at a wavelength of 430 nm.

C3. Interferences

Owing to the mild conditions employed not many substances interfere, especially if the reaction period is kept to the minimum necessary for say 99 per cent completion.

At the concentration levels of formaldehyde examined by the method, a solution containing 100 mg/l of any one of the following appears not to interfere:

acetone, methanol, formic acid, chloroform, phenol, nitrate, nitrite, ammonia, chloride, sulphate, potassium hydrogen phthalate, Di-n-butyl phthalate, benzaldehyde, acetaldehyde.

Chloral, fural, glucose and ninhydrin do not interfere with the manual technique (method A). It is assumed that they will not interfere with the automated procedure.

Turbidity and colour are removed from the sample at the dialysis stage. Oxidizing agents, reducing agents, and soluble metals (which could produce metal acetylacetonates) may interfere.

Hexamine in a concentration of 100 mg/l gives a response equivalent to 8.5 mg/l formaldehyde. It may be removed by preliminary extraction with chloroform[3] but if significant quantities are present it is preferable to correct for its interference by using the concentration of formaldehyde determined by both this method and by the automated total formaldehyde procedure (method D) in the following formula:

$$F = (F_f - 0.0659\ F_t) \times 1.07$$

where F = true free formaldehyde value
F_f = observed free formaldehyde value obtained by this method
F_t = observed total formaldehyde value obtained by method D

C4. Hazards

The precautions given in the essay review on continuous flow analysis[4] should be observed.

Sulphuric acid, sodium hydroxide, acetylacetone and acetic acid are corrosive. Eye protection and gloves should be worn when handling chemicals, and any spillage should be washed away with copious quantities of water.

C5. Reagents and Standards

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

C5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have a formaldehyde content which is negligible compared with the smallest concentration of formaldehyde to be determined in the samples. Distilled or deionized water will usually be suitable and a proprietary non-ionic wetting agent, 1 ml per litre of water, may be added to improve the flow characteristics of the liquid streams through the tubing of the system.

C5.2 0.5M Sulphuric acid solution

Cautiously add with stirring 27 ± 0.5 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water. Cool, make up to 1-litre with water in a calibrated flask and mix. Store in a glass stoppered bottle. This solution is stable for at least 3 months.

Standardize this acid solution against the 1.0M sodium hydroxide solution (Section C5.3).

C5.3 1.0M Sodium hydroxide solution

Dissolve 40 ± 0.5 g of sodium hydroxide pellets in about 600 ml of water. Cool, make up to 1-litre with water in a calibrated flask and mix. Store in a polyethylene stoppered bottle. This solution is stable for at least 1 month providing it is protected against attack by atmospheric carbon dioxide.

Standardize this alkali solution against a primary standard eg. potassium hydrogen phthalate, sulphamic acid.

C5.4 Sodium sulphite solution

Dissolve 125 ± 1 g of anhydrous sodium sulphite in about 600 ml of water and make up to 1.0 ± 0.01 litre with water. Store in a glass stoppered bottle. This solution is prepared fresh as required.

C5.5 Thymolphthalein indicator solution

Dissolve 1.0 ± 0.02 g thymolphthalein in 1.0 ± 0.01 litre of ethanol. Store in a glass stoppered bottle. This solution is stable indefinitely subject to evaporation losses of the ethanol.

C5.6 Acetylacetone solution

Dissolve 150 ± 1 g of ammonium acetate in about 800 ml of water, add 3.0 ± 0.1 ml of glacial acetic acid and 2.0 ± 0.1 ml of acetylacetone with stirring, make up to 1 litre with water in a calibrated flask and mix. This solution is stable for at least one week when stored in an amber-coloured glass stoppered bottle in a refrigerator between 1° and 5°C.

C5.7 Formaldehyde stock standard solution, 1 ml ≙ 20 mg formaldehyde

Weigh 6.0 ± 0.1 g of formaldehyde solution (40 per cent w/v) and transfer to a 100 ml calibrated flask. Add 10 ± 0.1 ml of 0.5M sulphuric acid solution. After 10 ± 0.1 min, add 10 ± 0.1 ml of 1M sodium hydroxide solution and dilute to the calibration mark with water. Standardize this stock solution by transferring 25 ± 0.1 ml into a flask and neutralizing to thymolphthalein indicator. Transfer 25 ± 0.1 ml of sodium sulphite solution into a second flask and neutralize to thymolphthalein indicator. Quantitatively add the neutral sodium sulphite solution to the neutral formaldehyde solution and titrate with 0.5M sulphuric acid solution.

1 ml of 0.5M sulphuric acid = 30.03 mg of formaldehyde, therefore the titration (t) will be approximately 20 ml.

1 ml of stock standard formaldehyde contains 30.03 t/25 mg formaldehyde.

C5.8 Formaldehyde working standard solution, 1 ml = 0.1 mg formaldehyde

Use a 5 ml pipette graduated in 0.05 ml units to transfer x ml of the stock standard formaldehyde solution (C5.7) containing 100 ± 1 mg formaldehyde to a l-litre calibrated flask. Make up to the mark with water and mix. Where x is given by:

$$x = \frac{100}{1.2012\ t}$$

1 ml of this working solution, which is stable for at least one month, contains 0.1 mg formaldehyde.

C5.9 Formaldehyde calibration standard solutions

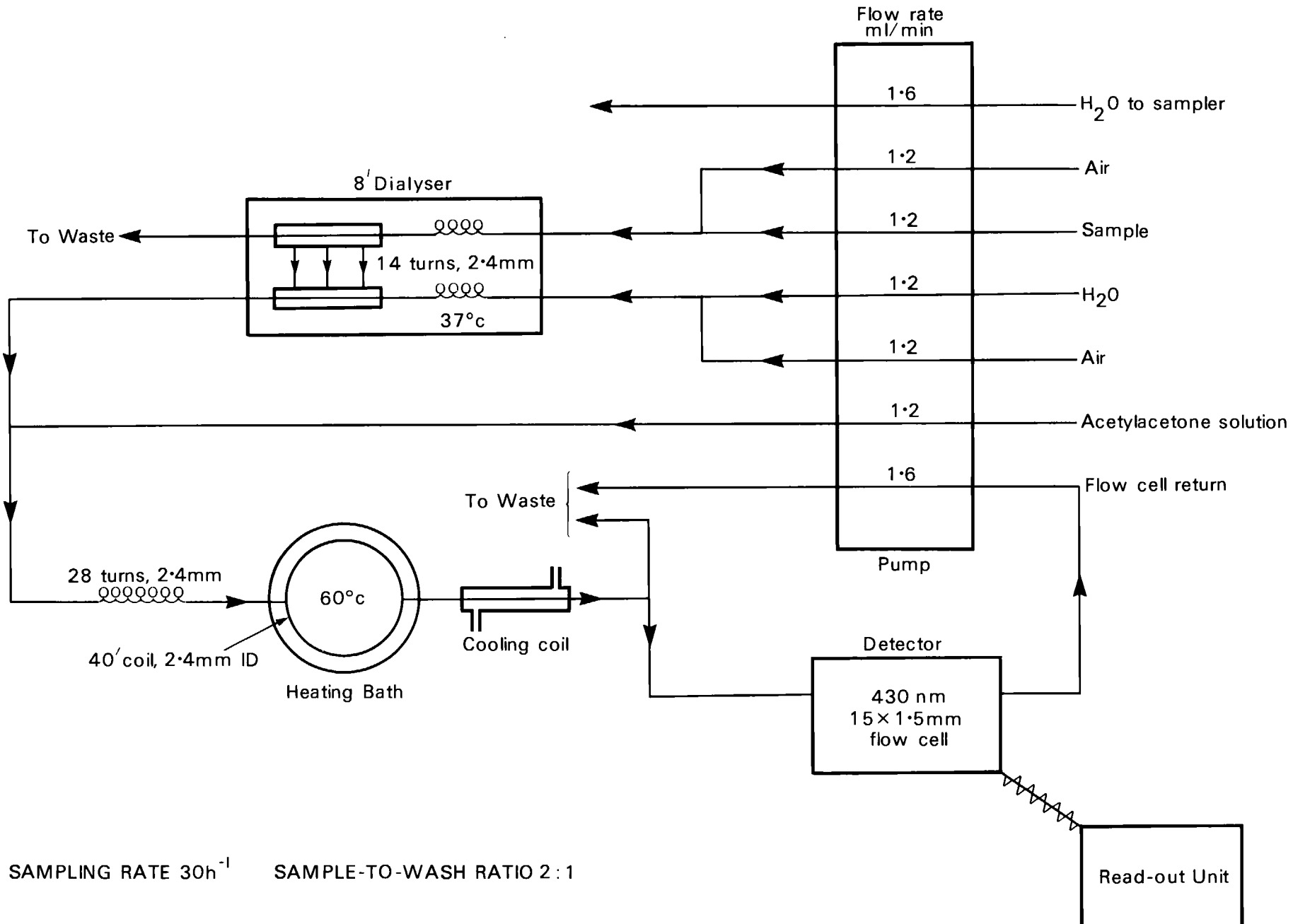
Prepare a series of standard solutions containing 2, 5, 10, 15, 20 and 25 mg formaldehyde/litre by adding 2.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml respectively of the working solution (5.8) to 100 ml calibrated flasks, making up to the mark with water and mixing well. These solutions are prepared fresh daily.

C6. Apparatus

The following apparatus, which is set up in figure 3 is required:

Sample presentation unit (sampler)
Multi-channel peristaltic pump (air inlet valve optional)
Analytical cartridge incorporating pump tubes, mixing coils and dialyser unit
Heating bath at 60 ± 2°C
Detector (colorimeter or spectrophotometer) which houses a flow-through cell
Read-out (measurement) unit (recorder or printer)

Figure 3 FLOW DIAGRAM



SAMPLING RATE $30h^{-1}$ SAMPLE-TO-WASH RATIO 2 : 1

C7. Analytical Procedure

Read Section 4 on hazards before starting this procedure

Step	Analytical Procedure	Notes
	Starting Operation	
C7.1	Connect the system as shown in the flow diagram (See fig. 3) (Notes a and b)	(a) Follow the manufacturers general operating instructions. (b) See Reference 4
C7.2	With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents. Start pump and switch on detection and measurement (read-out) units (Note c)	(c) Allow the system to equilibrate for at least 20 min and during this period check that the bubble pattern and hydraulic behaviour of the system are satisfactory. If not, eliminate difficulties before proceeding to Step C7.3
	Initial Sensitivity Setting	
C7.3	When an acceptably smooth baseline trace is given on the measurement unit, transfer the sample probe into a C_M standard solution (Note d) and adjust the baseline response to about 5 per cent of full scale (Note e)	(d) C_M is the greatest concentration that the calibration is intended to cover (e) An elevated setting of the baseline allows for any negative drift that may occur
C7.4	When there is a positive stable response at the measurement unit due to the colour produced from the C_M standard solution (Note f), adjust this response to read approximately 90 per cent of full scale (Note g).	(f) The sample probe need remain only in the C_M standard solution for sufficient time to give a stable reading. The response time is approximately 16 min (g) This may be directly possible on some units but others may require range expansion facilities
C7.5	Return the sample probe to rest in the wash receptacle solution (Note h)	(h) First remove any traces of standard solution from the outside of the sample probe
	Analysis of Samples	
C7.6	Load the sample turntable in the following order (Notes i and j) and start the sampler	(i) The turntable can be loaded during the initial stabilization period (Steps C7.2 to C7.4) (j) The order given is in current use. Alternative arrangements of solutions on the turntable are discussed in Reference 4

Position No. on turntable	Solution	
1–6	Calibration standards in ascending order of concentration	
7–8	Blank (Note k)	(k) Water from the same source as that used to prepare the calibration standards
9–18	Samples (Note l)	(l) A quality control standard should occupy one of the sample positions as a check of the system (see main Section 3 on checking the accuracy of analytical results)
19	Calibration standard (Note m)	(m) A 20 mg/l standard is used to check the calibration
20–21	Blank (Note k)	
22–31	Samples (Note l)	
32	Calibration standard (Note m)	
33–34	Blank (Note k)	

Repeat the sequence 9–34 until all samples have been processed (Notes n and o)

(n) If cross-contamination (sample interaction) occurs between two samples (visible on the measurement unit trace as incomplete separation of consecutive sample responses), both samples are re-analysed in reverse order and if necessary separated by a blank solution

(o) The complete calibration may be checked at the end if considered necessary

Step	Analytical Procedure	Notes
C7.7	When a steady baseline is obtained on the measurement unit (after step C7.5), re-adjust it to 5 per cent of full scale if necessary	
C7.8	When all the system responses due to the processed solutions have appeared on the measurement unit and a final baseline has been obtained, this unit can be switched off	
	Calculation of Results	
C7.9	Plot a calibration curve of measurement unit responses (y axis) against concentration of standard (x axis) (Note p)	(p) Providing the blank corrected responses of the calibration standard analysed at the end of each group of samples and those analysed at the end of the analytical run (if used) are all acceptably close to their respective initial calibration standard response. If not, refer to essay review (Reference 4) for suggested procedures to obtain the calibration curve
C7.10	Using the calibration curve convert the measurement unit responses due to the samples into concentration of free formaldehyde in the samples (Note q)	(q) The measurement unit responses of the samples are first corrected for any baseline and sensitivity changes The results are expressed as mg HCHO/litre
	Shut-down Procedure	
C7.11	Transfer the reagent line to water and continue pumping for 20 min. Switch off pump, detection and measurement units	

C8. Extension of the Concentration Range of the Method

Samples whose concentration of free formaldehyde is greater than the highest concentration that the calibration is intended to cover may be diluted accordingly prior to analysis without serious effect to the accuracy of the result. The dilution factor must be taken into account when calculating results.

D. Methods for The Determination of Total Formaldehyde using Air Segmented Continuous Flow Spectrophotometry

D1. Performance Characteristics of Method*

D1.1	Substance determined	Total formaldehyde (ie. free and combined forms of formaldehyde which includes hexamine)
D1.2	Types of sample	Raw, waste and potable waters
D1.3	Basis of method	Formaldehyde is a combined state (eg. hexamine)† is converted to free formaldehyde either by (a) direct hydrolysis or by (b) distillation under acidic conditions. The total free formaldehyde in solution reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, diacetyldihydrolutidine, whose concentration is measured spectrophotometrically
D1.4	Range of application	(a) Direct hydrolysis method; up to 25.0 mg formaldehyde/l (b) Distillation method; up to 5.0 mg hexamine/l (see Section D8.2.2.)
D1.5	Calibration curves	Linear

D1.6 Standard deviation (within batch) (9 degrees of freedom)

(a)

	Formaldehyde concentration (mg/l)	Standard deviation (mg/l)
Standards	5.0	0.21
	20.0	0.29
Samples		
Sewage effluent	5.3	0.07
Sewage	17.2	0.45

(b)

	Hexamine concentration (mg/l)	
Standards	0.5	0.02
	4.5	0.03
Samples		
River water	0.51	0.01
Sewage effluent	4.2	0.07

D1.7	Limit of detection** (9 degrees of freedom)	(a) 0.3 to 1.0 mg/l (b) 0.05 to 0.1 mg/l
D1.8	Bias	See Section D3
D1.9	Interferences	See Section D4

D1.10 Sensitivity	(a) A 25.0 mg formaldehyde/l standard gives an absorbance change of approximately 0.7 absorbance units using a 15 mm flowcell
	(b) A 5.0 mg hexamine/l standard gives an absorbance change of approximately 0.41 absorbance units using a 15 mm flowcell
D1.11 Time required for analysis	(a) Sampling rate 30 h^{-1}; response time 25 min
	(b) Sampling rate 30 h^{-1}; response time 16 min
	Operator time associated with both (a) and (b); approximately 1 h for 30 samples

*The information given in the above table was produced by the Anglian Water Authority (distillation procedure) and the Water Research Centre, Stevenage Laboratory (direct hydrolysis procedure).

†See Section D3

**The instrument baseline was too steady to estimate limits of detection from the analysis of blanks. The figures in the table are derived from:—

(i) The minimum discrimation interval of the recorder trace (1.0% of full scale deflection, 100% = 25 mg formaldehyde/l or 5 mg hexamine/l).

(ii) The variability of the low level samples or standards.

These figures may represent upper estimates.

D2. Principle

The method is based on the work of Nash([1]) which has been automated by Musselwhite and Petts([2]). Formaldehyde in a combined state is converted to free formaldehyde either by (a) direct hydrolysis or by (b) distillation under acidic conditions. The total free formaldehyde in solution reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, 3,5-diacetyl-l,4-dihydrolutidine, the concentration of which is measured spectrophotometrically at a wavelength of 430 nm.

D3. Bias

D3.1 Direct hydrolysis method (a) — not known

No recovery experiments were carried out as no suitable standards could be found to cover all the forms of formaldehyde which might be present in water. Recoveries of hexamine have been recorded as quantitative.

D3.2 Distillation method (b)

This method has lower detection limits than direct hydrolysis and has been written in the form in which it has been used in practice ie. for the determination of hexamine in water in the absence of detectable quantities of other forms of formaldehyde. When used in this manner using hexamine as the calibration standard the recoveries of hexamine given in table 4 were obtained (see section D8.2.2).

Table 4. Recovery of hexamine from 'Spiked' samples using distillation procedure (single determinations)

	Initial concentration as hexamine (mg/l)	Concentration of hexamine added (mg/l)	Concentration found as hexamine (mg/l)	% recovery of added hexamine
Sewage effluent	2.2	1.0	3.2	100
River water	0.6	1.0	1.6	100

It has been recorded that the conversion of hexamine to formaldehyde by distillation is 64%. These results have not been verified but could obviously lead to positive biases should free formaldehyde or forms of formaldehyde giving a higher yield of formaldehyde than hexamine be present. Negative biases would result if there were forms of formaldehyde present which gave lower yields of formaldehyde than hexamine.

D4. Interferences

At the concentration levels of formaldehyde examined by the method, a solution containing 100 mg/l of any one of the following appears not to interfere:

acetone, methanol, formic acid, chloroform, nitrate, nitrite, ammonia, chloride, sulphate, potassium hydrogen phthalate, Di-n-butyl phthalate, bezaldehyde, acetaldehyde.

Chloral, fural, glucose and ninhydrin do not interfere with the manual technique. It is assumed that they will not interfere with the automated procedure.

Turbidity and colour are removed from the sample by dialysis in the direct hydrolysis procedure. The distillation stage of the alternative procedure removes turbidity, but colour may distill over.

Oxidizing agents, reducing agents, and soluble metals (which could produce metal acetylacetonates) may interfere.

Phenol has been reported as showing a positive response (100 mg phenol/l gave a response equivalent to 0.58 mg formaldehyde/l) and although ethylene glycol has been shown not to be an interferent, diethylene glycol (100 mg diethylene glycol/l gave a response equivalent to 0.27 mg formaldehyde/l).

If the method is used to determine the concentration of formaldehyde in a combined state, the free formaldehyde which is originally present in the sample is considered as an interferent. Therefore, the concentration of free formaldehyde should be determined using method C and the concentration of formaldehyde in a combined state calculated as follows:

$$F_c = F_t - F_f$$

where F_c = the concentration of formaldehyde in a combined state
F_t = the concentration of total formaldehyde obtained by this method
F_f = the concentration of free formaldehyde obtained by method C.

D5. Hazards

The precautions given in the essay review on continuous flow analysis[4] should be observed.

Sulphuric acid, sodium hydroxide, acetylacetone and acetic acid are corrosive. Eye protection and gloves should be worn when handling chemicals, and any spillages should be washed away with copious quantities of water.

D6. Reagents and Standards

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

D6.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have a total formaldehyde content which is negligible compared with the smallest concentration of total formaldehyde to be determined in the samples. Distilled or deionized water will usually be suitable and a proprietary non-ionic wetting agent, 1.0 ± 0.1 ml per litre of water, may be added to improve the flow characteristics of the liquid streams through the tubing of the system.

D6.2 0.5M Sulphuric acid solution

Cautiously add with stirring 27 ± 0.5 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water. Cool, make up to 1-litre with water in a calibrated flask and mix. Store in a glass stoppered bottle. This solution is stable for at least 3 months.

Standardize this acid solution against the 1.0M sodium hydroxide solution (Section D6.5).

D6.3 0.9M Sulphuric acid solution (for distillation procedure)

Cautiously add with stirring 48 ± 1 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water. Cool, make up to 1-litre with water in a calibrated flask and mix. Store in a glass stopperd bottle. This solution is stable for at least 3 months.

Standardize this acid solution against the 1.0M sodium hydroxide solution (Section D6.5).

D6.4 3.15M Sulphuric acid solution (for direct hydrolysis procedure)

Cautiously add with stirring 170 ± 2 ml of sulphuric acid (d_{20} 1.84) to about 800 ml of water. Cool, make up to 1-litre with water in a calibrated flask and mix. Store in a glass stoppered bottle. This solution is stable for at least 3 months.

Standardize this acid solution against a standard sodium hydroxide solution.

D6.5 1.0M Sodium hydroxide solution

Dissolve 40 ± 0.5 g of sodium hydroxide pellets in about 600 ml of water. Cool, make up to 1-litre with water in a calibrated flask and mix. Store in a polyethylene stoppered bottle. This solution is stable for at least 1 month providing it is protected against attack by atmospheric carbon dioxide.

Standardize this alkali solution against a primary standard eg. potassium hydrogen phthalate or sulphamic acid.

D6.6 6.3M Sodium hydroxide solution

Dissolve 252 ± 2 g of sodium hydroxide pellets in about 600 ml of water. Cool, make up to 1-litre with water in a calibrated flask and mix. Store in a polyethylene stoppered bottle. This solution is stable for at least 1 month providing it is protected against attack by atmospheric carbon dioxide.

Standardize this alkali solution against a primary standard eg. potassium hydrogen phthalate or sulphamic acid.

D6.7 Sodium sulphite solution

Dissolve 125 ± 1 g of anhydrous sodium sulphite in about 600 ml of water and make up to 1.0 ± 0.01 litre with water. Store in a glass stoppered bottle. This solution is prepared fresh as required.

D6.8 Thymolphthalein indicator solution

Dissolve 1.0 ± 0.02 g thymolphthalein in 1.0 ± 0.01 litre of ethanol. Store in a glass stoppered bottle. This solution is stable indefinitely subject to evaporation losses of the ethanol.

D6.9 Acetylacetone solution

Dissolve 150 ± 1 g of ammonium acetate in about 800 ml of water, add 3.0 ± 0.1 ml of glacial acetic acid and 2.0 ± 0.1 ml of acetylacetone with stirring, make up to 1-litre with water in a calibrated flask and mix. This solution is stable for at least one week when stored in an amber-coloured glass stoppered bottle in a refrigerator between 1° and 5°C.

D6.10 Formaldehyde stock standard solution, 1 ml ≙ 20 mg formaldehyde

Weigh 6.0 ± 0.1 g of formaldehyde solution (40 per cent w/v) and quantitatively transfer to a 100 ml calibrated flask. Add 10 ± 0.1 ml of 0.5M sulphuric acid solution. After 10 ± 0.1 min, add 10 ± 0.1 ml of 1M sodium hydroxide solution and dilute to the calibration mark with water. Standardize this stock solution by transferring 25 ± 0.5 ml into a flask and neutralizing to thymolphthalein indicator. Transfer 25 ± 0.5 ml of sodium sulphite solution into a second flask and neutralize to thymolphthalein indicator. Quantitatively add the neutral sodium sulphite solution to the neutral formaldehyde solution and titrate with 0.5M sulphuric acid solution.

1 ml of 0.5M sulphuric acid = 30.03 mg formaldehyde, therefore the titration (t) will be approximately 20 ml.

1 ml of stock standard formaldehyde contains 30.03 t/25 mg formaldehyde.

D6.11 Formaldehyde working standard solution, 1 ml = 0.1 mg formaldehyde

Use a 5 ml pipette graduated in 0.05 ml units to transfer x ml of the stock standard formaldehyde solution (D5.10) containing 100 ± 1 mg formaldehyde to a 1-litre calibrated flask. Make up to the mark with water and mix. Where x is given by:

$$x = \frac{100}{1.2012\ t}$$

1 ml of this working solution, which is stable for at least one month, contains 0.1 mg formaldehyde.

D6.12 Calibration standard solutions

Prepare a series of standard solutions containing 1, 2, 3, 4, 5, 10, 15, 20 and 25 mg formaldehyde/l by adding 1.0, 2.0, 3.0, 4.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml respectively of the working solution (D6.11) to 100 ml calibrated flasks, making up to the mark with water and mixing well. These solutions are prepared fresh daily.

D7. Apparatus

The following apparatus, which is set up as shown in figures 4–6 or 7 is required

Sample presentation unit (sampler)
Multi-channel peristaltic pump (air inlet valve optional)
Analytical cartridge, incorporating pump tubes, mixing coils and dialyser unit
Heating baths at 60 ± 2°C and 150 ± 2°C.
Distillation coil and condenser unit
Detector (colorimeter or spectrophotometer) which houses a flow-through cell
Read-out (measurement) unit (recorder or printer)

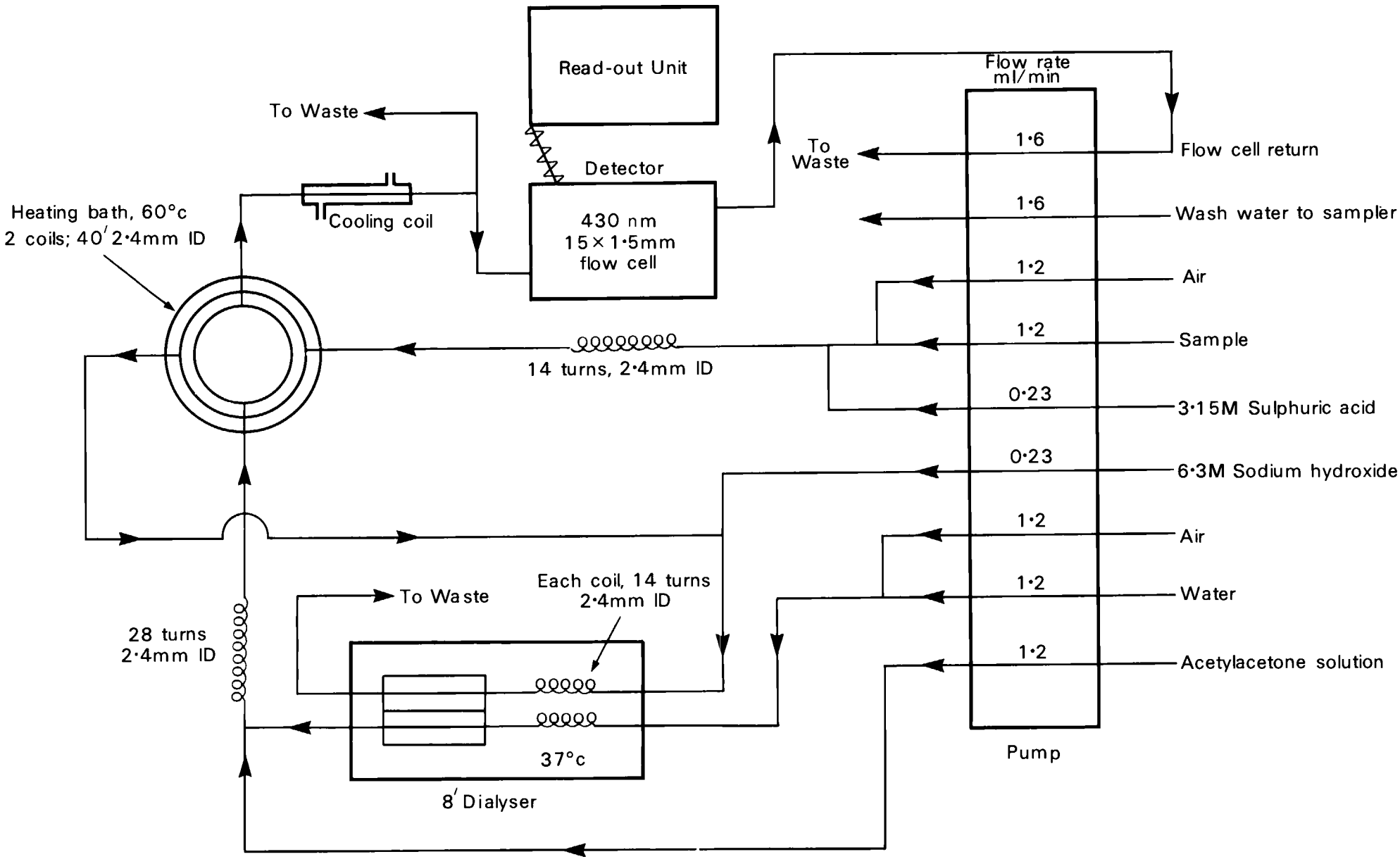
D8. Analytical Procedure

Read Section D4 on hazards before starting these procedures

D8.1 Hydrolysis and Dialysis Method

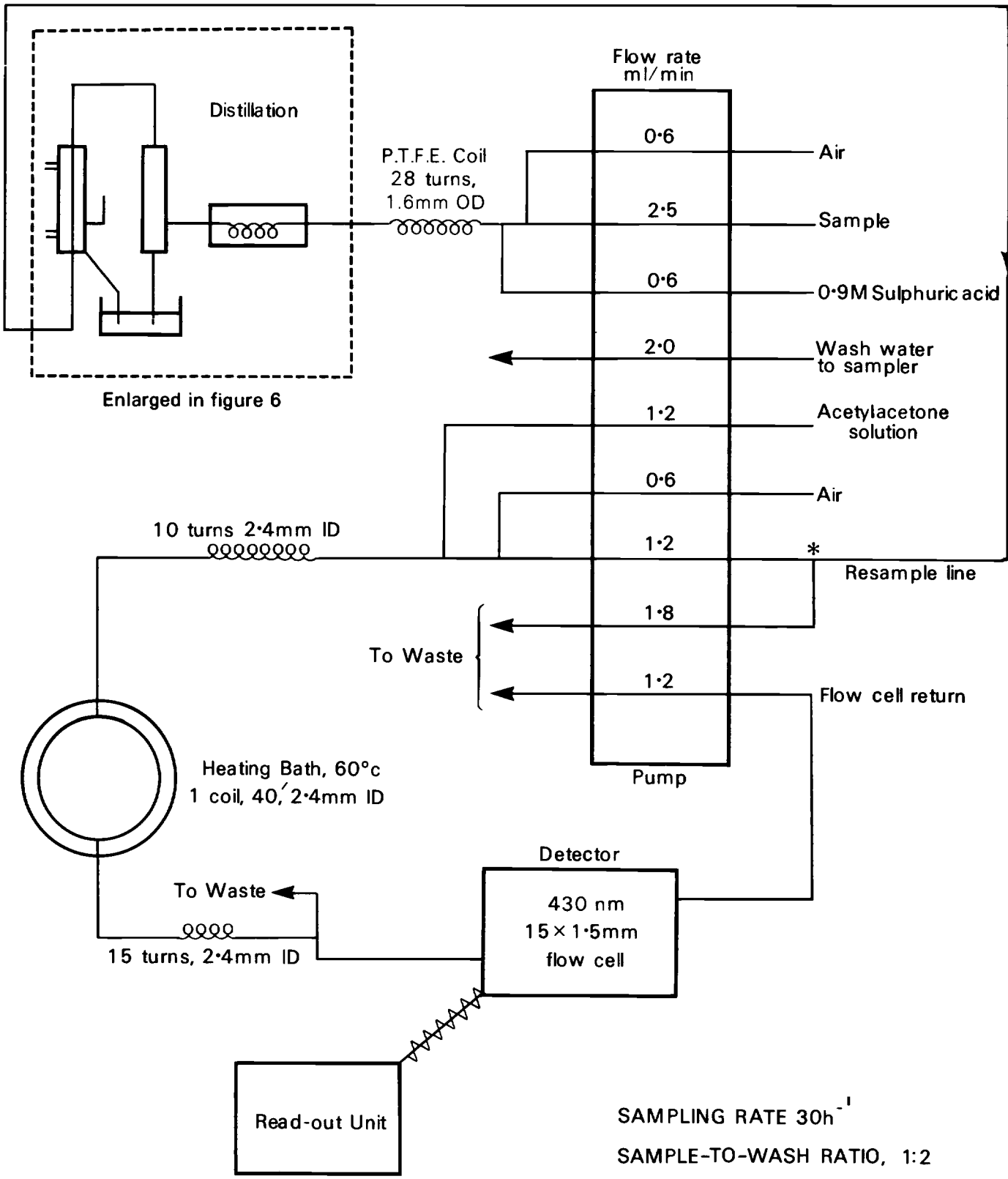
Step	Analytical Procedure	Notes
	Starting Operation	
D8.1.1	Connect system as shown in the flow diagram (See fig. 4) (Notes a and b)	(a) Follow the manufacturer's general operation instructions (b) See reference 4
D8.1.2	With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents. Start pump and switch on detection and measurement units (Notes c and d)	(c) At the beginning (and end) of the analytical run, the donor stream to the dialyser may not be neutral because of the longer distance travelled by the acid. To prevent damage to the membrane it is advisable to pump the donor stream to waste for 10 min (d) With the donor stream connected to the dialyser, allow the system to equilibrate for a further 15 min and during this period check that the bubble pattern and hydraulic behaviour of the system are satisfactory. If not, eliminate difficulties before proceeding to step D8.1.3
	Initial Sensitivity Setting	
D8.1.3	When an acceptably smooth baseline trace is given on the measurement unit, transfer the sample probe into a C_M standard solution (Note e) and adjust the baseline response to about 5 per cent of full scale (Note f)	(e) C_M is the greatest concentration that the calibration is intended to cover (f) An elvated setting of the baseline allows for any negative drift that may occur

Figure 4 FLOW DIAGRAM OF SYSTEM WITH HYDROLYSIS AND DIALYSIS



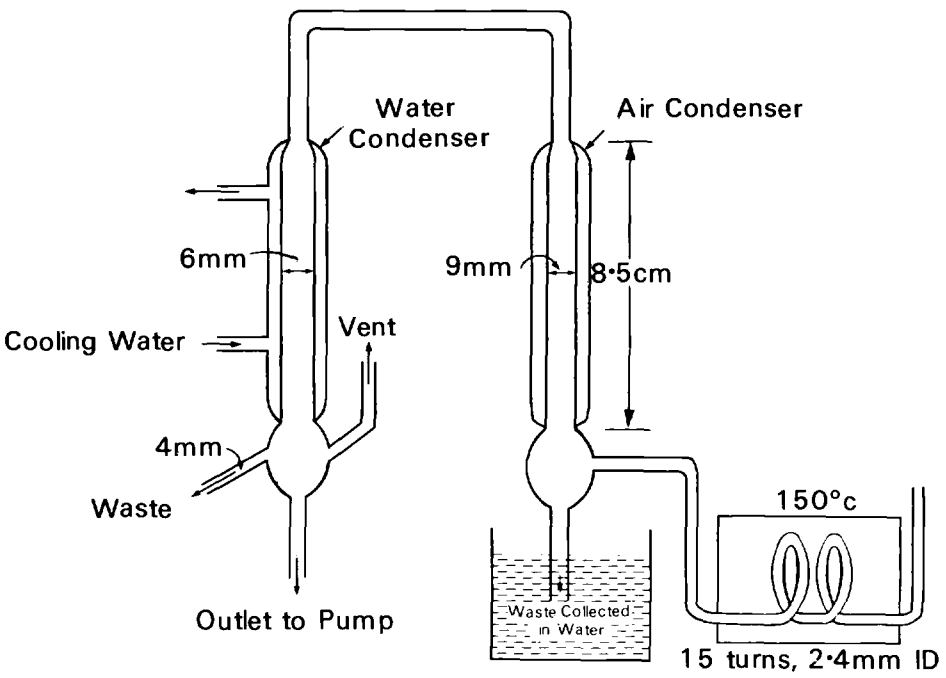
SAMPLING RATE 30h^{-1} SAMPLE-TO-WASH RATIO 2:1

Figure 5 FLOW DIAGRAM OF SYSTEM WITH DISTILLATION



*
Sample splitter; Segmentation of liquid stream by air vents at this point temporarily

Figure 6 DISTILLATION APPARATUS ENLARGED



Step	Analytical Procedure	Notes
D8.1.4	When there is a positive stable response at the measurement unit due to the colour produced from from the C_M standard solution (Note g) adjust this response to read approximately 90 per cent of full scale (Note h)	(g) The sample probe need remain only in the C_M standard solution for sufficient time to give a stable reading. The response time is approximately 25 min (h) This may be directly possible on some units but others may require range expansion facilities
D8.1.5	Return the sample probe to rest in the wash position (Note i)	(i) First remove any traces of standard solution from the outside of the sample probe
	Analysis of Samples	
D8.1.6	Load the sample turntable in the following order (Notes j and k) and start sampler	(j) The turntable can be loaded during the initial stabilization period (steps D8.1.2 to D8.1.4) (k) The order given is in current use. Alternative arrangements of solutions on the turntable are discussed in Reference 4.

Position No. on turntable	Solution	
1–5	Calibration standards in ascending order of concentration (Note l)	(l) 5, 10, 15, 20 and 25 mg formaldehyde/litre
6–7	Blank (Note m)	(m) Water from the same source as that used to prepare the calibration standards
8–17	Samples (Note n)	(n) A control standard should occupy one of the sample positions as a check of system control (see main Section 3 on checking the accuracy of analytical results)
18	Calibration standard (Note o)	(o) A 20 mg/l standard is used to check the calibration
19–20	Blank (Note m)	
21–30	Samples (Note n)	
31	Calibration standard (Note o)	
32–33	Blank (Note m)	

	Repeat the sequence 8–33 until all the samples have been processed (Notes p and q)	(p) If cross contamination (sample interaction) occurs between two samples (visible on the measurement unit trace as incomplete separation of consecutive sample responses) both samples are re-analysed in reverse order and separated by a blank solution (q) The complete calibration may be checked at the end if necessary
D8.1.7	When a steady baseline is obtained on the measurement unit (after Step D8.1.5) re-adjust the baseline to 5 per cent of full scale if necessary	
D8.1.8	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	
D8.1.9	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 analytical run (if used) are all acceptably close to their respective blank corrected initial calibration standard response. If not, refer to essay review (Reference 4) for suggested procedures to obtain the calibration curve(s)
D8.1.10	Using the calibration curve(s) convert the measurement unit responses due to the samples into concentration of total formaldehyde in the samples (Note s)	(s) The measurment unit responses of the samples are first corrected for any baseline and sensitivity changes. The results are expressed as mg HCHO/litre
	Shut-down Procedure	
D8.1.11	Transfer the reagent lines to water and continue pumping for 25 min (Note t). Switch off pump, detection and measurement units	(t) Refer to Note c, step D8.1.2.

D8.2 Distillation Method

The experimental procedure used is identical to the procedure used for the hydrolysis/dialysis method except for the 'Starting Operation' which for the distillation method reads:

D8.2.1 Connect system as shown in the flow diagram (See figs. 5 and 6).

D8.2.2 With the sample probe at rest in the wash receptacle solution, place all the reagent lines in their respective reagents. Start the pump, switch on heating bath units and set the flowrate of cold water through the condenser to approximately 750 ml/min (Note d).

'Note d' — 'Allow the system to equilibrate for 30 min and ...'

One other exception is the concentration range of the method. Here, the range of application is up to 5 mg formaldehyde/l. Therefore, step D8.1.6., Note (1) reads 1, 2, 3, 4 and 5 mg formaldehyde/l. However, since this distillation procedure is based on the method used at the Anglian Water Authority (Essex River Division) who use the technique primarily to monitor hexamine levels, hexamine standards may be used instead of formaldehyde standards. The results are then expressed as mg hexamine/litre.

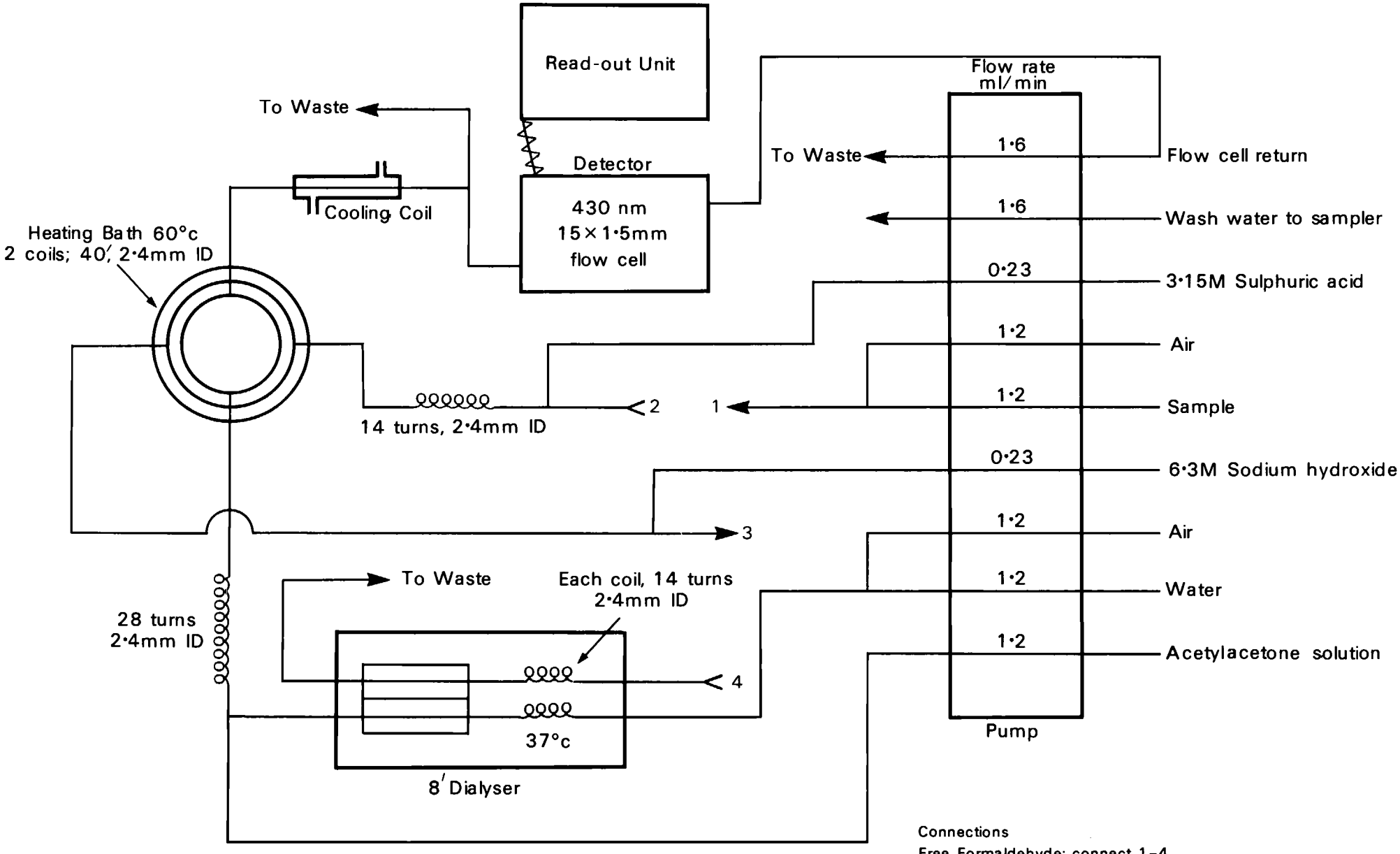
D8.3 Extension of the Analytical Procedure

Samples whose concentration of total formaldehyde is greater than the highest concentration that the calibration is intended to cover may be diluted accordingly prior to analysis without serious effect to the accuracy of result.

Since it is recommended that samples are subjected to a total formaldehyde procedure and a free formaldehyde procedure (method C in this booklet) the following information is worthy of consideration.

A system, based on the hydrolysis/dialysis procedure, can be set up whereby total or free formaldehyde can be determined with the minimum of change-over time (approximately 1 min) from one form of formaldehyde to the other. Unused pump tubes are allowed to pump air. The flow diagram of the system is given in Fig. 7.

Figure 7 FLOW DIAGRAM FOR A DUAL PURPOSE APPARATUS



Connections
Free Formaldehyde: connect 1–4
Total Formaldehyde: connect 1–2 and 3–4

SAMPLING RATE 30h^{-1} SAMPLE-TO-WASH RATIO 2:1

E. A Method for the Determination of Methanol using Air Segmented Continuous Flow Spectrophotometry

E1. Performance Characteristics of the Method*

E1.1	Substance determined	Methanol
E1.2	Type of sample	Raw, waste and potable waters
E1.3	Basis of method	Methanol is oxidised by potassium permanganate under acidic conditions to formaldehyde which reacts with acetylacetone in the presence of an excess of an ammonium salt to form a yellow compound, diacetyldihydrolutidine, whose concentrations is measured spectrophotometrically
E1.4	Range of application	Up to 20.0 mg/l
E1.5	Calibration curve	Linear

E1.6 Standard deviation (within batch) (9 degrees of freedom)

	Methanol concentration (mg/l)	Standard deviation (mg/l)
Standards		
	0.5	0.03
	20.0	0.30
Samples		
River water	1.0	0.10
Sewage works effluent	2.0	0.10
'Spiked' sewage works effluent	15.0	0.25

E1.7	Limit of detection† (9 degrees of freedom)	0.14 to 0.5 mg/l
E1.8	Bias	Less than 10% as indicated by recovery data from 'spiked' samples (see Table 5)
E1.9	Interferences	See Section E3
E1.10	Sensitivity	A 20.0 mg methanol/l standard gives an absorbance change of approximately 0.11 absorbance units using a 15 mm flowcell
E1.11	Time required for analysis	Sampling rate, 30 h^{-1}; response time 12 mins. Operator time approx 1 h for 30 samples

*The information given in the above table was produced by the Thames Water Authority (Lea Division).

† The instrument baseline was too steady to estimate a limit of detection from the analysis of blanks. The figures in the table were derived from:—

(i) The minimum discrimation interval of the recorder trace (1% full scale deflection, 100% = 20 mg/l).

(ii) The variability of the low level standard and sample.

These figures may be upper estimates.

Table 5. Recovery of methanol from 'spiked' samples (single determinations)

Sample	Initial concentration as Methanol (mg/l)	Concentration of Methanol added (mg/l)	Concentration of Methanol found (mg/l)	% Recovery of added Methanol
River water	1.0	5.5	6.5	100
Sewage effluent	2.5	13.8	15.6	94.9

E2. Principle

Methanol is oxidised to formaldehyde by potassium permanganate under acidic conditions[5] and the excess permanganate is reduced by hydrazinium sulphate[6]. The resultant formaldehyde is dialysed out of the acid stream into a neutral receiving stream at 37°C[6] and allowed to react with acetylacetone in the presence of an excess of an ammonium salt at 60°C to form a yellow compound 3,5-diacetyl-1,4-dihydrolutidine (DDL) whose concentration is measured spectrophotometrically at a wavelength of 420 nm[1,2]. (430 nm may be used, but the performance data may vary slightly.)

E3. Interferences

At the concentration levels of methanol examined by the method a solution containing 100 mg/l of any one of the following appears not to interfere:

sulphate, bicarbonate, orthophosphate, calcium, sodium, potassium, magnesium, chloride, and carbonate.

For turbid or coloured samples, filtration will not normally be necessary since a dialyser is employed. However, if the colour is due to the presence of soluble metals, then some interference may be expected due to formation of metal acetylacetonates.

Elevated levels of ammoniacal nitrogen, bromide, phenol and nitrite interfere seriously in the method. However, such high concentrations would not normally be found in the samples under test.

Oxidizing and reducing agents may interfere.

Hexamine at a concentration of 5.0 mg/l gives a response equivalent to 4.65 mg/l of methanol. It may be removed by preliminary extraction with chloroform[3] however, if significant quantities are present, it is preferable to correct for interference by analysing the sample with and without prior oxidation by potassium permanganate (see the determination of total formaldehyde, method D). The methanol concentration may be obtained by difference between the two results.

Free formaldehyde will also cause interference in the method. If the presence of free formaldehyde is suspected, than a subtractive procedure as described above, using method C, should be used to obtain the methanol concentration.

E4. Hazards

4.1 The precautions given in the essay review on continuous flow analysis[4] should be observed.

4.2 Hydrazinium sulphate (which also may be carcinogenic), sulphuric acid, acetylacetetone and acetic acid are corrosive. Eye protection and gloves should be worn when handling them, and wash any spillages with copious amounts of cold water.

4.3 Methanol is a toxic, volatile, inflammable solvent and should be handled with care, ensuring that no naked flames are in the vicinity.

E5. Reagents and Standards

Use only recognized analytical reagents grade chemicals unless stated otherwise. Volumetric (calibrated) glassware should meet the recognized criteria for accuracy.

E5.1 Water

The water used for blank determinations and for the preparation of reagents and standard solutions should have a methanol content which is negligible compared with the smallest concentration of methanol to be determined in the samples. Distilled or deionized water will usually be suitable.

The wash water should contain 1.0 ± 0.1 ml of a proprietary non-ionic wetting agent per litre to improve the flow characteristics of the liquid stream through the tubing of the system.

E5.2 0.5M Sulphuric acid solution

Add 27 ± 0.5 ml sulphuric acid (d_{20} 1.84) cautiously, with stirring, to approximately 800 ml of water. Cool to room temperature, dilute to 1 litre with water in a calibrated flask and mix. Store in a glass-stoppered bottle. This reagent is stable for at least 3 months.

E5.3 3.15M Sulphuric acid solution

Add 170 ± 2 ml sulphuric acid (d_{20} 1.84) cautiously, with stirring and cooling, to approximately 800 ml of water. Cool to room temperature, dilute to 1 litre with water in a calibrated flask and mix. Store in a glass-stoppered bottle. This reagent is stable for at least 3 months.

E5.4 0.70% m/V Potassium permanganate solution

Dissolve 7.0 ± 0.05 g potassium permanganate in approximately 800 ml of water with stirring. Transfer to a 1 litre calibrated flask, make up to the mark with water and mix. Filter through a medium porosity glass sinter or a 0.45 um filter. Store in an amber glass-stoppered bottle. This reagent is stable for at least 2 weeks.

E5.5 Hydrazinium sulphate in 0.06M sulphuric acid solution

Add 120 ± 1 ml of 0.5M sulphuric acid solution (E5.2) to approximately 800 ml of water and cool. Add 30 ± 1 g hydrazinium sulphate to the sulphuric acid solution and stir vigorously using a magnetic stirrer at room temperature for at least 2 hours. Make up to 1 litre in a calibrated flask and mix. Filter the solution through a fast filter paper to remove the undissolved hydrazinium sulphate. Store the solution in a glass-stoppered bottle. This reagent is stable for at least one week.

E5.6 Ammonium acetate buffer solution

Dissolve 150 ± 1 g ammonium acetate in approximately 800 ml of water. Add 3.0 ± 0.1 ml glacial acetic acid. Make up to 1.0 litre in a calibrated flask and mix. Add 0.15 ml of a proprietory non-ionic wetting agent and mix thoroughly. Filter if any cloudiness is apparent. Store in a glass stoppered bottle. Check that the pH is 6.6 ± 0.1 pH units, and adjust if necessary, with either acetic acid or ammonium hydroxide solution. This reagent is stable for at least 2 weeks.

E5.7 Acetylacetone solution

Dissolve 150 ± 1 g ammonium acetate in approximately 800 ml of water. Add 3.0 ± 0.1 ml glacial acetic acid followed by 3.0 ± 0.1 ml acetylacetone dilute to 1.0 litre in a calibrated flask with water and mix. This reagent is stable for at least one week if stored in a refrigerator between 1 and 5°C when not in use.

E5.8 Methanol stock standard solution, 1 ml = 10 mg methanol

Transfer quantitatively 10.00 ± 0.01 g of methanol into a 1 litre calibrated flask containing approximately 800 ml of water. Dilute to the mark with water and mix. Store in a glass-stoppered bottle in a refrigerator between 1 and 5°C when no in use. This solution is stable for at least one month under these conditions.

E5.9 Methanol working standard, 1 ml = 0.1 mg methanol

Add 10 ± 0.1 ml of stock standard methanol solution (E5.8) to a 1-litre calibrated flask, dilute to the mark with water and mix. Prepare this solution fresh daily.

E5.10 Methanol calibration standard solutions

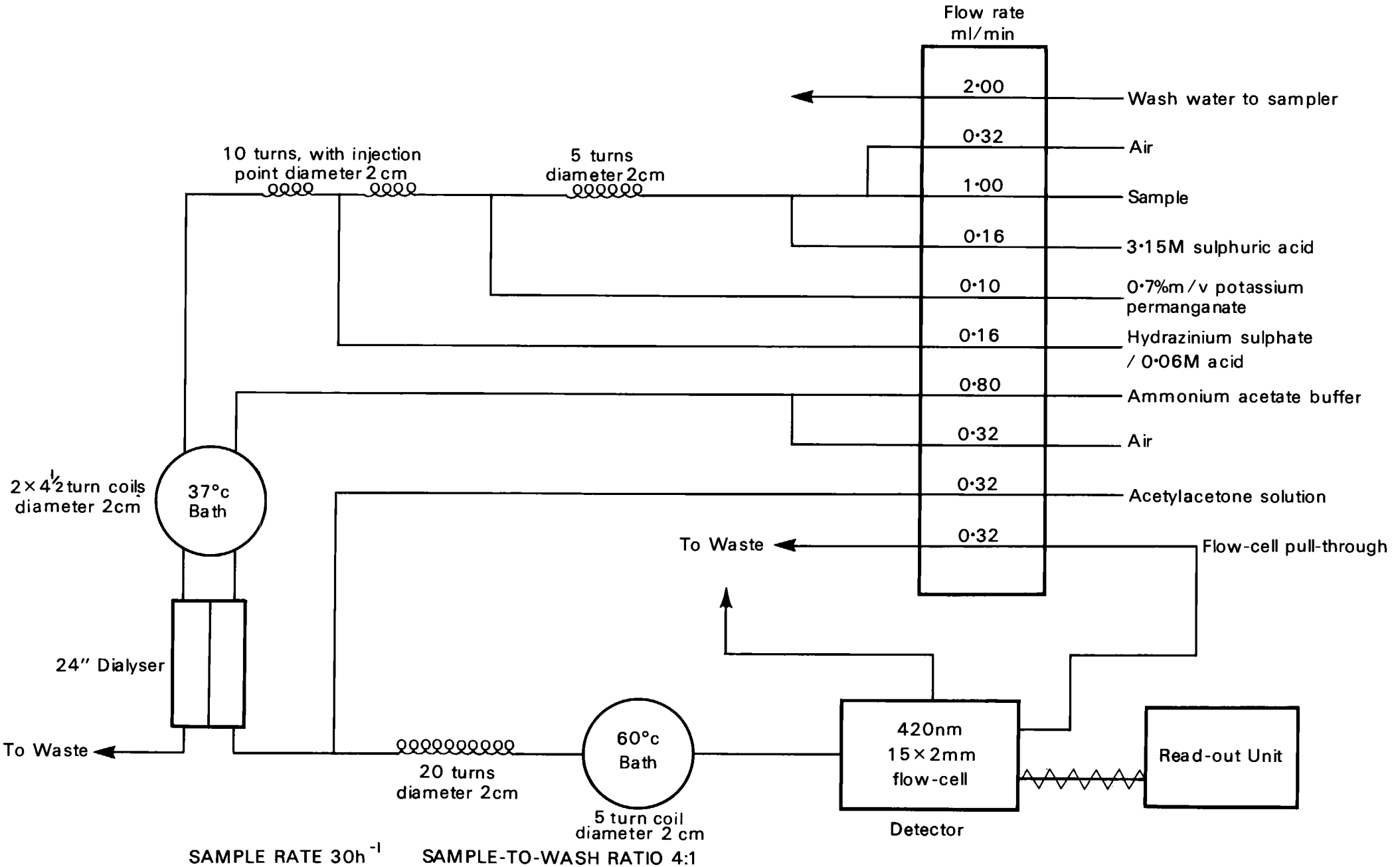
Prepare a series of standard solutions containing 0.5, 1, 2, 5, 10, 15 and 20 mg methanol/litre by adding 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ml working standard methanol solution (5.9) to 100 ml calibrated flasks, making up to the mark with water and mixing well. These solutions should be prepared fresh on the day of use.

E6. Apparatus

The following apparatus, which is set up as shown in figure 8, is required:

Sample presentation unit (sampler)
Multi-channel peristaltic pump with air inlet valve attachment
Analytical cartridge, incorporating pump-tubes, mixing coils, 37±1°C and 60±2°C heating baths, a 24" dialyser
Detector (colorimeter or spectrophotometer) incorporating a flow-cell
Read-out (measurement) unit (recorder or printer)

Figure 8 FLOW DIAGRAM



SAMPLE RATE 30h^{-1} SAMPLE-TO-WASH RATIO 4:1

E7. Analytical Procedure

Step	Analytical Procedure	Notes
	Starting operation	
E7.1	Arrange the apparatus as depicted in the flow diagram (Fig. 8) (Notes a and b)	(a) Follow the manufacturers general operating instructions (b) See Reference 4
E7.2	Place the reagent tubes in the respective reagent bottles with the sample probe in the wash receptacle solution. Start pump (Note c). Switch on measurement (read-out) and detection units.	(c) To avoid the formation of a dark brown precipitate, delay the introduction of the permanganate solution until the sulphuric acid and hydrazinium sulphate solutions have reached their respective first mixing coils as depicted in the flow diagram. Allow the system to equilibrate for at least 30 min and during this period check that the bubble pattern and hydraulic behaviour of the system are satisfactory. If not, eliminate difficulties before proceeding to Step E7.3.
	Initial Sensitivity Setting	
E7.3	When a satisfactory base-line has been obtained on the measurement unit, aspirate a 20 mg/l standard solution through the sample line for about 3 minutes. Adjust baseline response to about 5 per cent full scale (Note d). Return sample probe to the wash receptacle solution (Note e)	(d) An elevated baseline setting allows for any negative drift that may occur (e) First remove traces of the standard solution from probe
E7.4	After a period of about 12 minutes from the beginning of step E7.3 has elapsed, a positive response appears on the measurement unit. Adjust the response to give a reading at about 90 per cent of full scale (Note f)	(f) This may be directly possible on some units but others may require range expansion facilities
	Analysis of Samples	
E7.5	Arrange the solutions on the turntable in the following order and start the sampler (Notes g, h and i)	(g) the samples and standards can be loaded on the turntable during the setting up period (steps E7.2 to E7.4). (h) The order given is in current use. Alternative arrangements are given in Reference 4 (i) The cups containing solutions should be capped with aluminium foil before placing on the turntable to minimize losses of methanol by volatilization

Position no. on turntable	Solution	
1–7	Calibration standards in ascending order of concentration	
8	Blank colution (Note j)	(j) Use the same water as used to prepare the calibration standards
9	Calibration standard (Note k)	(k) A 20.0 mg/l stanad is used to check any variation in sensitivity
10–19	Samples (Note l)	(l) A quality control standard should occupy one batch as a check of the system. (See main section 3 on checking the accuracy of analytical results)

Step	Analytical Procedure	Notes
	20 Blank	
	21 Calibration standard (Note k)	
	22–31 Samples	
	32 Blank	
	33 Calibration standard (Note k)	
	Repeat the sequence 10–33 until al the samples have been processed (Note m). If it is thought necessary, repeat the calibration standards at the conclusion of the run of samples	(m) If cross-contamination is seen to occur (incomplete peak separation between consecutive sample responses) then separate the samples and reanalyse them in reverse order. If necessary separate them by a blank solution
E7.6	When the last sample or standard has been analysed, and all the responses have been registered on the measurement unit and the final baseline is obtained, switch off the measurement unit	
	Calculation of Results	
E7.7	Plot a calibration curve of measurement unit responses (y axis) against concentration (x axis) of the calibration standard solutions (Notes n and o)	(n) Providing that the response due to the intermittent blanks and calibration standards are acceptable close to their respective initial values. If not, refer to the essay review[4] for a suggested alternative procedure to obtain calibration curves
E7.8	Using the calibration curve, convert the measurement unit responses due to the samples into concentration of methanol in the samples (Note o)	(o) The measurement unit responses of the samples must first be corrected for any baseline and sensitivity changes The results are expressed as mg CH_3OH/litre
	Shut-down Procedure	
E7.9	Remove reagent lines, wipe dry with a tissue, and transfer to a beaker of water and continue pumping for 15 minutes (Note p). Switch off pump and detection units	(p) Pumping water through the system prolongs the life of the dialyser membrance and removes reagent and sample solutions from the tubing

E8. Extension of the Concentration Range of the Method

Samples with a methanol concentration in excess of 20 mg/l should be diluted accordingly, and subjected to re-analysis. The result corrected for blank and sensitivity should then be multiplied by the dilution factor to obtain the methanol concentration in the sample.

F. A Method for the Determination of Methanol by Gas-Liquid Chromatography

F1. Performance Characteristics of Method

F1.1	Substance determined	Methanol		
F1.2	Type of sample	Raw, waste and potable waters		
F1.3	Basis of method	Direct injection into a gas chromatograph using a flame ionization detector. Confirmed by using a second column.		
F1.4	Range of application	Up to 50 mg methanol/l		
F1.5	Calibration curve	Linear		
F1.6	Standard deviation* (within batch) (9 degrees of freedom)		Methanol concentration (mg/l)	Standard deviation (mg/l)
		Standards	5.0	0.13
			40.0	1.54
		Samples		
		Sewage effluent	3.9	0.14
		Sewage	20.3	0.20
F1.7	Limit of detection*† (9 degrees of freedom)	0.11 mg/l		
F1.8	Bias	No significant bias known		
F1.9	Interferences	See Section 3		
F1.10	Sensitivity	Typically 10 millivolts equivalent to 50 mg/l on the equipment used. Consult manufacturers manual.		
F1.11	Time required for analysis	15 minutes per determination (using primary column only); 35 minutes per determination when confirmatory column is used: operator time 5 minutes per sample		

*These values were obtained by autoinjection of solutions using the described procedure and concentrations of methanol were derived from peak measurements. All of the information was produced by the Welsh Water Authority (Bridgend Area Laboratory).

†This value was calculated from the standard deviation of a 0.3 mg methanol/l solution.

F2. Principle

Methanol is determined by gas chromatography using a primary column of Carbowax 1540 on Chromosorb W and flame ionization detection. Confirmation of the determination is obtained using a column of Chromosorb 102.

F3. Interferences

Volatile organic substances will interfere if they have similar retention times to methanol. On the primary column, butan-2-one has a very similar retention time to methanol, whilst acetone, ethanol and propan-2-ol may interfere if present in high concentrations. Use of the confirmatory column will enable a more confident identification of methanol to be achieved.

F4. Hazards

Methanol is highly flammable, therefore the use of naked flames must be prohibited. Avoid inhalation, ingestion and contact with skin and eyes.

F5. Reagents and Standards

Analytical reagent grade chemicals are used except where stated otherwise. Volumetric (calibrated) glassware should meet the recognised criteria for accuracy.

F5.1 Water

The water used for blank determinations and for the preparation of standard solutions should have a methanol content which is negligible compared with the smallest concentration of methanol to be determined in the samples.

The town mains supply will usually be suitable, but protection from atmospheric contamination should be ensured.

F5.2 Methanol stock standard solution, 1 ml = 1.0 mg methanol

Weight 1.000 ± 0.005 g of methanol and quantiatively transfer to a 1-litre calibrated flask. Make up to the mark with water and mix well, using a glass stopper. Prepare the solution fresh when required.

F5.3 Single point calibration standard, 1 ml = 0.05 mg methanol

Add 50.0 ± 0.05 ml of stock standard methanol solution (F5.2) to a l-litre calibrated flask, make up to the mark with water and mix well, using a glass stopper. Prepared this solution fresh when required.

F6. Apparatus

F6.1 A gas chromatograph fitted with an oven and flame ionisation detector. A chart recorder is a suitable form of read-out.

F6.2 Special apparatus†

F6.2.1 Primary Column

A stainless steel column of 2 m length and 3.2 mm bore packed with 15% Carbowax 1540 on Chromosorb W 80/100 mesh AW DMCS. A column efficiency of 1500 plates is desirable. (See reference 8).

F6.2.2 Confirmatory Column

For confirmation, a stainless steel column 2 m long and 3.2 mm bore packed with Chromosorb 102 80/100 mesh should be used.

F6.2.3 A 10 ul chromatographic syringe has been found to be most suitable.

† Dimensions of the column may vary slightly according to the make of instrument used.

F7. Analytical Procedures

Read Section F4 on Hazards before starting this procedure

Step	Analytical Procedure	Notes
	Preparation of the instrument (Note a)	
F7.1	Set up the instrument according to the manufacturer's instructions. The column oven temperature should be set at 70°C for the primary column and 150°C for the confirmatory column. The carrier gas should be oxygen free nitrogen set for a flow of 50 ± 5 ml/minute. The detector oven and injection port temperatures should be set at approximately 50°C above the column oven temperature	(a) See reference 8
F7.2	Equilibrate the column until an acceptably smooth baseline is obtained (Note b).	(b) The column must have been previously stabilized

Step	Analytical Procedure	Notes
	Sample Pretreatment	
F7.3	Allow the samples to stand for at least 15 minutes prior to removal of a portion of the liquid phase of the sample with the chromatographic syringe (Note c)	(c) This should ensure the settlement of any suspended matter which is capable of blocking the syringe needle
	Gas Chromatographic Procedure	
F7.4	Inject 5 μl of the calibration standard and allow it to elute for about 15 minutes. Repeat twice more and obtain the mean peak height H_c. (Notes d and e) (See fig. 9)	(d) Typical retention times are:— Column: No. 1 Carbowax 1540 — Retention Time (Mins) 3.8; No. 2 Chromosorb 102 — 1.3
		(e) Rinse the syringe several times between injections with methanol free water
F7.5	Inject 5 μl of water and allow it to elute for about 15 minutes. Measure the blank peak height for apparent methanol. Repeat once more and obtain the mean peak height H_b.	
F7.6	Inject 5 μl of the pretreated sample and allow it to elute for about 15 minutes. Measure the peak height for methanol H_s.	
	Calculation (Note f)	
F7.7	Methanol is identified by its retention time (see Figure 9) Calculate the concentration C of methanol in the sample from: $C = 50 \frac{(H_s - H_b)}{(H_c - H_b)}$ mg/l Where 50 is the concentration of methanol, in mg/l, in the single point calibration standard	(f) An alternative approach to the procedure used here involves the use of an internal standard* (eg. a higher alcohol such as butan-2-ol). This provides an aid to the identification of methanol and takes account of non-reproducibility of injections. With this approach, the concentration of methanol is expressed relative to the internal standard
	Confirmation Procedure	
F7.8	Confirmation of identity and quantity is necessary. The confirmatory column should be used repeating steps F7.2 — F7.7 above (Note g).	(g) See Figure 10 for typical trace

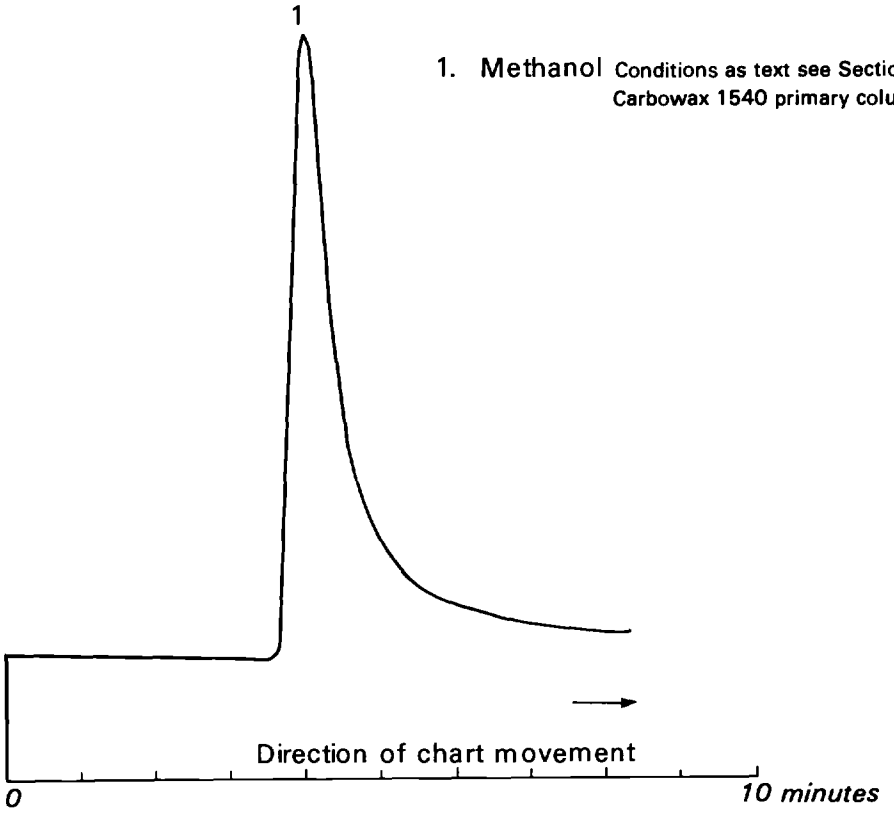
*For other internal standards Reference may be made to the Handbook of Chromatography, Vol. I, 1972, by G. Zweig, Ph.D and J Sherma, Ph.D Published by the Chemical Rubber Co., Ohio, US.

F8. Checking the Linearity of the Calibration Curve

The procedure in this section must be carried out on at least two occasions before application of the method to any samples and once per month thereafter during the life of the column.

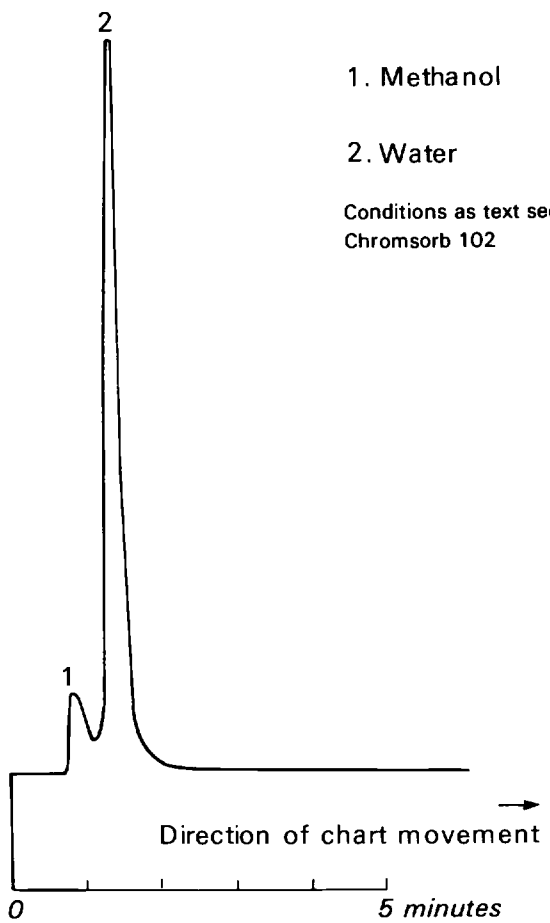
To a series of 100 ml calibrated flasks add 1.0, 2.0, 3.0, 4.0 and 5.0 ml of the stock standard solution and make up to the mark with water. These solutions contain respectively 10, 20, 30, 40 and 50 mg methanol/litre. Carry out the procedure described in Section 7, steps 1, 4 and 5 on each of the solutions. Plot the peak heights against mg methanol/litre. The calibration curve is linear up to 50 mg methanol/litre.

Figure 9 TYPICAL TRACE ON PRIMARY COLUMN



Note: Trace obtained by Welsh Water Authority, Bridgend Area Laboratory

Figure 10 TYPICAL TRACE ON CONFIRMATORY COLUMN



1. Methanol

2. Water

Conditions as text see Sections F6.2.2 and F7.1
Chromsorb 102

Note: Trace obtained by Welsh Water Authority, Bridgend Area Laboratory

Reference

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6. STICKLEY, D. P. Thames Water Authority (Lea Division), *Method of Analysis No. 64.*
7. SIMS, E. W. *J. Chromatog. Sci.*, 14, 1976, 65.
8. Gas Chromatography, an Essay Review 1981, HMSO London another publication in this series.

Estimating the Accuracy of Analytical Results

The methods contained in this publication have each been tested in only one laboratory, they can only be regarded as "Tentative Methods". Any further information on the performance of these methods would therefore be welcomed and should be forwarded to The Secretary. The Standing Committee of Analysts, Working Gorup 6, The Department of the Environment, Romney House, 43 Marsham Street, London, SW1P 3PY, England.

Because of the indeterminate nature of "total formaldehyde" it is not possible to recommend a comprehensive testing programme for the methods, however as a guide to the analyst information would be welcomed on the following:

(i) Standard deviations of replicate analyses of standards and samples both within and between days (dependant on solution stability).

(ii) Limits of detection.

(iii) Sources of bias.

(iv) Recoveries of formaldehyde and compounds comprising 'total formaldehyde' through the appropriate procedures.

(v) Information on inter-laboratory analytical quality control exercises.

Further information on the design of suitable experiments can be found in WRC TR 66, obtainable from The Water Research Centre, Medmenham, Marlow, Bucks, SL7 2HD, England.

Address for Correspondence

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

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

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