The Determination of Formaldehyde, Other Volatile Aldehydes, Ketones and Alcohols in Water 1988

Methods for the Examination of Waters and Associated Materials

Her Majesty's Stationery Office

The Determination of Formaldehyde, Other Volatile Aldehydes, Ketones and Alcohols in Water 1988

Methods for the Examination of Waters and Associated Materials

This booklet supplements but does not supercede Formaldehyde, Methanol and Related Compounds in Raw, Waste and Potable Waters 1982

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Methods for the Examination of Waters and Associated Materials

Chromatographic methods are highly dependent on the columns and packing materials used. This booklet mentions several proprietry packing materials which those evaluating the methods have found satisfactory. This in no way endorses these materials. It is suggested that users should evaluate columns with their own samples and spiked samples and determine limits of detection and extraction efficiences for themselves.

Contents

About This Series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes 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 technical staff 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 a committee of the Department of the Environment set up in 1972. Currently it has 9 Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1. General principles of sampling and accuracy of results.
2. Microbiological methods.
3. Empirical and physical methods.
4. Metals and metalloids.
5. General nonmetallic substances.
6. Organic impurities.
7. Biological monitoring.
8. Sewage Works Control Methods.
9. Radiochemical methods.

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee.

The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R Pittwell
Secretary and Chairman

11 August 1988

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 for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use. Lone working, whether in the laboratory or field, should be discouraged.

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 check-list, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', issued by the Royal Society of Chemistry, London: 'Safety in Biological 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.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods of contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

A. The Determination of Formaldehyde in Water by HPLC

1. Introduction

Formaldehyde, in various forms, may be present in river waters as a result of trade effluent discharges. Free formaldehyde is toxic and the standard methods of analysis[1], with a detection limit of approximately 100 $\mu g\ L^{-1}$, while satisfactory for effluents are inadequate for studies to monitor formaldehyde in rivers. This method determines free formaldehyde and any combined form which will react with 2,4-dinitrophenyl hydrazine to form the hydrazone[2]. It can also be used to determine other aldehydes and ketones which are separated chromatographically from the formaldehyde hydrazone e.g. acetaldehyde, propionaldehyde, acetone, and for compounds which can be converted to aldehydes or ketones, for example isopropanol.

2. Performance Characteristics of the Method

2.1 Substance determined

Formaldehyde

2.2 Type of sample

River and clean unchlorinated waters

2.3 Basis of method

Derivatisation of formaldehyde with 2,4-dinitrophenylhydrazine under acid conditions to form the hydrazone followed by reverse phase HPLC using ultra-violet detection.

2.4 Range of application

Upto at least 2000 $\mu g\ L^{-1}$.

2.5 Calibration curve

Linear (tested to 2000 $\mu g\ L^{-1}$).

2.6 Standard deviation

	Formaldehyde Concentration ($\mu g\ L^{-1}$)	Standard Deviations* Within Batch ($\mu g\ L^{-1}$)	Between Batch ($\mu g\ L^{-1}$)
Standards	10	1.32 (5)	2.24 (4)
	50	7.66 (5)	N.S. (4)
Samples			
River water	1.65	1.45 (5)	N.S. (4)
Spiked river water	24.95	2.52 (5)	3.29 (4)

*Figures in parentheses are the degree of freedom. N.S. indicates that the result is not statistically significant.

2.7 Limit of detection (5 degrees of freedom)

4.1 $\mu g\ L^{-1}$.

2.8 Bias

Less than 10% as indicated by a mean recovery of 93.2% from river waters (mean formaldehyde conc 1.65 $\mu g\ L^{-1}$) 'spiked' with 25 $\mu g\ L^{-1}$ of formaldehyde.

2.9 Interferences

Any compound which passes through the procedure, has similar LC characteristics to the determinand and absorbs at 254 nm.

3. Principle

The method is based on the formation of the 2,4-dinitrophenyl hydrazone derivative of formaldehyde by reaction of the formaldehyde carbonyl group with 2,4-dinitrophenylhydrazine under acidic conditions. The derivative is extracted into dichloromethane, evaporated to dryness and the residue dissolved in acetonitrile. Reverse phase HPLC with UV detection is used to separate and detect the formaldehyde derivative.

4. Interferences

Any compound which passes through the procedure, has similar LC characteristics to the determinand and absorbs UV at 254 nm. In practice the chromatographic separation eliminates interference from other low molecular weight aldehydes and ketones, e.g. acetaldehyde, propionaldehyde, acetone and butan-2-one, but it is known that low molecular weight intermediates formed during the polymerisation of urea and formaldehyde will react to form the formaldehyde 2,4-dinitrophenyl hydrazone.

5. Hazards

5.1 2,4-Dinitrophenylhydrazine, formaldehyde, acetonitrile and dichloromethane are all toxic and should be handled with care.

5.2 There is a risk of explosion by shock, friction, heat or other sources of ignition if 2,4-dinitrophenylhydrazine is allowed to dry out. It should be handled with care and eye protection, protective glasses and protective gloves should be worn when opening bottles. Any external dry material must be washed away, or if inside the bottle dampened with distilled water. All spillage should be wiped up immediately and rinsed to drain.

5.3 Hydrochloric acid is corrosive. Eye protection and gloves should be worn when handling and any spillages should be washed away with copious quantities of water.

5.4 Formaldehyde and acetonitrile are inflammable and should be handled with care, ensuring that no naked flames are in the vicinity.

6. Reagents

6.1 Water

Water used for standard and blank preparation should have a formaldehyde content which is negligible compared with the smallest concentration of formaldehyde to be determined in the samples. Unchlorinated borehole water was found to be the most suitable. (See Step 9.12 note d).

6.2 2,4-Dinitrophenylhydrazine Reagent

Dissolve 5.0 ± 0.1 g of powered 2,4-dinitrophenylhydrazine in a mixture of concentrated hydrochloric acid (80 ± 1.0 mL) and water (100 ± 1.0 mL) by gently heating on a water bath. Cool the solution and add a further 120 ± 1.0 mL water. If turbid the pale yellow solution should be filtered. Store in a dark glass screw-cap bottle. The solution is stable but will absorb formaldehyde and other aldehydes and ketones from the atmosphere. After use, do not allow liquid to remain in the screw threads of the bottle).

6.3 Acetonitrile

HPLC grade acetonitrile should be used.

6.4 Acetonitrile-water mixture

Add 550 ± 5 mL of HPLC grade acetonitrile to 450 ± 5 mL HPLC grade water, mix thoroughly and degas if necessary.

6.5 Dichloromethane

HPLC grade dichloromethane should be used.

6.6 0.5 M Sulphuric acid solution

Cautiously add with stirring 27.0 ± 0.5 mL of sulphuric acid (d_{20} 1.84) to about 800 mL of water. Cool, make up to 1 litre of water in a calibrated flask and mix. Standardize this solution against the 1.0 M sodium hydroxide solution (Section 6.7) and store in a glass stoppered bottle. This solution is stable for at least 3 months.

6.7 1.0 M 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. Standardize this solution against a primary standard acid such as potassium hydrogen phthalate or sulphamic acid, and store in polyethylene stoppered bottles. This solution is stable for at least one month provided it is protected from atmospheric carbon dioxide.

6.8 Sodium sulphite solution

Dissolve 125 ± 1 g of anhydrous sodium sulphite in about 600 mL of water and make up to 1 litre in a calibrated flask. Store in a glass stoppered bottle. This solution is made freshly as required.

6.9 Thymolphthalein indicator solution

Dissolve 1.00 ± 0.02 g of thymolphthalein in 1.00 ± 0.01 litre of ethanol. Store in a glass stoppered bottle. This solution is stable indefinitely subject to evaporation losses of ethanol, however many users will prefer to scale down the preparation to 100 mL.

6.10 Formaldehyde Stock Solution A

$$1 \text{ mL} = c20 \text{ mg formaldehyde}$$

Weigh out 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 ± 0.1 mL of 0.5 m sulphuric acid solution. After 10.0 ± 0.1 min add 10.0 ± 0.1 mL of 1 M sodium hydroxide solution and dilute to the calibration mark with water. Standardize this stock solution by transferring 25.0 ± 0.1 mL into a flask and neutralizing with acid (6.6) to thymolphthalein indicator. Transfer 25.0 ± 0.1 mL of sodium sulphite solution into a second flask and neutralize to thymolphthalein indicator using acid (6.6). Quantitatively add the neutral sodium sulphite solution to the neutral formaldehyde solution and titrate with 0.5 M sulphuric acid.

$$1 \text{ mL of } 0.5 \text{ M sulphuric acid} = 30.03 \text{ mg of formaldehyde.}$$

This solution should be prepared freshly each month.

6.11 Formaldehyde Intermediate Standard B

$$1 \text{ mL} = 2 \text{ mg formaldehyde}$$

Allow for any departure of Stock Solution A from the desired strength either by slight changes in the amount used or in the stated concentrations of the standard solutions B, C and D prepared from it.

Note: It is more convenient to make a set of dilutions of the standardized stock solution and plot the calibration curve to suit. For example, if the stock solution were 22.0 mg mL^{-1}, then the intermediate solution B would be 2.2 mg mL^{-1}.

Dilute 10.00 ± 0.01 mL of the stock solution (6.10) to 100 mL with water in a calibrated flask and mix. This solution is stable for at least one month.

6.12 Formaldehyde Intermediate Standard C

$$1 \text{ mL} = 10 \mu\text{g formaldehyde}$$

Dilute 5.00 ± 0.01 mL of the intermediate standard solution B to 1000 mL in a calibrated flask with water (6.1) and mix. This solution should be prepared freshly on the day of use.

6.13 Formaldehyde Working Standard
Solution D

$$1\ ml = 0.2\ \mu g\ formaldehyde$$

Dilute 5.00 ± 0.01 mL of the intermediate standard solution B to 250 mL with water (6.1) in a calibrated flask and mix. This solution should be prepared afresh immediately before use.

7. Apparatus

A high performance liquid chromatograph with UV detection at 254 nm and a 25 cm, 10 μm LiChrosorb RP-18 column. Samples are injected via a 20 μl sample loop. A water-bath at 60 ± 2°C together with a boiling water bath and assorted glassware are required.

8. 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.

As formaldehyde is a strong reducing agent and liberatable from a variety of common materials by hydrolysis, if its determination is needed, it is recommended that the sample should be subjected to three analyses, namely the determination of total formaldehyde, free formaldehyde and methanol.

Experience will dictate whether similar precautions are needed for other aldehydes and ketones; but it should be borne in mind that these compounds are volatile found in many natural products, and that along with the more volatile alcohols, some Ketones are common laboratory solvents.

9. Analytical Procedure

CAUTION
BEFORE PROCEEDING WITH ANALYSES READ SECTION 5 HAZARDS AND SECTION 10 CONTAMINATION

Step	Procedure	Notes
	HPLC Operating Conditions	
9.1	Start the HPLC using a mobile phase of acetonitrile-water (6.4) at a flow rate of 1.0 mL min^{-1} and allow the system to equilibrate and a steady baseline to establish. Set the UV detector to 254 nm.	

Step	Procedure	Notes
	Calibration	
9.2	Add 25.0, 50.0, 100.0, 150.0, and 200.0 mL aliquots of working standard C to each of five 250 mL glass stoppered borosilicate glass bottles and add appropriate amounts of water (6.1) to make up each bottle to 200 mL. Add 200 mL of water (6.1) to another bottle for a blank.	
9.2	Add 10.0 ± 0.1 mL of 2,4-dinitrophenylhydrazine reagent (6.2) to each bottle, replace stopper and shake to mix.	
9.3	Place the bottles in a 60°C water bath for 15 minutes then cool bottles rapidly in a water filled sink (note a).	(a) Take care to release any pressure build up
9.4	Transfer the contents of the bottles to 250 mL separating funnels (previously rinsed with dichloromethane) and add 20 ± 1 mL of dichloromethane. Shake the funnels for 5 minutes, venting frequently.	
9.5	Prepare a 50 mL filter funnel for each extract with anhydrous sodium sulphate supported on glass wool. Wash each with 20 mL dichloromethane.	
9.6	Pass the dichloromethane extract (from step 9.4) through the sodium sulphate (from step 9.5), wash the sodium sulphate with 10–15 mL dichloromethane and combine both extract and washings in a 100 mL pyrex beaker.	
9.7	Carefully evaporate the extract to dryness on a boiling water bath removing the beaker from the heat as soon as the solvent has evaporated.	
9.8	Allow the beaker to cool. Dissolve the residue in 2.00 ± 0.05 mL acetonitrile. Transfer this solution immediately to a stoppered 3.5 mL vial (notes b and c).	(b) This is to prevent loss by evaporation. Quantitative transfer is not necessary.
9.9	Chromatograph the standards and blank and prepare a calibration curve of peak area against concentration of the standards (corrected for the blank). Let the blank value be B (see step 9.12).	(c) If there is real risk of evaporative, loss the evaporate from step 9.7 may be dissolved in 1–1.5 mL of acetonitrile quantitatively transferred to a 2 mL calibrated flask and made up to volume with acetonitrile and well mixed just prior to analysis.
	Analysis of Samples	
9.10	Add 200 ± 1 mL of sample to a 250 mL glass stoppered borosilicate glass bottle and follow steps 9.2 to 9.8 inclusive.	
9.11	Chromatograph the sample and convert the peak area of the formaldehyde derivative peak to concentration (C) using the calibration graph (from step 9.9).	(d) This assumes that the concentration of formaldehyde in the water used to make the standards was initially negligible. If necessary this water should have been obtained by distillation of dilute acidified potassium permanganate solution (leaving ample residual liquid at the close of distillation).

Step	Procedure	Notes
	Calculation	
9.12	Deduct the blank value B from step 9.9 from the found value C (step 9.11) to find the actual concentration in the sample (note d).	

10. Contamination

Formaldehyde is used widely as a preservative, traces have also been detected from building materials. Hence, atmospheric concentrations can be significant in laboratories. Care must be taken to keep the 2,4-dinitrophenylhydrazine reagent bottle well stoppered and blanks should be monitored for signs of contamination.

B. Extension of Method A in this booklet to other Aldehydes and Ketones

The procedure is followed exactly as given above except that standards prepared from the appropriate aldehydes and ketones are used instead of or in addition to the formaldehyde standards given therein. Satisfactory separation and quantification has been confirmed for acetaldehyde, propionaldehyde, acetone, butan-2-one and pentan-3-one.

C. Extension of Method F in the 1982 booklet (1) to Aldehydes, Ketones and Alcohols

The method mentions interference effects in the determination of methanol from butan-2-one, acetone, ethanol, and propan-2-ol, but suggests the use of butan-2-ol as an internal standard. Variations in column type have been reported to achieve good separation, especially if used with a programmed temperature gradient as in Refs 3 and 4. Columns which have proved satisfactory for this type of separaton include Tenax GC, Tenax TA and the whole Chromosorb 100 series. Limits of detection are in the order of low ppm for direct sample injection.

D. Extension of Method A in this booklet to Alcohols and Compounds Decomposable to Aldehydes

The 1982 booklet (1) mentions that methanol and a number of aldehyde derivatives can be converted to aldehydes by oxidation or by acid hydrolysis. Hydrolysis procedures are given in Method D of Ref 1, which uses the acetylacetone colorimetric method of determining formaldehyde. It is possible to adapt this method as a pretreatment for Method A of this booklet.

Method F of Ref 1 uses sulphuric acid-potassium permanganate to oxidize alcohols to aldehydes with hydrazinium sulphate to remove excess permanganate, again with an acetylacetone colorimetric finish. It is possible to modify this, with the enclosed sample warmed to 65 ± 5°C after mixing with the acid permanganate, excess permanganate removed by *subsequent* addition of 0.2 M oxalic acid *after* the heating stage but while the sample is still kept at 65 ± 5°C. This warm solution is then reacted with 2,4-ninitrophenylhydrazone, cooled and submitted to HPLC and measurement of absorption at 254 nm. At least these last stages need batchwise operation or sufficient delay to allow the HPLC column to be cleared between sample injections. Care should be taken not to allow loss of aldehyde or ketone to atmosphere before reaction with 2,4-dinitrophenylhydrazone.

E. Estimation of the Accuracy of Analytical Results

1. Introduction

Quantitative investigation of the accuracy achievable when methods outlined in Sections B–D are used is limited. Before putting these methods into general use, it is desirable to know the accuracy achievable. It would, therefore, be of great value if any laboratory using them, or considering their use, could estimate the accuracy of its own analytical results and report the findings to the Secretary of the Department of the Environment's Standing Committee of Analysts (see address at the end).

The precision achieved and the effects of any interfering substances that may be present in samples are of particular interest. Any information would be greatly enhanced if it were obtained to a common plan so that the information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis of results are given in the following sections and it is strongly urged that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible; more complex designs are possible and would give more information.

2. Basis of suggested Tests

The limit of detection is governed by the within-batch variability of blank determinations. The precision of analytical results may depend on the relative concentration of the determinand in the sample analysed and on the type of sample, for instance worse precision may be obtained with samples than with standard solutions.

For these reasons the basic design recommended is the analysis of one portion of each of the following solutions on each of n days, where n is at least 4 and preferably up to 10.

Solution No	Description
1	Blank
2	Another blank
3	Standard solution with a concentration of the determinand at the lower end of the expected range
4	Standard solution with a concentration of the determinand at the high end of the expected range
5	Typical sample
6	Same sample spiked with a known amount of determinand (mid range)

It is essential that these solutions be treated exactly as if they were samples. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method. The same batch of water should be used on each day to prepare all 4 solutions. For solutions 5 and 6, a total of 5 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5. The total period of the tests may be any convenient time so long as the determinand concentration in solution 5 does not change appreciably. The results of the analyses of solutions 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of the added (spiked) determinand from 100% may give an indication of the presence of interfering substances.

3. Evaluation of Results

The raw experimental results should be sent direct to the Department of the Environment for evaluation together with the results obtained for the standards used to establish the calibration curve in each batch of analyses. However, for those laboratories wishing to make the calculations themselves, the details are given below.

3.1 Convert all results to concentrations as described in the method. Deduct the first of the 2 blank values (solution 1) from each of the other solution values.

3.2 Calculate the mean concentration of the n results for each solution.

3.3 Calculate the standard deviation, s, of the n results for each solution from:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

where x_i = the result from the ith batch
$\bar{x}$ = the mean value of x.

3.4 Calculate the within-batch standard deviation, s_w, of the blank from:

$$s_w = \sqrt{\frac{\sum (x_{ii} - x_{2i})^2}{2n}}$$

where x_{ii} = the 1st blank result (solution 1) from the ith batch

where x_{2i} = the 2nd blank result (solution 2) from the ith batch.

3.5 Calculate the mean percentage recovery, R, of the spiked determinand in solution 6 from:

$$R = \frac{(\bar{x}_6 - \bar{x}_5)}{C} \times 100$$

where x_5 = the mean value of the results for solution 5,

where $\bar{x}_6$ = the mean value of the results for solution 6,

and C is the concentration increase due to the addition (spike).

3.6 Summarise the results as in the following table:

Solution	No of results n	Mean Concentration	Standard Deviation	Mean Recovery %
2 Blank				–
3 Low Standard				–
4 High Standard				–
5 Sample of				–
6 Solution 5 + spike				–

The appropriate sample description should be entered in the space for solution 5. The standard deviations from step 3.3 are entered for solutions 3 to 6.

F Analytical Quality Control

Once the methods have been put into routine operation, many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check sources of inaccuracy should be made regularly. Many tests are possible and they should be used as appropriate. As a minimum, it is suggested that at least one sample of suitable concentration in each batch of samples be analysed at least in duplicate. Inclusion of a quality control standard of concentration unknown to the actual operator is also useful. Plots of the deviation between multiplicate samples, or of the control standard result, will facilitate detection of inadequate precision and allow the standard deviation of routine analytical results to be estimated. For further information see Refs 5 and 6.

References

1. *Formaldehyde, Methanol and Related Compounds in Raw, Waste and Potable Waters, 1982 Tentative Methods.* HMSO, London, in this series.

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3. *The Determination of Methane and other Hydrocarbon gases in Water 1988.* HMSO, London, in this series.

4. *The Tentative Identification of Volatilizable Organic Compounds by LTPRI etc 1988.* HMSO, London, in this series.

5. British Standards BS 5700 to 5703 inclusive and 5750.

6. Davey D J and Hunt D T E. The use of cumulative Sum Chartes in Analytical Quality Control. *WRC Technical Report TR174,* Water Research Centre, Medmenham, 1982.

Address for Correspondence

However thoroughly a method may be tested there is always the possibility of a user encountering a hitherto unreported problem or wishing to report observations.

Correspondence about these methods should be addressed to:

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The Standing Committee of Analysts
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