Environment Agency

The determination of metaldehyde in waters using chromatography with mass spectrometric detection (2009)

Methods for the Examination of Waters and Associated Materials

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Methods for the Examination of Waters and Associated Materials

This booklet contains six methods for the determination of metaldehyde in waters.

Each method has been validated in only one laboratory and consequently details are included for information purposes only as examples of the type of procedures that are available to analysts. Information on routine multi-laboratory use of these methods would be welcomed to assess their full capabilities.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as illustrative examples. Equivalent products are available and it should be understood that the performance characteristics of the methods might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

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About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soil (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials" and their continuing revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are

1 General principles of sampling and accuracy of results
2 Microbiological methods
3 Empirical and physical methods
4 Metals and metalloids
5 General non-metallic substances
6 Organic impurities
7 Biological methods
8 Biodegradability and inhibition methods
9 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with this booklet are listed at the back of the booklet.

Publication of new or revised methods will be notified to the technical press. If users wish to receive copies or advance notice of forthcoming publications, or obtain details of the index of methods then contact the Secretary on the Agency's internet web-page (http://www.environment-agency.gov.uk/nls) or by post.

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary. Users should ensure they are aware of the most recent version of the draft they seek.

Dr D Westwood
Secretary
December 2004

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and regulations made under this Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted

Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; "Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory", 1992, produced by the Royal Society of Chemistry; "Guidelines for Microbiological Safety", 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and "Safety Precautions, Notes for Guidance" produced by the Public Health Laboratory Service. Another useful publication is "Good Laboratory Practice" produced by the Department of Health.

The determination of metaldehyde in waters using chromatography with mass spectrometric detection

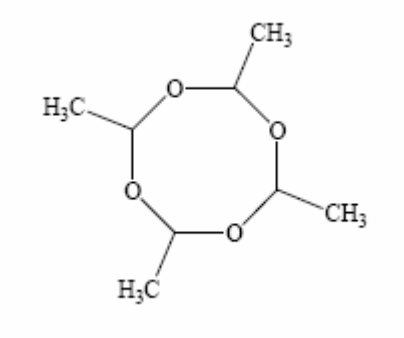
Introduction

Metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetraoxocanemetacetaldehyde) is an oligomer of acetaldehyde (CH_3CHO) see Figure I1. The compound is used principally as a contact molluscicide, commonly applied in the form of slug pellets. The compound is a white, crystalline solid which sublimes, with a melting point between 110 - 120 °C and boiling point of 246 °C.

Damage to crops from slugs and snails is a growing problem in the UK, which has been compounded in recent years by the mild, wet climate, and changes in agricultural practices. It is estimated that over 8 % of the area covered by arable crops is treated with metaldehyde. The principal crops at risk include wheat, potatoes and oil seed-rape.

Recent concerns have been raised that relatively high levels of metaldehyde (due to its persistence in the environment and its moderate solubility in water) are being found in surface waters. There is evidence indicating that some existing water treatment processes may be inadequate in reducing residual levels (up to 8 µg/l) found in some waters to below the regulatory limit for drinking water (i.e. 0.1 µg/l).

Figure I1 Structure of metaldehyde



Molecular weight of 176

A The determination of metaldehyde in waters using gas chromatography with mass spectrometric detection

A1 Performance characteristics of the method

A1.1	Substances determined	Metaldehyde.
A1.2	Type of sample	Raw waters, drinking waters and process waters.
A1.3	Basis of method	Metaldehyde is extracted from samples using solid phase extraction cartridges. Following elution using dichloromethane, the eluate is analysed using gas chromatography with mass spectrometric detection in selective ion monitoring mode.
A1.4	Range of application	Typically, up to 1 µg/l. The range may be extended (see section A7.11, note h).
A1.5	Standard deviation	See Table A1.
A1.6	Limit of detection	Typically, 0.005 µg/l, based on low level (0.01 µg/l) standard solutions.
A1.7	Bias	See Table A1.
A1.8	Interferences	Any co-extracted material which has a GC retention time similar to metaldehyde and which gives a detector response at the monitored masses will interfere. However, none are known at the m/z values selected.

A2 Principle

The sample, after dilution if required, is passed through a pre-conditioned styrene divinyl benzene polymer solid phase extraction column where metaldehyde is retained. The cartridge is then dried and eluted with dichloromethane. The extract is evaporated to a small volume and an internal standard added. Metaldehyde is determined by GC-MS using split-less injection and a single quadrupole mass spectrometer operating in SIM mode.

A3 Hazards

Methanol is highly flammable and metaldehyde is flammable. These compounds should be handled away from sources of ignition. Metaldehyde, methanol, dichloromethane, and deuterated 1,4-dichlorobenzene, i.e. 1,4-dichlorobenzene-d_4, should be considered toxic and handled with adequate ventilation and appropriate personal protective equipment.

A4 Reagents

All reagents should be of sufficient purity that they do not give rise to interferences during the analysis and distilled, deionised or similar grade water should be used throughout. A procedural blank should be run with each batch of samples.

A4.1 Methanol.

A4.2 Dichloromethane.

A4.3 Stock calibration metaldehyde standard solution (1000 mg/l). Dissolve 50.0 ± 0.5 mg of metaldehyde in 50.0 ml of methanol (A4.1). Cap and mix well. A stock AQC calibration metaldehyde standard solution (1000 mg/l) should also be prepared from a different batch or supplier of the metaldehyde used to prepare the stock calibration metaldehyde standard solution (1000 mg/l). These solutions may be stored between 1 - 10 °C for up to one year.

A4.4 Working calibration metaldehyde standard solution (1 mg/l). Add 50.0 ± 0.5 µl of stock calibration metaldehyde standard solution (A4.3) to 50.0 ml of dichloromethane (A4.2). Cap and mix well. An AQC working calibration metaldehyde standard solution (10 mg/l) should also be prepared from a different batch or supplier of the metaldehyde used to prepare the stock calibration metaldehyde standard solution (A4.3). In addition, an AQC working recovery calibration metaldehyde standard solution (10 mg/l) should also be prepared from the same batch or supplier of the metaldehyde used to prepare the stock calibration metaldehyde standard solution (A4.3). These solutions may be stored between 1 - 10 °C for up to one year.

A4.5 Stock internal standard solution (2000 mg/l). For example, add 200 ± 1 mg of deuterated 1,4-dichlorobenzene, i.e. 1,4-dichlorobenzene-d_4, to approximately 90 ml of methanol (A4.1) and mix well. Make to 100.0 ml with methanol. Mix well. This solution may be stored between 1 - 10 °C for up to two years. Pentachloronitrobenzene may also be suitable.

A4.6 Working internal standard solution (50 mg/l). Add 1.00 ± 0.01 ml of stock internal standard solution (A4.5) to approximately 35 ml of methanol (A4.1) and mix well. Make to 40.0 ml with methanol. Mix well. This solution may be stored between 1 - 10 °C for up to one year.

A5 Apparatus

In addition to normal laboratory glassware the following may be required.

A5.1 Solid phase cartridges. Baker SDB1 200 mg (3 ml) cartridges were used to generate the performance data. Other similar cartridges may be used, but their performance would need to be verified.

A5.2 Blow-down apparatus. Any device (capable of being set at 45 ± 3 °C) that can direct a gentle stream of air into a vial.

A5.3 Gas chromatograph. Fitted with an auto-injector, mass spectrometer capable of at least unit resolution and operating in SIM mode, with a data station. The suitability of the equipment will need to be evaluated.

The following conditions have been used in generating performance data.

Column:	HP5-MS, 30 m x 0.25 mm diameter, 0.25 µm film thickness.
Carrier gas:	Helium, 30 ml per second.
Injection temperature:	300 °C.
Injection volume:	1 µl (pulsed split-less injection)
Temperature programme:	Oven Initial temperature at 35 ° C for 1 minute, then 20 °C per minute to 260 °C, hold time for 0.5 minute,
Purge flow:	50 ml per minute.
Purge time:	1 minute.
Total flow:	52.7 ml per minute.

Using these conditions, the following apply

Compound	Approximate retention time (minutes)	Ions monitored	
		Target	Qualifier
1,4-dichlorobenzene-d_4	6.1	150.0	152.0
metaldehyde	6.3	45.0	89.0

Equivalent equipment and conditions may be used. See Figure A1 for a typical chromatogram.

A6 Sample collection and preparation

Samples may be taken in amber glass or plastic (for example polyethyleneterephthalate, PET) bottles with caps lined with an appropriate inert material. The volume taken should allow for at least one repeat analysis, i.e. a minimum of 500 ml of sample should be collected. Limited stability data indicate that samples may be stored for up to 21 days in PET bottles (or up to 35 days in glass bottles). See Tables A2 and A3.

A7 Analytical procedure

Step	Procedure	Notes
A7.1	Condition a solid phase cartridge (A5.1) using 10 ml of methanol (A4.1). Elute the cartridge and discard the eluate. Note a.	(a) Do not allow the cartridge to dry out at this stage, i.e. do not allow the meniscus of the solvent to fall below the level of the cartridge packing material.
A7.2	Add 2 ml of water and elute the cartridge. Discard the eluate. Note a.	
A7.3	Add Vs ml (typically, 250 ml) of sample (note b) and elute the cartridge. Discard the eluate. Note a.	(b) If the sample contains particulate matter, it may need to be filtered.
A7.4	Add 2 ml of water and elute the cartridge. Discard the eluate. Dry the cartridge by passing air through it. Note c.	(c) This may take approximately 45 minutes.

A7.5 Add 1 ml of dichloromethane (A4.2) and elute the cartridge collecting the eluate in a suitable vial. Add a further 1 ml quantity of dichloromethane and eluate the cartridge, combining the dichloromethane fractions.

Pass air through the cartridge and collect any residual dichloromethane in the vial.

A7.6 Remove the vial from the cartridge and evaporate (A5.2) the combined dichloromethane fraction to Vc ml (typically, 0.5 ml).

A7.7 Add 5.0 µl (note d) of working internal standard solution (A4.6) to the vial and cap. Mix well. The solution is now ready for GC-MS determination. Note e.

(d) This equates to 0.25 µg of internal standard.

(e) At this stage the solution may be stored in a refrigerator for up to one month before the GC-MS determination begins.

A7.8 Add 0.50 ml (note f) of working calibration metaldehyde standard solution (A4.4) to a suitable vial. Add 5.0 µl (note d) of working internal standard solution (A4.6) to the vial and cap. Mix well. See note g.

(f) This equates to 0.5 µg of metaldehyde.

(g) Since the standard solution is not eluted through the SPE cartridge, recovery estimates may need to be determined.

A7.9 Set up the GC-MS system according to manufacturer's instructions and construct a calibration graph of response versus amount of metaldehyde, monitoring the ions given in section A5.3.

A7.10 Analyse blank, AQC and recovery solutions using the entire procedure described in sections A7.1 - A7.7 replacing the sample with water.

A7.11 Analyse the sample extract and from the calibration graph, obtain the amount, Av, of metaldehyde in the vial and then calculate the concentration, Cs, of metaldehyde in the sample. Note h.

(h) If the response exceeds the calibration range, the analysis may be repeated using a smaller amount of sample (A7.3) and making the volume to 250 ml with water, or taking an aliquot of the volume, Vc ml (A7.6) and making to a known volume, i.e. 0.50 ml.

A8 Calculation

From the calibration graph determine the amount, Av, of metaldehyde in the vial and determine the concentration, Cs, in the sample using the equation:

$$Cs = (Av \times DF \times 1000) / Vs \quad \mu g/l$$

Where

Cs is the concentration (µg/l) of metaldehyde in the sample;
Av is the amount (µg) of metaldehyde obtained from the graph;
Vs is the volume (ml) of sample analysed (A7.3); and
DF is the dilution factor (A7.11, note h) if appropriate.

Blank correction is not normally necessary but should be considered if the blank control sample is above 0.005 ug/l.

Figure A1 Typical chromatogram of metaldehyde
(concentration of 1 µg/l)

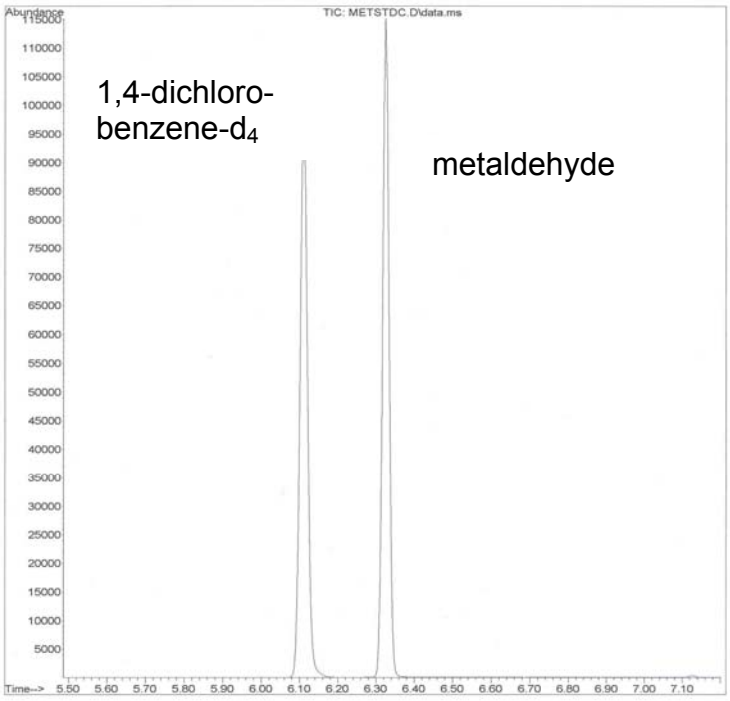


Table A1 Performance data

Concentration (nominal value) (µg/l)	Total standard deviation (degrees of freedom) (µg/l)	Relative standard deviation (%)	Recovery (%)	Bias (%)
0.01 (0.01)	0.001 (13)	13.2		1.3
0.095 (0.1)	0.008 (12)	9.0		-5.0
0.741 (0.8)	0.067 (16)	9.0		-7.3
Borehole sample spiked at 0.01 and 0.1 µg/l	0.011 (13) 0.012(13)	13.3 10.6	100.8	
Surface final sample spiked at 0.1 µg/l	0.002 (10) 0.009 (14)	12.9 7.6	106.5	
Surface raw sample spiked at 0.1 µg/l	0.001 (16) 0.01 (12)	10.2 8.5	105.8	

Performance data provided by Anglian Water Services, Huntingdon Central Laboratory

Table A2 Stability data in glass bottles at room temperature

	Metaldehyde concentrations (µg/l) at	
	Day 0	Day 35
	0.165	0.128
	0.159	0.147
	0.153	0.156
	0.137	0.165
	0.162	0.151
	0.150	0.162
Mean	0.15433	0.15150
Standard deviation	0.01015	0.01331
Pooled standard deviation	0.01184	
Mean absolute difference	0.00283	
Standard error (difference)	0.00683	
t statistic	0.41463	
Degrees of freedom	10	
Critical value (0.05)	2.22814	

The difference between the means is not statistically significant

Table A3 Stability data in PET bottles at room temperature

	Metaldehyde concentrations (µg/l) at	
	Day 0	Day 21
	0.162	0.157
	0.154	0.155
	0.155	0.146
	0.159	0.160
	0.166	0.153
	0.171	0.164
Mean	0.16117	0.15583
Standard deviation	0.00655	0.00618
Pooled standard deviation	0.00637	
Mean absolute difference	0.00533	
Standard error (difference)	0.00368	
t statistic	1.45036	
Degrees of freedom	10	
Critical value (0.05)	2.22814	

The difference between the means is not statistically significant

B The determination of metaldehyde in waters using gas chromatography with mass spectrometric detection

B1 Performance characteristics of the method

B1.1	Substances determined	Metaldehyde.
B1.2	Type of sample	Raw waters (treated and ground waters) and drinking waters.
B1.3	Basis of method	Metaldehyde is extracted from samples using solid phase extraction cartridges. Following elution using an ethyl acetate:acetone mixture and *iso*-octane, the eluate is analysed using gas chromatography with mass spectrometric detection (GC-MS) in selective ion monitoring (SIM) mode.
B1.4	Range of application	Typically, up to 0.5 µg/l. The range may be extended (see section B8.11, note i).
B1.5	Standard deviation	See Table B1.
B1.6	Limit of detection	Typically, 0.003 µg/l, based on low level (0.01 µg/l) spiked samples.
B1.7	Bias	See Table B1.

B2 Principle

The sample, after dilution if required, is passed through a pre-conditioned polymeric solid phase extraction column where metaldehyde is retained. The cartridge is then dried and eluted with an ethyl acetate:acetone solvent mixture followed by *iso*-octane. An internal standard is then added to the extract. Metaldehyde is determined by GC-MS using split-less injection and mass spectrometric detection operating in SIM mode.

B3 Interferences

Any compound that elutes under the conditions used, and has similar gas chromatographic and mass spectrometric properties to metaldehyde will interfere.

The procedure has been tested upon a variety of raw water matrices and no evidence has been recorded that interfering compounds are routinely encountered, even in samples containing high levels of humic substances. See also section B10 on use of tandem MS for additional confirmation.

B4 Hazards

Metaldehyde is considered harmful as a solid material, although in most laboratories it is obtained as a dilute solution in a common solvent.

Methanol is toxic and flammable; ethyl acetate and acetone are irritant and flammable and *iso*-octane is flammable. Solutions of the internal standard, obtained in dichloromethane are considered to be irritant and dangerous to the environment.

Waste solvents should be discarded according to documented procedures.

Appropriate safety procedures should be followed at all times.

B5 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interfering peaks in the chromatographic analysis. This should be checked for each batch of chemicals and reagents and verified by running procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography or pesticide use and normal analytical grade materials are normally suitable unless otherwise stated and details of preparation are given, where appropriate. Water should be distilled, deionised or of similar grade quality. Reagents should be stored appropriately in accordance with supplier's instructions and in suitable vessels.

B5.1 Ethyl acetate.

B5.2 Acetone.

B5.3 *iso*-Octane (2,2,4-trimethylpentane).

B5.4 Dichloromethane.

B5.5 Methanol.

B5.6 Stock calibration metaldehyde standard solution (100 mg/l). Dissolve 50.0 ± 0.5 mg of metaldehyde in 500.0 ml of acetone (B5.2). Cap and mix well. This solution may be stored between 4 ± 2 °C for up to six months.

B5.7 Working calibration metaldehyde standard solution (0.5 mg/l). Add 500 ± 5 µl of stock calibration metaldehyde standard solution (B5.6) to approximately 90 ml of acetone (B5.2). Mix well. Make to 100.0 ml with acetone. Cap and mix well. This solution may be stored at 4 ± 2 °C for up to one month.

B5.8 Stock internal standard solution (4000 mg/l). For example, add 40 ± 1 mg of deuterated 1,4-dichlorobenzene, i.e. 1,4-dichlorobenzene-d_4, to approximately 9 ml of dichloromethane (B5.4) and mix well. Make to 10.0 ml with dichloromethane. Mix well. This solution may be stored at 4 ± 2 °C for up to one year. Pentachloronitrobenzene may also be suitable.

B5.9 Intermediate internal standard solution (40 mg/l). Add 250 ± 2.5 µl of stock internal standard solution (B5.8) to approximately 20 ml of dichloromethane (B5.4) and mix well. Make to 25.0 ml with dichloromethane. Mix well. This solution may be stored between 4 ± 2 °C for up to 15 months.

B5.10 Working internal standard solution (0.5 mg/l). Add 1.25 ± 0.05 ml of intermediate internal standard solution (B5.9) to approximately 90 ml of *iso*-octane (B5.3)

and mix well. Make to 100.0 ml with *iso*-octane. Mix well. This solution may be stored between 4 ± 2 °C for up to three months.

B5.11 Ethyl acetate:acetone solvent mixture (1:1 v/v). Mix together 100 ± 5 ml of ethyl acetate (B5.1) and 100 ± 5 ml of acetone (B5.2).

B6 Apparatus

In addition to normal laboratory glassware the following may be required.

B6.1 Solid phase cartridges. Strata-X 200 mg (3 ml) cartridges were used to generate the performance data. Other similar cartridges may be used, but their performance would need to be verified.

B6.2 Gas chromatograph. Fitted with a heated injection system, mass spectrometer capable of operating with a resolution of 5000 (i.e. 10 % valley definition) and operating in SIM mode, with a data station. The suitability of the equipment will need to be evaluated.

The following conditions have been used in generating performance data.

Column:	DB5-MS, 30 m x 0.25 mm diameter, 0.25 µm film thickness.
Injector type:	Split:split-less
Carrier gas:	Helium, 2 ml per minute.
Injection volume:	2 µl.
Injector temperature:	250 °C.
Temperature programme:	Oven
	Initial temperature at 70 ° C for 5 minutes, then
	55 °C per minute to 250 °C, hold time for 0.75 minute,
Injector conditions:	
Mode:	Split-less
Initial Temperature:	250 °C.
Purge flow:	50 ml per minute.
Purge time:	2 minutes.
Total flow:	54.2 ml per minute.

Using these conditions, the following apply

Compound	Approximate retention time (minutes)	Ions monitored	
		Target	Qualifier
1,4-dichlorobenzene-d_4	5.5	150.0	115.0
metaldehyde	6	89.0	45.0

Equivalent equipment and conditions may be used. See Figures B1 - B5 for typical chromatograms.

B7 Sample collection and preparation

Samples may be collected in one-litre clear glass bottles with a screw cap lid containing a polytetrafluoroethylene liner. Samples may be stored in the refrigerator at 4 ± 2 °C and may be extracted up to two weeks after sampling.

Stability trials have shown that samples of metaldehyde in medium hardness borehole water (spiked at 100 ng/l) and stored for 14 days at 4 ± 2 °C, undergo no significant degradation. See Table B2.

B8 Analytical procedure

Step	Procedure	Notes
B8.1	Condition (note a) a solid phase cartridge (B6.1) using a cartridge volume of methanol (B5.5) i.e. approximately 2 ml. Elute the column and discard the eluate. Repeat this procedure with a further 2 ml quantity of methanol. Note b.	(a) Conditioning the column specifically identified in section B6.1 is to remove potential impurities rather than to activate it. (b) For columns other than those specifically identified in section B6.1, it may be necessary not to allow the cartridge to dry out at this stage, i.e. allow the meniscus of the solvent fall below the level of the cartridge packing material.
B8.2	Add a cartridge volume of water, i.e. approximately 2 ml, and elute the column, note a. Discard the eluate. Add a further 2 ml quantity of water and elute the column. Discard the eluate. Note b.	
B8.3	Add Vs ml (typically, 250 ± 10 ml) of sample (note c) and elute the column. Discard the eluate. Note b.	(c) If the sample contains particulate material, it may need to be filtered.
B8.4	Add 3.0 ± 0.2 ml of water and elute the column. Discard the eluate. Dry the column by passing air or nitrogen through it. Note d.	(d) This may take approximately 20 minutes.
B8.5	Add 0.40 ± 0.04 ml of the ethyl acetate:acetone solvent mixture (B5.11) and elute the column collecting the eluate in a suitable vial.	
B8.6	Add 1.00 ± 0.05 ml of *iso*-octane (B5.3) and eluate the column, combining the elution fractions. Dry the column by passing air through it and collect any residual solvent in the vial.	
B8.7	Remove the vial from the column and add 50 ± 5 µl of working internal standard solution (B5.10) see note e, to the vial and cap. Mix well. The solution is now ready for GC-MS determination. Note f.	(e) This is equivalent to 25 ng of internal standard. (f) At this stage the solution may be stored in a refrigerator for up to

		one month before the GC-MS determination begins.
B8.8	Prepare six calibrations solutions, For example, add 0, 10, 25, 50, 125 and 250 µl of the working calibration metaldehyde standard solution (B5.7) to separate vials. See note g. To each vial, add the same volume of *iso*-octane (B5.3) shown in section B8.6 and 50 ± 5 µl of working internal standard solution (B5.10). See note e. Cap the vial and mix well. The solutions are now ready for GC-MS determination, see note h.	(g) These six solutions are equivalent to 0, 20, 50, 100, 250 and 500 ng/l (based on a sample volume of 250 ml) and contain 0, 5, 12.5, 62.5 and 125 ng of metaldehyde respectively. (h) Since these standard solutions are not eluted through SPE cartridges, recovery estimates may need to be determined by adding appropriate amounts of standard solution (B5.7) to separate 250 ml quantities of water and processing the solutions as described in sections B8.1 - B8.7.
B8.9	Set up the GC-MS system according to manufacturer's instructions and construct a calibration graph of response versus concentration, monitoring the ions referred to in section B6.2.	
B8.10	Analyse blank and AQC solutions using the entire procedure described in sections B8.1 - B8.7 replacing the sample as appropriate.	
B8.11	Analyse the sample extract and from the calibration graph calculate the amount of metaldehyde in the sample. Note i.	(i) If the response exceeds the calibration range, the analysis may be repeated using a smaller quantity of sample (B8.3) or the volume of solvent (B8.6) increased.

B9 Calculation

From the calibration graph and using the response ratio for the internal standard between standards and samples, the amount, CE, of metaldehyde in the extract is given by

$$CE = (SR \times SC \times SISR) / (STDR \times STDISR)$$

where
SR is the sample response;
SC is the amount of the calibration standard in the extract;
SISR is the sample internal standard response;
STDR is the standard response; and
STDISR is the standard internal standard response.

The concentration of metaldehyde in the sample, CS, is given by

CS = CE / Vs

where
Vs is the volume of sample taken (section B8.3).

B10 Confirmatory tests

The procedure has been tested using a variety of water sources and there is no evidence of problems caused by interferences. However, gas chromatography triple quadrupole mass spectrometry (GC-MSMS) provides a high degree of specificity, because any selected ion (as would be measured in a standard “single quad” GC-MS) is allowed to undergo further collision, to produce a product ion, which is subsequently detected. The analyser acts as a filter, such that potential interferences are less likely to follow the same path of pre-cursor to product ion formation.

A suitable confirmatory procedure for the analysis of metaldehyde is to investigate the fragmentation of ions identified from the single MS procedure. Specifically, the 89 m/z response and, much lower response at m/z 117, can be used as the basis of multiple reaction monitoring analysis. The following multiple reaction monitoring transitions have been found suitable for the analysis of metaldehyde by GC-MSMS:

Transition 1	89 to 45
Transition 2	117 to 45

The collision energies are dependent on the particular instrumentation used.

Figure B1 Typical GC-MS chromatogram
(100 ng/l standard solution)

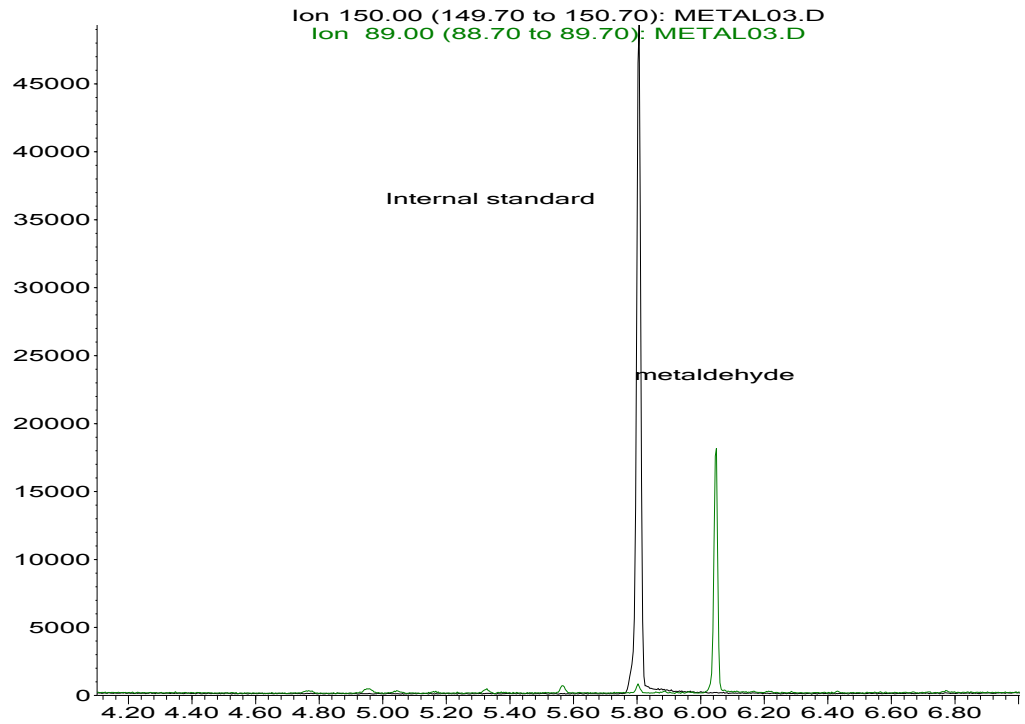


Figure B2 **Typical GC-MS chromatogram**
(100 ng/l AQC sample comprising borehole water)

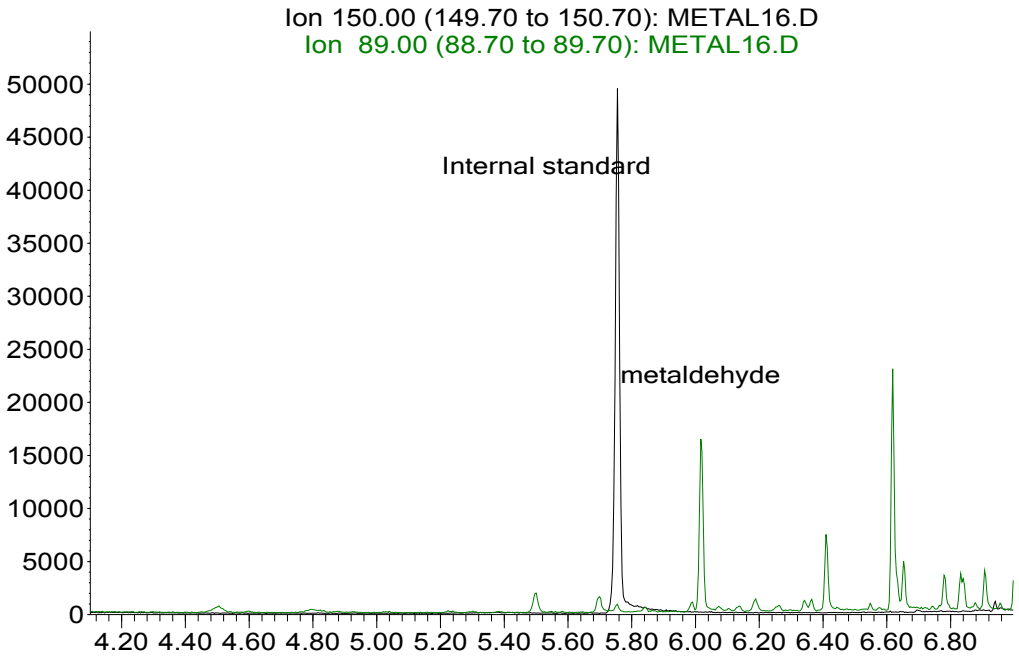


Figure B3 **Typical GC-MS chromatogram**
(29 ng/l in raw water)

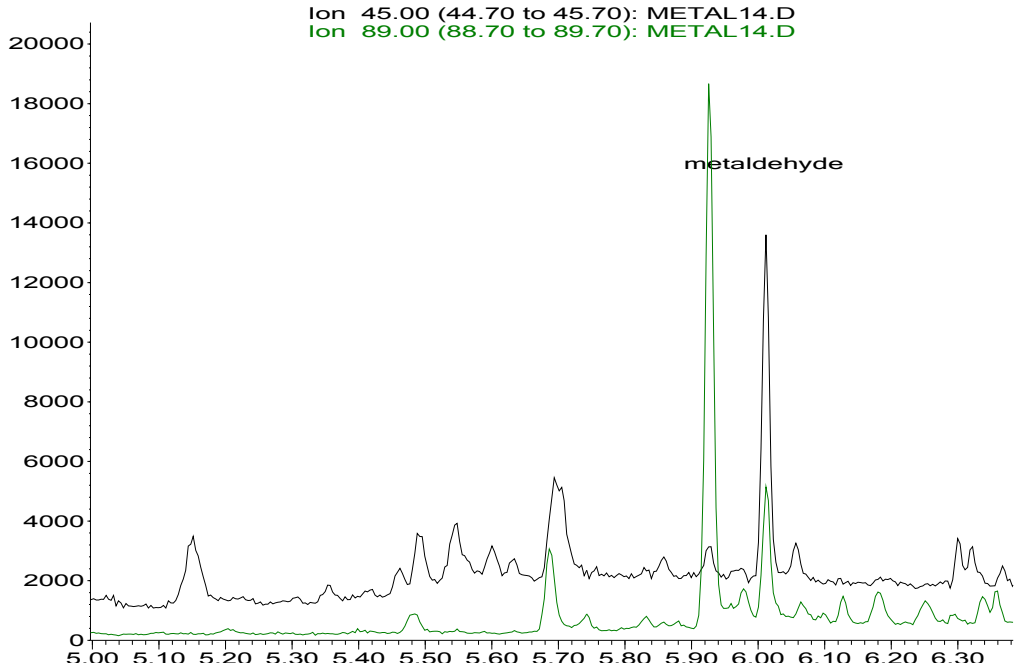


Figure B4 **Typical GC-MS chromatogram**
(2.1 ng/l in tap water - just below quoted detection limit)

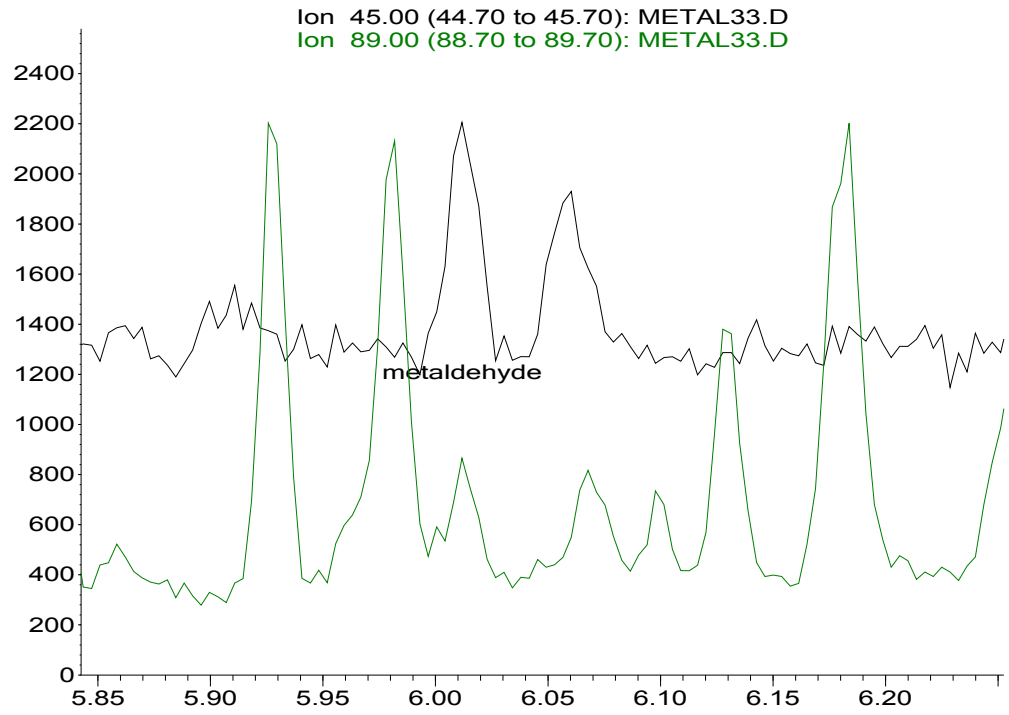


Figure B5 **Typical GC-MSMS chromatogram**
(confirmatory trace - 120 ng/l standard solution)

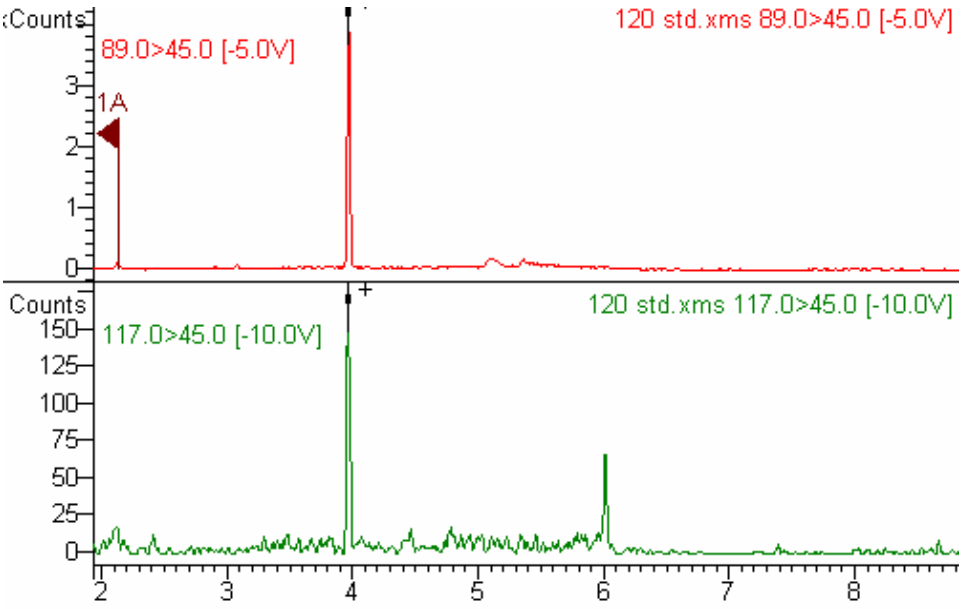


Table B1 Performance data

Spiking level (ng/l)	Standard solution					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	9.3	0.24	0.54	0.59	6.3	13
100	97.9	2.80	1.36	3.12	3.2	22
400	407.8	9.65	7.10	11.98	2.9	20
Spiking level (ng/l)	Soft purified water					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	10	0.49	0.31	0.58	5.8	21
100	98	2.39	2.49	3.45	3.5	17
400	401.3	15.97	15.75	22.44	5.6	18
Spiking level (ng/l)	Medium hardness borehole water					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	10.1	0.78	0.48	0.91	9.1	21
100	98.6	2.79	6.66	7.22	7.3	13
400	399.8	15.51	30.20	33.95	8.5	14
Spiking level (ng/l)	Hard borehole water					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	11.8	0.41	0.57	0.70	5.9	15
100	105.3	2.28	2.90	3.69	3.5	16
400	428.6	8.08	11.67	14.19	3.3	15

"Blank" samples spiked to low levels (nominal 10 ng/l)
Sw is within-batch standard deviation
Sb is between- batch standard deviation
St is total standard deviation
RSD is relative standard deviation
DOF is degrees of freedom
Data provided by Severn Trent Laboratories (STL)

Table B2 Stability data

Replicate analyses	Days storage				
(ng/l)	**0**	**4**	**7**	**11**	**14**
1	96.6	95.6	99.7	100.6	96.1
2	98.7	98.0	99.1	96.6	96.3
3	97.6	98.2	100.2	98.9	103.4
4	100.6	95.9	97.3	96.6	97.7
5	98.5	99.9	97.4	97.8	99.6
6	98.0	96.9	96.9	96.9	98.7
7	95.8	101.7	96.4	98.8	95.3
8	98.1	99.8	98.8	98.8	96.7
9	99.8	99.6	96.2	99.2	101.9
Mean	98.17	98.39	97.99	98.22	98.40
Standard deviation	1.468	2.028	1.482	1.367	2.756
Variance	2.155	4.112	2.197	1.868	7.598

C The determination of metaldehyde in waters using gas chromatography with mass spectrometric detection

C1 Performance characteristics of the method

C1.1	Substances determined	Metaldehyde.
C1.2	Type of sample	Raw waters, ground waters and drinking waters.
C1.3	Basis of method	Samples are buffered to a pH value of 7 and extracted using solid phase extraction cartridges. Following elution using ethyl acetate, the eluate is analysed using gas chromatography with mass spectrometric detection (GC-MS) in selective ion monitoring (SIM) mode.
C1.4	Range of application	Typically, up to 0.4 µg/l. The range may be extended (see section C8.9, note g).
C1.5	Standard deviation	See Table C1.
C1.6	Limit of detection	Typically, 0.006 µg/l.
C1.7	Bias	See Table C1.

C2 Principle

The sample, after dilution if required, is buffered to a pH value of 7. The buffered sample is then passed through a pre-conditioned solid phase extraction column where metaldehyde is retained. The cartridge is then eluted with buffer, and then dried and eluted with ethyl acetate. An internal standard is then added to the extract. Metaldehyde is determined by GC-MS using split-less injection and mass spectrometric detection operating in SIM mode.

C3 Interferences

Any compound that elutes under the conditions used, and has similar gas chromatographic and mass spectrometric properties to metaldehyde will interfere.

The selection of several mass ion fragments reduces the risk of positive bias.

C4 Hazards

Metaldehyde is considered harmful as a solid material, although in most laboratories it is obtained as a dilute solution in a common solvent.

Methanol is toxic and flammable; ethyl acetate and acetone are irritants and flammable. Solutions of the internal standard, obtained in dichloromethane are considered to be irritant and dangerous to the environment.

Waste solvents should be discarded according to documented procedures.

Appropriate safety procedures should be followed at all times.

C5 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interfering peaks in the chromatographic analysis. This should be checked for each batch of chemicals and reagents and verified by running procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography or pesticide use and normal analytical grade materials are normally suitable unless otherwise stated and details of preparation are given, where appropriate. Water should be distilled, deionised or of similar grade quality. Reagents should be stored appropriately in accordance with supplier's instructions and in suitable vessels.

C5.1 Ethyl acetate.

C5.2 Acetone.

C5.3 Methanol.

C5.4 Stock calibration metaldehyde standard solution (500 mg/l). Dissolve 50.0 ± 0.5 mg of metaldehyde in 100.0 ml of acetone (C5.2). Cap and mix well. This solution may be stored between 5 ± 3 °C for up to one year.

C5.5 Intermediate calibration metaldehyde standard solution (10 mg/l). Add 2000 ± 10 µl of stock calibration metaldehyde standard solution (C5.4) to approximately 90 ml of ethyl acetate (C5.1). Mix well. Make to 100.0 ml with acetone. Cap and mix well. This solution may be stored between 5 ± 3 °C for up to three months.

C5.6 Working calibration metaldehyde standard solutions. For example, in the concentration range 0.024, 0.05, 0.1, 0.24 and 0.4 mg/l, for example add 60, 125, 250, 600 and 1000 µl of intermediate calibration metaldehyde standard solution (C5.5) to approximately 20 ml of ethyl acetate (C5.1) contained in separate 25 ml volumetric flasks. To each flask, add 250 µl of stock internal standard solution (C5.8) i.e. 2.5 µg of internal standard (this equates to 0.1 mg/l). Mix well. Make to 25.0 ml with ethyl acetate. Cap and mix well. This solution may be stored between 5 ± 3 °C for up to three months.

C5.7 Stock internal standard solution (500 mg/l). For example, dissolve 50.0 ± 0.5 mg of 1,4-dichlorobenzene in 100.0 ml of ethyl acetate (C5.1). Cap and mix well. This solution may be stored between 5 ± 3 °C for up to one year. Pentachloronitrobenzene may also be suitable.

C5.8 Intermediate internal standard solution (10 mg/l). For example, add 2000 µl of stock internal standard solution (C5.7) in 100.0 ml of ethyl acetate (C5.1). Cap and mix well. This solution may be stored between 5 ± 3 °C for up to three months.

C5.9 Working internal standard solution (1 mg/l). For example, add 200 µl of stock internal standard solution (C5.7) in 100.0 ml of ethyl acetate (C5.1). Cap and mix well. This solution may be stored between 5 ± 3 °C for up to three months.

C5.10 Buffer solution (pH value of 7). Add 5.420 ± 0.001 g of potassium dihydrogen phosphate and 7.772 ± 0.001 g of disodium hydrogen phosphate to approximately 1500 ml

of water. Mix well to dissolve. Make to 2000 ml with water. Mix well. This solution may be stored at room temperature for up to one month.

C6 Apparatus

In addition to normal laboratory glassware the following may be required.

C6.1 Solid phase cartridges. 200 mg (3 ml) Isolute ENV cartridges were used to generate the performance data. Other similar cartridges may be used, but their performance would need to be verified.

C6.2 Gas chromatograph. Fitted with a heated injection system, mass spectrometer operating in SIM mode, with a data station. The suitability of the equipment will need to be evaluated.

The following conditions have been used in generating performance data.

Column:	DB5-MS, 30 m x 0.25 mm diameter, 0.25 µm film thickness.
Carrier gas:	Helium, 1.5 ml per minute.
Injection volume:	1 µl.
Injector temperature:	250 °C.
Temperature programme:	Oven Initial temperature at 50 ° C for 0.9 minutes, then 10 °C per minute to 110 °C, then 50 °C per minute to 240 °C
Injector conditions:	
Mode:	Split-less
Initial Temperature:	250 °C.
Purge flow:	50 ml per minute.
Purge time:	2 minutes.
Total flow:	54.2 ml per minute.

Using these conditions, the following apply

Compound	Approximate retention time (minutes)	Ions monitored	
		Target	Qualifier
1,4-dichlorobenzene	5.0	150.0	115.0
metaldehyde	6.0	89.1	117.1, 45.1

Equivalent equipment and conditions may be used.

C7 Sample collection and preparation

Samples may be collected in one-litre clear glass bottles with a screw cap lid containing a polytetrafluoroethylene liner. Samples may be stored in the refrigerator at 3 ± 2 °C and may be extracted up to two weeks after sampling. Stability data is presented in Tables C2 and C3. Sample extracts may be stored at 5 ± 3 °C for up to 10 days.

C8 Analytical procedure

Step	Procedure	Notes
C8.1	To 1000 ± 10 ml of sample, add 25.0 ± 0.5 ml of buffer solution (C5.10).	
C8.2	Condition (note a) a solid phase cartridge (C6.1) using 3.0 ± 0.5 ml of methanol (C5.3) followed by 3.0 ± 0.5 ml of buffer solution (C5.10). Elute the column and discard the eluate. See note a.	(a) Do not allow the meniscus of the solvent to fall below the level of the cartridge packing material.
C8.3	Add the buffered sample (C8.1) to the cartridge and elute the column, notes a and b. Discard the eluate. Add 3.0 ± 0.5 ml of buffer solution (B5.10) and elute the column. Discard the eluate. Dry the cartridge by applying a vacuum to the cartridge.	(b) Do not elute too quickly as this may lead to poor recoveries. A suitable flow rate may be approximately 10 ml per minute.
C8.4	Add 1.00 ± 0.05 ml of ethyl acetate (C5.1) to the dried cartridge and leave for approximately 5 minutes. Elute the column under gravity, collecting the eluate in a suitable tube. See note a.	
C8.5	Add 1.00 ± 0.05 ml of ethyl acetate (C5.1) and elute the column under gravity, collecting the eluate in the same tube.	
C8.6	Remove the tube from the column and add 100 ± 2 µl of working internal standard solution (C5.9) see note c, to the tube and cap. Mix well. The solution is now ready for GC-MS determination, see note d.	(c) This is equivalent to 0.1 µg of internal standard added to the tube. (d) At this stage the solution may be stored in a refrigerator for up to 10 days before the GC-MS determination begins.
C8.7	Set up the GC-MS system according to manufacturer's instructions. Using the five working calibration metaldehyde standard solutions (C5.6) construct a calibration graph of response versus amount of metaldehyde, monitoring the ions referred to in C6.2. See notes e and f.	(e) These five solutions are equivalent 0.024, 0.05, 0.1, 0.24 and 0.4 µg of metaldehyde respectively. (f) Since these standard solutions are not eluted through SPE cartridges, a recovery estimate may need to be determined by adding 0.1 µl of standard

solution (C5.7) to 1000 ml of water and processing the solutions as described in sections C8.1 - C8.6.

C8.8 Analyse blank and AQC solutions using the entire procedure described in sections C8.1 - C8.6 replacing the sample as appropriate.

C8.9 Analyse the sample extract (C8.6) and from the calibration graph, determine the amount of metaldehyde in the sample extract and hence in the sample, note g.

(g) If the response exceeds the calibration range, the analysis may be repeated using a smaller quantity of sample (C8.1) or the volume of solvent (sections C8.4 and C8.5) increased.

Figure C1 Typical GC-MS chromatogram (0.1 µg/l standard)

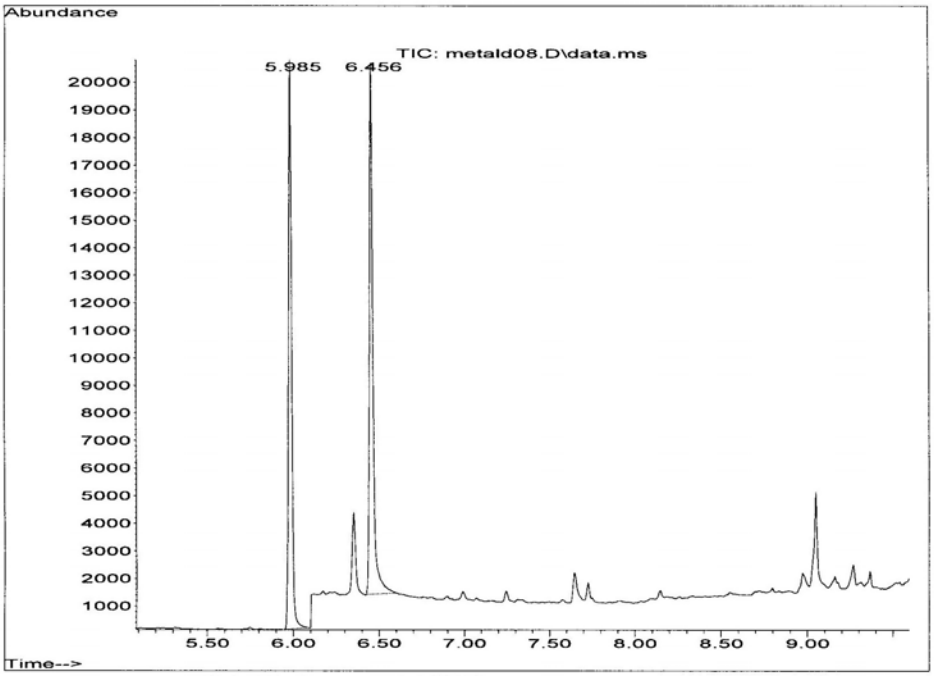


Figure C2 Typical GC-MS chromatogram (0.034 µg/l in river water sample)

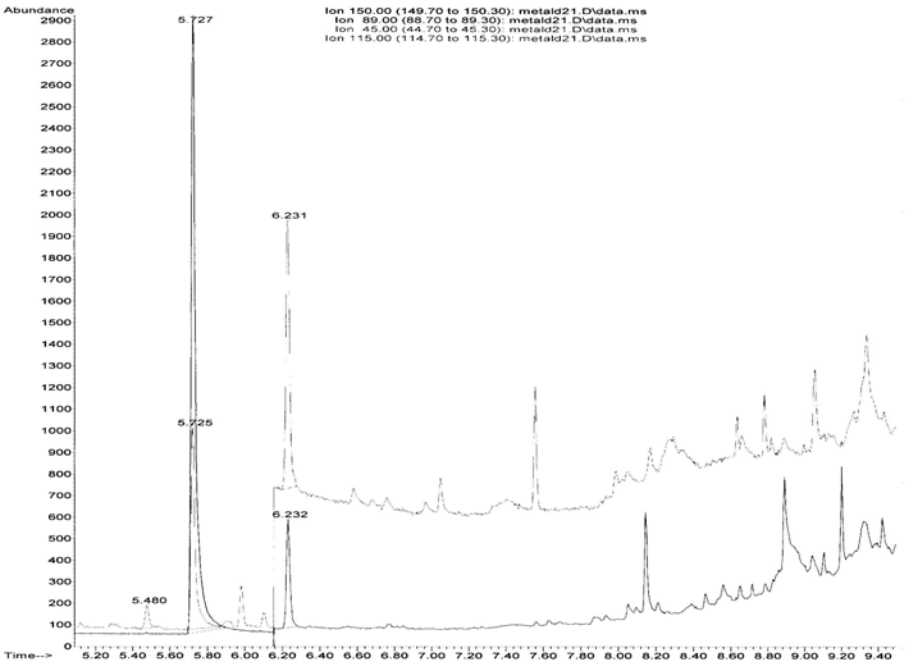


Figure C3 Typical GC-MS chromatogram (0.006 µg/l in hard water sample)

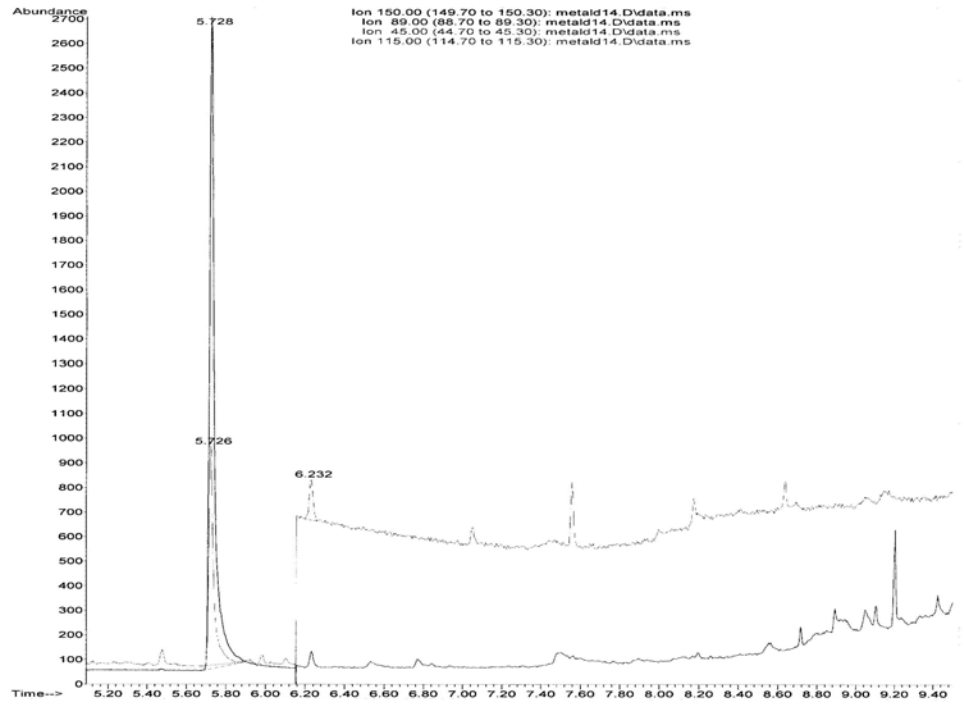


Table C1 Performance data

Spiking level (µg/l)	Standard solution					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	0	0	0	0	0	0
0.08	0.082	0.004	0.003	0.005	5.9	18
0.36	0.352	0.011	0.015	0.019	5.4	14

Spiking level (µg/l)	Hard surface water					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	0.156	0.007	0.0109	0.013	8.3	13
0.1	0.099	0.025	0	0.024	9.4	21

Spiking level (µg/l)	Hard borehole water					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	0	0	0	0	0	n/a
0.1	0.103	0.008	0.004	0.009	8.45	20

Spiking level (µg/l)	Soft borehole water					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	0.032	0.002	0.005	0.005	16.5	11
0.1	0.102	0.008	0.01	0.010	9.69	15

Spiking level (µg/l)	Soft Surface water					
	Mean	Sw	Sb	St	RSD(%)	DOF
Blank	0.038	0.002	0.005	0.006	14.5	12
0.1	0.095	0.006	0.005	0.008	6.1	18

"Blank" samples not spiked
Sw is within-batch standard deviation
Sb is between- batch standard deviation
St is total standard deviation
RSD is relative standard deviation
DOF is degrees of freedom

Data provided by Northumbrian Water Scientific Services, Hanningfield Laboratory (NWL)

Table C2 Stability data on metaldehyde solutions

	Day 0	Day 35
	0.165	0.128
	0.159	0.147
	0.153	0.156
	0.137	0.165
	0.162	0.151
	0.150	0.162
Mean	0.1543	0.1515
Standard deviation	0.0102	0.0133

Stored at room temperature in amber glass bottles.
Measurements expressed in µg/l.
The difference between the means is not significant

Table C3 Stability data on metaldehyde solutions

	Day 0	Day 35
	0.162	0.157
	0.154	0.155
	0.155	0.146
	0.159	0.160
	0.166	0.153
	0.171	0.164
Mean	0.1612	0.1558
Standard deviation	0.0066	0.0062

Stored at room temperature in amber plastic (PET) bottles.
Measurements expressed in µg/l.
The difference between the means is not significant

D The determination of metaldehyde in waters using liquid chromatography with on-line enrichment and mass spectrometric detection

D1 Performance characteristics of the method

D1.1	Substances determined	Metaldehyde.
D1.2	Type of sample	Raw and treated waters.
D1.3	Basis of method	Metaldehyde is analysed by direct aqueous injection with on-line enrichment using liquid chromatography (LC) with mass spectrometric (MS) detection. A triple quadruple mass spectrometer is used employing positive ion electrospray with multiple reaction monitoring (MRM).
D1.4	Range of application	Typically, up to 0.2 µg/l. The range may be extended (see section D8.5, note c).
D1.5	Standard deviation	See Table D1.
D1.6	Limit of detection	Typically, 0.007 µg/l, based on low level (0.02 µg/l) standard solutions.
D1.7	Bias	See Table D1.

D2 Principle

To the sample, after dilution if required, is added a known amount of internal standard Metaldehyde is then determined by LC with MS detection using positive ion electrospray and a triple quadruple mass spectrometer with MRM.

D3 Interferences

Any compound that elutes under the conditions used, and has similar chromatographic and mass spectrometric properties to metaldehyde will interfere.

The MS-MS technique of using a specific precursor to product ion reduces the risk of positive bias.

D4 Hazards

Metaldehyde is considered harmful as a solid material, although in most laboratories it is obtained as a dilute solution in a common solvent.

Methanol is toxic and flammable; acetone is irritant and flammable. Solutions of the internal standard, deuterated atrazine, i.e. atrazine-d_5, are considered to be irritant and dangerous to the environment. Formic acid is corrosive and causes burns, contact with eyes and skin should be prevented.

Waste solvents should be discarded according to documented procedures.

Appropriate safety procedures should be followed at all times.

D5 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interfering peaks in the chromatographic analysis. This should be checked for each batch of chemicals and reagents and verified by running procedural blanks with each batch of samples analysed. Analytical grade solvents for high performance liquid chromatography or pesticide use are normally suitable unless otherwise stated. Water should be distilled, deionised or of similar grade quality. Reagents should be stored appropriately in accordance with supplier's instructions and in suitable vessels.

D5.1 Acetone.

D5.2 Methanol.

D5.3 Formic acid.

D5.4 Sodium thiosulphate solution (18 g/l). Dissolve 9.00 ± 0.01 g of sodium thiosulphate pentahydrate in approximately 450 ml of water. Mix well. Make to 500 ml with water. Mix well. This solution is used to de-chlorinate the sample and may be stored at 5 ± 3 °C for up to one month.

D5.5 Stock solution of synthetic tap water. Add 0.90 ± 0.01 g of sodium thiosulphate pentahydrate, 2.00 ± 0.01 g of magnesium sulphate heptahydrate and 2.00 ± 0.01 g of calcium nitrate tetrahydrate to approximately 450 ml of water. Mix well to dissolve. When dissolved, make to 500 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to one month.

D5.6 Working solutions of synthetic tap water. To 6 separate 500 ml volumetric flasks (each containing 200 ± 10 ml of water) add 2.00 ± 0.01 ml of stock solution of synthetic tap water (D5.5). These solutions should be prepared on the day of use.

D5.7 Stock calibration metaldehyde standard solution (100 mg/l). Dissolve 10.0 ± 0.1 mg of metaldehyde in 100.0 ml of acetone (D5.1). Cap and mix well. This solution may be stored between 5 ± 3 °C for up to 12 months.

D5.8 Spiking calibration metaldehyde standard solution (0.2 mg/l). Add 100 ± 1 µl of stock calibration metaldehyde standard solution (B5.7) to approximately 9 ml of methanol (D5.2). Mix well. Make to 50.0 ml with methanol. Cap and mix well. This solution may be stored between 5 ± 3 °C for up to six months.

D5.9 Working calibration metaldehyde standard solutions. For example in the concentration range of 0.02 - 0.2 µg/l. To each of the six working solutions of synthetic tap water (D5.6) add 0, 20, 50, 100, 150 and 200 µl of spiking calibration metaldehyde standard solution (D5.8). Mix well. Each flask containing 200 ml of synthetic tap water contains 0, 0.004, 0.01, 0.02, 0.03 and 0.04 µg of metaldehyde. To each flask, add 50 ± 1 µl of internal standard spiking solution (D5.11). Mix well. These solutions contain 0.02 µg of internal standard. These solutions should be prepared on the day of use.

D5.10 Stock internal standard solution (100 mg/l). For example, add 10.0 ± 0.1 mg of deuterated atrazine to approximately 90 ml of methanol (D5.2) and mix well. Make to 100.0 ml with methanol. Mix well. This solution may be stored between 5 ± 3 °C for up to 12 months.

D5.11 Spiking internal standard solution (0.4 mg/l). Add 200 ± 2 µl of stock internal standard solution (D5.10) to approximately 40 ml of methanol (D5.2) and mix well. Make to 50.0 ml with methanol. Mix well. This solution may be stored between 5 ± 3 °C for up to 12 months.

D6 Apparatus

In addition to normal laboratory glassware the following may be required.

D6.1 Liquid chromatograph. Fitted with a quadrupole mass spectrometer capable of operating in MRM mode, with a data station. The suitability of the equipment will need to be evaluated.

The following conditions have been used in generating performance data.

SPE column	Zorbax SB-C18, 30 m x 2.1 mm internal diameter, 3.5 µm film thickness.
SPE mobile phase:	See table below..
Column:	Zorbax SB-C18, 150 m x 2.1 mm internal diameter, 3.5 µm film thickness.
Mobile phase A:	Water containing 0.25 % formic acid.
Mobile phase B:	Methanol containing 0.25 % formic acid.

Chromatography conditions.

Injection volume:	900 µl.
Flow:	0.4 ml per minute.

Time (minutes)	Mobile phase A (%)	Mobile phase B (%)
0	98	2
7.5	98	2
8.5	60	40
9.5	60	40
14.5	40	60
18	40	60
19	5	95
19.1	5	95
20	98	2

Using these conditions, the following apply

Compound	Approximate retention time (minutes)	Ions monitored	
		Precursor	Product
metaldehyde	10.8	199	67
atrazine-d_5	14.5	221	179

Equivalent equipment and conditions may be used. See Figures D1 and D2.

D7 Sample collection and preparation

Samples may be collected in one-litre clear glass bottles with a screw cap lid containing a polytetrafluoroethylene liner. Samples should be collected in bottles containing 1 ml of sodium thiosulphate solution (D5.4). Samples should be extracted as soon as possible after collection, but may stored in the refrigerator at 5 ± 3 °C and may be extracted up to 10 days after collection.

D8 Analytical procedure

Step	Procedure	Notes
D8.1	Add Vs ml (typically, 200 ± 10 ml) of sample (note a) to a 500 ml bottle. To this bottle add 50 ± 1 µl spiking internal standard solution (D5.11) see note b.	(a) If the sample contains particulate material, it may need to be filtered. (b) This equates to 0.02 µg of internal standard in 200 ml of sample.
D8.2	The solution is now ready for LC-MS determination.	
D8.3	Set up the LC-MS system according to manufacturer's instructions and construct a calibration graph of response versus amount of metaldehyde in the working calibration metaldehyde standard solutions (D5.9) monitoring the ions referred to in section D6.1.	
D8.4	Analyse blank and AQC solutions using the entire procedure described in sections D8.1 - D8.2 replacing the sample with water.	
D8.5	Analyse the sample extract and from the calibration graph, obtain the amount, Av, of metaldehyde in the bottle and then calculate the concentration, Cs, of metaldehyde in the sample. Note c.	(c) If the response exceeds the calibration range, the analysis may be repeated using a smaller volume of sample (D8.1) and making the volume to 200 ml with water.

D9 Calculation

From the calibration graph determine the amount, Av, of metaldehyde in the vial and determine the concentration, Cs, in the sample using the equation:

$$Cs = (Av \times DF \times 1000) / Vs \quad \mu g/l$$

Where

Cs is the concentration (µg/l) of metaldehyde in the sample;
Av is the amount (µg) of metaldehyde obtained from the graph;
Vs is the volume (ml) of sample analysed (D8.1);
DF is the dilution factor (D8.5, note c) if appropriate.

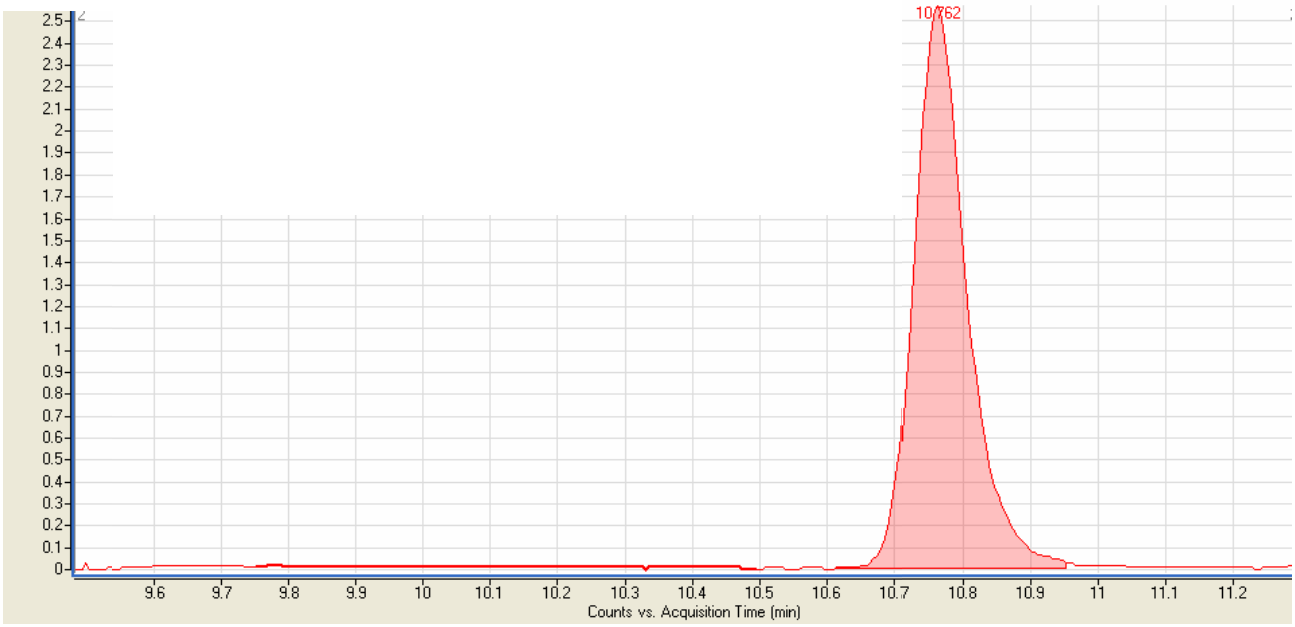
Table D1 Performance data

Sample with (spiking level, µg/l)	Water samples					
	Mean	Sw	Sb	St	RSD(%)	DOF
Standard solution (0.40)	0.047	0.002	0.003	0.004	8.4	12
Standard solution (0.16)	0.180	0.010	0.009	0.014	7.9	17
Untreated river water	0.01	0.001	0.002	0.002		10
Untreated river water spike (0.1)	0.111	0.007	0.006	0.009	8.0	16
Treated river water	0.025	0.001	0.003	0.004		11
Treated river spike (0.1)	0.127	0.009	0.009	0.012	9.6	16
Soft upland reservoir water	0.020	0.001	0.003	0.003		12
Soft upland reservoir water (0.1)	0.125	0.009	0	0.009	7.0	20
Hard river water	0.013	0.005	0.002	0.002		10
Hard river water spike (0.1)	0.116	0.009	0	0.009	7.8	20

Sw is within-batch standard deviation
Sb is between- batch standard deviation
St is total standard deviation
RSD is relative standard deviation
DOF is degrees of freedom
Data provided by Alcontrol Laboratories

Figure D1 **Typical chromatogram of metaldehyde transition**
MRM 199.1 → 67.0

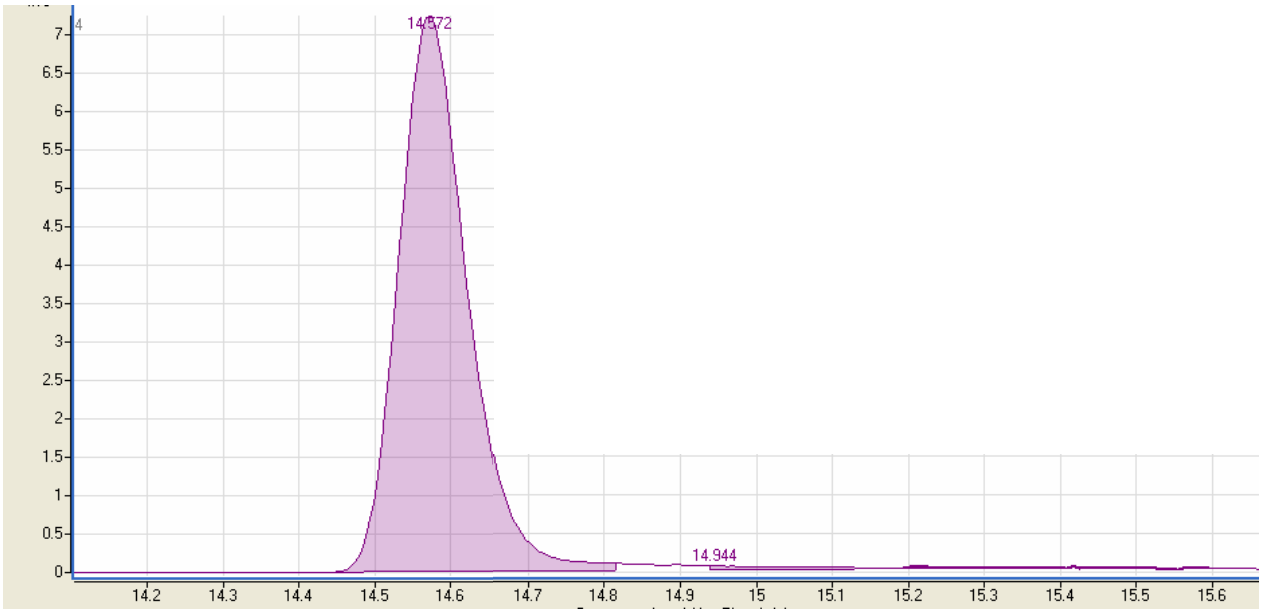
Counts x 100



Time (minutes)

Figure D2 **Typical chromatogram of internal standard transition**
MRM 221.1 → 179.0

Counts x 1000



Time(minutes)

E The determination of metaldehyde in waters using gas chromatography with mass spectrometric detection

E1 Performance characteristics of the method

E1.1	Substances determined	Metaldehyde.
E1.2	Type of sample	River waters, borehole waters, saline waters and drinking waters.
E1.3	Basis of method	Samples are extracted using solid phase extraction cartridges. Following elution using an acetone:ethyl acetate mixture, the eluate is analysed using gas chromatography with mass spectrometric detection (GC-MS) in selective ion monitoring (SIM) mode.
E1.4	Range of application	Typically, up to 0.4 µg/l. The range may be extended (see section E8.10, note h).
E1.5	Standard deviation	See Table E1.
E1.6	Limit of detection	Typically, 0.004 µg/l.
E1.7	Bias	See Table E1.

E2 Principle

The sample, after dilution if required, is passed through a pre-conditioned solid phase extraction column where metaldehyde is retained. The cartridge is then eluted with a 1:1 v/v acetone:ethyl acetate mixture. An internal standard is then added to the extract. Metaldehyde is determined by GC-MS using cool on-column injection and mass spectrometric detection operating in SIM mode.

E3 Interferences

Any compound that elutes under the conditions used, and has similar gas chromatographic and mass spectrometric properties to metaldehyde will interfere.

The selection of several mass ion fragments reduces the risk of positive bias.

E4 Hazards

Metaldehyde is considered harmful as a solid material, although in most laboratories it is obtained as a dilute solution in a common solvent.

Methanol and 2,2,4-trimethylpentane are toxic and flammable; ethyl acetate and acetone are irritants and flammable. Solutions of the internal standard, obtained in dichloromethane are considered to be irritant and dangerous to the environment.

Waste solvents should be discarded according to documented procedures.

Appropriate safety procedures should be followed at all times.

E5 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interfering peaks in the chromatographic analysis. This should be checked for each batch of chemicals and reagents and verified by running procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography or pesticide use and normal analytical grade materials are normally suitable unless otherwise stated and details of preparation are given, where appropriate. Water should be distilled, deionised or of similar grade quality. Reagents should be stored appropriately in accordance with manufacturer's instructions and in suitable vessels, and should be allowed to reach room temperature before use.

E5.1 Ethyl acetate.

E5.2 Acetone.

E5.3 Methanol.

E5.4 2,2,4-trimethylpentane.

E5.5 Aqueous methanol (10 % v/v). Mix one volume of methanol (E5.3) with nine volumes of water. Mix well. This solution may be stored at 20 °C for up to one month.

E5.6 Acetone:ethyl acetate mixture (1:1 v/v). Mix equal volumes of acetone (E5.2) and ethyl acetate (E5.1). This solution may be stored at 20 °C for up to one month.

E5.7 Stock calibration metaldehyde standard solution (1000 mg/l). Dissolve 50.0 ± 0.5 mg of metaldehyde in 50.0 ml of acetone (E5.2). Cap and mix well. An AQC stock calibration metaldehyde standard solution (1000 mg/l) should also be prepared from a different batch or supplier of the metaldehyde used to prepare the stock calibration metaldehyde standard solution (1000 mg/l). These solutions may be stored at -20 °C for up to one year.

E5.8 Intermediate calibration metaldehyde standard solution (10 mg/l). Add 1000 ± 10 µl of stock calibration metaldehyde standard solution (E5.7) to approximately 90 ml of acetone (E5.2). Mix well. Make to 100.0 ml with acetone. Cap and mix well. An AQC stock calibration metaldehyde standard solution (10 mg/l) should also be prepared from a different batch or supplier of the metaldehyde used to prepare the stock calibration metaldehyde standard solution (10 mg/l). This solution may be stored at -20 °C for up to six months.

E5.9 Working calibration metaldehyde standard solution (0.10 mg/l). Add 500 ± 5 µl of intermediate calibration metaldehyde standard solution (E5.8) to approximately 40 ml of acetone (E5.2) contained in a 50 ml volumetric flask. Mix well. Make to 50.0 ml with acetone. Cap and mix well. An AQC stock calibration metaldehyde standard solution (0.10 mg/l) should also be prepared from a different batch or supplier of the metaldehyde used to prepare the stock calibration metaldehyde standard solution (0.10 mg/l). These solutions may be stored at -20 °C for up to three months.

E5.10 Working calibration metaldehyde standard solutions. For example, in the concentration range of 0.01, 0.025, 0.05, 0.1, 0.2 and 0.4 µg/l. Into a series of six 250 ml bottles, add 10, 25, 50 100, 200 and 400 µl of working calibration metaldehyde standard solution (E5.9). This equates to 0.001, 0.0025, 0.005, 0.01, 0.02 and 0.04 µg of metaldehyde in each bottle. To each bottle add 100 ml of water. Cap and mix well. These solutions should be made on the day of use.

E5.11 Stock internal standard solution (100 mg/l). For example, dissolve 25.0 ± 0.5 mg of deuterated 1,3,5-trichlorobenzene-d_3 in 250.0 ml of acetone (E5.2). Cap and mix well. This solution may be available commercially. This solution may be stored at -20 °C for up to five years. Pentachloronitrobenzene may also be suitable.

E5.12 Working internal standard solution (0.2 mg/l). Add 100 ± 1 µl of stock internal standard solution (E5.11) in 50.0 ml of acetone (E5.2). Cap and mix well. This solution may be stored at -20 °C for up to six months.

E6 Apparatus

In addition to normal laboratory glassware the following may be required.

E6.1 Solid phase cartridges. 200 mg (3 ml) Strata X cartridges were used to generate the performance data. Other similar cartridges may be used, but their performance would need to be verified.

E6.2 Evaporator. Zymark Turbo Vap automated low volume evaporator set at 40 ± 2°C. Equivalent systems may be used.

E6.3 Gas chromatograph. Fitted with a heated injection system, mass spectrometer operating in SIM mode, with a data station. The suitability of the equipment will need to be evaluated.

The following conditions have been used in generating performance data.

Column:	HP-5MS 5% Phenyl methyl siloxane, 30 m x 0.25 mm diameter, 0.25 µm film thickness.
Carrier gas:	Helium, 1.0 ml per minute.
Injection volume:	1 µl.
Injector temperature:	Oven track mode.
Temperature programme:	Oven Initial temperature at 60 ° C for 5.0 minutes, then 10 °C per minute to 100 °C, then 50 °C per minute to 300 °C hold time for 7 minutes,
Injector conditions:	
Mode:	Cool on-column – oven track
Initial Temperature:	63 °C.

Using these conditions, the following apply

Compound	Approximate retention time (minutes)	Ions monitored	
		Target	Qualifier
metaldehyde	7.0	45	89
1,3,5-trichlorobenzene-d_3	9.5	183	185

Equivalent equipment and conditions may be used. See Figures E1 and E2.

E7 Sample collection and preparation

Samples may be collected in 250 ml clear plastic bottles with a screw cap lid containing a polytetrafluoroethylene liner. Samples may be stored in the refrigerator at 4 ± 2 °C and may be extracted up to 28 days after sampling.

E8 Analytical procedure

Step	Procedure	Notes
E8.1	Wash a solid phase cartridge (E6.1) using 3.0 ± 0.5 ml of 2,2,4-trimethylpentane (E5.4) and discard the eluate. Dry the cartridge under vacuum. Condition the cartridge using 3.0 ± 0.5 ml of acetone:ethyl acetate mixture (E5.6) allowing the solvent to elute under gravity. Discard the eluate. Note a.	(a) Do not allow the meniscus of the solvent to fall below the level of the cartridge packing material.
E8.2	Condition the cartridge using 3.0 ± 0.5 ml of water allowing the solvent to elute under gravity. Discard the eluate. Note a.	
E8.3	Elute the column (note b) with 100 ± 5 ml of sample discarding the eluate (note a). Wash the cartridge with 3.0 ± 0.5 ml of aqueous methanol (E.5.5) discarding the eluate. Dry the cartridge by applying a vacuum to the cartridge, note c.	(b) Do not elute too quickly as this may lead to poor recoveries. A suitable flow rate may be approximately 10 ml per minute. (c) This may take approximately 90 minutes. If the cartridge is not dried thoroughly, then poor recoveries may occur.
E8.4	Add 3.0 ± 0.5 ml of acetone:ethyl acetate mixture (E5.6) and allow the solvent to soak into the cartridge for about one minute before eluting the column and collecting the eluate, note a. Add 3.0 ± 0.5 ml of 2,2,4-trimethylpentane (E5.4) and allow the solvent to soak into the cartridge for about one minute before eluting the column allowing the solvent to elute under gravity. Collect the eluate in the same receiving tube.	

E8.5	Remove the tube from the column and add 50 ± 5 µl of working internal standard solution (E5.12) note d. Mix well to ensure the two solvent phases mix together. Note e.	(d) This equates to 0.01 µg of internal standard. (e) If the extract appears cloudy, this may indicate the presence of water in the mixture requiring the sample to be re-extracted.
E8.6	Evaporate (E6.2) the extract to 200 ± 50 µl. The solution is now ready for GC-MS determination, see note f.	(f) At this stage the solution may be stored in a refrigerator for up to 14 days before the GC-MS determination begins.
E8.7	Using the working calibration metaldehyde standard solutions (E5.10) in place of 100 ml samples repeat steps E8.1 - E8.6 .	
E8.8	Set up the GC-MS system according to manufacturer's instructions. Using the six working calibration metaldehyde standard solutions (E5.10) construct a calibration graph of response versus amount of metaldehyde, note g, moniotoring the ions referred to in E6.3.	(g) These six solutions are equivalent to 0.001, 0.0025, 0.005, 0.01, 0.02 and 0.04 µg of metaldehyde respectively.
E8.9	Analyse blank and AQC solutions using the entire procedure described in sections E8.1 - E8.6 replacing the sample as appropriate.	
E8.10	Analyse the sample extract and from the calibration graph, obtain the amount, Av, of metaldehyde in the vial and then calculate the concentration, Cs, of metaldehyde in the sample. Note h.	(h) If the response exceeds the calibration range, the analysis may be repeated using a smaller volume of sample (E8.3) and making the volume to 100 ml with water.

E9 Calculation

From the calibration graph determine the amount, Av, of metaldehyde in the vial and determine the concentration, Cs, in the sample using the equation:

$$Cs = (Av \times DF \times 1000) / Vs \quad \mu g/l$$

Where

Cs is the concentration (µg/l) of metaldehyde in the sample;
Av is the amount (µg) of metaldehyde obtained from the graph;
Vs is the volume (ml) of sample analysed (E8.3);
DF is the dilution factor (E8.10, note h) if appropriate.

Table E1 Performance data

Solution (Spiking concentration, µg/l)	Precision (%)	Trueness (%)	LOD (µg/l)	DOF
Blank water (0.005)			0.003	
Low standard (0.04)	14.6	98.9		13
High standard (0.36)	14.1	103.0		13
Treated river water (0.1)	19.0	101.1		14
Untreated river water (0.1)	12.6	102.5		15
Borehole water (0.1)	11.9	102.0		14
Saline water* (0.1)	12.5	99.9		14
Final effluent water (0.1)	16.2	102.1		16

Trueness calculated from 100 x (conc of spiked water - conc of un-spiked water) / (spiking conc).
Precision calculated from 2 x relative total standard deviation.
DOF is degrees of freedom
* Water containing 15 g/l sodium chloride.
Data provided by Thames Water

Figure E1 Typical chromatogram
(0.1 µg/l standard solution)

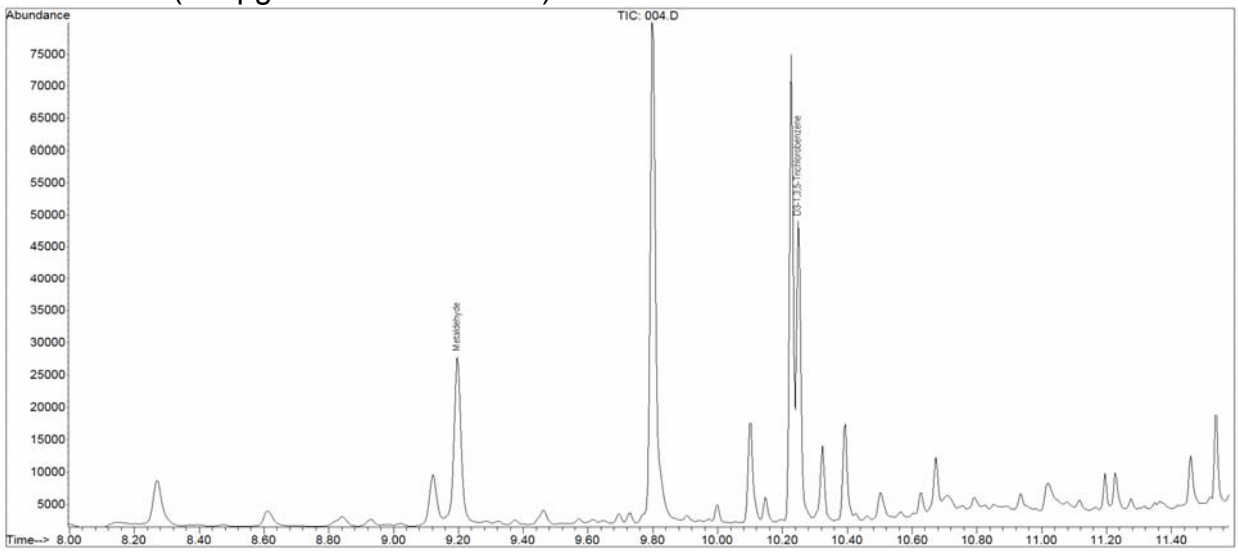
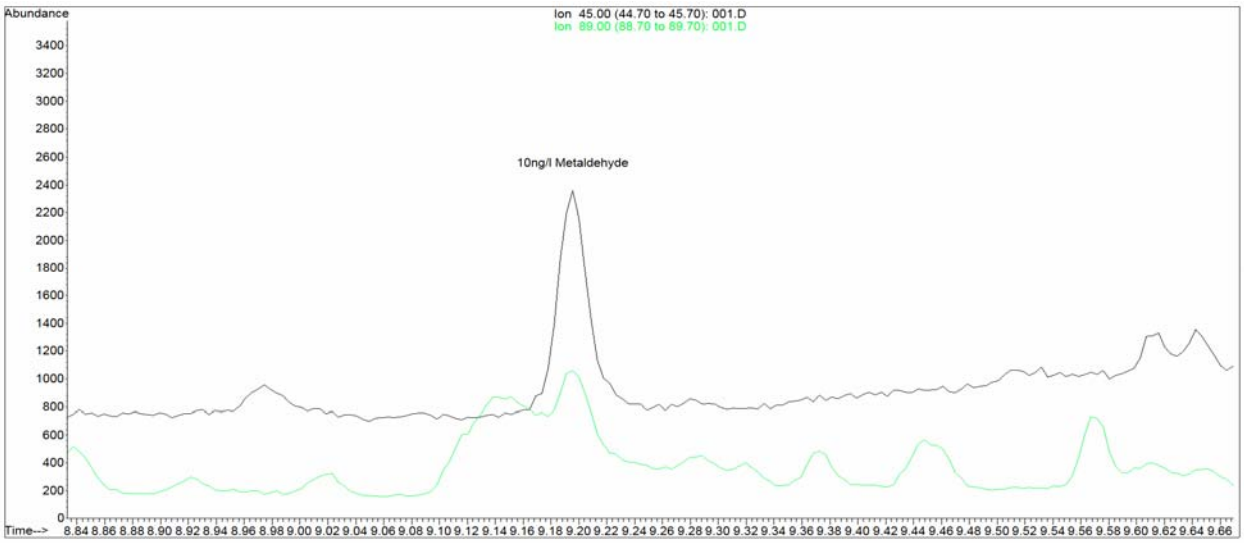


Figure E2 Typical extracted ion chromatogram
(0.01 µg/l standard solution)



F The determination of metaldehyde in waters using gas chromatography with mass spectrometric detection

F1 Performance characteristics of the method

F1.1	Substances determined	Metaldehyde.
F1.2	Type of sample	Potable waters, surface waters and ground waters.
F1.3	Basis of method	Metaldehyde is extracted from samples using solid phase extraction cartridges. Following elution using dichloromethane, the eluate is analysed using gas chromatography with mass spectrometric detection (GC-MS) in selective ion monitoring (SIM) mode.
F1.4	Range of application	Typically, up to 0.5 µg/l. The range may be extended (see section F8.10, note h).
F1.5	Standard deviation	See Table F1.
F1.6	Limit of detection	Typically, 0.004 µg/l, based on low level (0.020 µg/l) spiked samples.
F1.7	Bias	See Table F1.

F2 Principle

The sample, after dilution if required, is passed through a pre-conditioned polymeric solid phase extraction column where metaldehyde is retained. The cartridge is then dried and eluted with dichloromethane. An internal standard is then added to the extract. Metaldehyde is determined by GC-MS using split-less injection and mass spectrometric detection operating in SIM mode.

F3 Interferences

Any compound that elutes under the conditions used, and has similar gas chromatographic and mass spectrometric properties to metaldehyde will interfere.

The comparison of ion ratios assists in differentiating metaldehyde from interfering peaks in the chromatogram. See Figure F1.

F4 Hazards

Metaldehyde is considered harmful as a solid material, although in most laboratories it is obtained as a dilute solution in a common solvent.

Methanol is toxic and flammable. Solutions of the internal standard, obtained in dichloromethane are considered to be irritant and dangerous to the environment.

Waste solvents should be discarded according to documented procedures.

Appropriate safety procedures should be followed at all times.

F5 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interfering peaks in the chromatographic analysis. This should be checked for each batch of chemicals and reagents and verified by running procedural blanks with each batch of samples analysed. Solvents suitable for high performance liquid chromatography or pesticide use and normal analytical grade materials are normally suitable unless otherwise stated and details of preparation are given, where appropriate. Water should be distilled, deionised or of similar grade quality. Reagents should be stored appropriately in accordance with supplier's instructions and in suitable vessels.

F5.1 Dichloromethane.

F5.2 Methanol.

F5.3 Stock calibration metaldehyde standard solution (1000 mg/l). Dissolve 50.0 ± 0.5 mg of metaldehyde in 50.0 ml of methanol (F5.2). Cap and mix well. This solution may be stored at less than -5 °C for up to 1 year.

F5.4 Working calibration metaldehyde standard solution (0.5 mg/l). Add 50 ± 1 µl of stock calibration metaldehyde standard solution (F5.3) to approximately 90 ml of methanol (F5.2). Mix well. Make to 100.0 ml with methanol. Cap and mix well. This solution may be stored at 5 ± 3 °C for up to six months.

F5.5 Stock internal standard solution (1000 mg/l). For example, add 50 ± 1 mg of deuterated 1,4-dichlorobenzene, i.e. 1,4-dichlorobenzene-d_4, to approximately 45 ml of methanol (F5.2) and mix well. Make to 50.0 ml with methanol. Mix well. This solution may be stored at less than -5 °C for up to one year. Pentachloronitrobenzene may also be suitable.

F5.6 Working internal standard solution (0.5 mg/l). Add 50 ± 1 µl of stock internal standard solution (F5.5) to approximately 90 ml of dichloromethane (F5.1) and mix well. Make to 100.0 ml with dichloromethane. Mix well. This solution may be stored at less than -5 °C for up to three months.

F5.7 Sodium thiosulphate solution (3 % m/v). Dissolve 3.00 ± 0.01 g of sodium thiosulphate pentahydrate in approximately 80 ml of water and mix well. Make to 100.0 ml with water. Mix well. This solution may be stored at 5 ± 3 °C for up to three months.

F6 Apparatus

In addition to normal laboratory glassware the following may be required.

F6.1 Solid phase cartridges. Strata-X 200 mg (6 ml) cartridges were used to generate the performance data. Other similar cartridges may be used, but their performance would need to be verified.

F6.2 Blow-down apparatus. Any device (capable of being set at 40 ± 2 °C) that can direct a gentle stream of air or nitrogen into a vial.

F6.3 Gas chromatograph. Fitted with a heated injection system, mass spectrometer capable of operating with a resolution of 5000 (i.e. 10 % valley definition) and operating in SIM mode, with a data station. The suitability of the equipment will need to be evaluated.

The following conditions have been used in generating performance data.

Column:	DB5-MS, 30 m x 0.25 mm diameter, 0.25 µm film thickness.
Injector type:	Automated split-less.
Carrier gas:	Helium, 2 ml per minute.
Injection volume:	2 µl.
Injector temperature:	270 °C.
Temperature programme:	Oven Initial temperature at 50 ° C for 3 minutes, then 20 °C per minute to 150 °C, then 50 °C per minute to 270 °C, hold time for 3.6 minute,
Injector conditions:	
Mode:	Split-less
Initial Temperature:	270 °C.
Purge flow:	50 ml per minute.
Purge time:	2 minutes.
Total flow:	55 ml per minute.

Using these conditions, the following apply

Compound	Approximate retention time (minutes)	Ions monitored	
		Target	Qualifier
1,4-dichlorobenzene-d_4	6.2	150.0	115.0
metaldehyde	6.5	89.0	45.0 / 43.0

Equivalent equipment and conditions may be used. See Figure F1 for typical chromatograms.

F7 Sample collection and preparation

Samples may be collected in 2.5-litre amber glass bottles, containing 2.5 ml of sodium thiosulphate solution (F5.7), with a screw cap lid containing a polytetrafluoroethylene liner. Samples may be stored in the refrigerator at 5 ± 3 °C and may be extracted up to two weeks after sampling.

F8 Analytical procedure

Step	Procedure	Notes
F8.1	Condition a solid phase cartridge (F6.1) by passing (under gravity) 5 ml of dichloromethane (F5.1) through the cartridge. Using vacuum, dry the column by drawing air through it, note a.	(a) This usually takes about 5 minutes.

F8.2 Add about 5 ml of methanol (F5.2) to the cartridge and elute the column, note b. Discard the eluate. Add a further 5 ml quantity of methanol and elute the column, note b. Discard the eluate. Add 5 ml of water to the cartridge and allow the water to pass (under gravity) through the cartridge, note b. Discard the eluate. Close the tap and fill the cartridge with water.

(b) Do not allow the meniscus of the solvent to go below the level of the cartridge packing material.

F8.3 Add Vs ml (typically, 500 ± 5 ml) of sample (note c) and elute the column, note b. Discard the eluate. Add 5 ml of water to the cartridge and allow the water to pass (under gravity) through the cartridge, note b. Discard the eluate.

(c) If the sample contains particulate material, it may need to be filtered.

F8.4 Dry the column by passing nitrogen through it, note d.

(d) This may take approximately 45 minutes.

F8.5 Add 2.0 ± 0.2 ml of dichloromethane (F5.1) to the cartridge and leave for 5-10 minutes. Elute the column (under gravity) note b, collecting the eluate in a suitable test tube.

F8.6 Add 2.0 ± 0.2 ml of dichloromethane (F5.1) to the cartridge and eluate the column (under gravity) combining the elution fractions. Dry the column by drawing air through it and collect any residual solvent in the test tube.

F8.7 Remove the test tube from the column and add 50 ± 5 µl of working internal standard solution (F5.6) see note e, to the vial and cap. Mix well. Evaporate the mixture to about 0.5 ± 0.1 ml using nitrogen (F6.2).

The solution is now ready for GC-MS determination. Note f.

(e) This is equivalent to 25 ng of internal standard.

(f) At this stage the solution may be stored in a refrigerator for up to 2 weeks before the GC-MS determination begins.

F8.8 Prepare five calibrations solutions. For example, to each of 500 ± 5 ml of water, add 0.50 ± 0.05 ml of sodium thiosulphate solution (F5.7). To these solutions, add 0, 50, 100, 250 and 500 µl of the working calibration metaldehyde standard solution (F5.4) to separate bottles. See note g. These solutions are processed as described in sections F8.1 - F8.7. The solutions are

(g) These five solutions are equivalent to 0, 50, 100, 250 and 500 ng/l (based on a sample volume of 500 ml) and contain 0, 25, 50, 125 and 250 ng of metaldehyde respectively.

now ready for GC-MS determination, see note f.

F8.9 Set up the GC-MS system according to manufacturer's instructions and analyse the calibration extracts (F8.8). Construct a calibration graph of response versus concentration, monitoring the ions referred to in section F6.3.

F8.10 Analyse blank and AQC solutions using the entire procedure described in sections F8.1 - F8.7 replacing the sample as appropriate. Analyse the sample extract (F8.7) and from the graph (note h) determine the amount of metaldehyde in the extract.

(h) If the response exceeds the calibration range, the analysis may be repeated using a smaller quantity of sample (F8.3) but making the volume to 500 ml with water.

F8.11 Calculate the amount of metaldehyde in the sample.

F9 Calculation

From the calibration graph and using the response ratio for the internal standard between standards and samples, the amount, CS, of metaldehyde in the sample is given by

$$CS = (SE \times 1000) / (Vs)$$

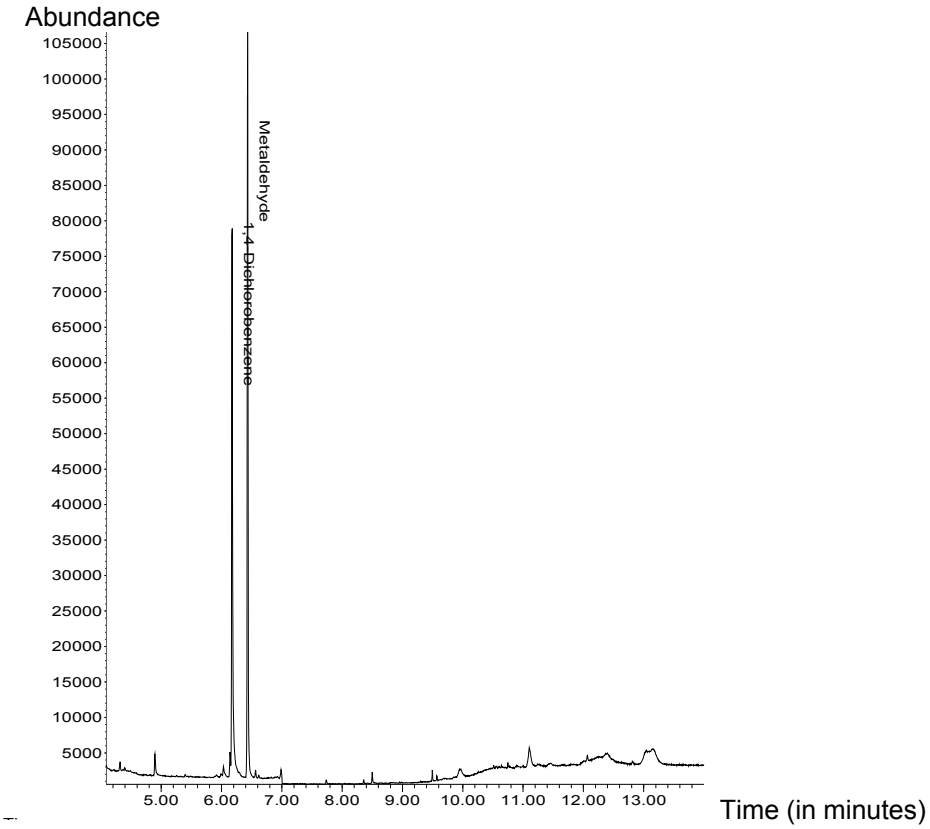
where
SE is the amount of metaldehyde in the sample extract;
Vs is the volume (ml) of sample extracted.

Table F1 Performance data

	Untreated borehole water	Treated river water	Untreated river water
Concentration of standard used for spiking (ng/l)	0.1	0.1	0.1
Volume of standard solution (ml)	0.1	0.1	0.1
Volume of sample used (ml)	499.9	499.9	499.9
Concentration added in spiking (ng/l)	100	100	100
Grand mean recovery (%)	102.3	109.6	94.5
Standard error of mean recovery(%)	1.95	5.36	6.19
95 % Confidence limits on mean recovery (%)	± 3.6	± 9.8	± 11.4
Best possible recovery (%)		99.8	105.9

Data based on 10 batches analysed in duplicate.
Data provided by South East Water

Figure F1 Typical GC-MS chromatogram
(100 ng/l standard solution)



Address for correspondence

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