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Determination of Long Alkyl Chain Quaternary Ammonium Compounds in Environmental Matrices by High Performance Liquid Chromatography 1996

Methods for the Examination of Waters and Associated Materials

HMSO

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Methods for the Examination of Waters and Associated Materials

Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of materials and apparatus used. The method in this booklet reports the materials actually used, but in no way endorses these materials as being superior to other similar materials. Equivalent materials are acceptable and it should be understood that the performance characteristics of the method may differ with other materials used. It is left to users to evaluate these procedures in their own laboratories. Only limited performance data are available for the procedures described.

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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, groundwater, river and seawater, waste water and effluents as well as sewage sludges, sediments and biota. In addition, short reviews of the more 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 reported for most parameters. 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 encompassing at least ten degrees of freedom 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. An indication of the status of the method is shown at the front of this publication on whether or not the method has undergone full performance testing.

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 in the series 'Methods for the Examination of Waters and Associated Materials' and their continuous revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is managed by the Drinking Water Inspectorate. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage treatment methods and biodegradability
9.0 Radiochemical methods

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

Publication of new or revised methods will be notified to the technical press. An index of methods and the more important parameters and topics is available from HMSO (ISBN 0 11 752669 X).

Every effort is made to avoid errors appearing in the published text. If, however, any are found please notify the Secretary.

Dr D WESTWOOD
Secretary

8 December 1995

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 any regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 1988 SI 1988/1657. 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, and these should be consulted and be readily accessible to all analysts. Amongst such publications are those produced by the Royal Society of Chemistry, namely 'Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', 5th edition, 1992; by Member Societies of the Microbiological Consultative Committee, 'Guidelines for Microbiological Safety', 1986, Portland Press, Colchester; and by the Public Health Laboratory Service 'Safety Precautions, Notes for Guidance'. Another useful publication is produced by the Department of Health entitled 'Good Laboratory Practice'.

The Determination of Long Alkyl Chain Quaternary Ammonium Compounds in Environmental Matrices by High Performance Liquid Chromatography

0 Introduction

The method describes the determination of dihardenedtallowdimethyl ammonium compounds (DHTDMAC) in environmental matrices. These compounds have been, until recently, the major components of fabric conditioning products. The procedure can be used to determine monoalkyltrimethyl ammonium and other dialkyldimethyl ammonium compounds. It may also be adapted for the determination of other cationic surfactants provided quantitative recovery can be demonstrated.

1 Performance characteristics of the method

1.1	Substance determined	Cationic surfactants of the monoalkyltrimethyl ammonium and dialkyldimethyl ammonium types (which have alkyl groups generally containing 10 or more carbon atoms), in particular dihardened-tallowdimethyl ammonium compounds. Other cationic surfactants may also be determined.
1.2	Type of sample	Sewage, sewage effluents, river waters, potable waters, sewage sludges, river sediments and sludge amended soils.
1.3	Basis of the method	Concentration and clean-up of cationic surfactant by a combination of simple evaporation, solvent extraction (solid-liquid and liquid-liquid extraction) and anion-exchange chromatography. Separation of the cationic surfactants by normal phase high performance liquid chromatography (HPLC). Detection by conductometry and quantification by peak height integration.
1.4	Range of application	Up to 10 μg of cationic surfactant expressed as some suitable reference surfactant such as DHTDMAC.
1.5	Calibration curve	Calibrations were linear or showed slight curvature.
1.6	Standard deviation	See Table 1. With the exception of final effluent samples, the inter-laboratory relative standard deviation of the procedure was shown to be less than 20% for liquor (raw sewage/settled sewage) and solid samples (primary/activated/digester sludges).
1.7	Limit of detection	The limits of detection for environmental liquor and solid samples are estimated to be 2.5 μg/l and 0.5 μg/g respectively based on typical sample sizes.
1.8	Bias	The recovery of standard additions of DHTDMAC at typical background concentrations is generally equal to or greater than 90%.
1.9	Interferences	Compounds not separated in the clean-up procedure that can ionise under non-aqueous conditions and have similar HPLC retention times to the cationic surfactants under investigation will interfere.

1.10	Time required for analysis	(i) Liquors	3-6 determinations—approximate total time 30 hours.
		(ii) Solids	3-6 determinations—approximate total time 25 hours.
		The operator time will be approximately half the total time.	

2 Principle

Liquor samples are extracted with methanoic hydrochloric acid from the residue remaining after evaporation of a suitable portion of the unfiltered liquor. Dried solid samples are similarly extracted with methanoic hydrochloric acid. The extracted surfactant is cleaned up using (i) water/chloroform liquid-liquid extraction (to remove inorganic ions and water soluble organic compounds), (ii) non-aqueous anion-exchange (to separate anionic interferences) and (iii) a chloroform/water back extraction step (to minimise the interference of ionic materials). The resulting cationic material is analysed by a normal phase HPLC system which separates quaternary ammonium compounds according to their degree of hydrophilicity. Detection is by conductivity measurement and quantification by peak height assessment using external standards.

3 Scope and limitations (including interferences)

The method can be used to determine low concentrations (down to μg/l) of long alkyl chain cationic surfactants (ie mono-, di- and trialkylmethyl ammonium compounds). It can be adapted to determine other cationic surfactants that are recovered quantitatively through the concentration/clean up steps. The procedure described is applicable to the determination of low concentrations of DHTDMAC found in samples from sewage treatment plants, rivers and soils. The limits of detection for environmental liquor and solid samples are estimated to be 2.5 μg/l and 0.5 μg/g respectively. Recoveries of standard additions are generally greater than or equal to 90% from all matrices (11.1). Its high specificity for the determination of DHTDMAC in a range of environmental samples was shown by comparing the results obtained with those for a standard non-specific colorimetric disulphine blue method (11.1). However, interferences can arise from organic compounds not separated in the clean-up steps which can ionise under non-aqueous conditions, and which have similar HPLC retention times to the cationic surfactants, for example long chain amines.

4 Hazards

Chloroform, methanol, hydrochloric acid and glacial acetic acid are hazardous. A high standard of hygiene should be maintained when working with sewage samples, in particular, primary, secondary and digested sewage sludges.

5 Reagents

Reagents should be analytical reagent quality except where otherwise specified.

5.1 Water—HPLC grade.

5.2 Methanol—HPLC grade.

5.3 Chloroform—HPLC grade.

5.4 Concentrated hydrochloric acid (d_{20} 1.18).

5.5 Glacial acetic acid.

5.6 Methanol/hydrochloric acid mixture, approximately 1 Molar.

Add 500 $\pm$ 10 ml methanol (5.2) to a 1000 ml volumetric flask. Cautiously add 89 $\pm$ 0.5 ml of concentrated hydrochloric acid (5.4) and mix. Dilute to the mark with methanol. Allow to cool and make to the mark with methanol again. Mix well.

5.7 Linear alkylbenzene sulphonate (LAS) aqueous solution, 1000 mg/l.

Dissolve 0.1 $\pm$ 0.005 g of a commercial secondary LAS, for example Marlon A350 in water (5.1) and dilute to the mark with water in a 100 ml volumetric

flask. This solution is stable for up to 3 months under normal laboratory conditions.

5.8 Standard long alkyl chain cationic surfactant reference compound.

The choice of reference compound will be dependent upon the particular application for the analytical method. For example, DHTDMAC with a typical alkyl chain length distribution of 5% C_{14}, 30% C_{16} and 65% C_{18}. The associated counter ion is either chloride or methosulphate.

5.8.1 Standard long alkyl chain cationic surfactant solutions.

5.8.1.1 Stock solution 1000 mg/l in chloroform.

Dissolve 0.1 $\pm$ 0.005 g of long alkyl chain cationic surfactant in chloroform (5.3) and dilute to the mark with chloroform in a 100 ml volumetric flask. This solution is stable for up to 3 months under normal laboratory conditions.

5.8.1.2 Working solution 1000 mg/l in mobile phase.

Pipette 5 $\pm$ 0.05 ml of stock solution (5.8.1.1) into a vial and evaporate to dryness on a heating block at 60°C under a stream of nitrogen. Re-dissolve the cationic surfactant in 5 $\pm$0.05 ml of HPLC mobile phase (6.1). This solution should be prepared fresh each day.

5.8.1.3 Stock solution 1000 mg/l in water.

Dissolve 0.1 $\pm$ 0.005 g of long alkyl chain cationic surfactant in water (5.1) and dilute to the mark with water in a 100 ml volumetric flask. This solution is stable for up to 3 months under normal laboratory conditions.

5.8.1.4 Working solution 5 mg/l in water.

Pipette 5.0 $\pm$ 0.05 ml of stock solution (5.8.1.3) into a 1000 ml volumetric flask and make up to the mark with water (5.1). This solution should be prepared fresh on the day of use.

5.9 Formalin, 40% v/v solution of formaldehyde.

5.10 Alcohol ethoxylate aqueous solution, 1000 mg/l.

Dissolve 0.1 $\pm$ 0.005 g of a linear alcohol ethoxylate (alkyl chain C_{14} and C_{15}, average of 7 ethoxylate units), for example Dobanol 45 7(EO), in water (5.1) and dilute to the mark with water in a 100 ml volumetric flask. This solution is stable for up to 3 months under normal laboratory conditions.

6 Apparatus

6.1 Liquid chromatography, ancillary equipment and chromatographic conditions.

A liquid chromatograph system (linked to a conductivity detector) capable of producing well separated peaks for the analytes of interest is suitable. An appropriate chromatographic data handling system may be used to assess peak heights.

Instrument	:	High performance liquid chromatograph capable of producing an isocratic solvent mixture.
Column	:	Partisil 5 PAC (Whatman) analytical column (amino/cyano bonded silica, 5 μm packing, 25 cm long x 4.6 mm i.d) or equivalent.
Guard column	:	Column packed with Co-Pell PAC (Chrompack) or equivalent material.

Mobile phase : A 89:10:1 mixture of chloroform (5.3)/methanol (5.2)/glacial acetic acid (5.5) is used.

Solvent programme : Isocratic.

Flow rate : 1 ml/min.

Detector : Conductivity detector.

Note:

It may be necessary to adjust the concentration of methanol in the mobile phase in order to obtain well resolved, sharp peaks. New columns may require conditioning to the mobile phase and typical sample extracts before the best results can be achieved. DHTDMAC typically has a retention time of about 4 min (see Figure 1). Under these conditions, trialkylmethyl and monoalkyltrimethyl ammonium compounds typically show retention times of approximately 2.5 and 7 minutes respectively.

6.2 Glassware.

6.2.1 Vials—used for reaction and storage—with solid top and polytetrafluoroethylene (PTFE) faced rubber liner (20 ml capacity), for example, Reacti-Vials or equivalent.

6.2.2 Beakers of various capacities.

6.2.3 Glass rods.

6.2.4 Centrifuge tubes, 25 ml capacity.

6.2.5 Pasteur pipettes.

6.2.6 Separating funnels each having a PTFE tap.

6.2.7 Conventional glass chromatographic columns—length 20–30 cm, internal diameter 10-15 mm.

6.2.8 Solvent filtration equipment.

6.3 Ancillary equipment.

6.3.1 Steam bath.

6.3.2 Heating block.

6.3.3 Laboratory centrifuge.

6.3.4 Nitrogen supply, oxygen-free grade.

6.3.5 Rotary sample mixer.

6.3.6 HPLC injection syringes, capacity 0-100 μl.

6.4 Anion-exchange resin.

Anion exchange resin in chloride form (50-100 mesh), for example Bio-Rad AGI-X2, Dowex 1-X2 or equivalent. Alternatively, solid phase extraction (SPE) cartridges pre-packed with a similar anion-exchange sorbent material may be used provided their performance has been validated.

6.4.1 Preparation of ion-exchange resins.

Soak 100 g of anion-exchange resin in methanol (5.2) overnight. Plug the column (6.2.7) above the tap with a small amount of glass wool and fill to approximately one-third of its volume with methanol. Slurry about 10 ml of the methanolic anion-exchange resin into the column with methanol. Remove any bubbles from the resin bed. Wash the resin bed with 50 ml of methanol at a rate of 1-2 ml/min. Do not allow the resin bed to dry out. The resin column can be re-used after washing for up to five liquor samples but should always be discarded once a solid sample extract has been ion-exchanged.

7 Cleaning and preparation of apparatus

7.1 All new glassware (beakers, separating funnels, ion-exchange columns, centrifuge tubes etc) should be pre-conditioned to cationic surfactant by soaking in 5 mg/l aqueous solution of DHTDMAC overnight in order to eliminate active sites. The glassware is then thoroughly rinsed (in succession) with deionised water, methanol, chloroform, methanol and deionised water to remove any surfactant which is not irreversibly bound to the glass surfaces. The conditioned equipment should be reserved solely for the determination of cationic surfactants.

7.2 Glassware should be cleaned by successively washing in tap water (twice) and deionised water (twice). Use a bottle brush to ensure beakers are completely free of sample residues. Allow apparatus to air dry before use. Any equipment, in particular beakers, that becomes noticeably scratched should be discarded in order to avoid the possibility of losses of cationic surfactant.

8 Sample collection and preservation

8.1 Liquor samples

Surfactants tend to become adsorbed onto suspended solids, as well as on the surface of containing vessels. The analyst should therefore ascertain the requirements of the analysis, ie whether the total or soluble surfactant concentration is to be determined. If the soluble fraction is to be determined centrifugation rather than filtration of the sample should be employed to remove suspended solids.

Sampling bottles should be filled with sample and if they are not to be analysed within a few hours of collection, the samples should be stored in a refrigerator at 1-5°C and sterilised, for example, by the addition of 1% v/v of a 40% formaldehyde solution (5.9). At the time of sampling, an addition of an alcohol ethoxylate (5.10) to samples at a concentration of 5 mg/l has been shown to minimise the adsorption of the cationic surfactant to the container surfaces. To obtain a representative sample, stir the whole sample with a magnetic stirrer or slowly invert the sample bottle before taking aliquots. As far as practicable, avoid the formation of foam during stirring or inversion, but in either case an aliquot should not be withdrawn while the bulk sample is foaming.

8.2 Sludges (primary, secondary and digested sludge)

Sludge samples should be collected in pre-washed glass jars to which 1-5% v/v of a 40% formaldehyde solution has been added and the contents mixed well. The samples should be stored in a refrigerator at 1-5°C. Sludge samples kept in this manner should remain stable for analysis for up to a month.

8.3 Soils

Soil samples should be thinly spread over trays and allowed to air-dry to constant weight. The soil is periodically broken up with a trowel to facilitate the drying process. The dried soil should be ground prior to being sieved to obtain soil with a particle size of less than 2 mm. The sieved samples can be

stored in sealable plastic bags or glass bottles at room temperature prior to analysis.

8.4 Sediments

Sediments can be treated as for soils except that they can be dried at 50°C to facilitate the removal of interstitial water.

9 Analytical procedure

Step	Procedure	Notes
9.1	**Extraction of Long Alkyl Chain Quaternary Ammonium Compounds from liquor samples**	
9.1.1	Take a suitable volume (Vs) of sample, up to 1000 ml containing 10–100μg of cationic surfactant (note a) and evaporate to dryness in a suitable beaker on a steam bath under a stream of nitrogen (6.3.4).	(a) Generally, up to 100 ml of sewage, 400 ml of sewage effluent or 1000 ml of river water can be taken for analysis.
9.1.2	Add 20 ml of methanol/hydrochloric acid mixture (5.6) and thoroughly dislodge all sample residues from the sides and bottom of the beaker using a glass rod. Reduce the volume of the solvent to about 10 ml on a steam bath. Transfer the supernatant liquor into a 25 ml centrifuge tube and centrifuge at 2000 g for 5 min. Remove the centrifuged extract from the tube with the aid of a Pasteur pipette and place in a 250 ml beaker. Repeat the extraction, centrifugation and transfer procedures with two further portions of methanol/ hydrochloric acid mixture (note b). Evaporate the combined extracts in the beaker to dryness on a steam bath under a stream of nitrogen. Clean up the cationic surfactant as outlined in section 9.3.	(b) After transferring the second and third extracts to the same centrifuge tube used for the first extract, any solid residue is broken up with the aid of a thin glass rod prior to centrifugation.
9.2	**Extraction of Long Alkyl Chain Quaternary Ammonium Compounds from solid samples**	
9.2.1	Ensure that the dried solids are well mixed before taking a sample for analysis. Accurately, weigh out approximately 0.5 g dried sludge (note c), 5 g air-dried sediment or 10 g air-dried soil into a 250 ml beaker.	(c) The procedure for preparing dried sludge has been described elsewhere (11.2). If, necessary, coarse solids are removed by sieving (about 5 mm). The dry weight of the sludge must be determined. Dried sludge is ground and sieved before use.
9.2.2	Add 50 ml of methanol/hydrochloric acid mixture (5.6) and heat the contents of the beaker on a steam bath. Stir with the aid of a glass rod until the total volume of solvent is reduced to about 25 ml. Transfer the supernatant liquor to a centrifuge tube with the aid of a Pasteur pipette and centrifuge at 2000 g for 5 min. Remove the centrifuged extract from the tube using the Pasteur pipette and place in a 250 ml beaker. Repeat the extraction of the solid residue remaining in the sample beaker with 50 ml portions of methanol/ hydrochloric acid mixture until the resulting extracts are essentially free of colour (usually 4 or more extraction steps are required to give quantitative recovery of DHTDMAC) (note b). Evaporate the combined extracts to dryness on a steam bath under a stream of nitrogen.	

9.3 **Clean up of cationic surfactant from liquor and solid extracts**

9.3.1 Transfer the cationic residue to a 250 ml separating funnel using four 25 ml portions of water (5.1). Dislodge the residue from the sides and bottom of the sample beaker with the aid of a glass rod. Rinse the beaker in turn with 5 ml of concentrated hydrochloric acid (5.4) and 50 ml of chloroform (5.3) and add each to the separating funnel. Add 1ml of a 1000 mg/l LAS solution (5.7) to the funnel (note d). Shake the contents of the separating funnel vigorously for one minute and allow the phases to separate completely. Transfer the lower chloroform phase to a 250 ml beaker. Use a further two 50 ml portions of chloroform to rinse the beaker and to extract the aqueous sample. Combine the three chloroform extracts and evaporate to dryness on a steam bath under a gentle stream of nitrogen.

(d) LAS is added to enhance the extractability of cationic surfactant via the formation of a more readily chloroform extractable ion-association compound.

9.3.2 Dissolve the extract residue in 2 ml of chloroform (5.3) using a glass rod to break up the residue and add 8 ml of methanol (5.2). Transfer the whole extract to the top of the prepared anion-exchange column (see 6.4.1).

9.3.3 Pass the sample through the resin bed at a rate of 1–2 ml/min (note e) and collect the eluate in a 250 ml beaker. Allow the whole extract to pass into the resin bed before using two 10 ml portions of methanol to ensure quantitative transfer of the sample to the column. Wash the sample through the column with 100 ml methanol at the same flow rate. Wash the column with a further 150 ml of methanol after each separation (see note f). Evaporate the column eluate to dryness carefully on a steam bath under a gentle stream of nitrogen.

(e) It may be helpful to use a spare column, regulated with a stop watch and measuring cylinder to establish the flow rates.

(f) Never allow the resin bed to become dry.

9.3.4 Dissolve the residue from the ion-exchange step in 5 ml of chloroform (5.3) and transfer to a 20 ml vial. Quantitatively transfer the cationic material using a further two 5 ml portions of chloroform. Reduce the volume of chloroform in the vial to about 10 ml by heating on a steam bath (or heating block) under a stream of nitrogen. Add 5 ml of water (5.1), securely cap the vial and shake contents vigorously for 30 seconds. Allow the layers to separate carefully, draw off most of the water layer with the aid of a Pasteur pipette without removing chloroform or any interfacial emulsion. Repeat the aqueous back extraction step two more times. Remove as much of the water phase as possible on the final extraction step. Evaporate the chloroform phase and any residual water to dryness on a steam bath (or heating block) under a gentle stream of nitrogen. Cap the vial and store the sample in a dry state prior to its determination by HPLC.

9.4 **High Performance Liquid Chromatography**

9.4.1 Filter and de-gas the HPLC mobile phase (6.1) by passing through an appropriate membrane filter prior to use.

9.4.2 Set up the liquid chromatograph and may ancillary equipment according to the general conditions given in section 6.1 and manufacturer's instructions. Ensure that stable, acceptable conditions are established for the subsequent analysis.

9.4.3 Add accurately to the evaporated extract (9.3.4), a volume (V_1) of mobile phase (6.1), generally between 250–5000 μl, so that an appropriate injection aliquot (5–25μl) can be taken, which should give a response similar to that for the reference standards used (9.4.5) (see note g).

(g) A degree of familiarity with the expected range of concentrations is required in order to ensure appropriate volumes are taken at this stage.

9.4.4 Re-cap the vial and mix the contents using a rotary mixer. Allow any particulate matter in the sample to settle and inject a suitable sample volume (V_2) into the chromatograph.

9.4.5 Prepare a calibration curve for the reference (5.8.1.2) standard by injecting between 1 to 10 μl of a 1000 mg/l working solution in mobile phase, corresponding to 1 to 10μg cationic surfactant injected on column (notes h and i).

(h) It has been found useful to inject standards and samples alternately during the analysis of a set of samples.

(i) The sensitivity of the conductivity detector employed will determine appropriate concentrations for the standard solution, the final extract volume and the injection volume used.

9.4.6 Construct a calibration plot of peak height versus the weight of reference cationic surfactant (note j). Determine the peak height for the analyte in the sample.

(j) Calibrations should be linear or possess slight curvature.

9.4.7 Derive the concentration of the analyte in samples by reference to the standard calibration and using the expressions given in section 10 (note k).

(k) A new calibration plot should be prepared for each series of samples analysed.

10 Calculation of results

If m_1 = mass of cationic surfactant in aliquot injected (μg)
V_1 = volume of mobile phase added to vial (μl)
V_2 = volume of sample injected (μl)
m_2 = mass of analyte in sample (μg)

then μg of analyte in sample, is given by

$$m_2 = \frac{m_1 \times V_1}{V_2}$$

If w = mass of dried solid sample taken for analysis, g
V_s = volume of aqueous liquor taken for analysis, ml

then concentration in mg/l analyte in aqueous liquor sample is given by

$$\frac{m_2}{V_s}$$

and the concentration in μg/g analyte in solid sample is given by

$$\frac{m_2}{w}$$

The performance of the method should be checked by determining the recovery of appropriate standards from spiked additions of real samples.

11 References

11.1 Gerike P, Klotz H, Kooijman J G A, Matthijs E and Waters J. (1994) The Determination of Dihardenedtallowdimethyl Ammonium Compounds (DHTDMAC) in Environmental Matrices Using Trace Enrichment Techniques and High Performance Liquid Chromatography with Conductometric Detection. Water Research, 28, 147-154.

11.2 The Sampling and Initial Preparation of Sewage and Waterworks Sludges, Soils, Sediments and Plant Materials and Contaminated Wildlife Prior to Analysis, 1986 (Second Edition) Methods for the Examination of Waters and Associated Materials, HMSO, London, in this series.

Table 1 Performance data

Laboratory	Sewage Treatment Samples				
	Raw Sewage (mg/l)	Settled Sewage (mg/l)	Final Effluent (mg/l)	Primary Sludge (mg/g)	Surplus Activated Sludge (mg/g)
1	0.99	0.76	0.05	2.7	4.0
2	-	-	0.02	2.0	3.0
3	0.71	0.62	0.02	2.3	2.6
4	-	-	-	1.7	3.2
5	0.8	0.65	0.03	2.2	3.7
Mean	0.83	0.68	0.03	2.2	3.3
SD	0.14	0.07	0.01	0.37	0.56
%RSD	17.2	10.9	47.1	17.0	16.9

Individual laboratory results are generally an average of two or more determinations.
SD Standard deviation
%RSD Percent relative standard deviation

Figure 1 Typical chromatograms for dihardenedtallowdimethyl ammonium compounds

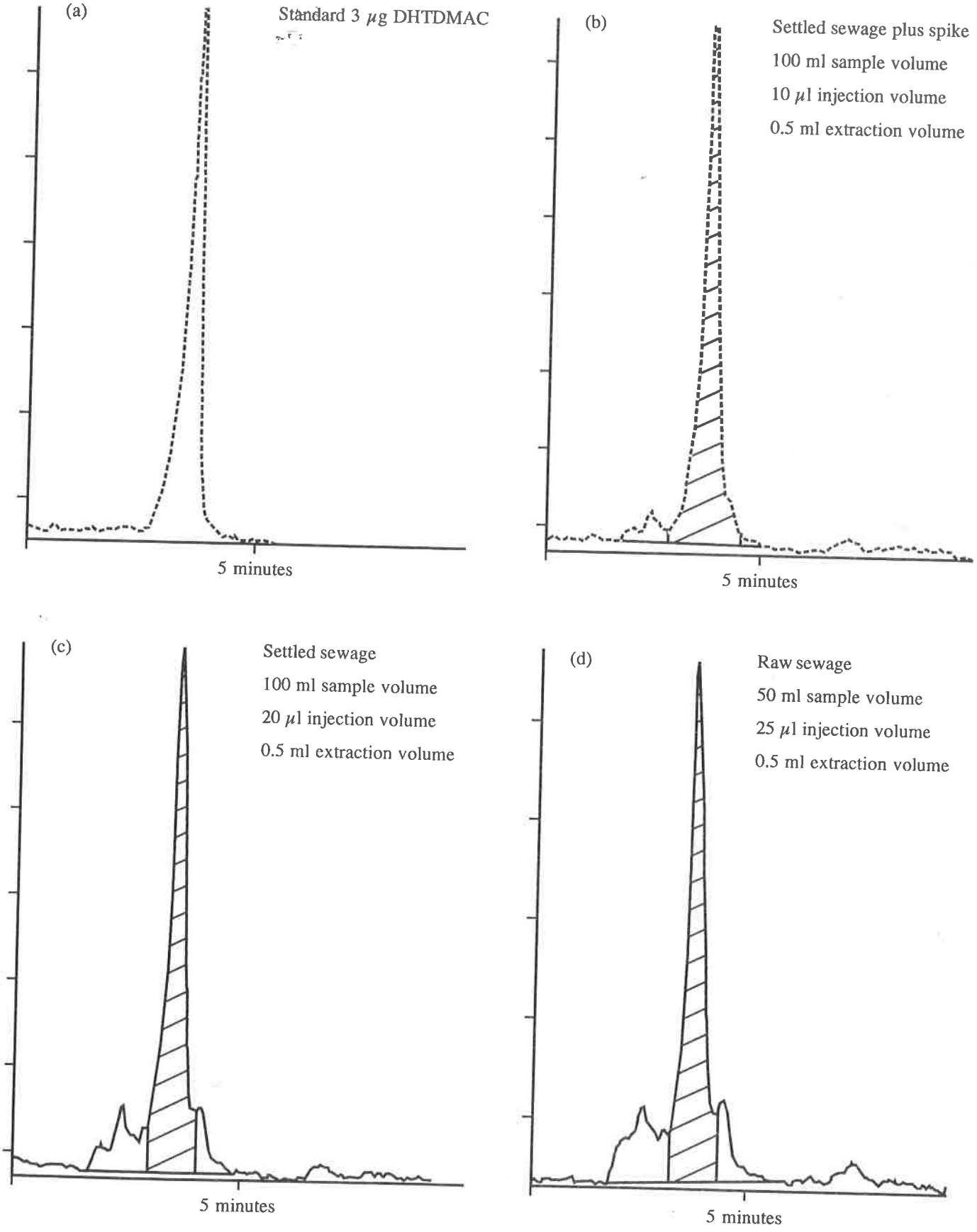
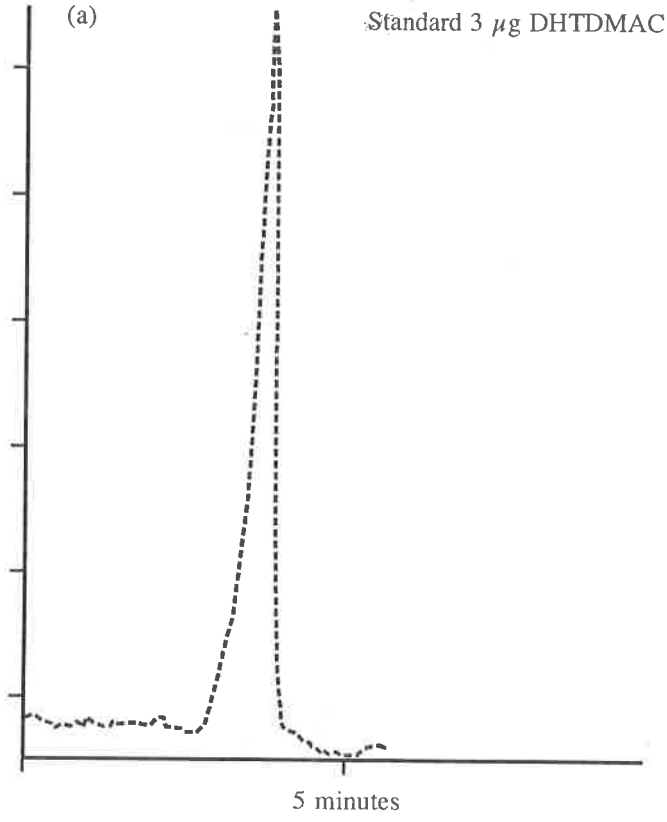
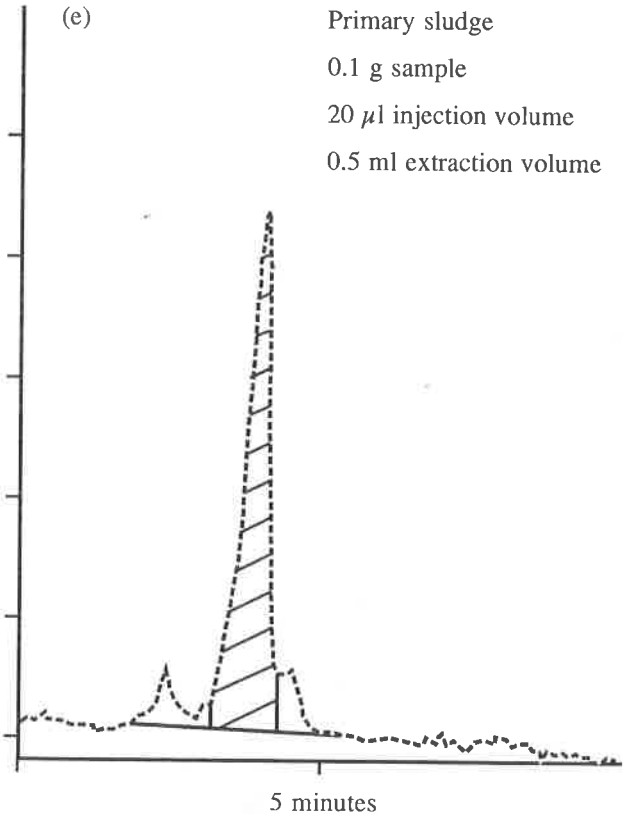
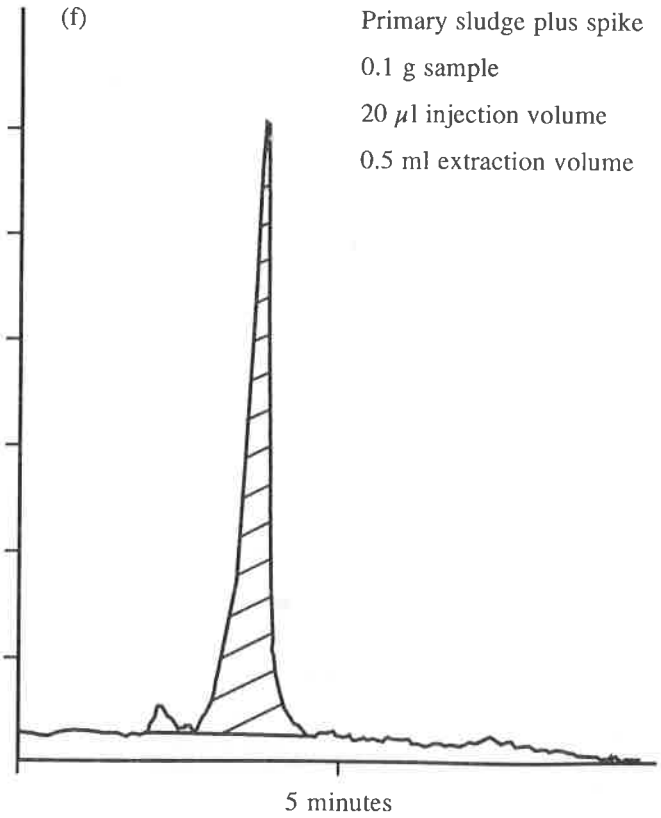
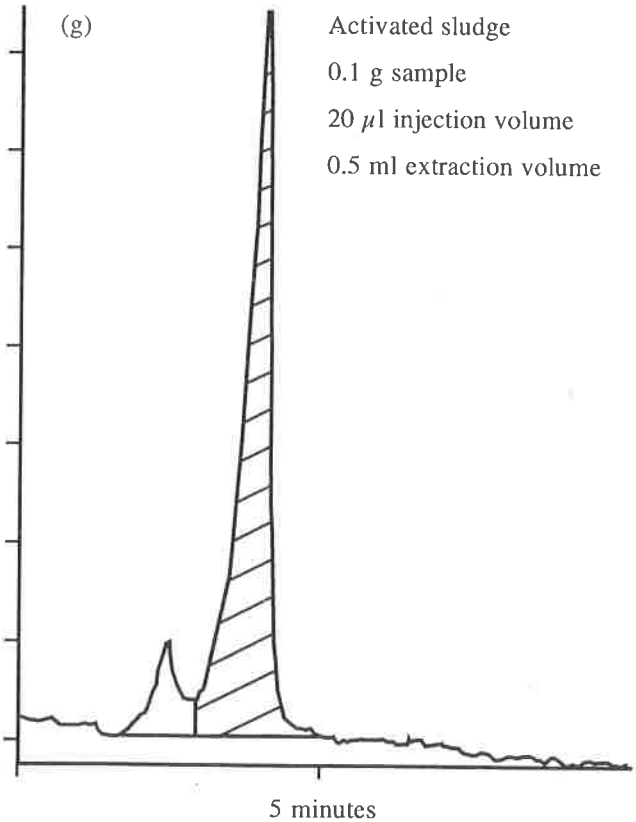


Figure 1 continued









Analytical Quality Control

1 Routine Control

Once a method has been selected for routine use, a system of analytical quality control should be adopted in order to validate the analysis. At least one control standard should be analysed with each batch of samples and the results plotted on a control chart. Corrective action should be taken if one value falls outside of the action limit (at $\pm$ 3s) or 2 consecutive values exceed the warning limit (at $\pm$ 2s). As more data are acquired, the standard deviation, s, should be updated and the control chart limits recalculated.

2 Estimation of the Accuracy of Analytical Results using these Methods

The method given in this booklet has not been thoroughly investigated and before general use, the accuracy achievable should be known. It would be of great value if any laboratory using or considering the use of this method would estimate the accuracy of its own analytical results and report the findings to the Secretary of the Standing Committee of Analysts.

Members assisting with this method

M H I Comber
M Daniel
M S Holt
S J Nash
H A Painter
J Waters

Address for correspondence

However well a method is tested, there is always the possibility of discovering a hitherto unknown problem. Users with information on these methods are requested to write to the address below.

The Secretary
The Standing Committee of Analysts
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