Determination of Aldicarb and other N-methyl carbamates in Waters 1994

Methods for the Examination of Waters and Associated Materials

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Determination of Aldicarb and other N-methyl carbamates in Waters 1994

Methods for the Examination of Waters and Associated Materials

This booklet contains two methods.

Method A: A method for the determination of aldicarb, aldicarb sulphoxide, aldicarb sulphone, carbaryl, carbofuran, ethiofencarb, methiocarb, methomyl, oxamyl and propoxur by reverse phase high performance liquid chromatography (HPLC) with post column derivatisation and fluorescence detection. A liquid chromatography-mass spectrometric (LC-MS) confirmation method is included.

Method B: A note on the determination of aldicarb, its sulphoxide and sulphone all expressed as sulphone, following oxidation and gas chromatography (GC) using a nitrogen selective detector. These and other determinands can also be determined directly by GC.

Only limited performance data is available for both methods described in this booklet.

Chromatographic methods are very sensitive to minor physical and chemical variations in the quality of materials and apparatus used. These methods report the use of materials actually used in the evaluation tests but this in no way endorses these materials as superior to other similar materials. Equivalent materials are acceptable and it should be understood that the performance characteristics may differ with other materials used. It is left to users to evaluate these methods in their own laboratories.

Contents

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 works control methods
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 these methods 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

18 February 1994

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'.

A Determination of aldicarb and other N-methyl carbamates in waters by HPLC

A1 Performance characteristics of the method

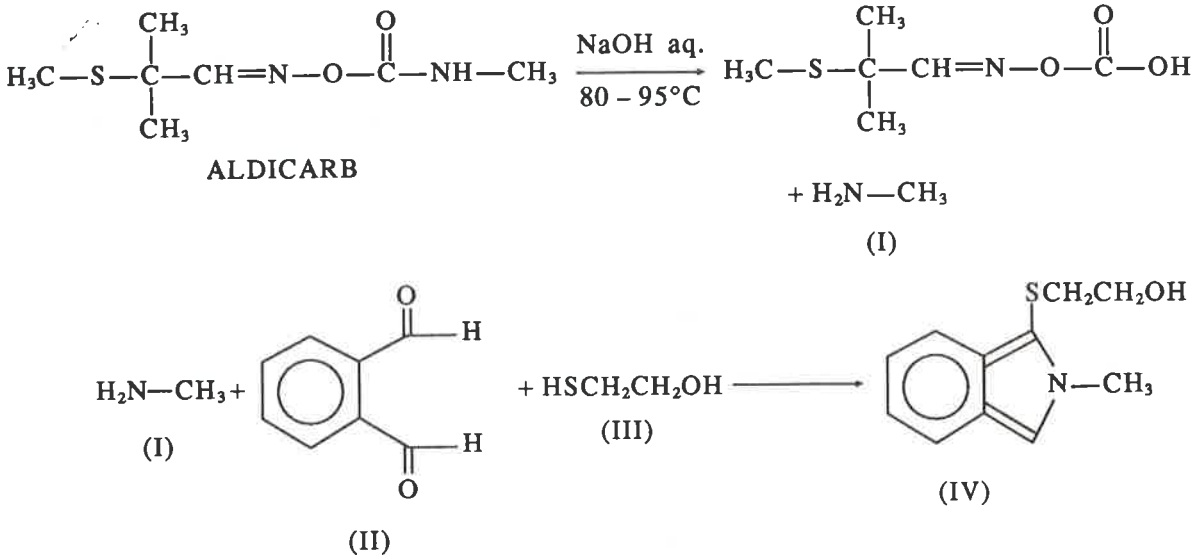
A1.1	Substances determined	Aldicarb, aldicarb sulphoxide, aldicarb sulphone, carbaryl, carbofuran, ethiofencarb, methiocarb, methomyl, oxamyl and propoxur (see Tables A1 and A2).
A1.2	Types of sample	Drinking, river and saline waters.
A1.3	Basis of method	Extraction of the sample into dichloromethane. Concentration and determination of the compounds by high performance liquid chromatography using post-column fluorometric detection, or thermospray high performance liquid chromatography-mass spectrometric detection (HPLC-MS).
A1.4	Range of application	Up to 2 μgL^{-1}. This may be extended by dilution of the sample extract or by taking a smaller sample volume.
A1.5	Calibration curves	Linear over the range of application for all determinands.
A1.6	Standard deviation	See Tables A3 and A4.
A1.7	Limit of detection	Typically < 0.04 μgL^{-1} for all determinands (see Tables A3 and A4).
A1.8	Sensitivity	Dependent on the instrument used.
A1.9	Bias	Extraction efficiencies are less than 100%. See Tables A3 and A4 for recovery data.
A1.10	Interferences	Any co-extracted material which responds to the detector and which has a similar retention time to any of the determinands will interfere.
A1.11	Time for analysis	Five samples may be analysed in 1 working day.

A2 Principle

The determinands are concentrated by solvent extraction and analysed by reverse phase HPLC with post column derivatisation and fluorescence detection. It is also possible to analyse the extracts using thermospray liquid chromatography-mass spectrometry.

N-methyl carbamates will release methylamine (I) when hydrolysed with sodium hydroxide, as demonstrated with aldicarb below. Methylamine (I) is known to react with o-phthalaldehyde (II) and 2-mercaptoethanol (III) to form the highly fluorescent product 1-(2-hydroxyethyl)thio-2-methyl isoindole (IV), see A10.

These reactions can be accomplished by a post-column reaction system and the isoindole (IV) quantified using a fluorescence detector.



A3 Interferences

Any compound which elutes close to any of the determinands and which contains a primary amino group (or a functional group which can be hydrolysed to a primary amine) will interfere. Figure A1 gives relevant retention data and Table A1 gives the structure and molecular weight of the determinands. Table A2 gives the structure and molecular weight of other N-methyl carbamates which may also be detected by this method.

A4 Hazards

Acetone, acetonitrile and methanol are flammable. Dichloromethane and methanol are narcotic and toxic. 2-mercaptoethanol and o-phthalaldehyde are toxic. The acid and alkali solutions used are corrosive. The pesticide standards are extremely toxic. Caution must be exercised when preparing the stock solutions. Skin contact, ingestion and inhalation must be avoided. Appropriate safety procedures should be followed.

A5 Reagents

All reagents must be of sufficient purity that they do not give rise to significant interference peaks during the HPLC analysis. This should be checked for each batch of materials and verified by running procedural blanks with each batch of samples analysed.

The water used for blank determination and preparation of control samples should show negligible interferences when compared with the smallest concentration to be determined.

Reagents may become contaminated by contact with air and/or other materials, particularly plastics, or by degradation caused by the action of light. Reagents should be stored in tightly sealed all glass containers or other suitable vessels and be kept in the dark if necessary.

A5.1 Acetone – Glass distilled.

A5.2 Acetonitrile – HPLC grade.

A5.3 Dichloromethane (DCM) – HPLC grade.

A5.4 2-Mercaptoethanol – Analytical reagent grade.

A5.5 Methanol – HPLC grade.

A5.6 Water – HPLC grade.

A5.7 Sodium chloride – Granular. Heat at 500 ± 20 °C for 4 hr ± 30 min. Cool to ambient temperature in a muffle. Store in a closed glass container.

A5.8 Sodium sulphate – Anhydrous and granular.

A5.8.1 Sodium sulphate – Anhydrous - heat at 500 ± 20 °C for 4 hr ± 30 min. Cool to about 200 °C in a muffle and then to ambient temperature in a desiccator. Store in a closed glass container.

A5.8.2 Sodium sulphate decahydrate – Granular, analytical reagent grade.

A5.9 Sodium hydroxide solution 0.05M – Weigh out 2.0 ± 0.1 g analytical reagent grade sodium hydroxide, dissolve in 1000 ± 10 mL of water with stirring.

A5.10 Sodium tetraborate solution 0.05M – Weigh out 19.1 ± 0.1 g of analytical reagent grade sodium tetraborate decahydrate, dissolve in 1000 ± 10 mL of water with stirring.

A5.11 o-Phthalaldehyde solution 0.05M (OPA) – Weigh out 50 ± 5 mg of analytical reagent grade o-phthalaldehyde, dissolve in approximately 5 mL methanol (A5.5) in a 500 mL volumetric flask and dilute to the mark with sodium tetraborate solution (A5.10). Add 25 ± 2 µL of 2-mercaptoethanol (A5.4) and mix thoroughly.

A5.12 Orthophosphoric acid solution (20% v/v) – Carefully add 20 ± 2 mL of concentrated (85%) analytical reagent grade orthophosphoric acid to 60 mL of deionised water with swirling and cooling. Cool to ambient temperature and dilute to 100 ± 1 mL with deionised water.

A5.13 Methanol : water 25:75 v/v.

A5.14 Ammonium acetate – Analytical reagent grade.

A5.15 Standards

A5.15.1 Stock solutions – Prepare separate stock solutions in acetone of each determinand at a concentration of 1000 mgL^{-1}. For example, in a volumetric flask dissolve 100.0 ± 0.1 mg pure or suitably certified material in 100.0 ± 0.1 mL of solvent (A5.1).

A5.15.2 Working standard solutions – Prepare a series of aqueous working standard solutions by dilution of the stock solutions (A5.15.1) with water. A useful working range is from 0.01 to 1.0 mgL^{-1}.

A6 Apparatus

Apparatus should be clean and dry.

A6.1 Sample Extraction

A6.1.1 Sample bottles – Glass bottles of 1.2 L capacity, marked at 1.0 L, fitted with glass stoppers or PTFE-lined screw caps.

A6.1.2 Kuderna – Danish evaporator – Fitted with 10 mL graduated tubes. Other equivalent evaporator systems may also be used.

A6.1.3 Measuring cylinders – Glass, 100, 500 and 1000 mL capacity.

A6.1.4 Separating funnels – Glass, 1 litre capacity, fitted with a grease-free glass or PTFE tap and stopper.

A6.1.5 Pipettes / syringes – Microlitre pipette or syringe capable of dispensing 25 µL.

A6.1.6 Mechanical shaker (optional) – Capable of taking the separating funnels or sample bottles.

A6.1.7 Drying columns – Glass, 15 × 1 cm.

A6.1.8 Nitrogen – Oxygen-free, dry and filtered.

A6.2 High Performance Liquid Chromatograph – A high performance liquid chromatograph with three solvent gradient capability. This should be operated in accordance with the manufacturer's instructions. The following conditions were used to generate the performance data. See Figure A1 for a typical chromatogram.

Column: Nova-Pak C_{18} 150 x 3.9 mm, 4 µm particle size (or equivalent).

Column temperature: 30 °C

Mobile phase gradient:

Time (min)	Water (%)	Methanol (%)	Acetonitrile (%)
0	88	12	0
4.0	88	12	0
4.1	68	16	16
16.1	30	35	35
19.0	88	12	0
30.0	88	12	0

Flow rate: 1.5 $mLmin^{-1}$.

Injection volume: 25 µL

Other HPLC equipment or conditions may be used provided equivalent performance can be demonstrated.

A6.3 Detection System – A post column reaction system capable of adding two reagents into the solvent flow and a heated reaction coil maintained at a fixed temperature between 80 and 95 °C. A fluorescence detector capable of excitation at a wavelength of 330 nm and emission at a wavelength of 445 nm.

A.6.3.1 Post Column Reaction System – A post column reaction system can be constructed as in Figure A2 or any equivalent commercial system employed.

A6.4 Thermospray HPLC-MS – The sample extract can also be analysed by thermospray HPLC-MS. No definitive performance data is available but all of the determinands can be detected by this procedure after separation using a suitable HPLC solvent system.

A6.4.1 HPLC Conditions – A requirement of thermospray ionisation is the presence of ammonium acetate in the HPLC mobile phase, therefore the following conditions (or similar) can be used:

Column:	250 × 4.6 mm ODS-2, 5 µm particle size.
Mobile phase:	Acetonitrile:water:ammonium acetate, 350 mL : 650 mL : 10 g.
Flow rate:	1.0 mLmin $^{-1}$.

Figure A3 shows the total ion current (TIC) chromatogram for some of the determinands obtained using the conditions above.

A6.4.2 Mass Spectrometer Conditions – Owing to the variation between equipment, exact operating conditions cannot be given here. These should be optimised for the determinands with the particular equipment used at the time of analysis, and the strongest ions chosen for the selected ion monitoring (SIM).

The positive ion thermospray mass spectra for the determinands all give [M+H], [M+NH_4] and [M+Ac] psuedo molecular ions. Typical mass spectra can be seen in Figure A4.

A6.4.3 Detection limits – These will depend upon the equipment/conditions being used. In SIM mode it is possible to detect aldicarb, aldicarb sulphoxide, aldicarb sulphone, carbaryl and methomyl directly at concentrations of less than 1 µgL^{-1} in extracts of water samples; full spectra can be obtained for concentrations of the order of 100 µgL^{-1}. The analysis of sample extracts with about 10-fold concentration (see section A8.4.1) should enable the confirmation of these compounds at 0.1 µgL^{-1}.

A7 Sample collection and storage

Samples should be taken in glass bottles with glass stoppers or PTFE-lined screw caps. They should be extracted and analysed as soon as possible after sampling. If this is impracticable they should be stored in a refrigerator at about 4 °C. They should not be stored in the vicinity of standard materials or their concentrated solutions.

A8 Analytical Procedure

Step	Procedure	Note
A8.1	Extraction	
A8.1.1	Aldicarb residues (note a) Measure 500 ± 1 mL of sample into a 1 litre separating funnel. Add 100 ± 5 g sodium sulphate decahydrate granules (A5.8.2) and mix to dissolve. Add 100 ± 5 mL DCM and shake for 2 minutes (note b). Allow the phases to separate. Proceed to A8.1.3.	(a) For total aldicarb residues the method of extraction described in section A8.1.1 affords better recoveries than that described in section A8.1.2 (see Tables A3 and A4). For other determinands, no performance data is available for this method of extraction, however, it is likely that these compounds will also be extracted. (b) A mechanical shaker may be used, but the extraction time should be increased to at least 10 minutes.
A8.1.2	Other determinands (note a) Measure 1000 ± 2 mL of sample into a 1 litre separating funnel. Add dilute orthophosphoric acid (A5.12) until the pH reaches 3 (note c). Add 50 ± 5 g of sodium chloride (A5.7) and mix to dissolve. Add 50 ± 5 mL DCM and shake for 2 minutes (note b). Allow the phases to separate.	(c) pH paper may be used.

A.8.1.3 Run off the organic layer into a drying column (notes d and e) containing anhydrous sodium sulphate (A5.8.1) and collect the eluate in a Kuderna - Danish evaporator fitted with a 10 mL graduated tube.

(d) If emulsions form, transfer the bulk of the solvent to a drying column. Transfer the interfacial cuff into a beaker and adsorb the water with sodium sulphate. Decant the dried solvent into the drying column. Wash the beaker with a few mL of DCM and transfer the washings to the drying column.

(e) Alternative procedures for drying the extracts with sodium sulphate may be used.

A8.1.4 Repeat the extraction of the aqueous phase with a further 50 ± 5 mL of DCM. Transfer the solvent to the same drying column.

A8.1.5 Wash the drying column after the extracts have passed through with 20 ± 2 mL of DCM collecting the solvent in the same Kuderna-Danish evaporator.

A8.2 Concentration of extracts

A8.2.1 Add an anti-bumping granule to the evaporator. Place the evaporator over a steam bath and reduce the volume of solvent to 3-5 mL (note f).

(f) Violent ebullition of the solvent may occur. Take care to avoid loss of extract.

A8.2.2 Remove the graduated tube from the evaporator (note g) and reduce the solvent to incipient dryness with a gentle stream of dry nitrogen (A6.1.8).

(g) If the extracts are not to be analysed immediately, then make up the extract to approximately 10 mL with DCM and store in a refrigerator at 4 °C or below.

A8.2.3 Dissolve the residue in 1.00 ± 0.01 mL of aqueous methanol (A5.13), (note h).

(h) The extracts should be analysed within 24 hours to reduce the risk of solvent evaporation.

A8.3 High performance liquid chromatography

A8.3.1 Inject 25 µL aliquots of the standards and extracts from samples, blanks and recoveries into the chromatograph. Record the retention times and peak areas (or heights).

A8.3.2 Using the standards prepare a calibration graph for each determinand of peak height or area versus concentration (mgL^{-1}).

A8.3.3 Read off the concentration of each determinand present from the corresponding calibration graph and calculate the amount present in the original sample (note i), see section A9.

(i) A direct calculation may be performed using a laboratory data system, by taking into account the volumes in steps A8.1.1, A8.1.2 and A8.2.3.

A8.4 Confirmation

A8.4.1 Change the HPLC conditions (note j). Re-analyse the extracts following similar procedures to those described in sections A8.3.1 to A8.3.3. HPLC-MS confirmation can also be carried out. Set up the HPLC-MS in the SIM mode under conditions given in section A6.4 after selecting suitable ions for monitoring. Concentrate extracts to achieve adequate sensitivity using procedures similar to those described in sections A8.2.2 and A8.2.3.

(j) This can include mobile phase composition or column type.

A8.5 Blanks

A8.5.1 Adequate blank values should be obtained using interference free water before analysing samples. At least one reagent blank should be analysed with each batch of samples.

A8.6 Recoveries

A8.6.1 Check the efficiency of the analytical procedure for each batch of samples analysed by adding suitable amounts of standard material to separate samples of interference free water, for example HPLC grade, immediately before extraction (note k). Process these solutions under conditions identical with those to be used for the samples under investigation.

A8.7 AQC

A8.7.1 Carry out the entire procedure using distilled water (or water of a similar nature to the sample being analysed) spiked at approximately 0.1 μgL^{-1} with individual standards. If the responses of extracted standards are used for comparison with those of the samples, an automatic correction is obtained. If not, the data from previous tests should be averaged and a mean correction factor determined to be used for correcting for recovery.

(k) Use up to 1 mL of an appropriate working solution (A5.15.2).

A9 Calculation

The concentration of each determinand, in μgL^{-1}, can be found from the following equation:

$$C_{sa} = (A_{sa} / A_{std}) \times (V_2 / V_1) \times C_{std}$$

If the calibration graph (see section A8.3.3) is used

C_{ext} should replace $C_{std} \times A_{sa}/A_{std}$

Where:

A_{sa} = Peak height or area for the determinand in the sample extract (A8.3.1).

A_{std} = Peak height or area for the determinand in the standard (A8.3.1).

V_1 = Volume of sample taken, mL (A8.1.1 or A8.1.2).

V_2 = Final volume of the extract for the determination, mL (A8.2.3).

C_{std} = Concentration of the determinand in the standard, μgL^{-1}.

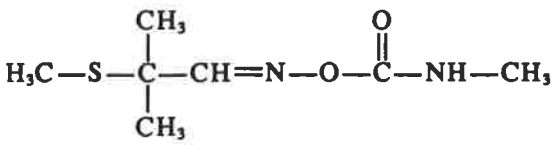
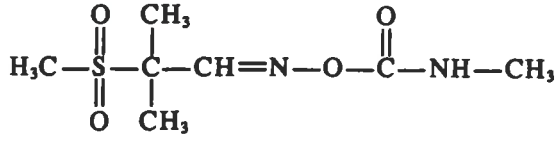
C_{sa} = Concentration of the determinand in the sample, μgL^{-1}.

C_{ext} = Concentration of the determinand in the sample extract, μgL^{-1}.

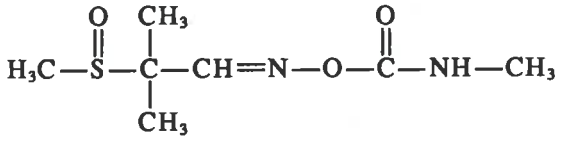
A10 Reference

R. T. Krause, J. Chrom, Sci. 16 (1978) 281-288.

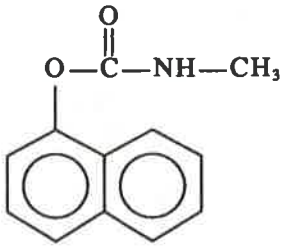
TABLE A1 Structures of the substances determined by this method

Compound (Molecular weight)	Structure
Aldicarb (190)	
Aldicarb sulphone (222)	

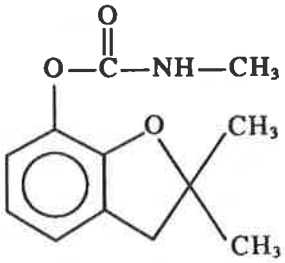
Aldicarb sulphoxide
(206)



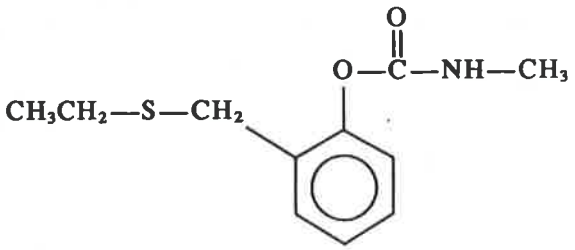
Carbaryl
(201)



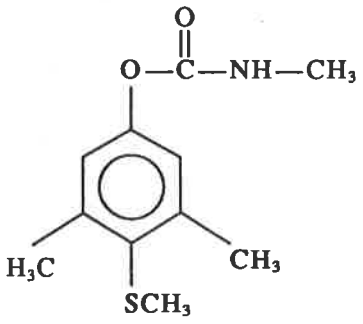
Carbofuran
(221)



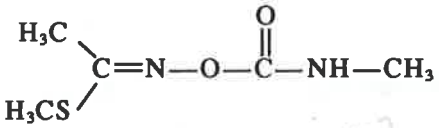
Ethiofencarb
(225)



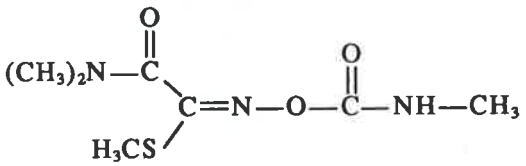
Methiocarb
(225)



Methomyl
(162)



Oxamyl
(219)



Propoxur
(209)

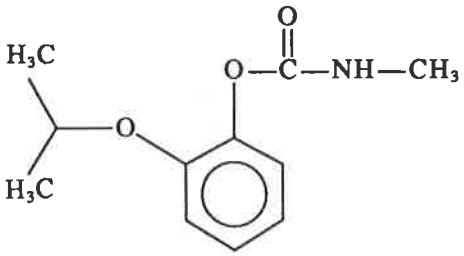
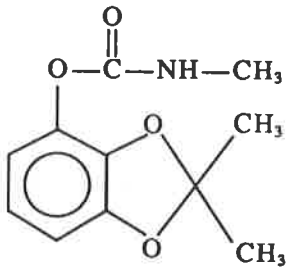
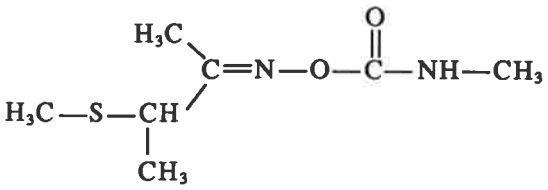
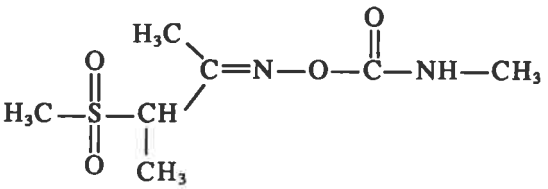
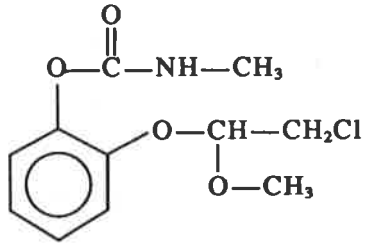
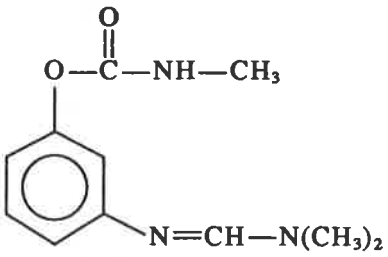
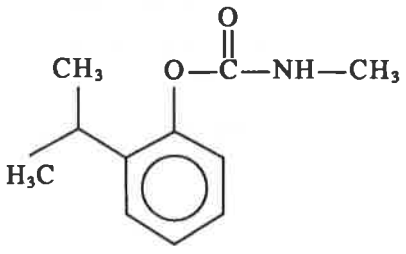
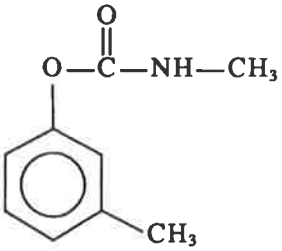
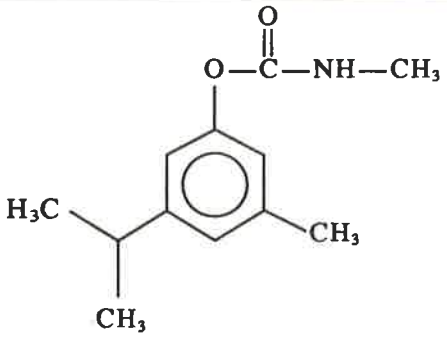


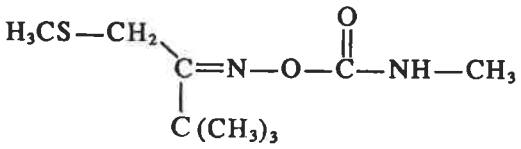
TABLE A2 Structures of other N-methyl carbamates which may also be determined by this method

Compound (Molecular weight)	Structure
Bendiocarb (223)	
Butocarboxim (190)	
Butoxycarboxim (222)	
Cloethocarb (259)	
Formetanate (221)	
Isoprocarb (193)	
Metolcarb (165)	

Promecarb
(207)



Thiofanox
(218)



Xylycarb
(179)

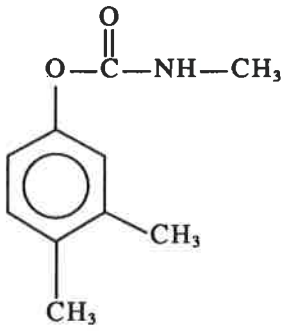


TABLE A3 Means, Standard deviations and Recoveries — extraction method A8.1.1

Compound	Sample	Concentration found	Recovery (%)	Standard deviation	Degrees of freedom
Aldicarb sulphoxide	Blank	<0.04			7
	0.1 spike	0.079	79	0.0077	7
	0.5 spike	0.374	75	0.0101	3
	1.0 spike	0.780	78	0.0248	3
Aldicarb sulphone	Blank	<0.01			7
	0.1 spike	0.089	89	0.0028	7
	0.5 spike	0.442	88	0.0077	3
	1.0 spike	0.873	87	0.0070	3
Aldicarb	Blank	<0.01			7
	0.1 spike	0.085	85	0.0030	7
	0.5 spike	0.436	87	0.0140	3
	1.0 spike	0.922	92	0.0120	3

Units expressed in μgL^{-1} unless otherwise stated.

High purity water was used in this analysis.

The data in Tables A3 and A4 were generated using a Waters Carbamate Analysis System, thermostated at 80 °C with reagent flow rates of 0.5 $mLmin^{-1}$.

Data provided by Rhône-Poulenc Agriculture Ltd.

TABLE A4 Means, Standard deviations and Recoveries — extraction method A8.1.2

Compound	Sample*	Concentration found	Recovery (%)	Standard deviation	Degrees of freedom
Aldicarb	Blank	<0.02			2
sulphoxide	0.1 spike	0.0308	31	0.00495	9
	Control	<0.02			5
	0.5 spike	0.0568	11	0.0168	5
Aldicarb	Blank	<0.01			2
sulphone	0.1 spike	0.0353	35	0.00193	9
	Control	<0.01			5
	0.5 spike	0.1754	35	0.00816	5
Oxamyl	Blank	<0.01			2
	0.1 spike	0.0545	55	0.00307	9
	Control	<0.01			5
	0.5 spike	0.2677	54	0.0142	5
Methomyl	Blank	<0.01			2
	0.1 spike	0.0687	69	0.00224	9
	Control	<0.01			5
	0.5 spike	0.3561	71	0.0188	5
Aldicarb	Blank	<0.04			2
	0.1 spike	0.0632	63	0.00782	9
	Control	<0.04			5
	0.5 spike	0.4334	87	0.0116	5
Propoxur	Blank	<0.03			2
	0.1 spike	0.0869	87	0.00560	9
	Control	<0.03			5
	0.5 spike	0.4709	94	0.0086	5
Carbaryl	Blank	<0.02			2
	0.1 spike	0.0941	94	0.00325	9
	Control	<0.02			5
	0.5 spike	0.4842	97	0.0134	5
Ethiofencarb	Blank	nr			2
	0.1 spike	nr	–	–	9
	Control	nr			5
	0.5 spike	0.2339	47	0.593	5
Methiocarb	Blank	<0.01			2
	0.1 spike	0.0838	84	0.00307	9
	Control	<0.01			5
	0.5 spike	0.4448	89	0.0096	5

Units expressed as μgL^{-1} unless otherwise stated.

nr = none recovered

*Blank = Deionised water

Control = River water

Data provided by NRA (Anglian Region).

Figure A1 **Typical HPLC chromatogram of a N-methyl carbamates mixed standard (0.2 mgL^{-1} each compound)**

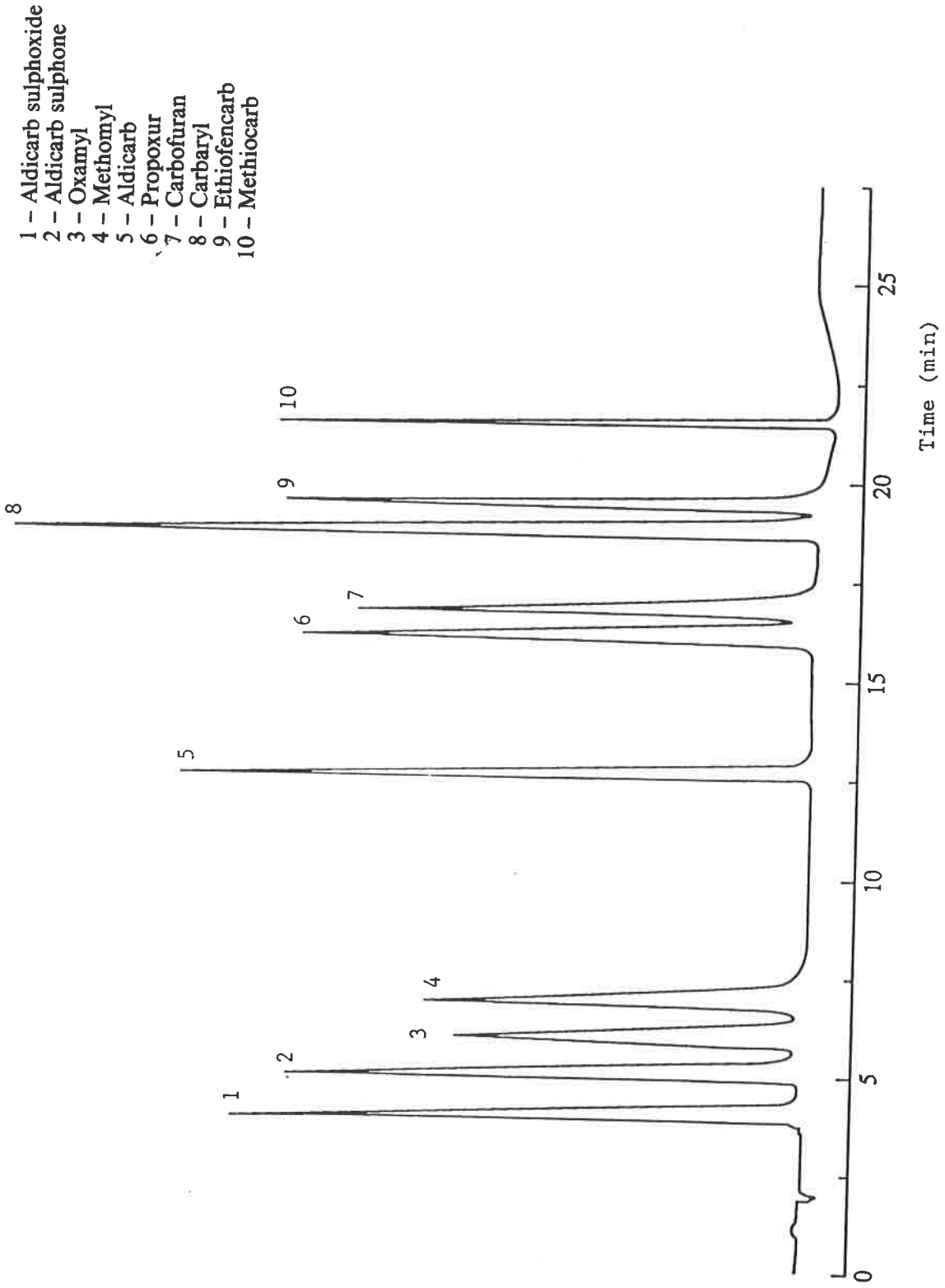
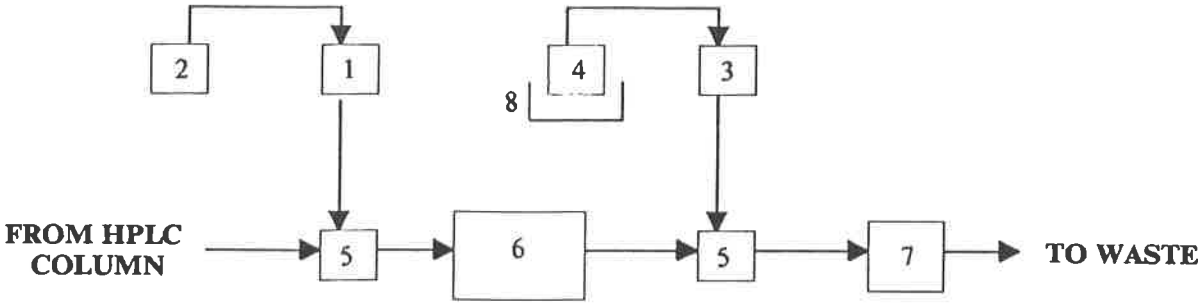
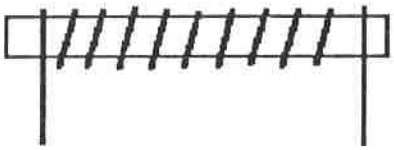


Figure A2 HPLC and post-column reaction/detection system



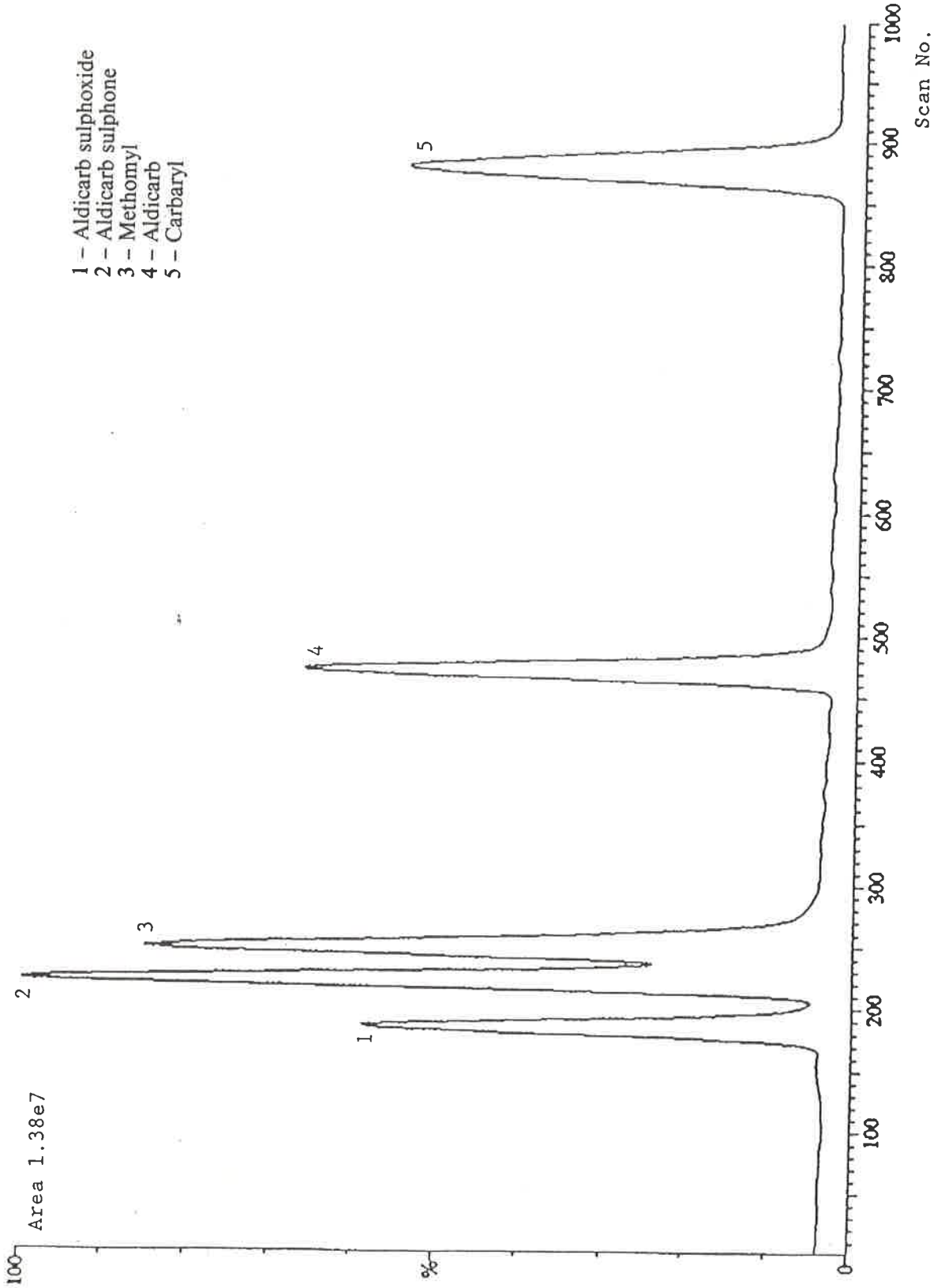
1 Reagent pump for sodium hydroxide solution. Flow rate = 0.2 $mLmin^{-1}$.
2 Reagent bottle containing sodium hydroxide solution (A5.9).
3 Reagent pump for OPA reagent. Flow rate = 0.2 $mLmin^{-1}$.
4 Reagent bottle containing OPA reagent (A5.11).
5 Mixing tee.
6 Heated reaction coil. PTFE tubing 3 m × 0.25 mm id, maintained at a fixed temperature between 80 and 95 °C, either in an oil bath or in a column oven, see below).
7 Fluorescence detector, Excitation = 330 nm, Emission = 445 nm.
8 Ice bucket for the OPA reagent

By tightly winding the PTFE reaction coil onto a 250 × 3 mm stainless steel or copper tube as below, it is possible to use an HPLC column oven to effect the hydrolysis.



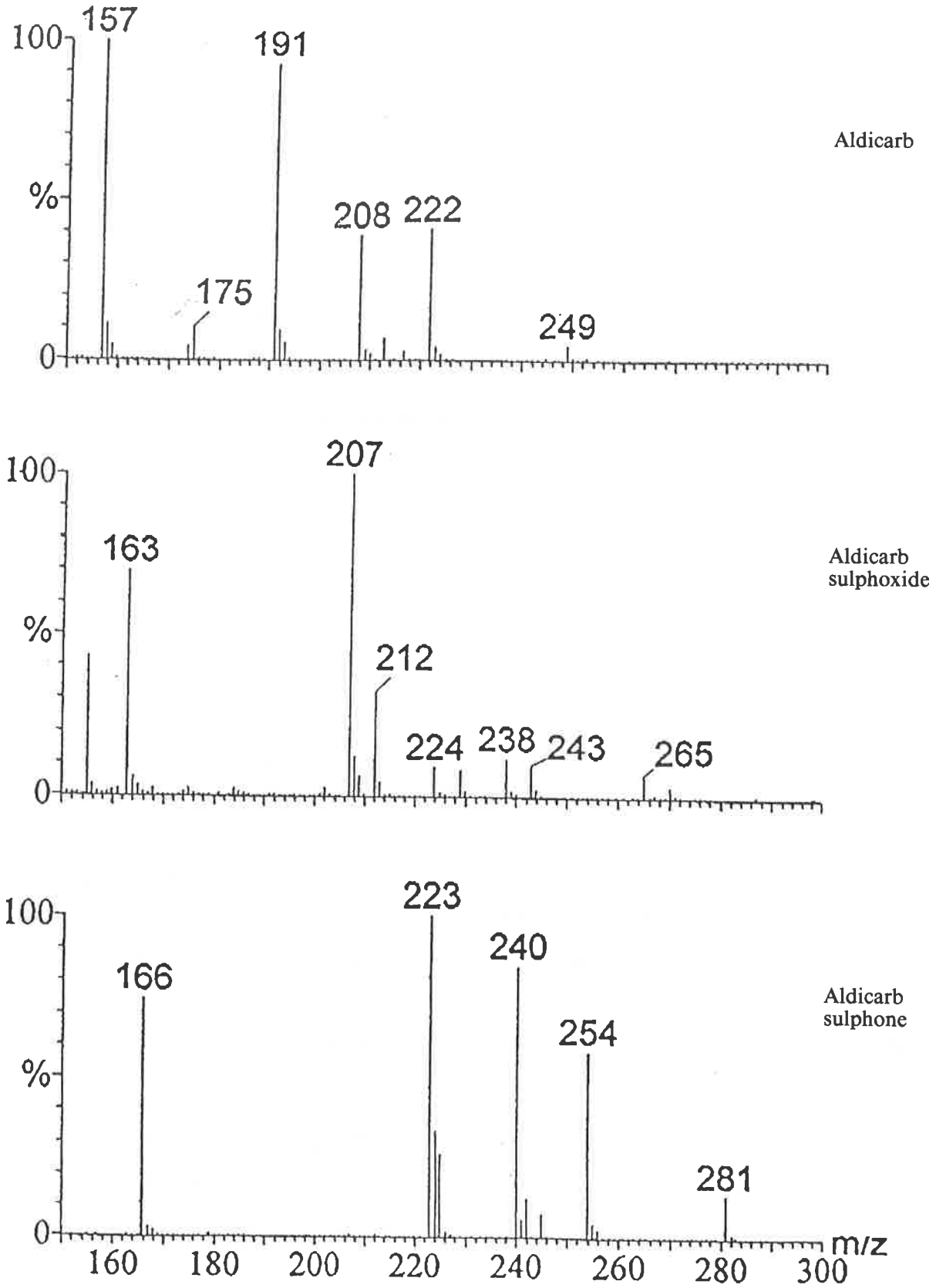
Secure the ends with copper wire to prevent the tube uncoiling.

Figure A3 **Thermospray HPLC-MS TIC chromatogram for a N-methyl carbamates mixed standard (10 mgL^{-1} each compound)**



Note: The scan rate was 1 scan per second.

Figure A4 **Thermospray HPLC-MS mass spectra for aldicarb, aldicarb sulphoxide and aldicarb sulphone**



Note: These spectra were obtained using a 10 mgL^{-1} mixed standard.

B Confirmation of total aldicarb residues and other N-methyl carbamates in waters by GC (a note)

B1 Performance characteristics of the method

B1.1	Substances determined	Aldicarb, aldicarb sulphoxide and aldicarb sulphone. All are converted to and analysed as aldicarb sulphone. Most of the other determinands (Method A, Tables A1 and A2) can also be determined by GC using the extract from method A.
B1.2	Types of sample	Drinking and river water.
B1.3	Basis of method	For total aldicarb residues, the sample is oxidised with peracetic acid, extracted with dichloromethane and purified using a Florisil column. For other determinands, the extract from method A is used. Analysis is by GC with a nitrogen selective detector.
B1.4	Calibration curve	The range of linearity depends upon the equipment in use and is typically up to 1 μgL^{-1}.
B1.5	Standard deviation	Typically 0.008 μgL^{-1}.
B1.6	Limit of detection	Typically 0.012 μgL^{-1}.
B1.7	Interferences	Any co-extracted material which responds to the detector and which has a similar retention time to the determinands will interfere.

B2 Principle

For total aldicarb residues, the determinands are all converted to aldicarb sulphone by oxidation with peracetic acid and then extracted with dichloromethane. The extract is further purified by using a Florisil column and the final determination carried out by gas chromatography with a nitrogen selective detector (GC-NPD).

B3 Interferences

Any co-extracted material which responds to the detector and which has a similar retention time to the determinands will interfere.

B4 Hazards

Acetone is flammable. Dichloromethane is narcotic and toxic. Acetic anhydride and peracetic acid are flammable and corrosive. Diethyl ether is toxic, narcotic and flammable. Hydrogen peroxide and sulphuric acid are corrosive. The pesticide standards are extremely toxic. Caution must be exercised when preparing the stock solutions. Skin contact, ingestion and inhalation must be avoided. Appropriate safety procedures should be followed.

B5 Reagents

All reagents must be of sufficient purity that they do not give rise to significant interference peaks in the chromatograms. This should be checked for each batch of materials and verified by running procedural blanks with each batch of samples analysed.

The water used for blank determination and preparation of control samples should show negligible interferences when compared with the smallest concentration to be determined.

Reagents may become contaminated by contact with air and/or other materials, particularly plastics, or by degradation caused by the action of light. Reagents should be stored in all glass containers or other suitable vessels and be kept in the dark if necessary.

B5.1 Acetic anhydride – Analytical reagent grade.

B5.2 Acetone – Glass distilled.

B5.3 Dichloromethane (DCM) – HPLC grade.

B5.4 Diethyl ether – Glass distilled.

B5.5 Hydrogen peroxide (100 vol) – Analytical reagent grade.

B5.6 Sulphuric acid (98%) – Analytical reagent grade.

B5.7 Water – HPLC grade.

B5.8 Florisil (100-200 μm) – Analytical reagent grade, activated at 160 °C.

B5.9 Peracetic acid (40% v/v) – To a stirred, cooled solution of 100 ± 1 mL hydrogen peroxide (B5.5) add slowly 1.0 ± 0.1 mL sulphuric acid (B5.6) followed by the slow addition of 100 ± 2 mL acetic anhydride (B5.1). The solution is left at about 4 °C overnight.

B5.10 Sodium hydrogen carbonate solution 1M – Weigh out 84.0 ± 0.5 g analytical grade sodium hydrogen carbonate and dissolve in 1000 ± 10 mL water.

B5.11 Sodium sulphate – Anhydrous - heat at 500 ± 20 °C for 4 hr ± 30 min. Cool to about 200 °C in a muffle and then to ambient temperature in a desiccator. Store in a closed glass container.

B5.12 Standard Solutions

B5.12.1 Stock solution – Prepare a stock solution of aldicarb sulphone in acetone at a concentration of 1000 mgL^{-1}. For example, in a volumetric flask dissolve 100.0 ± 0.1 mg pure or suitably certified material in 100.0 ± 0.1 mL of solvent.

B5.12.2 Working standard solutions – Prepare a series of working standard solutions by dilution of the stock solution (B5.12.1) with acetone. A useful working range is from 0.01 to 1.0 mgL^{-1}.

B5.13 Solvent mixtures

B5.13.1 Solvent Mixture 1 – In a 1 litre measuring cylinder dilute 50 mL acetone to 1 litre with diethyl ether.

B5.13.2 Solvent Mixture 2 – In a 1 litre measuring cylinder dilute 250 mL acetone to 1 litre with diethyl ether.

B6 Apparatus

Glassware should be clean and dry.

B6.1 Sample Extraction

B6.1.1 Sample bottles – Glass bottles of 250 mL capacity, marked at 200 mL, fitted with glass stoppers or PTFE-lined screw caps.

B6.1.2 Measuring cylinders – Glass, 10, 50 and 100 mL capacity.

B6.1.3 Separating funnels – Glass, 500 mL capacity, fitted with a grease-free glass or PTFE tap and stopper.

B6.1.4 Drying columns – Glass, 15 × 1 cm.

B6.1.5 Rotary evaporator – Fitted with a cold-trap condenser and a water bath.

B6.1.6 Mechanical shaker (optional) – Capable of taking the sample bottles.

B6.1.7 Round bottom flasks – Glass, 250 mL capacity.

B6.2 Gas Chromatography – A gas chromatograph fitted with a split/splitless injector and a nitrogen selective detector.

The following conditions have been found suitable:

Column:	25 m × 0.32 mm id fused silica capillary, SE54, 0.2 μm film thickness or equivalent.
Column temperature:	190 °C (isothermal).
Injector temperature:	250 °C.
Detector temperature:	250 °C.
Carrier gas:	Helium at 1.5 $mLmin^{-1}$.
Injection volume:	2 μL, 10:1 split injection.

Under these conditions aldicarb sulphone has a retention time of approximately 3 minutes.

B7 Sample collection and storage

Samples should be taken in glass bottles with glass stoppers or PTFE-lined screw caps. They should be extracted and analysed as soon as possible after sampling. If this is impracticable they should be stored in a refrigerator at about 4 °C. They should not be stored in the vicinity of standard materials or their concentrated solutions.

B8 Analytical Proceture

Step	Procedure	Note
B8.1	Extraction	
B8.1.1	Total aldicarb residues. Add 4 ± 0.5 mL peracetic acid solution (B5.9) to 200 ± 1 mL of sample in the sample bottle and shake for 30 minutes. (note a)	(a) A mechanical shaker may be used
B8.1.2	Quantitatively transfer the mixture to a 500 mL separating funnel using 100 ± 5 mL sodium hydrogen carbonate solution (B5.10). Extract the sample with 100 ± 5 mL DCM and allow the phases to separate.	
B8.1.3	Run the DCM layer through a drying column containing anhydrous sodium sulphate (B5.11) into a 250 mL round bottom flask. Extract the aqueous phase with a further 40 ± 2 mL DCM and collect as before. Finally, wash the sodium sulphate column with 20 mL DCM and collect the solvent in the round bottom flask.	
B8.2	Clean-up and concentration	
B8.2.1	Prepare a 6g Florisil column in DCM and add 1-2 g of anhydrous sodium sulphate (B5.11).	
B8.2.2	Pass the combined DCM extracts from B8.1.3 through the Florisil column and discard the eluate.	
B8.2.3	Elute the column with 100 ± 2 mL solvent mixture 1 (B5.13.1) and discard the eluate.	
B8.2.4	Elute the column with 70 ± 2 mL solvent mixture 2 (B5.13.2) and collect the eluate. Evaporate to incipient dryness and re-dissolve the residue in 1.0 ± 0.1 mL acetone.	

B8.3 Gas chromatography

B8.3.1 Inject 2 µL aliquots of standards and extracts of samples, blanks and recoveries into the gas chromatograph. Record the retention times and peak heights or areas.

B8.3.2 Using the standards prepare a calibration graph of peak height or area versus concentration (mgL^{-1}).

B8.3.3 Read off the concentration of aldicarb sulphone present from the calibration graph and calculate the total aldicarb residue expressed as sulphone in the original sample, see section B9.

B9 Calculation

The concentration of total aldicarb residues in μgL^{-1} (expressed as aldicarb sulphone equivalents) in the sample can be found from the following formula:

$$C_{sa} = (A_{sa} / A_{std}) \times (V_2 / V_1) \times C_{std}$$

If the calibration graph (section B8.3.3) is used

C_{ext} should replace $C_{std} \times A_{sa}/A_{std}$.

Where:

A_{sa} = Peak height or area for the determinand in the sample extract (B8.3.1).

A_{std} = Peak height or area for the determinand in the standard (B8.3.1).

V_1 = Volume of sample taken, mL (B8.1.1).

V_2 = Final volume of extract for the determination, mL (B8.2.4).

C_{std} = Concentration of aldicarb sulphone in the standard, μgL^{-1}.

C_{sa} = Concentration of aldicarb as sulphone equivalents in the sample, μgL^{-1}.

C_{ext} = Concentration of aldicarb as sulphone equivalents in the sample extract, μgL^{-1}.

To express the results for total aldicarb residues as aldicarb equivalents (C_{eq}, μgL^{-1}) use the following formula:

$$C_{eq} = C_{sa} \times (190/222)$$

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 ± 3s) or 2 consecutive values exceed the warning limit (at ± 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

None of the methods given in this booklet have 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 any of these methods would estimate the accuracy of its own analytical results and report the findings to the Secretary of the Department of the Environment's Standing Committee of Analysts.

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