Determination of Synthetic Pyrethroid Insecticides in Waters by Gas Liquid Chromatography 1992 (Tentative Method)

Methods for the Examination of Waters and Associated Materials

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Contents

About This Series

This booklet is part of a series intended to provide recommended methods for determining the quality of water and associated materials. In addition short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series is published as a series of booklets on single or related topics, thus allowing for the replacement or addition of methods as quickly as practicable without the need for waiting for the next edition. The rate of publication is also related to the urgency of the requirement for that particular method.

Although ideally, all methods published should be fully tested, this is not often possible without delay in publication. Furthermore, the limit of detection, range, precision and interference effects applying to instrumental methods can depend on the actual instrument used, as well as on sample type, reagent purity and operator skill, etc. Even methods tested in many laboratories have been known to acquire problems when new products appear (introducing new substances into effluents), changes in production methods affecting reagent quality, or the method used to analyse new types of sample (despite apparent similarity to samples already evaluated). As a guide, the following categories have been given to methods:

(i) tested, usually in five or more laboratories
— no grade indicated;

(ii) tested in one to three or four laboratories
— Tentative;

(iii) evaluated, but not fully tested, but publication is urgently required
— Note;

(iv) tested and found to be satisfactory by several laboratories, but in the opinion of experts requires a high degree of skill or has some other difficulty such that the method would be replaced if a better method were discovered.
— Provisional.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users and senior technical staff, to decide which method to use for the determination in hand. Whilst the attention of users is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has nine working groups, each responsible for one section or aspect of water cycle 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 nonmetallic 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 the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press. A current list of publications can be obtained from the Secretary.

Every effort is made to prevent errors from occurring in the published text. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically. However, should any errors be found, please notify the Secretary.

DR D WESTWOOD
Secretary

16 October 1991

Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety and COSHH Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

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

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

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

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

Safety while Sampling

Prior consideration must be given, especially when sampling in confined spaces or where access is difficult, to guard against suffocation, drowning, falls and poisoning or infection by ingestion, inhalation or skin contact.

Good Laboratory Practice

The Department of Health issues a booklet entitled: Good Laboratory Practice; the United Kingdom Compliance Programme, 1989. This can be obtained by writing to that Department in London. It deals chiefly with toxicity studies, but much can be applied to analytical chemistry.

Introduction

The method in this booklet is expected to be applicable to most synthetic pyrethroids including, fenpropathrin, permethrin, cyhalothrin, cyfluthrin, cypermethrin, fenvalerate and deltamethrin and their isomers. Resmethrin is not included because of low sensitivity (notes a and b).

The method is based on removal of the pyrethroids from water by solvent extraction, clean-up of the extract by adsorption chromatography followed by determination using capillary GC with electron capture detection (GC/ECD).

Three clean-up procedures are given using Florisil, an aminopropyl bonded phase silica or alumina.

Florisil cartridges have been evaluated for permethrin, cypermethrin and alphacypermethrin in ground water. A Florisil column is also expected to be suitable and column conditions are given for guidance.

Aminopropyl bonded phase cartridges have been similarly tested for all the pyrethroids listed above except for fenpropathrin, cyfluthrin and cyhalothrin. This procedure has been optimised for simultaneous determination of organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) in the same extract as pyrethroids. In this case, compounds are quantified against decachlorobiphenyl as an internal standard.

The alumina column has been examined for recovery of all the pyrethroids as reference materials. Both alumina and Florisil clean-up should also allow simultaneous determination of other insecticides with appropriate calibration.

Notes (a) For the relationship between the common names, trademarks and the chemical structures of these compounds see the Appendix.

(b) If the determination of resmethrin is required, the method should be evaluated using a mass spectrometer operating in electron impact (EI) mode with selected ion monitoring (SIM) as detector.

A generally applicable set of capillary GC/ECD conditions which can be used for pyrethroids, OCs and PCBs is given in the method. GC conditions which have been used for the determination of individual pyrethroids are also included.

Confirmation of positive results is by gas chromatography-mass spectrometry (GC–MS) operating in the negative ion chemical ionisation (CI) mode with SIM. This provides a sensitive and selective means of confirming results and provides greater certainty of identity in these cases. When a GC-MS instrument with this capability is not available, results should be confirmed, as necessary, by GC using a column with a different stationary phase. The GC-MS procedure may also be used as the primary method of determination; in this case clean-up of some extracts may prove unnecessary.

An alternative solid phase extraction procedure has been developed by ICI Agrochemicals, based on use of cartridges to sample and extract water. It has not been included in this booklet because it is too complex for routine use. This method has been evaluated individually for cyhalothrin, cypermethrin and permethrin and is available from ICI on request.

Determination of Synthetic Pyrethroid Insecticides in Waters by Gas Liquid Chromatography

1 Performance Characteristics of the Method

1.1	Substances determined	Most synthetic pyrethroids. The compounds for which water test data are given include permethrin, cypermethrin, alphacypermethrin fenvalerate and deltamethrin. The method may also be used for fenpropathrin, cyhalothrin and cyfluthrin.
1.2	Types of sample	River and drinking water.
1.3	Basis of method	Solvent extraction of the sample followed by concentration, chromatographic clean-up and capillary gas chromatography using electron-capture detection (GC/ECD). Confirmation is by gas chromatography-mass spectrometry (GC-MS) operating in the negative ion chemical ionisation (CI) mode.
1.4	Range of application	Typically up to 10μg/l
1.5	Calibration curve	Linearity depends on the detector in use but is normally up to about 1 ng for the compounds tested.
1.6	Standard deviation	See Tables 1 and 2.
1.7	Limit of detection	Typically 0.01μg/l (See Tables 1 and 2).
1.8	Sensitivity	Depends on the instrument in use. See Table 4.
1.9	Bias	Recovery efficiencies are less than 100%. See Tables 1 to 3.
1.10	Interferences	Any electron capturing material which passes through the procedure and has similar GC characteristics to any determinand will interfere. Certainty of identity in the case of positive results is improved by negative ion CI GC-MS analysis.
1.11	Time required for analysis	Assuming the apparatus and equipment is prepared, eight samples can be analysed in 1.5 days.

2 Principle

Samples are extracted with hexane. The extracts are concentrated, cleaned-up (as necessary) using Florisil, an aminopropyl bonded phase silica or alumina, before analysis by capillary column GC with electron capture detection (GC/ECD).

3 Interferences

Any substance which passes through the procedure and produces a response on the electron capture detector at a retention time similar to any of the determinands will interfere. Clean-up of extracts and the use of a high resolution wall coated open tubular (WCOT) column assists in separation of the determinands from interfering material. Use of GC-MS operating in the negative ion CI mode with SIM will also reduce such problems.

4 Hazards

Hexane, acetone, methyl tertiary-butyl ether and diethyl ether are flammable. Ethers can form explosive peroxides. The pyrethroids and their solutions should be considered as toxic. Ensure adequate ventilation and work in a flame and spark free area. Spark proof refrigerators should be used to store organic solvent extracts.

5 Reagents

The reagents vary with the procedure chosen. All reagents should be of sufficient purity to give chromatograms free from interfering peaks. They should be checked to confirm that they are interference free and if necessary a different source of supply found.

5.1 Hexane—Pesticide grade or equivalent.

5.2 Acetone—Pesticide grade or equivalent.

5.3 Methyl tertiary-butyl ether (MTBE)—HPLC grade.

5.4 Diethyl ether—analytical grade reagent.

5.5 n-Decane—glass distilled.

5.6 Water—for use in preparation of blanks, controls and Florisil should be glass distilled and checked for absence of significant interference.

5.7 Cotton wool—washed with hexane.

5.8 Sodium sulphate—granular, anhydrous analytical grade reagent. Heat at 500 ± 20°C for 4 hours ± 30 minutes. Cool to about 200°C in a muffle furnace and then to ambient temperature in a desiccator containing magnesium perchlorate or equivalent alternative. (Washing thoroughly with acetone, air drying followed by drying in an oven at 200 ± 5°C overnight before use has also proved satisfactory). Store in a closed glass container.

5.9 Florisil cartridges—pre-packed containing 1 g of adsorbent, such as Spe-ed or equivalent.

5.10 Florisil—60–100 mesh. Heat to 120 ± 5°C overnight. Cool, add 10% by weight of glass distilled water and agitate in closed glass vessel until a free flowing powder is obtained. Store in a closed glass container.

5.11 Aminopropyl cartridges—pre-packed containing 500 mg of adsorbent, Bond Elut or equivalent.

5.12 Alumina

5.12.1 Woelm A Super 1 (acidic) or equivalent

Heat at 500 ± 20°C for 4 hours ± 30 minutes. Cool to about 200°C in a muffle furnace then cool in a desiccator containing magnesium perchlorate or equivalent. Deactivate the alumina by adding 7% by weight of water and agitating in a closed glass container until an even consistency is obtained. Store in a closed glass container.

5.12.2 Woelm B Super 1 (basic) or equivalent

Prepared and deactivated as for acidic alumina in section 5.12.1. Store in a closed glass container.

5.13 Eluting solvents

5.13.1 Methyl tertiary-butyl ether + hexane (5 + 95 v/v).

5.13.2 Diethyl ether + hexane (15 + 85v/v and 10 + 90 v/v).

5.14 Standard solutions

5.14.1 Stock solution of pyrethroids:

Prepare a stock solution of each pyrethroid of 1000 or 100 μg/ml by dissolving an accurately weighed amount of pure or suitable certified material in acetone + hexane (10 + 90 v/v).

5.14.1.1 Working standards:

Prepare working solutions by serial dilution of stock solutions in hexane. A useful working range is 0.005 to 0.2 μg/ml.

5.14.1.2 When retention times of each pyrethroid have been determined, preparation of a mixed standard is convenient for routine work.

5.14.2 If the internal standard method with clean-up on the aminopropyl cartridge is to be used, prepare the following additional standard solutions using the procedures described in sections 5.14.1 and 5.14.1.1

5.14.2.1 A working standard solution of decachlorobiphenyl of 0.5 μg/ml in acetone.

5.14.2.2 Mixed working standard solutions of pyrethroids and decachlorobiphenyl in the concentration range as in section 5.14.1.1 but each containing 0.05 μg/ml of decachlorobiphenyl. In this case n-decane should be substituted for hexane as solvent.

6 Apparatus

All apparatus should be checked for contamination before use. Some brands of detergents can give rise to interferences. A suitable cleaning procedure for glassware is as follows:—Wash with a suitable detergent, rinse with pesticides-free water and dry in an oven (60–120°C). Immediately before use rinse with acetone and then hexane and allow to drain.

6.1 Glass sample bottles—1 or 2 litre nominal capacity (to contain a minimum of 1.2 or 2.2 litres and marked for sampling at 1 or 2 litres as appropriate) with PTFE (Teflon) lined screw caps or glass stoppers.

6.2 Glass columns—200 mm long by 7–8 mm internal diameter.

6.3 Kuderna-Danish Evaporator—(250 ml).

6.4 Graduated tubes—(10 ml, 0.1 ml graduations) tapered, glass stoppered.

6.5 Nitrogen line—gas cleaned by passage through molecular sieve type 13X pellets or activated charcoal/silica gel terminating in a fine jet of glass or metal.

6.6 Separating funnels—pear-shaped 2 litre and 1 litre capacity, used with a grease-free tap or fitted with a PTFE tap.

6.7 Florisil Column. Plug a glass column with cotton wool. Fill the column with hexane. Slowly, with gentle tapping, add 5 ± 0.1 g Florisil (section 5.10) followed by granular anhydrous sodium sulphate (1 g). Drain the hexane level to the top of column bed.

6.8 Alumina column. Plug a glass column with cotton wool. Add 2 g acidic alumina (section 5.12.1), 1 g basic alumina (section 5.12.2) and a 5 mm cap of sodium sulphate (section 5.8) to the column. Wash the column with 15 ml hexane, tapping to remove bubbles. The whole column should be prepared immediately before use.

6.9 Gas chromatograph—fitted with an electron capture detector and a capillary (WCOT) column (5% phenyl methyl silicone eg DB5 or SE54 are suitable but other phases such as OV1701 or OV101 may be used). Availability of an auto injector is an advantage. The system must have an electronic integrator for peak area or peak height determination. Three different sets of GC conditions have been used to obtain the test data for pyrethroids. An applicable set of conditions used to obtain the data in Table 2 is given in Figure 1. Under these conditions pyrethroids are eluted after OCs and PCBs and in the case of isomer mixtures are separated into their respective enantiomeric pairs. A chromatogram showing the elution pattern for these compounds including permethrin, cypermethrin, fenvalerate and deltamethrin is given in Figure 1.

Chromatograms for pyrethroids used to obtain the test data in Tables 1 and 3 are shown in Figures 2 and 3 respectively. The conditions used in Figure 3 are also generally applicable. Relative retention times for pyrethroids chromatographed under the conditions given in Figure 1 are given in Table 5.

Other chromatographic conditions may be used where these have been proved to be suitable.

6.10 GC–MS Equipment—capable of operating in the negative ion chemical ionisation (CI) mode with selected ion monitoring (SIM). Details of suitable ions are given in Table 6 and examples of mass spectra and mass chromatograms are shown in Figures 4 to 8.

7 Sample collection and storage

Sample bottles should be glass with PTFE lined screw caps or glass stoppers. Each bottle should be checked by rinsing with a small volume of hexane and examining the rinsings by GC/ECD. Bottles showing contamination should be rejected. Bottles should be filled to the 1 or 2 litre mark.

The pyrethroids may become adsorbed on the walls of the sample bottle. Samples should not be subdivided before analysis. Sample bottles should be stored in a refrigerator at about 4°C. It is recommended that samples should be extracted within 24 to 48 hours of sampling.

8 Analytical procedure

Step	Procedure	Notes
8.1	Extraction	
8.1.1	To a 1 litre sample of water in the sample bottle, add 100 ± 5 ml of hexane. Shake the bottle vigorously for 1 minute (notes a and b).	(a) Up to 2 litres of a sample of water may be extracted under the same conditions and the extraction (steps 8.1.1 to 8.1.4) may also be carried out in a separating funnel, shaking vigorously for 1 minute. A machine for shaking bottles in a horizontal plane may be used but then the shaking period must be extended to at least 5 minutes. (b) If the aminopropyl cartridge clean-up procedure is to be used, add 100 ± 2μl of decachlorobiphenyl solution in acetone (section 5.14.2.1) in step 8.1.1 before extraction with hexane.
8.1.2	Pour the contents into a 1 litre separating funnel. Rinse the bottle with a further 20 ± 2 ml of hexane and transfer the washings to the same separating funnel. Allow the layers to separate and run the lower aqueous layer back into the sample bottle.	
8.1.3	Dry the hexane extract in the separating funnel by passing it through 20 ± 2 g granular anhydrous sodium sulphate supported by a plug of cotton wool in a short column or filter funnel. Collect the dried extract in a 250 ml round bottom flask.	
8.1.4	Add a further 50 ± 5 ml of hexane to the sample bottle and shake vigorously for 1 minute. Repeat steps 8.1.2 and 8.1.3. If not already known measure the volume of water sampled to ± 5ml.	
8.1.5	Wash the sodium sulphate with 20 ± 2 ml hexane and collect in the flask with the rest of the extract.	
8.2	Concentration	
8.2.1	Reduce the combined hexane extracts just to dryness by rotary evaporation (note c). Proceed as soon as possible to step 8.3.	(c) Various methods of solvent evaporation can be used and the extract may be evaporated in a Kuderna Danish evaporator. This procedure should be used if OCs and PCBs are to be determined in the same extract as pyrethroids as care is needed to avoid loss of the more volatile OCs during the evaporation stage (see also organochlorine insecticides method in this series [1,2]). In the case of the aminopropyl clean-up (section 8.3.2), n-decane (1 ± 0.1 ml) is added as keeper, to minimise loss of the more volatile OCs and the extract is rotary evaporated to approximately 4 ml as in section 8.2.1 and not to dryness.
8.2.2	For some clean waters where clean-up is unnecessary, take the sample up in 1 ± 0.05 ml hexane or n-decane and pass directly to step 8.4.	

Step	Procedure	Notes
8.3	Clean-up	
	Three alternative clean-up procedures may be used.	
8.3.1	**Florisil**	
8.3.1.1	Prepare a Florisil cartridge by washing successively with a mixture of methyl tertiary-butyl ether (MTBE) + hexane (5 + 95 v/v, 10 ± 0.5 ml) and hexane (10 ± 0.5 ml) (note d).	(d) Solvent flow can be speeded up through the cartridge if necessary by applying slight positive air pressure to the top.
8.3.1.2	Using 1 ± 0.05 ml aliquot portions of hexane to wash out the flask containing the sample residue, carefully transfer any residuum from Step 8.2.1 to the cartridge bed. Use a total of 3 ml of hexane in the transfer ensuring each portion is adsorbed into the packing before adding the next one. Elute the cartridge with a further 7 ± 0.2 ml of hexane (note e). Collect all the hexane in a 10 ml tapered tube (Fraction 1) (note f).	(e) A portion of this 7 ml of hexane can be used to rinse the flask if necessary before eluting the column. (f) This fraction may be retained for analysis of other insecticides including OCs.
8.3.1.3	Elute the cartridge with a mixture of MTBE + hexane (5 + 95 v/v) collecting 12 ± 0.2 ml in a 10 ml tapered tube (Fraction 2) (note g). Evaporate this fraction just to dryness with a stream of clean dry nitrogen with the tube placed on a warm bath. Pipette 1 ± 0.05 ml of hexane into the tube to re-dissolve the residuum (1ml equivalent to 1 litre of water) (note h).	(g) The calibration of the Florisil cartridge has been established for cypermethrin, alphacypermethrin and permethrin. It is given as a guide and should be checked for each batch of cartridges used. It should be adjusted as necessary in the case of other pyrethroids and checked for any other insecticides to be analysed. (h) A Florisil column prepared as described in section 6.7 may be used in place of a cartridge. In the case of cypermethrin, alphacypermethrin and permethrin it should be eluted with hexane 16 ± 0.2 ml (Fraction 1) and diethyl ether + hexane (10 + 90 v/v) 20 ± 0.2 ml (Fraction 2). Fraction 2, containing the pyrethroids, should be progressed as in section 8.3.1.3. The same guidance on calibrating the column as given in note (g) for cartridges also applies.
8.3.2	**Aminopropyl silica**	
8.3.2.1	Prepare an aminopropyl cartridge by washing with hexane (6 ± 0.5 ml) (note d).	
8.3.2.2	Transfer the extract from the flask in Step 8.2.1 (note c) to the cartridge bed and collect the eluate in a tapered tube. Wash out the flask with a total of 6 ± 0.2 ml of diethyl ether + hexane (15 + 85 v/v) and transfer the washings to the cartridge. Collect the eluate in the same tapered tube (note i).	(i) This clean-up procedure has been optimised for simultaneous determination of OCs and pyrethroids in the same extract. The calibration should be checked for each batch of cartridges and should be adjusted as necessary if only pyrethroids are to be determined.
8.3.2.3	Evaporate the contents of the tube to 1 ± 0.05 ml using a stream of clean dry nitrogen.	

Step	Procedure	Notes
8.3.3	**Alumina**	
8.3.3.1	Prepare an alumina column as described in section 6.8. Run off the surplus hexane.	
8.3.3.2	Transfer the residuum from Step 8.2.1. to the top of the column as described in Step 8.3.1.2. Allow the hexane level to reach the top of the packing.	
8.3.3.3	Elute the column with diethyl ether + hexane (10 + 90 v/v) (35 ± 0.5 ml). Collect the total eluate from the column (note j). Evaporate the eluate and adjust to 1 ± 0.05 ml with hexane using the procedures previously described (notes c, f).	(j) The calibration of the alumina column has been established for each pyrethroid. It is given as a guide and should be checked for each batch of alumina used.
8.4	GC/ECD determination	
8.4.1	Set up the machine in accordance with the manufacturer's instructions using the conditions given in Figure 1.	
8.4.2	Inject aliquots of appropriate standard solutions and sample extracts (section 8.3.1.3, 8.3.2.3 or 8.3.3.3) into the GC using a microlitre syringe (note k).	(k) If the internal standard method with aminopropyl cartridge clean-up is being followed, procedures in Sections 8.4.2 to 8.4.4 should be adapted accordingly and standard solutions in n-decane should be used.
8.4.3	Measure, using an integrator, the total area of the separated isomer peaks for each pyrethroid or determine the heights of the peaks (notes l, m) (refer to Figures 1 and 3).	(l) The ratio of peaks for separated isomers arising from water samples may differ from that in the corresponding standard due to degradation or interference. In these circumstances, results should be confirmed using an alternative GC column or GC-MS as described elsewhere in this booklet. (m) Where sufficient resolution is achieved, separated isomers may be determined if necessary.
8.4.4.	Construct a calibration graph of peak area or peak height for the standards versus concentration (μg/ml) of pyrethroid injected (note n).	(n) If the internal standard was used construct a calibration graph of peak ratios relative to the internal standard versus mass ratios relative to the internal standard for each pyrethroid injected.
8.4.5	Read the concentration of the pyrethroid in the sample extracts from the calibration graph (or mass ratio in the case of the internal standard) and calculate the concentration present in the original sample (See section 9).	
8.5	GC-MS determination/confirmation	
8.5.1	Set up the multiple ion detector in the negative ion CI mode with methane reagent gas to select the appropriate ions for the pyrethroids to be determined. Suitable ions are shown in Table 6. Follow similar procedures to those described in section 8.4.1 to 8.4.5 (notes o, p).	(o) GC-MS may be used in place of GC/ECD for quantitative determination of pyrethroids in extracts. In this case less clean-up may be necessary. (p) Where GC-MS with negative ion facilities is not available, results should be confirmed by GC/ECD using a capillary (WCOT) column with a different stationary phase.

Step	Procedure	Notes
8.6	Blanks	
8.6.1	Adequate blank values should be obtained using interference free water before analysing samples and one reagent blank should be analysed alongside each set of samples.	
8.7	Recoveries	
8.7.1	Check the efficiency of the analytical procedure for each batch of samples analysed by adding suitable known amounts of standard materials to a separate sample of interference free water immediately before extraction (note q). Process this sample under conditions identical with those to be used for the samples under analysis.	(q) Use up to 1 ml of a dilute standard solution for the addition and allow the solvent to evaporate before extraction.

9 Calculation

9.1 External standard procedure

$$C = \frac{c \times v}{V}$$

If a 1 litre sample of water is extracted into 1 ml before GC determination then:

$$C = c$$

9.2 Internal standard procedure

If the procedure in Section 8 note (n) has been followed then:—

$$C = \frac{R \times A}{V}$$

where C = Concentration in the original sample (μg/l)
c = Concentration determined in the extract (μg/ml)
V = Volume of the original sample (litres)
v = Volume of the extract for the determination (ml)
R = Mass ratio of the determinand to internal standard from the calibration graph.
A = Amount of internal standard added to the original sample (μg).

The value of C may be calculated for individual pyrethroid isomer peaks separated or peaks for each pyrethroid may be summed to give the total of each pyrethroid present. Identification is aided by examining the pattern of peaks in each case (refer also to note l in section 8).

References

1. Organochlorine Insecticides and Polychlorinated Biphenyls in Waters 1978. HMSO, London, in this series.

2. The Determination of Organochlorine Insecticides and Polychlorinated Biphenyls in Sewages, Sludges, Muds and Fish, 1978. Organochlorine Insecticides and Polychlorinated Biphenyls in Water, an addition 1984. HMSO, London, in this series.

Table 1 Recoveries and limits of determination for ground water—Florisil cartridge clean-up

Pyrethroid	Spiking concentration (μg/l)	Mean concentration found (μg/l)	Number of determinations	Standard deviation (μg/l)	Mean recovery (%)
Cypermethrin	—	<0.01	9	—	—
	0.05	0.047	5	0.003	94
	0.10	0.098	2	0.005	98
	0.20	0.20	8	0.013	100
	0.50	0.46	5	0.011	92
Alphacypermethrin	—	<0.01	4	—	—
	0.10	0.090	2	0.002	90
	0.20	0.19	2	0.004	95
Permethrin	—	<0.01	4	—	—
	0.10	0.087	4	0.002	87

Notes: (a) Samples were taken from ground water sources and spiked, where appropriate, with the pyrethroids. The number of different waters used was 8 in the case of cypermetherin and 4 each in the case of alphacypermethrin and permethrin. The volume of water extracted in each case was 500 ml. Recoveries are uncorrected and are based on total isomers in the case of cypermethrin and permethrin.

(b) The limit of determination was set at 0.01 μg/l for each pyrethroid and none of the pyrethroids was found above this value in any of the waters used.

(c) In addition, in the case of cypermethrin 5 reagent blanks were all <0.01 μg/l.

(d) The following GC/ECD conditions were used to obtain these results in the case of cypermethrin: fused silica capillary (WCOT) 30 m × 0.33 mm ID, DB-5, (0.25 μm thickness), helium 3.8 ml/min, oven temperature 240°C, injection split ratio 10:1, retention time 7.8, 8.1, 8.3, 8.5 min (separated isomers). Similar GC conditions with a 5% phenyl methyl silicone column were used for alphacypermethrin and permethrin but with an oven temperature of 200°C in the latter case. Chromatograms for standards obtained under the conditions used are shown in Figure 2.

Table 2 Recoveries and limits of determination for ground water—aminopropyl cartridge clean-up

Pyrethroid		Spiking concentration (μg/l)	Mean concentration found (μg/l)	Number of determinations	Standard deviation (μg/l)	Mean recovery (%)
Permethrin	cis	0.04	0.040	4	0.002	100
	trans		0.039	4	0.002	98
Permethrin	cis	0.02	0.019	1	—	95
	trans		0.016	1	—	80
Cypermethrin	peak 1	0.08	0.062	4	0.011	78
	peak 2		0.054	4	0.009	68
	peak 3		0.061	4	0.021	76
	peak 4		0.043	4	0.009	54
Cypermethrin	peak 1	0.04	0.028	1	—	70
	peak 2		0.035	1	—	88
	peak 3		0.028	1	—	70
	peak 4		0.018	1	—	45
Fenvalerate	peak 1	0.04	0.022	4	0.003	55
	peak 2		0.017	4	0.002	43
Fenvalerate	peak 1	0.02	0.018	1	—	90
	peak 2		0.010	1	—	50
Deltamethrin		0.04	0.018	4	0.004	45
		0.02	0.014	1	—	70

Notes: (a) Samples were taken from ground water sources and spiked with the pyrethroids. The volume of water extracted was 2 litres. Recoveries were determined using the internal standard procedure and are uncorrected.

(b) The GC/ECD conditions used are given in detail in Figure 1.

(c) The limits of determination for ground water were:

Permethrin cis	0.005 μg/l
Permethrin trans	0.005 μg/l
Cypermethrin	0.007 μg/l
Fenvalerate	0.005 μg/l
Deltamethrin	0.003 μg/l

(d) This clean-up procedure has been optimised for simultaneous determination of organochlorine insecticides, PCBs and pyrethroids in the same extract (refer section 8, Note i).

Table 3 Recovery Data for the Alumina Column

Pyrethroid		Recovery %
Fenpropathrin		102
Cyhalothrin		51
Permethrin	cis	97
	trans	100
Cyfluthrin	peak 1	85
	peak 2	51
	peak 3	86
	peak 4	78
Cypermethrin	peak 1	86
	peak 2	70
	peak 3	92
	peak 4	80
Fenvalerate	peak 1	94
	peak 2	84
Deltamethrin		68

Note (a) Improved recovery of pyrethroids can be obtained by eluting the column with an eluent containing a larger proportion of diethyl ether than 10% (v/v) but in this case a less efficient clean-up would be expected.

Table 4 Sensitivity

Pyrethroid		Quantity (ng)	% Full scale deflection at a base-line noise level of 2.7%.
Fenpropathrin		—	—
Cyhalothrin		—	—
Permethrin	cis	0.02	31
	trans	0.02	35
Cyfluthrin		—	—
Cypermethrin	peak 1	0.04	69
	peak 2		63
	peak 3		80
	peak 4		59
Fenvalerate	peak 1	0.02	60
	peak 2		39
Deltamethrin		0.01	70

Note These data were obtained under the conditions set out in Figure 1 using a Varian 3500 GC.

Table 5 Relative retention times for pyrethroids chromatographed under conditions used for Figure 1

Pyrethroid		Retention time relative to decachlorobiphenyl
		Figure 1
Fenpropathrin		—
Cyhalothrin		—
Permethrin	cis	0.895
	trans	0.905
Cyfluthrin	peak 1	—
	peak 2	—
	peak 3	—
	peak 4	—
Cypermethrin	peak 1	0.965
	peak 2	0.973
	peak 3	0.979
	peak 4	0.982
Fenvalerate	peak 1	1.036
	peak 2	1.053
Deltamethrin		1.094

Table 6 Suitable ions for negative ion chemical ionisation GC-MS of pyrethroids

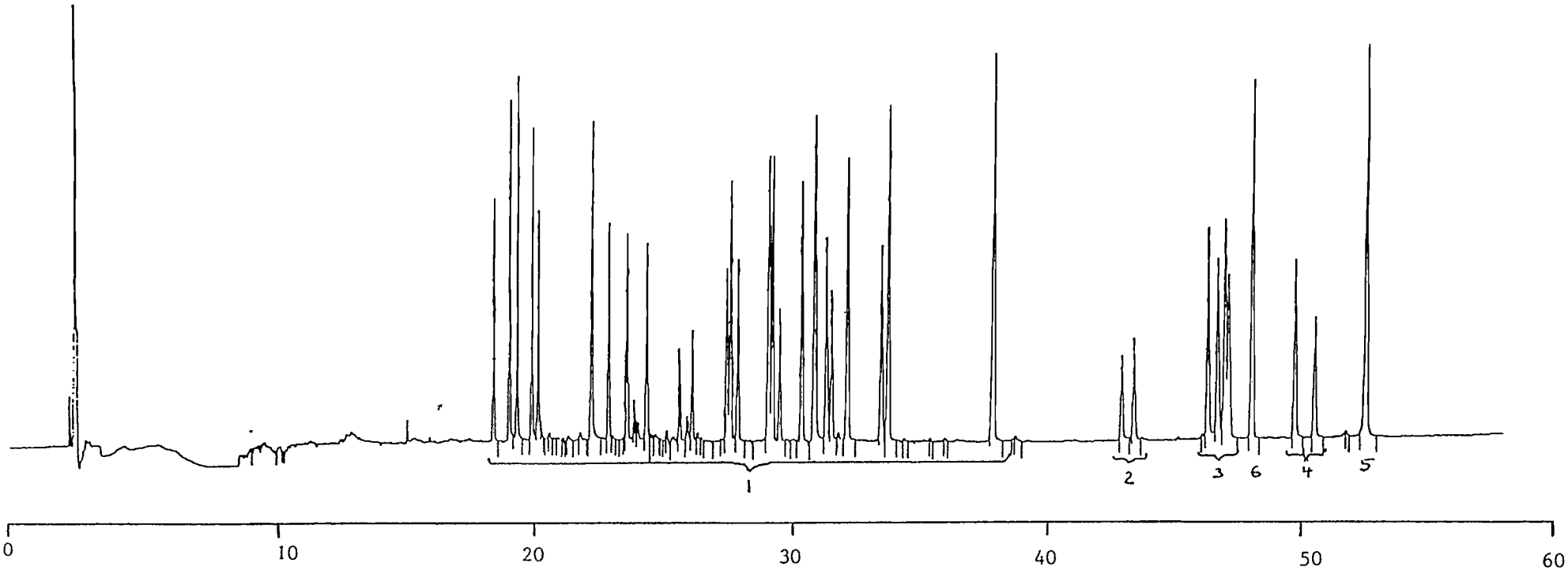
Pyrethroid	Ions (m/z)
Fenpropathrin	—
Cyhalothrin	205, 241
Permethrin	207, 209
Cyfluthrin	207, 209
Cypermethrin	207, 209
Fenvalerate	—
Deltamethrin	79, 81

Notes: (a) The structures of the ions are shown, as appropriate in Figures 5 to 8. In the case of each pyrethroid, the ions are common to separated isomer pairs.

(b) Methane reagent gas.

(c) In the case of fenvalerate and fenpropathrin no data is available.

Fig 1. GC/ECD Chromatogram of Organochlorine Pesticides, PCBs and Pyrethroids



Time (min.)

Notes: (a) 1–Organochlorine pesticides and PCBs.
2–Cis- and trans-permethrin.
3–Cypermethrin,
4–Fenvalerate,
5–Deltamethrin.
6–Internal standard, DCBP.

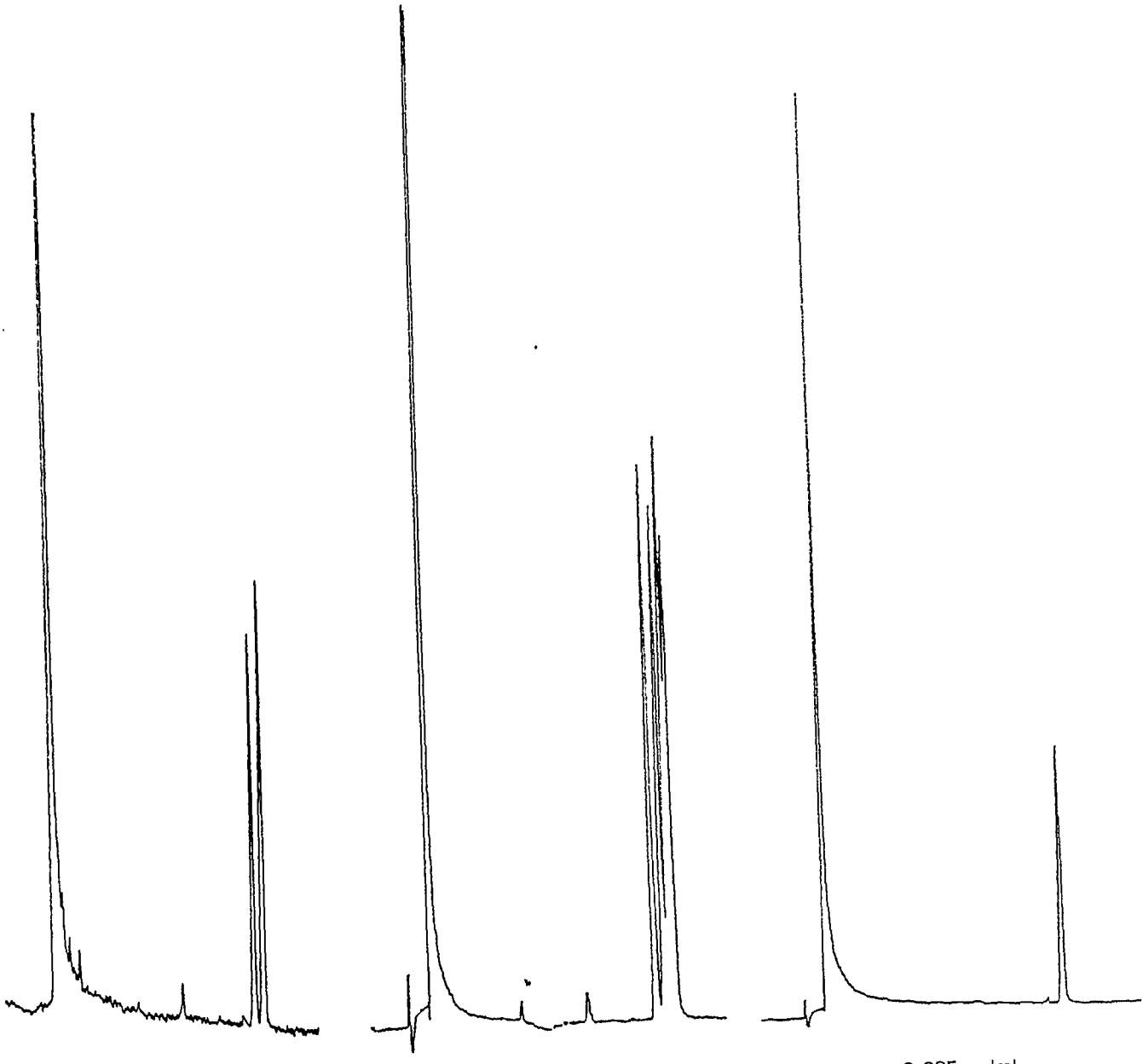
(b) Amount injected on column

Cis-permethrin	0.16 ng
Trans-permethrin	0.16 ng
Cypermethrin	0.32 ng
Fenvalerate	0.16 ng
Deltamethrin	0.16 ng

(c) GC conditions used to obtain the data in Table 2

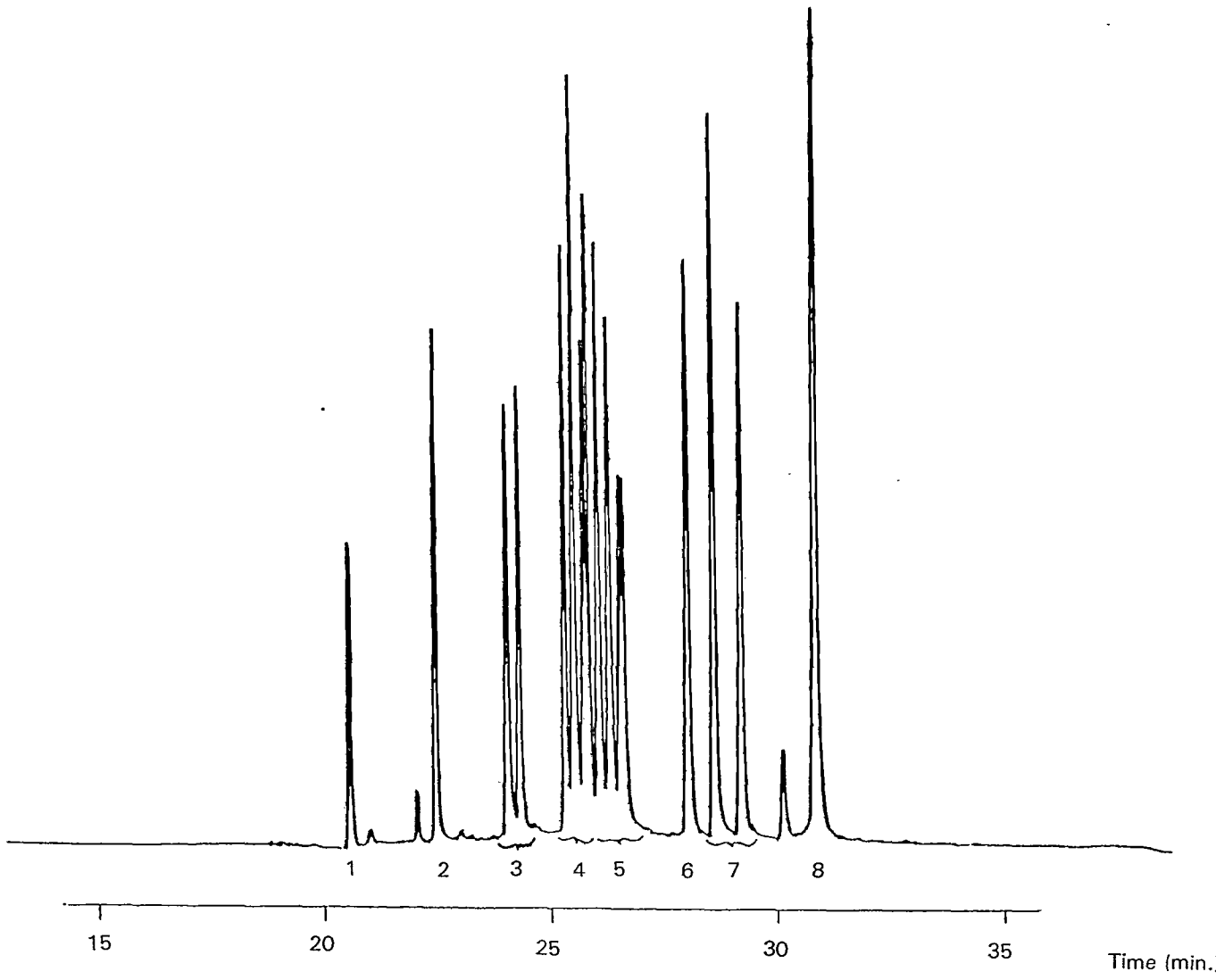
Column	:	Fused silica WCOT capillary 60 m × 0.25 mm ID
Stationary phase	:	DB5 (0.25 μm thickness)
Mobile phase	:	Helium
Flow rate	:	1.5 ml/min
Injection mode	:	On-column
Column temperature	:	80°C for 2 min, 80–200°C at 7.5°C/min, 200–300°C at 2.5°C/min
Injector temperature	:	60°C to 320°C at 90°C/min, held at 320°C for 2 min.
Detector temperature	:	350°C.

Fig 2. GC/ECD Chromatograms of Permethrin, Cypermethrin and Alphacypermethrin.



Note (a) GC conditions similar to those given in Table 1 Note (d) were used.

Fig 3. GC/ECD chromatogram of pyrethroids.



Notes:

(a)

1 Fenpropathrin
2 Cyhalothrin
3 Cis- and trans-permethrin
4 Cyfluthrin (4 peaks)
5 Cypermethrin (4 peaks)
6 Internal standard, DCBP
7 Fenvalerate (2 peaks)
8 Deltamethrin

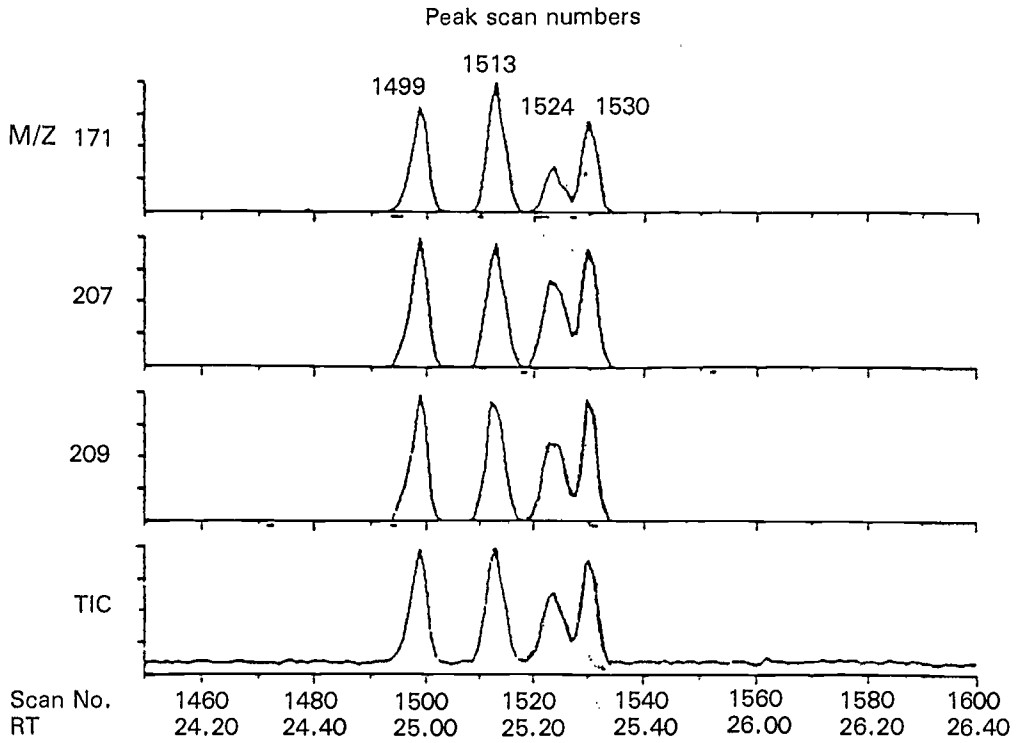
(b) GC conditions used for alumina column recoveries

Column	:	Fused silica WCOT capillary 30 m × 0.25 mm ID
Stationary phase	:	DB5 (0.25 μm thickness)
Mobile phase	:	Hydrogen
Flow rate	:	1.0 ml/min
Injection mode	:	Splitless
Column temperature	:	50°C for 1 minute, 35°C/min to 200°C. Hold 5 minutes at 200°C, then 4°C/min to 280°C. Hold 5 minutes at 280°C.
Injector temperature	:	270°C
Detector temperature	:	320°C

(c) Amount injected on column

Fenpropathrin	1.6 ng
Cyhalothrin	2.0 ng
Cis-permethrin	4.3 ng
Trans-permethrin	3.5 ng
Cyfluthrin	4.4 ng
Cypermethrin	4.9 ng
Fenvalerate	0.3 ng
Deltamethrin	1.2 ng

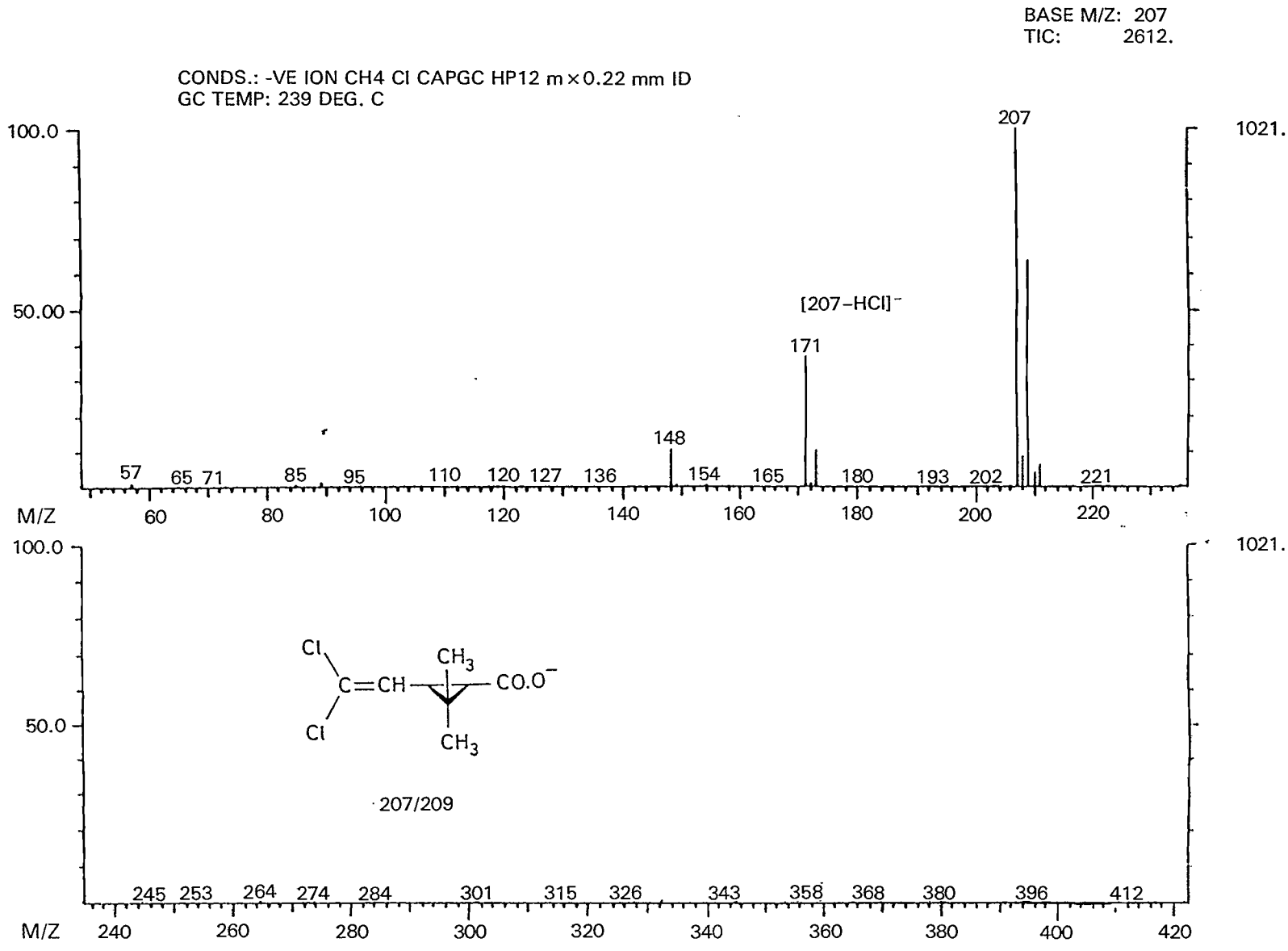
Fig. 4. Selected ion scan mass chromatogram for cypermethrin



Notes (a) The GC Column used was a capillary WCOT OV1, 25 m × 0.32 mm ID with helium carrier gas, splitless injection, temperature programmed: 45°C for 2 minutes, 10°C/min to 240°C. Hold 34.5 min at 240°C, then 10°C/min to 265°C. Hold 2.5 minutes.

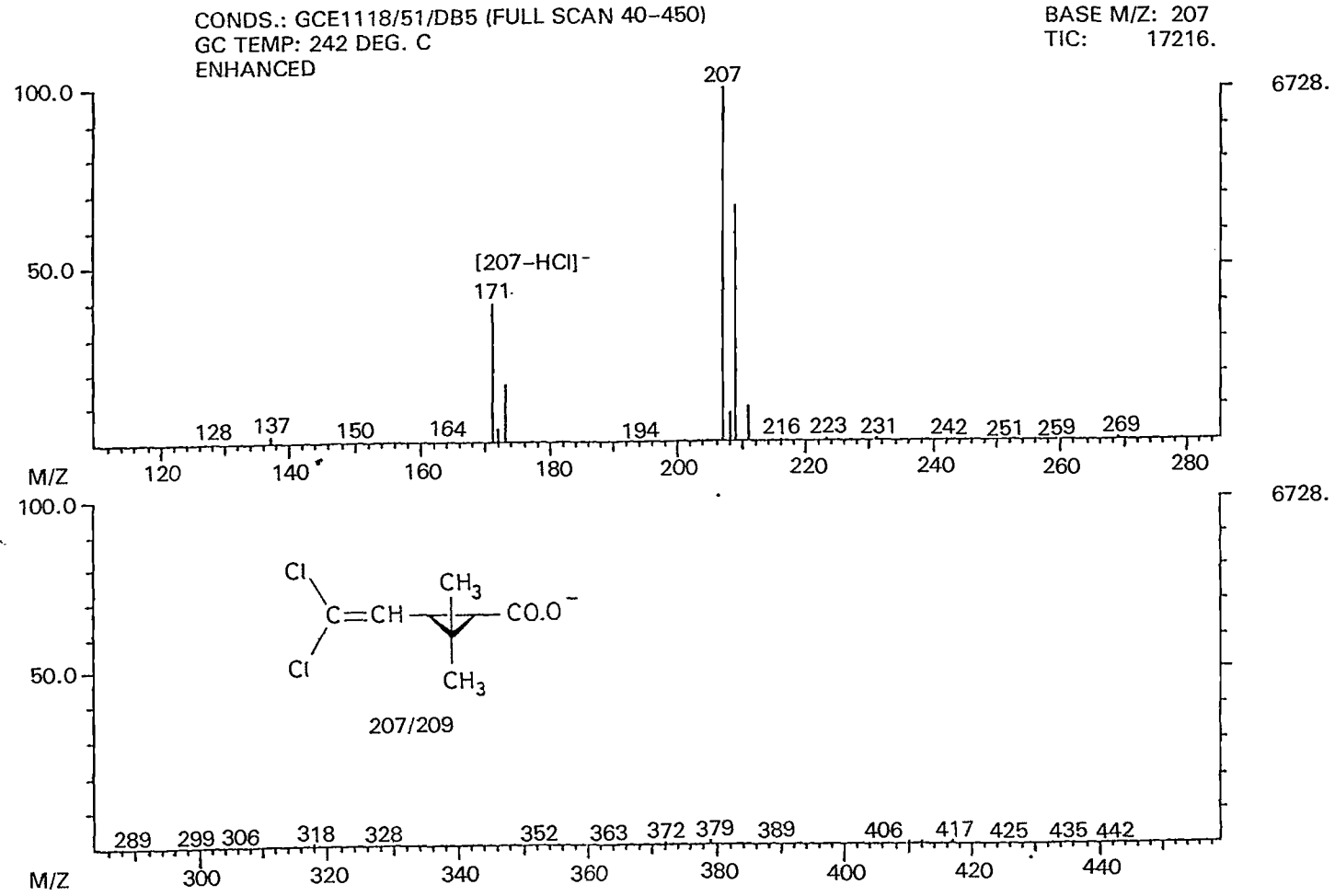
(b) The mass spectrometer used was a Finnigan 4600 operating under the following conditions: Mode negative ion CI, reagent gas methane, source pressure 2.1×10^{-5} torr, electron energy 100 eV, filament current 0.3 amps, EM voltage 1300 volts, ioniser pressure 0.22 torr, ioniser temperature 120°C, sensitivity 10^{-7} amps/volt.

Fig 5 Mass Spectrum of Cypermethrin



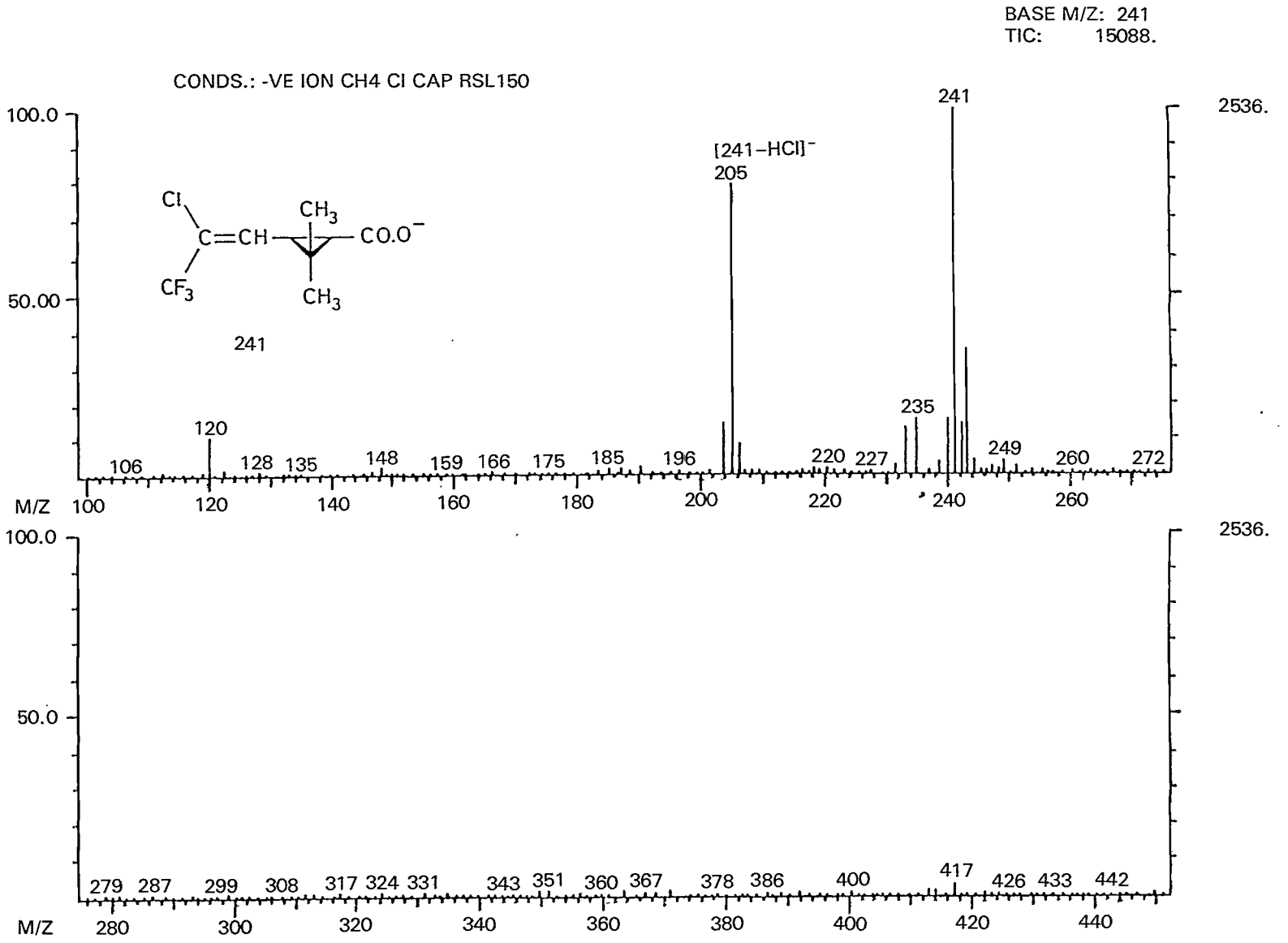
Note (a) The mass spectrometer conditions are given in Figure 4 note (b).

Fig 6 Mass Spectrum of Mixed Permethrin, Cyfluthrin, Cypermethrin Standard



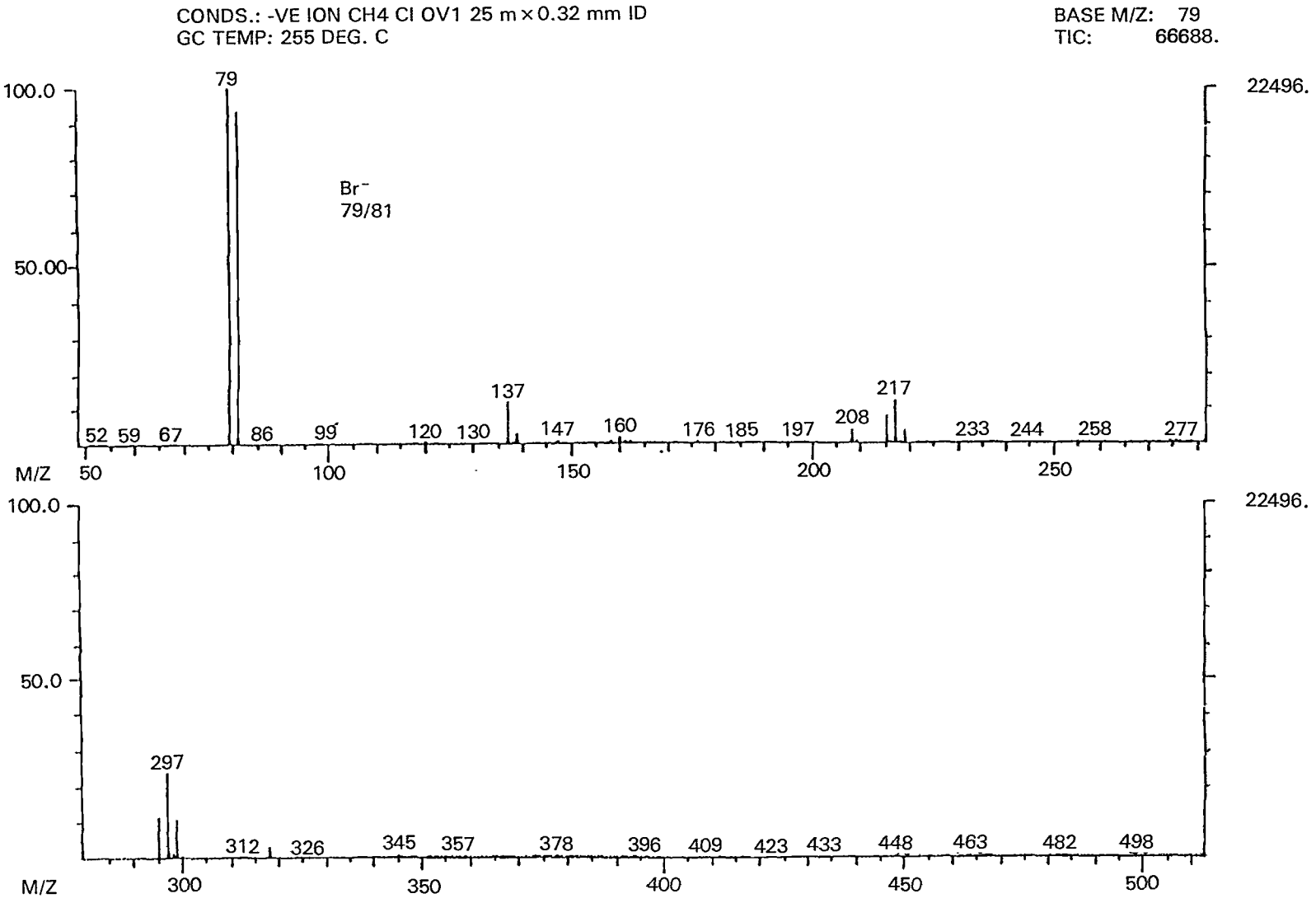
Note (a) This spectrum was obtained using a Finnigan 8200 mass spectrometer operating in the negative ion CI mode with methane reagent gas.

Fig 7 Mass Spectrum of Cyhalothrin



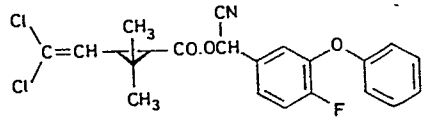
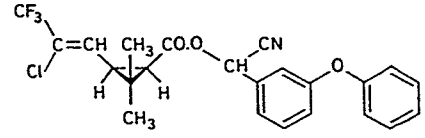
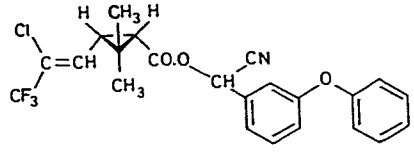
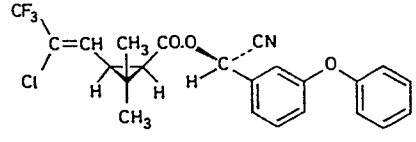
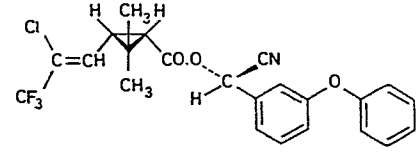
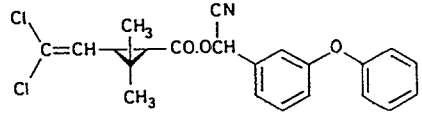
Note (a) The mass spectrometer conditions are given in Figure 4 note (b).

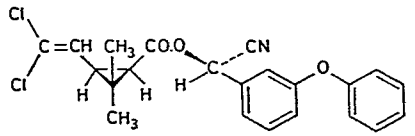
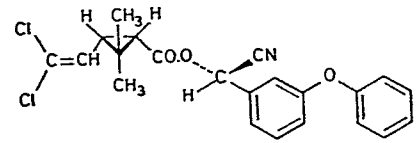
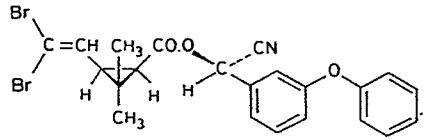
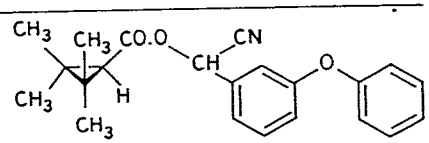
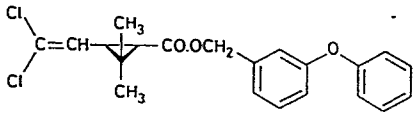
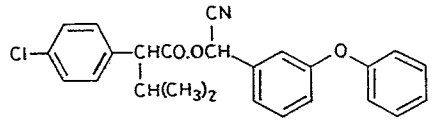
Fig 8 Mass Spectrum of Deltamethrin

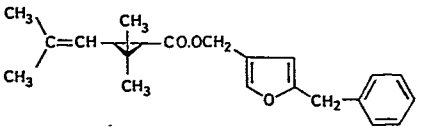
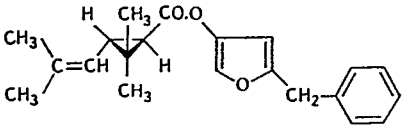


Note (a) The mass spectrometer conditions are given in Figure 4 note (b).

Appendix of common names, trademarks and chemical structures for synthetic pyrethroid insecticides referred to in the method

COMMON NAME	TRADE MARKS*	CHEMICAL FORMULA	CHEMICAL STRUCTURE
Cyfluthrin	'Baythroid', 'Baythroid H', 'Responsar', Solfac 'Muscatox' (mixture with phoxim) for public health, 'Baygon Spray' (mixture with dichlorovos and propoxur), 'Eulan SP' as IR agent (all to Bayer).	$C_{22}H_{18}Cl_2FNO_3$	
Cyhalothrin	'Grenade' for veterinary use, 'Cirrasol MPW' as IR agent (both to ICI)	$C_{23}H_{19}ClF_3NO_3$	 (Z)-(1R)-cis-  (Z)-(1S)-cis-
Cyhalothrin ((S) (Z)-(1R)-cis- and (R) (Z)-(1S)-cis-isomers)	'Karate' for agronomic use (to ICI)	as above	 (S) (Z)-(1R)-cis-  (R) (Z)-(1S)-cis-
Cypermethrin	'Polytrin' (to Ciba-Geigy AG), 'Ambush C', 'Cymbush', 'Imperator', 'Kafil Super', 'CCN52' (all to ICI), 'Cyperkill' (to Mitchell Cotts), 'Ripcord' for agronomic use, 'Barricade', 'Flectron', 'Stockade' for veterinary use and 'Folcord' for public health use (all to Shell), 'Sherpa' (to Rhone-Poulenc), 'Toppel' (to Farm Protection), 'Ammo', 'Arrivo' (both to FMC).	$C_{22}H_{19}Cl_2NO_3$	

COMMON NAME	TRADE MARKS*	CHEMICAL FORMULA	CHEMICAL STRUCTURE
Cypermethrin (S 1R-cis- and R 1S-cis-isomers) (Alphacypermethrin)	'Concord', 'Fastac' for agronomic use, 'Fendona' for public health use and 'Renegade' for veterinary use (all to Shell).	$C_{22}H_{19}Cl_2NO_3$	 (S) (1R)-cis-  (R) (1S)-cis-
Deltamethrin	'Decis' for agronomic uses, 'K-Othrine' for domestic industrial public health and stored product uses, 'Butox', 'Butoflin' both for veterinary uses (all to Roussel Uclaf).	$C_{22}H_{19}Br_2NO_3$	
Fenpropathrin	'Rody', 'Danitol', 'Meothrin' (all to Sumitomo).	$C_{22}H_{23}NO_3$	
Permethrin	'Ambushfog', 'Kafil', 'Perthrine', 'Picket', 'Picket G' (all ICI or SOPRA), 'Dragnet', 'Pounce' (both to FMC), 'Pramex' (Penick), 'Talcord' for agronomic and public health use, 'Outflank', 'Stockade' for veterinary use (all Shell), 'Eksmin' (to Sumitomo), 'Coopex', 'Peregin', 'Stomoxin', 'Stomoxin P', 'Qamlin' and 'Perigen' as IR agent (all to Wellcome Foundation), 'Corsair', 'Tornade' (both to Rhone-Poulenc), 'Eulan SPN' as IR agent (to Bayer), 'SMA-V' as IR agent (to Vickers), 'Antitarma NTC' as IR agent (to Dalton), 'Mitin BC' and 'Mitin AL' (mixture with a hexahydropyrimidine derivative) as IR agents (both to Ciba Geigy).	$C_{21}H_{20}Cl_2O_3$	
Fenvalerate	'Sumicidin' (to Sumitomo), 'Belmark', in USA 'Pydrin' (both to Shell).	$C_{25}H_{22}ClNO_3$	

COMMON NAME	TRADE MARKS*	CHEMICAL FORMULA	CHEMICAL STRUCTURE
Resmethrin	'Benzylfuroline', 'Chryson' (both to Sumitomo).	$C_{22}H_{26}O_3$	
Bioresmethrin	'Combat White Fly Insecticide' (to Fisons), 'Resbuthrin' (to Welcome), 'Biobenzyfuroline', 'Chryson Forte' (to Sumitomo).	$C_{22}H_{26}O_3$	 *(1R)—trans*

Information taken from:

1. The Pesticide Manual, eighth edition, 1987 Ed. C R Worthing.
2. Insect proofing of wool. Lewis D M and Shaw T Rev Prog Coloration, 1987, **17**, 86.

* For guidance purposes only and may not represent a complete list. Further details are now available from the ninth edition of the Pesticide Manual.

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However thoroughly a method may be tested there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:

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