

Chlorphenylid, Flucofuron and Sulcofuron in Waters (Tentative Methods) 1993

Methods for the Examination of Waters and Associated Materials

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Chlorphenylid, Flucofuron and Sulcofuron in Waters (Tentative Methods) 1993

Methods for the Examination of Waters and Associated Materials

This booklet contains tentative methods for chlorphenylid, flucofuron and sulcofuron and a note on the determination of flucofuron by hydrolysis to 4-chloro-3-trifluoromethylaniline.

Method A is for chlorphenylid.

Method B is for flucofuron and sulcofuron.

Method C (the note) is for flucofuron by hydrolysis to 4-chloro-3-trifluoromethylaniline.

Methods A and B are tentative.

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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 These volumes inevitably took some years to prepare so that they were often partially out of date before they appeared in print.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 requirements 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 be dependent 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, for example, when new products appear (introducing new substances into effluents), when changes in production methods affect reagent quality, or when the methods are used to analyse new types of samples (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 was 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

United 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 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 quality analysis. They are as follows:

- 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 members associated with these methods are listed at the back of this booklet.

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

11 June 1992

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. Similar warnings 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 specialised 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.

A Chlorphenylid in waters by methylation and GC-ECD (tentative method)

A0 Introduction

The active ingredient, chlorphenylid, consists mainly of a mixture of the tetrachloro-, pentachloro- and hexachloro- 2-(chloromethylsulphonamide)diphenyl ethers (PCSD). The chlorine atoms are substituted on both benzene rings and the sulphonamide group is situated at position 2 relative to the ether bond.

A1 Performance characteristics of the method

A1.1	Substances determined	Chlorphenylid (Trade name Eulan WA New). PCSD.
A1.2	Type of sample	River and drinking waters.
A1.3	Basis of the method	A two litre water sample is acidified and extracted into dichloromethane (DCM). The concentrated extract is methylated with diazomethane and analysed by gas chromatography (GC) with electron capture detection (ECD).
A1.4	Range of application	0–5 µg/L ⁻¹ . The upper limit may be extended by dilution of the sample extracts or by taking a smaller sample volume.
A1.5	Calibration curve	The range of linearity depends on the detector in use. The instrument used in performance tests gave a linear response over the range of 0–500 pg injected.
A1.6	Standard deviation	See Table 1.
A1.7	Limit of detection	0.019 µg/L ⁻¹ .
A1.8	Sensitivity	Dependent upon the instrument in use. For the instrument used in the performance tests, with a baseline count of 2,500 area counts, injection of 500 pg of derivatised standard gave a total response of 137,000 area counts, with the highest peak giving approximately full scale deflection (FSD) on the analogue trace.
A1.9	Bias	The extraction efficiency is less than 100%. For recoveries see Table 1.
A1.10	Interferences	Any electron capturing material which passes through the procedure and which has a similar retention time to any of the derivatised peaks will interfere.
A1.11	Time required for analysis	Six samples may be analysed per day.

A2 Principle

The sample is acidified to pH 2 and extracted with DCM. After separation, drying and concentration, the solvent is removed by evaporation with a stream of nitrogen and the residue methylated with a solution of diazomethane in diethyl ether. After removal

of excess reagent, the prepared sample is analysed by capillary column GC with ECD. The areas of major peaks in the standard chromatograms are compared with the areas of the same peaks in the sample chromatograms.

A3 Interferences

No serious interference occurred when the method was tested with relatively clean samples. If interference does occur, (indicated by gross distortion of the pattern of peaks), it may be possible to quantify the chlorphenylid by changing to a different column. See also section A8.4.

A4 Hazards

The diazomethane reagent is toxic, carcinogenic and possibly explosive. The sulphonamide reagent used in its preparation has been shown to produce tumours in laboratory animals. Skin contact, ingestion and inhalation must be avoided. All operations involving diazomethane preparation or use, should be carried out in a fume cupboard. DCM and diethyl ether are toxic and narcotic. Diethyl ether and acetone are extremely flammable. Diethyl ether forms explosive peroxides. For information on their detection and removal see A10.1 sections A5.1 and B5.2. Chlorphenylid is toxic. Sulphuric acid is corrosive.

A5 Reagents

All reagents must be of sufficient purity such that they do not give rise to significant interfering peaks in the chromatograms ultimately obtained. This should be verified by running procedural blanks with each batch of samples analysed.

A5.1 Sulphuric acid approximately 5M. (CARE). Add 250 ± 5 mL concentrated sulphuric acid ($d_{20} 1.84$) to about 600 mL distilled water with swirling and cooling. Cool to ambient temperature and dilute to 1 litre with distilled water.

A5.2 Dichloromethane. Pesticide grade.

A5.3 Diethyl ether. Pesticide grade.

A5.4 Acetone. Pesticide grade.

A5.5 N-methyl-N-nitrosotoluene-4-sulphonamide. Analytical reagent grade.

A5.6 Sodium hydroxide. (CARE). Dissolve 60 ± 5 g sodium hydroxide in 100 ± 5 mL distilled water.

A5.7 Acetic acid (glacial).

A5.8 Standards.

A5.8.1 Stock solution. Prepare a stock solution of suitably certified chlorphenylid in acetone. A concentration of 1gL^{-1} is suitable. The solution is stable for at least 1 year at about 4°C . It should be checked for loss of solvent (by evaporation) before use.

A5.8.2 Working solutions. Using the stock solution (A5.8.1) prepare by dilution with ether, standards containing appropriate amounts of chlorphenylid. Suitable solutions are 0.05, 0.1, 0.5, 1.0, 2.5 and 5.0mgL^{-1} . These should be stored in a refrigerator and discarded after 1 month.

A5.9 Granular anhydrous sodium sulphate. Heat at $500 \pm 20^\circ\text{C}$ for $4\text{hr} \pm 30$ min. Cool to about 200°C in a muffle furnace and then to ambient temperature in a desiccator. The roasted material may be stored in a screw topped jar with a PTFE or metal lined cap.

A5.10 Anti-bumping granules. Acetone washed.

A5.11 Nitrogen. Oxygen free, filtered and dry.

A6 Apparatus

A6.1 Sample bottles. All glass or with PTFE lined screw caps, 2 litre capacity, marked at 2 litres.

A6.2 Shaking machine. To shake bottles in a horizontal plane.

A6.3 Separating funnels. 2 litre capacity with ungreased glass or PTFE taps.

A6.4 Methylation apparatus. Apparatus for the generation of diazomethane is available commercially.

A6.5 Kuderna-Danish evaporators. 250 mL.

A6.6 Graduated centrifuge tubes. Glass 10 mL with 0.1 mL graduations, glass stoppered, tapered.

A6.7 Gas Chromatograph. A GC fitted with a capillary column, a suitable injector and with an electron capture detector is required. The instrument should be operated in accordance with the manufacturer's instructions. Suitable columns are DB5, OV1, OV17 or equivalents. Other columns may also be suitable.

A6.8 GC-MS Equipment. A GC-MS capable of operating in the electron impact mode (EI) with selected ion monitoring. Examples of mass spectra are shown in Figures 2 to 4.

Capillary GC conditions appropriate to the determination are DB5 (0.2 μ m) 30 m \times 0.25 mm id.

GC temperature: 60 °C for 0.5 min; 5 °C per minute to 300 °C; hold for 15 min.

A7 Sample Storage

Samples should be extracted as soon as possible after sampling. If it is impractical to analyse the samples at once, they should be stored at about 4 °C. The acid and solvent should be added and the sample shaken before storage if immediate analysis is impossible. The sample bottles should be protected from contamination by covering the top and shoulders of the bottle with metal foil. Samples should not be placed in the proximity of pure standards or their concentrated solutions.

A8 Analytical Procedure

Step	Procedure	Notes
A8.1	Extraction	
A8.1.1	To 2000 \pm 20 mL of sample in the sample bottle, add 5M sulphuric acid (A5.1) until the pH is approximately 2 (note a).	(a) pH paper may be used.
A8.1.2	To the bottle, add 70 \pm 5 mL DCM (A5.2). Shake on a shaking machine with the bottles in a horizontal plane for 5 minutes (note b).	(b) If a bottle rolling machine is used, the extraction time should be extended to 40 min. Hexane may be used as an alternative extraction solvent. The use of a second separating funnel will be necessary to account for the difference in solvent densities.
A8.1.3	Transfer the contents of the bottle to a 2 litre separating funnel. Rinse the bottle with a further 10 \pm 1 mL DCM and transfer the washings to the separator. Run off the lower DCM layer into a flask containing 5–10 g sodium sulphate (A5.9). Add a further 20 mL DCM to the separator, shake for 1 min, allow the layers to separate and add the DCM layer to the flask containing the sodium sulphate. Discard the aqueous layer.	
A8.1.4	Swirl the flask and leave to stand for at least 20 min, swirling occasionally (note c).	(c) Residual water in the extract should be scrupulously avoided.

Step	Procedure	Notes
A8.1.5	Transfer the extract to a Kuderna-Danish evaporator fitted with a graduated tube. Wash the sodium sulphate with 10 ± 1 mL DCM and decant washings into the Kuderna. Add an anti-bumping granule and concentrate the extract to about 2 mL using a steam bath (note d).	(d) DCM boils violently and care is necessary to ensure that the extract boils evenly without bumping.
A8.1.6	Remove the Kuderna from the steam bath, allow to drain and cool, remove the centrifuge tube containing the extract from the Kuderna and blow down the extract to incipient dryness using a stream of purified nitrogen.	
A8.2	Methylation	
A8.2.1	Set up the methylation apparatus and prepare a solution of diazomethane in diethyl ether.	
A8.2.2	To the residue from A8.1.6 add approximately 2 mL of the diazomethane solution in diethyl ether and allow to stand for 15 min. Blow off the excess reagent and reduce the volume to 1.00 ± 0.02 mL. The methylated extract is now ready for GC analysis.	
A8.3	Preparation of standards	
A8.3.1	Ethereal solutions of the standards (1.00 ± 0.02 mL) covering the expected range of levels to be found in the samples, together with a reagent blank are methylated by following steps A8.2.1 and A8.2.2. A concentration range of $0.05\text{--}5$ mgL ⁻¹ will be adequate for most samples.	
A8.4	GC-ECD determination	
A8.4.1	Set up the GC in accordance with the manufacturer's instructions using the conditions given in Figure 1.	
A8.4.2	Inject a suitable volume of the methylated standard solutions and the sample extracts into the GC.	
A8.4.3	The standards should show multiple peaks and the last four major peaks are normally the most suitable for quantification (see Figure 1). Measure the areas of these peaks (note e).	(e) The ratio of the separated peaks from water samples may differ from that in the standards due to degradation or interference. In these circumstances although initial quantification may be undertaken using those peaks which appear free from interference, results should be confirmed using an alternative GC column or by GC-MS as described in section A8.6.
A8.5	Construct a calibration graph of total peak area for the peaks measured in the standards versus the concentration of chlorphenylid (mgL ⁻¹). Read the concentration of chlorphenylid in the sample extracts from the calibration graph and calculate the concentration present in the original sample (see section A9).	

Step	Procedure	Notes
A8.6	GC-MS determination and confirmation	
A8.6.1	Set up the mass spectrometer in the EI mode to select suitable ions (see Figures 2 to 4). Follow similar procedures to those described in sections A8.4 and A8.5.	
A8.7	Blanks Blank values should be obtained using interference free water before analysing samples and at least one reagent blank should be analysed with each batch of samples.	
A8.8	Recoveries	
A8.8.1	Check the efficiency of the analytical procedure for each batch of samples analysed, by adding suitable known amounts of standard material to separate samples of interference-free water immediately before extraction (note f). Process these solutions under identical conditions to those used for the samples.	(f) Use an appropriate volume of dilute standard solution for the addition and allow the solvent to evaporate before extraction.

A.9 Calculation

Calculate the concentration (C) of chlorophenylid in the initial sample using

$$C = \frac{c \times v}{V} \mu\text{gL}^{-1}$$

Where C = concentration in the original sample (μgL^{-1})

c = concentration determined in the extract (mgL^{-1})

V = volume of the original sample (litres) and

v = volume of the extract for the determination (mL).

The calculations are more easily performed using a laboratory data system to integrate the relevant peaks and to calculate the results automatically.

Table 1 Means, Standard deviations and Recoveries

Sample		Mean	S_w	S_b	S_t	Recovery %
Distilled water	Unspiked	0.017			0.004	
	0.1	0.078	0.0038(3)	n.s	0.0005(3)	78[61]
	1.0	0.79	0.030 (3)	n.s	0.035 (4)	79[77]
River water	Unspiked	0.017				
	0.1	0.084	0.014 (3)	n.s	0.018 (4)	84[67]
	1.0	0.90	0.111 (3)	0(2)	0.111 (5)	90[88]

[] = Corrected for blank.

() = Degrees of freedom.

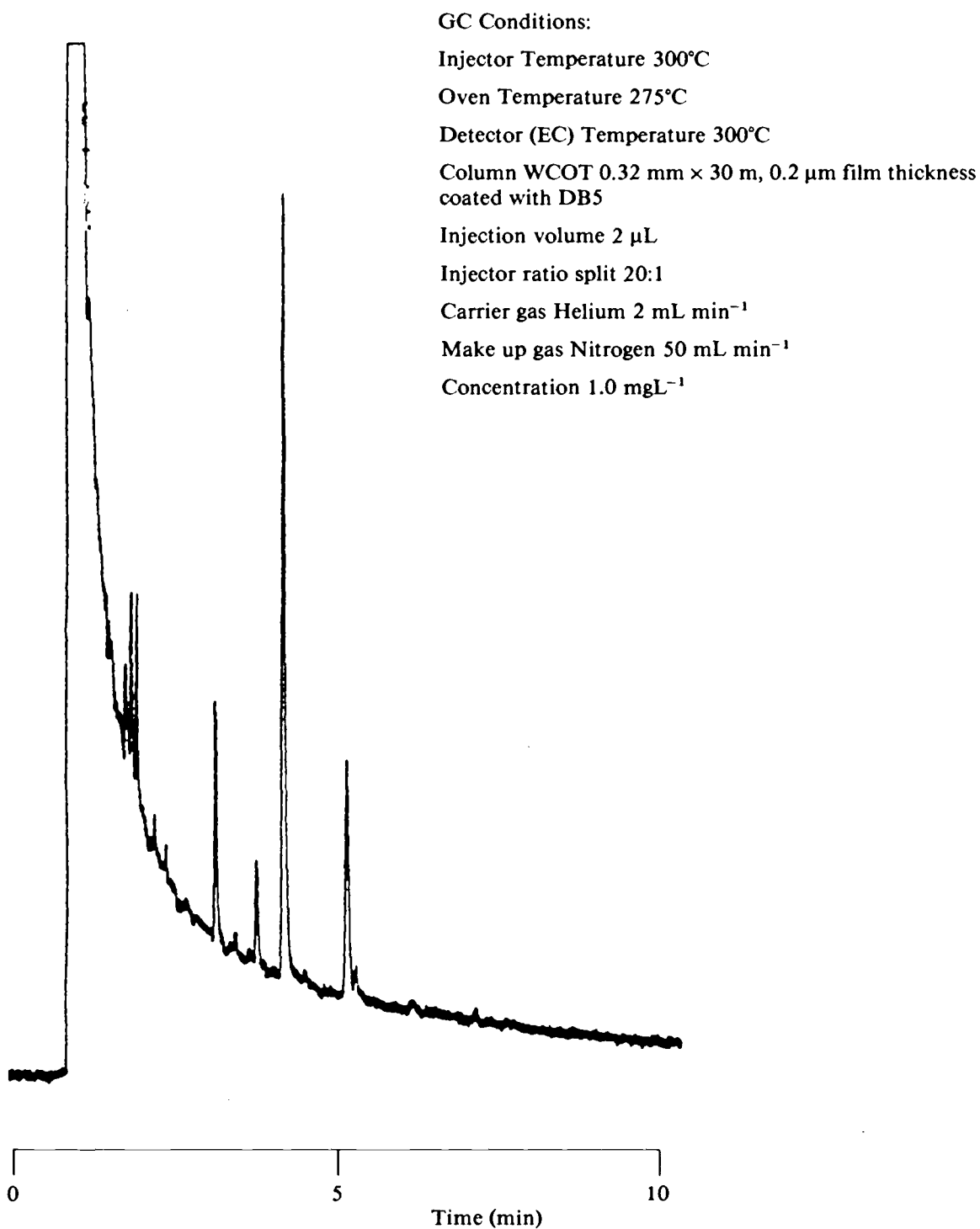
Except for recoveries, all results expressed in units of μgL^{-1} .

A10 References

A10.1 Chlorophenoxy Acidic Herbicides, Trichlorobenzoic acid, Chlorophenols, Triazines and Glyphosate in Water 1985 (ISBN 0117518867) in this series.

A10.2 D E Wells, A A Cowan *Analyst* 1981 **106** 862-868.

Figure 1 GC-ECD chromatogram of chlorphenylid



Note: Chlorphenylid gives multiple peaks using this procedure and the commercial material may also contain minor impurities.

Figure 2
Mass spectrum of methyltetrachloro-2-(chloromethylsulphonamide)diphenyl ether

Base M/Z: 159
RIC:18080

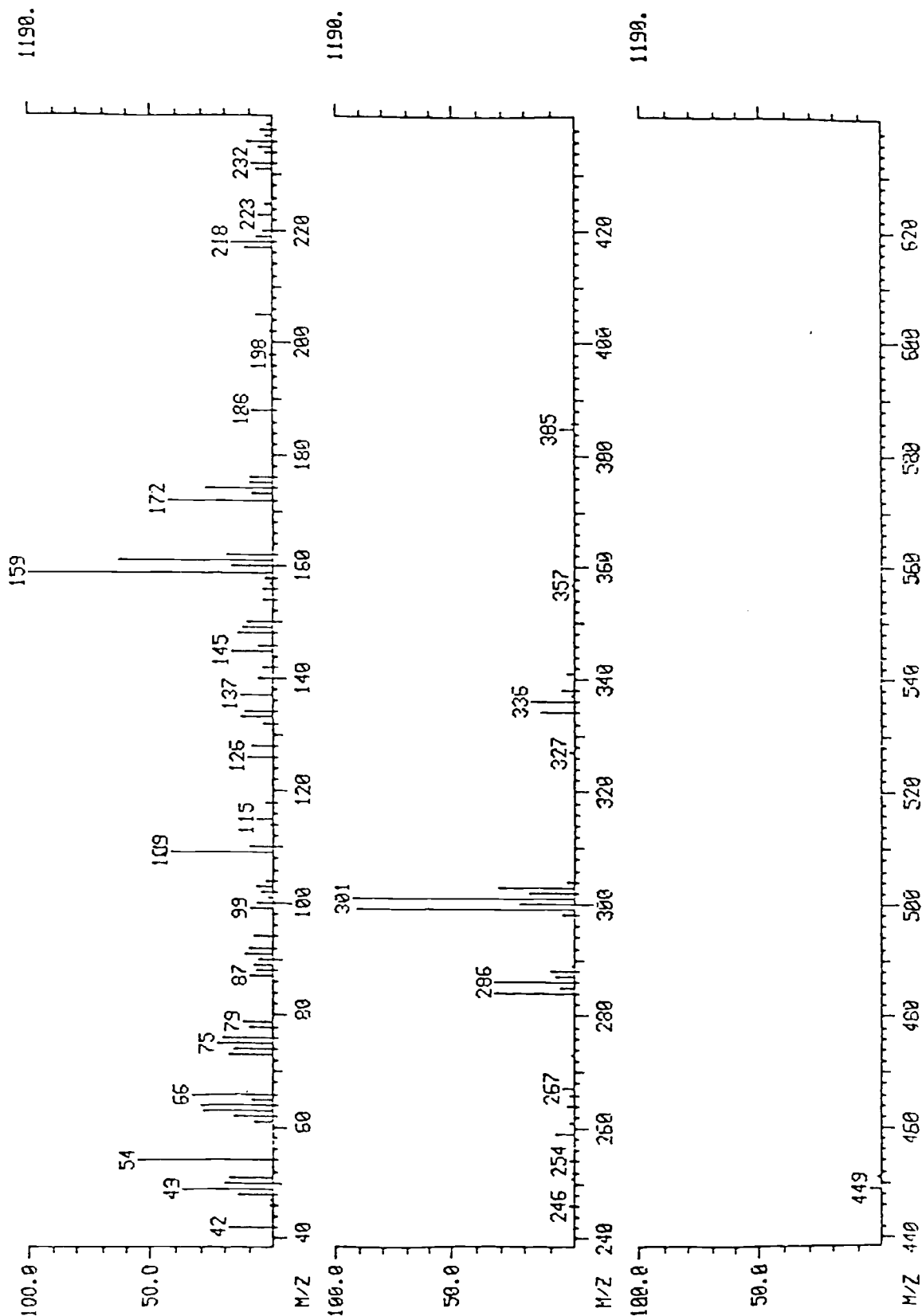


Figure 2
Mass spectrum of methyltetrachloro-2-(chloromethylsulphonamide)diphenyl ether

Figure 3

Mass spectrum of methylpentachloro-2-(chloromethylsulphonamide)diphenyl ether

Base M/Z: 159

RIC:103680

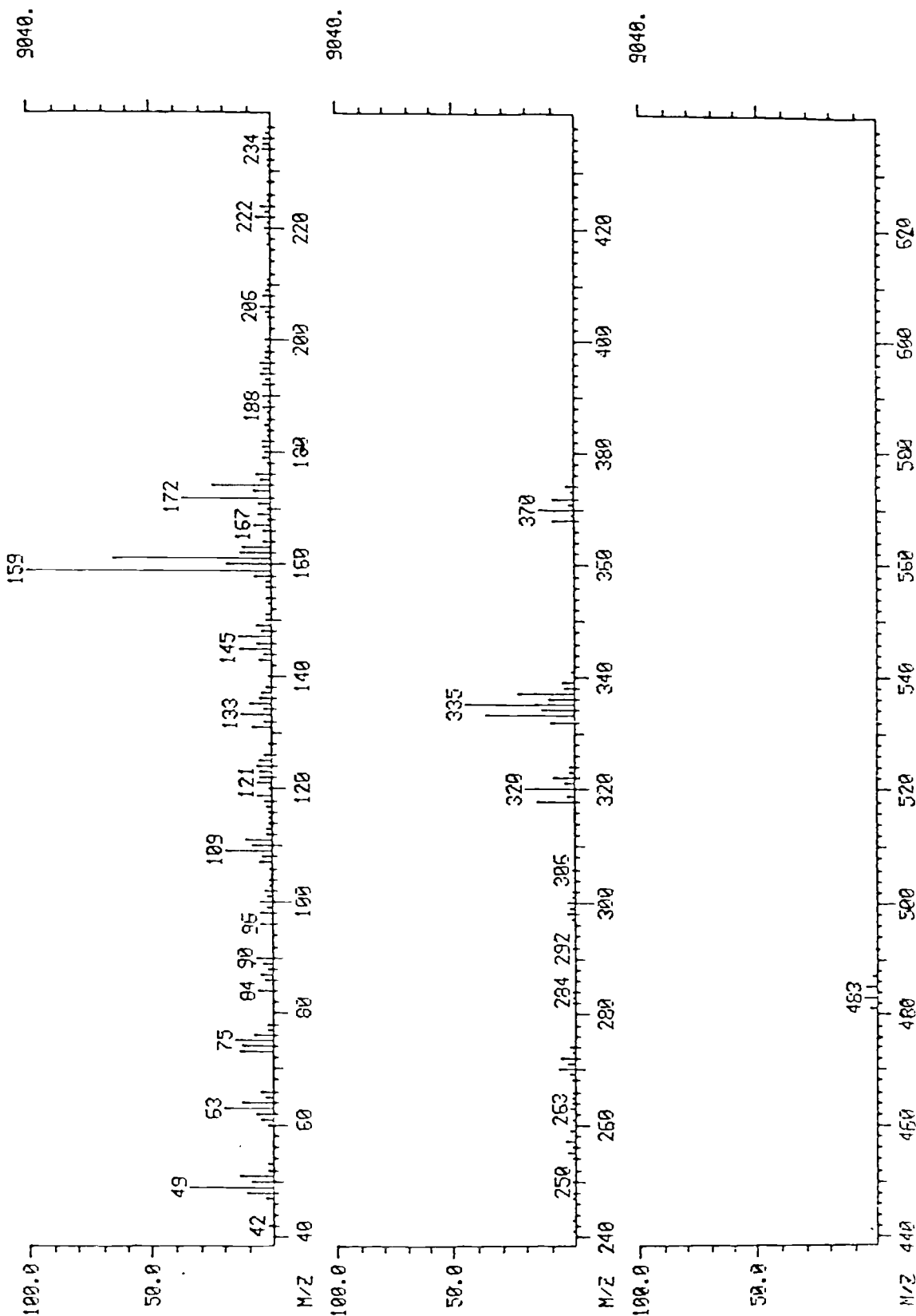


Figure 3
Mass spectrum of methylpentachloro-2-(chloromethylsulphonamide)diphenyl ether

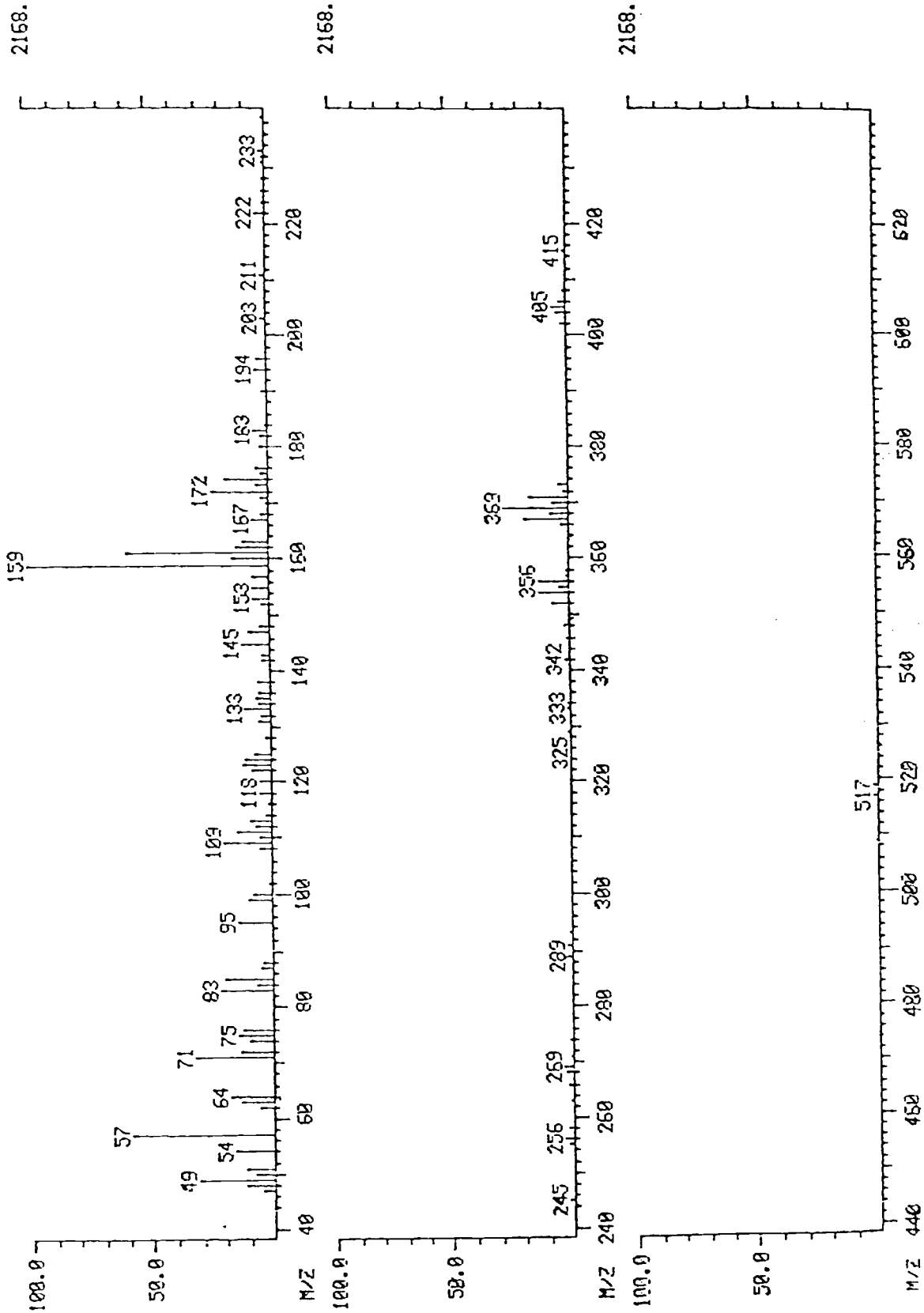


Figure 4
Mass spectrum of methylhexachloro-2-(chloromethylsulphonamide)diphenyl ether

B Flucofuron and Sulcofuron in waters by ion-pair HPLC (tentative method)

B1 Performance characteristics of the method

B1.1	Substances determined	Flucofuron, N,N'-bis[4-chloro-3-(trifluoromethyl)phenyl]-urea (Trade name: Mitin N) and Sulcofuron, 5-chloro-2-[4-chloro-2-[3-(3,4-dichlorophenyl)ureido]phenoxy]benzenesulphonic acid (Trade name: Mitin FF).
B1.2	Type of sample	River and drinking waters.
B1.3	Basis of the method	After addition of tetraethylammonium bromide (TEAB) to the sample, the compounds of interest are extracted from water with dichloromethane (DCM). The extract is concentrated and analysed by reverse phase high performance liquid chromatography (HPLC) on a C18 column using a methanol/water mobile phase containing TEAB. Detection is by UV at 266nm.
B1.4	Range of application	Up to 2 μgL^{-1} . The range may be extended by taking a smaller sample or by dilution of the extract with the mobile phase.
B1.5	Calibration curve	Linear up to 2 μgL^{-1} .
B1.6	Standard deviation	See Table 2.
B1.7	Limit of detection	Typically 0.02–0.03 μgL^{-1} in the sample.
B1.8	Sensitivity	A 1.0 mgL^{-1} standard gave a response of 1400 area units for flucofuron with a baseline fluctuation of 20 area units.
B1.9	Bias	Extraction efficiencies are less than 100%. See Table 2.
B1.10	Interferences	Any material with a UV response at the wavelength used and having a similar retention time to either of the determinands.
B1.11	Time required for analysis	Eight samples may be analysed per day.

B2 Principle

Flucofuron and sulcofuron are extracted from water with DCM after addition of TEAB to the sample to give an ion pair. The DCM extract is concentrated by evaporation to incipient dryness and the residue taken up in the mobile phase. The sample is analysed by reverse phase HPLC with a C18 column. Quantification is by comparison of peak areas with those of external standards analysed in the same manner.

B3 Interferences

None known. No serious interference occurred when the method was tested.

B4 Hazards Flucufuron, sulcofuron and methanol are toxic. DCM is toxic and narcotic. Methanol is flammable.

B5 Reagents

B5.1 Dichloromethane. HPLC grade.

B5.2 Tetraethylammonium bromide (TEAB). Analytical reagent grade.

B5.3 Methanol. HPLC grade.

B5.4 HPLC Mobile phase. Prepare a solution of methanol in water (4:1 v/v) and add 4.2 gL^{-1} of TEAB. Stir until dissolved.

B5.5 Anhydrous sodium sulphate. Heat at $500 \pm 20 \text{ }^\circ\text{C}$ for $4 \text{ hr} \pm 30 \text{ min}$. Cool to about $200 \text{ }^\circ\text{C}$ in a muffle furnace and then to ambient temperature in a desiccator. The roasted material may be stored in a screw topped jar with a PTFE or metal lined cap.

B5.6 Standards

B5.6.1 Stock solutions. Prepare stock solutions of pure or suitably certified flucufuron and sulcofuron in methanol. (B5.3) at concentrations of 100 mgL^{-1} .

B5.6.2 Working Solutions. Using the stock solutions (B5.6.1) prepare working mixed standards in the mobile phase (B5.4) containing 0.05, 0.1, 0.5, 1.0, 2.5 and 5.0 mgL^{-1} . Solutions from B5.6.1 and B5.6.2 are stable for at least 1 month when stored at about $4 \text{ }^\circ\text{C}$.

B5.7 Anti bumping granules.

B5.8 Nitrogen. Oxygen free, filtered and dry.

B6 Apparatus

B6.1 Sample bottles. All glass or with PTFE lined screw caps, 2 litre capacity, marked at 2 litres.

B6.2 Shaking machine. To shake the bottles in a horizontal plane.

B6.3 Kuderna-Danish evaporators. 250 mL.

B6.4 Graduated centrifuge tubes. Glass 10 ml with 0.1 mL graduations, glass stoppered, tapered.

B6.5 HPLC system with UV detector. Operated in reverse phase mode with a C18 column and with a detector operating at 266 nm.

B7 Sample Storage

Samples should be analysed as soon as possible after sampling. If it is impractical to analyse the samples at once, they should be stored at about $4 \text{ }^\circ\text{C}$.

B8 Analytical Procedure

Step	Procedure	Notes
B8.1	To $2000 \pm 20 \text{ mL}$ of sample in the sample bottle, add $4.0 \pm 0.5 \text{ g}$ TEAB (B5.2). Shake until dissolved.	
B8.2	Add $100 \pm 10 \text{ mL}$ DCM (B5.1) and shake on a shaking machine (B6.2) for 10 min (note a). Transfer the contents of the bottle into a 2 litre separating funnel and allow the layers to separate.	(a) If a bottle rolling machine is used the extraction time should be extended to 40 min.

Step	Procedure	Notes
B8.3	Run off the lower DCM layer into a flask containing approximately 10 g of sodium sulphate (B5.5). Rinse the bottle with a further 50 ± 5 mL DCM and add to the separator, shake for 5 min and allow the layers to separate. Run the lower DCM layer into the flask containing the sodium sulphate and discard the aqueous layer.	
B8.4	Swirl the flask and leave for a minimum of 20 min, swirling occasionally (note b).	(b) As much of the water as possible should be removed at this stage.
B8.5	Decant the DCM extract into a Kuderna-Danish evaporator (B6.3) fitted with a centrifuge tube (B6.4). Wash the sodium sulphate with a further 10 ± 1 mL DCM and add the washings to the Kuderna. Add an anti-bumping granule and evaporate the extract to 1-2 mL on a steam bath (note c).	(c) Care is necessary as DCM boils violently.
B8.6	Remove the tube from the Kuderna and evaporate the extract to incipient dryness using a stream of purified nitrogen.	
B8.7	Add 1.00 ± 0.01 mL of the HPLC mobile phase (B5.4) and allow the residue to dissolve. The sample is now ready for HPLC analysis.	
B8.8	HPLC/UV determination	
B8.8.1	Set up the HPLC in accordance with the manufacturer's instructions using the conditions given in Figure 5.	
B8.8.2	Inject aliquots of standards and extracts into the HPLC.	
B8.8.3	Construct separate calibration graphs for flucofuron and sulcofuron of the peak areas measured for the standards versus the concentration of each determinand (mgL^{-1}) injected.	
B8.8.4	Read the concentration of flucofuron and sulcofuron in the sample extracts from the corresponding calibration graphs and calculate the concentration of each determinand in the original sample (see section B9).	
B8.9	Confirmation	
B8.9.1	Change the HPLC conditions (notes d and e). Re-analyse extracts following similar procedures to those described in sections B8.8.1 to B8.8.4.	(d) This can include mobile phase composition, column type or detector system or a combination of these. (e) Detailed alternative HPLC conditions are not currently available.

Step	Procedure	Notes
B8.10	Blanks Blank values should be obtained using interference free water before analysing samples and at least one reagent blank should be analysed with each batch of samples.	
B8.11	Recoveries	
B8.11.1	Check the efficiency of the analytical procedure for each batch of samples analysed, by adding suitable known amounts of standard material to separate samples of interference-free water immediately before extraction (note f). Process these solutions under identical conditions to those used for the samples.	(f) Use an appropriate volume of a dilute standard solution for the addition.

B9 Calculation

Calculate the concentration (C) of either flucofuron or sulcofuron in the initial sample using

$$C = \frac{c \times v}{V} \mu\text{gL}^{-1}$$

where C = concentration in the original sample (μgL^{-1})

c = concentration determined in the extract (mgL^{-1})

V = volume of the original sample (litres) and

v = volume of the extract for the determination (mL).

The calculations are more easily performed using a laboratory data system to integrate the relevant peaks and to calculate the results automatically.

Table 2 Means, Standard deviations and Recoveries

Sulcofuron

Sample	Spiked Concentration	Mean Found	S_w	S_b	S_t	Recovery %
Distilled water	Unspiked	0.019			0.0045(9)	
Distilled water	0.1	0.088	0.017(3)	ns	0.019 (4)	88
Distilled water	1.0	0.75	0.087(3)	ns	0.182 (3)	75
River water	0.1	0.080	0.018(3)	0(2)	0.018 (5)	80
River water	1.0	0.74	0.153(3)	0(2)	0.153 (5)	74

Flucofuron

Sample	Spiked Concentration	Mean Found	S_w	S_b	S_t	Recovery %
Distilled water	Unspiked	0.019			0.007(9)	
Distilled water	0.1	0.091	0.010(3)	0(2)	0.010(5)	91
Distilled water	1.0	0.83	0.138(3)	0(2)	0.158(5)	83
River water	0.1	0.094	0.020(3)	0(2)	0.020(5)	94
River water	1.0	0.74	0.123(3)	ns	0.128(5)	74

() = Degrees of freedom.

Except for recoveries, all results expressed in units of μgL^{-1} .

Figure 5 HPLC chromatogram of flucofuron and sulcofuron

HPLC Conditions:

Reverse phase

Column—Lichrocart RP₁₈

Detector—UV 266 nm

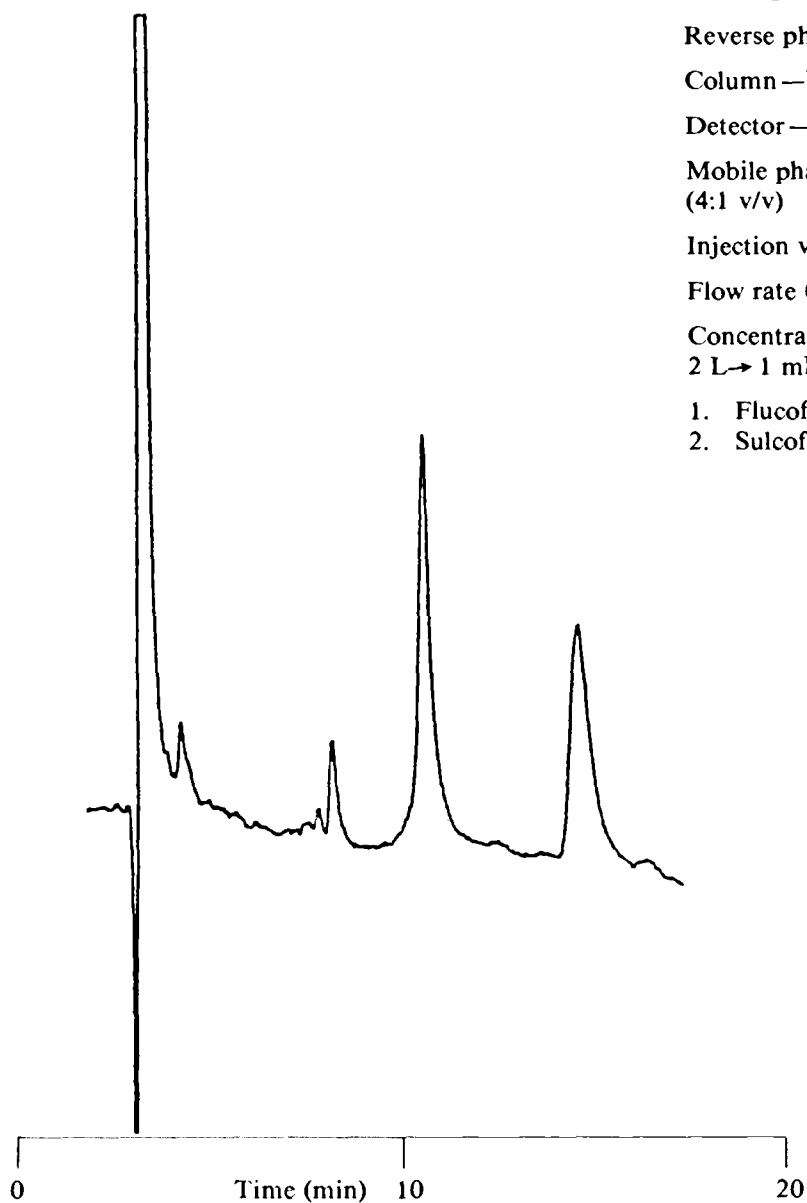
Mobile phase—0.42% TEAB in Methanol: Water
(4:1 v/v)

Injection volume 20 μ L

Flow rate 0.8 mL min⁻¹

Concentration 0.1 μ g L⁻¹ in distilled water,
2 L \rightarrow 1 mL

1. Flucofuron approximately 10 min
2. Sulcofuron approximately 14 min



C Flucofuron in waters by hydrolysis to 4-chloro-3-trifluoromethylaniline by GC–ECD (a note)

C1 Performance characteristics of the method	C1.1 Substances determined	Flucofuron. See B1.1.
	C1.2 Types of sample	Drinking and river water of low solids content.
C2 Principle	Flucofuron is extracted from the sample with dichloromethane (DCM). The extract is evaporated to incipient dryness and the residue hydrolysed under reflux with a mixture of acetic and sulphuric acids. The hydrolysed sample is made alkaline with potassium hydroxide and the 4-chloro-3-trifluoromethylaniline hydrolysis product is extracted with hexane. Determination is by GC-ECD.	
C3 Interferences	Any co-extracted material, or material formed on hydrolysis, which has a similar retention time to the determinand and which gives a detector response, will interfere.	
C4 Hazards	DCM is toxic and narcotic. Acetic and sulphuric acids are corrosive. Methanol and hexane are flammable. Potassium hydroxide and its solutions are caustic. Flucofuron and methanol are toxic.	
C5 Reagents	C5.1 Dichloromethane.	Glass distilled grade.
	C5.2 Sulphuric acid approximately 5M. (CARE).	Add 250 ± 5 mL concentrated sulphuric acid ($d_{20} 1.84$) to about 600 mL distilled water with swirling and cooling. Cool to ambient temperature and dilute to 1 litre with distilled water.
	C5.3 Acetic acid (glacial).	Analytical reagent grade.
	C5.4 Acid mixture for hydrolysis.	Measure 400 ± 5 mL of water into a 2 L beaker. Slowly, with external cooling, add 450 ± 5 mL of sulphuric acid (C5.2). When cool add 150 ± 5 mL of glacial acetic acid and mix well.
	C5.5 Methanol.	Analytical reagent grade.
	C5.6 Hexane.	Fraction from petroleum. Boiling range not less than 95% between 67°C and 70°C or pesticide grade.
	C5.7 Potassium hydroxide solution (5M).	Dissolve 28 ± 1 g potassium hydroxide (analytical reagent grade) in 100 ± 5 mL water. Allow to cool.
	C5.8 Standards.	
C5.8.1 Stock solution.	Dissolve sufficient pure or suitably certified flucofuron in methanol to make a 100 mgL^{-1} solution. This solution is stable for up to 1 month when stored at about 4 °C.	
C5.8.2 Working solutions.	Using the stock solution prepare appropriate working standards in methanol. Suitable concentrations are 0.02, 0.05, 0.1, 0.5, and 1.0 mgL^{-1} .	

C5.9 Granular anhydrous sodium sulphate. Heat at 500 ± 20 °C for 4 hr \pm 30 min. Cool to about 200 °C in a muffle furnace and then to ambient temperature in a desiccator. The roasted material may be stored in a screw topped jar with a PTFE or metal lined cap.

C5.10 Anti bumping granules.

C5.11 Nitrogen. Oxygen free, filtered and dry.

C6 Apparatus

C6.1 Sample bottles. All glass or with PTFE lined screw caps, 2 litre capacity and marked at 2 litres.

C6.2 Shaking machine. To shake bottles in a horizontal plane.

C6.3 Separating funnels. 2 litre capacity with ungreased or PTFE taps.

C6.4 Kuderna-Danish evaporators. 250 mL.

C6.5 Centrifuge tubes. Glass 10 mL with 0.1 mL graduations, glass stoppered, tapered.

C6.6 Reflux apparatus. Micro-scale with boiling vessel of 10-25 mL capacity fitted with an air condenser of 30 cm length. Ground glass joints may seize with the alkali and screw/PTFE joints are preferred. A screw-capped test tube makes a suitable reaction flask.

C6.7 Gas chromatograph. A GC fitted with a capillary column, a suitable injector and an electron capture detector. The instrument should be operated in accordance with the manufacturer's instructions. A suitable column would be a 25 m WCOT Carbowax 20M or equivalent.

C7 Sample Storage

Samples should be extracted as soon as possible after sampling. If it is impractical to analyse the samples at once, they should be stored at 4 °C.

C8 Analytical Procedure

Step	Procedure	Notes
C8.1	Extraction	
C8.1.1	To 2000 \pm 20 mL of sample in the sample bottle, add sulphuric acid (C5.2) until the pH is approximately 2 (notes a and b).	(a) Cartridge extraction may be used. (b) pH paper may be used.
C8.1.2	To the bottle, add 100 \pm 5 mL DCM (C5.1). Shake on a shaking machine with the bottles in a horizontal plane for 5 minutes (note c).	(c) If a bottle rolling machine is used the extraction time should be extended to 40 min.
C8.1.3	Transfer the contents of the bottle to a 2 litre separating funnel. Rinse the bottle with a further 10 \pm 1 mL DCM and transfer the washings to the separator. Run off the lower DCM layer into a flask containing 5-10 g sodium sulphate (C5.9). Add a further 50 mL DCM to the separator, shake for 2 min, allow the layers to separate and add the DCM layer to the flask containing the sodium sulphate. Discard the aqueous layer.	
C8.1.4	Swirl the flask and leave to stand for at least 20 min, swirling occasionally (note d).	(d) Residual water in the extract should be scrupulously avoided.

Step	Procedure	Notes
C8.1.5	Transfer the extract to a Kuderna-Danish evaporator fitted with a graduated tube. Wash the sodium sulphate with 10 ± 1 mL DCM and decant washings into the Kuderna. Add an anti-bumping granule and concentrate the extract to about 2 mL using a steam bath (note e).	(e) DCM boils violently and care is necessary to ensure that the extract boils evenly without bumping.
C8.1.6	Remove the Kuderna from the steam bath, allow to drain and cool, remove the centrifuge tube containing the extract from the Kuderna and blow down the extract to 1–2 mL using a stream of purified nitrogen (note f).	(f) Any 4-chloro-3-trifluoromethylaniline already present in samples which are extracted under these conditions will also be determined by this procedure.
C8.2	Set up a reflux apparatus (C6.6). Transfer the extract to the reaction vessel rinsing the tube with 2–3 mL DCM and adding the washings to the vessel.	
C8.3	Evaporate the extract in the reaction vessel (C6.6) to incipient dryness using a stream of purified nitrogen.	
C8.4	Set up the reflux condenser and to the reaction vessel add 1.0 ± 0.05 mL of the acetic/sulphuric acid solution (C5.4). Swirl and fit the condenser to the flask. Heat at $150 \text{ }^\circ\text{C}$ for 30 ± 5 min.	
C8.5	Remove the apparatus and cool the flask in iced water.	
C8.6	Add 2.00 ± 0.02 mL hexane (C5.6) down the condenser tube.	
C8.7	Add 5.0 ± 0.1 mL 5M potassium hydroxide solution (C5.7) and 1.0 ± 0.1 mL water to rinse the wall of the condenser. Keep the contents of the flask cool to avoid loss of hexane.	
C8.8	Remove the condenser from the reaction vessel. Stopper and shake vigorously for 5 min. Allow the layers to separate (note g). The hexane phase is now ready for gas chromatography.	(g) If emulsification occurs, the reaction vessel may be centrifuged at 3000 rpm to help separate the layers.
C.8.9	Hydrolyse suitable amounts of standards for GC calibration using the hydrolysis procedure	
C8.10	Inject suitable aliquots of hydrolysed standard solutions and samples into the GC and compare the retention times and peak areas given by the determinand in samples and standards (note h).	(h) An oven temperature of about $150 \text{ }^\circ\text{C}$ is suitable, but a temperature programme may also be used.
C8.11	Construct a calibration graph of peak area for the peaks measured in the standards versus concentration of flucofuron (mgL^{-1}).	
C8.12	Read the concentration of flucofuron from the calibration graph and calculate the concentration present in the original sample as given in section C9.	

Step	Procedure	Notes
C8.13	Blanks	
	Blank values should be obtained using interference free water before analysing samples and at least one reagent blank should be analysed with each batch of samples.	
C8.14	Recoveries	
C8.14.1	Check the efficiency of the analytical procedure for each batch of samples analysed, by adding suitable known amounts of standard material to separate samples of interference free water immediately before extraction (note i). Process these solutions under identical conditions to those used for the samples.	(i) Use an appropriate volume of a dilute standard solution for the addition.

C9 Calculation

Calculate the concentration (C) of flucofuron in the initial sample using

$$C = \frac{c \times v}{V} \mu\text{gL}^{-1}$$

Where C = concentration in the original sample (μgL^{-1})

c = concentration determined in the extract (mgL^{-1})

V = volume of the original sample (litres) and

v = volume of the extract for the determination (mL).

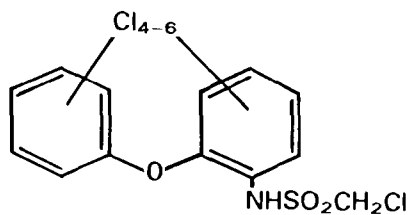
The calculations are more easily performed using a laboratory data system to integrate the relevant peaks and to calculate the results automatically.

Common names and chemical structures

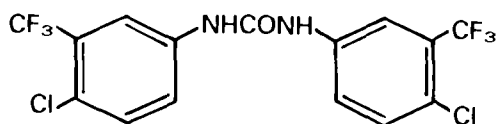
Common Name

Structure

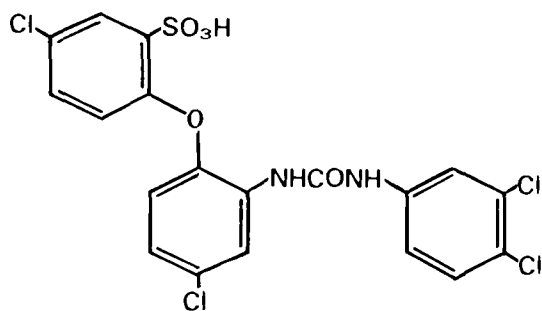
Chlorphenylid



Flucofuron



Sulcofuron



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

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.

Address for correspondence

1. 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.
2. At the present time, thorough test data is not available. Additional test data would be welcomed and results should be sent to the address below.

The Secretary
The Standing Committee of Analysts
The Department of the Environment
Drinking Water Inspectorate

43 Marsham Street
LONDON SW1P 3PY
England

Department of the Environment

Standing Committee of Analysts

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