



CSIRO LAND and WATER



***A Method for the Collection, Preservation and
Analysis of Water Samples for Agricultural Chemicals
(Pesticides) used in the Murrumbidgee Irrigation Area***

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1 Introduction

1.1 Background

This technical report details the steps required to collect, preserve and analyse water samples for pesticides. The method was developed for the conditions experienced in the Murrumbidgee Irrigation Area (MIA) by Dr. Wolfgang Korth¹, and has been in use at CSIRO Land and Water (formerly CSIRO Division of Water Resources), Griffith since 1991. Our particular local conditions include waters that can be very turbid, as well as containing a vast array of different pesticides at varying concentrations. For reference to field experiments that have used this method see Korth *et al*, 1995a and Korth *et al*, 1995b.

2 Methods

2.1 Sample Bottle Preparation

Samples should be collected in 1L amber glass bottles. Prior to collection, used sample bottles must undergo a rigorous cleaning regime (as follows). New bottles are used without cleaning.

- thoroughly rinse bottle in hot tap water
- soak overnight in a detergent bath (5% “extran 300”)
- rinse 3 times in hot tap water
- soak overnight in 10% HCl bath
- rinse 3 times in hot tap water
- rinse 3 times in distilled or MilliQ water
- rinse in methanol
- allow to dry

¹ Dr. Wolfgang Korth moved to the Bureau of Resource Sciences in 1995 to take up a position as the Residues Program Chemist within the National Residues Survey.

- place aluminium foil over opening and replace the lid
- place a piece of water proof tape on bottle to use as a label

2.2 Sample Collection

Prior to the collection of the sample a volume of sample water of approximately 100 mL is allowed to enter the bottle by immersing the bottle in the body of water. If the site is difficult to access, either collect the sample in a stainless steel bucket attached to a rope (which is thoroughly rinsed with the sample to be collected prior to filling the sample bottle), or attach the bottle to the extendable metal pole, specifically constructed to hold the bottle in place and allow it to be lowered into the water body. Place the lid on the bottle and rinse. Discard contents in a way that will not disturb the sample about to be taken. Repeat this rinse step 2 more times. Re-immerses the bottle and allow it to fill to the top of the bottle to minimise head space. Cover the opening with aluminium foil and seal with the screw-on lid. Once collected, samples should be stored on ice in an esky for transport to the laboratory.

2.3 Buffering and storage

Once in the laboratory, the samples need to be buffered (pH 6.9) and stored ($\sim 4^{\circ}\text{C}$) to minimise pesticide degradation. Samples are buffered by the addition of 10 mL of concentrated phosphate buffer (see 2.3.1 for buffer preparation) to 1L of sample. A 5 mL pipette is used to dispense the buffer. A small volume ($\sim 10\text{-}15\text{ mL}$) of the sample must be discarded, after thorough mixing, to allow for addition of the buffer. Once buffered, samples are stored at $\sim 4^{\circ}\text{C}$.

2.3.1 Preparation of Phosphate Buffer

Place ~ 800 mL of MilliQ water in a beaker with a magnetic stirrer bar and place on a magnetic stirrer plate.

Weigh out the following:

AR grade Na₂HPO₄ 353.3 g

AR grade KH₂PO₄ 338.7 g

place one of the above in the MilliQ water with constant stirring. Once this has dissolved, add the second. Continue stirring until all has dissolved. Transfer to a 1L volumetric flask and dilute to 1L with MilliQ water. Store at room temperature in a labelled glass container². This solution is stable for at least 6 months.

3 Preparation of Surrogate and Internal Standards

All standards can be purchased from commercial suppliers specialising in pesticide standards. The standards are supplied with documentation regarding their purity, hazard information, storage requirements and expiry date.

Stock solutions of pesticides should be prepared from primary standard materials in a fume cupboard and gloves should be worn during the preparation process to avoid skin contact.

Care should be taken to minimise the physical handling of glassware which will be weighed as some glove types leave powder residues which may contribute to weighing errors.

3.1 Preparation of fenchlorphos (surrogate standard)

- place a clean, dry 50 mL volumetric flask on a 4 decimal place electronic balance
- tare

² Do not use a glass container with a quick-fit stopper as this will be difficult to remove if buffer solidifies between stopper and neck of container.

- add an amount of fenchlorphos (~ 0.0900g) to the tared flask. Record the weight accurately and note the purity of the fenchlorphos. (eg. 0.0942g weighed, 95.5% pure)
- dilute to the mark with acetone (HPLC grade)
- calculate the concentration of fenchlorphos and correct for purity
 (eg. $0.0942\text{g}/50\text{ mL}$
 $= 1884\text{ mgL}^{-1}$, but since purity is 95.5%
 $= 1799\text{ ppm}$)
- this solution is stored at -18°C and is kept as the stock solution for the subsequent preparation of working standards.

3.1.1 Preparation of fenchlorphos spiking mix

- weigh ~ 5 g of fenchlorphos stock solution into a 50 mL volumetric flask, accurately record weight. (eg. 4.5744g)
- convert weight to volume using specific gravity of acetone (0.7899)
 (eg. $4.5744/0.7899 = 5.79\text{ mL}$)
- dilute to 50 mL with acetone (HPLC grade), calculate new concentration of fenchlorphos spiking mix. (eg. $5.79\text{ mL} \times 1799\text{ ppm} / 50\text{ mL} = 208\text{ ppm}$)

3.2 Preparation of 1-chlorotetradecane (1-Cl-C₁₄) (internal standard)

- place a clean, dry 50 mL volumetric flask on a 4 decimal place electronic balance
- tare
- add an amount of 1-Cl-C₁₄ (~ 0.0900g) to the tared flask. Record the weight accurately and note the purity of the 1-Cl-C₁₄. (eg. 0.0548g weighed, 99% pure)

- dilute to the mark with dichloromethane (HPLC grade)
- allowing for purity, calculate the concentration of 1-Cl-C₁₄

(eg. 0.0548g/50 mL

= 1096 mgL⁻¹, but since purity is 99%

= 1085 ppm)

This solution is stored at -18°C and is kept as the stock solution for the subsequent preparation of working standards.

3.2.1 Preparation of 1-Cl-C₁₄ spiking mix

- weigh ~ 5 g of 1-Cl-C₁₄ stock into a 50 mL volumetric flask, accurately record weight

(eg. 6.8705g)

- convert weight to volume using specific gravity of dichloromethane (1.3266)

(eg. 6.8705/1.3266 = 5.18 mL)

- dilute to 50 mL with dichloromethane (HPLC grade), calculate new concentration of 1-Cl-C₁₄ spiking mix (eg. 5.18 mL x 1085 ppm / 50 mL = 112.4 ppm)

4 Preparation of pesticide standards

The choice of which pesticides should be monitored was in part determined following discussions with farmers, retailers and agronomists regarding the usage patterns of these compounds in the study area. In addition, the following factors were also considered:

- toxicity
- potential downstream human health or ecosystem impact

- likelihood of partitioning into dichloromethane
- suitability for gas chromatographic analysis

Table 1 lists the pesticides that were chosen to be monitored in the 1995/96 irrigation season based on the ability to detect these pesticides by the methods described, and their potential use in the study site.

Table 1. Pesticides analysed for in 1995/96.

atrazine	diazinon	lambda-cyhalothrin	monocrotofos
bensulfuron	dicofol	linuron	profenfos
bifenthrin	diuron	malathion	propanil
bromacil	α -endosulfan	methidathion	simazine
chlorpyrifos	β -endosulfan	methomyl	terbufos
cypermethrin	endosulfan-sulfate	metolachlor	thiobencarb
deltamethrin	fluazifop-butyl	molinate	trifluralin

Pesticide analysis can be both quantitative and qualitative. To determine the actual concentration of pesticides, a number of standards containing a range of concentrations must be prepared. Stock standards containing high pesticide concentrations are initially prepared from the purchased primary standard, and further diluted to prepare working standards.

4.1 Preparing a stock pesticide solution from a primary standard

4.1.1. If the primary standard is a solid

- place a clean, dry 50 mL volumetric flask on a 4 decimal place electronic balance
- tare
- transfer ~100 mg of the solid into the flask with a clean spatula
- record weight accurately

- dilute to 50 mL with a suitable solvent. Eg acetone (HPLC grade)
- allowing for purity, calculate concentration which is generally between 1000 and 2000 ppm and record on label with compound name, date, solvent and expiry date.

This process is repeated for all solid standards. Record all steps in the preparation process in a standards preparation book.

4.1.2 If the primary standard is a liquid

- place a clean, dry 50 mL volumetric flask on a 4 decimal place electronic balance
- tare
- transfer ~100 mg of the liquid into the flask using a glass pasteur pipette
- record weight accurately
- dilute to 50 mL with a suitable solvent. Eg acetone (HPLC grade)
- allowing for purity, calculate concentration which is generally between 1000 and 2000 ppm and record on label with compound name, date, solvent and expiry date.

This process is repeated for all liquid standards. Record all steps in the preparation process in the standards preparation book.

4.2 Spiking Standards

4.2.1 High level standard (HLS)

Once stock standards have been prepared, they may be used in various combinations to prepare spiking standards.

Given that all stock standards were prepared in the same solvent (ie. acetone), spiking mixtures are prepared on a w/w basis.

- weigh a clean, dry 50 mL volumetric flask
- tare

- use a clean pasteur pipette to transfer ~ 1 mL of each pesticide stock to the flask and record the weight. Re-tare between each pesticide addition
- after the addition of all pesticides calculate the new concentrations.

NOTE Do not make up to volume

4.2.2 Low level standard (LLS)

A second, low level working stock is prepared by diluting the high level standard ~ 1/10:

- weigh a clean, dry 10 mL volumetric flask
- tare
- weigh accurately ~1g of high level standard into flask, record weight
- convert weight to volume based on specific gravity of acetone
- dilute to 10 mL with acetone, calculate new concentrations of each component

4.2.3 Matrix Working Standards

Prepare six working standards by spiking the high level and low level standards into MilliQ water.

- add 400 mL of MilliQ to each of 6 x 500 mL glass separating funnels
- spike each separating funnel with volumes of HLS and LLS as described below:

Separating funnel	Volume of HLS (µL)	Volume of LLS (µL)	Capacity (µL) of syringe used in spiking procedure
1		1.6	10
2		6.0	10
3	1.6		10
4	13.5		25
5	50.0		100
6	150		250

- spike each separating funnel with the fenchlorphos surrogate spiking mix (5.6 µL)
- spiking is achieved using HPLC syringes of varying capacity (generally 50% greater than the volume to be dispensed) using the “air-sandwich” technique (see 4.2.4)
- the matrix standards are extracted in the same manner as pesticide samples including the addition of the 1-Cl-C₁₄ internal standard, detailed in Section 5 (see 5.4).
- The amount of pesticide added to each matrix standard is determined and recorded in a table that is referred to when calculating the actual concentration of pesticide in each sample. Table 2 is an example of the composition of the matrix standards used in the 1995/6 season.

Table 2. Composition of pesticide matrix standards prepared for the 1995/6 Irrigation season.

Pesticide	µg pesticide / volume extracted (400 mL)					
	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6
atrazine	0.013	0.050	0.140	1.18	4.37	13.1
bensulfuron	0.012	0.044	0.125	0.980	3.90	11.7
bromacil	0.011	0.043	0.120	1.01	3.74	11.2
chlorpyrifos	0.013	0.050	0.140	1.19	4.39	13.2
cypermethrin	0.016	0.060	0.169	1.43	5.29	15.9
deltamethrin	0.014	0.052	0.147	1.24	4.61	13.8
dicofol	0.015	0.055	0.155	1.31	4.85	14.5
diuron	0.012	0.044	0.124	1.05	3.88	11.6
α-endosulfan	0.013	0.049	0.138	1.17	4.32	13.0
β-endosulfan	0.014	0.052	0.145	1.22	4.54	13.6
endosulfan-SO ₄	0.012	0.044	0.123	1.03	3.83	11.5
lambdacyhalothrin	0.017	0.065	0.184	1.55	5.75	17.3
malathion	0.018	0.067	0.188	1.59	5.89	17.7
metolachlor	0.014	0.054	0.151	1.28	4.73	14.2
molinate	0.013	0.050	0.140	1.18	4.38	13.1
simazine	0.016	0.061	0.196	1.10	5.00	14.7
thiobencarb	0.015	0.058	0.161	1.36	5.03	15.1

trifluralin	0.011	0.042	0.118	0.990	3.68	11.0
fenchlorphos	1.16	1.16	1.16	1.16	1.16	1.16
1-Cl-C ₁₄ *	0.63	0.63	0.63	0.63	0.63	0.63

* added to final extract (see 5.4)

4.3 Air-Sandwich Technique

To ensure an accurate transfer of a given spiking solution into a water sample a HPLC syringe and the air-sandwich technique are used. The air-sandwich technique involves initially drawing ~1µL of air into the syringe followed by the required volume of spiking solution, and finally another ~2 µL of air. Using this technique the entire volume of spiking solution to be dispensed (including the volume in the syringe needle {~0.6 µL}) is visible in the barrel of the syringe sandwiched between separate volumes of air. The volume of spiking solution to be dispensed can be accurately determined by reading the scale on the syringe barrel. The entire spiking solution is dispensed into the water by holding the syringe needle below the water surface before pushing the plunger down. The volume of air behind the spiking solution in the barrel of the syringe ensures that all liquid in the syringe needle is also dispensed. After dispensing the spiking solution, the needle is kept below the surface of the water and the syringe is rinsed 3 times with the water just spiked.

NOTE: To enable all of the spiking solution, plus adequate volumes of air both behind and in front of the solvent to fit adequately into the syringe barrel, the capacity of the syringe to be used for spiking purposes needs to be ~50% greater than the volume to be dispensed.

5 Preparation of samples

Dichloromethane (DCM) is the preferred solvent used in this extraction because it is not miscible with water and extracts most organics (eg. pesticides) easily from water samples.

An added advantage of DCM is that it is more dense than water. Consequently, once phase separation has occurred in the separation funnel the DCM layer is easily removed from the bottom of the separating funnel leaving the aqueous sample behind for subsequent extractions.

Prior to extraction, field samples are prepared as follows:

⇒ remove samples from cold storage and allow them to equilibrate to room temperature.

Thoroughly mix each sample and place 400 mL into a separating funnel (500 to 1000 mL capacity) using a measuring cylinder. Rinse the measuring cylinder between each sample transfer with tap water and then pre-rinse with a small portion of the current sample

⇒ ensure all relevant sample information is recorded in the extraction log book

⇒ add a volume (5.6 μ L) of fenchlorphos (surrogate standard) into each sample using the “air sandwich technique”(see 4.3). The container holding the fenchlorphos standard should remain uncovered for as short a time as possible, and should be covered in aluminium foil to reduce evaporation

⇒ clean the syringe between each sample by drawing acetone into the barrel 10 times and dispensing it onto a tissue. The final volume of acetone is dispensed into a syringe cleaner (SGE @200°C) attached to a vacuum pump, and the barrel is drawn in and out a few times to ensure the syringe is clean.

5.1 First Extraction

◇ Add ~40 mL of DCM to each sample.

- ◇ Briefly shake the separating funnel and inverted holding the stopper firmly in place.
Open the tap slowly to allow any pressure to be released.
- ◇ Commence the extraction procedure. **NOTE:** To ensure uniformity, all separating funnels are inverted 180° and given 3 quick shakes. This is repeated 30 times. The final shake should be in a swirling manner with the funnel upright to ensure all solvent runs down into the bottom of the separating funnel. While the separating funnel is upright, remove the stopper briefly to allow any build up pressure to be released.
- ◇ Organic and aqueous phases are allowed to separate, the duration will vary depending on the turbidity of the sample, eg for highly turbid samples it may be necessary to let the samples sit overnight. The length of time required for phase separation is reduced with each subsequent extraction. Once separation has occurred, the stopper is removed and the bottom (organic) layer is allowed to run into a round bottom flask. Approximately 1 cm of emulsion is left in the separating funnel.
- ◇ Using a glass funnel, approximately 1 teaspoon of anhydrous sodium sulphate (Na_2SO_4) is added to each round bottom flask. Shake the flask to dry the organic layer, if the solvent is still “wet”, a second teaspoon of Na_2SO_4 may be added. “Wet” solvent can be identified by a lack of free flowing Na_2SO_4 .
- ◇ Filter the contents of the round bottom flasks through a funnel containing a glass wool plug and a teaspoon of Na_2SO_4 into evaporating tubes (see Figure 1 for an example of a Zymark[®] TURBOVAP[™] evaporating tube {Cat. No. ZA7516}).
- ◇ Filter the contents of each round bottom flask through the funnel into the evaporating tubes.

5.2 Second Extraction

The steps outlined for the First Extraction are repeated, but the addition of Na₂SO₄ to the glass funnel is omitted unless it is obvious that the sodium sulphate is totally wet.

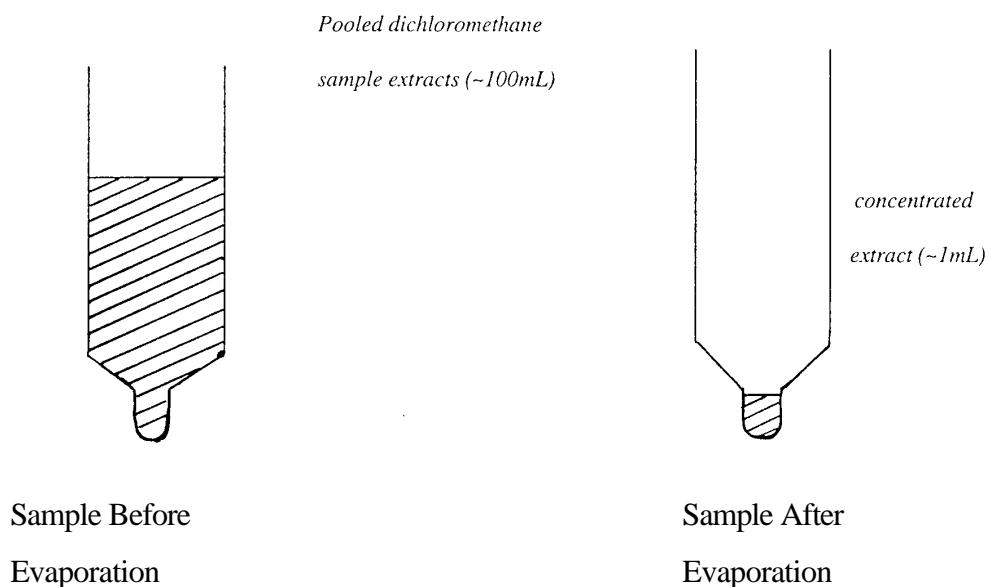
5.3 Third Extraction

The steps outlined for the First Extraction are repeated.

5.4 Concentration of extract “Sample Blow Down”

- ◆ Turn on the Zymark[®] TurboVap[™] Evaporator P/N and allow to warm up.
- ◆ Turn on the nitrogen at the cylinder, and adjust the regulator until it reads 250 kPa.
- ◆ Place the evaporating tubes into the TurboVap and close the lid. Once the lid is closed, a stream of nitrogen is delivered into each tube speeding up the evaporation process.
- ◆ Monitor the evaporation process and when the liquid fills the “nipple” section of the evaporating tubes (see Figure 1) stop the evaporation process and remove the tube.
- ◆ Place evaporation tubes into the holding rack.
- ◆ Add a volume of 5.6 μL of 1-Cl-C₁₄ to the extract using the “air sandwich” technique (see 4.3).
- ◆ Transfer the spiked extract carefully to a 2 mL labelled glass vial using a pasteur pipette.
- ◆ Store extracts in the freezer.

Figure 1. Evaporating tubes (TurboVap™) showing sample before and after “blow down”.



5.5 Glassware Cleaning

Glassware is initially rinsed in hot tap water and then soaked (for at least 2 h, but generally overnight) in detergent. Glassware removed from the detergent bath is then thoroughly rinsed in tap water and soaked in de-ionised water (for at least 2 h) followed by MilliQ water rinsing and drying at 105 °C. Separating funnels are placed in their rack to drip dry. Taps from separating funnels are wiped with acetone.

6 Analysis

6.1 GC-MSD

Samples are analysed by GC-MSD using the Selective Ion Monitoring (SIM) mode. The instrument used at Griffith laboratory of CSIRO Land and Water is a Hewlett Packard

5890 Series II gas chromatograph (analytical column HP-5 MS; 30 m x 0.25 mm, film 0.25 μm) coupled to a Hewlett Packard 5972 Mass Selective Detector. Chromatographic conditions are: 2 μL injection (splitter off 1 min); injector temperature 200°C; column temperature, 50°C (isocratic 1 min) ramped at 20°C min^{-1} to 160°C (isocratic 1 min), ramped at 4°C min^{-1} to 190°C (isocratic 4 min) and ramped at 7°C to a final temperature of 250°C (isocratic 2 min).

Run all standards with the mass spectrometer in full scan mode to obtain a clean mass spectrum of each compound and to establish their retention times. Choose the best target and qualifying ions for multiple ion detection (MID) of each compound and set the appropriate retention time windows as shown in Appendix 1. Run all standards again with the mass spectrometer in MID mode to confirm that the correct parameters have been set. See Appendix 5 for an example of a typical chromatogram of standards. Prior to analysis of samples or standards, ensure that they are at room temperature. This is important as some of the less soluble compounds could have dropped out of solution during storage in the freezer.

6.2 Calculations

Quantification is based on the ratio of the fenchlorphos surrogate standard to the pesticide of interest determined for the sample and the ratio of surrogate to the same pesticide determined for the matrix standards (see Appendix 4 for malathion example). The 1-Cl-C14 internal standard added to the extract just prior to analysis is used to monitor fenchlorphos recovery. If the ratio of 1-Cl-C14 to fenchlorphos for any sample or standard differs by more than 20% the extract of the sample should be repeated. Following the successful analysis of a sample and standards the actual concentration of each pesticide present can be determined. However, each peak should be examined prior to quantification

to check the retention times and the presence of characteristic ions at the expected ratios. Once all peaks have been checked and integrated, generate a report detailing the “area count” of each peak. This “area count” figure is listed as “Resp” in the table which appears on the computer monitor. This figure is recorded in a table, an example of which is presented in Appendix 2. This same process is repeated for the standards. These area counts are then divided by the value recorded for fenchlorphos (the surrogate standard) and recorded in a separate table (an example of which is Appendix 3). These values are then transferred to a separate sheet for each pesticide, Appendix 4 presents Malathion as an example. Sample and standard results are listed together with the volume of solution extracted (usually 400 mL) and the area ratio to fenchlorphos. Values for the amount of pesticide present in each of the standards are recorded in the “ $\mu\text{g}/\text{vol}$ ” column (taken from Table 2 as an example). To determine the concentration of pesticide in a given sample, the area ratio of that sample is divided by the area ratio of one of the standards (preferably one with a similar area ratio to fenchlorphos). This value is then multiplied by the “ $\mu\text{g}/\text{vol}$ ” value of the standard. To determine the concentration per litre, this value is divided by 0.4 - the volume expressed in litres (see Appendix 4).

Concentrations of analytes outside of the linear range of the standards should not be determined by extrapolation. If the concentration is too high, the extraction should be repeated on an appropriately diluted sample. If the concentration is too low it should be reported as <Limit Of Detection (LOD). However, if necessary concentrations below LOD may be estimated by extrapolation and reported in parenthesis eg <LOD (0.02) to indicate that they are semi quantitative.

6.3 Limit of Detection (LOD), Limit of Reporting (LOR), Precision, Accuracy

Establish the limit of LOD for each analyte by the repeated analysis ($n \geq 5$) of each analyte spiked into matrix blanks at low levels. The lowest concentration giving a signal to noise ratio of 3:1 and at which the identity of the analyte can be confirmed is taken as the LOD. The LOR is generally set at a level of ~ 2 -3 times LOD. Appendix 6 presents the LOR's for the pesticides monitored in the 1995/96 Irrigation season. The precision and accuracy of the method for each analyte is determined by the repeated analysis ($n \geq 10$) of matrix blanks spiked at LOR concentrations. The mean concentration of these analyses for each analyte is an indication of the accuracy of the method, while precision is indicated by the associated variation of the mean (%cv). Generally the mean concentration determined for an analyte at an LOR of $0.05 \mu\text{g/L}$ is within 20% of the expected value.

References

- Korth, W., Thomas, M., Foster, S., McCorkelle, G., and Bowmer, K.H. (1995a). Toxicity of Rice and Maize Pesticides to *Ceriodaphnia* sp.: Implications for Management of Irrigation Drainage Water in Australia. *Australasian Journal of Ecotoxicology*. **1**, 55-62.
- Korth, W., Thomas, M., McCorkelle, G and Foster, S. (1995b). Pesticide and Toxicity Testing of MIA Drainage Water (5 October to 30 November, 1994). CSIRO Division of Water Resources, Griffith Laboratory, Consultancy Report No. 95/25.

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Cheryl Orr. Many thanks to Jane Roberts for proof reading this document.

A p p e n d i x 1
GC-MS Method File

TOPLEVEL PARAMETERS

Method Information For: C:\HPCHEM\1\METHODS\PESTSIM.M

Method Sections To Run:

- Save Copy of Method With Data
- Pre-Run Cmd/Macro =
- Data Acquisition
- Data Analysis
- Post-Run Cmd/Macro =

Method Comments:

Organophosphorus pesticides (SIM)

END OF TOPLEVEL PARAMETERS

ACQUISITION PARAMETERS

General Information

Inlet : GC
Tune File : MAXTUNE.U
Acquisition Mode : Sim

MS Information

Solvent Delay : 3.00 min
EM Absolute : False
EMV Offset : 0.0
Resulting Voltage : 2023.5

[Sim Parameters]

GROUP 1
Group ID : methomyl b/d 1+
Dwell Per Ion : 60 msec.
Low Resolution : Yes
Group Start Time : 3.50
Plot 1 Ion : 105.00
Ions In Group : 58.00 71.00 88.00 105.00

GROUP 2

Method: PESTSIM.M

Group ID : dichlorvos,BEN1
Dwell Per Ion : 40 msec.
Low Resolution : Yes
Group Start Time : 5.90
Plot 1 Ion : 109.00
Ions In Group :109.00 145.00 185.00 180.00 181.00
151.00

GROUP 3
Group ID : diuron,BEN2
Dwell Per Ion : 40 msec.
Low Resolution : Yes
Group Start Time : 6.50
Plot 1 Ion : 186.70
Ions In Group :159.00 186.70 189.00 154.00 155.00
68.00

GROUP 4
Group ID : molinate, methom
Dwell Per Ion : 40 msec.
Low Resolution : Yes
Group Start Time : 8.00
Plot 1 Ion : 125.90
Ions In Group : 98.00 125.90 187.00 58.00 105.00
88.00

GROUP 5
Group ID : dicamba
Dwell Per Ion : 60 msec.
Low Resolution : Yes
Group Start Time : 10.10
Plot 1 Ion : 173.00
Ions In Group :173.00 175.00 220.00 222.00

GROUP 6
Group ID : 1-C1-C14
Dwell Per Ion : 60 msec.
Low Resolution : Yes
Group Start Time : 11.90
Plot 1 Ion : 91.00
Ions In Group : 91.00 93.00 97.00 105.00

GROUP 7
Group ID : Monocr, triflu,
Dwell Per Ion : 30 msec.
Low Resolution : Yes
Group Start Time : 12.15
Plot 1 Ion : 90.90
Ions In Group :127.00 192.00 193.00 306.00 264.00
290.00 90.90 93.00 97.00

GROUP 8
Group ID : atraz,simaz
Dwell Per Ion : 50 msec.
Low Resolution : Yes
Group Start Time : 13.40
Plot 1 Ion : 199.90
Ions In Group :199.90 201.00 202.00 217.00 215.00

Method: PESTSIM.M

Mon Apr 21 11:26:55 1997

GROUP 9
Group ID : Terbufos
Dwell Per Ion : 60 msec.
Low Resolution : Yes
Group Start Time : 14.00
Plot 1 Ion : 231.00
Ions In Group : 97.00 153.00 231.00 288.00

GROUP 10
Group ID : Diazinon
Dwell Per Ion : 60 msec.
Low Resolution : Yes
Group Start Time : 15.10
Plot 1 Ion : 137.00
Ions In Group :137.00 179.00 199.00 304.00

GROUP 11
Group ID : fenchlor, propa
Dwell Per Ion : 60 msec.
Low Resolution : Yes
Group Start Time : 17.00
Plot 1 Ion : 284.70
Ions In Group :125.00 284.70 287.00 161.00 163.00
217.00

GROUP 12
Group ID : bromac, thio
Dwell Per Ion : 50 msec.
Low Resolution : Yes
Group Start Time : 19.15
Plot 1 Ion : 257.00
Ions In Group :257.00 125.00 127.00 188.00 190.00
100.00

GROUP 13
Group ID : linuron,mal,me
Dwell Per Ion : 30 msec.
Low Resolution : Yes
Group Start Time : 19.40
Plot 1 Ion : 173.00
Ions In Group :173.00 146.00 238.00 162.00 248.00
160.00 61.00 125.00 127.00

GROUP 14
Group ID : chlorpyrifos
Dwell Per Ion : 70 msec.
Low Resolution : Yes
Group Start Time : 19.90
Plot 1 Ion : 196.70
Ions In Group :196.70 199.00 314.00

GROUP 15
Group ID : endol,methidat
Dwell Per Ion : 40 msec.
Low Resolution : Yes
Group Start Time : 22.50
Plot 1 Ion : 170.00
Ions In Group :170.00 195.00 237.00 241.00 85.00
125.00 145.00 302.00

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GROUP 16
 Group ID : PRO, DDE, DIEL
 Dwell Per Ion : 30 msec.
 Low Resolution : Yes
 Group Start Time : 24.00
 Plot 1 Ion : 139.00
 Ions In Group : 139.00 97.00 208.00 246.00 176.00
 318.00 79.00 108.00 263.00

GROUP 17
 Group ID : endo2, Fluaz
 Dwell Per Ion : 40 msec.
 Low Resolution : Yes
 Group Start Time : 25.15
 Plot 1 Ion : 170.00
 Ions In Group : 170.00 195.00 146.00 254.00 282.00
 237.00

GROUP 18
 Group ID : endo sulfate
 Dwell Per Ion : 60 msec.
 Low Resolution : Yes
 Group Start Time : 26.60
 Plot 1 Ion : 229.00
 Ions In Group : 229.00 272.00 274.00 387.00

GROUP 19
 Group ID : bifen, dicofol
 Dwell Per Ion : 40 msec.
 Low Resolution : Yes
 Group Start Time : 28.00
 Plot 1 Ion : 181.00
 Ions In Group : 181.00 166.00 165.00 139.00 111.00
 251.00

GROUP 20
 Group ID : L-Cyhalomethrin
 Dwell Per Ion : 60 msec.
 Low Resolution : Yes
 Group Start Time : 29.00
 Plot 1 Ion : 181.00
 Ions In Group : 181.00 197.00 208.00 449.00

GROUP 21
 Group ID : cypermethrins
 Dwell Per Ion : 70 msec.
 Low Resolution : Yes
 Group Start Time : 31.00
 Plot 1 Ion : 181.00
 Ions In Group : 163.00 181.00 209.00

GROUP 22
 Group ID : Delta-Methrin
 Dwell Per Ion : 40 msec.
 Low Resolution : Yes
 Group Start Time : 33.00
 Plot 1 Ion : 180.80
 Ions In Group : 180.80 297.00 174.00 172.00 93.00

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91.00

[Real Time Plot Parameters]

Time Window : 14 min
Iconize Real Time Display : True
Plot 1 type : Single ion
Scale minimum : 0
Scale maximum : 2000000
Plot 2 type : No plot

GC Inlet Information
-- -----

[Inlet A Temperature Program Information]

Oven Track : Off
Initial Temp. : 250 C
Initial Time : 480.00 min

Level	Rate (C/min)	Final Temp. (C)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Inlet B Temperature Program Information]

Oven Track : Off
Initial Temp. : 200 C
Initial Time : 480.00 min

Level	Rate (C/min)	Final Temp. (C)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Inlet A Pressure Program Information]

Constant Flow : Off
Initial Pres. : 83 kPa
Initial Time : 480.00 min

Level	Rate(kPa/min)	Final Pres.(kPa)	Final Time (min)
1	0		

Total Program Time: 480.00 min
Pressure Units : kPa

[Inlet A Flow Settings]

Column length : 25.00 m
Column diameter : 0.220 mm
Gas : He
Vacuum compensation : On
Pressure : 21 kPa
Flow : 0.5 ml/min
Linear velocity : 26.7 cm/sec

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Split flow : 30 ml/min
Split ratio : 66.3

[Inlet B Pressure Program Information]

Constant Flow : Off
Initial Pres. : 21 kPa
Initial Time : 480.00 min

Level	Rate(kPa/min)	Final Pres.(kPa)	Final Time (min)
1	0		

Total Program Time: 480.00 min
Pressure Units : kPa

[Inlet B Flow Settings]

Column length : 30.00 m
Column diameter : 0.530 mm
Gas : He
Vacuum compensation : On
Pressure : 0 kPa
Flow : 0.0 ml/min
Linear velocity : 0.0 cm/sec

[Auxiliary Channel C Information]

Comment:

Pressure Program:
Initial Pres. : 0 kPa
Initial Time : 480.00 min

Level	Rate(kPa/min)	Final Pres.(kPa)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Auxiliary Channel D Information]

Comment:

Pressure Program:
Initial Pres. : 0 kPa
Initial Time : 480.00 min

Level	Rate(kPa/min)	Final Pres.(kPa)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Auxiliary Channel E Information]

Comment:

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Pressure Program:
Initial Pres. : 0 kPa
Initial Time : 480.00 min

Level	Rate(kPa/min)	Final Pres.(kPa)	Final Time (min)
1	0		

Total Program Time: 480.00 min

[Auxiliary Channel F Information]

Comment:

Pressure Program:
Initial Pres. : 0 kPa
Initial Time : 480.00 min

Level	Rate(kPa/min)	Final Pres.(kPa)	Final Time (min)
1	0		

Total Program Time: 480.00 min

GC Temperature Information

[GC Zone Temperatures]

Inj. A : 250 C
Inj. B : 200 C
Det. A : 50 C Off
Det. B : 290 C
Aux. : 290 C

[Oven Parameters]

Oven Equib Time : 0.50 min
Oven Max : 325 C
Oven : On
Cryo : Off
Ambient : 25 C
Cryo Blast : Off

[Oven Program]

Initial Temp. : 50 C
Initial Time : 1.00 min

Level	Rate (C/min)	Final Temp. (C)	Final Time (min)
1	20.00	150	1.00
2	3.00	190	1.00
3	10.00	310	3.00

Next Run Time : 36.33 min

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Injector Information

Injection Source : Auto
Injection Location : Front

Sample Washes : 1
Sample Pumps : 2
Sample Volume : 2 stop(s)
Viscosity Delay : 1 sec
Solvent A Washes : 5
Solvent B Washes : 5
On Column : No

[Purge Information]

Purge A/B	Init. Value	On Time	Off Time
A	Off	1.00	0.00
B	Off	1.00	0.00

END OF ACQUISITION PARAMETERS

DATA ANALYSIS PARAMETERS

Method Name: C:\HPCHEM\1\METHODS\PESTSIM.M

Percent Report Settings

Sort By: Retention Time

Output Destination

Screen: No
Printer: Yes
File: No

Integration Events: Meth Default

Generate Report During Run Method: No

Signal Correlation Window: 0.020

Qualitative Report Settings

Peak Location of Unknown: Apex

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5 not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

2) Methomyl b/d 1 ()

Ret. Time 4.92 min., Extract & Integrate from 4.42 to 5.42 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 105.00			*** METH DEFAULT ***
Q1 58.00	100.00	20.0	*** METH DEFAULT ***
Q2 88.00	40.00	20.0	*** METH DEFAULT ***
Q3 71.00	10.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	
2	not used for this compound	
3	not used for this compound	
4	not used for this compound	
5	not used for this compound	

Qualifier Peak Analysis ON
Curve Fit: Quadratic

3) Diuron ()

Ret. Time 6.74 min., Extract & Integrate from 6.24 to 7.24 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 186.90			*** METH DEFAULT ***
Q1 189.00	98.20	20.0	*** METH DEFAULT ***
Q2 159.00	50.40	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	0.770	54340
2	1.790	159376
3	4.280	300602
4	8.530	497392
5	20.980	1047873

Qualifier Peak Analysis ON
Curve Fit: Linear

4) Bensulfuron b/d ()

Ret. Time 6.91 min., Extract & Integrate from 6.41 to 7.41 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 154.00			*** METH DEFAULT ***
Q1 155.00	83.00	20.0	*** METH DEFAULT ***
Q2 68.00	90.00	20.0	*** METH DEFAULT ***
Q3 187.00	0.40	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	

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2 not used for this compound
3 not used for this compound
4 not used for this compound
5 not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

5) Molinate ()

Ret. Time 9.56 min., Extract & Integrate from 9.06 to 10.06 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 125.90			*** METH DEFAULT ***
Q1 187.00	16.50	20.0	*** METH DEFAULT ***
Q2 98.00	14.20	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	0.870	152341
2	2.020	423406
3	4.800	902531
4	9.600	1483638
5	23.600	4755734

Qualifier Peak Analysis ON
Curve Fit: Linear

6) Methomyl ()

Ret. Time 10.13 min., Extract & Integrate from 9.63 to 10.63 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 105.00			*** METH DEFAULT ***
Q1 58.00	95.00	20.0	*** METH DEFAULT ***
Q2 88.00	40.00	20.0	*** METH DEFAULT ***
Q3 162.00	3.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	
2	not used for this compound	
3	not used for this compound	
4	not used for this compound	
5	not used for this compound	

Qualifier Peak Analysis ON
Curve Fit: Quadratic

7) Dicamba ()

Ret. Time 10.25 min., Extract & Integrate from 9.75 to 10.75 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 173.00			*** METH DEFAULT ***
Q1 175.00	80.00	20.0	*** METH DEFAULT ***
Q2 220.00	80.00	20.0	*** METH DEFAULT ***
Q3 222.00	50.00	20.0	*** METH DEFAULT ***

Method: PESTSIM.M

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Lvl ID	Conc ()	Response
1	not used	for this compound
2	not used	for this compound
3	not used	for this compound
4	not used	for this compound
5	not used	for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

8) 1-Chlorotetradecane ()

Ret. Time 12.01 min., Extract & Integrate from 11.51 to 12.51 min

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 90.90			*** METH DEFAULT ***
Q1 93.00	34.20	20.0	*** METH DEFAULT ***
Q2 97.00	20.60	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	1.200	1478011
2	1.200	195561
3	1.200	164441
4	1.200	128402
5	1.200	187341

Qualifier Peak Analysis ON
Curve Fit: Linear

9) trifluralin ()

Ret. Time 12.26 min., Extract & Integrate from 11.76 to 12.76 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 306.00			*** METH DEFAULT ***
Q1 264.00	94.30	20.0	*** METH DEFAULT ***
Q2 290.00	23.10	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used	for this compound
2	not used	for this compound
3	not used	for this compound
4	not used	for this compound
5	not used	for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

10) Monocrotophos ()

Ret. Time 12.47 min., Extract & Integrate from 11.97 to 12.97 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 127.00			*** METH DEFAULT ***
Q1 192.00	15.00	20.0	*** METH DEFAULT ***

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Signal	Rel Resp.	Pct.	Unc.(rel)	Integration
Tgt 231.00				*** METH DEFAULT ***
Q1 97.00	50.00		20.0	*** METH DEFAULT ***
Q2 153.00	45.00		20.0	*** METH DEFAULT ***
Q3 288.00	10.00		20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound
4		not used for this compound
5		not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

14) Diazinon ()

Ret. Time 15.23 min., Extract & Integrate from 14.73 to 15.73 min.

Signal	Rel Resp.	Pct.	Unc.(rel)	Integration
Tgt 137.00				*** METH DEFAULT ***
Q1 179.00	75.00		20.0	*** METH DEFAULT ***
Q2 199.00	60.00		20.0	*** METH DEFAULT ***
Q3 304.00	50.00		20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound
4		not used for this compound
5		not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

15) propanil ()

Ret. Time 17.23 min., Extract & Integrate from 16.73 to 17.73 min.

Signal	Rel Resp.	Pct.	Unc.(rel)	Integration
Tgt 161.00				*** METH DEFAULT ***
Q1 163.00	70.00		20.0	*** METH DEFAULT ***
Q2 217.00	30.00		20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound
4		not used for this compound
5		not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

16) Fenchlorphos (ISTD)

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Ret. Time 18.02 min., Extract & Integrate from 17.52 to 18.52 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 284.70			*** METH DEFAULT ***
Q1 287.00	84.90	20.0	*** METH DEFAULT ***
Q2 125.00	112.10	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	1.260	126702
2	1.260	175425
3	1.260	157893
4	1.260	125411
5	1.260	157401

Qualifier Peak Analysis ON ISTD conc: 0.000
Curve Fit: Linear

17) Linuron ()

Ret. Time 19.43 min., Extract & Integrate from 18.93 to 19.93 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 248.00			*** METH DEFAULT ***
Q1 160.00	100.00	20.0	*** METH DEFAULT ***
Q2 61.00	1000.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	
2	not used for this compound	
3	not used for this compound	
4	not used for this compound	
5	not used for this compound	

Qualifier Peak Analysis ON
Curve Fit: Quadratic

18) Bromacil ()

Ret. Time 19.25 min., Extract & Integrate from 18.75 to 19.75 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 190.00			*** METH DEFAULT ***
Q1 188.00	100.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	1.110	15067
2	2.580	49844
3	6.150	107064
4	12.250	176332
5	27.700	605796

Qualifier Peak Analysis ON
Curve Fit: Linear

19) Thiobencarb ()

Method: PESTSIM.M

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Ret. Time 19.34 min., Extract & Integrate from 18.84 to 19.84 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 257.00			*** METH DEFAULT ***
Q1 125.00	265.00	20.0	*** METH DEFAULT ***
Q2 127.00	110.00	20.0	*** METH DEFAULT ***
Q3 257.00	1200.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	0.510	140793
2	1.450	523505
3	3.170	980047
4	6.150	1515371
5	16.000	5809845

Qualifier Peak Analysis ON
Curve Fit: Linear

20) Malathion ()

Ret. Time 19.60 min., Extract & Integrate from 19.10 to 20.10 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 172.90			*** METH DEFAULT ***
Q1 125.00	150.50	20.0	*** METH DEFAULT ***
Q2 127.00	136.80	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	1.350	96431
2	3.140	315454
3	7.480	676829
4	14.900	1106969
5	36.700	3844661

Qualifier Peak Analysis ON
Curve Fit: Linear

21) Metolachlor ()

Ret. Time 19.66 min., Extract & Integrate from 19.16 to 20.16 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 162.00			*** METH DEFAULT ***
Q1 238.00	42.00	20.0	*** METH DEFAULT ***
Q2 146.00	14.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	0.550	79622
2	1.570	341221
3	3.430	705540
4	6.670	1224637
5	17.300	5223449

Qualifier Peak Analysis ON
Curve Fit: Linear

Method : PESTSIM.M

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22) Chlorpyrifos

()

Ret. Time 19.99 min., Extract & Integrate from 19.49 to 20.49 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 196.70			*** METH DEFAULT ***
Q1 199.00	119.50	20.0	*** METH DEFAULT ***
Q2 314.00	54.20	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	0.670	32194
2	1.550	96658
3	3.690	218918
4	7.360	361496
5	18.100	1110307

Qualifier Peak Analysis ON

Curve Fit: Linear

23) Methidathion

()

Ret. Time 22.68 min., Extract & Integrate from 22.18 to 23.18 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 145.00			*** METH DEFAULT ***
Q1 85.00	80.00	20.0	*** METH DEFAULT ***
Q2 125.00	20.00	20.0	*** METH DEFAULT ***
Q3 302.00	5.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	
2	not used for this compound	
3	not used for this compound	
4	not used for this compound	
5	not used for this compound	

Qualifier Peak Analysis ON

Curve Fit: Quadratic

24) endosulfan I

()

Ret. Time 23.23 min., Extract & Integrate from 22.73 to 23.73 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 195.00			*** METH DEFAULT ***
Q1 237.00	81.30	20.0	*** METH DEFAULT ***
Q2 241.00	84.10	20.0	*** METH DEFAULT ***
Q3 170.00	91.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	
2	not used for this compound	
3	not used for this compound	
4	not used for this compound	
5	not used for this compound	

Method: PESTSIM.M

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Qualifier Peak Analysis ON
Curve Fit: Quadratic

25) Profenofos ()

Ret. Time 24.19 min., Extract & Integrate from 23.69 to 24.69 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 139.00			*** METH DEFAULT ***
Q1 97.00	95.00	20.0	*** METH DEFAULT ***
Q2 208.00	60.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used	for this compound
2	not used	for this compound
3	not used	for this compound
4	not used	for this compound
5	not used	for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

26) Dieldrin ()

Ret. Time 24.33 min., Extract & Integrate from 23.83 to 24.83 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 79.00			*** METH DEFAULT ***
Q1 108.00	15.00	20.0	*** METH DEFAULT ***
Q2 263.00	10.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used	for this compound
2	not used	for this compound
3	not used	for this compound
4	not used	for this compound
5	not used	for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

27) DDE ()

Ret. Time 24.42 min., Extract & Integrate from 23.92 to 24.92 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 246.00			*** METH DEFAULT ***
Q1 176.00	50.00	20.0	*** METH DEFAULT ***
Q2 318.00	55.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used	for this compound
2	not used	for this compound
3	not used	for this compound
4	not used	for this compound
5	not used	for this compound

Method: PESTSIM.M

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Qualifier Peak Analysis ON
Curve Fit: Quadratic

28) Fluazifop ()

Ret. Time 25.25 min., Extract & Integrate from 24.75 to 25.75 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 282.00			*** METH DEFAULT ***
Q1 254.00	60.00	20.0	*** METH DEFAULT ***
Q2 146.00	45.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound
4		not used for this compound
5		not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

29) endosulfan II ()

Ret. Time 25.39 min., Extract & Integrate from 24.89 to 25.89 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 195.00			*** METH DEFAULT ***
Q1 170.00	74.20	20.0	*** METH DEFAULT ***
Q2 237.00	70.70	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound
4		not used for this compound
5		not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

30) endosulfan sulfate ()

Ret. Time 26.71 min., Extract & Integrate from 26.21 to 27.21 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 272.00			*** METH DEFAULT ***
Q1 229.00	71.90	20.0	*** METH DEFAULT ***
Q2 274.00	79.00	20.0	*** METH DEFAULT ***
Q3 387.00	28.60	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound

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4 not used for this compound
5 not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

31) Bifenthrin ()

Ret. Time 28.18 min., Extract & Integrate from 27.68 to 28.68 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 181.00			*** METH DEFAULT ***
Q1 166.00	0.00	20.0	*** METH DEFAULT ***
Q2 165.00	0.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound
4		not used for this compound
5		not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

32) Dicofol ()

Ret. Time 28.38 min., Extract & Integrate from 27.88 to 28.88 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 139.00			*** METH DEFAULT ***
Q1 111.00	40.00	20.0	*** METH DEFAULT ***
Q2 251.00	75.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound
2		not used for this compound
3		not used for this compound
4		not used for this compound
5		not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

33) Lambda-Cyhalomethrin ()

Ret. Time 29.63 min., Extract & Integrate from 29.13 to 30.13 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 181.00			*** METH DEFAULT ***
Q1 197.00	90.00	20.0	*** METH DEFAULT ***
Q2 208.00	60.00	20.0	*** METH DEFAULT ***
Q3 449.00	10.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1		not used for this compound

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2 not used for this compound
3 not used for this compound
4 not used for this compound
5 not used for this compound

Qualifier Peak Analysis ON
Curve Fit: Quadratic

34) cypermethrin ()

Ret. Time 31.57 min., Extract & Integrate from 31.07 to 32.07 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 163.00			*** METH DEFAULT ***
Q1 181.00	68.30	20.0	*** METH DEFAULT ***
Q2 209.00	25.60	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	
2	not used for this compound	
3	not used for this compound	
4	not used for this compound	
5	not used for this compound	

Qualifier Peak Analysis ON
Curve Fit: Quadratic

35) Delta-Methrin ()

Ret. Time 33.23 min., Extract & Integrate from 32.73 to 33.73 min.

Signal	Rel Resp.	Pct. Unc.(rel)	Integration
Tgt 181.00			*** METH DEFAULT ***
Q1 209.00	40.00	20.0	*** METH DEFAULT ***
Q2 253.00	80.00	20.0	*** METH DEFAULT ***
Q3 172.00	30.00	20.0	*** METH DEFAULT ***

Lvl ID	Conc ()	Response
1	not used for this compound	
2	not used for this compound	
3	not used for this compound	
4	not used for this compound	
5	not used for this compound	

Qualifier Peak Analysis ON
Curve Fit: Quadratic

END OF DATA ANALYSIS PARAMETERS

Method: PESTSIM.M

Mon Apr 21 11:26:55 1997

Appendix 2. Table used to record area count values from the GC-MS (MID) trace.

Area count:

SAMPLE ID	LU 13	LUG 13	LU 14	LUG 14	LD 13	LD 14	STD 2	STD 3	STD 4	STD 5	LM 13	LM 14
FILE NAME	EUW 700	EUW 701	EUW 702	EUW 703	EUW 704	EUW 705	EUW 706	EUW 707	EUW 708	EUW 709	EUW 710	EUW 711
diuron b/d	5392	1447	2747	7052	2699	2017	167	735	7272	18049	3871	1806
bensulfuron												
molinate	57967	14067	21378	43366	27737	29738	1122	4663	42270	101492	31878	14706
1-Cl-C ₁₄ *	44497	27973	29528	27399	23081	29626	13603	18174	23010	11186	28836	28928
trifluralin												
simazine	9703	1627	3589	9947	8469	3245	327	1632	12031	34007	10983	2143
atrazine	140	59	90	102	90	69	449	2029	19584		114	80
fenchlorphos**	40720	26392	27584	24794	22650	28305	11332	16067	16688	9503	26995	28053
bromacil	832	36	471	1861	566	258		117	1810	5338	773	329
thiobencarb												
malathion	2214	1556	754	3557	484	699	406	1729	19727		516	581
metolachlor												
chlorpyrifos												
α-endosulfan												
β-endosulfan												
endosulfan-SO ₄												
dicofol												
lambda-cyhalothrin												
cypermethrin (various isomers)												
deltamethrin												

* internal standard

** surrogate/internal standard

Appendix 3. Table used to express area ratio of analytes detected to fenchlorfos.

Area ratio to fenchlorphos:

SAMPLE ID	LU 13	LUG 13	LU 14	LUG 14	LD 13	LD 14	STD 2	STD 3	STD 4	STD 5	LM 13	LM 14
FILE NAME	EUW 700	EUW 701	EUW 702	EUW 703	EUW 704	EUW 705	EUW 706	EUW 707	EUW 708	EUW 709	EUW 710	EUW 711
diuron b/d	0.132	0.055	0.10	0.284	0.119	0.071	0.0147	0.046	0.436	1.9	0.14	0.064
bensulfuron												
molinate	1.42	0.533	0.775	1.75	1.22	1.05	0.099	0.29	2.53	10.68	1.18	0.52
1-Cl-C ₁₄ *	1.1	1.06	1.07	1.10	1.01	1.05	1.2	1.13	1.38	1.18	1.07	1.03
trifluralin												
simazine	0.238	0.062	0.130	0.40	0.374	0.115	0.029	0.10	0.72	3.58	0.406	0.086
atrazine	0.003	0.002	0.003	0.004	0.004	0.002	0.040	0.126			0.004	0.003
fenchlorphos**												
bromacil	0.020	0.0014	0.017	0.075	0.025	0.009		0.007	0.108	0.56	0.029	0.0117
thiobencarb												
malathion	0.054	0.059	0.027	0.143	0.021	0.025	0.036	0.108	1.18		0.019	0.021
metolachlor												
chlorpyrifos												
α-endosulfan												
β-endosulfan												
endosulfan-SO ₄												
dicofol												
lambda-cyhalothrin												
cypermethrin (various isomers)												
deltamethrin												

* internal standard

** surrogate/internal standard

Appendix 4. Form used to calculate the concentration of malathion in each sample.

Malathion					
Sample	Volume Extracted (mL)	Area Ratio v Fenchlorfos	µg/Vol.	µg/L	
LU 13	400	0.054	0.105	0.25*	
LUG 13	400	0.059	0.11	0.27*	
LU 14	400	0.027	0.05	0.13*	
LUG 14	400	0.143	0.25	0.62*	
LD 13	400	0.021	0.039	0.10*	
LD 14	400	0.025	0.046	0.12*	
STD 2	400	0.036	0.067	STD	
STD 3	400	0.108	0.188	STD	
LM 13	400	0.019	0.005	0.09*	
LM 14	400	0.021	0.039	0.10*	

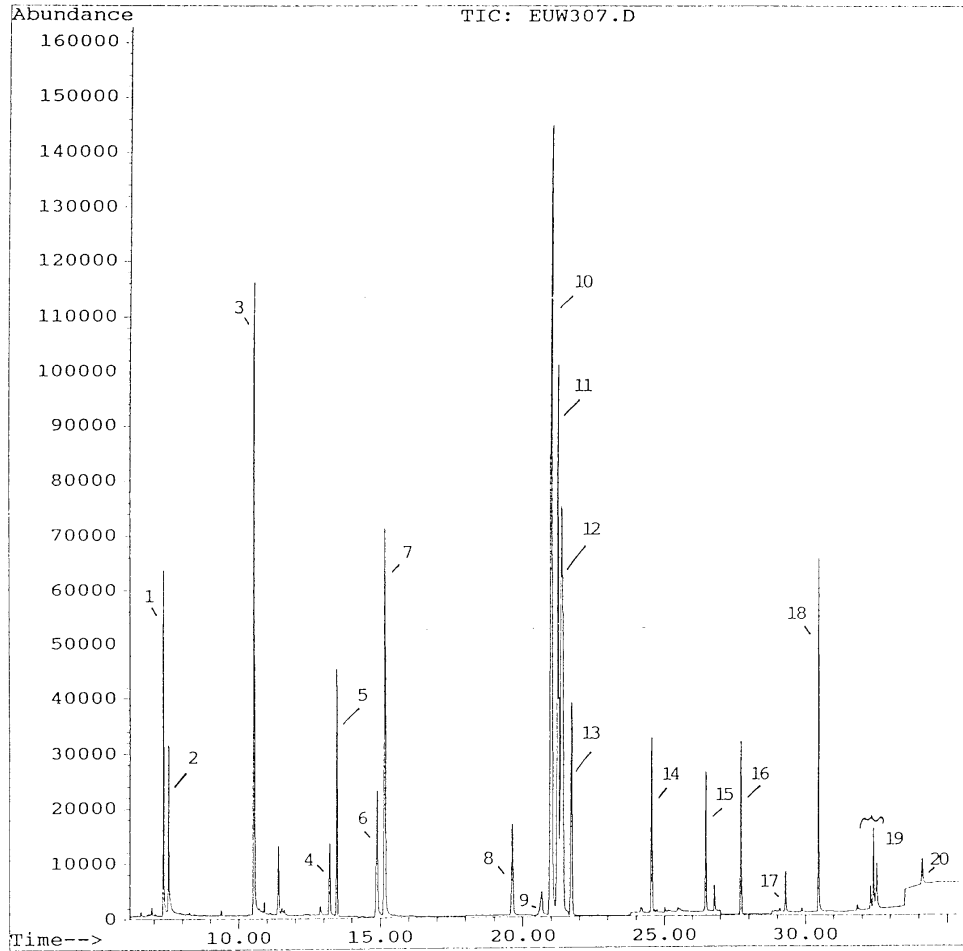
* calculated using area ration of standards and sample concentration of standards (see example)

Calculation example: LU13

$$\text{malathion } (\mu\text{g/L}) = \frac{0.054 \times 0.067}{0.036} \times \frac{1}{0.4} = 0.25$$

Appendix 5. Example of a chromatogram of a pesticide standard.

File : C:\HPCHEM\1\DATA\EUW307.D
Operator :
Acquired : 29 Sep 95 7:54 pm using AcqMethod PESTSIM
Instrument : 5972 - In
Sample Name: SEPSTD 5
Misc Info :
Vial Number: 10



See over for key.

Key:

1. diuron
2. bensulfuron
3. molinate
4. 1-chlorotetradecane
5. trifluralin
6. simazine
7. atrazine
8. fenchlorfos
9. bromacil
10. thiobencarb
11. malathion
12. metolachlor
13. chlorpyrifos
14. α -endosulfan
15. β -endosulfan
16. endosulfan-SO₄
17. dicofol
18. lambda cyhalothrin
19. cypermethrins
20. deltamethrin

Appendix 6. Limit of Reporting (LOR) for pesticides analysed for in the 1995/96 Irrigation season.

Pesticide	LOR ($\mu\text{g/L}$)
atrazine	0.03
bensulfuron	0.10
bromacil	0.30
chlorpyrifos	0.03
cypermethrin	0.15
deltamethrin	0.15
dicofol	0.40
diuron	0.03
α-endosulfan	0.03
β-endosulfan	0.03
endosulfan -SO₄	0.03
lambda-cyhalothrin	0.03
malathion	0.03
metolachlor	0.03
molinate	0.03
simazine	0.03
thiobencarb	0.03
trifluralin	0.03