

STUDY TITLE PAGE

INSECTICIDES: MCPB
Analytical Method for the Determination of
Residues of MCPB and its metabolite MCPA in Peas - Interim Report

DATA REQUIREMENTS

FIFRA Subdivision O, Part 171-4 (c)
Magnitude of the Residues
Method of Analysis - Plants

AUTHOR

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REPORT COMPLETED ON

15th September 1995

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STATEMENT OF NO DATA CONFIDENTIALITY CLAIM

No claim of confidentiality is made for any information in this study on the basis of its falling within the scope of FIFRA Section 10(d) (1) (A), (B) or (C).

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Good Laboratory Practice, The United Kingdom Compliance Programme, 1989

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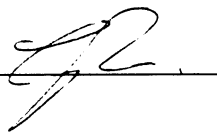
Sponsor :

pp B.M.Luscombe

Title:

Manager, Analytical Chemistry Department, Rhône-Poulenc Agriculture Limited.

Signature: _____



Date: 15/9/95

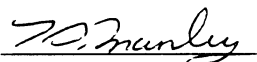
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Date: 15th September, 1995

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QUALITY ASSURANCE STATEMENT

The study described in this report was inspected on the following dates:-

13/10/94 Data Audit
03/03/95 Sample Processing

The findings of these inspections were reported formally to the Study Director and Line Management on:-

19/10/94
03/03/95

Routine and repetitive procedures relevant to this study have been selected at random and inspected periodically. The findings were reported promptly to the Study Director and laboratory management.

In an audit which was completed on 15th September 1995, this report was found to describe accurately the methods and SOPs used, and to reflect accurately the results recorded in the raw data.

Signed: 

Quality Assurance GLP

Dated: 15 September 1995

STUDY PERSONNEL AND DATES

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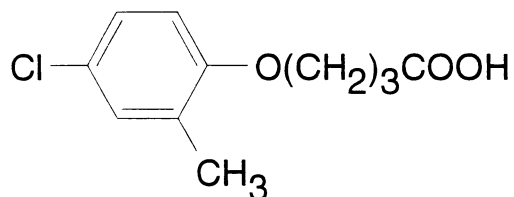
SUMMARY

An analytical method is described for the analysis of MCPB and its metabolite MCPA in peas. Free MCPB and MCPA are extracted by sequential maceration with acetone then aqueous acetone, followed by liquid-liquid partition into diethyl ether. Following clean-up by Gel Permeation Chromatography, the compounds are derivatised to give substances suitable for quantification by gas-chromatography with mass selective detection monitoring ions m/z 267 and 380.

Recovery of MCPB and MCPA was determined over the range 0.04 to 1 mg kg⁻¹ (ppm). Mean recoveries of 103 and 99 % for MCPB and MCPA respectively were obtained from six recoveries. The limit of detection is estimated at 0.02 mg kg⁻¹ for both MCPB and MCPA.

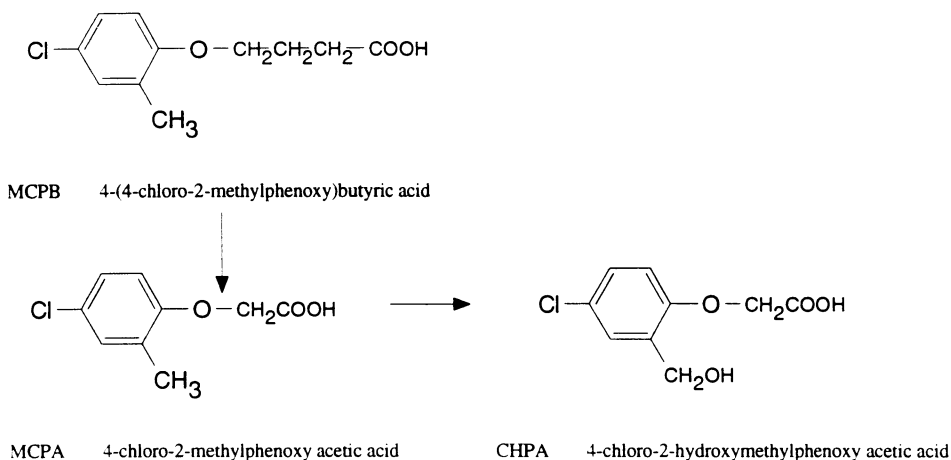
1. INTRODUCTION

The herbicide MCPB, 4-(4-chloro-2-methylphenoxy) butyric acid is used to control broadleaf weeds in peas.



4-(4-Chloro-2-methylphenoxy)butyric acid

Metabolism studies on peas and plants (1, 2) have shown that MCPB is metabolised by β -oxidation of the side chain to MCPA which undergoes further degradation by methylhydroxylation (2). In addition, conjugation of the hydroxymethyl occurs to form glycosides.



The analytical method developed and described in this report determines free MCPB and MCPA in Peas. This is an interim report giving details of the method for use in residue studies and only limited validation data on peas themselves are presented. The final report will include methodology for conjugated metabolites and extended validation data, including pods and vines. The properties of MCPB and MCPA are given below:

Table 1

Compound	mw	mp (°C)	Solubility in water	Log P	pKa	CAS RN
MCPB	228.7	100	44 mg l ⁻¹	4.26	4.84	94-81-5
MCPA	200.6	119	825 mg l ⁻¹		3.07	94-74-6
CHPA	216.6	148	2 g l ⁻¹			6386-63-6

2. PRINCIPLE

Free MCPB and MCPA are extracted by maceration sequentially with acetone then aqueous acetone, followed by liquid-liquid partition into diethyl ether. Following clean-up by Gel Permeation Chromatography, the compounds are derivatised to give substances suitable for quantification by gas-chromatography with mass selective detection.

3. REAGENTS AND DISPOSABLE ITEMS

MCPB, MCPA	Analytical reference standards
Hydrochloric acid	Laboratory reagent grade ^a
Potassium carbonate	Laboratory reagent grade ^a
Sodium hydrogen carbonate	Laboratory reagent grade ^a
Sodium sulphate (as the anhydrous salt)	Laboratory reagent grade ^a
Pentafluorobenzyl bromide (PFBB)	Laboratory reagent grade ^b
Acetone	Glass distilled grade ^c
Cyclohexane	Glass distilled grade ^c
Diethyl ether	Glass distilled grade ^c
Ethyl acetate	Glass distilled grade ^c

^a Rhône-Poulenc Laboratory Products, Manchester, UK.

^b Pierce Chemicals, Rockford, Illinois, USA.

^c Rathburn Chemicals Ltd., Walkerburn, UK.

3.1 Specialised Apparatus

Robot-Coupe vertical cutter/blender or equivalent apparatus.

Ultra-Turrax macerator (Type T45/N) or equivalent apparatus.

MSE centrifuge type GF-8 equivalent.

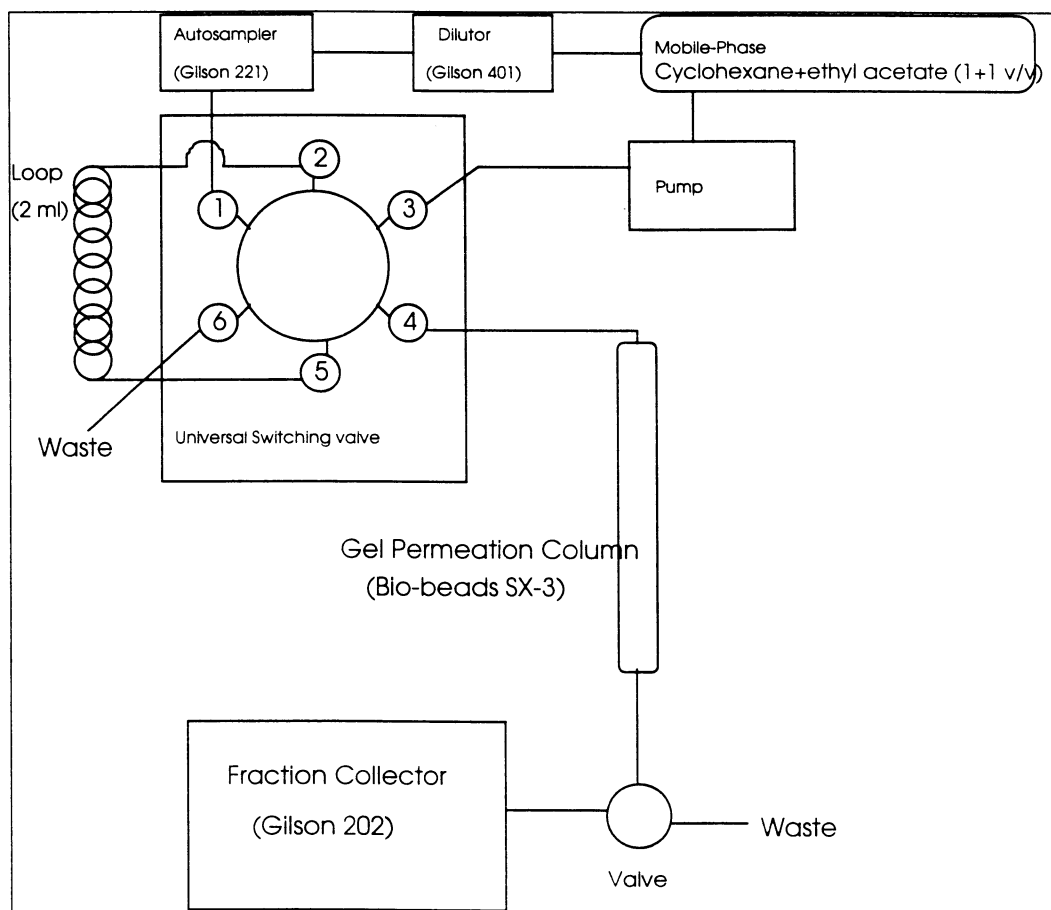
Rotary film evaporator.

TurboVap and TurboVap LV evaporators

Gel Permeation Chromatography (GPC) System

Packing:	Bio-beads SX-3.
Column:	10 mm x 50 cm.
Mobile phase:	Cyclohexane+ethyl acetate (1+1 v/v)
Flow rate:	0.5 ml min. ⁻¹ .
Injection Volume:	500 µl

Block Diagram of GPC System



4. PREPARATION OF STANDARD SOLUTIONS

Standard reference materials used to prepare the solutions should be of an analytical grade with a purity of at least 98 %.

4.1 Fortifying Solutions (MCPB and MCPA)

- 4.1.1** Accurately weigh into a volumetric flask (100 ml capacity) a portion (0.1g) of pure analytical standard. Dissolve in acetone and dilute to 100.0 ml at 20°C.
- 4.1.2** Serially dilute accurately pipetted portions of this solution with acetone at 20°C to give solutions containing 100 µg ml⁻¹, 50 µg ml⁻¹ and 10 µg ml⁻¹.

4.2 Standards for Gas Chromatography (MCPB and MCPA)

- 4.2.1** Derivatise a portion (5000 µg) of MCPB and MCPA using the procedures given in Section 6.5.1. Dissolve the derivative obtained in acetone and quantitatively transfer to a volumetric flask (20.0 ml) and dilute to volume at 20°C.
- 4.2.2** Serially dilute accurately pipetted portions of this master solution to give solutions containing 0.1, 0.2, 0.4, 0.8 and 1.0 µg ml⁻¹ MCPB or MCPA equivalent.

4.3 Storage and Stability

- 4.3.1** Store all solutions in a freezer when not in use.
- 4.3.2** Prepare fresh stock solutions of MCPB and MCPA and their respective serial dilutions each month. Do not use any solution more than 1 month after the preparation of the parent stock solution.
- 4.3.3** Derivatise fresh portions of MCPB and MCPA for each batch of samples analysed.

5. GAS CHROMATOGRAPHIC CONDITIONS

Instrument:	HP 5890 series II plus with EPC, HP 7673 auto sampler and HP 5972 mass selective detector
Column :	HP 5, 5% phenyl methyl silicone, 30 m x 0.25 mm, 0.25 µm film thickness
Temperatures :	Column :120 °C for 3 minutes, 15 °C/minute to 245 °C, hold 8 minutes, then 25 °C/minute to 280 °C, hold 20 minutes. Injector : 175 °C Detector Interface : 280 °C
Gas flows :	Column : He, pressure set at 15 psi. Vacuum compensation on.
Inlet :	EPC 15 psi for 0.75 min, 50 psi/min to 8 psi.
MSD :	Selective Ion Mode using Ion m/z 267 for MCPB Selective Ion Mode using Ion m/z 380 for MCPA Dwell 100 msec. Solvent delay 5 min.
Injection :	Auto, 1 µl, fast, splitless. Purge on 1.0 minute

Typical retention time for MCPB derivative is 15.0 minutes. For MCPA derivative typical retention time is 12.4 minutes

The MSD is tuned prior to a run using the maximum sensitivity autotune facility. Ions m/z 267 and m/z 380 are integrated and the areas measured.

5.1 Linearity of Detector Response

Determine the linearity of the detector response to solutions of the derivatives of MCPB and MCPA (as prepared in Section 4.2.1) under the gas-chromatographic conditions described (see Figure 2, Appendix II).

6. ANALYTICAL PROCEDURE

6.1 Preparation of Samples

Blend the samples in a Robot-Coupe cutter/blender or other suitable food processor using dri-ice to render them homogeneous. Take care not to allow the sample to thaw.

6.2 Extraction of Free Metabolites

- 6.2.1** Into a glass macerator jar, weigh a portion of homogeneous sample (50 g for fresh or frozen peas or 25 g for dried peas). For dried peas, add water (50 ml) and leave overnight prior to extraction. Add acetone (100 ml) and macerate for 1-2 minutes.
- 6.2.2** Centrifuge at 2000 rpm for 5 minutes. Decant supernatant into a round-bottomed flask (500 ml capacity).
- 6.2.3** Re-macerate sample with aqueous acetone (1+1 v/v, 100 ml), centrifuge and decant supernatant into round-bottomed flask.

6.3 Liquid-Liquid Partition

- 6.3.1** Evaporate off acetone using rotary film evaporation. Add concentrated hydrochloric acid (1 ml), filter through Whatman No.1 paper and extract with diethyl ether (2 x 100 ml).
- 6.3.2** Dry combined ether partitions with anhydrous sodium sulphate (40 g). Decant the ether into a TurboVap tube and evaporate to ~5 ml.
- 6.3.3** Quantitatively transfer the contents of the tube into a 16 x 100 mm test tube with acetone rinsings, and evaporate to dryness using a TurboVap LV evaporator. Continue with GPC clean-up.

6.4 Gel Permeation Chromatography Clean-up

- 6.4.1** Dissolve the residue in the GPC mobile phase (cyclohexane + ethyl acetate, 1+1 v/v, 2 ml), centrifuge and inject 500 µl onto the GPC system. Collect the fraction between 49 and 75 minutes in a 16 x 100 mm test tube.
- 6.4.2** Evaporate to dryness using a TurboVap LV evaporator.

6.5 Derivatisation

- 6.5.1** Dissolve the residue in acetone (1.0 ml). Add pentafluorobenzyl bromide (PFBB) (20 µl) and potassium carbonate (5 mg). Shake and allow to react for 60 minutes (with periodic shaking) at 70°C.
- 6.5.2** Transfer to a GC Vial prior to injecting onto the Gas Chromatograph.

7. QUANTIFICATION OF RESIDUES

The amounts of MCPB and MCPA present in the extracts are calculated by quantifying the corresponding GC/MSD peaks by comparison with standard solutions of appropriate concentration injected onto the GC, preferably adjacent to the samples. Whenever necessary dilute the extracts so that peak height obtained is within the linear working range of the detector (see Section 12). Inject each sample extract twice, bracketed between injection of standard solutions.

Compound	Quantifying Ion (m/z)
MCPB	267
MCPA	380

- 7.1 Measure the peak areas of MCPB and MCPA using the data capture system. The area of the peak should be used to calculate the results.
- 7.2 Calculate the result, C_1 , $\mu\text{g ml}^{-1}$ from the sample injection using the adjacent standard solutions or the average for the particular run if consistent.

$$C_1 = \frac{H_s \times C}{H_i} \quad \mu\text{g ml}^{-1} \text{ MCPB or MCPA}$$

Where:

- H_s = Measured area of sample peak
- H_i = Measured area of standard peak or mean
- C = Concentration of standard in $\mu\text{g ml}^{-1}$

The mean value for $\frac{C}{H_i}$ for a series of standards in a calibration can be used to calculate the results of samples if it is constant throughout the chromatographic run.

- 7.3 Calculate the levels of MCPB and MCPA in the samples taking into account any dilutions and the weight of plant material used. Report the results in terms of $\mu\text{g kg}^{-1}$ (ppb) MCPB and MCPA.

$$\frac{C_1 \times D \times V}{W} \quad \mu\text{g kg}^{-1} \text{ MCPB and MCPA}$$

Where:

- C_1 = Concentration of analyte in sample in $\mu\text{g ml}^{-1}$
- D = Dilution factor
- V = Volume of extract (ml) prior to dilution.
- W = Weight of sample (g)

8. METHOD VALIDATION

The analytical method has been validated by spiking control samples of peas with MCPB and MCPA at levels between 0.04 and 1 mg kg⁻¹. Six recovery determinations have been performed for both MCPA and MCPB. In addition, data from control samples analysed from pea controls have been reported.

9. LIMIT OF DETECTION

The limit of detection is defined as the mean value for the control plus three times the standard deviation. The absolute limit of detection using the GC conditions given in Section 5 is estimated as 0.05 µg ml⁻¹ for MCPA and 0.02 µg ml⁻¹ for MCPB. Analysis of a 50 g sample represents residues of 0.004 mg kg⁻¹ for MCPA and 0.002 mg kg⁻¹ for MCPB. Residues in control samples (Section 11) ranged from 0.001 to 0.042 mg kg⁻¹, but were generally below 0.02 mg kg⁻¹. The mean of 0.007 mg kg⁻¹ and standard deviation of 0.006 mg kg⁻¹ has been used to calculate the limit of detection of 0.02 mg kg⁻¹. Thus this has been estimated as the method limit of detection for both analytes.

10. LIMIT OF QUANTIFICATION

The limit of quantification is defined as the mean value for the control plus ten times the standard deviation. The calculated level (Section 9) is thus 0.06 mg kg⁻¹. However, recoveries have been satisfactorily validated at 0.04 mg kg⁻¹ and is thus estimated as the limit of quantification.

11. LEVELS FOUND IN CONTROL SAMPLES

During development of this analytical method, control samples from a variety of sources were found to contain significant apparent residues at the same retention time as MCPA. In order to validate the method control samples known not to have been treated with MCPB or MCPA were obtained. Apparent residue levels of MCPB or MCPA above the level of 0.001 mg kg⁻¹ have been reported in order to accurately calculate the limit of detection. Apparent residues above the limit of detection (0.02 mg kg⁻¹) should be expressed in terms of mg kg⁻¹. Residue levels in control samples ranged from 0.001 to 0.042, but were generally below 0.02 mg kg⁻¹. Summary results of analyses of control samples are given in Table 2. Specimen chromatograms are shown in Appendix III.

Table 2 Analysis of Control Pea Samples

Sample Reference	Apparent residue (mg kg ⁻¹)	
	Apparent MCPB residue (mg kg ⁻¹)	Apparent MCPA residue (mg kg ⁻¹)*
T95/242	0.017, 0.010	0.002, 0.002, 0.001
T95/175	0.008, 0.042*	0.005, 0.014*
Mean	0.007 (0.011)*	
Std.Dev.	0.006 (0.013)*	

* Control sample probably contaminated during analysis and hence not used to calculate limit of detection.

12. LINEARITY OF DETECTOR RESPONSE

Determine the linear range of the detector response to MCPB or MCPA by injections of known amounts of compound. Use the detector within the linear range thus determined, diluting any sample solutions if necessary. Mass selective detectors have a good linear working range usually over three orders of magnitude or more. A specimen linearity plot over the range 0.12 to 2.5 µg ml⁻¹ is given in Figure 2.

13. DETERMINATION OF RECOVERIES

Fortify portions of control sample at levels of between 0.04 and 1 mg kg⁻¹ preferably using 1.0 ml of an appropriate standard solution.

Appropriate level (µg ml⁻¹) = weight of control sample (g) x spiking level (µg g⁻¹)

Recovery determinations should be carried out at levels which bracket any levels found in the samples. The fortified level should not be less than three times the apparent level found in the control samples.

13.1 Spiking the Samples

13.1.1 Weigh out a portion (50 g) of control sample. Add, accurately, by pipette, a portion (1.0 ml) of standard fortifying solution (see Section 4.1.2) of each component, of appropriate concentration so as to give the desired residue level.

13.1.2 Add acetone (100 ml) and complete the analytical method.

Recoveries were determined by adding known amounts of MCPB or MCPA to portions of control samples and analysing by the method detailed. The results are summarised in Table 3. The overall mean recoveries from 6 individual recovery analyses were 103 and 99 % for MCPB and MCPA respectively.

Specimen chromatograms are given in Appendix III.

Table 3 Recovery of MCPB and MCPA

Level (mg kg ⁻¹)	MCPB Recovery (%)	MCPA Recovery (%)
0.04	96, 76	104, 84
0.16	152, 128	117, 110
1.0	84, 82	91, 88
Mean	103.0	98.9
Std.dev.	30	13.2
Coeff.Var.	30	13.4
Number	6	6

14. REFERENCES

1. Goodyear, A., 1993. (14C)-MCPB: METABOLISM IN PEAS, Hazleton UK report No. 68/137-1015.
2. Cole, D.J., and Loughman, B.C., 1983. The metabolic fate of (4-chloro-2-methylphenoxy)acetic acid in higher plants. *Journal of Experimental Botany*, 34, 1299-1310.
3. *Statistics for Analytical Chemistry*, 2nd Edition, J.C.Miller, J.N.Miller, Published by Ellis Horwood Limited, 1988.

APPENDIX I

Figure 1

Summary of Analytical Method for Analysis of MCPB and MCPA

50 g Fresh/Frozen, or 25 g Dried Pea material

Add 100 ml acetone. Macerate 1-2 min. Centrifuge for 5 min. 2000 rpm

Decant acetone to a round-bottomed flask

Re-extract with aqueous acetone (1+1 v/v, 100 ml). Centrifuge for 5 min. 2000 rpm

Decant aqueous acetone to round-bottomed flask

Rotary evaporate off acetone

Add conc. hydrochloric acid (1 ml)

Extract with diethyl ether (2 x 100 ml)

Dry ether over anhydrous sulphate (40 g)

Evaporate off ether using TurboVap

Dissolve in cyclohexane + ethyl acetate (1+1 v/v, 2 ml)

Centrifuge prior to GPC clean-up

Collect fraction between 49 and 75 minutes

Evaporate off solvent using TurboVap

Dissolve residue in acetone (1.0 ml)

Add PFBB (20 µl) and potassium carbonate (5 mg)

Shake and leave 60 minutes at 70°C

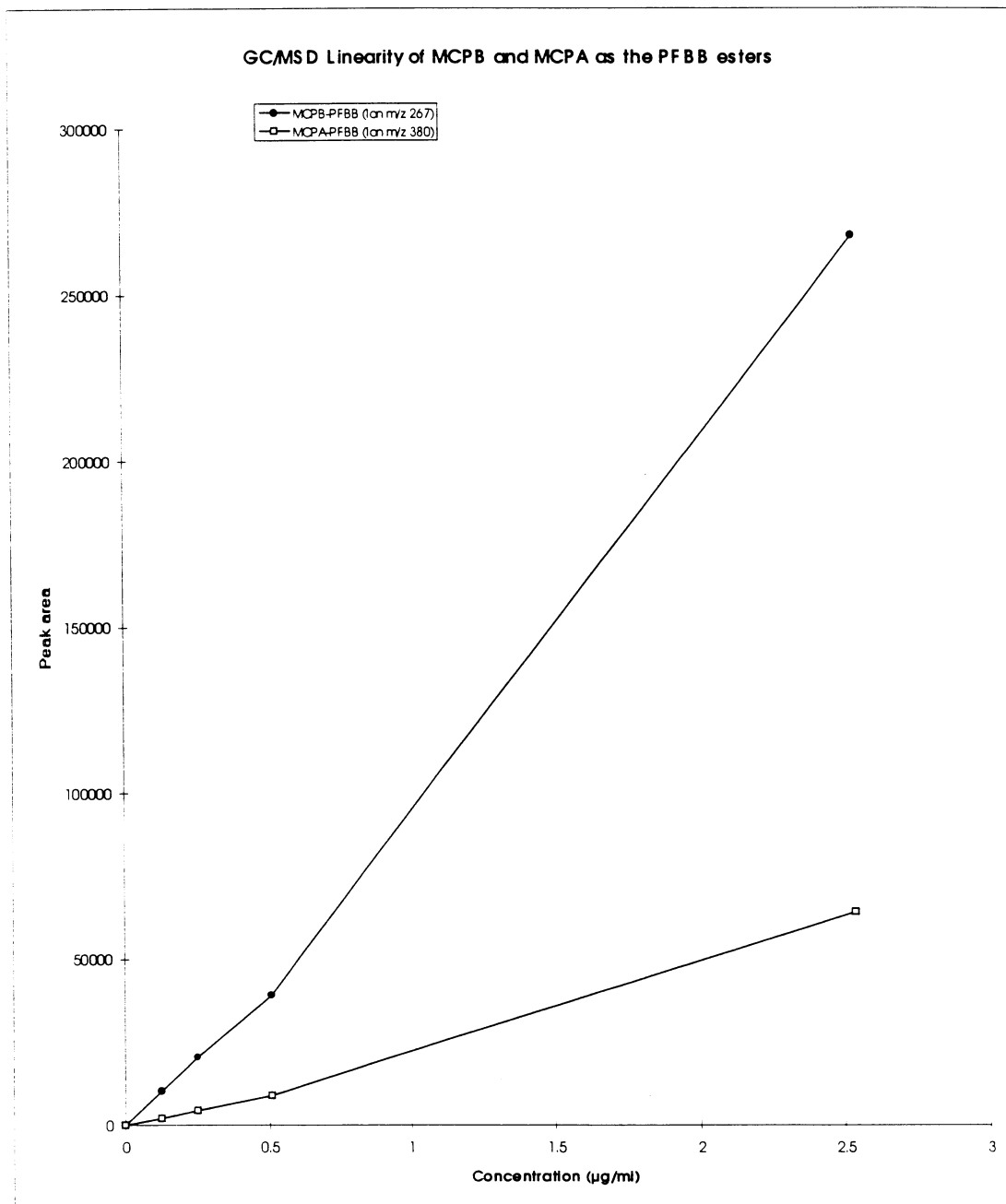
Transfer solvent to GC Vial

GC using MSD (Ions m/z 267 and 380)

APPENDIX II

Figure 2

Linearity of Detector Response to derivatives of MCPB and MCPA



APPENDIX III

TYPICAL CHROMATOGRAMS

Typical chromatograms have been included as examples of the chromatography in this method report.

Table 4

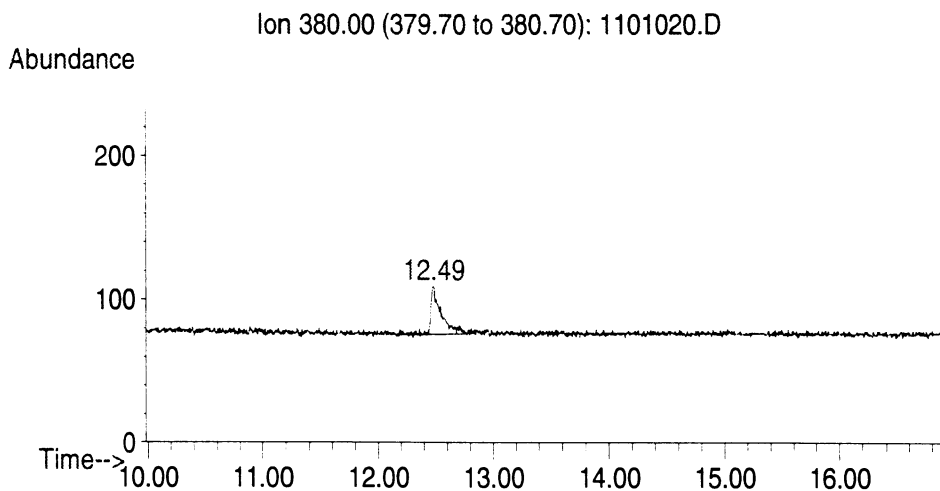
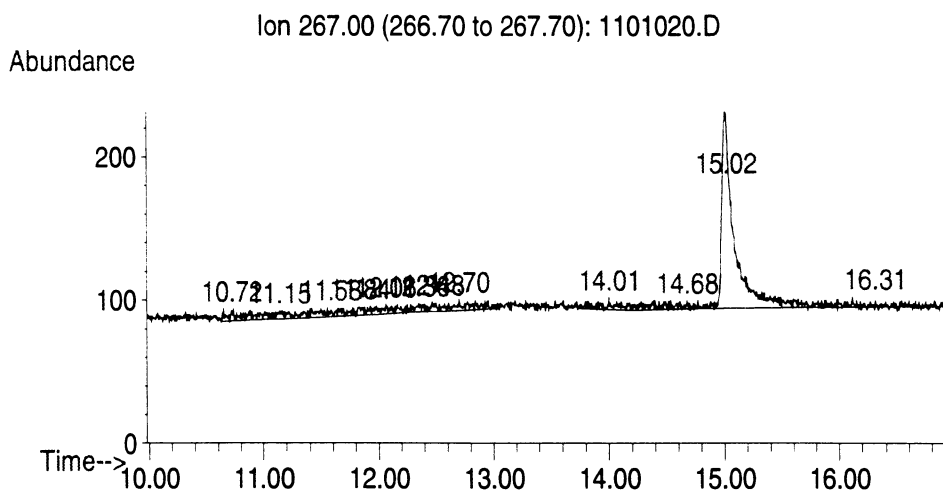
Figure	Sample type	Details
3	Standard	~0.125 $\mu\text{g ml}^{-1}$ MCPB and MCPA
4	Standard	~0.50 $\mu\text{g ml}^{-1}$ MCPB and MCPA
5	Control Peas	0.010 mg kg^{-1} MCPB and 0.001 mg kg^{-1} MCPA
6	Recovery Peas	0.04 mg kg^{-1} MCPB (96 %), MCPA (104 %)
7	Recovery Peas	0.16 mg kg^{-1} MCPB (152 %), MCPA (117 %)
8	Recovery Peas	1.00 mg kg^{-1} MCPB (84 %), MCPA (91 %)

APPENDIX III

Figure 3

Standard ~0.125 µg ml⁻¹ MCPB and MCPA

File : C:\HPCHEM\1\DATA\1995\AUGUST\110895\1101020.D
Operator : A.M.Oddy
Acquired : 12 Aug 95 5:30 am using AcqMethod P92191A
Sample Name: P92/191/7/8/95/4 std
Misc Info : Project Number P92/191
Vial Number: 11
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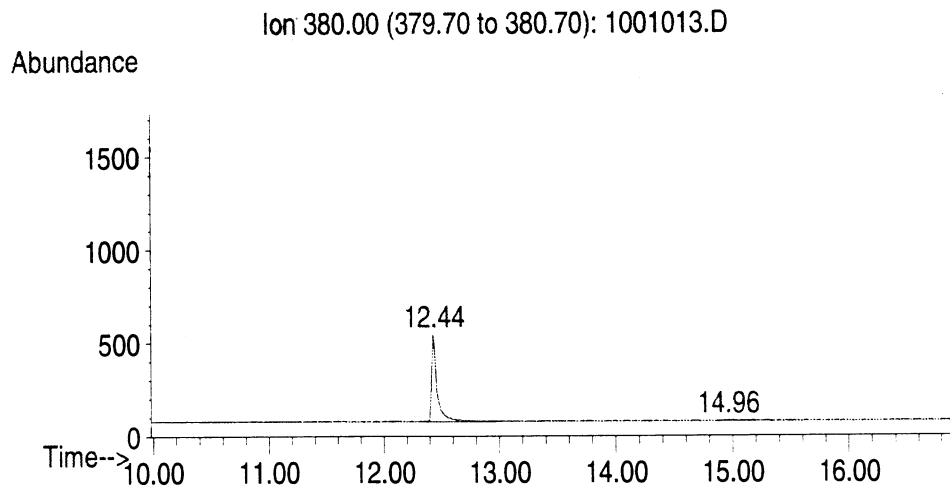
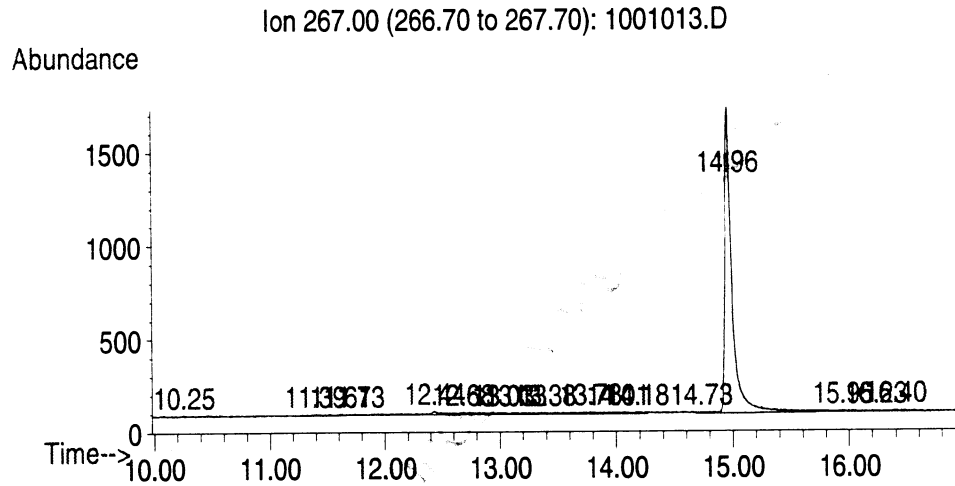


APPENDIX III

Figure 4

Standard $\sim 0.50 \mu\text{g ml}^{-1}$ MCPB and MCPA

File : C:\HPCHEM\1\DATA\1995\AUGUST\110895\1001013.D
Operator : A.M.Oddy
Acquired : 12 Aug 95 12:06 am using AcqMethod P92191A
Sample Name: P92/191/7/8/95/3 std
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Vial Number: 10
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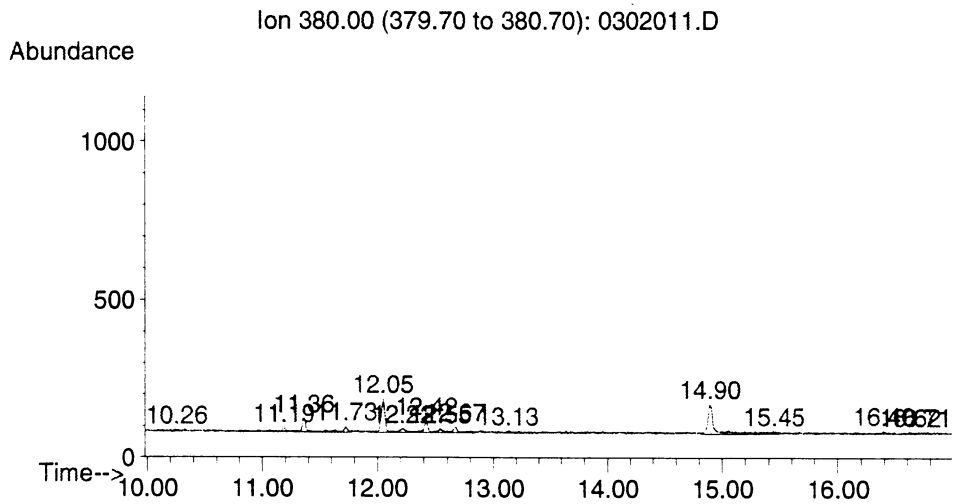
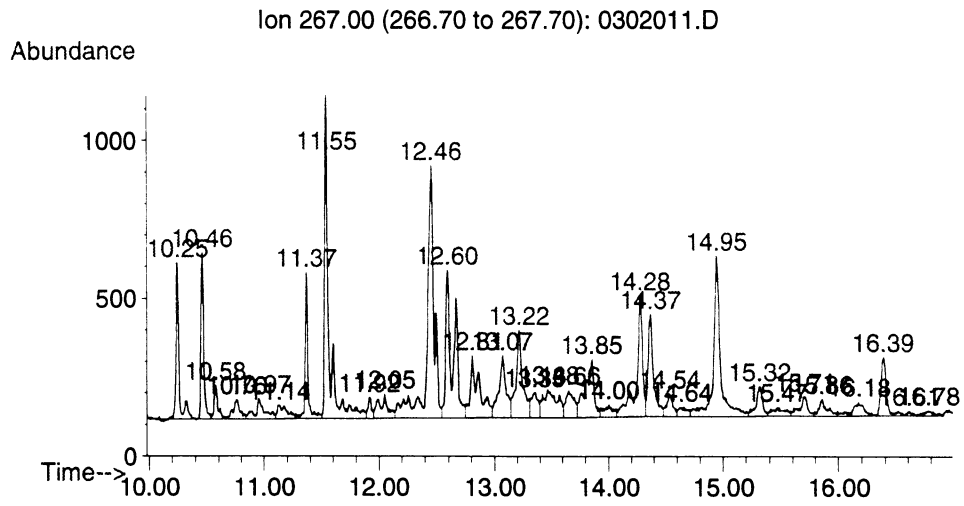


APPENDIX III

Figure 5

Control Peas 0.010 mg kg⁻¹ MCPB and 0.001 mg kg⁻¹ MCPA

File : C:\HPCHEM\1\DATA\1995\AUGUST\090895\0302011.D
Operator : A.M.Oddy
Acquired : 9 Aug 95 9:41 pm using AcqMethod P92191A
Sample Name: t95/242/8/4/2 CONTROL
Misc Info : Project Number P92/191
Vial Number: 3
CurrentMeth: C:\HPCHEM\1\METHODS\HP5\P92191A.M



APPENDIX III

Figure 6

Recovery Peas 0.04 mg kg⁻¹ MCPB (96 %), MCPA (104 %)

File : C:\HPCHEM\1\DATA\1995\AUGUST\090895\0601019.D

Operator : A.M.Oddy

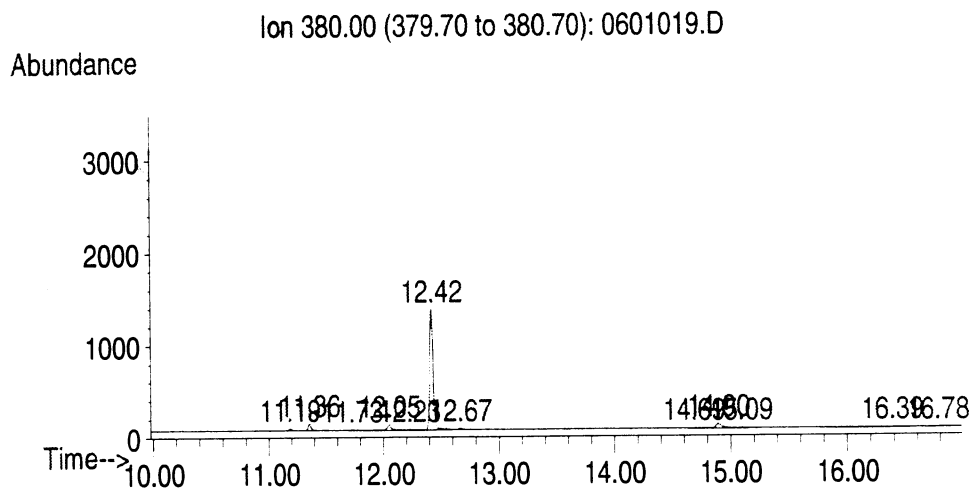
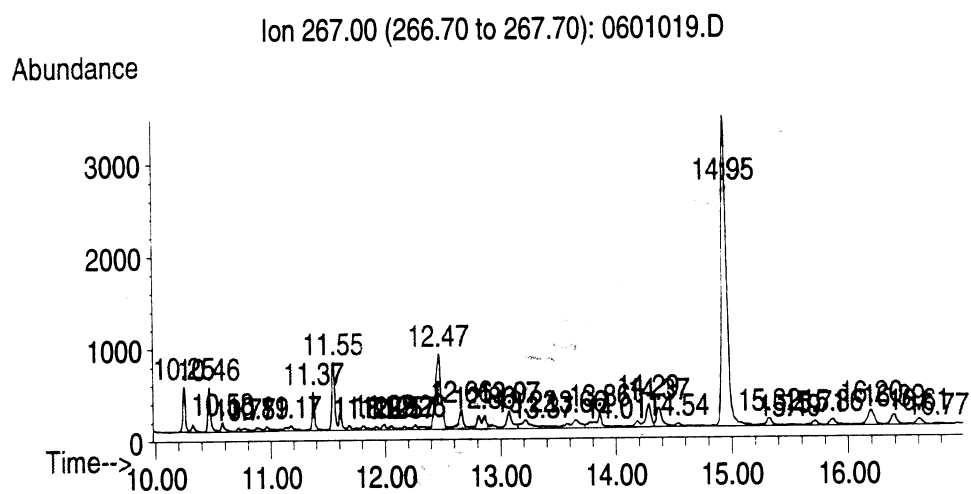
Acquired : 10 Aug 95 3:51 am using AcqMethod P92191A

Sample Name: t95/242/8/4/4 0.04MG/KG

Misc Info : Project Number P92/191

Vial Number: 6

CurrentMeth: C:\HPCHEM\1\METHODS\HP5\P92191A.M

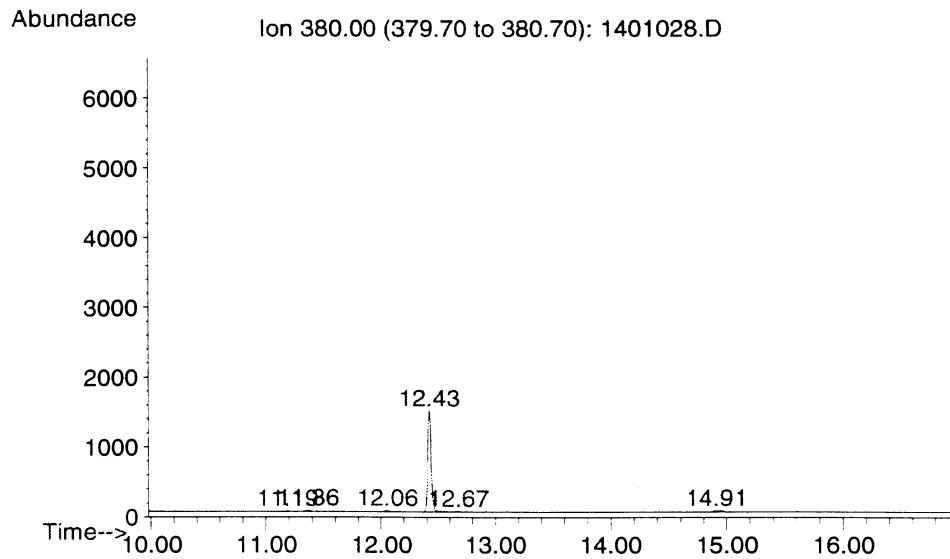
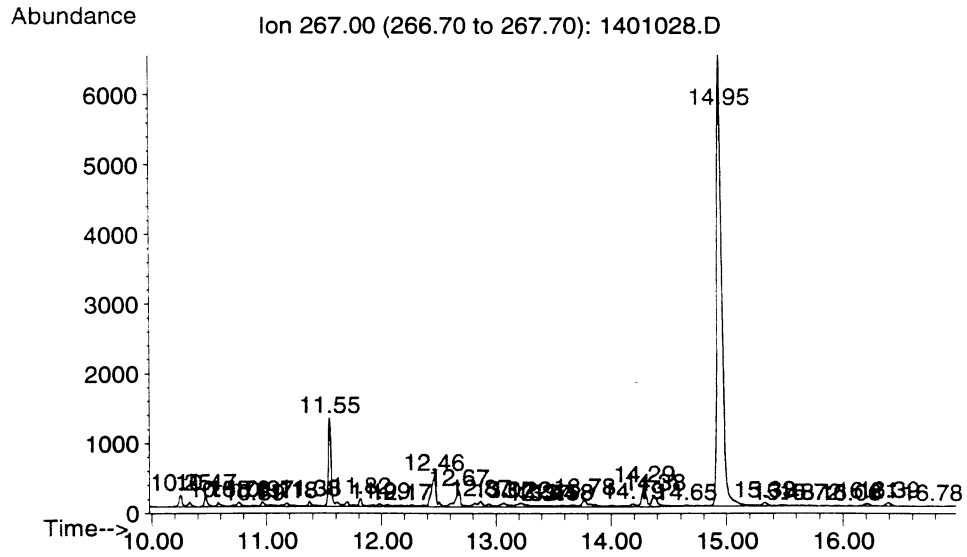


APPENDIX III

Figure 7

Recovery Peas 0.16 mg kg⁻¹ MCPB (152 %), MCPA (117 %)

File : C:\HPCHEM\1\DATA\1995\AUGUST\110895\1401028.D
Operator : A.M.Oddy
Acquired : 12 Aug 95 11:40 am using AcqMethod P92191A
Sample Name: t95/242/8/10/1 0.16 MG/KG
Misc Info : Project Number P92/191
Vial Number: 14
CurrentMeth: C:\HPCHEM\1\METHODS\HP5\P92191A.M

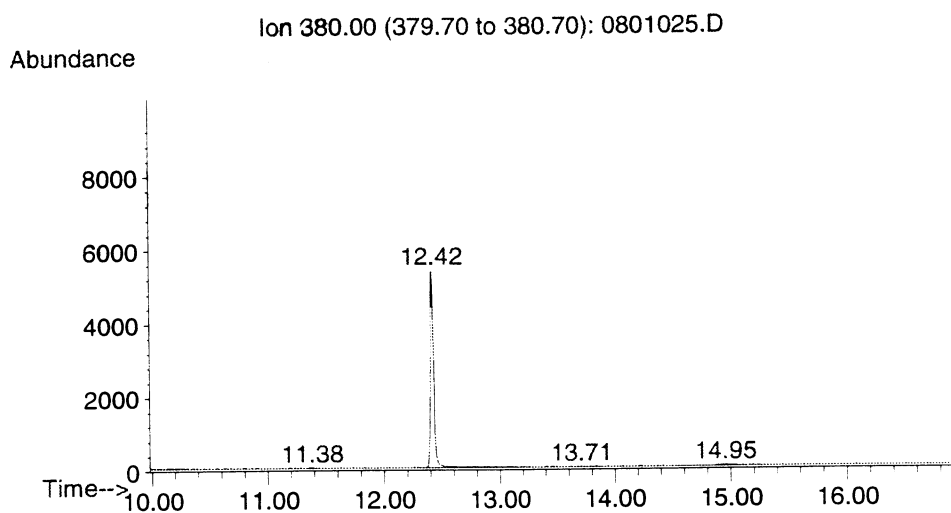
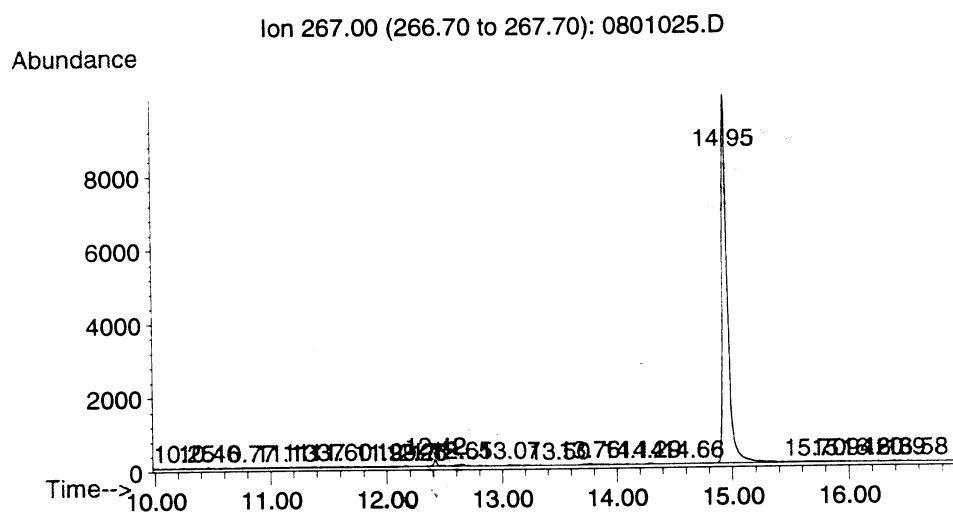


APPENDIX III

Figure 8

Recovery Peas 1.00 mg kg⁻¹ MCPB (84 %), MCPA (91 %)

File : C:\HPCHEM\1\DATA\1995\AUGUST\090895\0801025.D
Operator : A.M.Oddy
Acquired : 10 Aug 95 8:29 am using AcqMethod P92191A
Sample Name: t95/175/8/7/4 1-10D 1.0 MG/KG
Misc Info : Project Number P92/191
Vial Number: 8
CurrentMeth: C:\HPCHEM\1\METHODS\HP5\P92191A.M



APPENDIX IV

CONTROL OF SUBSTANCES HAZARDOUS TO HEALTH (COSHH) ASSESSMENT

Table 5

Materials Used	Hazard
MCPB and MCPA	Toxic by inhalation, and if swallowed.
Acetone	Highly flammable. Harmful by inhalation. Avoid contact with eyes.
Cyclohexane	Highly flammable. Harmful by inhalation. Degreases skin. Avoid contact with skin and eyes
Diethyl ether	Extremely flammable. Avoid sources of ignition especially electrical equipment. Harmful by inhalation.
Ethyl acetate	Highly flammable. Harmful by inhalation. Avoid contact with eyes.
Pentafluorobenzyl bromide	Lachromator, hence avoid contact with eyes. Very toxic.
Hydrochloric acid	Causes severe burns. Irriating to eyes and skin.
Potassium carbonate	Harmful by ingestion
Sodium sulphate	Harmful by ingestion
Sodium hydrogen carbonate	Harmful by ingestion

AUTHENTICATION

Study Number: P 92/191

I hereby declare that this study was performed under my direction and that this report represents a true and accurate record of the results obtained.

Study Director: J.D. Manley
J.D. Manley
Leading Analyst
Analytical Chemistry Department
Rhône-Poulenc Agriculture Ltd.

Date: 15th September, 1995

Approval: G. Buddle
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Date: 15/9/95

Approval: B.M. Luscombe
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Date: 15/9/95

All raw data, documentation, chromatograms, records, related correspondence, protocol and amendments, and the final report will be retained in the Rhône-Poulenc Agriculture Ltd. Archives.