Cover Sheet for

ENVIRONMENTAL CHEMISTRY METHOD

Pestcide Name: Metolachlor

MRID #: 413098-05

Matrix: Soil

Analysis: GC/MS

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413098-05 GC/MS

STUDY TITLE

Summary of Gas Chromatography
Mass Spectrometry Confirmations
Of Metolachlor Field Dissipation Study,
California- Site C
Agrisearch Study No. 1265C

STUDY REQUIREMENT

Field Dissipation Study For Metolachlor

AUTHOR

James E. Whetzel

ANALYTICAL PHASE COMPLETED

November, 1989

ANALYTICAL REPORT ISSUED

November, 1989

CONDUCTED BY

EMS Laboratories, Inc.
4132 Pompano Rd.
Charlotte, N. C. 28216

EMS PROTOCOL

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EMS LABORATORIES, INC. 4132 POMPANO ROAD CHARLOTTE, NC 28216/(704) 393-1853

GOOD LABORATORY PRACTICE STATEMENT

To the best of my knowledge, the analytical data reported within was generated by EMS Laboratories, Inc. in compliance with generally accepted EPA Good Laboratory Practice Standards, 40 CFR Part 160, July 1, 1988.

Study Director: _____ Date: 11/3/89
James E. Whetzel
EMS Laboratories, Inc.

Study Initiation Date: October 1989
Study Completion Date: November 1989

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QUALITY ASSURANCE STATEMENT

The analytical portion of this study was inspected by the EMS Quality Assurance Unit for compliance with GLP standards and EMS Standard Operating Procedures as follows:

Inspection Dates	Dates Submitted To Study Director And To The Management
6-19-89	10-18-89
11-6-89	11-10-89

Helmuth Janssen
Helmuth Janssen
Quality Assurance Officer

11-16-89
Date

EMS

STUDY PERSONNEL

James Whetzel	-	Study Director
Steven H. Guptill	-	Senior Scientist
Helmuth M.B. Janssen	-	Quality Assurance Officer
Lynn Butler	-	Document Control Officer/ Sample Custodian
Michele E. Sakwa	-	Laboratory Director

EMS

I. Introduction

The purpose of this report is to summarize the results of gas chromatography-mass spectrometry (GC/MS) confirmation of selected soil samples from metolachlor field dissipation study, California-Site C. Samples for GC/MS confirmation were provided by Agrisearch, Inc., Frederick, Maryland after gas chromatography analyses using a flame ionization detector (GC/FID). Representative sample extracts showing positive detections of metolachlor or any of the metabolites of metolachlor: CGA-50720, CGA-40919, CGA-40172 or CGA-51202, were analyzed by GC/MS using single ion monitoring (SIM) approach. The screening level for GC/MS confirmation was 0.1ng/ul. This report describes the procedure used and summary of data for GC/MS confirmation of samples requested by Ciba-Geigy Corporation, Greensboro, North Carolina. Questions regarding the GC/MS confirmations mentioned in this report can be directed to James E. Whetzel, EMS Laboratories, phone number 704/393-1853.

II. Experimental

A). Materials

1) Autosampler vials, 100 ul
2) Hexane (pesticide grade)
3) Gas Chromatographic Standards which were prepared from an Agrisearch, Inc. 25 ug/ml stock solution of metolachlor, metabolites: CGA-40172, CGA-40919, and methylated metabolites: CGA-51202, CGA-50720.

B). Shipping

1) All extracts were shipped (in dry ice) over night in coolers from Agrisearch, Inc. to EMS Laboratories.
2) Extracts were accompanied by a sample transmittal form (chain-of-custody) that had been filled out by the person relinquishing the extracts. A signed copy of this form was returned to Agrisearch, Inc.
3) Extracts were logged into the LIMS (Laboratory Information Management System) and given unique identification numbers. Extracts were stored under refrigeration until removal for analysis. All retainer extracts were kept under refrigeration for 90 days after issuance of final report.

C). Analytical Method

Analyses were performed using a gas chromatograph/mass spectrometer (GC/MS) in single ion monitoring (SIM) mode to specifically detect and confirm the presence of metolachlor and metabolites: CGA-50720, CGA-40172, CGA-40919 or CGA-51202.

Ions used for SIM analysis were chosen from mass spectra produced by scanning from 35 to 500 AMU each compound of interest. For each compound, the five most abundant ions greater than 100 AMU were chosen as the group to monitor. The most abundant ion of the group was chosen to be the quantitation ion. (Ions less than 100 AMU were disqualified to minimize interferences). Due to the close elution pattern and low sensitivity of CGA-40172 and CGA-51202, one group of four ions was selected to monitor both metabolites.

1) Gas Chromatographic Conditions

Instrument: Hewlett Packard 5890 Gas Chromatograph
Column: Capillary J & W DB-5, 0.25mm ID, 30m length, 0.25um film
Injector Temperature: 285°C
Oven Temperature: 180°C
Analysis Time: 19 minutes
Carrier Flow: Helium at 1-2ml/min. at 10 psi

2) Detector Conditions

Detector: Hewlett Packard 5970 Mass Selective Detector in SIM mode.
Detector Temp: 285°C
Multiplier Voltage: 2200 volts
Number of groups: 4

Group 1 start/stop scan: 5.00/7.50

	M/Z	Dwell (MSEC)
Quant ion CGA-50720	134.1	100
	146.0	100
	162.1	100
	163.1	100
	221.1	100

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Group 2 start/stop scan:		7.50/10.00
	M/Z	Dwell (MSEC)
	146.0	100
	160.1	100
Quant ion CGA-40919	161.1	100
	188.1	100
	233.1	100

Group 3 start/stop scan:		10.00/13.00
	M/Z	Dwell (MSEC)
	146.1	125
Quant ion CGA-40172	162.1	125
	220.1	125
Quant ion CGA-51202	248.1	125

Group 4 start/stop scan:		13.00/19.00
	M/Z	Dwell (MSEC)
	146.1	100
Quant ion Metachlor	162.1	100
	211.1	100
	238.1	100
	240.1	100

3. Instrument Calibration
Prior to the analysis of extracts, known quantities of metolachlor and the metabolites of interest were injected to construct an initial calibration curve for each compound. Calibration curves for concentrations between 0.10ng and 2.00ng were prepared by plotting the concentration of the standard versus the peak area of quantitation ion. Second degree equations of the curves were determined and used in all low level calculations. Standards containing metolachlor and each of the metabolites of interest were analyzed throughout the run to check the calibration.

4. Detection Limits
The method detection limit (MDL) was determined by the method listed in 40 CFR Part 136, App. B. The detection limit reported for the analysis is 0.1ng/ul.

5. Calculation Method
The ng/ul values found for each extract were determined by the external standard method. The area of the quantitation ion of each compound found was substituted into the appropriate second degree equation as determined by the initial calibration, and ng/ul value was generated.

D. Quality Control and Archiving of Data

1) All analyses were performed in compliance with Good Laboratory Practices (40CFR, Part 160). All raw data was audited and approved by the Quality Assurance Officer.

2) All original raw data has been stored in the archives at EMS Laboratories, 4132 Pompano Rd., Charlotte, NC 28216. Copies of raw data have been provided to Ciba-Geigy Corporation.

III. Results and Discussion

A summary of the analytical results of the GC/MS confirmation and blind sample analysis is provided in Table 1 and 2 respectively. These tables provide information regarding sample code by Agrisearch and EMS Laboratories, Agrisearch project number, dates samples were received and analyzed and GC/MS results in units of ng/ul. The individual reports for the analyses of samples were provided to Ciba-Geigy Corporation.

The data in Table 1 and 2 show the use of the term "BDL". This expression means that the quantity is less than the detection limit.

The following Figures have been included:

Figures 1-5:	Typical calibration curves used for quantitation.
Figures 6:	Typical standard chromatogram.
Figures 7-11:	Reference spectra for Metolachlor and the metabolites of interest.
Figure 12:	Example chromatogram of sample with confirmed presence of CGA-51202.
Figure 13:	Example chromatogram of sample with all compounds of interest below the detection limit.

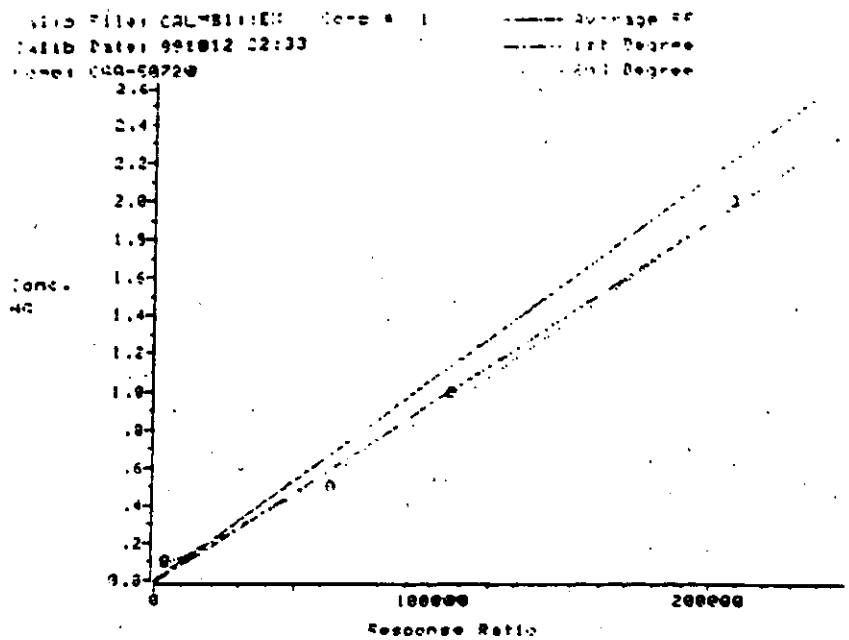
Figure 14: Example of sample spectrum with confirmed CGA-51202.
Figure 15: Ion chromatograms of sample with confirmed presence of CGA-51202.
Figure 16: Ion chromatograms of sample showing absence of CGA-40172.

Positive confirmation was noted only if the following criteria was met:

1) Retention time of sample peak had to be comparable to the reference standard.
2) All ions of reference standard had to be present in the sample spectrum.
3) Ion chromatograms of each ion of interest had to be comparable to those of the reference standard.
4) After appropriate background subtraction, intensity ratios had to be reasonably comparable to those of the reference standard.

00002

FIGURE 1



Compound # 1 Calib File: CALMB1::EX

Compound: CGA-50720
Istd:

File:	>84506	>84505	>84504	>84503
Conc:	.10	.50	1.00	2.00
Rf:	38440.	125694	106463	193782

Average of 4 Rfs: 93595 (40.65 % Rsd) Rw: .0000000 Ry: .0000000
1st Degree Equation: y = -.005814 + .0000095(x)
1st Degree Corr Coef: .9964559
2nd Degree Equation: y = .0538667 + .0000074(x) + .0000000(x^2)
2nd Degree Corr Coef: .9985181

In the above equations:

$$y = \frac{\text{Conc Std}}{\text{Conc Istd}} \qquad x = \frac{\text{Area Std}}{\text{Area Istd}}$$

Istd Conc for all calibration points is: 1.00

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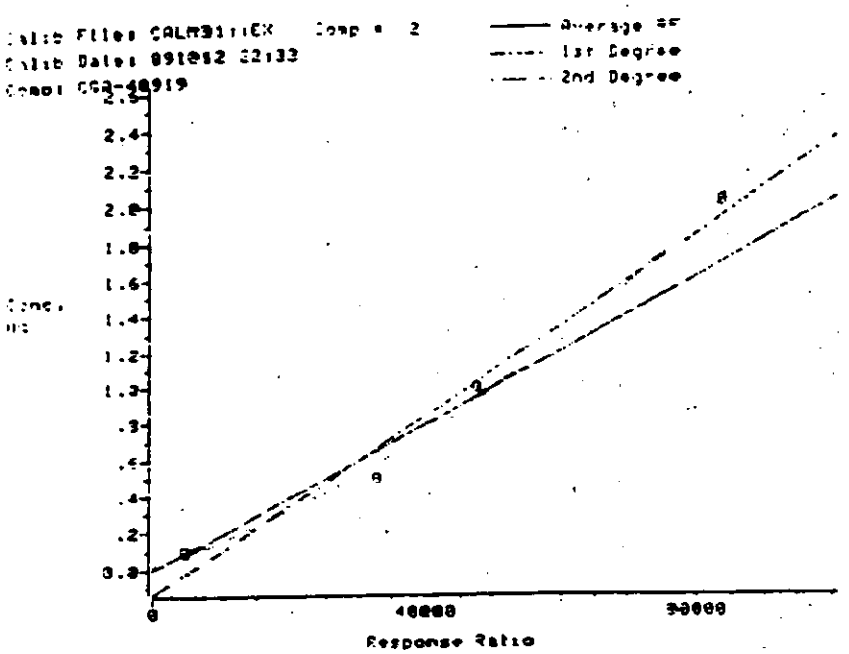
FIGURE 2



00003

Compound # 2 Calib File: CALMBI::EX

Compound: CGA-40919
Istd:

Rate: .84506 .84505 .84504 .84503
Conc: .10 .50 1.00 2.00
RF: 45600. 46210. 47450. 51976.

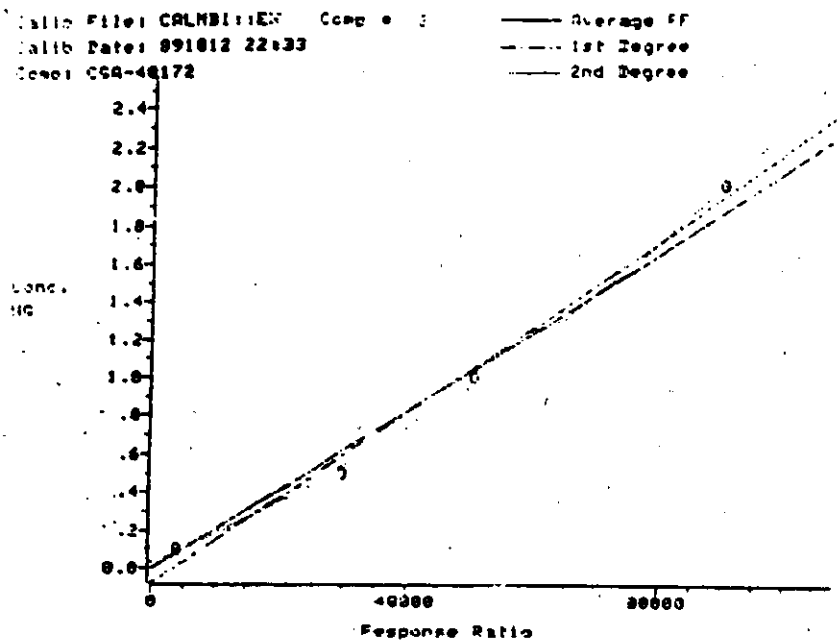
Average of 4 RFs: 50059. (20.68 % Std) R=: 0000000 Sy=: 0000000
1st Degree Equation: y = -.133131 + .0000045(x)
1st Degree Corr Coef: .9878231
2nd Degree Equation: y = .0196653 + .0000171(x) + 0000000(x^2)
2nd Degree Corr Coef: .9968977

In the above equations:

$$y = \frac{\text{Conc Std}}{\text{Conc Istd}} \qquad x = \frac{\text{Area Std}}{\text{Area Istd}}$$

Istd Conc for all calibration points is: 1.00

FIGURE 3



00004

Compound # 3 Calib File: CALMBI::EX

Compound: CGA-40172
Istd:

File: >84506 >84505 >84504 >84503
Conc: .10 .50 1.00 2.00
RF: 38140. 59622. 50239. 45110.

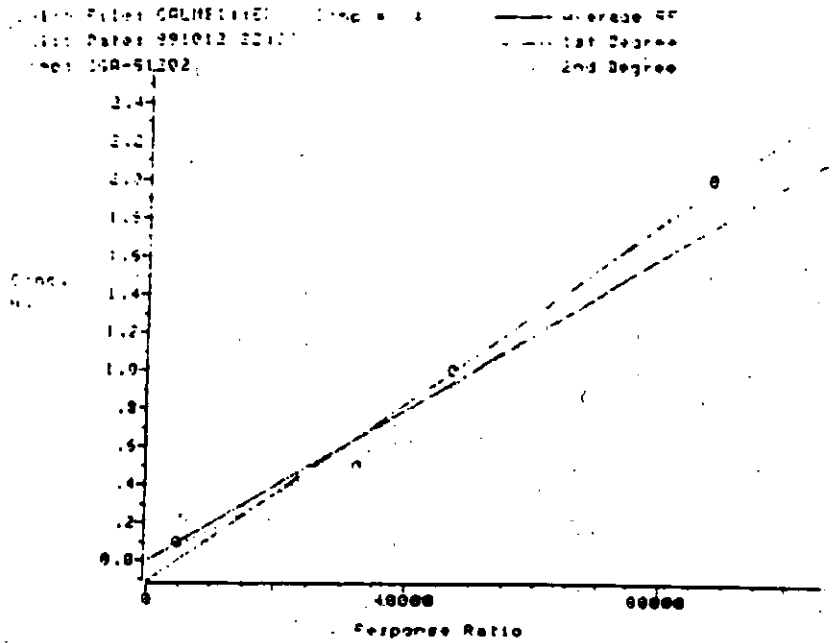
Average of 4 Rfs: 48278. (18.73 % Rsd) Rx: .000000 Ry: .000000
1st Degree Equation: y = -.073799 + .0000224(x)
1st Degree Corr Coef: .9945191
2nd Degree Equation: y = .0316397 + .0000146(x) + .000000[illegible](x^2)
2nd Degree Corr Coef: .9993496

In the above equations:

$$y = \frac{\text{Conc Std}}{\text{Conc Istd}} \qquad x = \frac{\text{Area Std}}{\text{Area Istd}}$$

Istd Conc for all calibration points is: 1.00

FIGURE 4



00005

Compound # 4 Calib File: CALMB1**EX

Compound: CGA-51202
Table:

File:	84506	84505	84504	84503
Conc:	.10	.50	1.00	2.00
Rf:	46170.	64560.	46747.	43864.

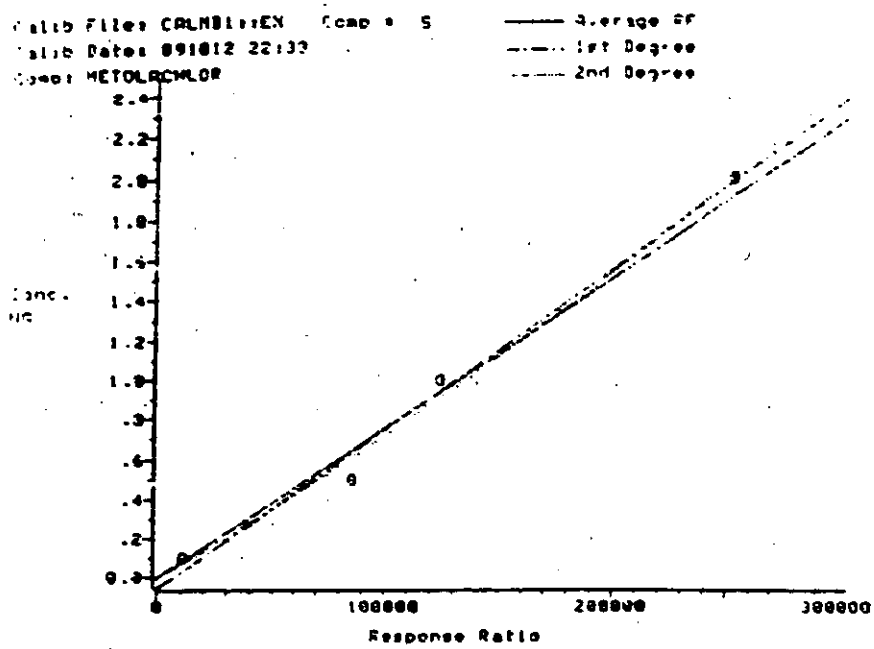
Average of 4 Rfs: 50335. (19.00 % Rsd) Rx= .0000000 Ru= .0000000
1st Degree Equation: y = -.105702 + .0000275(x)
1st Degree Corr Coef: .7913462
2nd Degree Equation: y = .0042794 + .0000156(x) + .0000000(x^2)
2nd Degree Corr Coef: .9958446

In the above equations:

$$y = \frac{\text{Conc Std}}{\text{Conc Istd}} \qquad x = \frac{\text{Area Std}}{\text{Area Istd}}$$

Istd Conc for all calibration points is: 1.00

FIGURE 5



00006

Compound # 5 Calib File: CALMB1::EX

Compound: METOLACHLOR
Istd:

File:	>84506	>84505	84504	>84503
Conc:	.10	.50	1.00	2.00
Rf:	107800	167832	123802	126467

Average of 4 Rfs: 132475 (19.59 % Rsd) Rx: .0000000 Ry: .0000000
1st Degree Equation: y = -.051207 + .0000081(x)
1st Degree Corr Coef: .9938732
2nd Degree Equation: y = -.000501 + .0000068(x) + .0000000(x^2)
2nd Degree Corr Coef: .9948670

In the above equations:

$$y = \frac{\text{Conc Std}}{\text{Conc Istd}} \qquad x = \frac{\text{Area Std}}{\text{Area Istd}}$$

Istd Conc for all calibration points is: 1.00

FIGURE 6

Typical chromatogram of standard solution of all five compounds at a concentration of 2.0ng/ul

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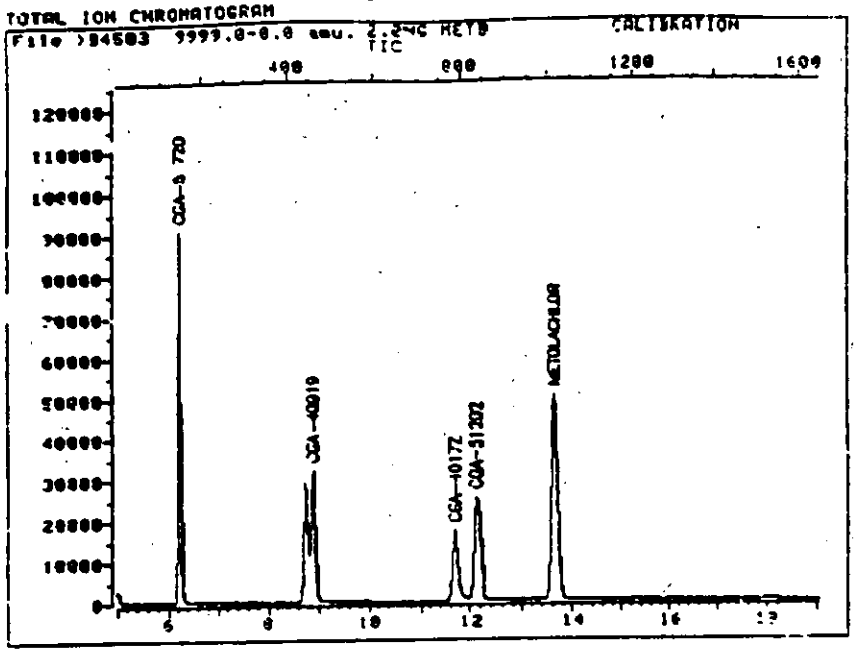


Data File: >B4503::D8
Name: 2.0NG METB
Misc: CALIBRATION

Quant Output File: 'B4503::QT

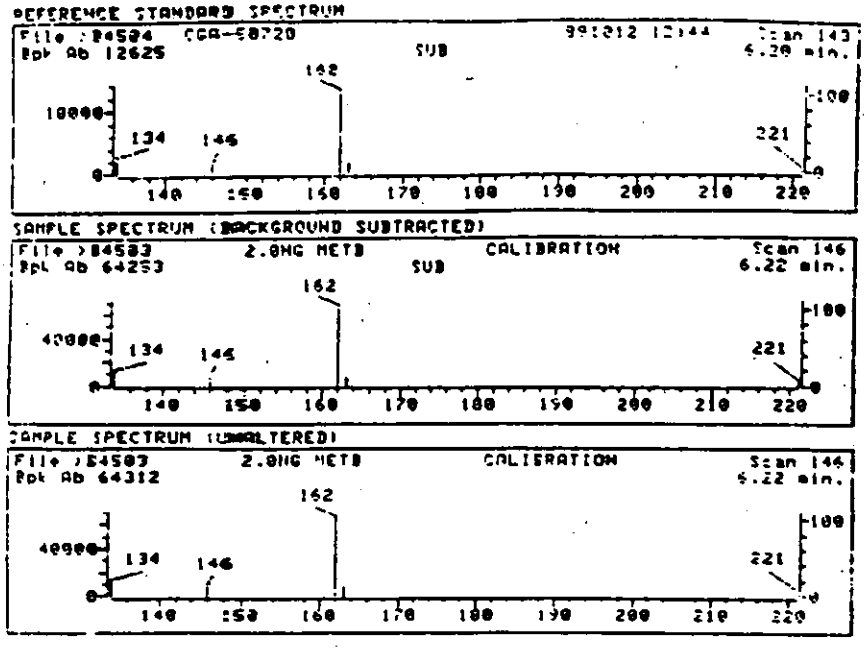
ST # 1

Id File: MTBID::D8
Title: METOLACHLOR-METABOLITES ID FILE
Last Calibration: 891012 16:12

Operator ID: JIM
Quant Time: 891012 22:13
Injected at: 891012 19:01

FIGURE 7

Reference spectra for CGA-50720



Data File: >84503::08 Quant Output File: ^84503::QT
Name: 2.0NG METB
Misc: CALIBRATION BTL# 3
Quant Time: 891012 22:13 Quant ID File: MTBID::08
Injected at: S91012 19:01 Last Calibration: 891012 16:12

Compound No: 1
Compound Name: CGA-50720
Scan Number: 146
Retention Time: 6.22 min.
Quant Ion: 162.1
Area: 207563
Concentration: 2.23 NG
q-value: 100

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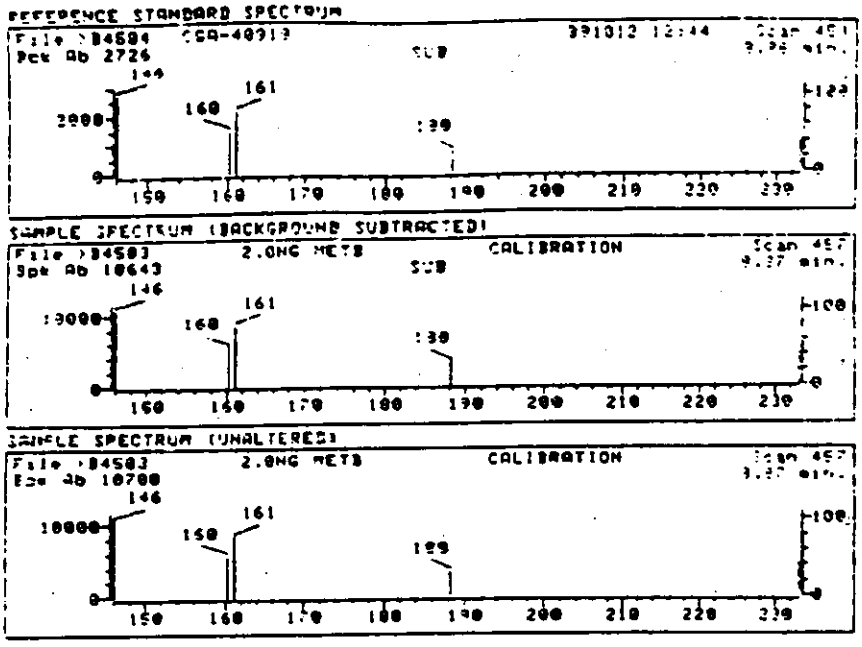
FIGURE 8

Reference spectra for CGA-40919



00012

Data File: >84503::08
Name: 2.0NG METB
Misc: CALIBRATION
Quant Time: 891012 22:13
Injected at: 891012 19:01

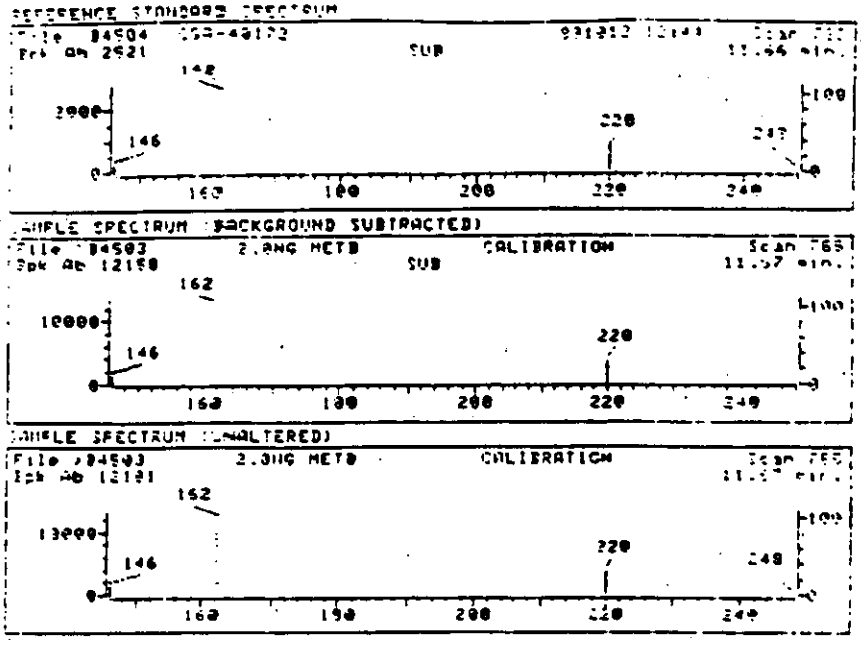
Quant Output File: '84503::QT

STL# 3
Quant ID File: MTBID::08
Last Calibration: 891012 16:12

Compound No: 2
Compound Name: CGA-40919
Scan Number: 457
Retention Time: 3.87 min
Quant Ion: 161.1
Area: 83953M
Concentration: 2.22 NG
Q-value: 100

FIGURE 9

Reference spectra for CGA-40172



00014

Data File: B4503::D8 Quant Output File: [illegible]

Name: 2.0NG METB

Misc: CALIBRATION Style 7

Quant Time: 891012 22:13 Quant ID File: MTBID::D8

Injected at: 891012 19:01 Last Calibration: 891012 14:12

Compound No: 3

Compound Name: CGA-40172

Scan Number: 785

Retention Time: 11.67 min.

Quant Ion: 162.1

Area: 90221

Concentration: 2.34 NG

q-value: 100

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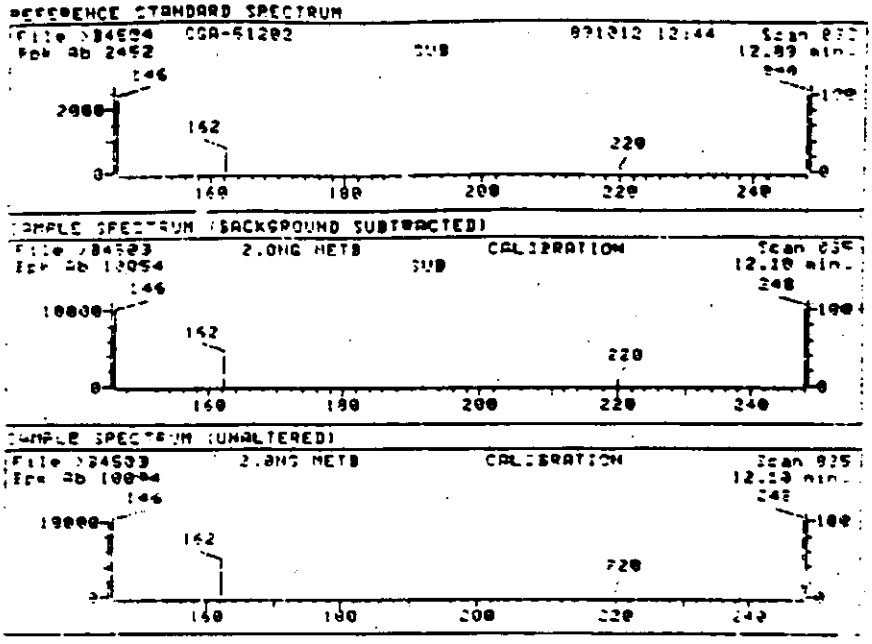
FIGURE 10

Reference spectra for CGA-51202



Data File: 84503::08 Quant Output File: 84503::07

Name: 2.0NG METB

Misc: CALIBRATION

Quant Time: 891012 22:13 Quant ID File: ...

Injected at: 891012 19:01 Last Calibration: ...

Compound No: 4

Compound Name: CGA-51202

Scan Number: 935

Retention Time: 12.10 min.

Quant Ion: 248.1

Area: 87727

Concentration: 2.28 NG

Value: 100

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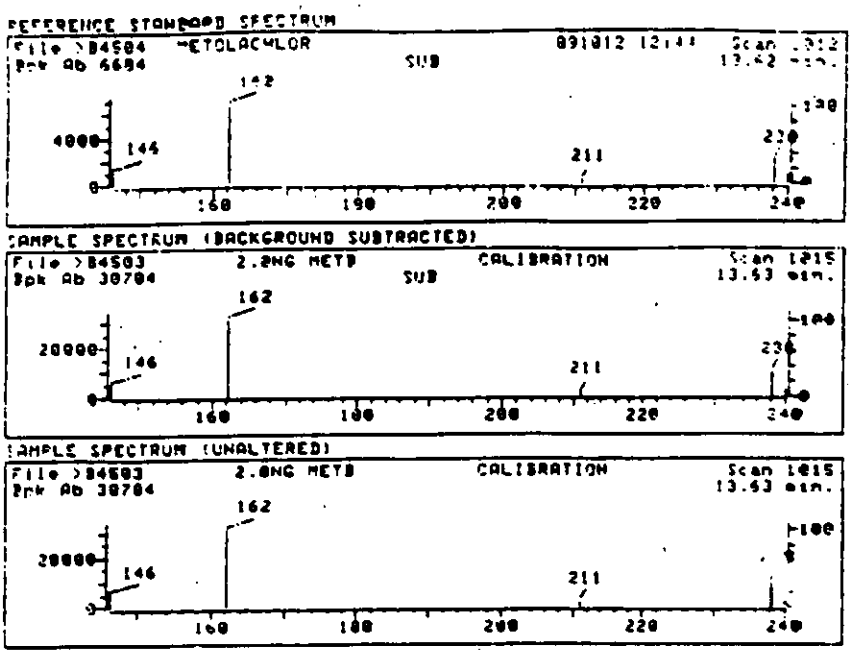
FIGURE 11

Reference spectra for Metolachlor

00018



Data File: >B4503::08 Quant Output File: >B4503::QT

Name: 2.0NG METB

Misc: CALIBRATION BTL# 3

Quant Time: 891012 22:13 Quant ID File: MTBID::08

Injected at: 891012 19:01 Last Calibration: 891012 16:12

Compound No: 5

Compound Name: METOLACHLOR

Scan Number: 1015

Retention Time: 13.63 min.

Quant Ion: 162.1

Area: 252934

Concentration: 2.44 NG

Q-value: 100

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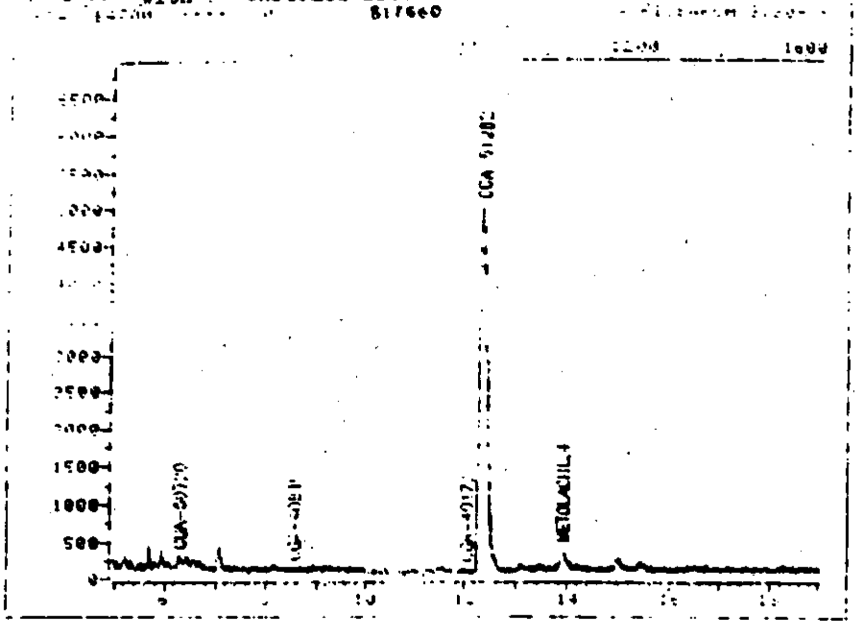
FIGURE 12

Example chromatogram of sample extract (Agrisearch sample 2720-9R) with a confirmed detection of CGA-51202 above the detection limit.

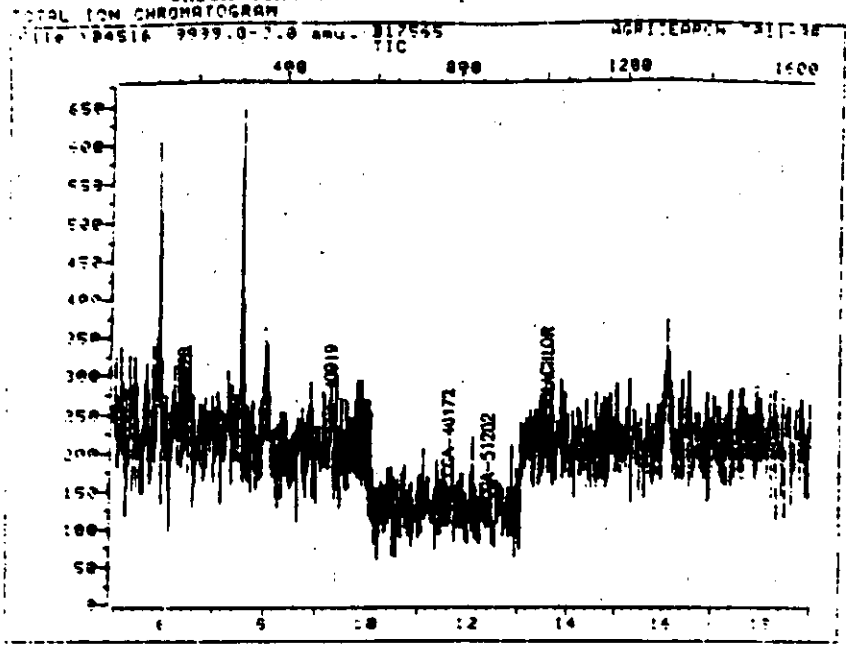


Data File: B4?00??03   Quant Output File: ?????????
Name: B1??60
Misc: AGRISEARCH 2720-9R

Last Calibration: ???

FIGURE 43

Example chromatogram of a sample extract (Agrisearch sample No. 7011.8R) which contained no compounds of interest above the detection limit.



Data File: S4516::09 Quant Output File: S4516::Q1
Name: S17545
Misc: AGRISEARCH 7011-8R

ID File: MISID::08
Title: METOLACHLOR-METABOLITES ID FILE
Last Calibration: 891012 22:37

Operator ID: JIM
Quant Time: 891013 01:11
Injected at: 891013 00:47

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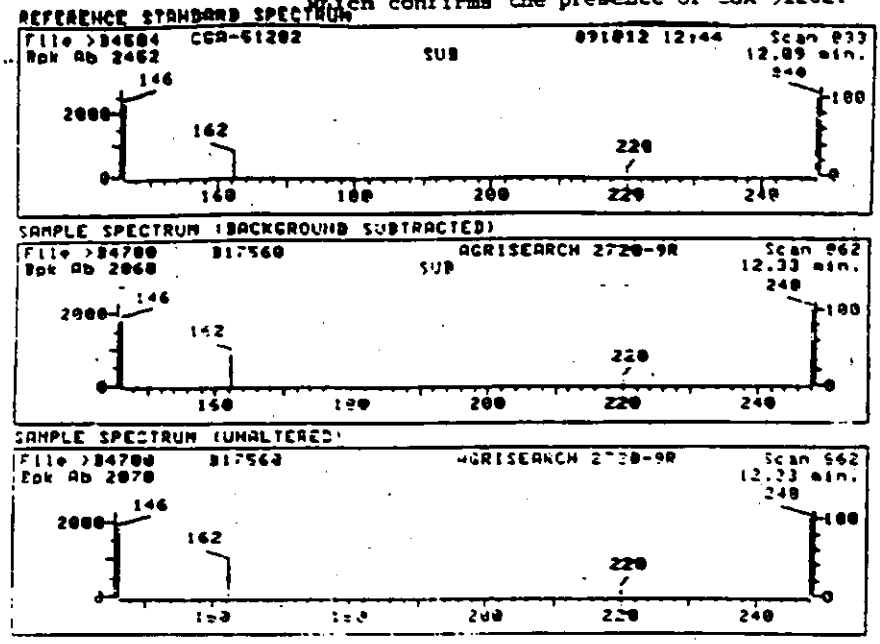
Example of sample spectrum (Agrisearch sample No. 2720-9R) which confirms the presence of CGA-51202.



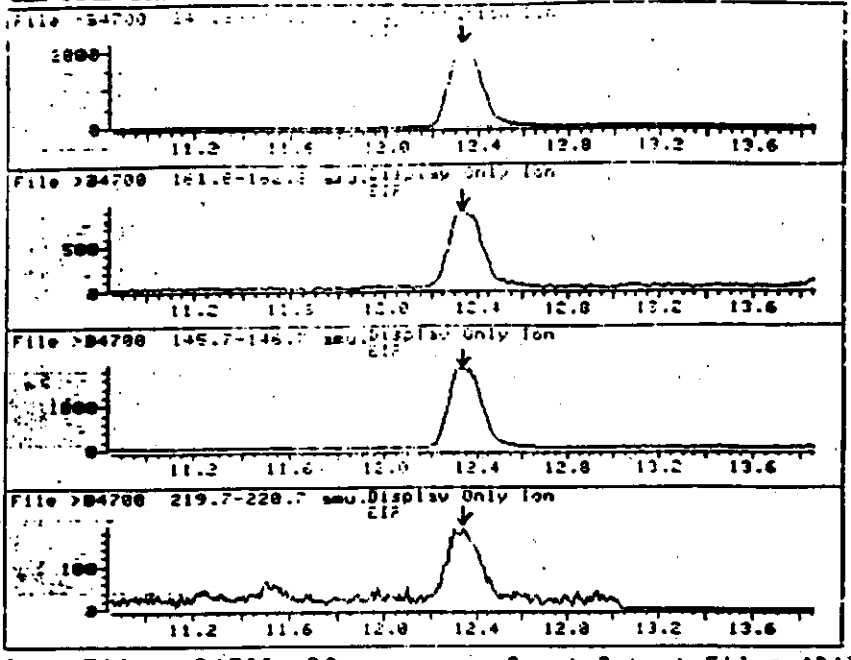
Data File: >B4700::DA
Name: B17560
Misc: AGRISEARCH 2720-9R
Quant Time: 891...
Injected at: 891107 ...

Quant Output File: *B4700::QT
BTL# 1
Quant ID File: MT810::D2
Last Calibration: 891102 09:07

Compound No: 4
Compound Name: CGA 51202
Scan Number: 844
Retention Time: ...
Quant Ion: 248.1
Area: 20450n
Concentration: .31 NG
q-value: 100

FIGURE 15

Ion chromatogram of Agrisearch sample No. 2720-9R showing the presence of all four ions monitored for CGA-51202 at the CGA-51202 retention time of 12.33 minutes.



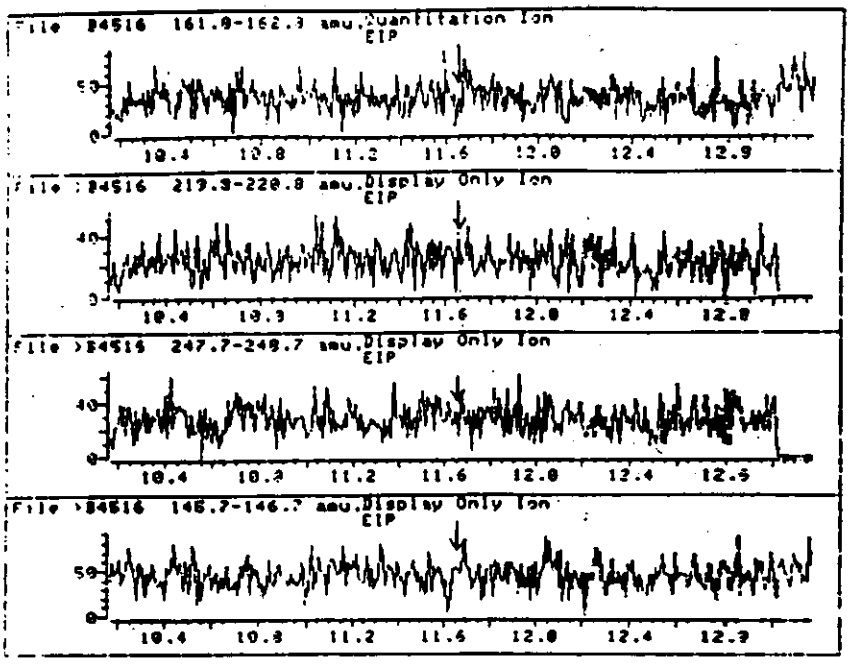
Data File: >84700::DA Quant Output File: ^84700::QT
Name: 817560
MrSE: AGRISEARCH 2720-9R BTL# 1
Quant Time: 891102 10:24 Quant ID File: MTBID::D2
Injected at: 891102 10:00 Last Calibration: 891102 09:03

Compound No: 4
Compound Name: CGA-51202
Quant Ion: 248.1

Hit	R.T.	Scan#	Area	Conc	Units	q
1	12.33	863	20450M	.31	NG	100

FIGURE 16

Ion chromatograms of Agrisearch sample No. 7011.8R showing the absence of the four ions monitored for CGA-40172.



Data File: >84516::08 Quant Output File: *84516::08
Name: B17565
Misc: AGRISEARCH 7011-8R BT_#15
Quant Time: 891013 01:11 Quant ID File: MISID::09
Injected at: 891013 00:47 Last Calibration: 891012 22:17

Compound No: 3
Compound Name: CGA-40172
Quant Ion: 162.1

Hit	R.T.	Scan#	Area	Conc	Units	q
1	11.59	775	89	.03	NG	102