

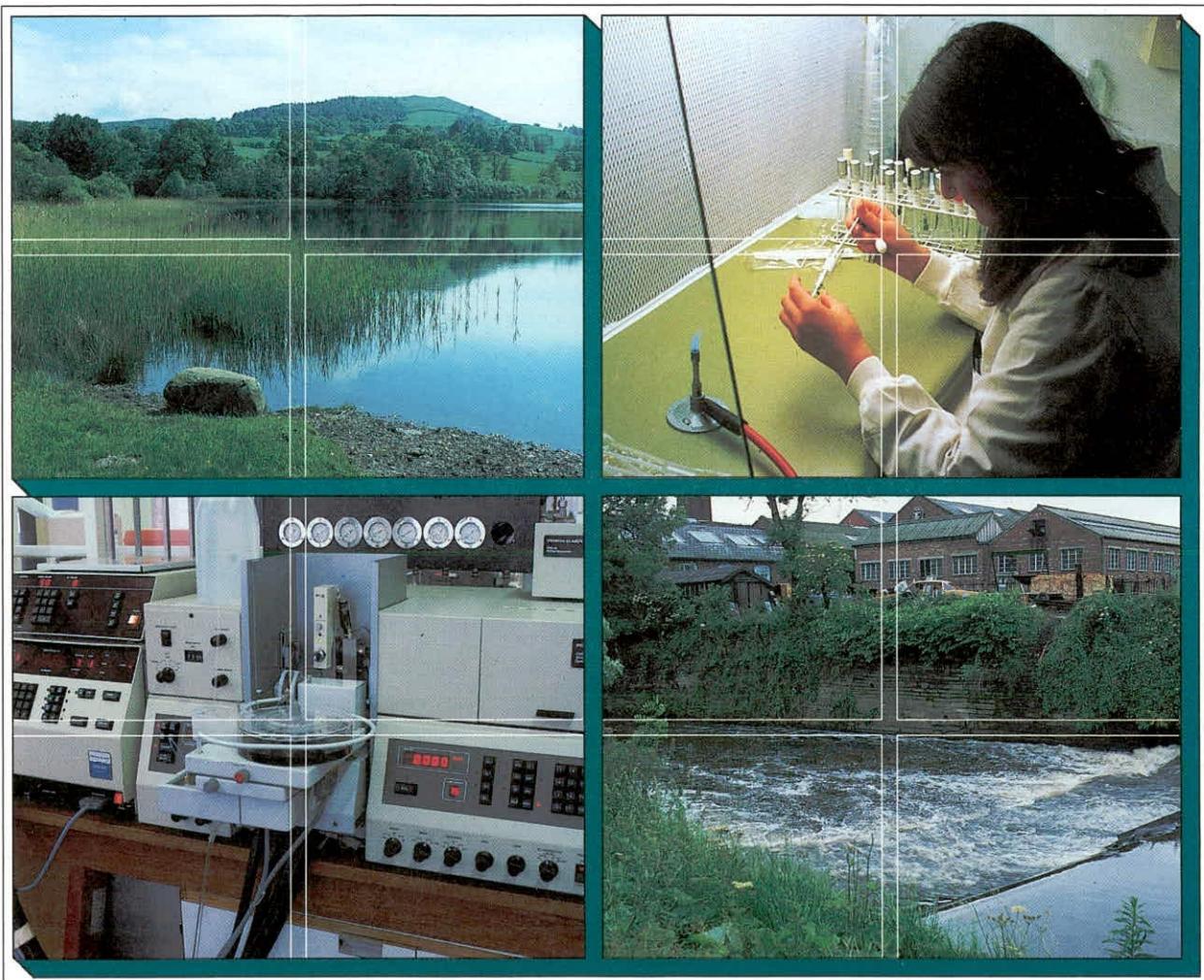


Institute of
Freshwater
Ecology

Intercalibration of pesticides in two batches of lyophilized water

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**INTERCALIBRATION OF PESTICIDES IN TWO BATCHES OF
LYOPHILIZED WATER**

by

W.A. House & D.R. Orr

| | |
|-----------------|---|
| Project leader: | W.A. House |
| Report date: | 1 October 1992 |
| Report to: | Commission of the European Communities Community Bureau of Reference Rue de la Loi 200 B-1049 Brussels |
| IFE Report Ref: | RL/T04053O1/5 |
| TFS Project No: | T04053O1 |

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The Institute of Freshwater Ecology is part of the Terrestrial and Freshwater
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SUMMARY

Five samples from both batch A and batch B together with two blanks were reconstituted, extracted using C18 disks, concentrated, dried and analysed by capillary glc with PTV or split-splitless injection and detection by NPD, ECD or mass spectrometry (GC/MS). The following pesticides were determined: atrazine, simazine, fenitrothion, parathion and permethrin. The *cis* and *trans* isomers of permethrin were detected by GC/MS operated in SIM mode and quantified using the 183 amu target ion. The results of the pH and conductivity measurements of the water immediately after reconstitution are given together with the concentration of the pesticides in the water samples.

Information on reconstitution of the samples

| BCR# | mass /g | volume water /ml | conductivity @ 25°C/ µS cm ⁻¹ | pH |
|-------------|--------------|------------------|---|-------------|
| 5,blk | 1.999 | 959.75 | 59.83 | 4.63 |
| A158 | 2.400 | 960.23 | 60.07 | 4.63 |
| A159 | 2.401 | 960.20 | 61.13 | 4.85 |
| A160 | 2.400 | 960.47 | 67.43 | 4.64 |
| A161 | 2.401 | 960.04 | 65.11 | 4.84 |
| A162 | 2.400 | 960.23 | 61.44 | 4.79 |
| Mean | 2.400 | 960.15 | 62.50 | 4.73 |
| 4, blk | 2.001 | 960.04 | 58.67 | 4.64 |
| B160 | 2.401 | 960.34 | 50.27 | 5.17 |
| B161 | 2.401 | 959.97 | 64.47 | 4.72 |
| B162 | 2.401 | 960.17 | 62.64 | 4.76 |
| B174 | 2.401 | 959.60 | 67.04 | 4.67 |
| B189 | 2.401 | 960.29 | 59.7 | 4.87 |
| Mean | 2.401 | 960.07 | 60.82 | 4.84 |

The mean conductivity of samples from batch A based on 2.4 g of powder was $63.04 \pm 3.11 \mu\text{S cm}^{-1}$ (CV = 4.9%). This compares with $65.24 \pm 13.95 \mu\text{S cm}^{-1}$ obtained in the stability study with this sample.

The mean conductivity for batch B based on 2.6 g of powder was $65.89 \pm 6.48 \mu\text{S cm}^{-1}$ (CV 9.8%). This compares with a mean of $63.51 \pm 10.21 \mu\text{S cm}^{-1}$.

CALIBRATION

Indicate below the concentration of the pesticides in the calibration standard(s) used and absolute quantities injected. If you use one calibration standard solution enter values in column 1. If you use upper and lower bracketing standards use columns 1 and 2. For calibration curves enter in columns 1,2,3, etc.

| PAH | Standard 1 | | Standard 2 | | Standard 3 | | Standard 4 | |
|------------|-----------------|----|-----------------|----|-----------------|----|-----------------|----|
| Pesticides | $\mu\text{g/g}$ | ng | $\mu\text{g/g}$ | ng | $\mu\text{g/g}$ | ng | $\mu\text{g/g}$ | ng |

| | | | | | | | | |
|-------------------|-------|-------|------|------|------|------|---|---|
| Carbaryl | - | - | - | - | - | - | - | - |
| Atrazine | 0.050 | 0.075 | 0.50 | 0.75 | 1.0 | 1.5 | | |
| Simazine | 0.050 | 0.075 | 0.50 | 0.75 | 1.0 | 1.5 | | |
| Fenitrothion | 0.032 | 0.048 | 0.32 | 0.48 | 0.64 | 0.96 | | |
| Parathion ethyl | 0.048 | 0.072 | 0.48 | 0.72 | 0.96 | 1.44 | | |
| Fenamiphos | - | - | - | - | - | - | - | - |
| Propanil | - | - | - | - | - | - | - | - |
| Linuron | - | - | - | - | - | - | - | - |
| Permethrin c t | 0.050 | 0.075 | 0.50 | 0.75 | 1.14 | 1.71 | | |
| | 0.051 | 0.077 | 0.51 | 0.77 | 1.02 | 1.53 | | |

Description of the method to evaluate the efficiency of the extraction and the possible losses during the clean up :

ESTIMATE OF RECOVERY (%)

| compound | Test1 | Test2 | Test3 | Mean | SD |
|-------------------------|--------------|--------------|--------------|--------------|--------------|
| Carbaryl | - | - | - | - | - |
| Atrazine | 65.4 | 84.6 | 83.6 | 77.9 | 10.8 |
| Simazine | 64.6 | 84.2 | 83.5 | 77.4 | 11.1 |
| Fenitrothion | 47.0 | 78.0 | 80.4 | 68.5 | 18.6 |
| Parathion-ethyl | 66.7 | 82.9 | 83.3 | 77.6 | 9.5 |
| Fenamiphos | - | - | - | - | - |
| Propanil | - | - | - | - | - |
| Linuron | - | - | - | - | - |
| Permethrin cis trans | 41.7 50.1 | 51.6 64.6 | 74.6 87.2 | 66.8 67.3 | 17.0 18.7 |

Description of the method to evaluate the efficiency of the extraction and the possible losses during the clean up:

- 1 litre pyrex bottle spiked with 2 ml of multistandard of: atrazine 0.50 µg/ml, simazine 0.50 µg/l, fenitrothion 0.32 µg/l, parathion 0.48 µg/ml as in 5% acetone/hexane. An aliquot of 2 ml of 0.5 µg/ml of *cis* and *trans* permethrin was added.
- The solvent was evaporated using a stream of oxygen-free dry-nitrogen gas. This took approximately 15 mins.
- 1 litre of HPLC grade water was added to each bottle and mixed on an orbital shaker in the dark at 20°C for 1 hour.
- 5 ml of HPLC grade methanol added and then immediately extracted using C18 disks.
- Extraction procedure as attached.

Average amount of pesticides (ng) in sample aliquot injected for quantification.

| | Batch A | Batch B |
|------------------|---------|---------|
| Carbaryl | - | - |
| Atrazine | 0.23 | 0.73 |
| Simazine | 0.72 | 0.40 |
| Fenitrothion | 0.034 | 0.031 |
| Parathion ethyl | 0.31 | 0.91 |
| Fenamiphos | | |
| Propanil | | |
| Linuron | | |
| cis-permethrin | 0.009 | 0.009 |
| trans-permethrin | 0.057 | 0.014 |

REPORTING SHEET

Batch A

RESULTS: RAW DATA

Mass concentration ng/g

| Replicate | 1 | 2 | 3 | 4 | 5 | Mean | SD |
|--------------|-------|-------|-------|-------|-------|-------|-------|
| Carbaryl | - | - | - | - | - | - | - |
| Atrazine | 0.306 | 0.336 | 0.298 | 0.489 | 0.441 | 0.374 | 0.086 |
| Simazine | 0.989 | 1.081 | 0.963 | 1.348 | 1.412 | 1.158 | 0.208 |
| Fenitrothion | 0.055 | 0.063 | 0.057 | 0.037 | 0.065 | 0.056 | 0.011 |
| Parathion.et | 0.397 | 0.465 | 0.415 | 0.600 | 0.616 | 0.499 | 0.103 |
| Fenamiphos | | | | | | | |
| Propanil | | | | | | | |
| Linuron | | | | | | | |
| cis-perm | 0.009 | 0.008 | 0.007 | 0.017 | 0.025 | 0.013 | 0.007 |
| trans-perm | 0.151 | 0.126 | 0.118 | 0.037 | 0.039 | 0.094 | 0.053 |

REPORTING SHEET

Batch B

RESULTS: RAW DATA

Mass concentration ng/g

| Replicate | 1 | 2 | 3 | 4 | 5 | Mean | SD |
|--------------|-------|-------|-------|-------|-------|-------|-------|
| Carbaryl | - | - | - | - | - | - | - |
| Atrazine | 1.30 | 1.20 | 1.40 | 1.06 | 1.02 | 1.19 | 0.16 |
| Simazine | 0.753 | 0.635 | 0.738 | 0.560 | 0.555 | 0.648 | 0.095 |
| Fenitrothion | 0.115 | 0.045 | 0.028 | 0.049 | 0.010 | 0.049 | 0.041 |
| Parathion.et | 1.98 | 1.58 | 1.64 | 1.05 | 1.15 | 1.48 | 0.38 |
| Fenamiphos | | | | | | | |
| Propanil | | | | | | | |
| Linuron | | | | | | | |
| cis-perm | 0.014 | 0.011 | 0.013 | 0.018 | 0.018 | 0.015 | 0.003 |
| trans-perm | 0.021 | 0.017 | 0.022 | 0.029 | 0.028 | 0.023 | 0.005 |

REPORTING SHEET

Batch A

RESULTS: DATA CORRECTED FOR BLANK AND RECOVERY AND TO :

2.461g FOR BATCH A
2.663g FOR BATCH B

Mass concentration ng/g

| Replicate | 1 | 2 | 3 | 4 | 5 | Mean | SD |
|--------------|-------|-------|-------|-------|--------|-------|-------|
| Carbaryl | - | - | - | - | - | - | - |
| Atrazine | 0.221 | 0.239 | 0.229 | 0.326 | 0.313 | 0.266 | 0.050 |
| Simazine | 0.930 | 0.983 | 0.957 | 1.075 | 1.213 | 1.032 | 0.115 |
| Fenitrothion | 0.039 | 0.045 | 0.045 | 0.016 | 0.0432 | 0.038 | 0.012 |
| Parathion.et | 0.393 | 0.444 | 0.433 | 0.500 | 0.551 | 0.464 | 0.062 |
| Fenamiphos | | | | | | | |
| Propanil | | | | | | | |
| Linuron | | | | | | | |
| cis-perm | <0 | <0 | <0 | 0.001 | 0.009 | <0 | 0.007 |
| trans-perm | 0.130 | 0.101 | 0.103 | 0.015 | 0.017 | 0.073 | 0.053 |

The results given for parathion have not been corrected for the blank. For sample this is 0.797 ug/g.

REPORTING SHEET

Batch B

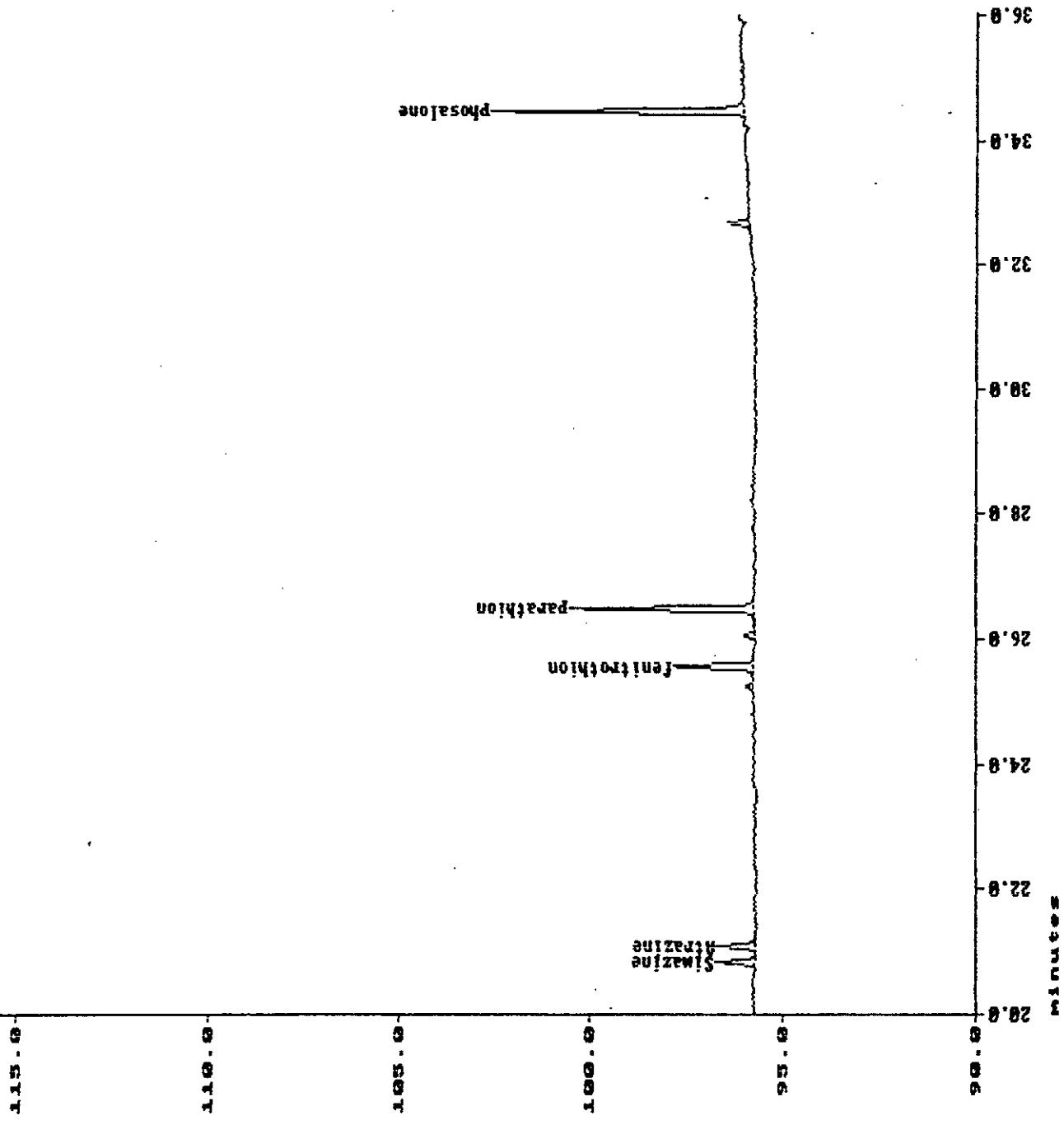
RESULTS: DATA CORRECTED FOR BLANK AND RECOVERY AND TO :

2.461g FOR BATCH A
2.663g FOR BATCH B

Mass concentration ng/g

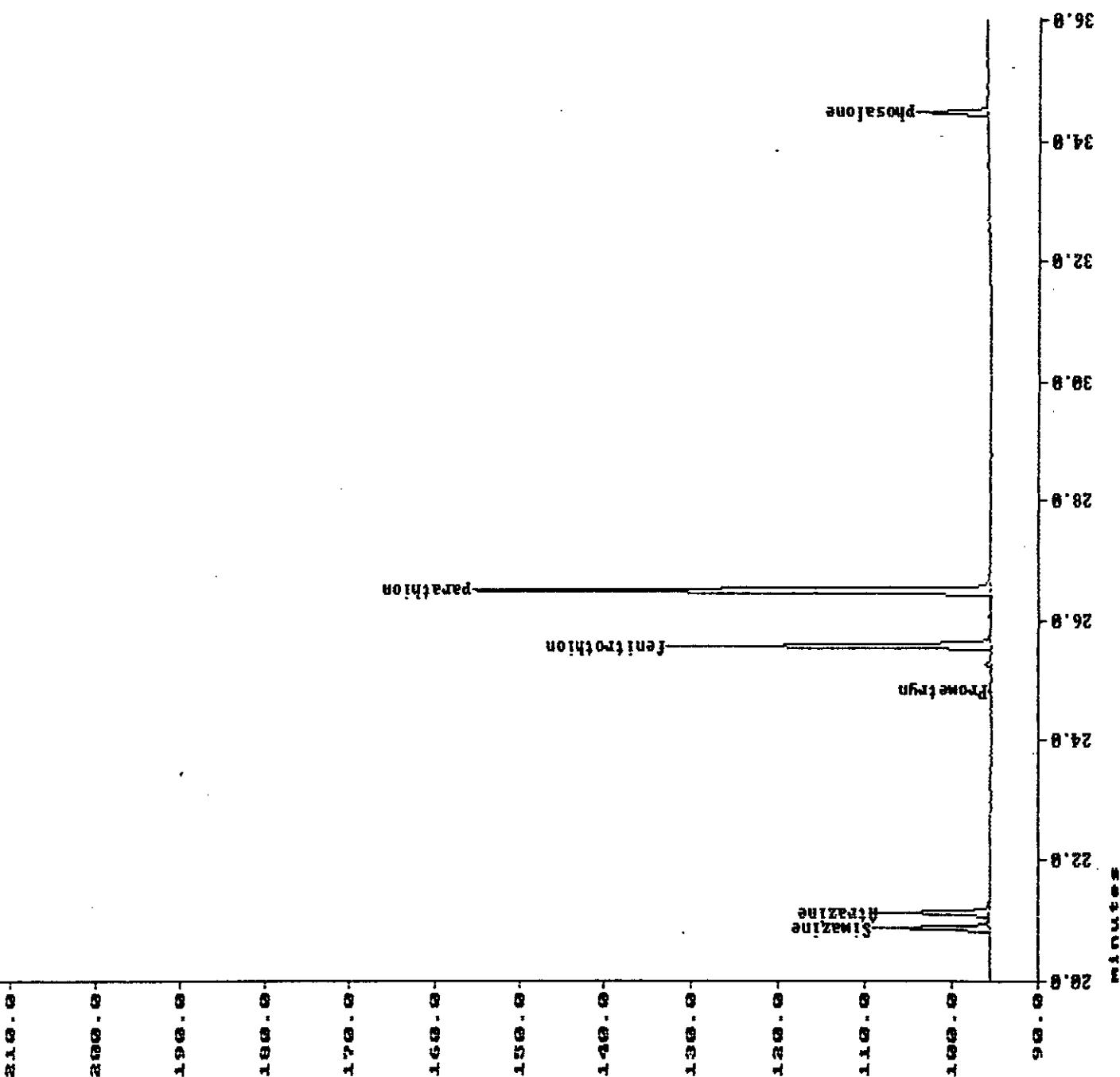
| Replicate | 1 | 2 | 3 | 4 | 5 | Mean | SD |
|--------------|-------|-------|-------|-------|--------|-------|-------|
| Carbaryl | - | - | - | - | - | - | - |
| Atrazine | 1.23 | 1.25 | 1.28 | 1.16 | 1.14 | 1.21 | 0.06 |
| Simazine | 0.710 | 0.654 | 0.665 | 0.607 | 0.614 | 0.650 | 0.042 |
| Fenitrothion | 0.103 | 0.035 | 0.013 | 0.044 | -0.002 | 0.039 | 0.040 |
| Parathion.et | 2.04 | 1.79 | 1.61 | 1.26 | 1.40 | 1.62 | 0.31 |
| Fenamiphos | | | | | | | |
| Propanil | | | | | | | |
| Linuron | | | | | | | |
| cis-perm | 0.014 | 0.012 | 0.013 | 0.022 | 0.022 | 0.017 | 0.005 |
| trans-perm | 0.022 | 0.019 | 0.021 | 0.035 | 0.034 | 0.026 | 0.008 |

The results given for parathion have not been corrected for the blank. For sample B this is 0.770 ug/g.



(RUN#_B3.DAT) #1

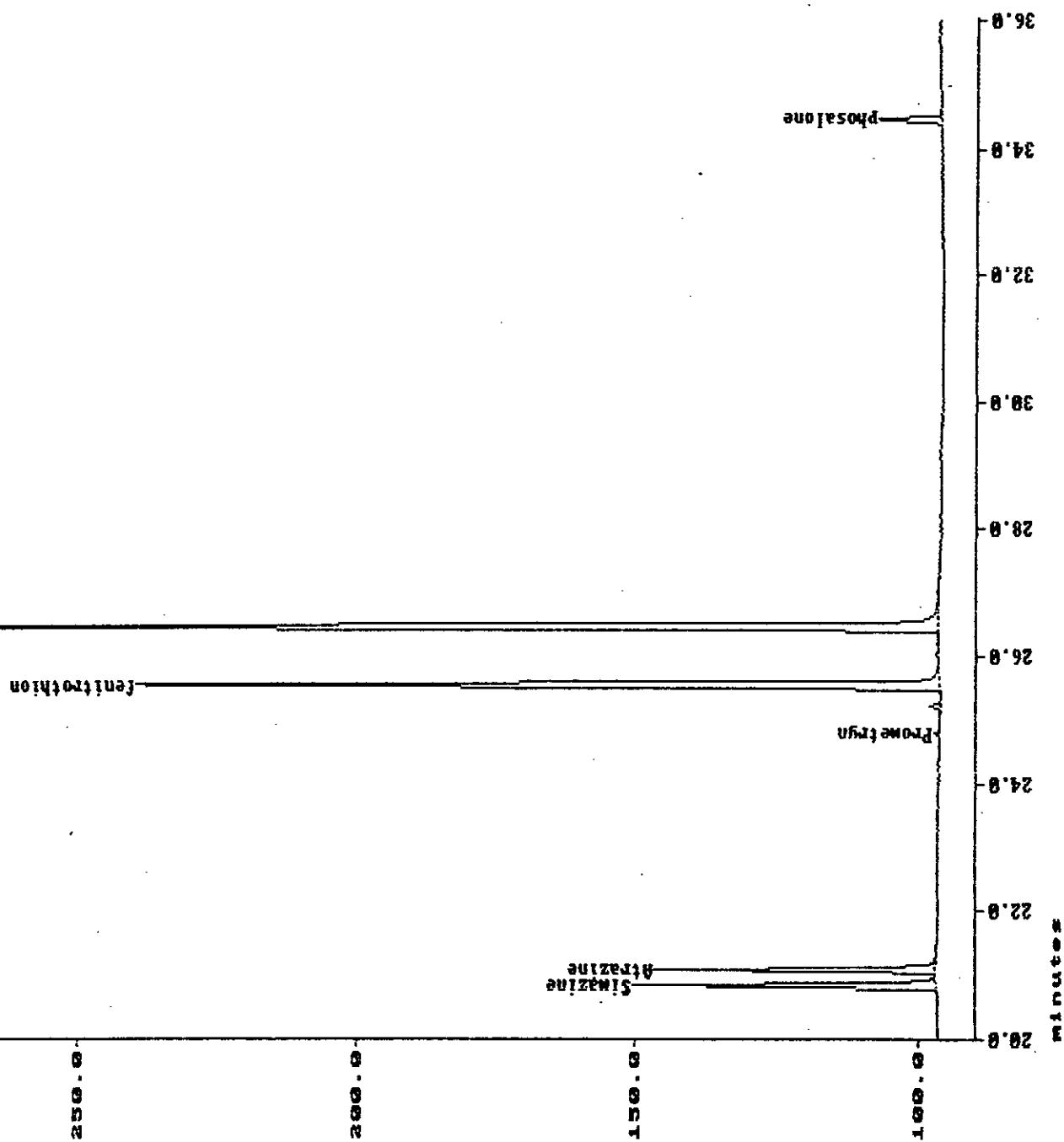
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Collection : 16:03:23 Sep 10 1992 Method : BCROPT 1 14:22:55 Sep 10 1992 1
0.05 ml/min 0.05 ml/min



(RUN#_04.D01) MU

11

File : RUN#_04.D01 Date : 16:58:51 Sep 18 1992 Method : BCROPT [14:22:55 Sep 18 1992]
Run : 01 Queue : DOUG Set Number : 1 Type : Sample
Collection : 16:58:51 Sep 18 1992

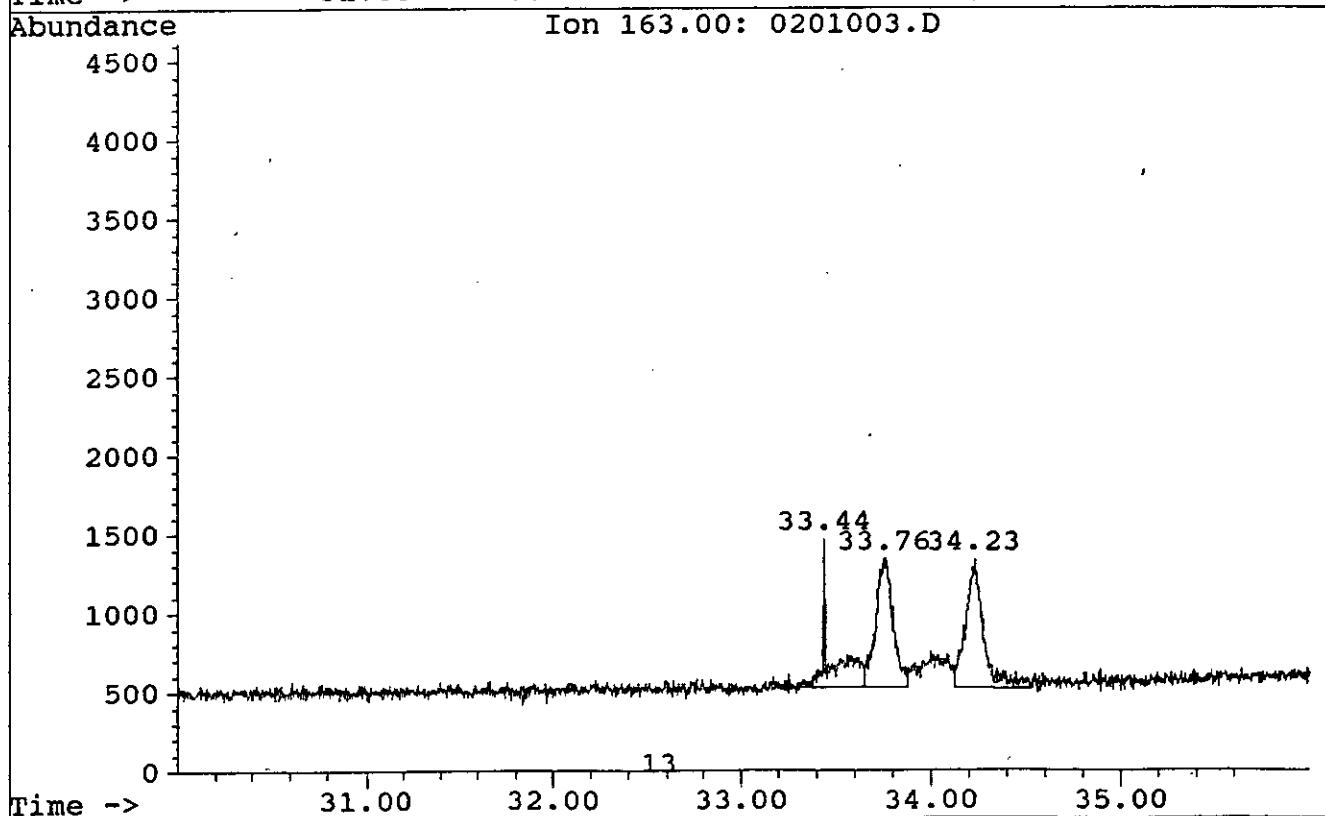
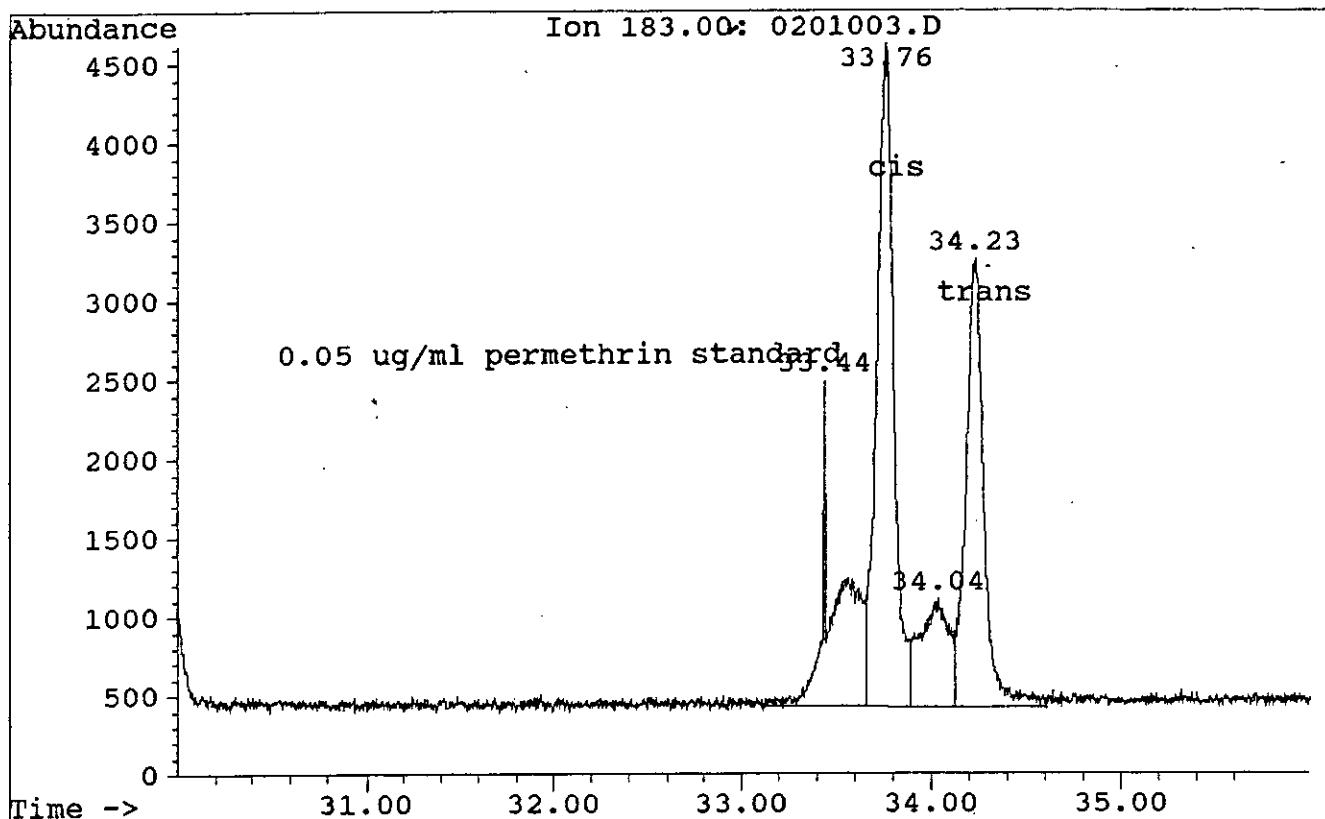


(RUNS_05.D01) MU

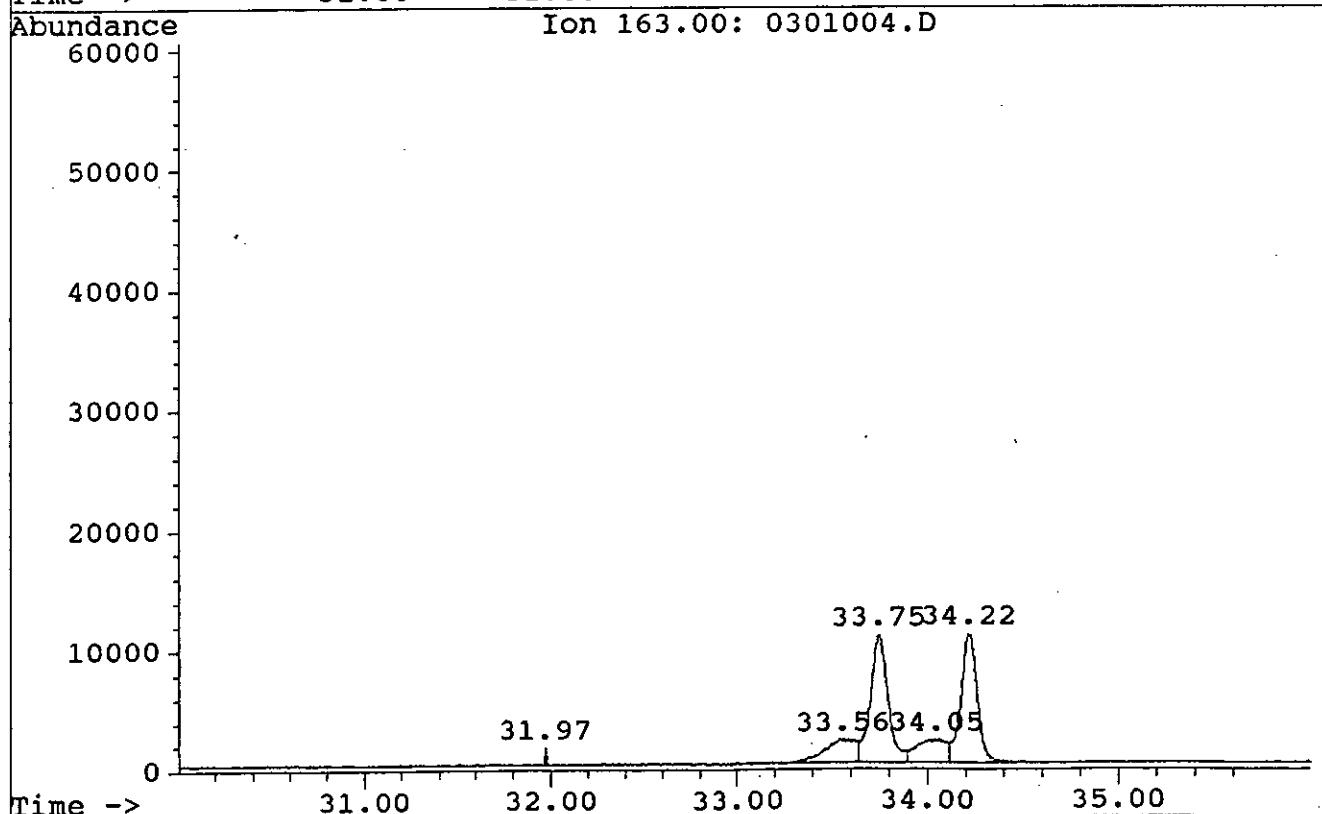
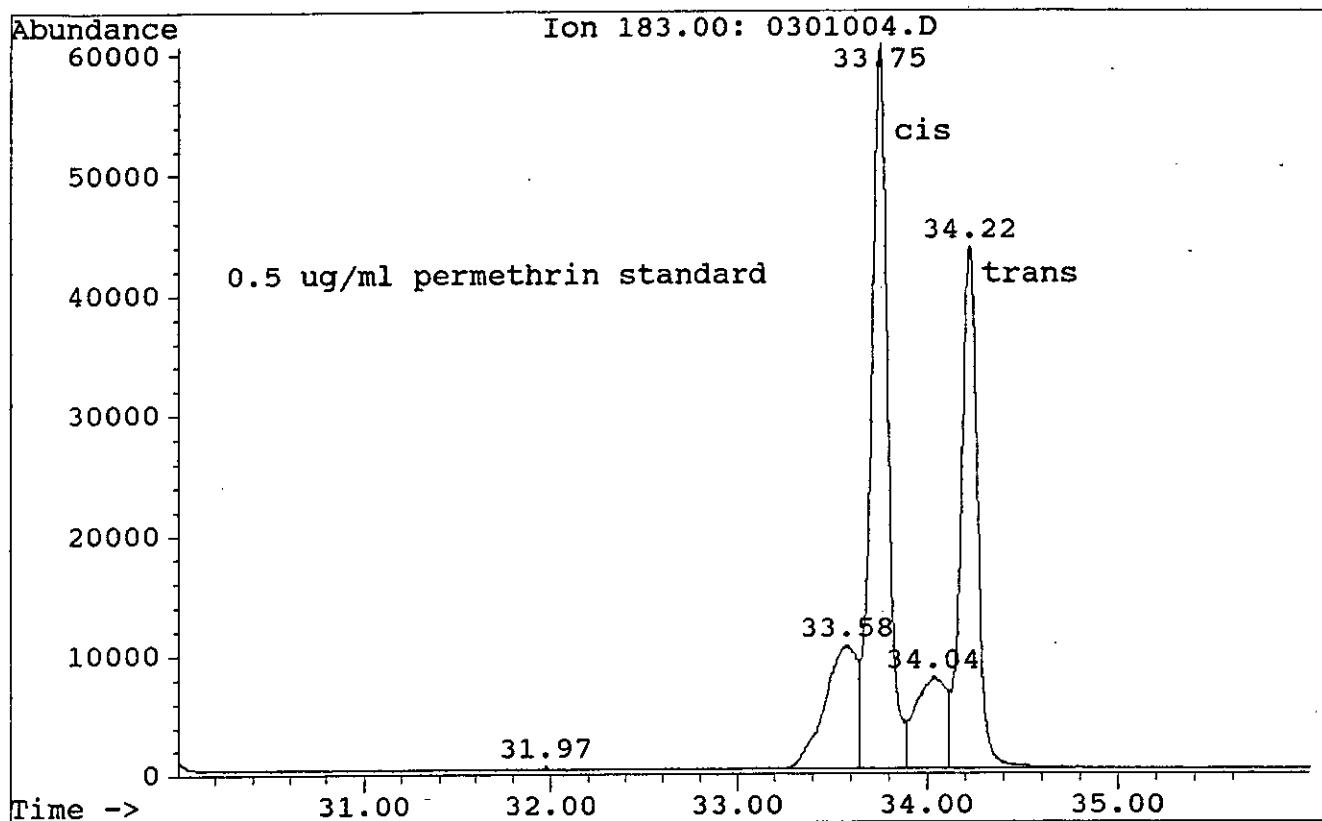
12

File : RUNS_05.D01 Queue : DOUG Set Number : 1 Type : Sample
Run : 01 Method : REPORT Date : 17:46:43 Sep 18 1992
Collection : 17:46:43 Sep 18 1992 Set Number : 1 Type : Sample

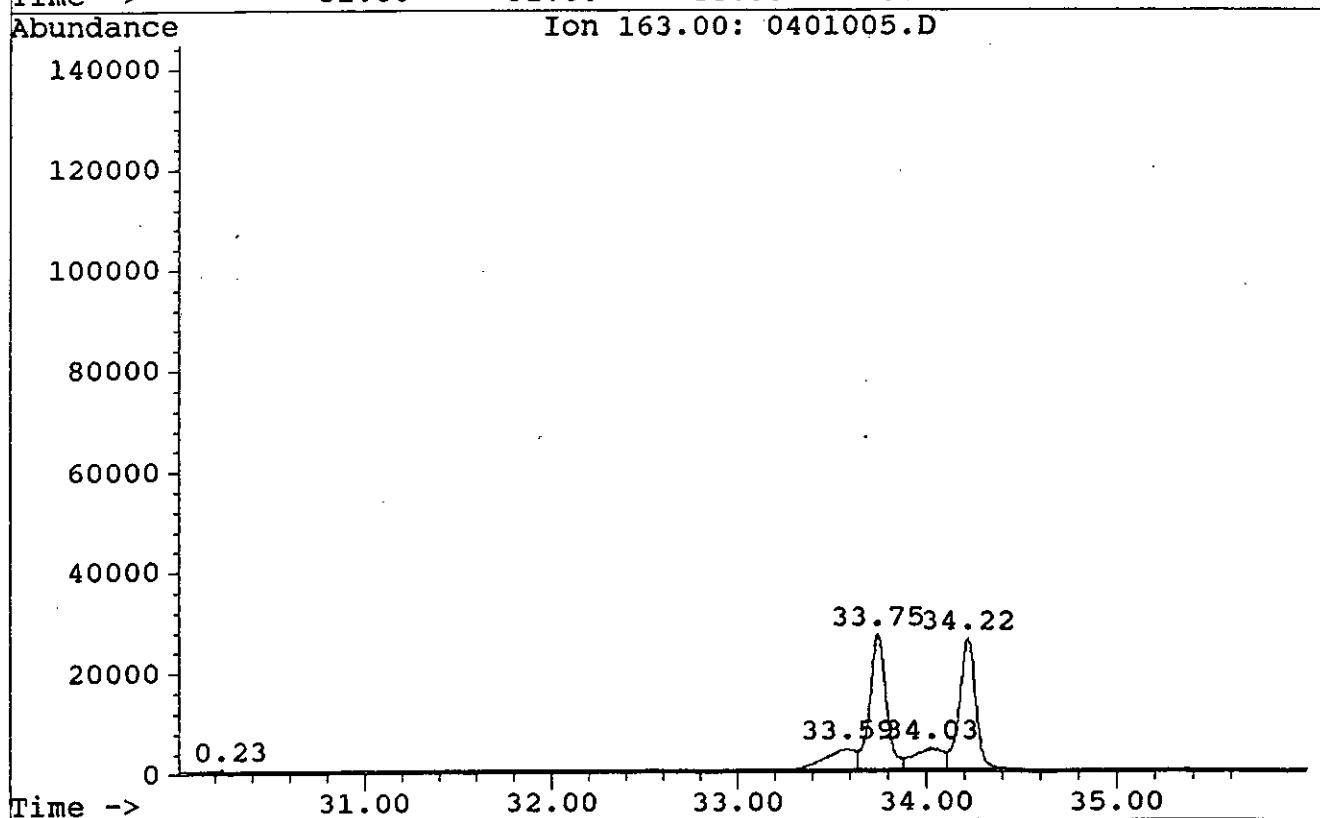
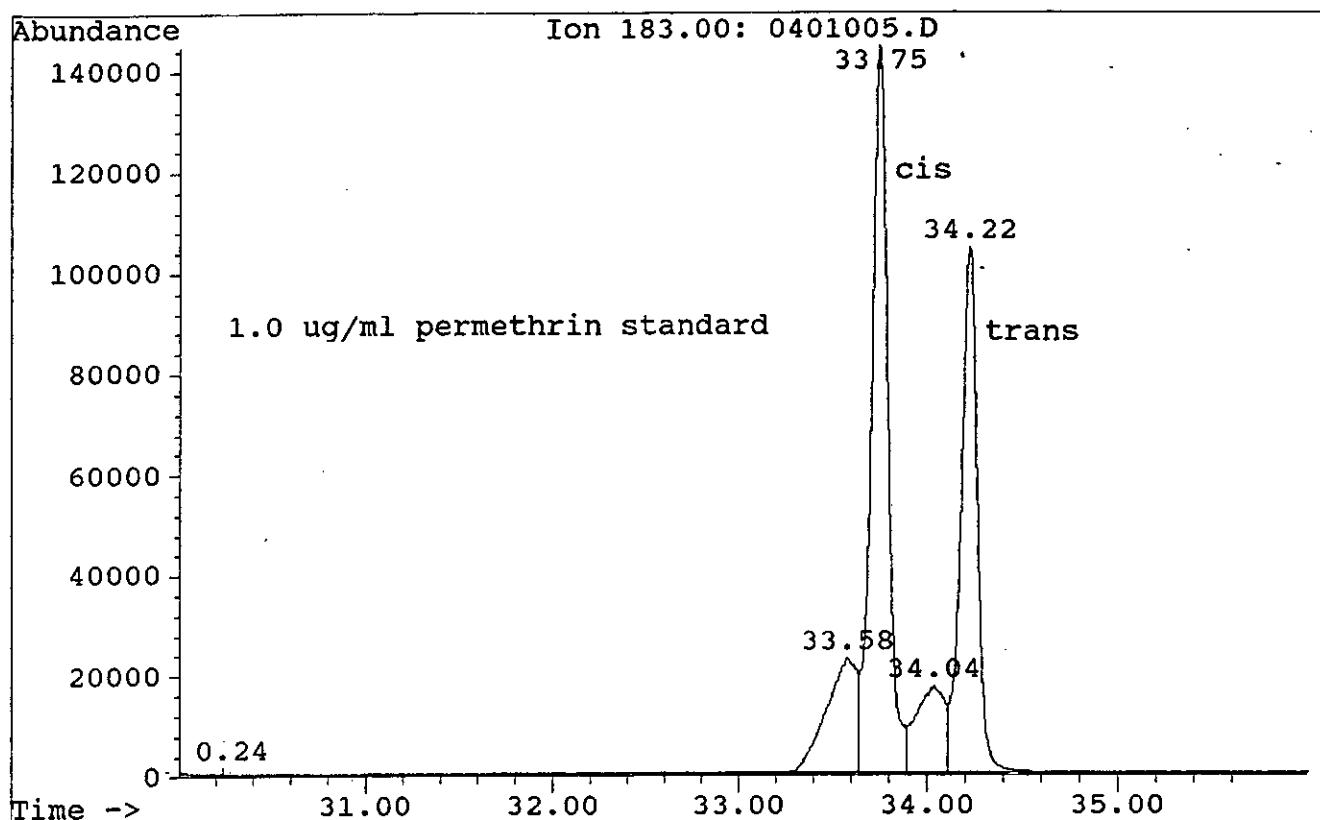
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Operator: wah
Date Acquired: 18 Sep 92 11:28 am
Method File: permalan.M
Sample Name: 0.05 std
Misc Info:
ALS vial: 2

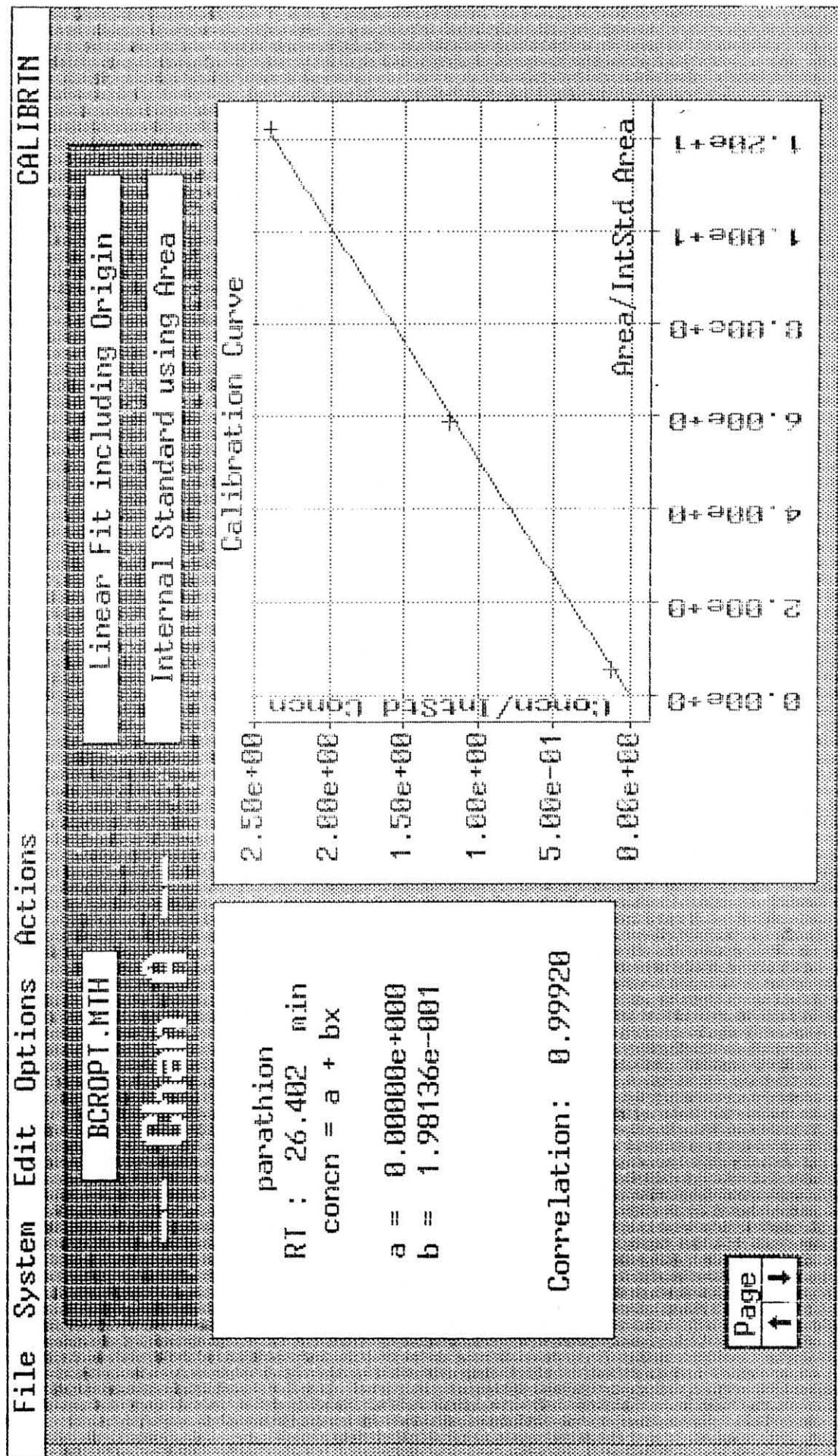


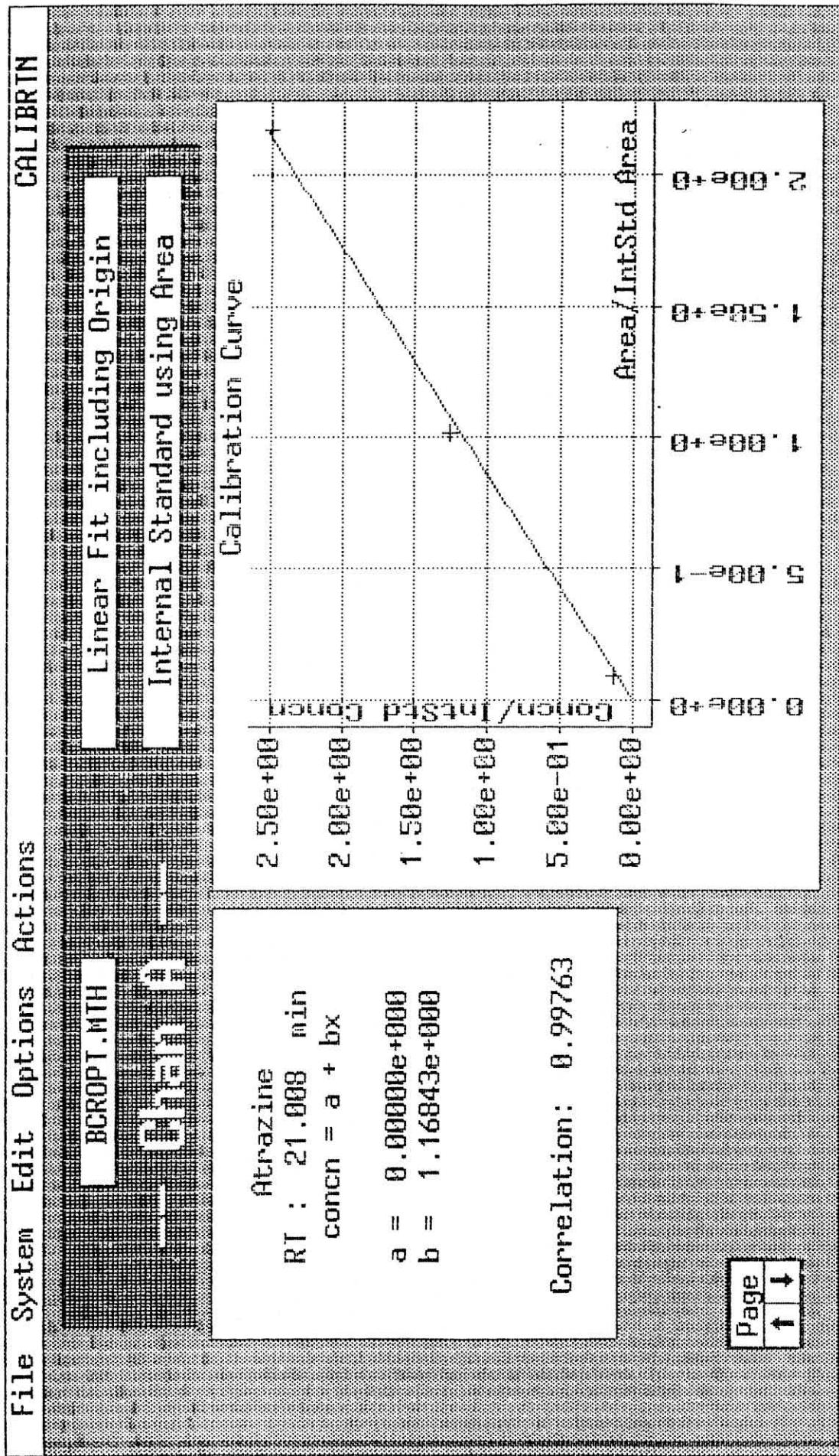
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Operator: wah
Date Acquired: 18 Sep 92 12:26 pm
Method File: permalan.M
Sample Name: 0.5 std
Misc Info:
ALS vial: 3

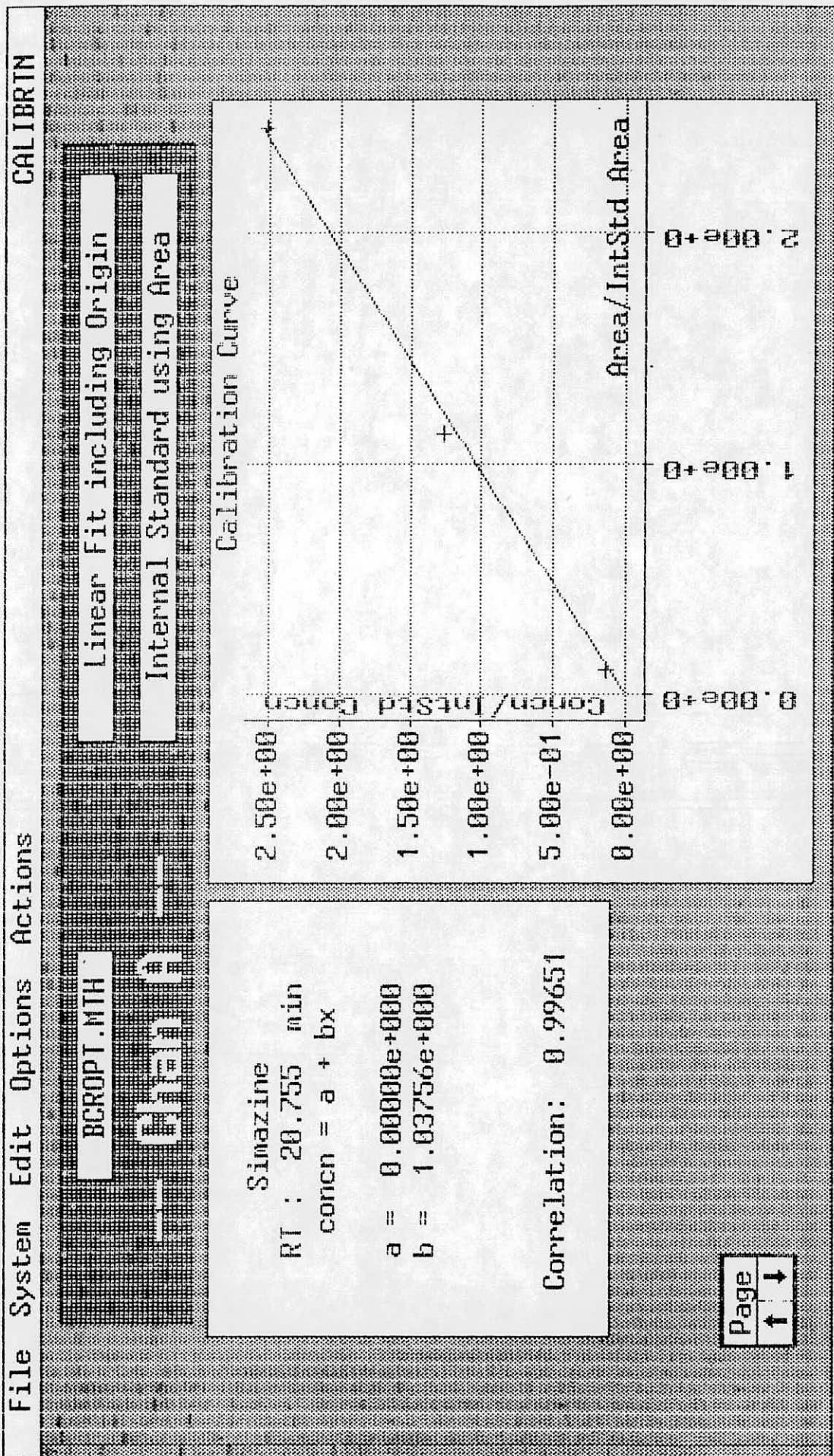


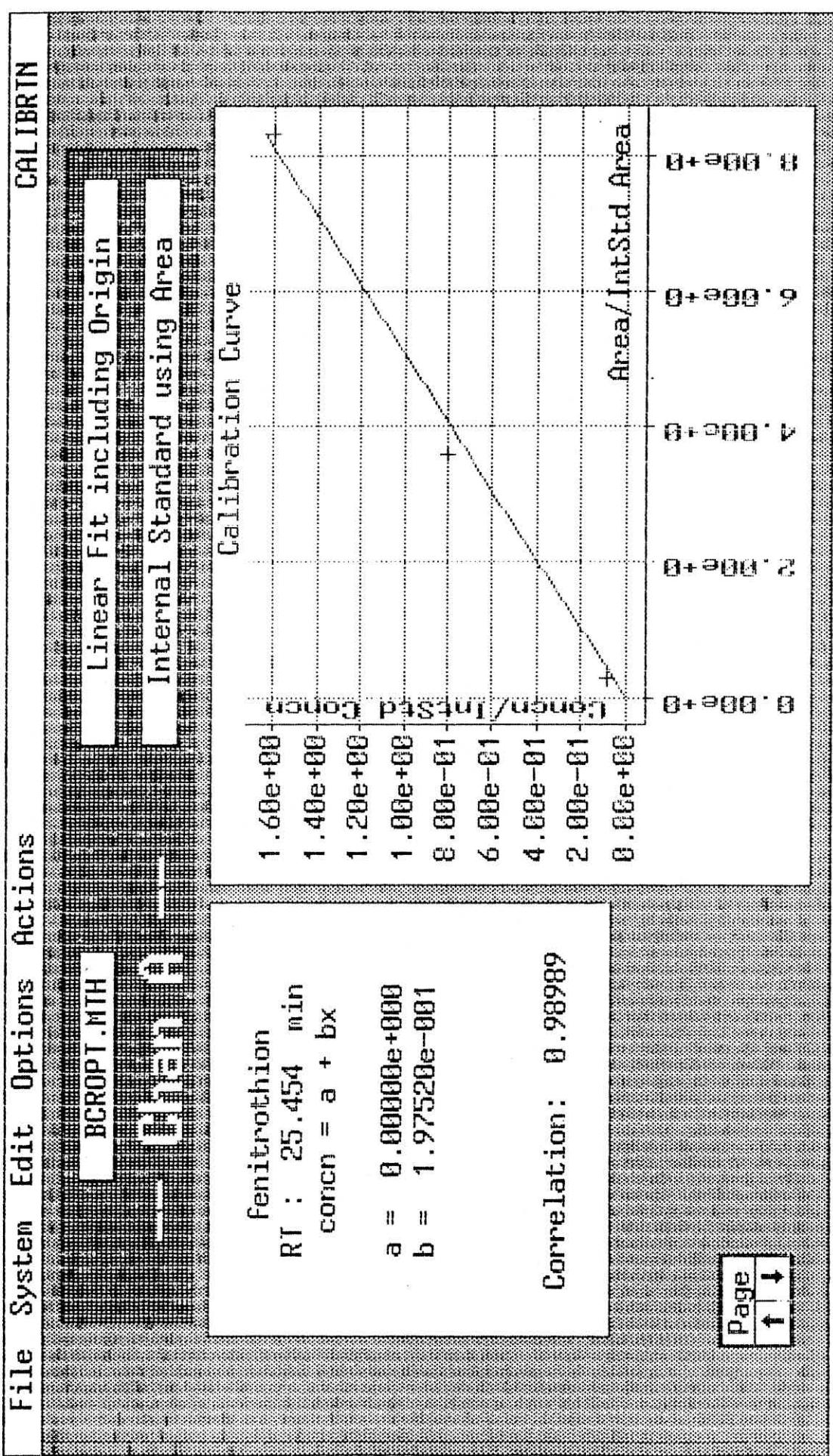
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Operator: wah
Date Acquired: 18 Sep 92 1:23 pm
Method File: permalan.M
Sample Name: 1.0
Misc Info:
ALS vial: 4

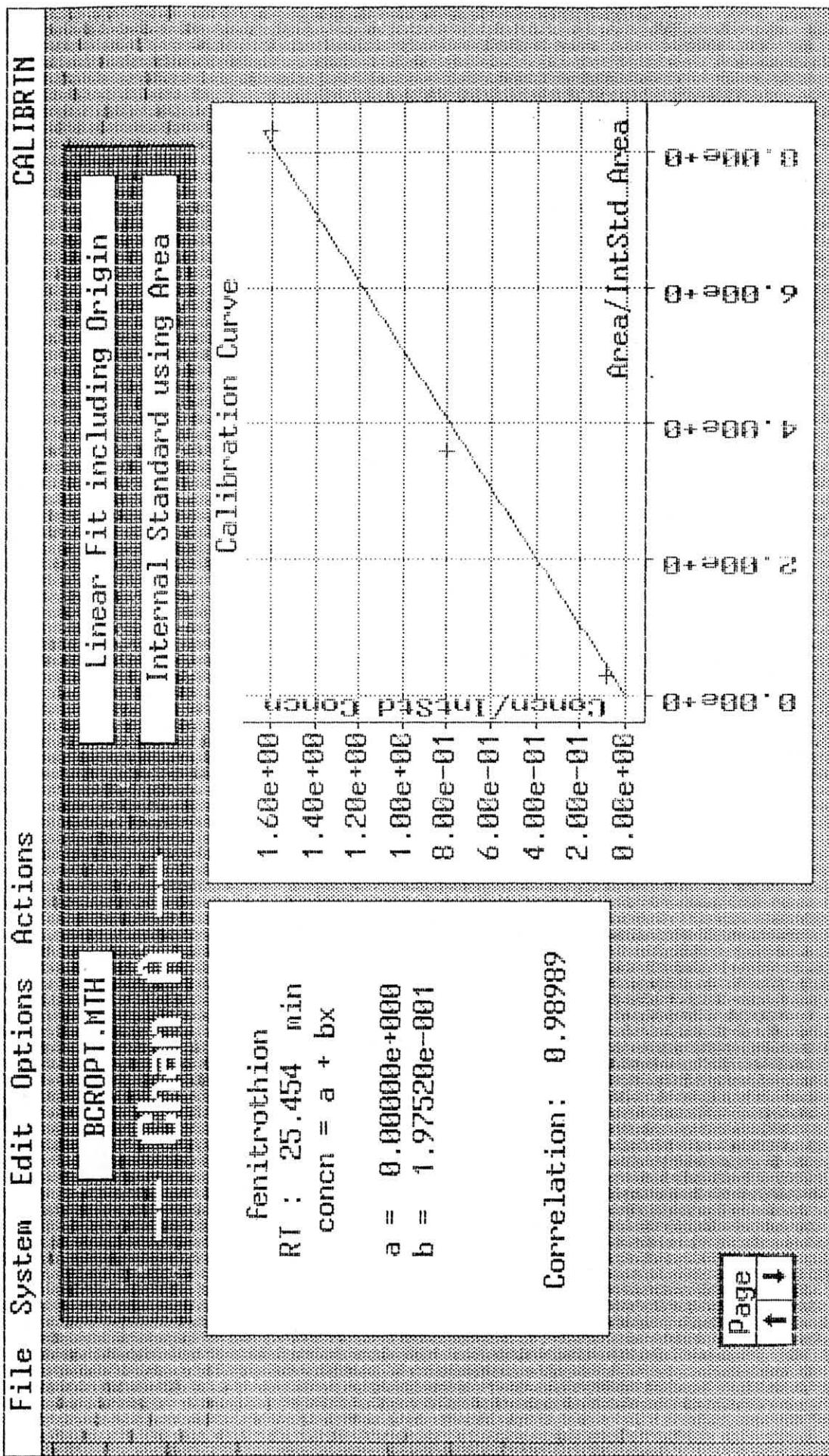


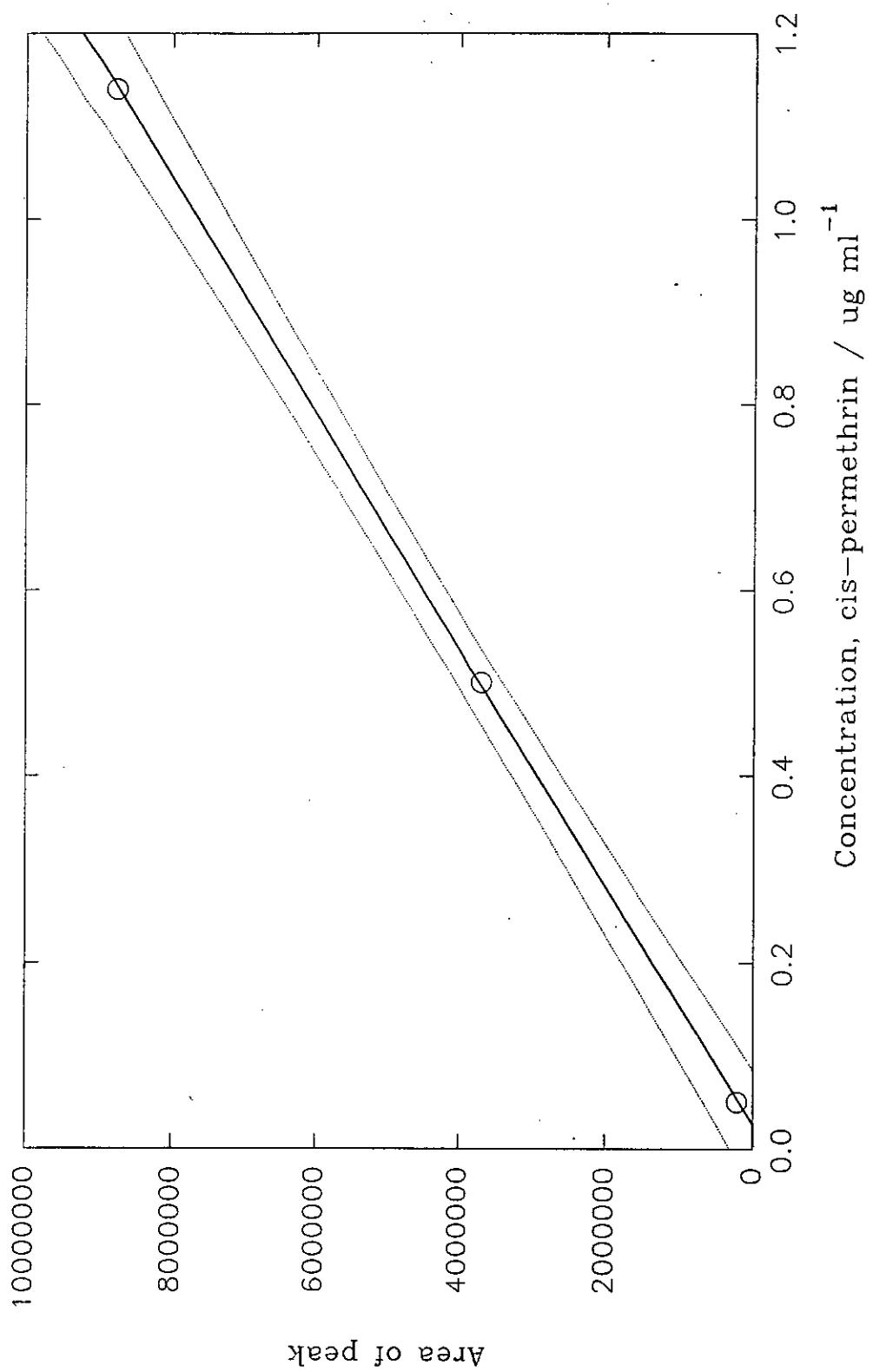


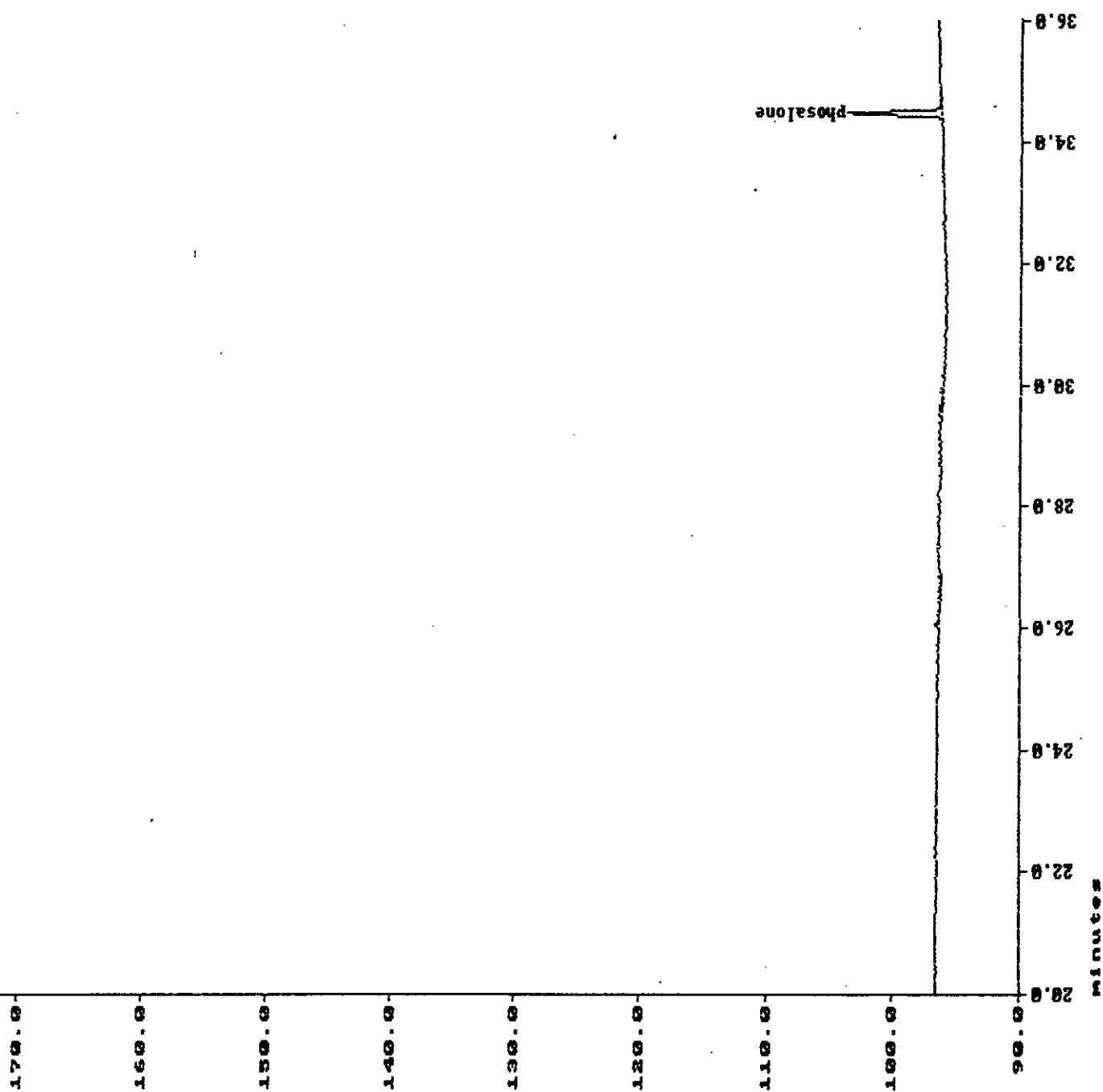






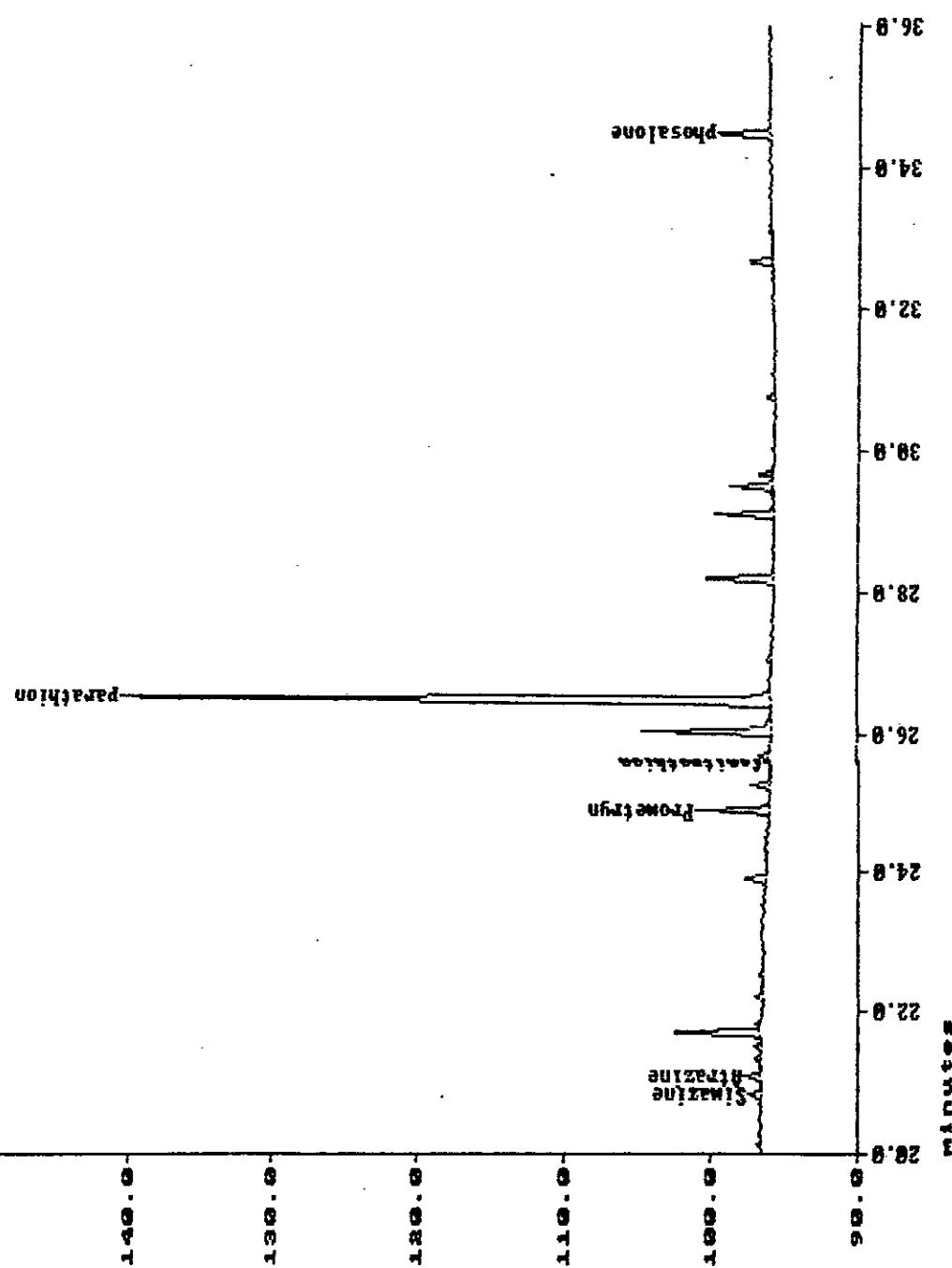




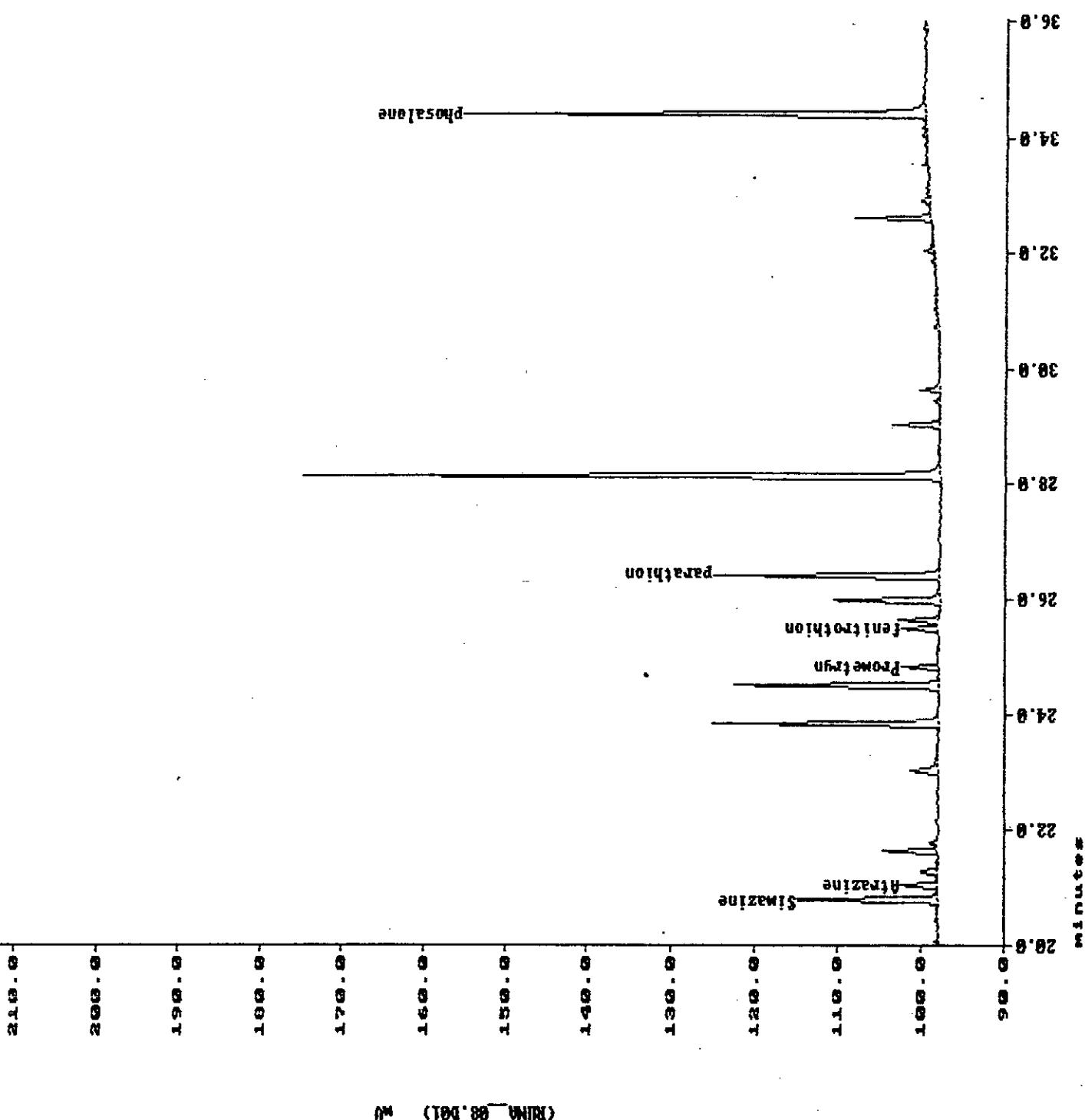


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Collection : 18:34:58 Sep 18 1992 Method : BCORT [14:22:55 Sep 18 1992]
Run : 81 Queue : DOUG Set Number : 1 Type : Sample
Title : RUN#_81.DAT Author : cd Date : 8.0.92

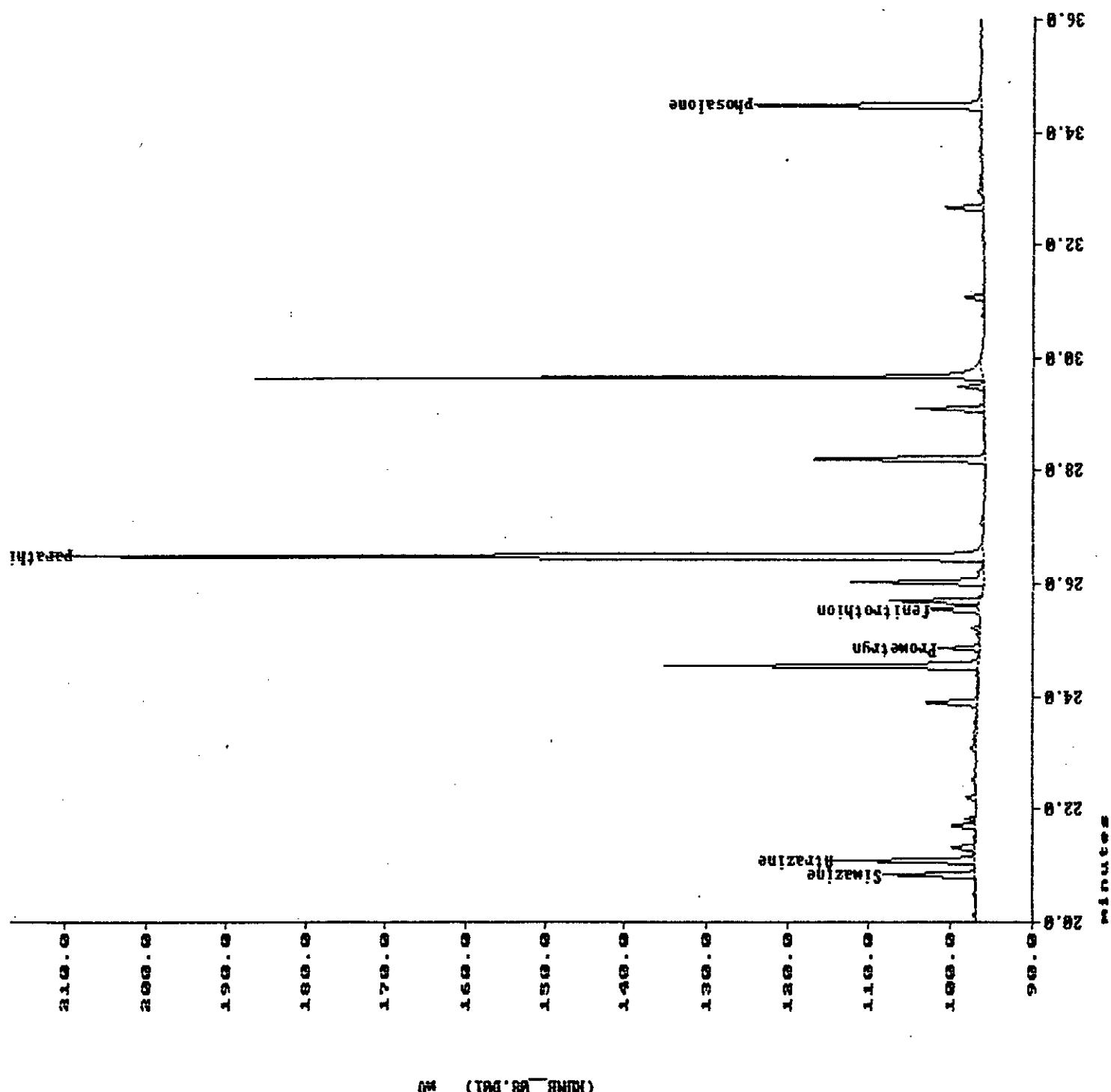


File : MINES_87.DAT Queue : DOUG Set Number : 1 Type : Sample
Run : 01 Method : BCROPT [19:22:55 Sep 18 1992] [14:22:55 Sep 18 1992]



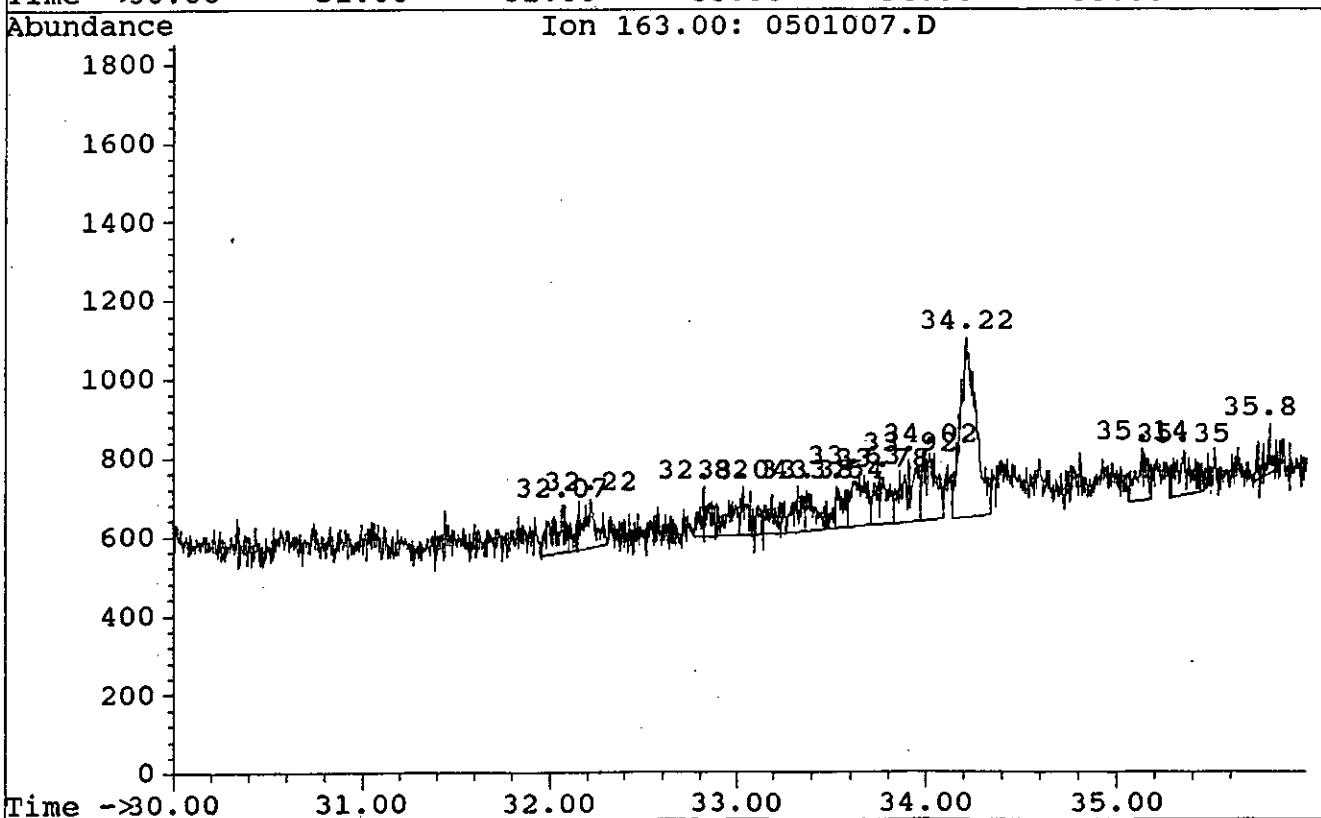
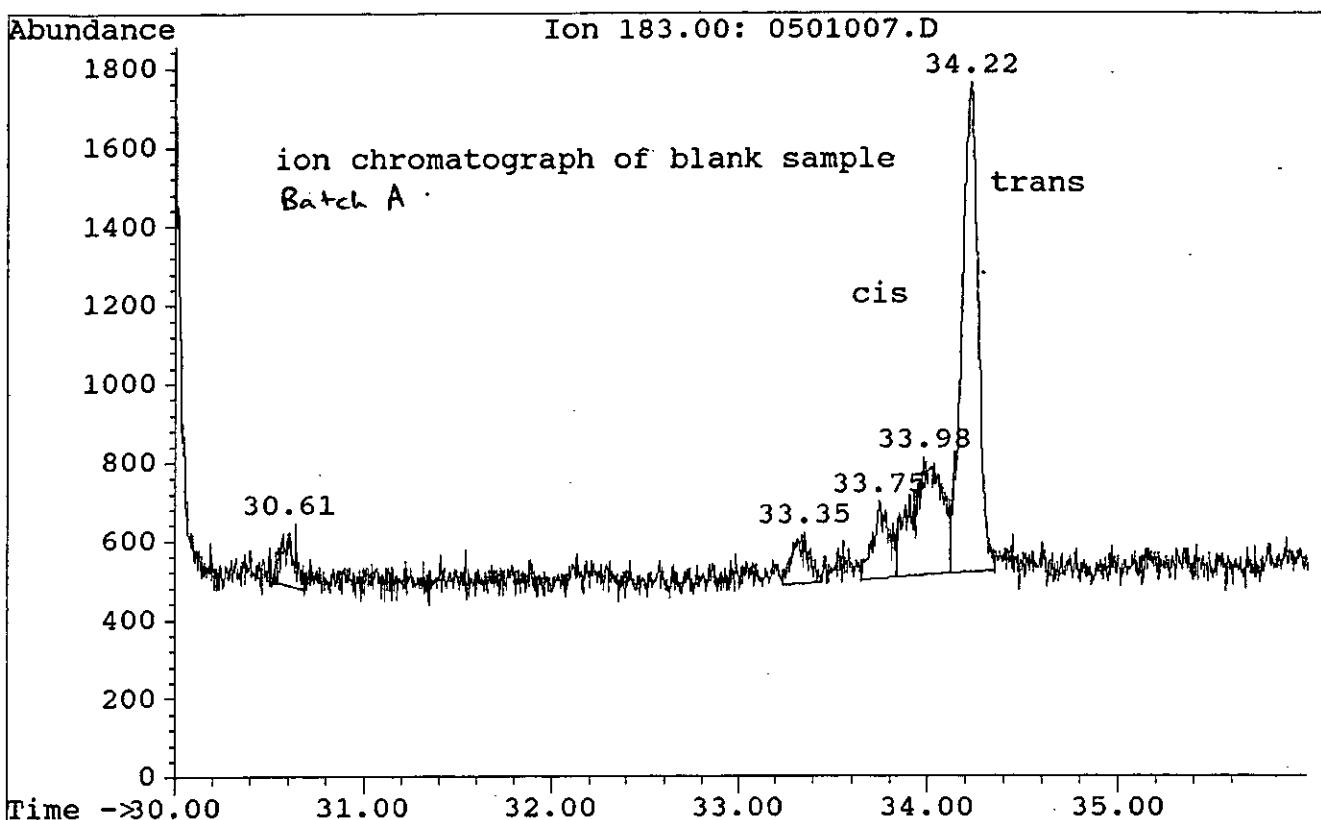
(WINA_88.DAT) NO

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 Run : 01 Collection : 22:46:39 Sep 08 1992 Method : OPTIMA I 10:18:12 Sep 03 1992]
 "D01C"

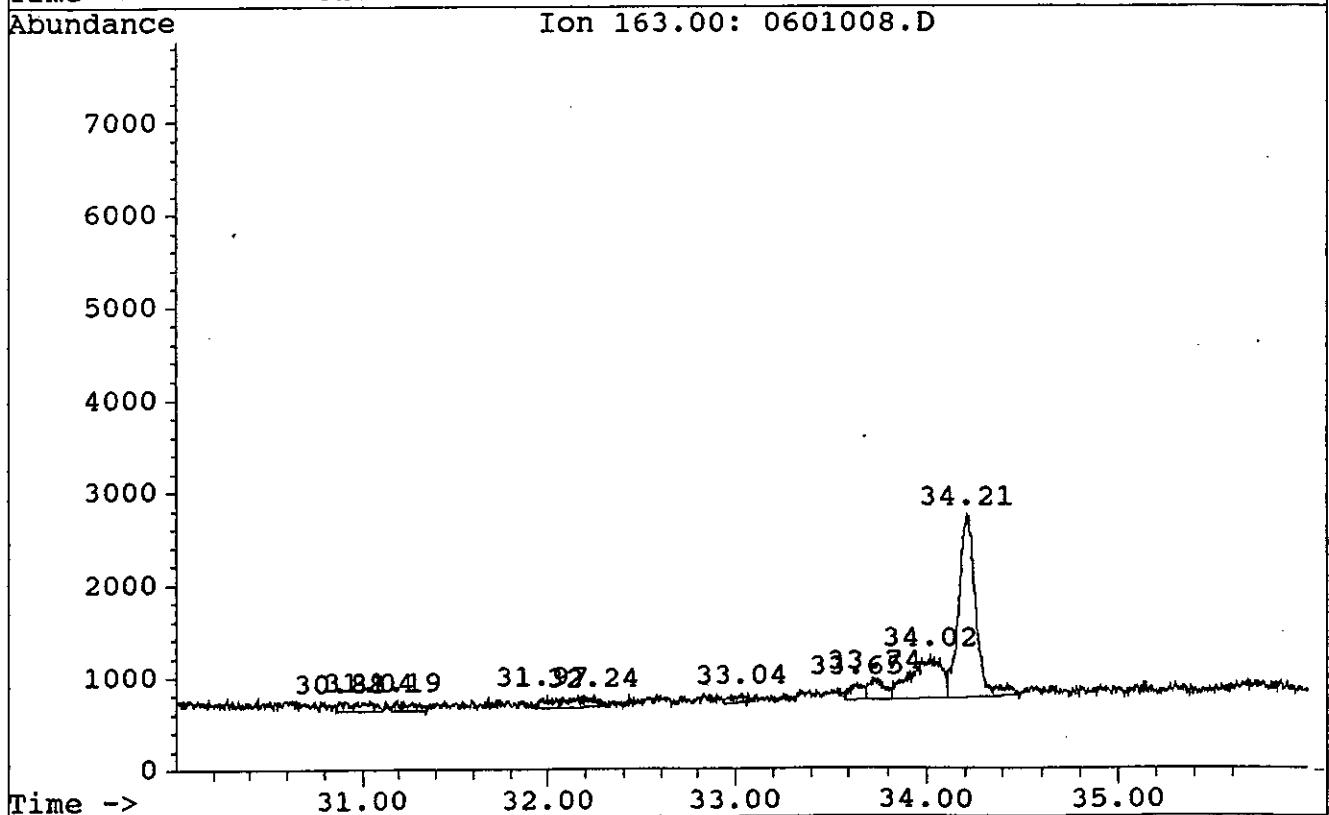
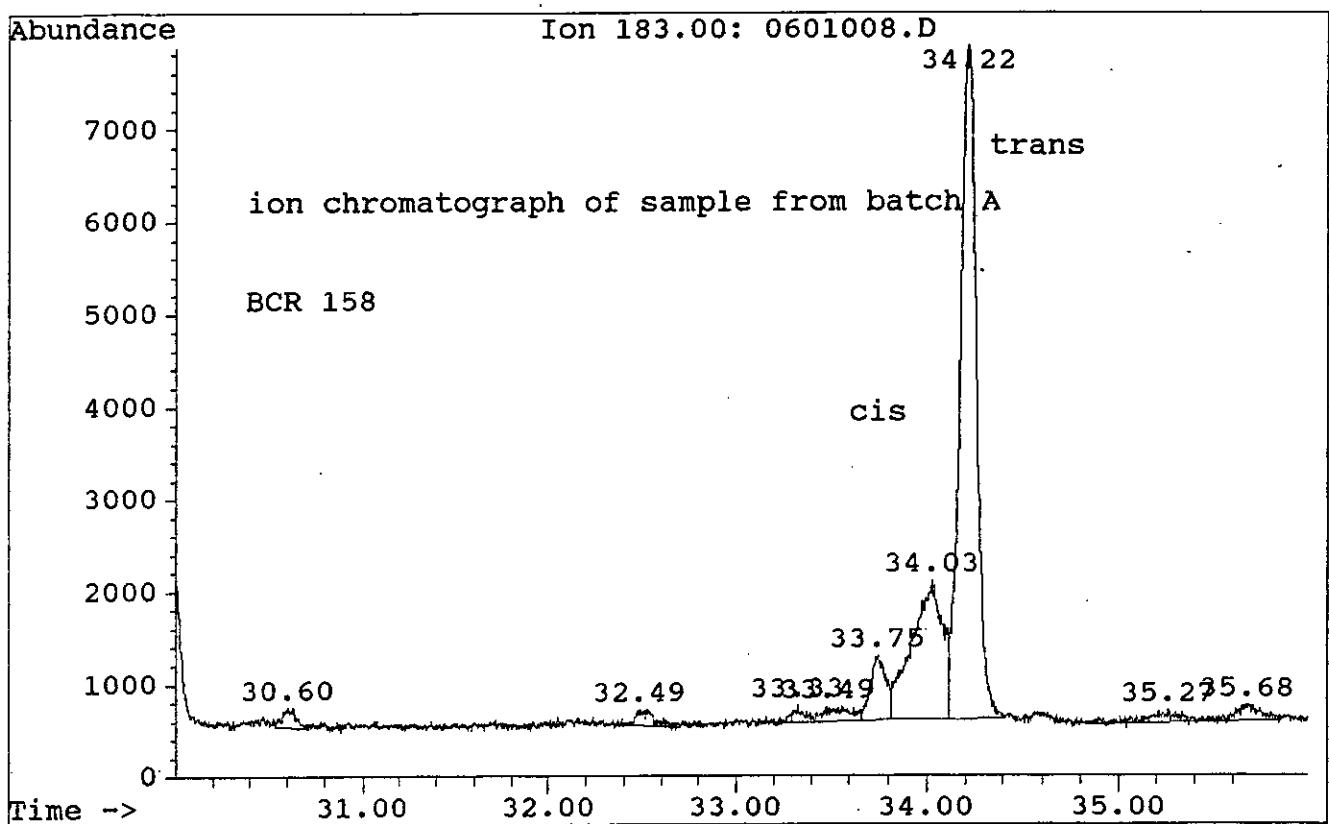


Batch : RUNS_98.DAT Date : 10/09/98 Queue : DOUG Set Number : 1 Type : Sample
 Run : 01 Method : BC9169 Report : 14:22:55 Sep 18 1992 Collection : 20:10:54 Sep 18 1992

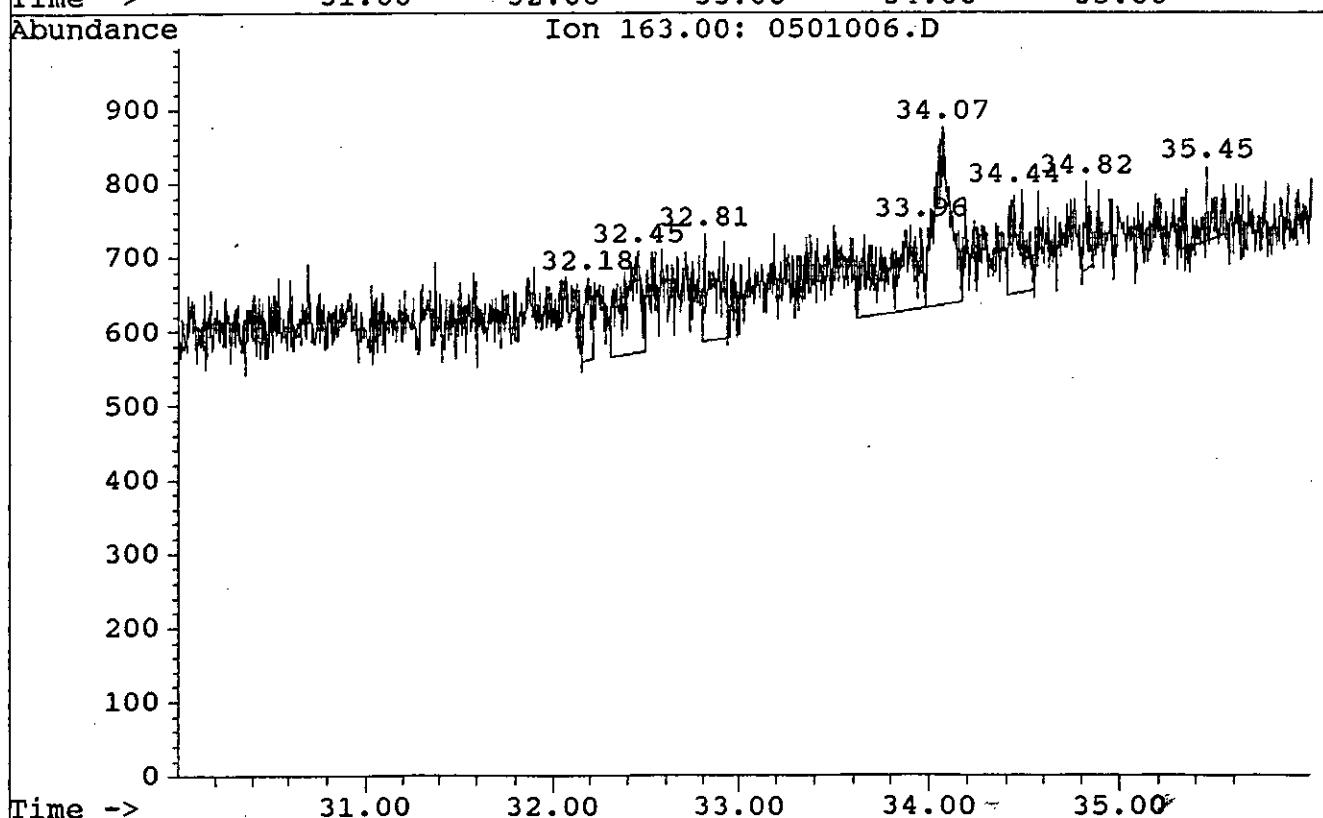
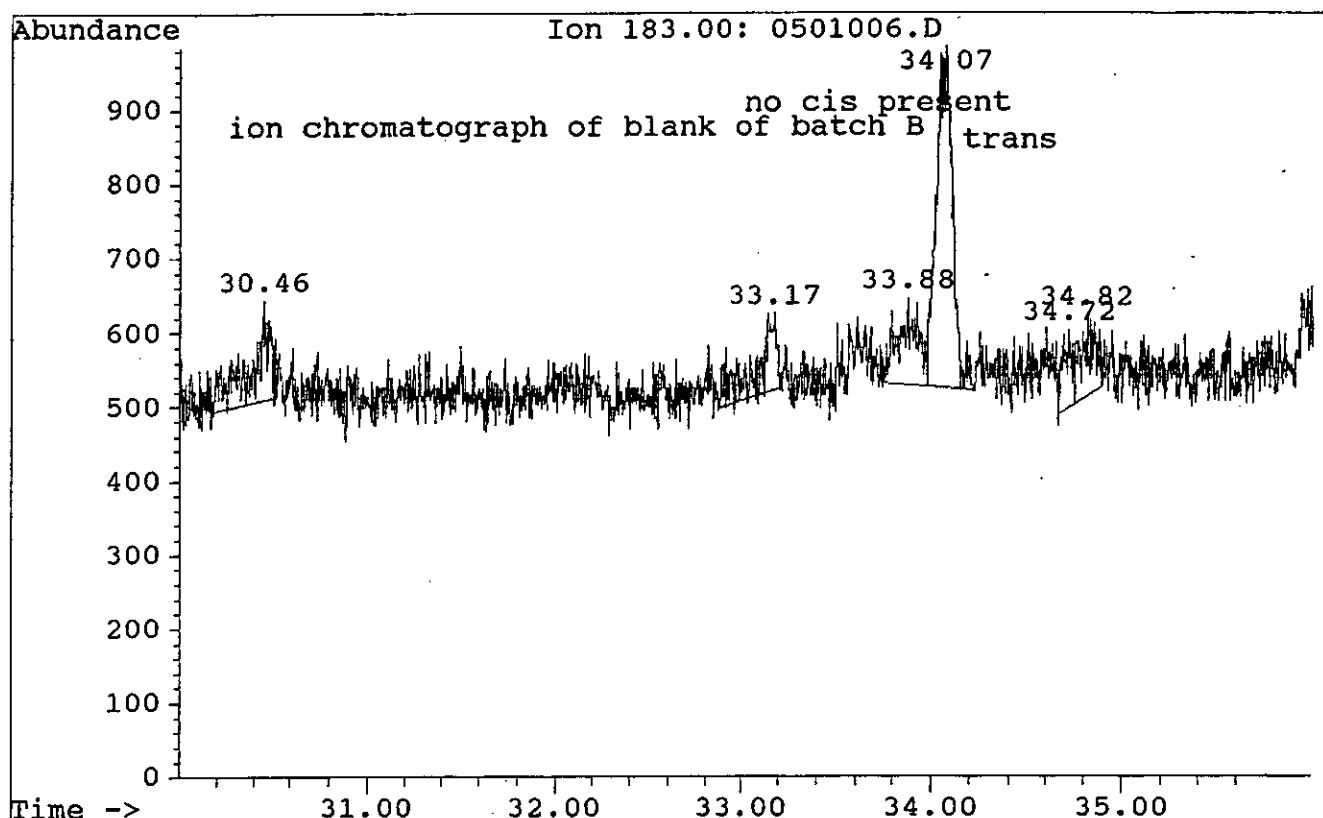
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Operator: wah
Date Acquired: 18 Sep 92 3:18 pm
Method File: permalan.M
Sample Name: blank
Misc Info:
ALS vial: 5



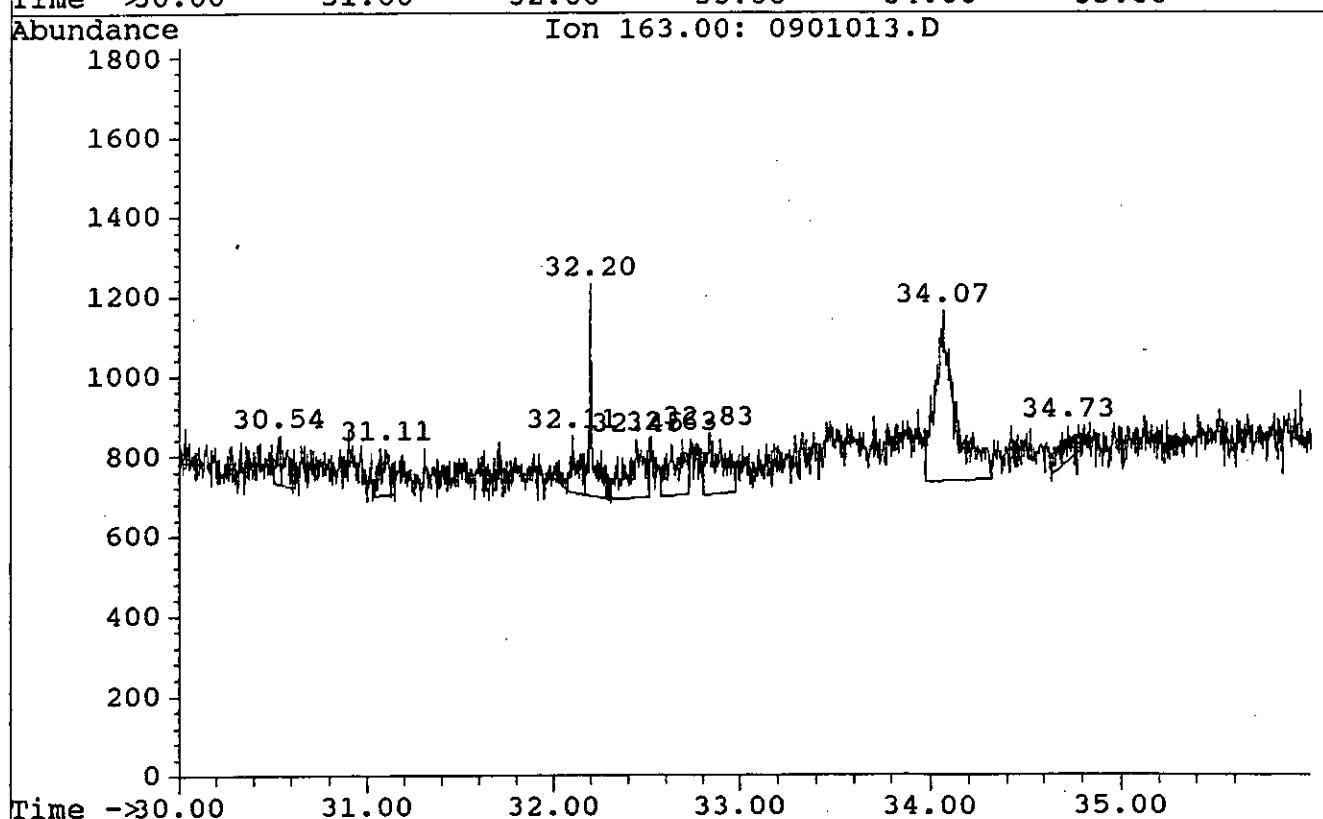
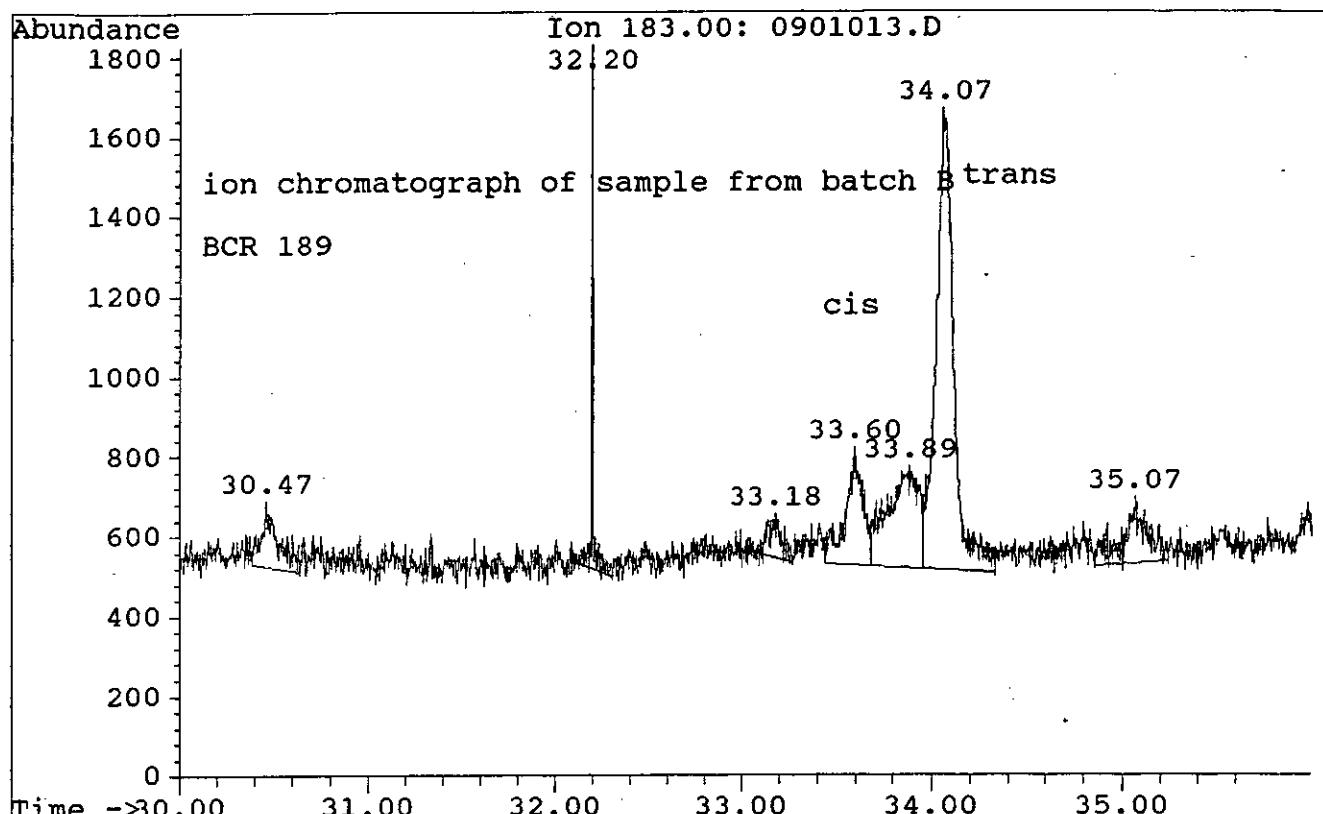
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Operator: wah
Date Acquired: 18 Sep 92 4:16 pm
Method File: permalan.M
Sample Name: 158
Misc Info:
ALS vial: 6



File: C:\CHEMPC\DATA\BCR4\0501006.D
Operator: wah
Date Acquired: 19 Sep 92 7:25 pm
Method File: permalan.M
Sample Name: blank
Misc Info:
ALS vial: 5



File: C:\CHEMPC\DATA\BCR4\0901013.D
Operator: wah
Date Acquired: 20 Sep 92 2:10 am
Method File: permalan.M
Sample Name: 189
Misc Info:
ALS vial: 9



BCR INTERCALIBRATION OF PESTICIDES IN TWO BATCHES OF LYOPHILISED
WATER (A and B)

Protocol for reporting the results

1.General

- 1.1. Five independent analyses should be done. One from each of the five bottles for each batch (Batch A and B) by adequate chromatographic technique (GC or LC) with an appropriate detector.
- 1.2 An estimation of the recovery of the pesticides from one liter of water will be made by a standard addition of a known amount of each pesticide or by reextraction. The final concentration of pesticides spiked in the water varies between 0.1-10 ppb. It is recommended that this recovery is estimated at least in triplicate.
- 1.3. The pesticides which will be determined are: Carbaryl, Atrazine, Simazine, Fenitrothion, Parathion-ethyl, Fenamiphos, Propanil, Linuron. Although the lyophilised water showed inhomogeneity for Permethrin, its concentration can be estimated.
- 1.4. Reconstitution of the freeze-dried water samples
The reconstitution process will be performed according to the reconstitution method given in annex 2 of the minutes of the meeting held in Brussels on the 19 February 1992. It should be considered that the amounts of freeze-dried water corresponding to one liter sample are:
for batch A..... 2.461 g
for batch B..... 2.663 g
for blank..... 2.268 g
- 1.5 The analyses will be performed by an extraction, clean-up and fractionation method chosen by the laboratory given in the proposal work.
- 1.6. The final determinations will be made by capillary GC or LC using an appropriate detector.
- 1.7. In gas chromatography at least two columns of different polarity or different detectors must be used to confirm the identity and purity of each pesticide. The choice of the columns and detectors is left to the participants. For HPLC the use of two columns is recommended.
- 1.8. For GC analysis at least one internal standard will be used for the final determination. For HPLC the use is recommended.

- 1.9. In addition to the attached forms being completed the participants will provide the following:
- a) a linearity plot of peak height/mass injected against mass injected for each pesticide
 - b) a chromatogram of the own standard solution
 - c) a chromatogram of the sample
 - d) a chromatogram of the blank

1.10. All basic data should be provided on the forms supplied. The results should be given with at least three significant figures. Additional information is welcomed, but should be appended in an annex to the forms supplied.

1.11. All reports to be in Brussels before 1 October 1992.

Annex 1

PROCEDURE

0 Tick with x if appropriate

1 SAMPLE INTAKE FOR RECONSTITUTION (POWDER AND WATER) 0

Blank sample: 2.000 g 1000 ml Hplc grade water
Batch A 2.400 ± 0.001 g 1000 ml Hplc grade water
Batch B 2.400 ± 0.001 g 100 ml Hplc grade water

2 EXTRACTION

2.1 - Sample size 960 ml

2.2 - Internal standard for extraction efficiency

. compound Prometryn
. quantity 0.5 ug ng
. final concentration in sample 0.5 ng/g ng/g

2.3 - Extractant(s) Octadecyl C18 extraction disks

2.4 - Volume of extractant(s)

1st step ml

2st step ml

3st step ml

2.5 - Solid phase extraction

- . off line ✓
- . on line
- . material used

2.6 - Mixing during extraction(s)

- . shaking by hand ✓ 0
- . ultrasonic 0
- . mechanical 0
- . soxhlet 0

2.7 - Drying of the raw extract (specify) 0

. Sodium sulphate column dried at 160°C
...and eluted with ethyl acetate
.....

2.8 - Concentration of the raw extract (specify) 0

...Nitrogen... oxygen... water free...
surface of solvent
.....

2.9 - Final volume of the raw extract....2.3.....ml

Concentration sample in extractant.....mg/ml

2.10 - Remarks

.....
.....
.....

3 CLEAN UP OF THE RAW EXTRACT None

- GPC 0

- . type of column:
- . eluent:
- flow rate: ml/min
- . volume (main) fraction(s): 1st ml
- 2st ml
- 3st ml

- HPLC (specify) 0

- . adsorbent:
- . eluent:
- flow rate: ml/min
- . volume (main) fraction(s): 1st ml
- 2st ml
- 3st ml

- column chromatography (specify) 0

- . adsorbent
 - Florisil (specify) 0
 -
- Silicagel (specify) 0
-

Alumina (specify) 0

.....

Other(s) (specify) 0

.....

. eluent(s) (specify): 1st
2st
3st

. volume fraction(s): 1stml
2stml
3stml

- Other(s) (specify) 0
.....
.....

- remarks
.....
.....

3.1 Amount of sample used for clean-up:mg

4 CONCENTRATION OF THE FRACTION(S):

. rotary evaporation 0
. open flask evaporation 0
temperature:°C
. adsorption/elution (specify) 0
.....
.....
.....

4.1 Final volume fraction(s): 1st fraction.....ml
2st fractionml
3st fractionml

5 STORAGE OF THE EXTRACT BEFORE ANALYSIS

- . glass
- . quarts 0
- . polymers (specify) 0

5.1 Temperature 6...°C

Light conditions (specify) ..dark.....
.....
.....

6 FINAL ANALYSIS (see for detailed reporting 7.)

- . GC:
: capillary columns
- . LC: 0
.....
.....

6.1 Use Internal Standard for GC analysis 0

- . name: ..~~Phenol~~.....
- . concentration in final fraction ..~~0.4~~.....^Mµg/ml

6.2 Eventual dilutions 0

- 1st fraction
- 2st fraction
- 3st fraction

GAS CHROMATOGRAPHY

GC Column No.: DB-S
1225032

| | 1 | 2 | 3 |
|-------------------------------|------------|---------------------|-------|
| Quantitative Determ. | 0 | 0 | 0 |
| <u>Column characteristics</u> | | | |
| - Length (m) | ...30..... | ...30..... | |
| - Glass column | 0 | 0 | 0 |
| - Fused silica | X | X | 0 |
| - Int. diameter (mm) | .0.252... | ...0.252... | |
| - stationary phase | ...DB5... | ...DB5... | |
| - Chemical bonded | X | X | 0 |
| - Load (%) | | | |
| - Film thickness (um) | 0.25..... | 0.25.... | |
| - Support type | | | |
| - Particle size (mesh) | | | |
| <u>Carrier gas type</u> | | | |
| - Flow (ml/min) | ..50..... | 50..... | |
| <u>Make-up gas type</u> | | | |
| - Flow (ml/min) | ..30..... | 160..... | |
| <u>Injector temp. (°C)</u> | | | |
| | ...300.... | ..100→250 (PTV).... | |
| <u>Detector temp. (°C)</u> | | | |
| | ..350.... | 300..... | |
| <u>Column temp. (°C)</u> | | | |
| | ..450.... | 100..... | |

Temperature Program

| | | | |
|------------------------|-------|-------|-------|
| - Isoth. temp. (°C) | 0 | 0 | 0 |
| period (min) | 50 | 100 | |
| - Progr. rate (°C/min) | 20 | 5 | |
| period (min) | 10 | | |
| - Isoth. temp. (°C) | 220 | 240 | |
| period (min) | 0 | 0 | |
| - Progr. rate (°C/min) | 5 | 30 | |
| period (min) | | | |
| - Isoth. temp. (°C) | 285 | 290 | |
| period (min) | 17 | 10 | |
| | 30 | | |

Injections

| | | | |
|------------------------|-------|-------|-------|
| - On-column injection | 0 | 0 | 0 |
| - Splitless injection | X | X | 0 |
| - Split closing (min) | 0.5 | 1 | |
| - Split injection | 0 | 0 | 0 |
| - Split ratio | | | |
| - Injected volume (ul) | 1.5 | 1.5 | |

GLC apparatus (type)

(1) P-E 8700 ... 8700
 (2) HP 5871A
 MSID

Precolumn systems

(specify)

Detection

| | | | |
|--------------------|------------------------------|-------|-------|
| - M.S. (type) | M.S. 5871A mass-selective | | |
| - Electron capture | X | 0 | 0 |

| | | | |
|-----------------------|---|---|---|
| - Nitrogen phosphorus | 0 | X | 0 |
| - Others (specify) | 0 | 0 | 0 |

.....

Quantitation

| | | | |
|-------------|---|----------------|---|
| Peak height | 0 | Peak area | X |
| Manually | 0 | Electronically | X |

Integration over whole chromatogram 0

Internal standard: 0.4 mg/ml ... External standard 0.05, 0.5, 1 mg/ml

How many points (different concentrations for each compound in your standard Solutions) were used for the calibration curve?

| | | | |
|------------|---|------------|---|
| 1 (+ zero) | 0 | 3 (+ zero) | X |
| 2 (+ zero) | 0 | more | 0 |

Nr.....

METHOD 3 OPTIMA

DATE LAST WRITTEN 6/09/02

SECTION 1 GC CONTROL

| | 1 | 2 | 3 |
|-----------------------|-----|------|------|
| OVEN TEMP (DEG C) | 100 | 240 | 290 |
| ISO TIME (MIN) | 1.0 | 0.0 | 10.0 |
| RAMP RATE (DEG C/MIN) | 5.0 | 30.0 | |

NPD 1 SENS HIGH
 NPD 1 BEAD 3
 NPD 1 ZERO ON
 ECD 2 ZERO ON

INJ 2 TEMP 290
 DET 1 TEMP 300
 DET 2 TEMP 350

CARRIER 1 15.0 PSIG
 CARRIER 2 15.0 PSIG

EQUILIB TIME 0.0 MIN
 TOTAL RUN TIME 40.6 MIN

SECTION 2 TIMED EVENTS

| TIME | DET | EVENT |
|--------|-----|--------------|
| - 3.00 | 1 | NPD OPTIM |
| - 2.00 | | RELAY 0 ON |
| 0.01 | | PTV TEMP 100 |
| 1.00 | | RELAY 0 OFF |
| 1.01 | | PTV TEMP 250 |
| 2.00 | | RELAY 0 ON |
| 5.00 | | PTV TEMP 150 |

SECTION 3 DATA HANDLING

DATA ACQUISITION 1

REPORT 1

| | | | |
|---------------|-----------|---------------|----------|
| ENABLED | YES | REPORT TYPE | SEPARATE |
| START TIME | 0.00 MIN | CALC TYPE | % |
| END TIME | 40.66 MIN | CALIB FIT | ZERO |
| WIDTH | -4 | AREA/HT CALC | AREA |
| SKIM SENS | 0 | OUTPUT | |
| BASELINE CORR | V-V | PRINT TOL | 0.0000 |
| AREA SENS | 350 | SCREEN | YES |
| BASELINE SENS | 12 | PRINTER | NO |
| | 40 | NO PEAK ALARM | NO |

PEAK IDENTIFICATION 1

QUANTITATION 1

| | |
|------------------|----------|
| UNRETD PEAK TIME | 0.00 MIN |
| AREA/HT REJECT | 0.0000 |
| MULTIPLE REF PK | NO |
| REF PK: TIME | 0.00 MIN |
| TIME TOL | 0.10 MIN |

| | |
|----------------|--------|
| SCALING FACTOR | 1.0000 |
|----------------|--------|

SECTION 3 DATA HANDLING

DATA ACQUISITION 2

REPORT 2

| | | | |
|----------------|-----------|---------------|--------|
| ENABLED | NO | CALC TYPE | % |
| START TIME | 0.00 MIN | CALIB FIT | ZERO |
| END TIME | 40.66 MIN | AREA/HT CALC | AREA |
| WIDTH | -4 | OUTPUT | |
| SKIM SENS | 0 | PRINT TOL | 0.0000 |
| BASELINE CORR | V-V | SCREEN | YES |
| AREA SENS | 350 | PRINTER | NO |
| BASELINE SENS. | 12 | NO PEAK ALARM | NO |

PEAK IDENTIFICATION 2

QUANTITATION 2

| | | | |
|------------------|----------|----------------|--------|
| UNRETD PEAK TIME | 0.00 MIN | SCALING FACTOR | 1.0000 |
| AREA/HT REJECT | 0.0000 | | |
| MULTIPLE REF PK | NO | | |
| REF PK: TIME | 0.00 MIN | | |
| TIME TOL | 0.10 MIN | | |

METHOD 2 PERMETHRIN DATE LAST WRITTEN 6/09/14

SECTION 1 GC CONTROL

| | 1 | 2 | 3 | 4 |
|-----------------------|------|-----|------|------|
| OVEN TEMP (DEG C) | 50 | 220 | 285 | 300 |
| ISO TIME (MIN) | 2.0 | 0.0 | 17.0 | 10.0 |
| RAMP RATE (DEG C/MIN) | 20.0 | 5.0 | 30.0 | |

NPD 1 SENS LOW
NPD 1 BEAD OFF
NPD 1 ZERO OFF
ECD 2 ZERO ON

INJ 2 TEMP 300
DET 1 TEMP OFF
DET 2 TEMP 350

CARRIER 1 15.0 PSIG
CARRIER 2 15.0 PSIG

EQUILIB TIME 0.0 MIN
TOTAL RUN TIME 51.0 MIN

SECTION 2 TIMED EVENTS

| TIME | DET | EVENT | |
|--------|-----|-----------|-----|
| - 1.00 | | RELAY 2 | ON |
| - 0.50 | 2 | ATTN | 64 |
| - 0.10 | | RELAY 2 | OFF |
| 0.50 | | RELAY 2 | ON |
| 10.00 | 2 | INTEG | ON |
| 11.00 | 2 | BASE CODE | V-V |

SECTION 3 DATA HANDLING

DATA ACQUISITION 1

REPORT 1

| | | | |
|---------------|-----------|---------------|----------|
| ENABLED | NO | REPORT TYPE | SEPARATE |
| | | CALC TYPE | % |
| START TIME | 0.00 MIN | CALIB FIT | ZERO |
| END TIME | 51.00 MIN | AREA/HT CALC | AREA |
| WIDTH | 4 | OUTPUT | |
| SKIM SENS | 0 | PRINT TOL | 0.0000 |
| BASELINE CORR | B-B | SCREEN | YES |
| AREA SENS | 200 | PRINTER | NO |
| BASELINE SENS | 4 | NO PEAK ALARM | NO |

PEAK IDENTIFICATION 1

QUANTITATION 1

| | | | |
|------------------|----------|----------------|--------|
| UNRETD PEAK TIME | 0.00 MIN | SCALING FACTOR | 1.0000 |
| AREA/HT REJECT | 0.0000 | | |

MULTIPLE REF PK

NO

REF PK: TIME 0.00 MIN
TIME TOL 0.10 MIN

SECTION 3 DATA HANDLING

DATA ACQUISITION 2

ENABLED YES
START TIME 0.00 MIN
END TIME 51.00 MIN
WIDTH -4
SKIM SENS 0
BASELINE CORR V-V
AREA SENS 350
BASELINE SENS 12

REPORT 2

| CALC TYPE | % |
|--------------|------|
| CALIB FIT | ZERO |
| AREA/HT CALC | AREA |

OUTPUT
PRINT TOL 0.0000
SCREEN YES
PRINTER NO
NO PEAK ALARM NO

PEAK IDENTIFICATION 2

UNRETD PEAK TIME 0.00 MIN
AREA/HT REJECT 0.0000
MULTIPLE REF PK NO
REF PK: TIME 0.00 MIN
TIME TOL 0.10 MIN

QUANTITATION 2

SCALING FACTOR 1.0000