

3791



## UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, D.C. 20460

Analytical Chemistry Section  
Building 306, BARC-East  
Beltsville, Maryland 20705

SEP 14 1995

OFFICE OF  
PREVENTION, PESTICIDES AND  
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Glyphosate Trimesium in or on Corn, Soybeans, Citrus Fruit, Stone Fruit and the Nut Crop Group (except Almonds). (MRID#s: 432736-04 and -05. Barcode D216509. Chemical No 128501. CBTS# 15715.)

FROM: Douglas Swineford, Chemist *DS*  
Analytical Chemistry Section

THRU: Harvey K. *Harvey K. Hundley* Hundley, Head  
Analytical Chemistry Section

THRU: Donald A. Marlow, Chief *DM*  
Analytical Chemistry Branch  
Biological and Economic Analysis Division (7503W)

TO: F. D. Griffith, Acting Section Head  
Tolerance Petition Section III  
Chemistry Branch I, Tolerance Support  
Health Effects Division (7509C)

Introduction

The Analytical Chemistry Laboratory (ACL) validated the method: "Determination of Residues of the Trimethylsulfonium Cation in Agricultural Crops by Gas Chromatography" (Study Number GLYP-93-AM-04/Document Number RR93-105B). The matrices validated were pecans, corn grain, corn fodder, soybean seed and oranges.

Method Summary

The samples were extracted with an aqueous phosphate buffer and filtered. The extract is treated with basic anion-exchange resin to neutralize acids followed by phenylisocyanate and barium hydroxide to remove amino acids. The samples were cleaned up with cation-exchange resin and dealkylated prior to quantitation by gas chromatography (GC) using a flame photometric detector (FPD).

Comments

1. Two experienced chemists can process a set of six samples in 12 hours, excluding the optional thermal cleanup (sec. 3.5) that may be necessary for some matrices. GC analysis time is approximately 5 minutes per injection.
2. The limit of detection from visual inspection of the chromatograms is estimated to be 0.01 ppm for the matrices tested.
3. No special safety hazards were noticed. Normal laboratory safety procedures were followed.
4. Standards were obtained from the registrant (Zeneca Ag Products, Richmond, CA 94840-0023). The EPA standards repository in RTP, North Carolina indicated they have a small amount of the standard available.
5. ACL has received various analytical methods this year for the validation of the trimethylsulfonium cation from Zeneca Ag Products for multiple raw agricultural commodities. Has the registrant considered the feasibility of combining the various approaches into a single method?
6. If the above comments are taken into consideration and incorporated with additional comments noted in the laboratory pre-review, the method would meet 40 CFR 158 and EPA's requirements as published in the Pesticide Assessment Guidelines, Subdivision "O" for Residue Chemistry, Part 171-4(b) as an enforcement method.
7. Recovery data, example chromatograms, pre-review checklist and pre-review comments are attached.

*See pre-review  
comments*

VALIDATION REPORT TRIMETHYLSULFONIUM CATION (TMS)

| <u>Commodity</u> | <u>Chemical<br/>Added</u> | <u>PPM<br/>Added</u> | <u>PPM<br/>Found</u> | <u>%Recovery</u> |
|------------------|---------------------------|----------------------|----------------------|------------------|
| Corn Grain       | Control                   | 0                    | N.D.*                | ---              |
|                  | Control                   | 0                    | N.D.*                | ---              |
|                  | TMS                       | 0.05                 | 0.0463               | 92.6             |
|                  | TMS                       | 0.05                 | 0.0465               | 93.0             |
|                  | TMS                       | 0.10                 | 0.0854               | 85.4             |
|                  | TMS                       | 0.10                 | 0.0820               | 82.0             |

\* N.D. = &lt; 0.01 ppm

| <u>Commodity</u> | <u>Chemical<br/>Added</u> | <u>PPM<br/>Added</u> | <u>PPM<br/>Found</u> | <u>%Recovery</u> |
|------------------|---------------------------|----------------------|----------------------|------------------|
| Corn Fodder      | Control                   | 0                    | N.D.*                | ---              |
|                  | Control                   | 0                    | N.D.*                | ---              |
|                  | TMS                       | 0.10                 | 0.1030               | 103              |
|                  | TMS                       | 0.10                 | 0.1021               | 102              |
|                  | TMS                       | 1.0                  | 1.0119               | 101              |
|                  | TMS                       | 1.0                  | 0.8960               | 89.6             |
|                  | TMS                       | 2.0                  | 1.9367               | 96.8             |
|                  | TMS                       | 2.0                  | 1.8282               | 91.4             |

N.D.\* = &lt; 0.01 ppm

VALIDATION REPORT TRIMETHYLSULFONIUM CATION (TMS) (continued)

| <u>Commodity</u> | <u>Chemical<br/>Added</u> | <u>PPM<br/>Added</u> | <u>PPM<br/>Found</u> | <u>%Recovery</u> |
|------------------|---------------------------|----------------------|----------------------|------------------|
| Soybean Seed     | Control                   | 0                    | N.D.*                | ---              |
|                  | Control                   | 0                    | N.D.*                | ---              |
|                  | TMS                       | 0.05                 | 0.0426               | 85.2             |
|                  | TMS                       | 0.05                 | 0.0478               | 95.6             |
|                  | TMS                       | 0.50                 | 0.4017               | 80.3             |
|                  | TMS                       | 0.50                 | 0.4447               | 88.9             |
|                  | TMS                       | 1.0                  | 0.9494               | 94.9             |
|                  | TMS                       | 1.0                  | 0.9743               | 97.4             |

\* N.D. = &lt; 0.01 ppm

| <u>Commodity</u> | <u>Chemical<br/>Added</u> | <u>PPM<br/>Added</u> | <u>PPM<br/>Found</u> | <u>%Recovery</u> |
|------------------|---------------------------|----------------------|----------------------|------------------|
| Oranges          | Control                   | 0                    | N.D.*                | ---              |
|                  | Control                   | 0                    | N.D.*                | ---              |
|                  | TMS                       | 0.05                 | 0.0450               | 90.0             |
|                  | TMS                       | 0.05                 | 0.0437               | 87.4             |
|                  | TMS                       | 0.50                 | 0.5290               | 106              |
|                  | TMS                       | 0.50                 | 0.5050               | 101              |
|                  | TMS                       | 1.0                  | 1.1752               | 118              |
|                  | TMS                       | 1.0                  | 1.1115               | 111              |

\* N.D. = &lt; 0.01 ppm

VALIDATION REPORT TRIMETHYLSULFONIUM CATION (TMS) (continued)

| <u>Commodity</u> | <u>Chemical<br/>Added</u> | <u>PPM<br/>Added</u> | <u>PPM<br/>Found</u> | <u>%Recovery</u> |
|------------------|---------------------------|----------------------|----------------------|------------------|
| Pecans           | Control                   | 0                    | N.D.*                | ---              |
|                  | Control                   | 0                    | N.D.*                | ---              |
|                  | TMS                       | 0.05                 | 0.0510               | 102              |
|                  | TMS                       | 0.05                 | 0.0544               | 109              |
|                  | TMS                       | 0.10                 | 0.1070               | 107              |
|                  | TMS                       | 0.10                 | 0.1026               | 103              |

\* N.D. = < 0.01 ppm

Modifications to method:

None.

Special precautions to be taken:

Handle all chemicals in a safe manner.

Source of analytical standard:

Zeneca Ag Products, Richmond, CA 94804-0023.

If derivatized standard, give source:

N/A

Instrument for quantitation:

GC/FPD

Instrument for confirmation:

N/A

If instrument parameters differ from those given in method, list parameters used:

N/A

Commercial sources of any special chemicals of apparatus:

N/A

Additional comments:

See report.

Chromatograms:

Copies attached.

TMV Pre-Review of Glyphosate- Trimesium

Reviewed By: Dallas Wright, Jr. *DW*

Date: June 15, 1995

Laboratory Assignment Number: B95-34,36,37,38,39

Analyte: Trimethylsulfonium Cation

Commodities: Pecans, Corn grain, <sup>*Corn Fodder*</sup> ~~Soybean Hay~~, Soybean Seed, and Oranges

Petitioner: Zeneca Ag Products

Method: "Determination of Residues of the Trimethylsulfonium Cation in Agricultural Crops by Gas Chromatography;" Dec. 30, 1993; RR 93-105B

Section 3: Analytical Procedure

3.2.2: In the note for this step there are suggestions for filtering the extract; however, there is no filtration step in the extraction for oily crops.

3.3.5: Is it necessary to continue the evacuation of the flask for 1-2 minutes as in step 3.3.4? Should the filter cake be removed before the second filtration? *(DWS: ACS what they did + with registration equipment)*

3.5 Thermal Cleanup: Normally ACL safety regulations do not allow overnight heating or extractions. However, this step should be included in the validation. Is it possible to reduce the time to 8 or 9 hours? *(1)*

3.6 Dealkylation: 1) Since the toluene is added before the sample is heated, it is possible that the volume will change due to leaking during the heating. Since there is only 0.5 to 1 ml of toluene to start with, a small loss during heating could result in a large percentage change to the final volume used for calculations.

Section 5: Calculations: The instructions are misleading and seem to indicate that it would be appropriate to use the average response factor when using an FPD. The average response factor method for calculating cannot be used when the samples are quantitated on an FPD in sulfur mode, since the response is not linear. The method should clearly state that the analyst must use either a linear regression based on the square root of the response or closely match standard and sample responses.

Section 8.4 Lower Limit of Quantitation: 1) The LOQ for this method is 0.05 ppm for food crops and 0.1 ppm for feed items.

Section 9 Conclusions: The method has not been tested for samples less than the LOQ and greater than 10 times the LOQ. Some of the requested spiking levels are greater than 10 times the LOQ. The following table summarizes the data for each commodity requested, the LOQ, and the requested spiking levels:

| Commodity    | LOQ (PPM) | 10x LOQ (PPM) | Data Provided (PPM) | Requested Levels (PPM) |
|--------------|-----------|---------------|---------------------|------------------------|
| Pecans       | 0.05      | 0.5           | 0.05; 0.1           | 0.05; 0.10             |
| Corn Grain   | 0.05      | 0.5           | 0.05; 0.5           | 0.05; 0.10             |
| Corn Fodder  | 0.1       | 1.0           | 0.1; 1.0            | 0.1; 1.0; 2.0          |
| Soybean Seed | 0.1       | 1.0           | 0.05; 0.1           | 0.05; 0.5; 1.0         |
| Oranges      | 0.05      | 0.5           | 0.05; 0.09; 0.23    | 0.05; 0.5; 1.0         |

Recovery Data: Not all recovery data was within the range of 70-120%. The following list summarizes the data: Pecans: 62-112%; Corn grain: 81-118%; Corn Fodder: 85-115%; Soybean seed: 74-110%; Oranges: 104-125%

ILV Data: The Independent Laboratory Validation was run by Morse Laboratories, Inc. on corn grain (0.05 and 0.5 ppm), forage (0.1, and 1.0 ppm), and fodder (0.1, and 1.0 ppm). Acceptable recoveries were obtained on the first set of samples run.

ANALYTICAL CHEMISTRY BRANCH  
SCREEN FOR RESIDUE METHODS FOR TMV

1. LABORATORY ASSIGNMENT NUMBER: B95-34, 36-39
2. PP#: 9F03796, 0F03866, 3F04238, 4F04343
3. TECHNICAL REVIEWER: Dallas Wright, Jr.
4. DATE: June 19, 1995
5. ANALYTES/LEVEL: See Review
6. COMMODITIES: Pecans, Corn Grain, Corn Fodder, Soybean Seed, Oranges
7. METHOD: Determination of Residue of the Trimethylsulfonium Cation in Agricultural crops by Gas Chromatography

The Analytical Chemistry Section has been asked to screen the residue chemistry methods submitted by the registrant in order to determine if they contain the essential requirements identified in the Residue Chemistry Guidelines. Full scientific review and laboratory evaluation of those methods will take place after the initial screen. The following items need to be resolved before the analytical method can be evaluated.

- |                                                                                                                                                  | <u>YES</u>  | <u>NO</u>   |
|--------------------------------------------------------------------------------------------------------------------------------------------------|-------------|-------------|
| 1. Does the method use exotic equipment and/or supplies that are not commercially available in the U.S.?                                         | _____       | _____/_____ |
| 2. Does the method require any new equipment before the laboratory work begins?                                                                  | _____       | _____/_____ |
| 3. Are chromatograms included?                                                                                                                   |             |             |
| a. Is (are) peak(s) of interest sufficiently resolved from other peaks?                                                                          | _____/_____ | _____       |
| b. Has registrant included chromatograms of analyses at or below tolerance on all crop types for which tolerance is requested by HED? See Review | _____/_____ | _____/_____ |
| c. Do the control samples have reasonably low levels of the analyte in relation to the proposed tolerance?                                       | _____/_____ | _____       |
| d. Is the method sufficiently sensitive and specific to measure and identify the residues at levels specified by HED in the TMV request?         | _____/_____ | _____       |

- N/A

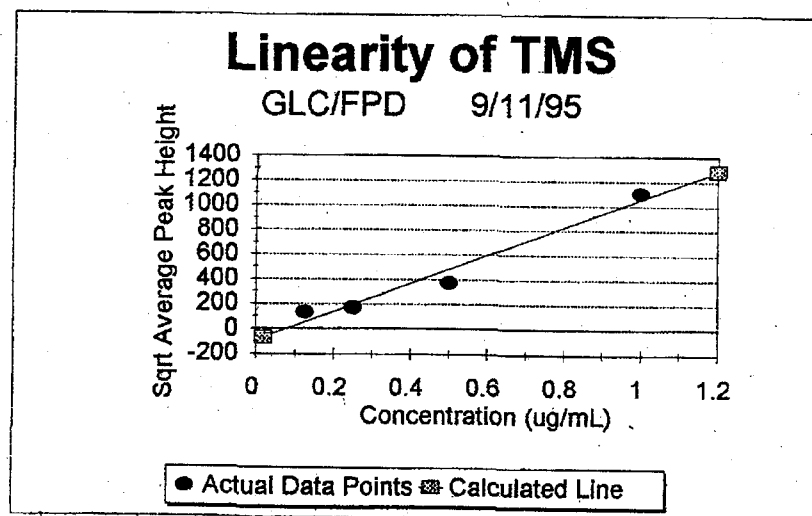
B95-34-35

# Linearity of TMS GLC/FPD 9/11/95

| ug/mL  | PK. HT. 1 | PK. HT. 2 | AVE PK. HT. | Sqrt Avg Pk Ht | Sqrt CALC. PK. HT. |
|--------|-----------|-----------|-------------|----------------|--------------------|
| 0.1250 | 18082.0   | 17314.0   | 17698.0     | 133.0338       |                    |
| 0.2500 | 29935.0   | 29323.0   | 29629.0     | 172.1308       |                    |
| 0.5000 | 128467.0  | 146861.0  | 137664.0    | 371.0310       |                    |
| 1.0000 | 1223028.0 | 1223179.0 | 1223103.5   | 1105.9401      |                    |
| 0.0200 |           |           |             |                | -69.6693           |
| 1.2000 |           |           |             |                | 1285.0712          |

## Regression Output:

|                     |             |
|---------------------|-------------|
| Constant            | -92.6310293 |
| Std Err of Y Est    | 104.8272386 |
| R Squared           | 0.964211424 |
| No. of Observations | 4           |
| Degrees of Freedom  | 2           |
| X Coefficient(s)    | 1148.08523  |
| Std Err of Coef.    | 156.4030464 |



B-34,35,36,37,38,39

Linearity of TMS  
GLC - FPD  
7/5/95

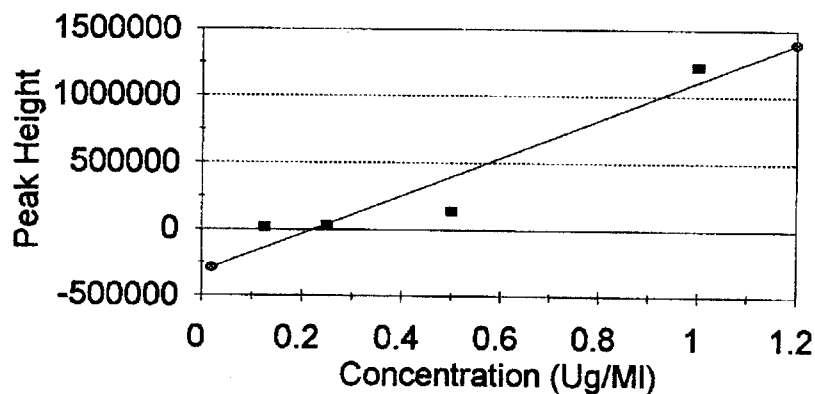
| ug/mL | PK. HT 1  | PK. HT 2  | AVG PK. HT | CALC. PK. HT |
|-------|-----------|-----------|------------|--------------|
| 0.125 | 18082.0   | 17314.0   | 17698.0    |              |
| 0.250 | 29935.0   | 29323.0   | 29629.0    |              |
| 0.500 | 128467.0  | 146861.0  | 137664.0   |              |
| 1.000 | 1223028.0 | 1223179.0 | 1223103.5  |              |
| 0.020 |           |           |            | -288817.68   |
| 1.200 |           |           |            | 1396291.48   |

| Regression Output:  |                |
|---------------------|----------------|
| Constant            | -317378.847826 |
| Std Err of Y Est    | 228393.556228  |
| R Squared           | 0.89776271334  |
| No. of Observations | 4              |
| Degrees of Freedom  | 2              |
| Std Err of Coef.    | 0.089136462    |
| X Coefficient(s)    | 1428058.609    |
| Std Err of Coef.    | 340764.943     |

# LINEARITY OF TMS

GLC/FPD

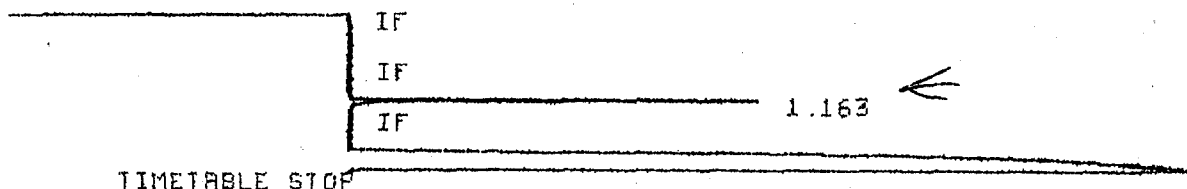
7/5/95



■ Actual Data Points —♦— Calculated Line

12

RUN # 545      AUG 5, 1995 13:32:16  
START



RUN# 545      AUG 5, 1995 13:32:16

SAMPLE NAME: DMSS STD      SAMPLE# 1  
0.25 UG/ML

B95/34 THRU 39 (SOYBEAN SEED) 2UL INJ

HEIGHT%

| RT    | HEIGHT | TYPE | WIDTH | HEIGHT%   |
|-------|--------|------|-------|-----------|
| 1.163 | 49240  | BU   | .015  | 100.00000 |

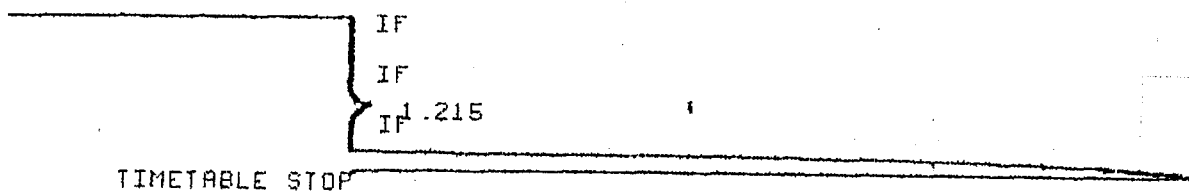
*TMS*

TOTAL HEIGHT= 49240  
MUL FACTOR=1.0000E+00

RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRS = 3  
PK WD = 0.02

RUN # 546      AUG 5, 1995 13:35:56  
START



RUN# 546      AUG 5, 1995 13:35:56

SAMPLE NAME: CONTROL #1      SAMPLE# 2  
FINAL VOL 1ML/50 ALIQUOT

B95/34 THRU 39 (SOYBEAN SEED) 2UL INJ

NO RUN PEAKS STORED

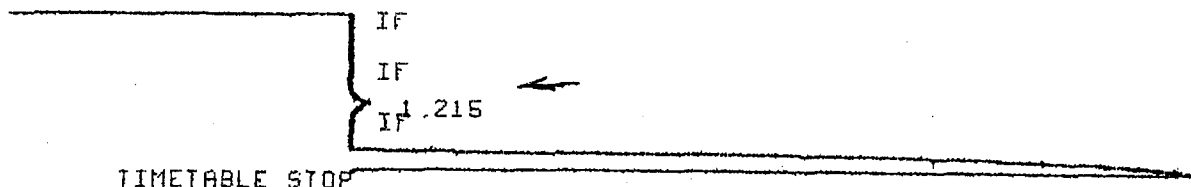
RUN PARAMETERS

13

RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 546 AUG 5, 1995 13:35:56  
START



TIMETABLE STOP

RUN# 546 AUG 5, 1995 13:35:56

SAMPLE NAME: CONTROL #1 SAMPLE# 2  
FINAL VOL 1ML/5G ALIQUOT

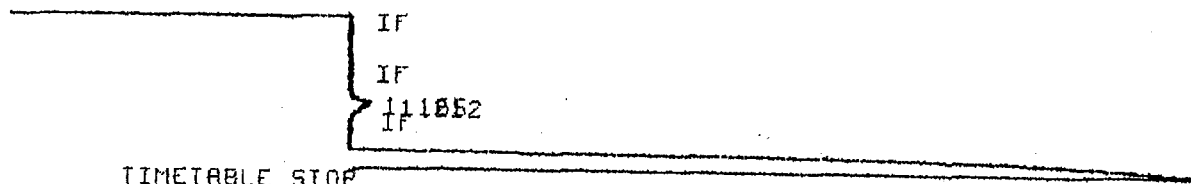
B95/34 THRU 39 (SOYBEAN SEED) 2UL INJ

NO RUN PEAKS STORED

RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 547 AUG 5, 1995 13:39:36  
START



TIMETABLE STOP

RUN# 547 AUG 5, 1995 13:39:36

SAMPLE NAME: CONTROL #1 SAMPLE# 2  
FINAL VOL 1ML/5G ALIQUOT

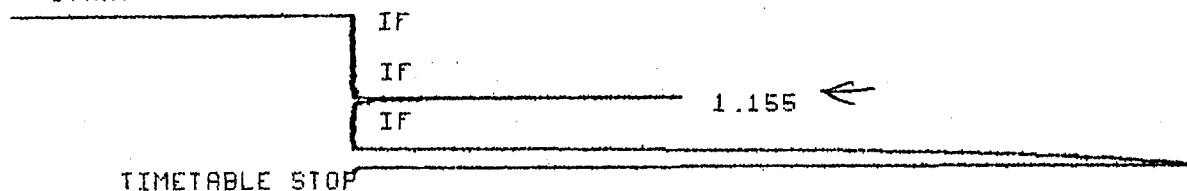
B95/34 THRU 39 (SOYBEAN SEED) 2UL INJ

14

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSR = 3  
PK WD = 0.02

RUN # 554      AUG 5, 1995 14:05:18  
START



TIMETABLE STOP

RUN# 554      AUG 5, 1995 14:05:18

SAMPLE NAME: 0.05PPM SPK#      SAMPLE# 6  
FINAL VOL 1ML/5G ALIQUOT

B95/34 THRU 39 <SOYBEAN SEED> 2UL INJ

## HEIGHTX

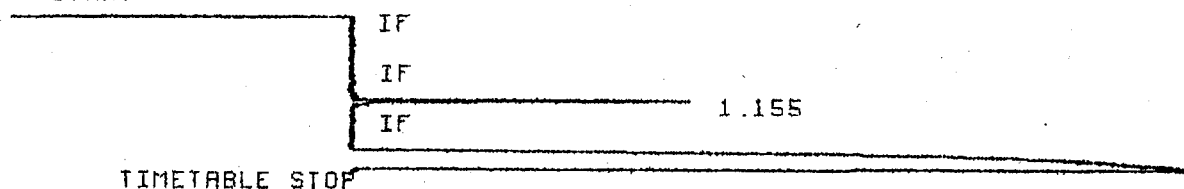
| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX   |
|-------|--------|------|-------|-----------|
| 1.155 | 40259  | PU   | .018  | 100.00000 |

TOTAL HEIGHT= 40259  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSR = 3  
PK WD = 0.02

RUN # 555      AUG 5, 1995 14:09:01  
START



TIMETABLE STOP

RUN# 555      AUG 5, 1995 14:09:01

SAMPLE NAME: 0.05PPM SPK#      SAMPLE# 6  
FINAL VOL 1ML/5G ALIQUOT

15

TOTAL HEIGHT= 27393  
MUL FACTOR=1.0000E+00

RUN PARAMETERS  
ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 560 AUG 5, 1995 14:27:22  
START

IF

IF

IF

1.152

TIMETABLE STOP

RUN# 560 AUG 5, 1995 14:27:22

SAMPLE NAME: 0.5PPM SPK#2 SAMPLE# 9  
FINAL VOL 10ML/5G ALIQUOT

B95/34 THRU 39 (SOYBEAN SEED) 2UL INJ

HEIGHT%

| RT    | HEIGHT | TYPE | WIDTH | HEIGHT%   |
|-------|--------|------|-------|-----------|
| 1.152 | 34198  | PU   | .017  | 100.00000 |

TOTAL HEIGHT= 34198  
MUL FACTOR=1.0000E+00

RUN PARAMETERS  
ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 561 AUG 5, 1995 14:31:03  
START

IF

IF

IF

1.152

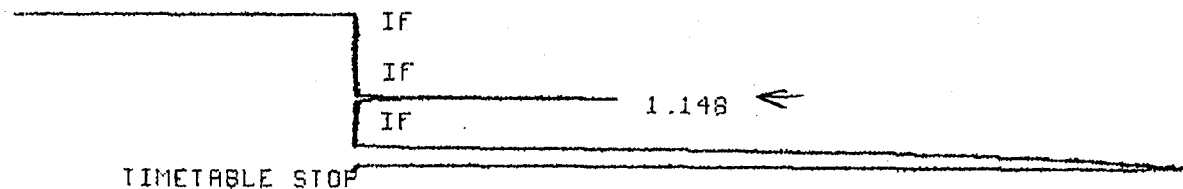
14

TOTAL HEIGHT= 32333  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 567 AUG 5, 1995 14:53:11  
START



RUN# 567 AUG 5, 1995 14:53:11

SAMPLE NAME: 1PPM SPK#2 SAMPLE# 12  
FINAL VOL 20ML/56 ALIQUOT

B95/34 THRU 39 <SOYBEAN SEED> 2UL INJ

## HEIGHT%

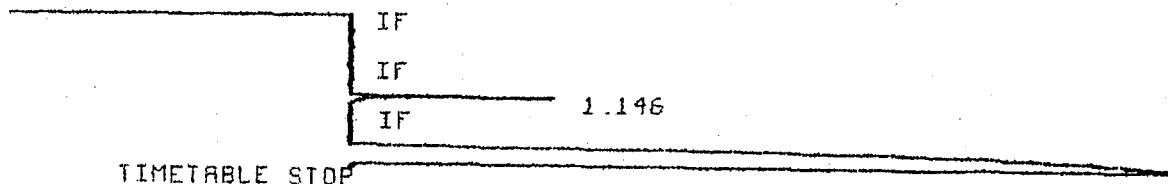
| RT    | HEIGHT | TYPE | WIDTH | HEIGHT%   |
|-------|--------|------|-------|-----------|
| 1.148 | 32041  | PV   | .018  | 100.00000 |

TOTAL HEIGHT= 32041  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 568 AUG 5, 1995 14:56:48  
START



B95/34 THRU 39 (CORN FODDER) 2UL INJ

HEIGHTX

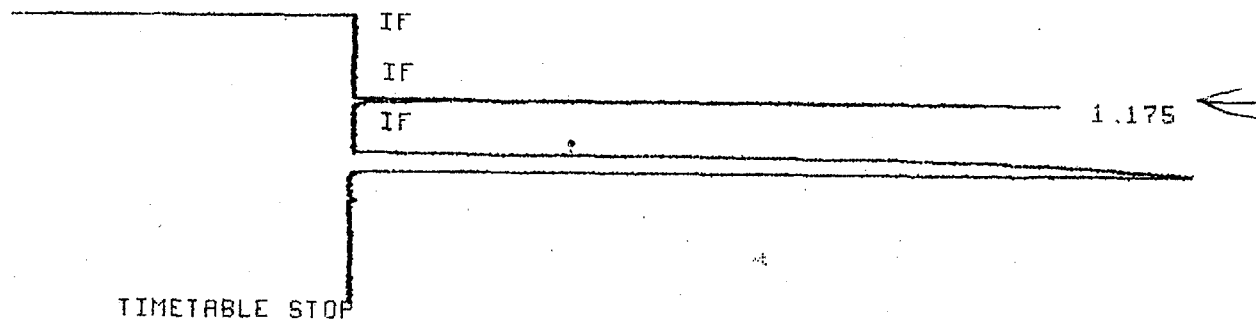
| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX   |
|-------|--------|------|-------|-----------|
| 1.174 | 95550  | UV   | .015  | 100.00000 |

TOTAL HEIGHT= 95550  
MUL FACTOR=1.0000E+00

RUN PARAMETERS

ZERO = 20  
ATT 2° = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 371 JUL 27, 1995 16:34:23  
START



RUN# 371 JUL 27, 1995 16:34:23

SAMPLE NAME: QMS STD SAMPLE# 7  
0.25 UG/ML *2ul inj*

B95/34 THRU 39 (CORN FODDER) 2UL INJ

HEIGHTX

*TMS*

| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX   |
|-------|--------|------|-------|-----------|
| 1.175 | 84906  | PB   | .014  | 100.00000 |

TOTAL HEIGHT= 84906  
MUL FACTOR=1.0000E+00

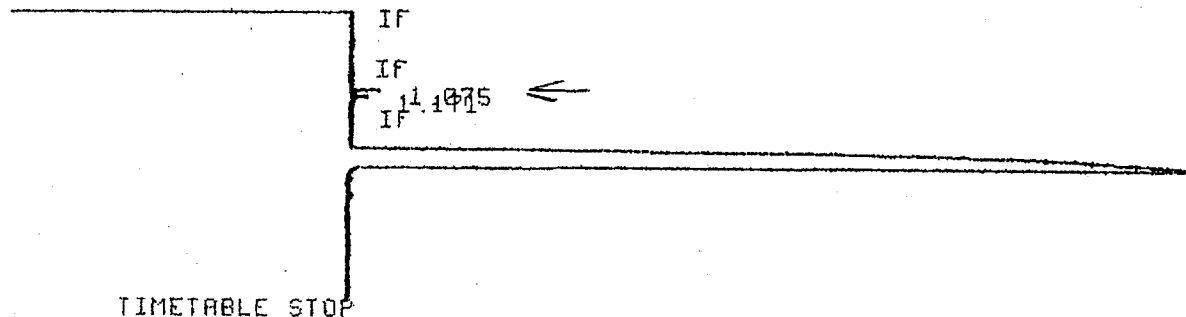
RUN PARAMETERS

ZERO = 20  
ATT 2° = 4  
CHT SP = 1.0  
-----

18

RUN PARAMETERS  
 ZERO = 20  
 ATT 2^ = 4  
 CHT SP = 1.0  
 AR REJ = 6000  
 THRSH = 3  
 PK WD = 0.02

RUN # 361 JUL 27, 1995 15:39:45  
 START



RUN# 361 JUL 27, 1995 15:39:45

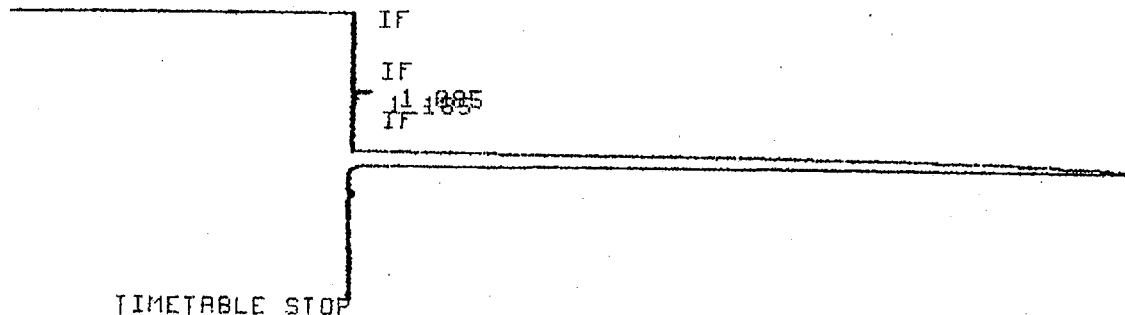
SAMPLE NAME: CONTROL #1 SAMPLE# 2  
 FINAL VOL 2ML/5G ALIQUOT

B95/34 THRU 39 (CORN FODDER) 2UL INJ

NO RUN PEAKS STORED

RUN PARAMETERS  
 ZERO = 20  
 ATT 2^ = 4  
 CHT SP = 1.0  
 AR REJ = 6000  
 THRSH = 3  
 PK WD = 0.02

RUN # 362 JUL 27, 1995 15:45:10  
 START



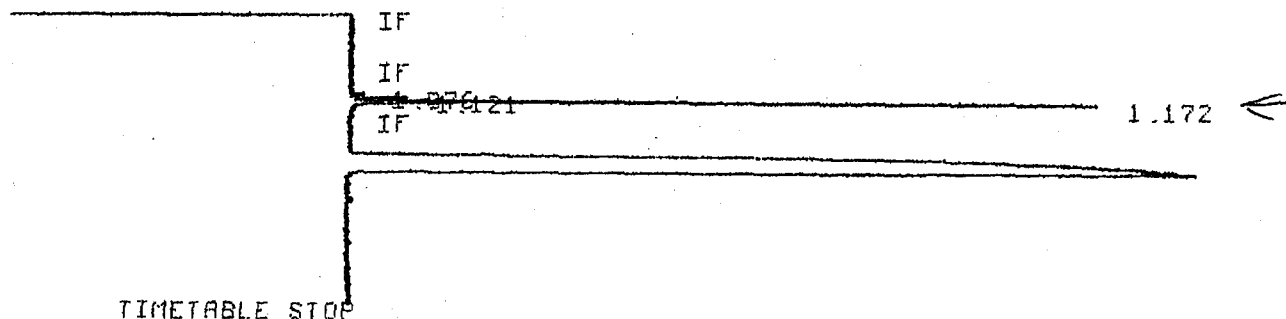
RUN# 362 JUL 27, 1995 15:45:10

SAMPLE NAME: CONTROL #2 SAMPLE# 3

## RUN PARAMETERS

ZERO = 20  
 ATT 2^ = 4  
 CHT SP = 1.0  
 AR REJ = 6000  
 THRSH = 3  
 PK WD = 0.02

RUN # 367 JUL 27, 1995 16:12:25  
 START



TIMETABLE STOP

RUN# 367 JUL 27, 1995 16:12:25

SAMPLE NAME: 0.1 SPK#1 SAMPLE# 5  
 FINAL VOL 2ML/5G ALIQUOT

B95/34 THRU 39 (CORN FODDER) 2UL INJ

## HEIGHTX

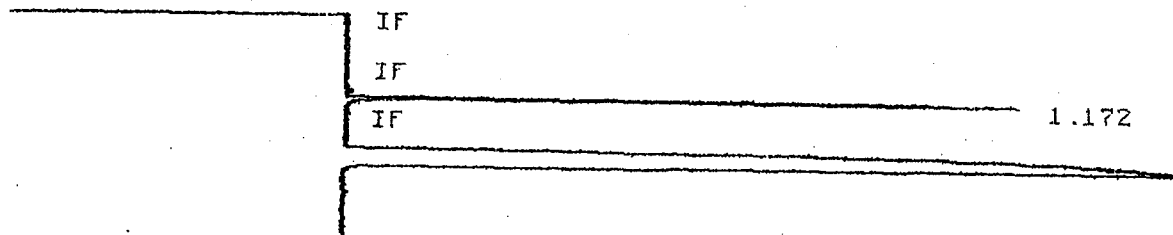
| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX  |
|-------|--------|------|-------|----------|
| 1.121 | 6857   | PU   | .015  | 7.12342  |
| 1.172 | 89403  | UB   | .014  | 92.87658 |

TOTAL HEIGHT\* 96260  
 MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
 ATT 2^ = 4  
 CHT SP = 1.0  
 AR REJ = 6000  
 THRSH = 3  
 PK WD = 0.02

RUN # 368 JUL 27, 1995 16:17:57  
 START



20

ATT 2  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 373 JUL 27, 1995 16:45:17  
START

IF

IF

IF

1.176

TIMETABLE STOP

RUN# 373 JUL 27, 1995 16:45:17

SAMPLE NAME: 1PPM SPK#1 SAMPLE# 8  
FINAL VOL 20ML/5G ALIQUOT

B95/34 THRU 39 (CORN FODDER) 2UL INJ

HEIGHTX

| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX   |
|-------|--------|------|-------|-----------|
| 1.176 | 87658  | PB   | .014  | 100.00000 |

TOTAL HEIGHT= 87658  
MUL FACTOR=1.0000E+00

RUN PARAMETERS

ZERO = 20  
ATT 2 = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 374 JUL 27, 1995 16:50:45  
START

IF

IF

1.077

IF

1.174

TIMETABLE STOP

21

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 380 JUL 27, 1995 17:23:36  
START

IF

IF

IF

1.180

TIMETABLE STOP

RUN# 380 JUL 27, 1995 17:23:36

SAMPLE NAME: 2PPM SPK#2 SAMPLE# 12  
FINAL VOL 40ML/56 ALIQUOT

B95/34 THRU 39 (CORN FODDER) 2UL INJ

## HEIGHTX

| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX   |
|-------|--------|------|-------|-----------|
| 1.180 | 76587  | PB   | .013  | 100.00000 |

TOTAL HEIGHT= 76587  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 4  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 381 JUL 27, 1995 17:29:03  
START

IF

IF

IF

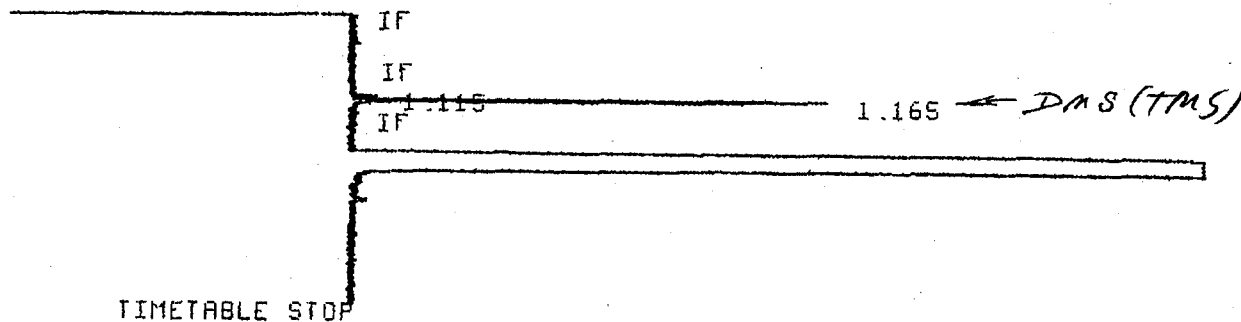
1.176

22

## RUN PARAMETERS

ZERO = 20  
 ATT 2^ = 3  
 CHT SP = 1.0  
 AR REJ = 6000  
 THRSH = 3  
 PK WD = 0.02

RUN # 147 JUL 12, 1995 09:24:13  
 START



RUN# 147 JUL 12, 1995 09:24:13

SAMPLE NAME: TMS STD SAMPLE# 1  
 0.25 UG/ML *2 ul inj*

B95-34 THRU 39<CORN GRAIN>

## HEIGHTX

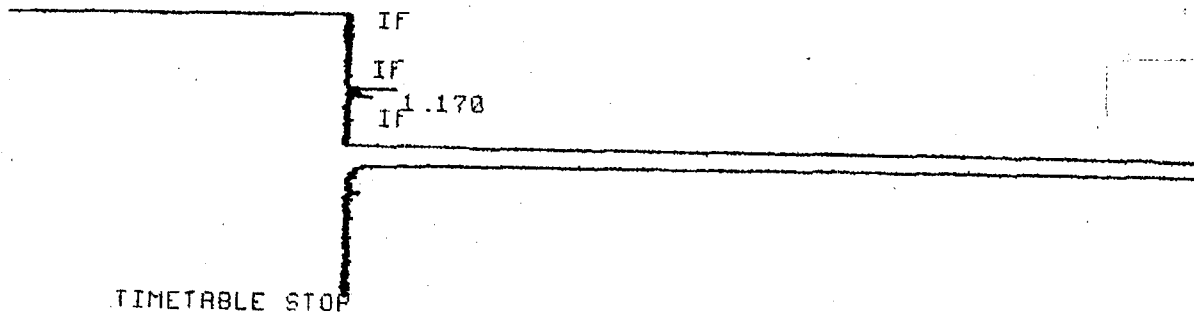
| RT               | HEIGHT | TYPE | WIDTH | HEIGHTX   |
|------------------|--------|------|-------|-----------|
| <i>TMS</i> 1.165 | 28482  | PB   | .015  | 100.00000 |

TOTAL HEIGHT= 28482  
 MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
 ATT 2^ = 3  
 CHT SP = 1.0  
 AR REJ = 6000  
 THRSH = 3  
 PK WD = 0.02

RUN # 148 JUL 12, 1995 09:29:43  
 START



TOTAL HEIGHT= 28482  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 3  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 148 JUL 12, 1995 09:29:43  
START

IF

IF

If 1.170 ←

TIMETABLE STOP

RUN# 148 JUL 12, 1995 09:29:43

SAMPLE NAME: CONTROL#1 SAMPLE# 2  
2UL INJ/FINAL VOL 1ML/5G ALIQUOT

B95-34 THRU 39&lt;CORN GRAIN&gt;

NO RUN PEAKS STORED

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 3  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 149 JUL 12, 1995 09:35:12  
START

HEIGHT%

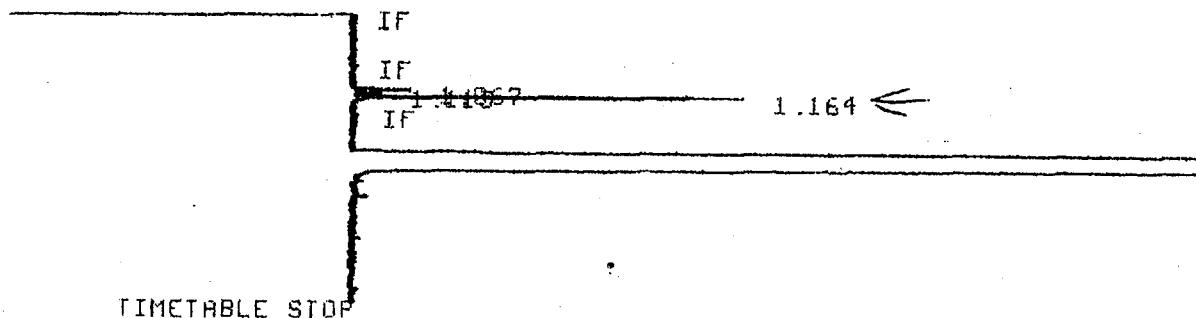
| RT    | HEIGHT TYPE | WIDTH | HEIGHT%   |
|-------|-------------|-------|-----------|
| 1.164 | 25518 UU    | .016  | 100.00000 |

TOTAL HEIGHT= 25518  
MUL FACTOR=1.0000E+00

RUN PARAMETERS

ZERO = 20  
ATT 2^ = 3  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 154 JUL 12, 1995 10:02:31  
START



RUN# 154 JUL 12, 1995 10:02:31

SAMPLE NAME: 0.05PPM SPK1 .SAMPLE# 5  
2UL INJ/ FINAL VOL 1ML/ 5G ALIQUOT

B95-34 THRU 39<CORN GRAIN>

HEIGHT%

| RT    | HEIGHT TYPE | WIDTH | HEIGHT%   |
|-------|-------------|-------|-----------|
| 1.164 | 23776 UU    | .015  | 100.00000 |

TOTAL HEIGHT= 23776  
MUL FACTOR=1.0000E+00

RUN PARAMETERS

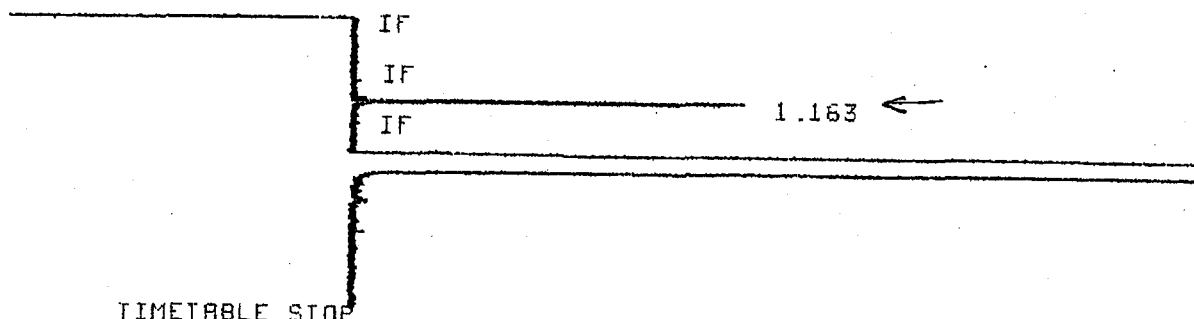
ZERO = 20  
ATT 2^ = 3  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

25

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 3  
CHT SP = 1.0  
AR REJ = 6000  
THRSH = 3  
PK WD = 0.02

RUN # 161 JUL 12, 1995 10:41:03  
START



RUN# 161 JUL 12, 1995 10:41:03

SAMPLE NAME: 0.1SPK1 SAMPLE# 8  
ZUL INJ/ FINAL VOL2ML/ 5G ALIQUOT

B95-34 THRU 39(CORN GRAIN)

## HEIGHT%

| RT    | HEIGHT | TYPE | WIDTH | HEIGHT%   |
|-------|--------|------|-------|-----------|
| 1.163 | 23813  | PU   | .016  | 100.00000 |

TOTAL HEIGHT= 23813  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

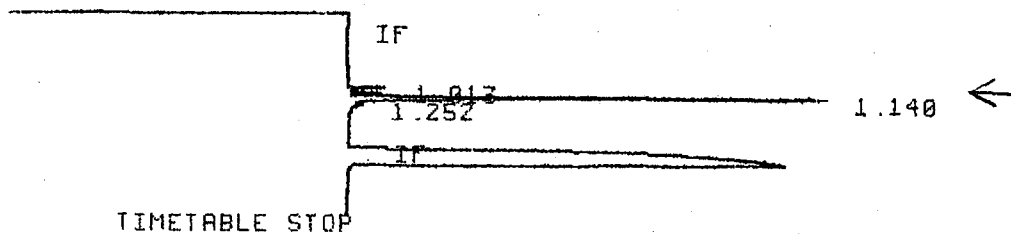
26

TOTAL HEIGHT= 158790  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRS = 3  
PK WD = 0.06

RUN # 1217      AUG 29, 1995 10:54:38  
START



Storing processed peaks to A:Q14398EF.PRO

RUN# 1217      AUG 29, 1995 10:54:38

SAMPLE NAME: 0.25UG/ML      SAMPLE# 1  
DMS STD

PEAK FILE : A:Q14398EF.PRO

B95/34-39 (PECANS) 2UL INJ

## HEIGHTX

|            | RT    | HEIGHT        | TYPE | WIDTH | HEIGHTX  |
|------------|-------|---------------|------|-------|----------|
|            | 1.013 | 8814          | BB   | .015  | 6.79301  |
| <i>TMS</i> | 1.140 | <u>118403</u> | BB   | .022  | 91.25402 |
|            | 1.252 | 2534          | BB   | .016  | 1.95297  |

TOTAL HEIGHT= 129751  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRS = 3  
PK WD = 0.06

RUN # 1218      AUG 29, 1995 10:59:49  
START

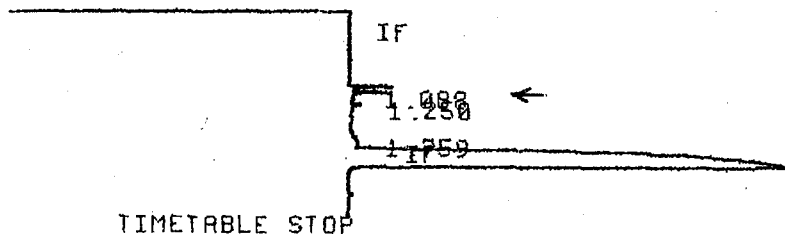
IF

27

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRS = 3  
PK WD = 0.06

RUN # 1221      AUG 29, 1995 11:15:13  
START



Storing processed peaks to A:Q1439DC2.PRO

RUN# 1221      AUG 29, 1995 11:15:13

SAMPLE NAME: CONTROL#2      SAMPLE# 3  
FINAL VOL 1ML/5G ALIQUOT

PEAK FILE : A:Q1439DC2.PRO

B95/34-39 (PECANS) 2UL INJ

## HEIGHTX

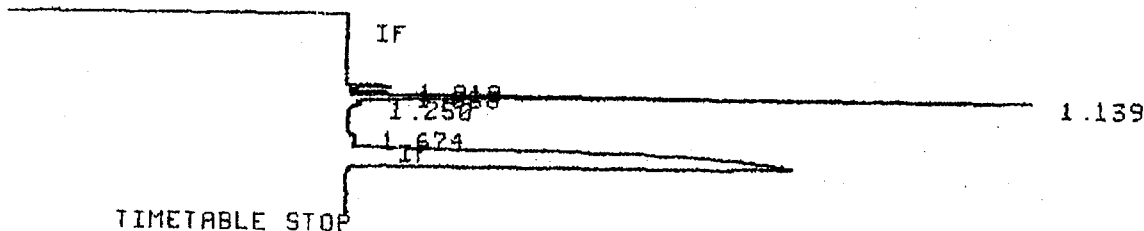
| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX  |
|-------|--------|------|-------|----------|
| 1.088 | 10119  | PB   | .017  | 66.63373 |
| 1.250 | 2913   | BV   | .031  | 19.10214 |
| 1.759 | 2154   | PV   | .162  | 14.18412 |

TOTAL HEIGHT= 15186  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRS = 3  
PK WD = 0.06

RUN # 1222      AUG 29, 1995 11:20:24  
START

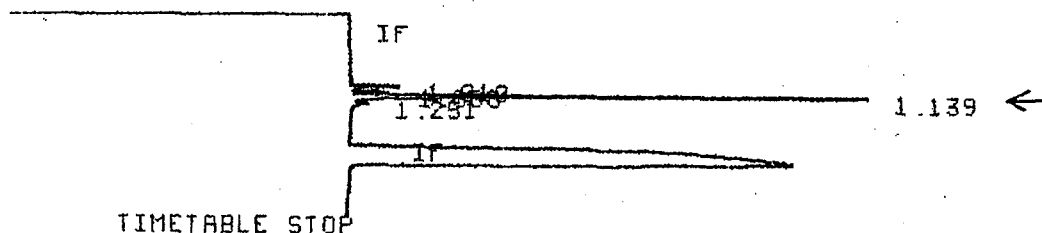


28

## RUN PARAMETERS

ZERO = 20  
 ATT 2^ = 5  
 CHT SP = 1.0  
 AR REJ = 2000  
 THRSH = 3  
 PK WD = 0.06

RUN # 1232 AUG 29, 1995 12:34:18  
 START



Storing processed peaks to A:Q143B04B.PRO

RUN# 1232 AUG 29, 1995 12:34:18

SAMPLE NAME: 0.05PPM SPK#/ SAMPLE# 5  
 FINAL VOL 1ML/5G ALIQUOT

PEAK FILE : A:Q143B04B.PRO

B95/34-39 (PECANS) 2UL INJ

## HEIGHT%

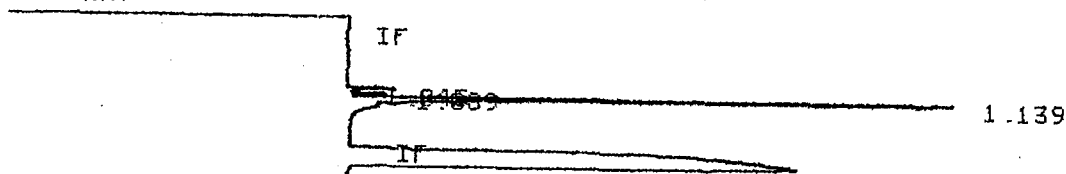
| RT           | HEIGHT        | TYPE | WIDTH | HEIGHT%  |
|--------------|---------------|------|-------|----------|
| 1.010        | 12107         | PP   | .020  | 7.97368  |
| 1.088        | 9140          | PP   | .014  | 6.01961  |
| <u>1.139</u> | <u>127017</u> | PB   | .021  | 83.65354 |
| 1.251        | 3573          | PB   | .023  | 2.35318  |

TOTAL HEIGHT= 151837  
 MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
 ATT 2^ = 5  
 CHT SP = 1.0  
 AR REJ = 2000  
 THRSH = 3  
 PK WD = 0.06

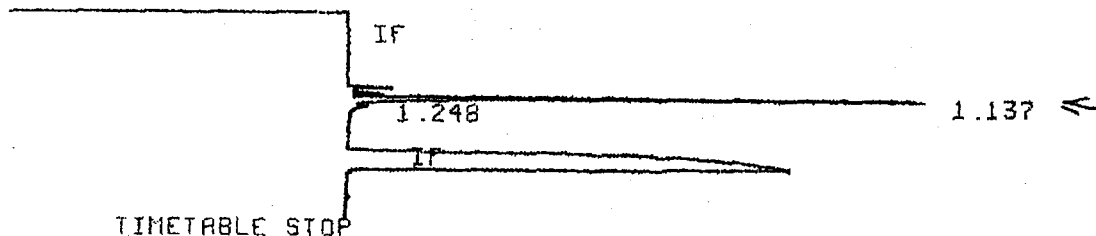
RUN # 1233 AUG 29, 1995 12:39:39  
 START



## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRSH = 3  
PK WD = 0.06

RUN # 1239      AUG 29, 1995 13:11:46  
START



Storing processed peaks to A:Q143B913.PRO

RUN# 1239      AUG 29, 1995 13:11:46

SAMPLE NAME: 0.1PPM SPK#1      SAMPLE# 8  
FINAL VOL 2ML/5G ALIQUOT

PEAK FILE : A:Q143B913.PRO

B95/34-39 (PECANS) 2UL INJ

## HEIGHT%

| RT    | HEIGHT        | TYPE | WIDTH | HEIGHT%  |
|-------|---------------|------|-------|----------|
| 1.137 | <u>136306</u> | PB   | .022  | 97.70829 |
| 1.248 | 3197          | BB   | .013  | 2.29171  |

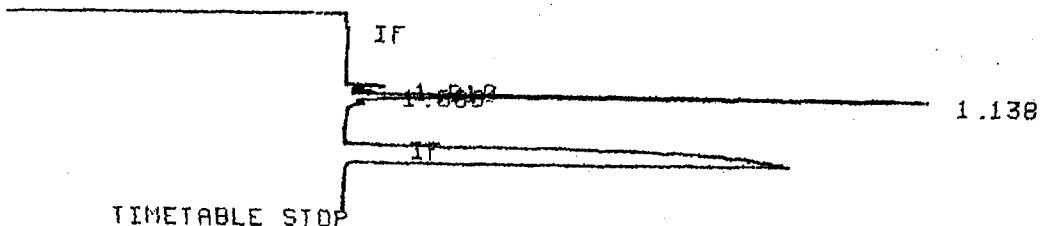
TOTAL HEIGHT= 139503

MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRSH = 3  
PK WD = 0.06

RUN # 1240      AUG 29, 1995 13:17:06  
START



30

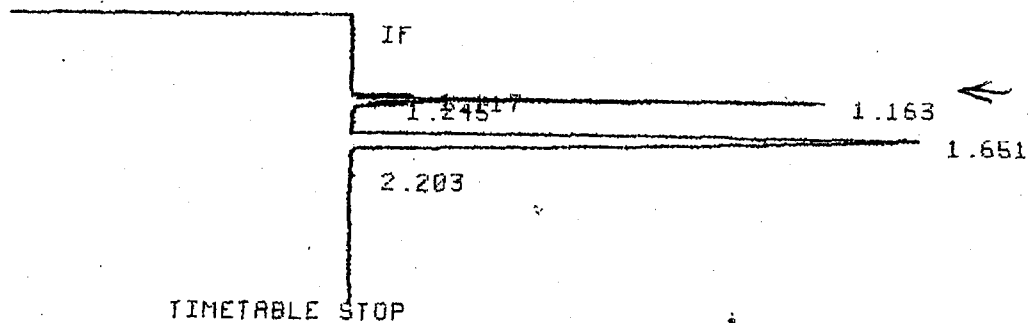
|       |        |    |      |          |
|-------|--------|----|------|----------|
| 1.165 | 110459 | PB | .020 | 43.91850 |
| 1.653 | 124705 | PB | .048 | 49.58272 |
| 2.207 | 1251   | PP | .034 | .49740   |

TOTAL HEIGHT= 251509  
MUL FACTOR=1.0000E+00

# RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRS = 3  
PK WD = 0.04

RUN # 1075 AUG 19, 1995 13:40:50  
START



Storing processed peaks to A:Q13690E3.PRO

RUN# 1075 AUG 19, 1995 13:40:50

SAMPLE NAME: 0.25UG/ML SAMPLE# 7  
DMS STD

PEAK FILE : A:Q13690E3.PRO

B95/34-39 (ORANGES) 2UL INJ

# HEIGHTX

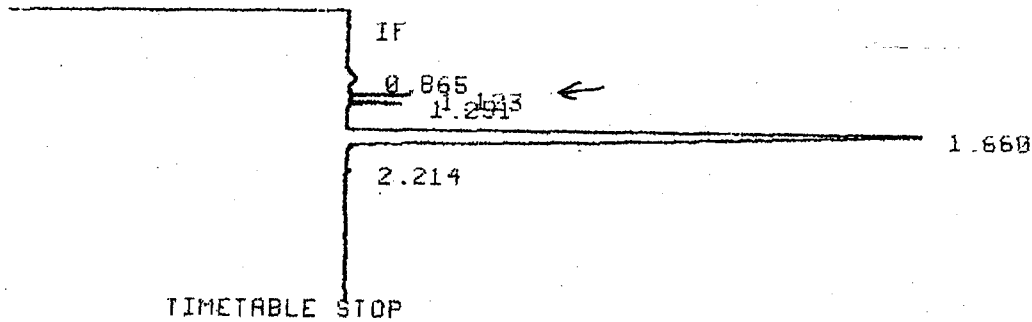
| RT        | HEIGHT | TYPE | WIDTH | HEIGHTX  |
|-----------|--------|------|-------|----------|
| 1.117     | 15068  | PU   | .017  | 6.15988  |
| TMS 1.163 | 118768 | UU   | .021  | 48.55302 |
| 1.245     | 13158  | UB   | .021  | 5.37907  |
| 1.651     | 96244  | PB   | .027  | 39.34509 |
| 2.203     | 1377   | PP   | .052  | .56293   |

TOTAL HEIGHT= 244615  
MUL FACTOR=1.0000E+00

# RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0

RUN # 1064      AUG 19, 1995 12:36:40  
START



Storing processed peaks to A:Q1368109.PRO

RUN# 1064      AUG 19, 1995 12:36:40

SAMPLE NAME: CONTROL#1      SAMPLE# 2  
FINAL VOL1ML/5G ALIQUOT

PEAK FILE : A:Q1368109.PRO

B95/34-39 (ORANGES) 2UL INJ

HEIGHT%

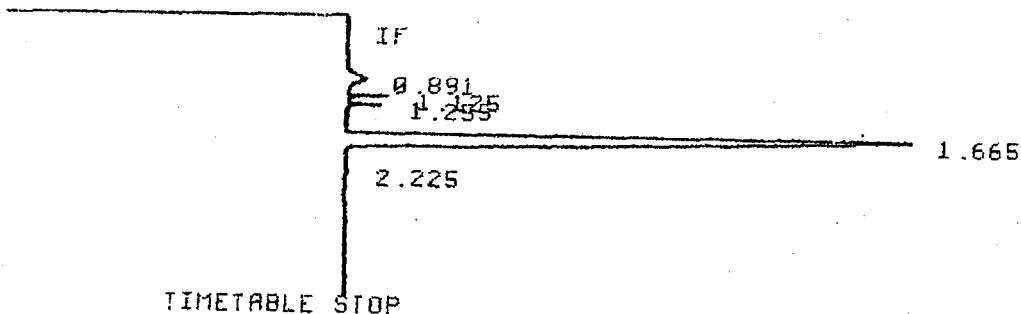
| RT    | HEIGHT | TYPE | WIDTH | HEIGHT%  |
|-------|--------|------|-------|----------|
| .865  | 2353   | BU   | .142  | 1.65205  |
| 1.123 | 16199  | UU   | .016  | 11.37339 |
| 1.251 | 13339  | UU   | .021  | 9.36537  |
| 1.660 | 109064 | PB   | .052  | 76.57430 |
| 2.214 | 1474   | UP   | .039  | 1.03490  |

TOTAL HEIGHT= 142429  
MUL FACTOR=1.0000E+00

RUN PARAMETERS

ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
RR REJ = 2000  
THRSH = 3  
PK WD = 0.04

RUN # 1065      AUG 19, 1995 12:42:32  
START



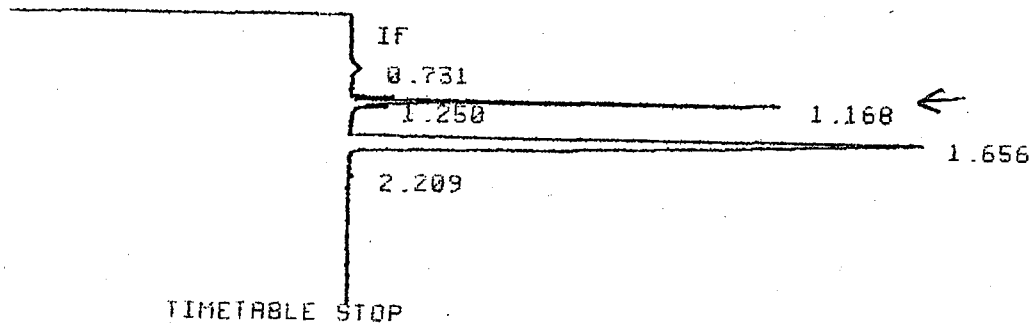
32

TOTAL HEIGHT= 109984  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2<sup>^</sup> = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRS = 3  
PK WD = 0.04

RUN # 1071      AUG 19, 1995    13:17:02  
START



Storing processed peaks to A:Q1368B4F.PRO

RUN# 1071      AUG 19, 1995    13:17:02

SAMPLE NAME: 0.05PPM SPK#      SAMPLE# 5  
FINAL VOL IML/5G ALIQUOT

PEAK FILE : A:Q1368B4F.PRO

095/34-39 (ORANGES) 2UL INJ

## HEIGHT%

| RT    | HEIGHT | TYPE | WIDTH | HEIGHT%  |
|-------|--------|------|-------|----------|
| .731  | 2239   | UP   | .135  | .91650   |
| 1.168 | 103408 | BU   | .021  | 42.32862 |
| 1.250 | 8494   | UB   | .021  | 3.47690  |
| 1.656 | 128806 | BB   | .056  | 52.75770 |
| 2.209 | 1271   | BU   | .045  | .52027   |

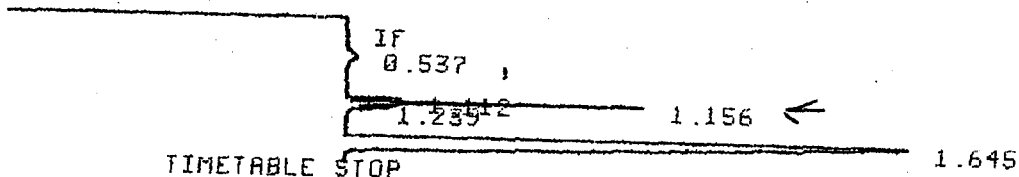
TOTAL HEIGHT= 244298  
MUL FACTOR=1.0000E+00

## RUN PARAMETERS

ZERO = 20  
ATT 2<sup>^</sup> = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRS = 3  
PK WD = 0.04

RUN PARAMETERS  
ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRSH = 3  
PK WD = 0.04

RUN # 1091 AUG 19, 1995 14:57:23  
START



Storing processed peaks to A:Q136A204.PRO

RUN# 1091 AUG 19, 1995 14:57:23

SAMPLE NAME: 0.5PPM SPK#1 SAMPLE# 0  
FINAL VOL 10ML/5G ALIQUOT

PEAK FILE : A:Q136A204.PRO

895/34-39 (ORANGES) 2UL INJ

| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX  |
|-------|--------|------|-------|----------|
| .537  | 1096   | BP   | .110  | .79938   |
| 1.112 | 13316  | PU   | .017  | 5.61418  |
| 1.156 | 75239  | UU   | .023  | 31.72165 |
| 1.239 | 11545  | UU   | .023  | 4.06751  |
| 1.645 | 135109 | BP   | .122  | 56.99728 |

TOTAL HEIGHT= 237185  
MUL FACTOR=1.0000E+00

RUN PARAMETERS  
ZERO = 20  
ATT 2^ = 5  
CHT SP = 1.0  
AR REJ = 2000  
THRSH = 3  
PK WD = 0.04

RUN # 1092 AUG 19, 1995 15:01:23  
START

IF  
0.460

NO RUN PEAKS STORED

## RUN PARAMETERS

ZERO = 20  
 ATT 2^ = 5  
 CHT SP = 1.0  
 AR REJ = 2000  
 THRSH = 3  
 PK WD = 0.04

## \* EDIT SEQ

- 1 = ALS INFORMATION
- 2 = EQUILIBRATION TIME DELAY
- 3 = METHOD FILE SPECIFICATION
- 4 = SAMPLE INFORMATION TABLE

SECTION TO BE EDITED: 1

## ALS INFORMATION

INET SAMPLER CONTROL [Y\*/H]:

7673A SAMPLER:  
 LOOP ADDRESS: 8

## FRONT INJECTOR

INJ/BOTTLE 2 --> @  
 FIRST BOTTLE 7 --> 12 @  
 LAST BOTTLE 13 --> BREAK

## \* SEQ START

RUN # 1099 AUG 19, 1995 15:27:39  
 START

IF

1.175

1.098

1.566

TIMETABLE STOP

Storing processed peaks to A:Q136A9EC.PRO

RUN# 1099 AUG 19, 1995 15:27:39

SAMPLE NAME: 1PPM SPK#2 SAMPLE# 12  
 FINAL VOL 20ML/5G ALIQUOT

PEAK FILE : A:Q136A9EC.PRO

B95/34-39 (ORANGES) 2UL INJ

## HEIGHTX

| RT    | HEIGHT | TYPE | WIDTH | HEIGHTX  |
|-------|--------|------|-------|----------|
| 1.055 | 16919  | PV   | .016  | 7.69164  |
| 1.098 | 62111  | UV   | .023  | 28.23663 |
| 1.175 | 14077  | UB   | .019  | 6.39962  |
| 1.566 | 126859 | PB   | .056  | 57.67210 |

TOTAL HEIGHT: 110000

35