

# DIFENOCONAZOLE - 1


ANALYTICAL METHOD FOR THE DETERMINATION OF  
CGA-169374 IN WHEAT RAW AGRICULTURAL COMMODITIES BY  
GAS CHROMATOGRAPHY WITH NITROGEN/PHOSPHORUS DETECTION

Method No. AG-575B  
(Supersedes Method AG-575A)  
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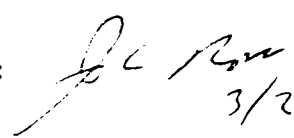
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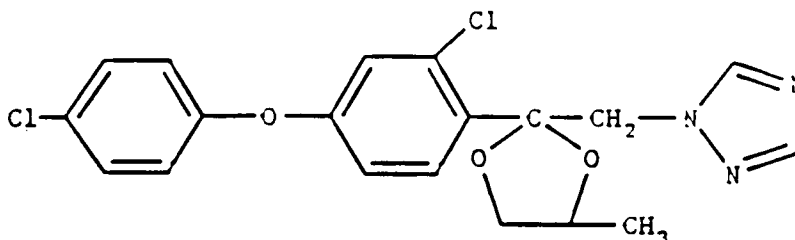
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I. INTRODUCTION/SUMMARY

A. SCOPE

This method is used for the determination of parent residues of CGA-169374 (1-[[2-[2-chloro-4-(4-chloro-phenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole) in wheat raw agricultural commodities. The limit of sensitivity of the method is 0.10 ng of CGA-169374. The limit of determination for CGA-169374 residues is 0.01 ppm for wheat grain and 0.05 ppm for wheat forage and wheat straw, as demonstrated by fortification experiments. The chemical structure of CGA-169374 is presented below.



Method AG-575B is a re-issue of Method AG-575A as a result of an EPA data review and method trial. The outcome of the method trial was a request to add a confirmatory procedure generated by EPA as part of the methodology (see Section II.F.). Reference to a method specificity study requested as part of the data review, in which sixty-eight compounds which have tolerances in wheat, barley and rye grain were examined for potential interference with the analysis of CGA-169374 by the procedures of the method, has also been included (see Section II.E.3). The procedures of Method AG-575A remain unaltered in this re-issue.

B. PRINCIPLE

A representative crop sample is extracted by refluxing in 8:2 (v/v) methanol:conc. ammonium hydroxide. After filtering, an aliquot of the extract is diluted with water and saturated sodium chloride, and

partitioned with hexane. The hexane fraction is partitioned with acetonitrile and the acetonitrile fraction is cleaned up on a silica gel Sep-Pak. The sample is then cleaned up on a phenyl Bond-elut, followed by a charcoal:magnesium oxide:celite column clean-up step. The extract is analyzed by packed column gas chromatography using nitrogen/phosphorus detection.

A flow diagram for the method is presented in Figure 1.

## II. MATERIALS AND METHODS

### A. APPARATUS

- 1.0. Chromatography Column, 19-mm i.d., with teflon stopcock.
- 2.0. Condenser, Allihn, 60-cm.
- 3.0. Bond-elut, phenyl (Analytichem, #608303-1210-2032).
- 4.0. Bottle, Boston round, 8-oz.
- 5.0. Filter paper, Reeve Angel 802 (coarse porosity), and Whatman 2V (medium porosity), 24-cm.
- 6.0. Flask, Erlenmeyer, 250-ml.
- 7.0. Flask, round bottom, 50-ml, 100-ml, 250-ml and 500-ml.
- 8.0. Funnel, filter, 10-cm.
- 9.0. Funnel, separatory, 250-ml.
- 10.0. Heating mantle, 500-ml.
- 11.0. Rotary evaporator, Buchi, or equivalent.
- 12.0. Scintillation vial, 20-ml.
- 13.0. Sep-Pak, silica gel (Waters Assoc. #51900).

- 14.0. Syringe, 20-ml, Luer-Lok.
- 15.0. Visiprep solid phase extraction manifold (Supelco #57030 or equivalent).

B. REAGENTS

- 1.0. Acetone, reagent grade (Fisher cat. #A18SK-4).
- 2.0. Acetonitrile, HPLC grade (Fisher cat. #A998-4).
- 3.0. Ammonium hydroxide, concentrated (28-30%), reagent grade (Fisher cat. #A669-212).
- 4.0. Celite 545 (Fisher cat. #C212-500).
- 5.0. Charcoal, Norit SX-2 (formerly called Norit SG-Extra), acid washed (American Norit, prepared according to the U.S. Food and Drug Administration Pesticide Analytical Manual, Vol. I, PAM I, Section 232.32a).
- 6.0. 1:2:4 (w/w/w) Charcoal:magnesium oxide:Celite 545 (PAM I, Section 232.32b).
- 7.0. Ethyl ether, anhydrous, Reagent A.C.S. (Fisher Cat. #E138-1).
- 8.0. Hexane, HPLC grade (Fisher Cat. #H302-4).
- 9.0. Magnesium oxide, 98%, A.C.S. Reagent, (Aldrich Cat. #24,338-8, or equivalent).
- 10.0. Methanol, HPLC grade (Fisher Cat. #A452-4).
- 11.0. 8:2 (v/v) Methanol:conc. ammonium hydroxide.
- 12.0. Sodium chloride, reagent grade (Fisher cat. #S271-500).

- 13.0. Sodium chloride, saturated solution in distilled water.
- 14.0. Toluene, HPLC grade (Fisher cat. #T290-4).
- 15.0. 85:15 (v/v) Toluene:acetone.
- 16.0. 1:1 (v/v) Toluene:acetonitrile.
- 17.0. 9:1 (v/v) Hexane:ethyl ether.
- 18.0. Water, distilled.
- 19.0. CGA-169374 Analytical Standard, Ciba-Geigy Corporation, P. O. Box 18300, Greensboro, NC, 27419.

C. ANALYTICAL PROCEDURE

1.0. Sample Preparation

Samples are prepared under the general guidelines of the U.S. Food and Drug Administration Pesticide Analytical Manual Volume I, Section 141. Frozen forage and straw are chopped in a Hobart food chopper. Frozen grain is ground in a Wiley Mill.

2.0. Extraction

- 2.1. Weigh a 20-g subsample from a well-homogenized chopped or ground crop sample into a 500-ml round bottom flask. Add 200 ml of 8:2 methanol:concentrated ammonium hydroxide solution to grain or forage, and 300 ml to straw samples, along with several boiling chips.
- 2.2. Fit the round bottom flask onto an Allihn condenser, place the flask in a heating mantle and reflux at a rapid boil for two hours.

2.3. Cool the sample to room temperature and filter the sample extract through a Reeve Angel 802 filter paper placed inside a Whatman 2V filter paper into an 8-oz. Boston round bottle.

3.0. Partition Cleanup

- 3.1. Place a 40-ml aliquot of the filtered extract solution for grain or forage, or a 60-ml aliquot for straw in a 250-ml separatory funnel. Add 100 ml of distilled water and 4 ml of saturated sodium chloride to the separatory funnel.
- 3.2. Partition the aqueous methanol with 50 ml of hexane by shaking the separatory funnel for 30 seconds. Allow the layers to separate, draw the lower layer into a 250-ml Erlenmeyer flask, leaving any emulsion in the separatory funnel. Add 4 ml of saturated sodium chloride to the separatory funnel to break most of the emulsion remaining. Draw off the aqueous layer and any remaining emulsion and combine it with the aqueous layer in the 250-ml Erlenmeyer flask.
- 3.3. Pour the hexane layer from the top of the separatory funnel carefully, so as not to transfer any water droplets, into a second 250-ml separatory funnel.
- 3.4. Transfer the aqueous fraction back into the first 250-ml separatory funnel and partition with hexane a second time as in Section II.C.3.2.

3.5. Combine the hexane fraction from Section II.C.3.4 with that from Section II.C.3.3 in the second 250-ml separatory funnel. Partition the hexane with two 50-ml portions of acetonitrile, combine the acetonitrile fractions in a 250-ml round bottom flask and evaporate the contents of the flask to dryness on a rotary evaporator at a bath temperature of approximately 40°C.

4.0. Silica Sep-Pak Cleanup

- 4.1. Dissolve the residue in the round bottom flask in Section II.C.3.5 in 5 ml of toluene.
- 4.2. Connect a silica Sep-Pak to the Luer fitting on a 20-ml Luer Lok syringe barrel and prewash the Sep-Pak with 5 ml of toluene. Load the toluene solution from Section II.C.4.1 onto the Sep-Pak. Discard the eluate.
- 4.3. Rinse the 250 ml round bottom flask with 5 ml of toluene and load the toluene onto the silica Sep-Pak. Discard the eluate.
- 4.4. Elute the compound, CGA-169374, from the Sep-Pak with 15-ml of 85:15 toluene:acetone and collect the eluate in a 50-ml round bottom flask.
- 4.5. Evaporate the contents of the flask to dryness on a rotary evaporator at a bath temperature of approximately 40°C.

5.0. Phenyl Bond-Elut Cleanup

- 5.1. Dissolve the residue in the 50 ml round bottom flask from Section II.C.4.5 with 3 ml of hexane.
- 5.2. Connect the phenyl Bond-elut column to a Vac-elut assembly and prewash with 3 ml of hexane and discard the eluate. Note that all Bond-elut operations are performed under low vacuum suction applied to the Vac-elut assembly.
- 5.3. Load the hexane solution from Section II.C.5.1 onto the Bond-elut and rinse the 50-ml round bottom flask with 3 ml of hexane and load onto the Bond-elut column. Repeat the rinse and load with an additional 3 ml of hexane. Discard the eluates.
- 5.4. Wash the Bond-elut column with 3 ml of 9:1 hexane:ethyl ether and discard the eluate. Repeat this wash three more times, discarding the eluate.
- 5.5. Elute the compound, CGA-169374, from the Bond-elut with 2 ml of methanol into a scintillation vial. Repeat this step three more times, collecting 8 ml of methanol in the scintillation vial.
- 5.6. Transfer the contents of the scintillation vial to a 50-ml round bottom flask. Rinse the scintillation vial with 3 ml of methanol and add to the 50-ml round bottom flask.
- 5.7. Evaporate the contents of the flask to dryness on a rotary evaporator at a bath

temperature of approximately  
40°C.

6.0. Charcoal Column Cleanup

- 6.1. Dissolve the residue in the 50-ml round bottom flask of Section II.C.5.7 in 5 ml of toluene.
- 6.2. Set up the chromatographic column according to the U.S. Food and Drug Administration Pesticide Analytical Manual (PAM), Vol. I, Section 232.34. Place a plug of glass wool at the bottom of the column. Add 1 g of Celite 545 to the column, tamp, add 6 g of adsorbent mixture (see PAM I, Section 232.32b), 1:2:4 (w/w/w) charcoal:magnesium oxide:Celite 545. Place a small glass wool plug on top of the adsorbent.
- 6.3. Prewash the column with 100-ml of 1:1 toluene:acetonitrile. Load the toluene solution from Section II.C.6.1 onto the column. Collect the load solution in a 250-ml round bottom flask.
- 6.4. Rinse the 50-ml round bottom flask with 10 ml of toluene. Collect the rinse as described in Section II.C.6.3. Repeat with another 10 ml rinse of the 50-ml round bottom flask.
- 6.5. Elute the column with 120 ml of 1:1 toluene:acetonitrile and collect the eluate in the 250-ml round bottom flask.
- 6.6. Evaporate the contents of the 250-ml round bottom flask to dryness on a rotary evaporator at a bath temperature of approximately 40°C. For wheat

grain samples, dissolve the residue in the flask in 1.0 ml of toluene. For forage and straw samples, dissolve in 2.0 ml of toluene.

D. INSTRUMENTATION

1.0. Description and Operating Conditions

See Table I.

2.0. Calibration and Standardization

2.1. The GC system is calibrated with each analytical run by checking the retention time and detector response relative to previous runs. Retention times should not vary by more than 5% and detector response should not vary more than 10% between runs.

2.2. The GC system is standardized by injecting aliquots of standard solutions of CGA-169374 in a working range of 0.1-2.5 ng/injection. A linear regression function is generated from the data comparing detector response and ng injected. Typical standardization data are presented in Table II and typical standard chromatograms are shown in Figure 2.

2.3. As with any packed column GC system, the column should be sufficiently primed to give an optimal peak shape by deactivating any active sites on the column. This is accomplished by making several injections of sample matrix extracts from Section II.C.6.6 until a constant peak shape and sensitivity are obtained for CGA-169374.

2.4. It may be necessary to increase the N/P element power beyond the recommended operating range in order to obtain sufficient peak height of the lowest calibration standard. A baseline of ca. 100 pA was used to acquire the chromatograms in Figures 2 through 5, using a Hewlett-Packard 5880A gas chromatograph.

#### E. INTERFERENCES

- 1.0. Some interferences have been observed as a result of carryover when large standard injections precede control and reagent blank injections. These interferences are particularly pronounced when other than "packed on-column" injection techniques are used. These problems can be minimized by properly maintaining the GC system (frequently changing the septum and glass wool at the head of the column), using direct "on-column" injection, and injecting samples and standards in a sequence where samples and standards of like concentration are adjacent.
- 2.0. Analysis of control samples of wheat forage and straw has shown no significant interferences at a screening level of 0.05 ppm. Analysis of control samples of wheat grain has shown no significant interferences at a screening level of 0.01 ppm. No interferences have been observed in reagent blanks.
- 3.0. As part of a review of data for an import tolerance petition<sup>8</sup>, EPA requested that the specificity of the method be demonstrated. A method specificity study<sup>9</sup> was conducted in which 68 compounds having tolerances in wheat, barley and rye were examined for potential interferences with the analysis of CGA-169374 by

the procedures of this method. Upon examination, eight compounds were eliminated from further testing based on chemical or physical properties. The remaining sixty compounds were fortified at the tolerance level on wheat grain and the samples analyzed by the procedures of the method. None of the compounds tested was found to interfere with the determination of CGA-169374 residues at its proposed tolerance level.

F. CONFIRMATORY TECHNIQUES

A successful confirmatory method trial was conducted at the EPA Methods Lab in Beltsville, MD<sup>10</sup>. As part of this trial, an alternate megabore gas chromatography column was used to demonstrate an improved separation of CGA-169374 from background in forage and straw. A copy of the EPA method trial including the gas chromatography conditions and representative chromatograms is presented in Appendix I.

G. TIME REQUIRED

A skilled analyst can carry out the extraction, cleanup and analysis of a set of 4-6 samples in a 24-hour period including GC analysis.

H. MODIFICATIONS

None.

I. PREPARATION OF STANDARD CGA-169374 SOLUTIONS

- 1.0. Weigh 100 mg of CGA-169374 analytical standard into a 100-ml volumetric flask and dilute to the mark with acetone.
  - 1.1. Make serial dilutions of the 1 mg/ml standard solution with toluene to give a series of injection standards in a range of 0.02 to 0.5 ng/ $\mu$ l of CGA-169374.

J. DETERMINATION OF SAMPLE RESIDUES

1.0. Inject aliquots of sample extracts from Section II.C.6.6 into the gas chromatograph under the same conditions as for standards. Make appropriate dilutions of the samples (if necessary) with toluene to bring the sample peak heights within the range of the standard curve. Compare the peak heights of the unknown samples to the standard curve or enter the peak height into the least squares program to determine the nanograms of CGA-169374 in the injected aliquot. Typical chromatograms for control and procedural recovery wheat samples are shown in Figures 3 through 5.

2.0. Calculate the residue results in terms of ppm of CGA-169374 by the following equation:

$$(1) \text{ PPM CGA-169374} = \frac{\text{CGA-169374 found (ng)}}{\text{mg sample injected}} \times \frac{100}{R\%}$$

where mg sample injected is calculated as follows:

$$(2) \frac{G}{V} \times V_a \times \frac{V_i}{V_f} \times \frac{V}{V + (W \times M/100)} = \text{mg inj.}$$

G = milligrams of sample extracted

V = the volume of the extraction solvent (ml)

V<sub>f</sub> = total volume of final injection solution (μl)

R% = recovery ratio given by equation (3)

V<sub>i</sub> = injection volume (μl)

V<sub>a</sub> = aliquot volume (ml)

W = weight of sample extracted (g)

M = moisture content of sample (%)

\*Moisture correction is needed for crop samples with a moisture content >20%. (The percent moisture is taken from PAM, Vol. I, Section 202).

### 3.0. Fortification Experiments

The method is validated for each set of samples analyzed by including an untreated control sample and one or more control samples fortified prior to extraction. Wheat forage and straw samples are typically fortified at 0.05 ppm CGA-169374. Wheat grain samples are typically fortified at 0.01 ppm.

- 3.1. Add up to 2.0 ml of the appropriate standard solution of CGA-169374 to 20 g of the wheat substrate prior to the addition of the extraction solvent for reflux in Section II.C.2.1. Allow the sample to sit for a few minutes before adding the extraction solvent. Adjust the concentration of the fortification solution so that no more than 2 mL of solution is added to 20-g of substrate if a higher concentration spike is desired.
- 3.2. Analyze the samples through the procedures of the method as for treated samples.
- 3.3. Calculate the ppm of CGA-169374 in the samples using Equation 1 excluding the 100/R% recovery factor. Determine the recovery factor by first subtracting the detector response for CGA-169374, if any, in the control sample from the CGA-169374 response in the recovery sample. Then calculate the recovery factor expressed as a percentage (R%) by the equation:

$$(3) \quad R\% = \frac{\text{CGA-169374 found (ng)}}{\text{ppm CGA-169374 added}} \times 100\%$$

### III. RESULTS AND DISCUSSION

To date, this method has been used for the analysis of control and CGA-169374-fortified samples of wheat forage, straw, and grain, as well as for field-incurred residues of CGA-169374 on the same crop fractions. A summary of procedural recoveries from fortification experiments appears in Table III.

This method is an extension of AG-537A<sup>2</sup>, in which the extractability of <sup>14</sup>C-labelled weathered residues has been addressed. Refer to AG-537A for more extensive fortification and recovery information.

The ruggedness of this method has been demonstrated and documented during ruggedness trials of methods AG-537A<sup>4</sup> and AG-575<sup>5</sup>.

### IV. CONCLUSION

Analytical Method AG-575B is a valid and accurate method for the determination of parent residues of CGA-169374 in wheat forage, straw, and grain.

V. CERTIFICATION

The reports and experimental results included in this study, Laboratory Project I.D. AG-575B, are certified to be authentic accounts of the experiments.

3-26-93  
Date

W. T. Beidler  
W. T. Beidler, Ph.D.  
State Reg. Manager,  
Regulatory Affairs  
(Formerly Study Monitor)  
919-632-2976

VI. CERTIFICATION OF GOOD LABORATORY PRACTICES

The analytical work cited as Supplemental Fortification Data, Table III AG-575B was performed in accordance with Good Laboratory Practice Standards, 40 CFR Part 160.

Appendix I is data generated by the USEPA and is thus not compliant with GLP and 40 CFR Part 160.

3/24/93  
Date

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Study Director

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Table I: Gas Chromatographic Conditions for Analysis  
of CGA-169374

Instrument: Hewlett-Packard 5880A Gas Chromatograph  
with a 7673A Autosampler and N/P Detector

Carrier Gas: Helium, Flow Rate 22 ml/min.

Detector Gases: Hydrogen, 3-4 ml/min.  
Air, 60 ml/min.

NPD Element Power 80-100 pA

Column: 3% OV-17 on 80/100 Mesh  
Chromo- sorb W-HP (2 ft. X 2.0 mm  
I.D.)

Injection: Packed column injection,  
Autosampler (5µl)

Injector Temperature: 290°C

Detector Temperature: 300°C

Column Oven Temperature: 245°C

Retention Time: ~5 min.

Table II: Typical Standardization Data for a  
CGA-169374 Standard Curve

<u>ng Injected</u>	<u>Peak Height (µv)</u>
0.10	128
0.10	102
0.20	198
0.20	195
0.50	576
1.00	1104

Linear regression analysis with VG Multichrom  
(Version 1.8), linear through zero fit selected.

(Analysis File = 23 AG575-2)

Slope: 1.10573E + 3

Intercept: 0.00000

Coefficient of Determination: 0.99758

Table III: Summary of Recovery Data for Wheat Samples Fortified with CGA-169374

A. Fortification Data\*

<u>Substrate</u>	<u>Fortification, ppm</u>	<u>Recovery (%)</u>
Forage	0.0	<0.05 ppm
	0.05	(76%)
Straw	0.0	<0.05 ppm
	0.05	(122%)
	0.075	(85%)
	Avg =	(104%)
Grain	0.0	<0.01 ppm
	0.0	<0.01 ppm
	0.01	(70%)
	0.01	(85%)
	0.01	(83%)
	0.01	(79%)
Avg =	(79%)	

B. Supplemental Fortification Data\*\*

<u>Substrate</u>	<u>Fortification, ppm</u>	<u>Recovery (%)</u>	<u>Field Test #</u>
Grain	0.01	(79%)	MW-FR-703-89
	0.01	(89%)	MW-FR-504-89
04-FR-001-89	0.01	(67%)	
	0.01	(88%)	04-FR-001-89
	0.05	(83%)	MW-FR-603-89
	0.05	(87%)	MW-FR-503-89
	0.05	(70%)	OW-FR-609-89
	0.20	(75%)	04-FR-001-89
	0.10	(109%)	OW-FR-614-89
	1.00	(97%)	OS-FR-103-89
	1.00	(100%)	OS-FR-505-89
	1.00	(78%)	OS-FR-208-89
	0.05	(100%)	05-FR-004-89
	0.05	(102%)	MW-FR-304-89
	0.01	(91%)	OW-FR-504-89
	0.05	(90%)	02-FR-008-89
Avg =	(88%)		

\*Results generated during Method AG-575 validation, RTR  
No. RI-MV-011-90

\*\*Supplemental results were generated as part of Study  
Protocol 19-89 Part-B2 Amendment No. 9, and are reported  
in ABR-90043 and ABR-90043 Amendment No. 1.

Figure 1: Flow Diagram For Analytical Method AG-575B

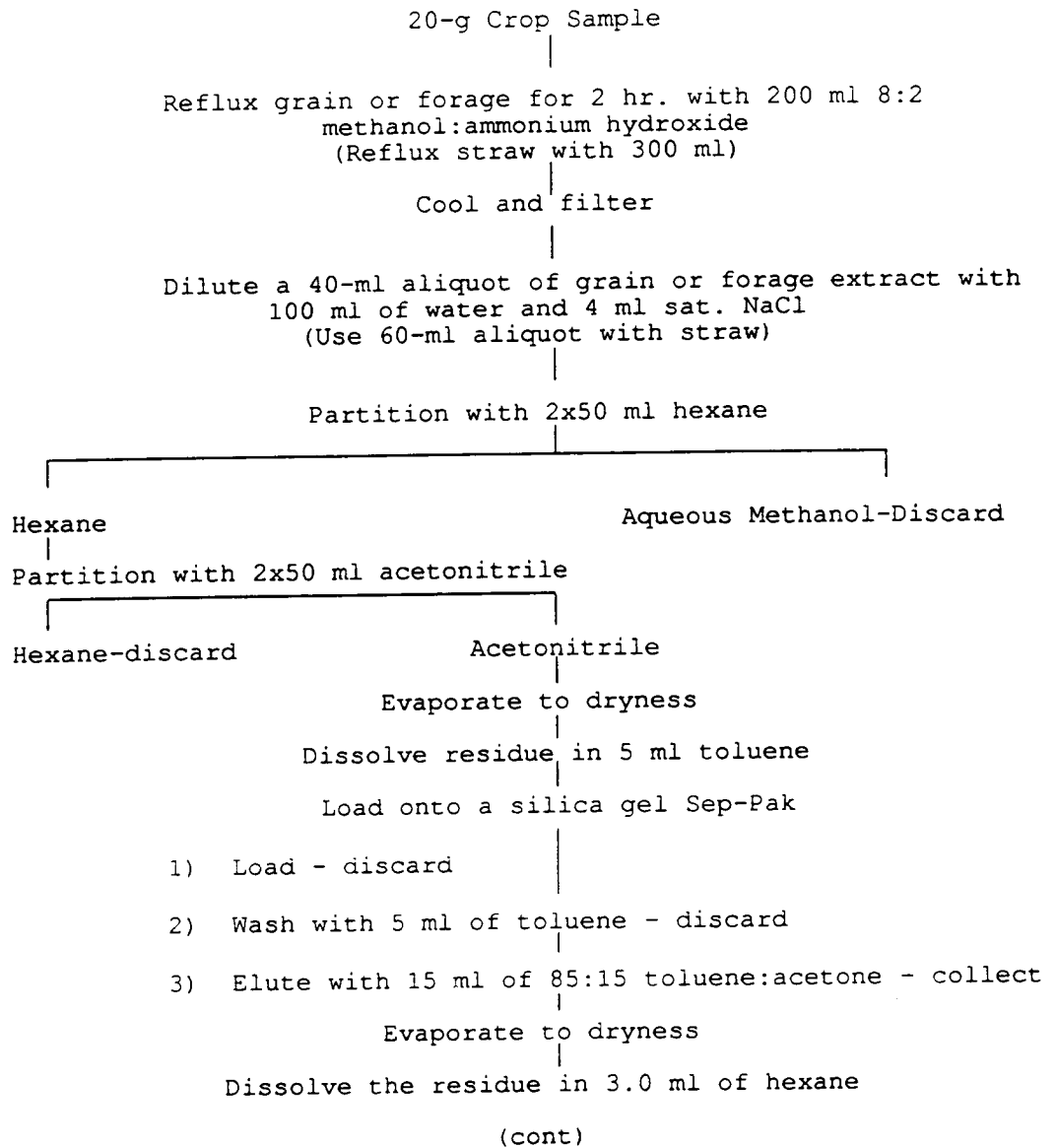


Figure 1: Flow Diagram For Analytical Method AG-575B

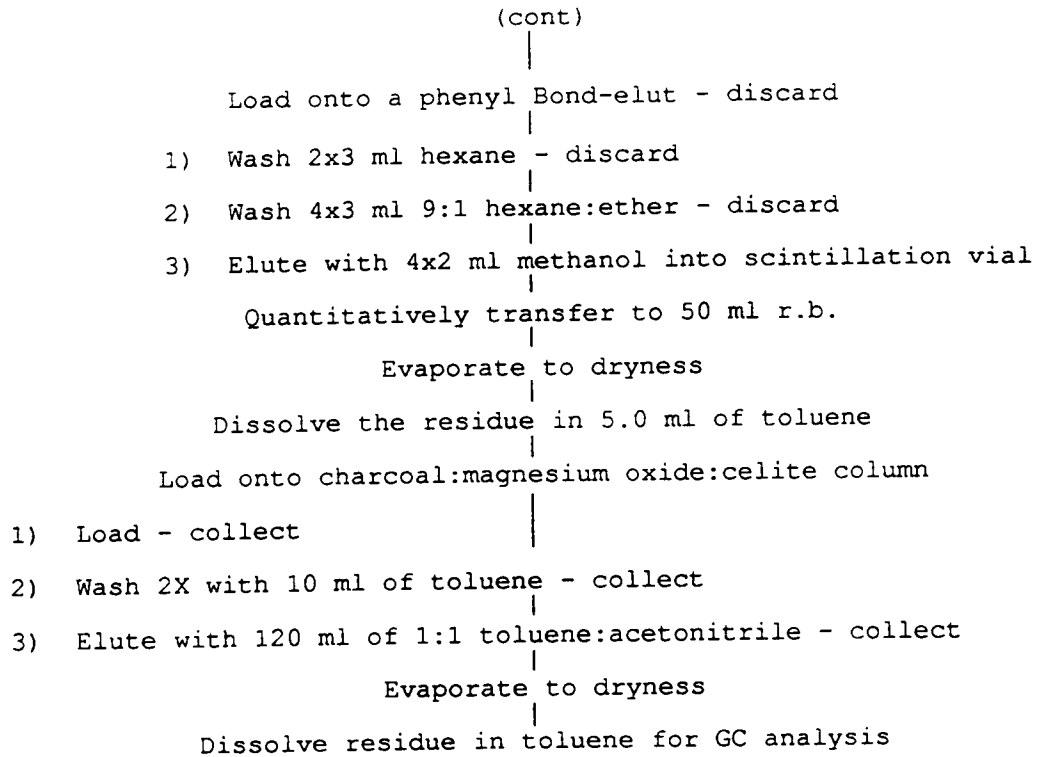
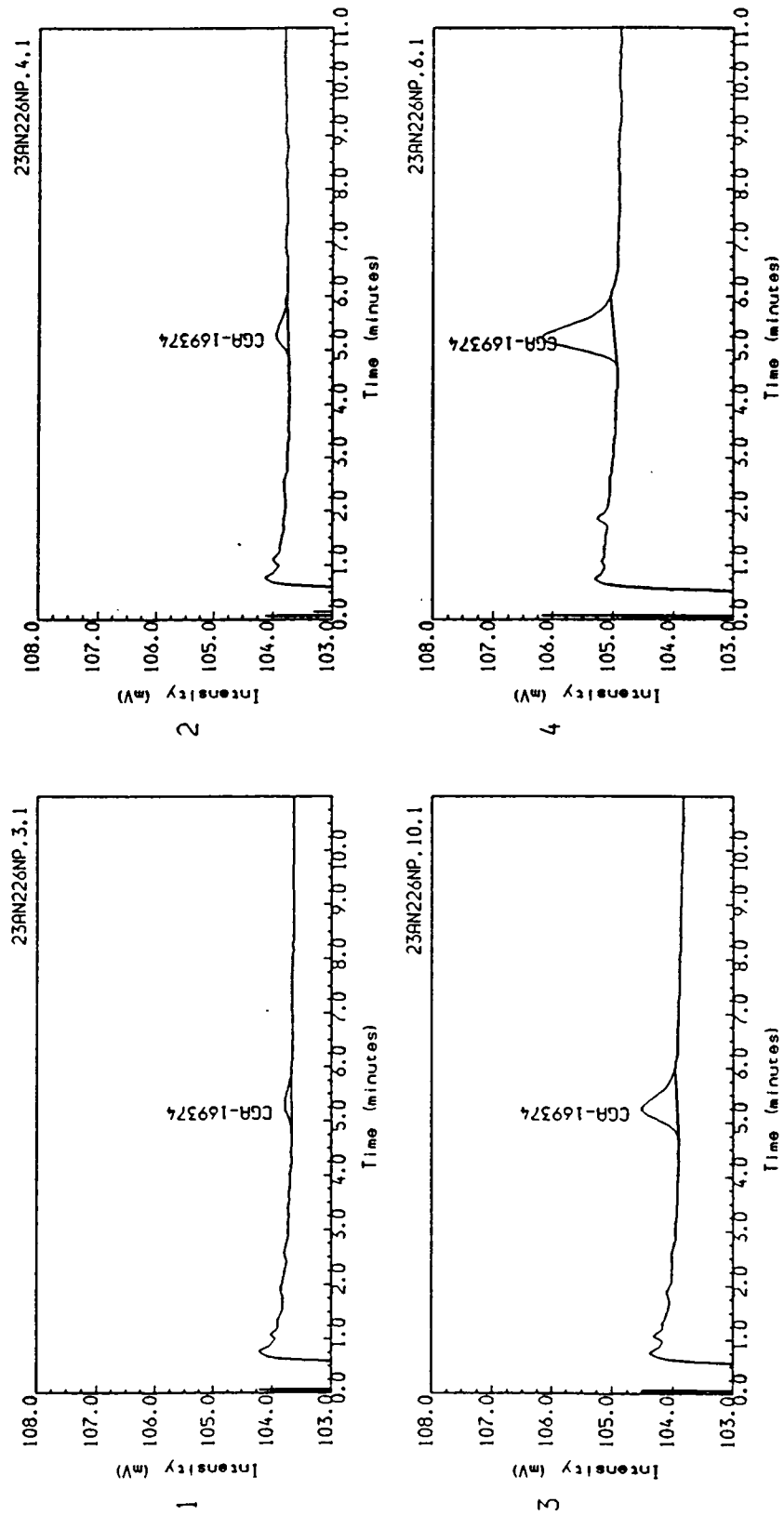
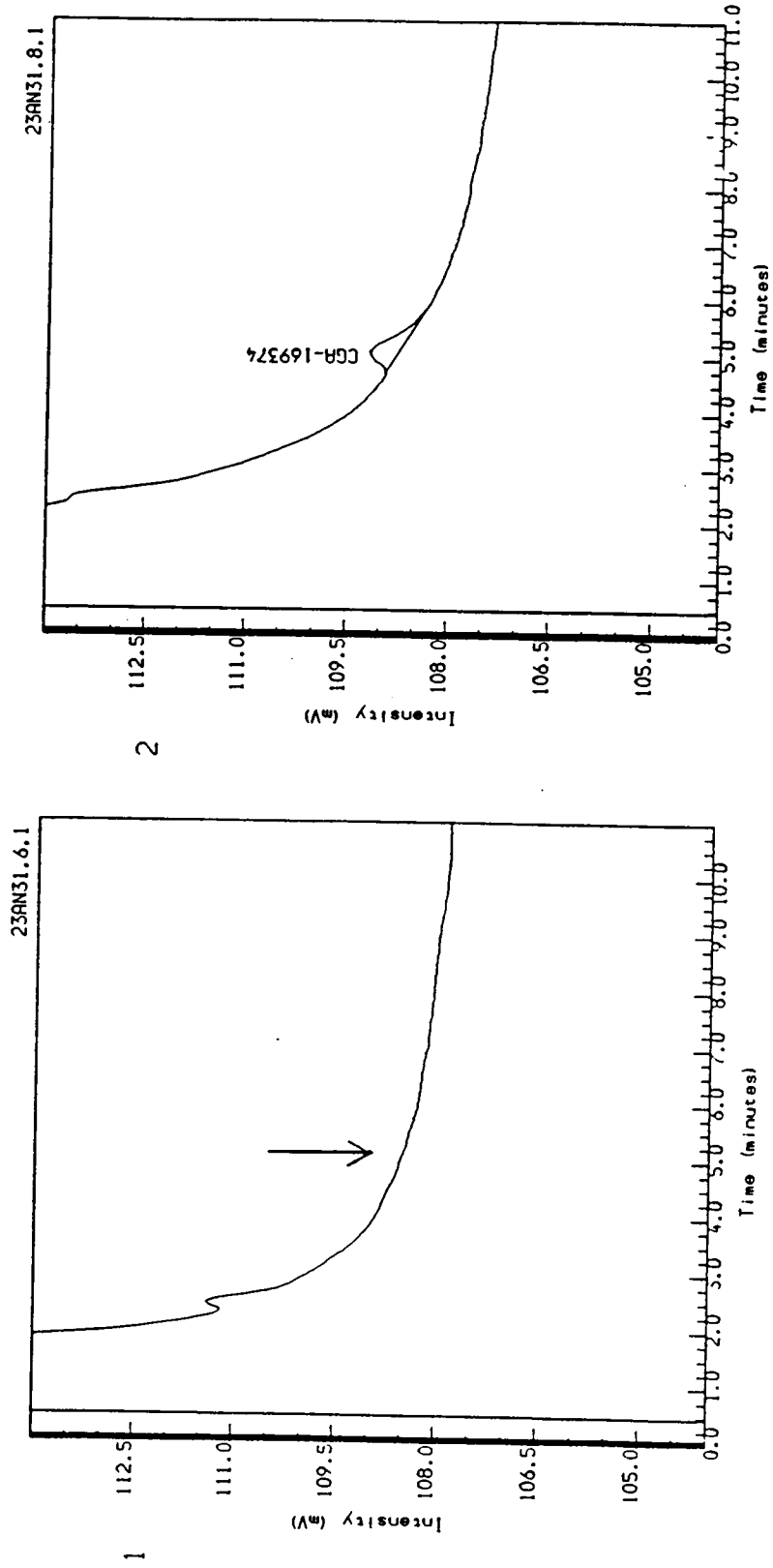


Figure 2. Typical Standard Chromatograms of CGA-169374 Under Analytical Conditions Specified in Table I



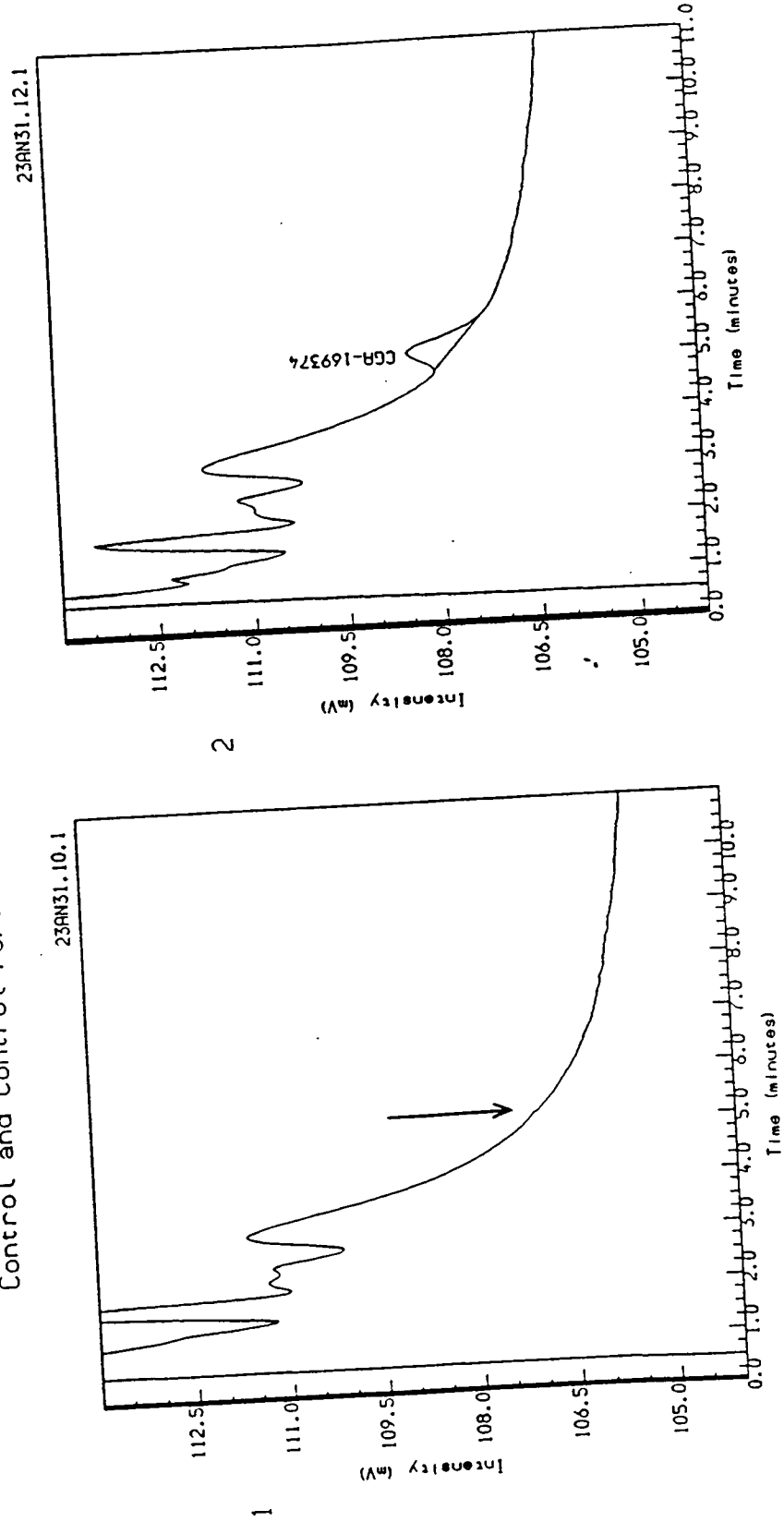
- 1. 0.10 ng Standard CGA-169374 (Detector response = 109 uV)
- 2. 0.20 ng Standard CGA-169374 (Detector response = 225 uV)
- 3. 0.50 ng Standard CGA-169374 (Detector response = 575 uV)
- 4. 1.00 ng Standard CGA-169374 (Detector response = 1186 uV)

Figure 3. Typical Chromatograms of CGA-169374 in Wheat Forage  
Control and Control Fortified with 0.05 ppm CGA-169374



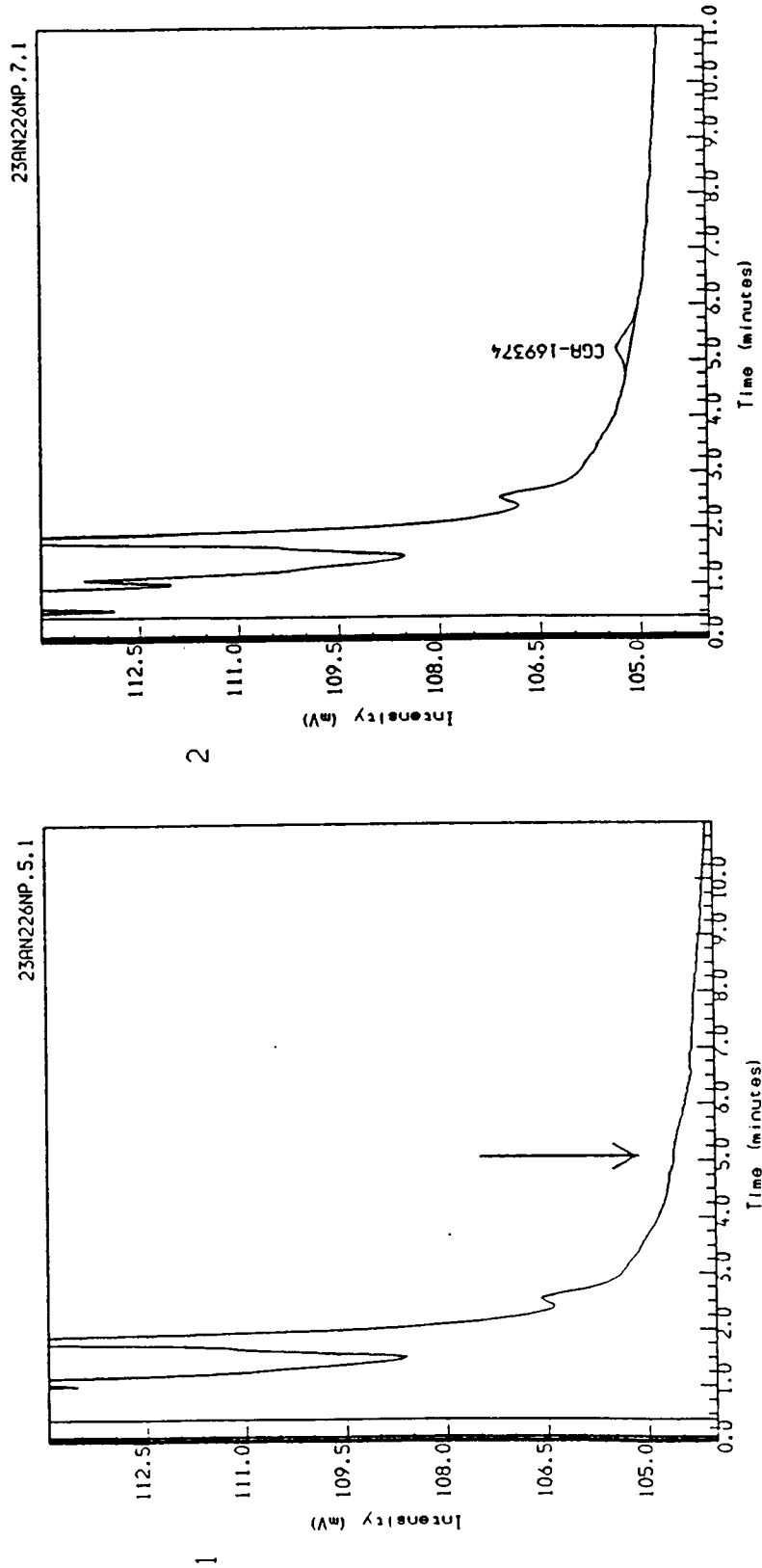
1. Control Forage, 10 mg injected, (0.01 ppm CGA-169374
2. Control Forage + 0.050 ppm CGA-169374, 10 mg injected, 76% Recovery

Figure 4. Typical Chromatograms of CGA-169374 in Wheat Straw  
Control and Control Fortified with 0.075 ppm CGA-169374



1. Control Straw. 10 mg injected. (0.01 ppm CGA-169374
2. Control Straw + 0.075 ppm CGA-169374. 10 mg injected. 85% Recovery

Figure 5. Typical Chromatograms of CGA-169374 in Wheat Grain  
Control and Control Fortified with 0.01 ppm CGA-169374



1. Control Grain, 20 mg injected, (0.01 ppm CGA-169374)
2. Control Grain + 0.01 ppm CGA-169374, 20 mg injected, 85% Recovery

VIII. REFERENCES

1. Darnow, J. and Sayers, L., Ciba Residue Dept. Method No. AG-575, "Analytical Method for the Determination of CGA-169374 in Wheat Raw Agricultural Commodities by Gas Chromatography with Nitrogen/Phosphorus Detection."
2. Williams, W. L., Ciba Residue Dept. Method No. AG-537A, "Analytical Method for the Determination of CGA-169374 in Wheat Raw Agricultural Commodities by Gas Chromatography."
3. Kuhne, H. and Merlini, R., Ciba-Geigy LTD. Method No. REM 7/86, "CGA-169374/Determination of Parent Compound by Gas Chromatography."
4. Whetzel, J. E., EMS Heritage Laboratories Report No. EMS9003.1, "Method Ruggedness Trial for Ciba Analytical Method No. AG-537A for the Determination of CGA-169374 in Wheat Raw Agricultural Commodities by Gas Chromatography."
5. Yarko, J., CYAL Report No. 900201, "Independent Laboratory Confirmation of a Proposed Tolerance Enforcement Method for the Determination of CGA-169374 in Wheat Raw Agricultural Commodities by Gas Chromatography, Ciba Method No. AG-575."
6. Cheung, M. W., Oakes T. L., Moore, M. E., and Smith, J. W., Ciba Residue Dept. ABR-90043, "CGA-169374 (Difenoconazole) - Magnitude of Residues in Spring Wheat and Processed Grain Fractions Following Seed Treatment with Dividend® 3FS."
7. Senzel, A. J. and Ross, J. A., Ciba Residue Dept. ABR-90043, "CGA-169374 (Difenoconazole) - Magnitude of Residues in Spring Wheat and Processed Grain Fractions Following Seed Treatment with Dividend 3FS. Amendment 1 to Incorporate Residue Results for CGA-169374 (Difenoconazole) in Winter Wheat Forage, Straw, and Grain Following Seed Treatment with Dividend 3FS."

8. Memorandum dated November 4, 1992 from Cynthia Giles-Parker, PM-22, Fungicide Herbicide Branch, Registration Division (H7505C) to Eileen D. King-Watson, Ph.D., Ciba re PP#2E4051. CGA-169374 (Difenoconazole, Dividend) in Imported Wheat Barley and Rye Grain.
9. Yokley, R. A., Specificity of Analytical Method AG-575A For The Determination of CGA-169374 in Small Grains. ABR-92084 March 9, 1993.
10. Memorandum (with attachments) dated January 7, 1993 from Cynthia Giles-Parker, PM-22, Fungicide Herbicide Branch, Registration Division (H7505C) to Greg Watson, Ph.D., Ciba re PP#2E4051. CGA-169374 (Difenoconazole, Dividend) Petition Method Validation Trial of Analytical Method AG-575A. MRID No. 420920-52,-53.

JAN 11 1993

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Appendix I



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

OFFICE OF  
PREVENTION, PESTICIDES  
AND TOXIC SUBSTANCES

JAN 7 1993

Greg Watson Ph.D.  
Agricultural Division  
Ciba-Geigy Corporation  
P.O. Box 18300  
Greensboro, NC 277419

Dear Dr. Watson:

Subject: Petition for Import Tolerance for Wheat, Barley and Rye  
Technical CGA-169374/Dividend  
Pesticide Petition 2E4051  
Your Submission Dated October 14, 1991

Chemistry Branch I - Tolerance Support (CBTS) and Analytical  
Chemistry Branch have completed review of the method validation  
trial and have the following comments:

The analytical method, as submitted, is suitable for use as an  
enforcement method, for the purpose of the subject petition for  
wheat, barley and rye grains. For future petitions on wheat (and  
barley and rye) straw and forages, you should amend the method to  
allow for use of a DB-17 megabore column instead of a packed  
column.

For your assistance enclosed is a copy of the scientific  
review.

Sincerely yours,

A handwritten signature in cursive script, appearing to read "C. Giles-Parker".

Cynthia Giles-Parker  
Product Manger (22)  
Fungicide Herbicide Branch  
Registration Division (H7505C)

Enclosure



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

DEC 28 1992

OFFICE OF  
PESTICIDES AND TOXIC  
SUBSTANCES

Memorandum

**Subject:** PP#2E4051. CGA-169374 (Difenoconazole, Dividend) Petition Method Validation Trial of Analytical Method AG-575A. No CBTS#. MRID# 420900-52, -53. No DP Barcode#.

**From:** Robert Lascola, Chemist  
Chemistry Branch I - Tolerance Support *Rob Lascola*  
Tolerance Petition Section III  
Health Effects Division (H7509C)

**Through:** P. V. Errico, Section Head *P. V. Errico for*  
Chemistry Branch I - Tolerance Support  
Tolerance Petition Section III  
Health Effects Division (H7509C)

**To:** Jim Stone/Cynthia Giles-Parker (PM22)  
Fungicide/Herbicide Branch  
Registration Division (H7505C)

CIBA-GEIGY has requested the establishment of tolerances for residues of the fungicide CGA-169374 (difenoconazole) (1-{2-[4-(4-chlorophenyl)-2-chlorophenyl]-4-methyl-1,3-dioxolan-2-yl-methyl}-1H-1,2,4-triazole) in or on the imported RACs wheat, barley, and rye grain at 0.1 ppm. The original petition was reviewed in R. Lascola's memo of 10/26/92. In that review, several deficiencies were noted, including several concerning the analytical enforcement method. That method is CIBA-GEIGY Analytical Method AG-575A, "Analytical Method for the Determination of CGA-169374 in Wheat Raw Agricultural Commodities by Gas Chromatography with Nitrogen/Phosphorus Detection", 5/17/91, by Mark Grunewald, MRID# 420900-52. CBTS noted in that review that the method would be forwarded to the EPA Beltsville laboratories for validation, and that if any additional deficiencies were noted as a result of that trial, they would be forwarded to the petitioner.

CBTS requested the petition method validation trial on 5/27/92. The reply was received recently. Recoveries from grain, straw, and forage matrices are listed in Table 1. Specific comments about the running of the method included the following:

- 1) As stated in the PAM Vol I (Section 232.34) it is necessary to apply vacuum to the charcoal

column in order to elute the sample at a faster rate. ACL did not use vacuum for the wheat grain extracts, but did use vacuum for the other two commodities. The use of vacuum, while significantly speeding up the analysis, had no apparent effect on the recoveries.

2) ACL preferred to transfer and store the cleaned up extracts in 10 or 25 mL Mills tubes rather than in 250 mL round bottom flasks. Also, in order to increase sensitivity, ACL used 1 mL as the final volumes for wheat straw and wheat forage rather than 2 mL.

Commodity	Spike Added (ppm)	Residue Found (ppm)	% Recovery
Wheat Grain	Control	0.011, ND	---
	0.055	0.063, 0.060	115, 109
	0.11	0.130, 0.120	118, 109
Wheat Forage	Control	ND, ND	---
	0.055	0.062, 0.057	112, 104
	0.11	0.098, 0.111	90, 101
Wheat Straw	Control	ND, ND	---
	0.055	0.057, 0.058	103, 107
	0.11	0.114, 0.108	103, 98

3) Although ACL had acceptable results using the recommended packed column with all commodities, Dividend showed up on the chromatograms as a shoulder peak in wheat straw and in wheat forage extracts. With these two commodities it was necessary to measure the peak height by hand, rather than using the values from the GC integrator. ACL investigated the use of a 15 meter DB-17 megabore column in order to achieve better chromatographic resolution between the analyte and interferences in the commodity. The enclosed chromatograms (see Attachment) show that a megabore column would give better separation than the recommended packed column.

ACL had the following general conclusions:

- 1) While the submitted method for the analysis of Dividend in wheat raw agricultural commodities gave satisfactory recoveries at the requested spiking levels, the chromatographic separation in the straw and forage samples was marginal at best. Although the method gave acceptable results for wheat forage and wheat straw, the registrant might consider using a megabore column for better GC separations for those commodities.
- 2) Two chemists can prepare six (6) samples and analyze them on the GC within 24 hours.
- 3) Moisture content data for the forage was not listed in PAM, Vol. I., Section 202. ACL used a value of 70% moisture, which was provided by the registrant.

- 4) Based on GC chromatograms of the controls ACL estimates the detection limits to be 0.01 ppm in wheat grain, wheat straw, and wheat forage.
- 5) This method meets 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.

**CBTS comments:** This method, as submitted is suitable for use as an enforcement method, for the purposes of this petition for wheat, barley, and rye grains. For future petitions on wheat (and barley and rye) straw and forages, the petitioner should amend the method to allow for use of a DB-17 megabore column instead of a packed column.

CBTS continues to recommend against the proposed import tolerances of 1.0 ppm for wheat, barley, and rye grains for the reasons stated in Conclusions 1(a-e, i, and k), 5(a-b), and 8 in our 10/26/92 review. There are no "additional deficiencies" as referred to in Conclusion 5c.

We recommend that this entire review, including the attachment, be sent to the petitioner.

**Attachment:** ACL report of petition method validation trial.

**cc w/Attachment:** PP#2E4051.

**cc without Attachment:** R. Lascola, RF, Circulation, D. Edwards.

H7509C:CBTS:RLascola/rjl:CM#2:Rm805B:305-7478:12/21/92

**RDI:** J. Garbus: 12/22/92; R.Loranger:12/23/92.

☐:Disk\DIFENO2.PMV



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

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Appendix I

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

OFFICE OF  
PREVENTION, PESTICIDES  
AND TOXIC SUBSTANCES

MEMORANDUM

DEC 28 1992

SUBJECT: PP#2E4051. CGA-169374 (Difenoconazole, Dividend).  
Petition Method Validation Trial of  
Analytical Method AG-575A. MRID# 420900-52,-53.  
HED# 9029.

FROM: Alex Krynitsky, Chemist *AK*  
Dallas P. Wright, Chemist *DPW*  
Analytical Chemistry Section

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

THRU: Donald A. Marlow, Chief *DM*  
Analytical Chemistry Branch

TO: Philip V. Errico, Section Head  
Tolerance Petition Section III  
Chemistry Branch I- Tolerance Support  
Health Effects Division (H7509C)

INTRODUCTION

Chemistry Branch I requested that the Analytical Chemistry Laboratory run a method validation on Dividend (1-[[2-[2-chloro-4-(4-chloro-phenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole) in wheat grain, wheat forage, and wheat straw using the following method: "Analytical Method for the Determination of CGA-169374 in Wheat Raw Agricultural Commodities by Gas Chromatography with Nitrogen/Phosphorus Detection", 5/17/91, by Mark Grunewald, CIBA-Geigy Corporation, Greensboro, NC, MRID# 420900-52.

## METHOD SUMMARY

A representative crop sample is extracted by refluxing in 8:2 (v/v) methanol:conc. ammonium hydroxide. After filtering, an aliquot of extract is diluted with water and saturated sodium chloride, and partitioned with hexane. The hexane fraction is partitioned with acetonitrile and the acetonitrile fraction is cleaned up on a silica gel Sep-Pak. The sample is then cleaned up on a phenyl Bond-elut, followed by charcoal:magnesium oxide:celite column cleanup step. The extract is analyzed by packed column gas chromatography using nitrogen/phosphorus detection.

## COMMENTS

### 1) Charcoal Column Cleanup:

As stated in the PAM Vol I (Section 232.34) it is necessary to apply vacuum to the charcoal column in order to elute the sample at a faster rate. ACL did not use vacuum for the wheat grain extracts, but did use vacuum for the other two commodities. The use of vacuum, while significantly speeding up the analysis, had no apparent affect on the recoveries.

### 2) Evaporation of Samples prior to GC analysis:

A) ACL preferred to transfer and store the cleaned up extracts in 10 or 25 mL Mills tubes rather than in 250 mL round bottom flasks.

B) In order to increase sensitivity, ACL used 1 mL as the final volumes for wheat straw and wheat forage rather than 2 mL.

### 3) ACL's GC Conditions:

Column - 2 ft. x 2 mm I.D. OV-17 80/100 mesh Chromosorb WHP Supelco packed column.

Column Temp. - 255 Deg. C  
Detector Temp. - 300 Deg. C  
Injector Temp. - 290 Deg. C

Helium Flow - 25 mL/min.  
Hydrogen Flow - 3.4 mL/min.  
Air Flow - 105 mL/min.

#### 4) GC Column and Chromatography:

Although ACL had acceptable results using the recommended packed column with all commodities, Dividend showed up on the chromatograms as a shoulder peak in wheat straw and in wheat forage extracts. With these two commodities it was necessary to measure the peak height by hand, rather than using the values from the GC integrator. ACL investigated the use of a 15 meter DB-17 megabore column in order to achieve better chromatographic resolution between the analyte and interferences in the commodity. The enclosed chromatograms (see Exhibit A) show that a megabore column would give better separation than the recommended packed column.

GC Conditions using the DB-17 megabore:

Column: DB-17 Megabore; 15 m x 0.53 mm I.D.; Film Thickness 1.0 micron.

The other GC parameters were the same as with the packed column.

General Comments

1. While the submitted method for the analysis of Dividend in wheat raw agriculture commodities gave satisfactory recoveries at the requested spiking levels, the chromatographic separation in the straw and forage samples was marginal at best.

2. Two chemists can prepare six (6) samples and analyze them on the GC within 24 hours.

3. Moisture content data for the forage was not listed in PAM, Vol. I, Section 202. ACL used a value of 70% moisture, which was provided by the registrant.

4. Based on GC chromatograms of the controls ACL estimates the detection limits to be 0.01 ppm in wheat grain, wheat straw and wheat forage.

5. ACL is enclosing a copy of the method validation pre-review as additional information.

6. The method meets 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.

ANALYTICAL RESULTS FOR WHEAT GRAIN

ppm Dividend Added	ppm Found	% Recovery
Control	0.011	-
Control	N.D.*	-
0.055	0.063	115
0.055	0.060	109
0.11	0.130	118
0.11	0.120	109

\*N.D. = < 0.01 ppm

ANALYTICAL RESULTS FOR WHEAT FORAGE

ppm Dividend Added	ppm Found	% Recovery
Control	N.D.*	-
Control	N.D.	-
0.055	0.062	112
0.055	0.057	104
0.11	0.098	90
0.11	0.111	101

\*N.D. = < 0.01 ppm

ANALYTICAL RESULTS FOR WHEAT STRAW

ppm Dividend Added	ppm Found	% Recovery
Control	N.D.*	-
Control	N.D.	-
0.055	0.057	103
0.055	0.058	107
0.11	0.114	103
0.11	0.108	98

\*N.D. = < 0.01 ppm

Modification to method (major or minor):

See Comments Section

Special precautions to be taken:

The usual precautions when handling hazardous materials.

Source of Analytical reference standards:

U.S. EPA Pesticide and Industrial Chemicals Repository  
Research Triangle Park, NC 27709

Derivatized Standards and Source:

None

Instrumentation for quantitation:

Hewlett Packard 5890 GC with Nitrogen Phosphorous Detector.

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

See comment section.

Commercial sources for any special chemicals or apparatus:

N/A

Additional Comments:

Although method gave acceptable results for wheat forage and wheat straw, registrant might consider using a megabore column for better GC separations for those commodities (see comment section).

Chromatograms:

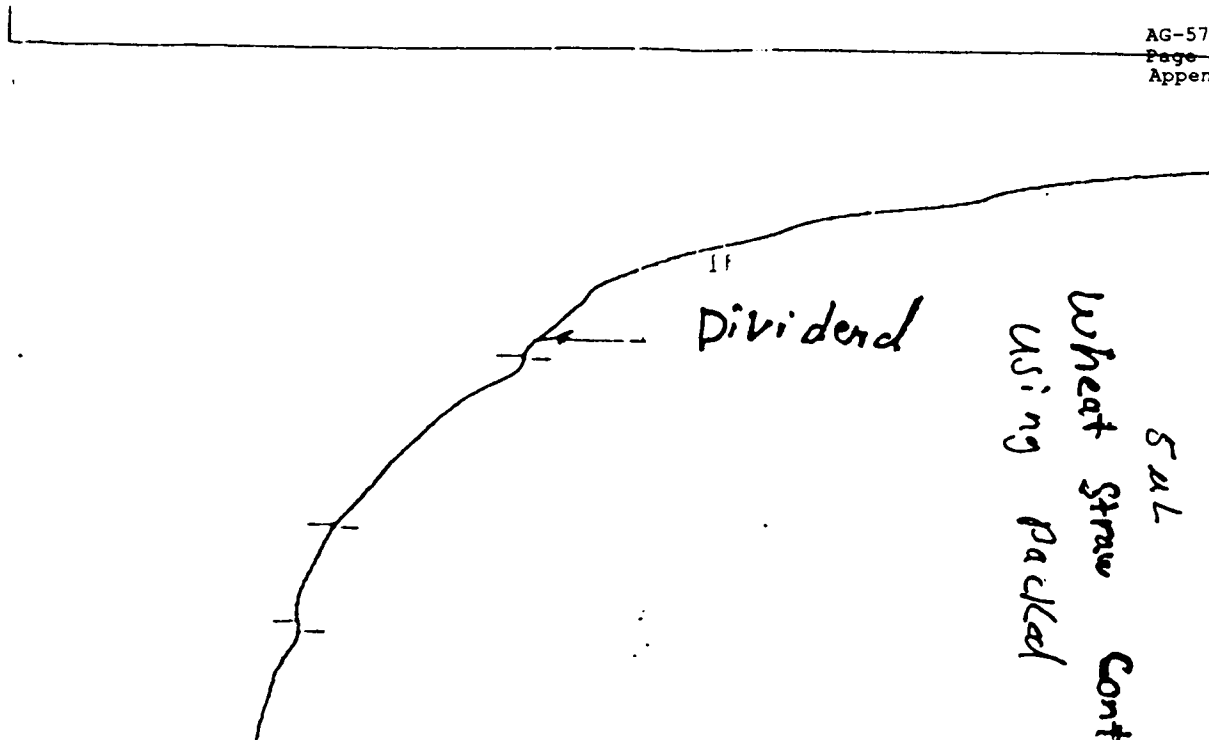
Representative chromatograms from the validation study are attached along with chromatograms showing the improvement in chromatography using a DB-17 megabore column for wheat straw and wheat forage.

EXHIBIT A

- a. Sample Chromatograms of controls and 0.11 ppm spikes in wheat straw and wheat forage using packed column G.C.
  
- b. Sample chromatograms of controls and 0.11 ppm spikes in wheat straw and wheat grain using DB-17 Megabore Column.

Exhibit A

Wheat Straw Control  
5AL  
Using Packed Column GC.



TINCTABLE STOP

Closing signal file B:\01E87029.BNA

RUN# 4 JAN 1, 1901 01:00:24

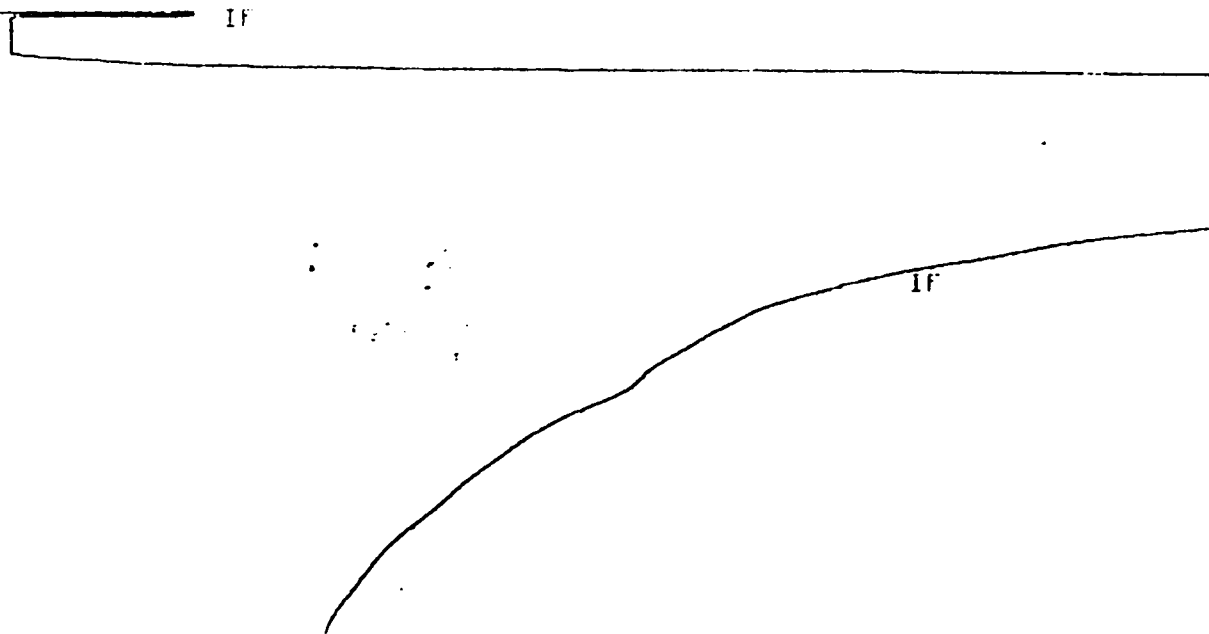
SAMPLE NAME: US-1 SAMPLE# 2  
BAC-19: 5 UL CONTROL

SIGNAL FILE: B:\01E87029.BNA

MON 1900 THU

NO RUN PERMS STORED

RUN # 5 JAN 1, 1901 01:12:17  
START



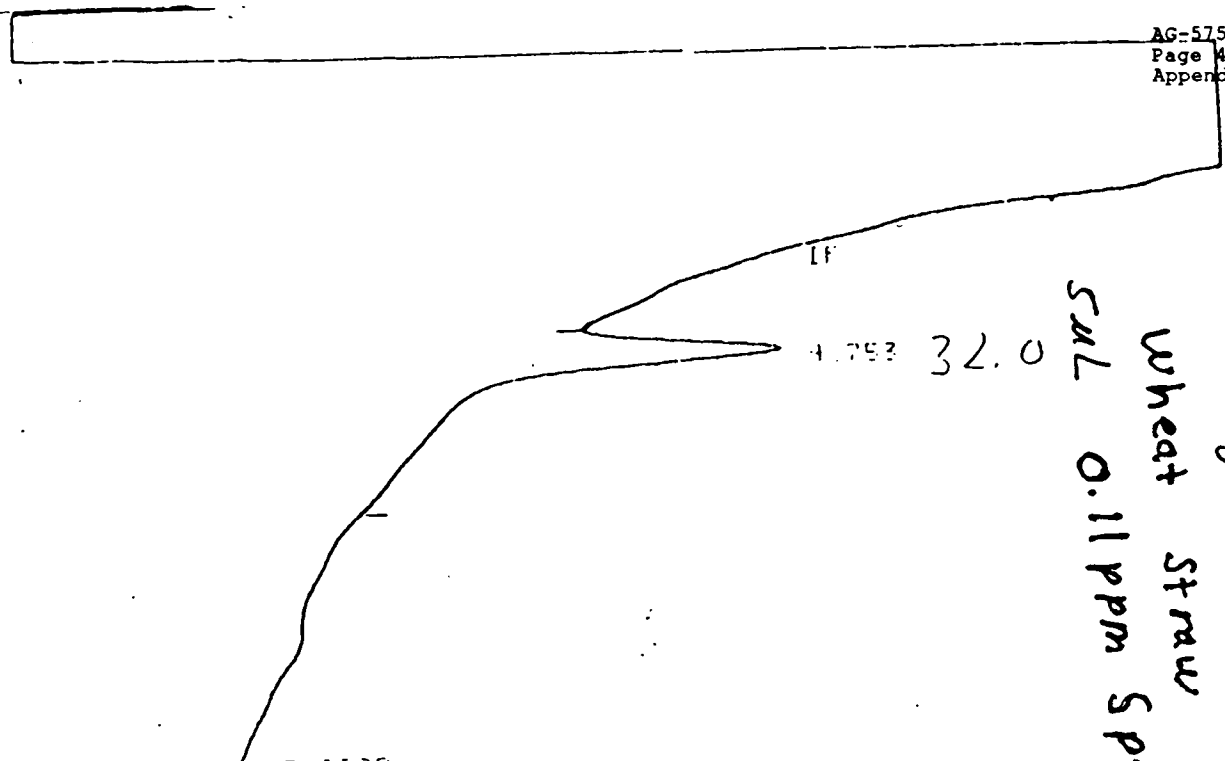


Exhibit A  
Using Packed Column GC.  
Wheat Straw  
5ul 0.11ppm Spike

TIMEABLE STOP

Closing signal file B:010ARREF.BUR

RUN# 20 JAN 1, 1901 04:11:26

SAMPLE NAME: US-6 SAMPLE# 10  
SAC-19: 5 UL 0.11 ppm SPI

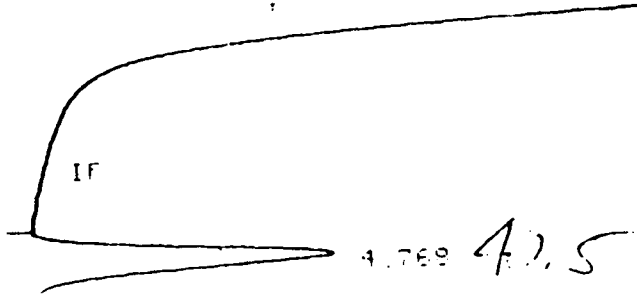
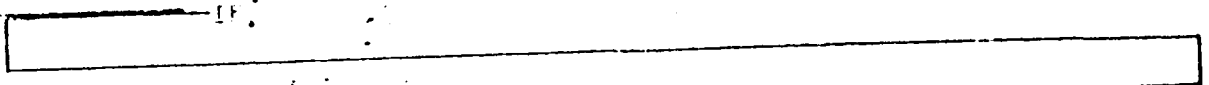
SIGNAL FILE: B:010ARREF.BUR

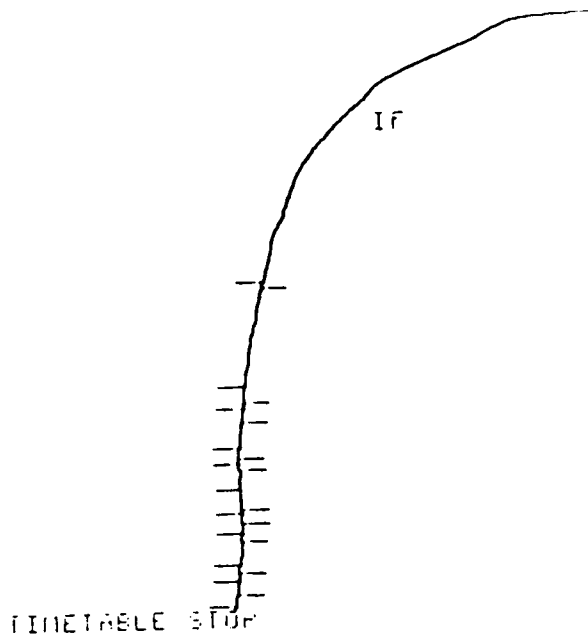
TIME 1900 TIME

HEIGHT	RT	HEIGHT	AREA	WIDTH	HEIGHT%
	4.753	3186	88	.125	100.00000

TOTAL HEIGHT= 3186  
INFL FACTOR=1.0000E+00

RUN# 21 JAN 1, 1901 04:23:26  
START





Closing signal file B:\09501435.BNC

RUN# 174 OCT 9, 1992 16:37:08

SAMPLE NAME: F-1 SAMPLE# 2  
SAL-19: S OL CONTROL

SIGNAL FILE: B:\09501435.BNC

NOV 1990 THU

NO RUN PEAR'S STOPED

RUN # 175 OCT 9, 1992 16:48:57  
START

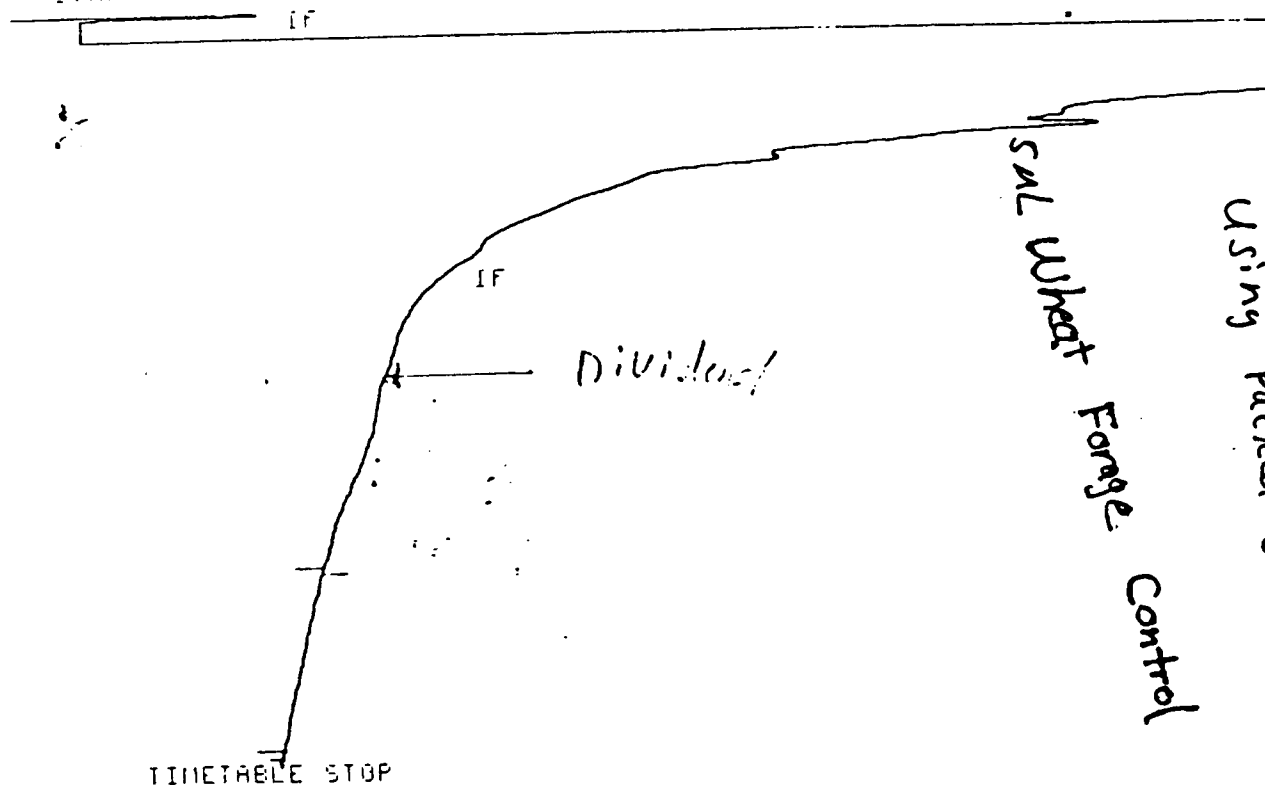


Exhibit A  
Using Packed Column G-C.



Exhibit A  
SAL Wheat Forage  
0.11 ppm Spike  
Using Packed Column. GC.

Closing signal file B:\055E948E.BNC

FORM 135 OCT 10, 1990 15:38:13

SAMPLE NAME: F-8 SAMPLE# 3  
E82-19: 5 UL 0.11 PPM SPIKE P600

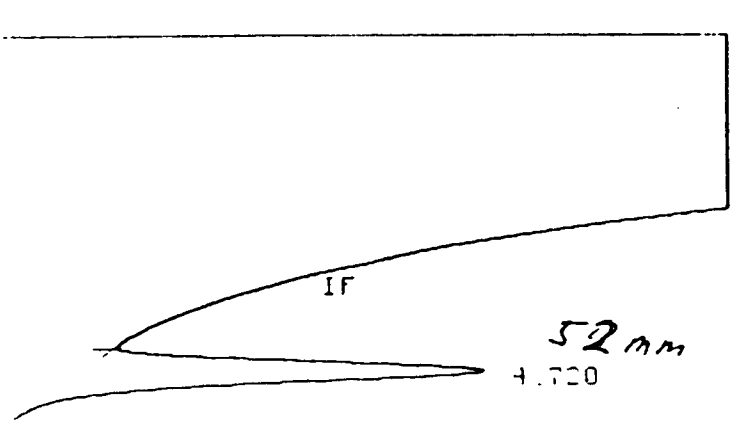
SIGNAL FILE: B:\055E948E.BNC

TIME 13900 MIN

HEIGHT	RT	HEIGHT	TYPE	WIDTH	HEIGHT
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TOTAL HEIGHT= 1917  
GUL FACTOR=1.00000E+00

FORM # 136 OCT 10, 1990 15:40:11  
START



B 92-19

DB-17 Megabarc GC column  
15 m x 0.53 mm I.D.  
Film Thickness 1.0 micron  
Exhibit A

WELCOME TO THE HP 3396 BATCH REPROCESSING PROGRAM (Rev. B.01.00)

AT ANY PROMPT: 'Q' [ENTER] Quits  
'S' [ENTER] Starts Over

Method file for reprocessing [Current active\*]:

Calibration file for reprocessing [Current active\*]:

Use Sequence Sample Table for reprocessing [Y\*/N]:

Sequence file with Sample Table [Current active\*]:

Enter the first signal data file name: B:05710346.BNC

Enter the last signal data file name: B:0571178D.BNC

VOLUME NAME: DIU DRIVE: B  
DATE: NOV 4, 1992 10:44:51

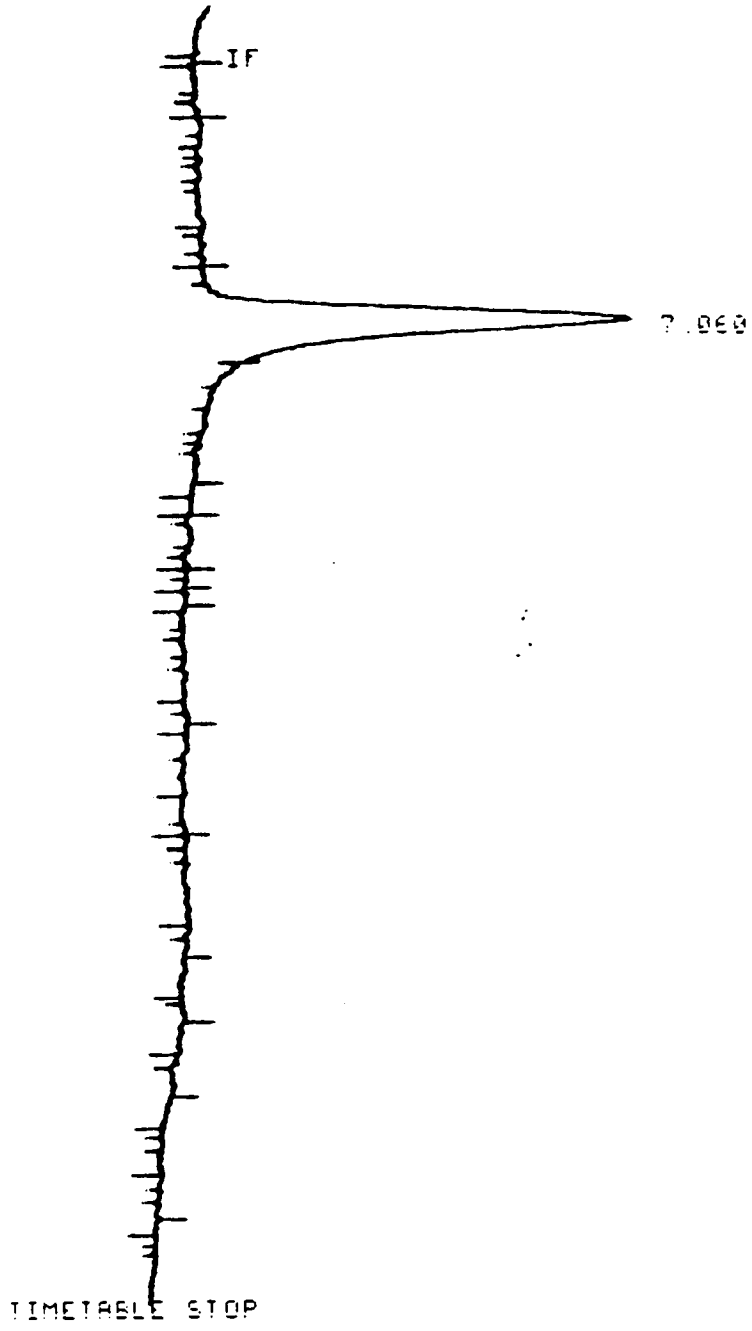
PROCESSING!

RUN # 55 NOV 3, 1992 15:01:25  
START

\_\_\_\_\_ IF  
\_\_\_\_\_

Exhibit A  
DB-11 Megabore Column

ul 0.551g/ml Dividend Std.



Closing signal file B:\05710346.BNR

RUN# 55 NOV 3, 1992 15:01:25

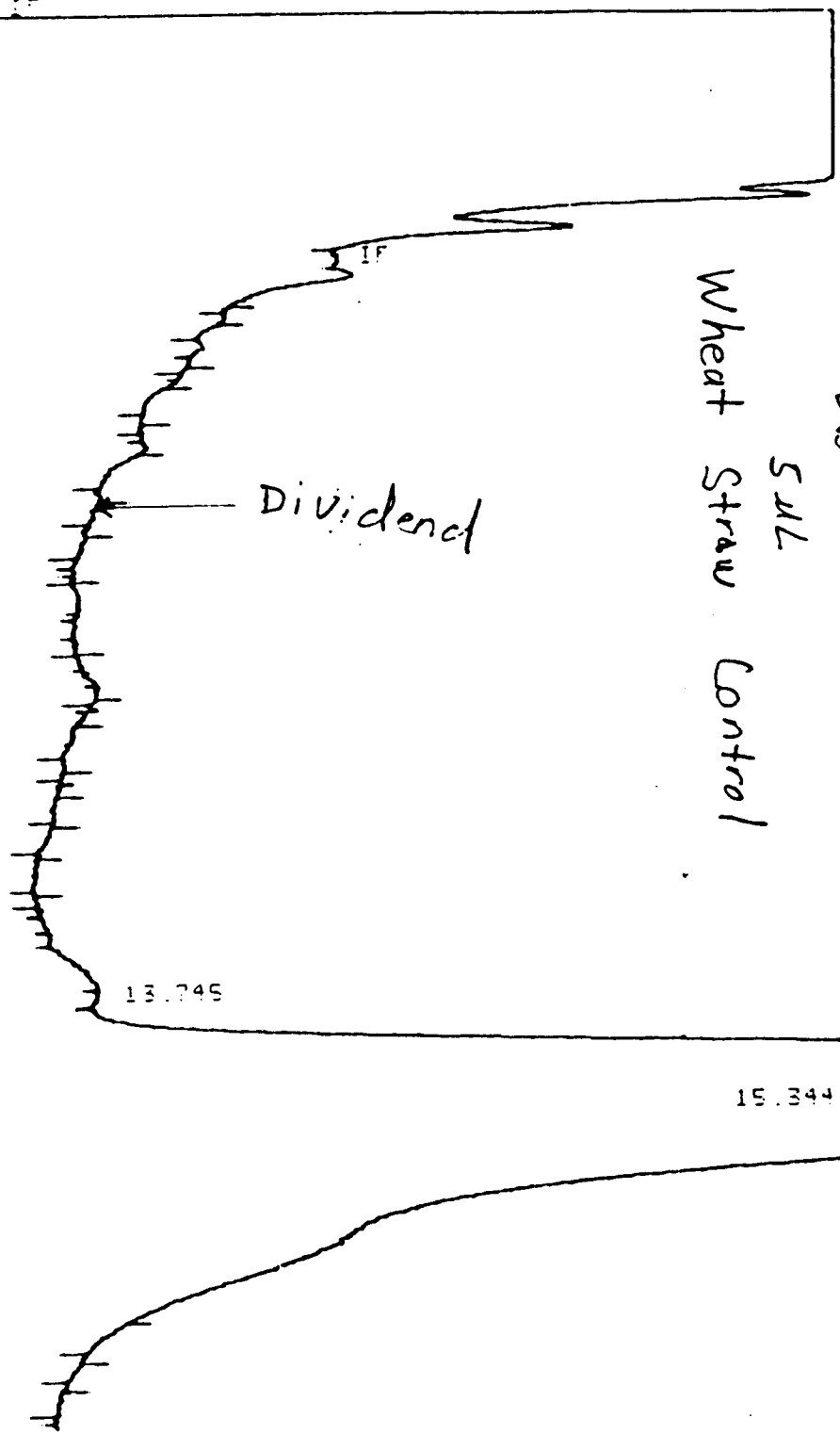
SAMPLE NAME: STD SAMPLE# 1  
BAC-15: S UL 0.551 UG/ML DIU

SIGNAL FILE: B:\05710346.BNR

MOD 12900 TMU

HEIGHTX	RT	HEIGHT	TYPE	WIDTH	HEIGHTX
	7.068	1511	UU	.491	100.00000

TOTAL HEIGHT= 1511  
MUL FACTOR=1.0000E+00



TIMETABLE STOP

Closing signal file B:\05710863.BNA

RUN# 56 NOV 3, 1992 15:23:14

SAMPLE NAME: CONTROL SAMPLE# 2  
B92-19: STRAW CONTROL

SIGNAL FILE: B:\05710863.BNA

MON 13908 TMU

TOTAL HEIGHT= 21064  
MUL FACTOR=1.0000E+00

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START

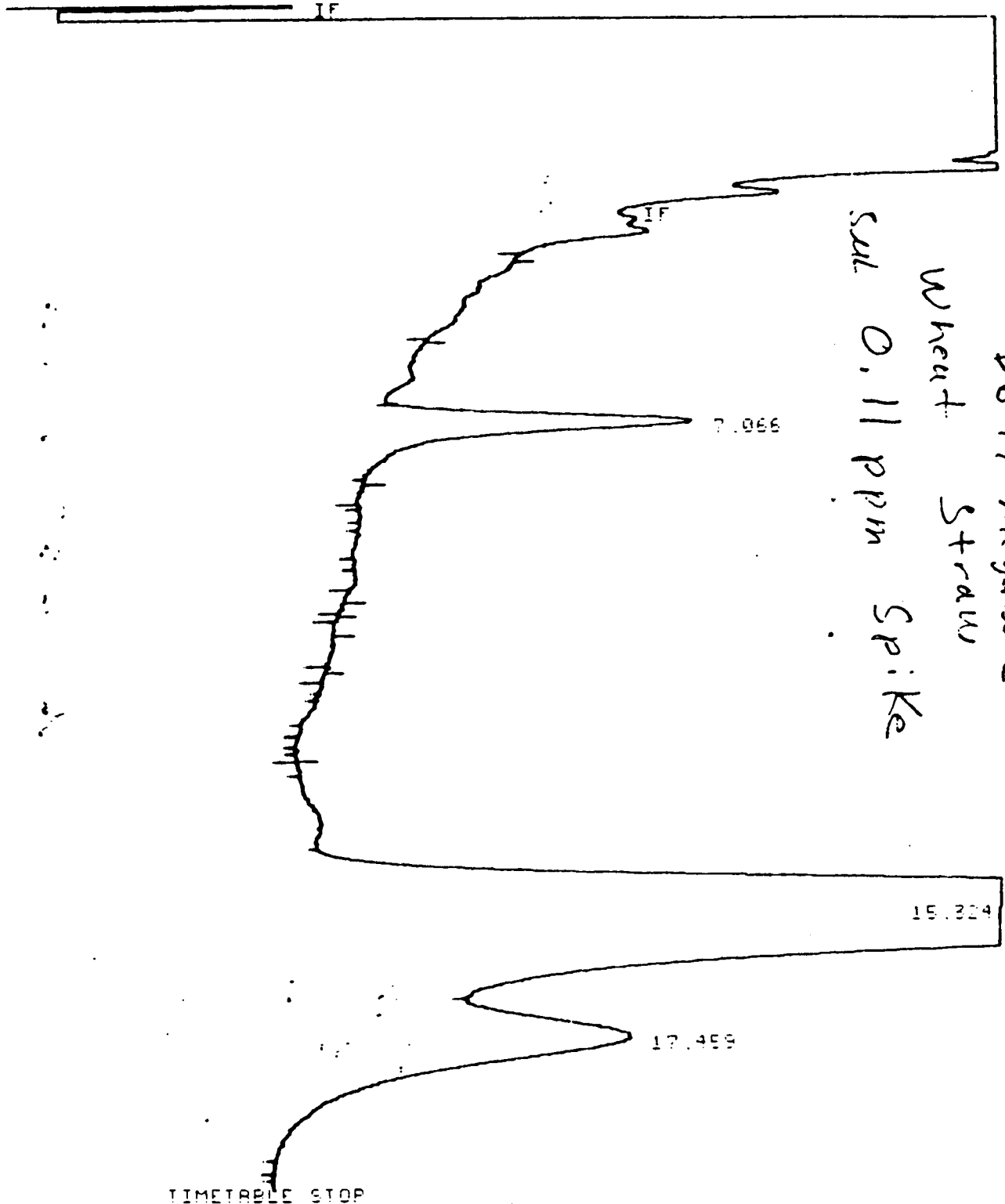


Exhibit A  
DB-17 Megalor  
Column  
Wheat Straw  
Spike

TIMETABLE STOP

SIGNAL FILE: B:\09710001.BNA

MON 13900 TMU

HEIGHTX	RT	HEIGHT	TYPE	WIDTH	HEIGHTX
	7.066	1392	BP	.367	10.26746
	15.324	10466	UU	.984	77.74886
	17.499	1613	UP	1.094	11.99366

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MUL FACTOR=1.0000E+00

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START

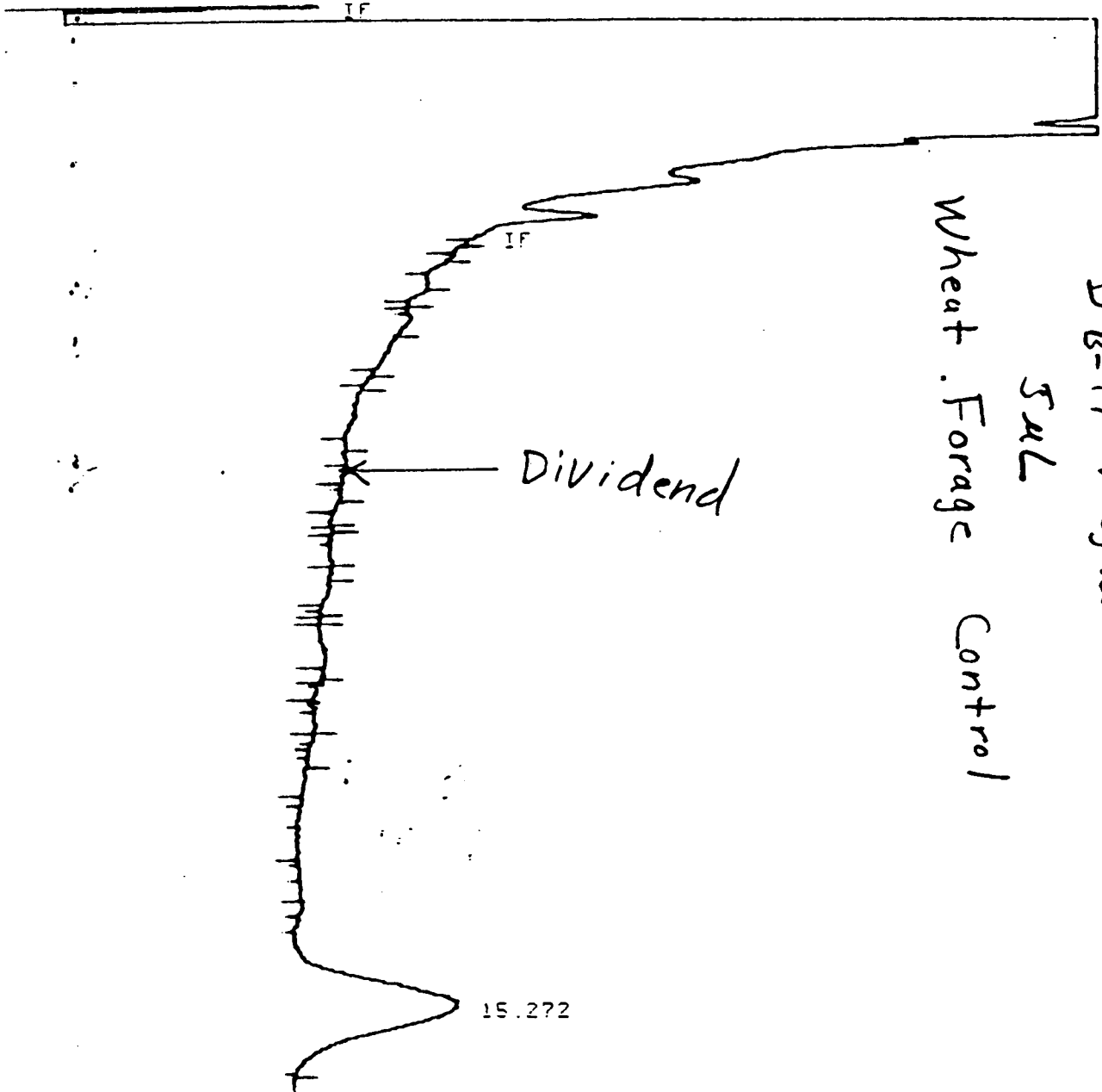


Exhibit A  
DB-17 megabar Column  
SAL  
Wheat Forage Control

15.272

TIMETABLE STOP

Closing signal file B:\Q571129E.BNA

RUN# 58 NOV 3, 1992 16:06:53

SAMPLE NAME: CONTROL SAMPLE# 4  
B92-19: FORAGE CONTROL

SIGNAL FILE: B:\Q571129E.BNA

MON 13900 TMU

HEIGHT%	RT	HEIGHT	TYPE	WIDTH	HEIGHT%
15.272		685	FU	.869	100.00000

TOTAL HEIGHT= 685  
MUL FACTOR=1.0000E+00

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START

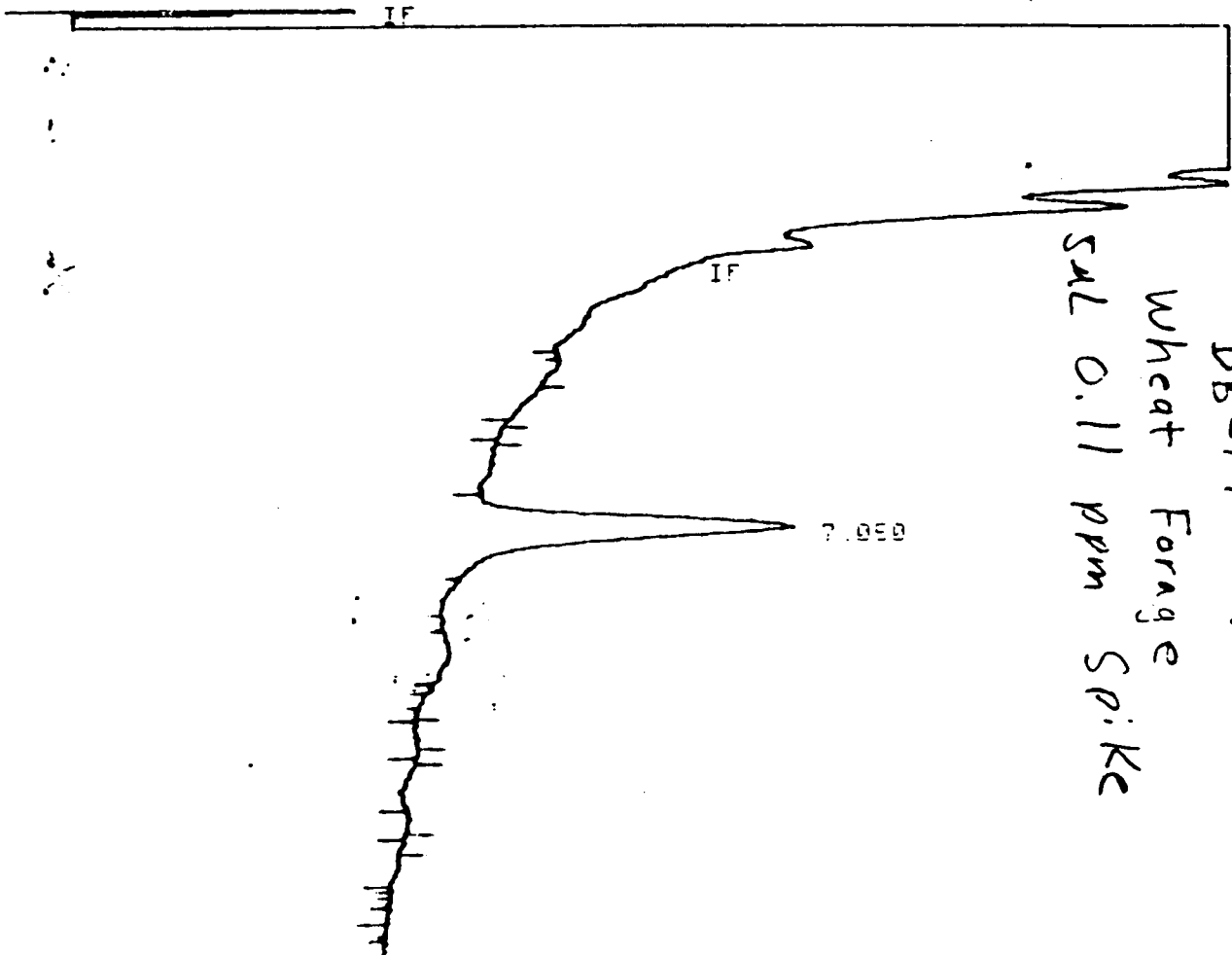
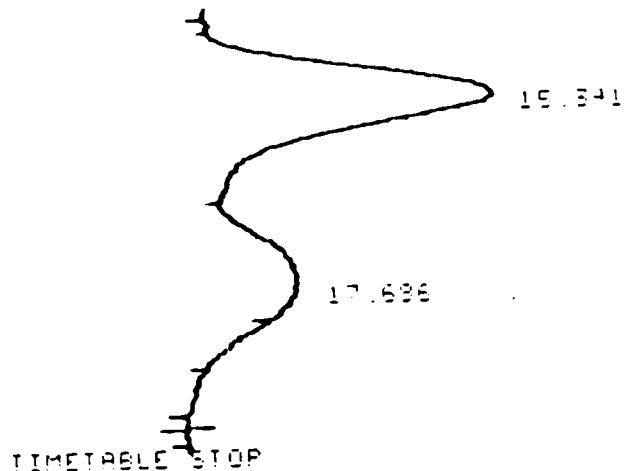


Exhibit A  
DB-171 Megaloc Column  
Wheat Forage  
SAL 0.11 ppm Spike



Closing signal file: B:\05711780.BNR

PUNB 59 NOV 3, 1992 18:29:44

SAMPLE NAME: F-6 SAMPLE# 5  
B91-19: 0.11 RPM SPK WHEAT FORAGE

SIGNAL FILE: B:\05711780.BNR

MDM 13900 IMU

HEIGHTX	PT	HEIGHT	TYPE	WIDTH	HEIGHTX
	7.050	1127	BU	.360	45.67141
	15.341	1044	UU	.956	40.16930
	17.686	368	UU	1.159	14.15930

TOTAL HEIGHT= 2539  
MUL FACTOR=1.0000E+00

Do you want to reprocess another sequence of data files [Y/N]: N

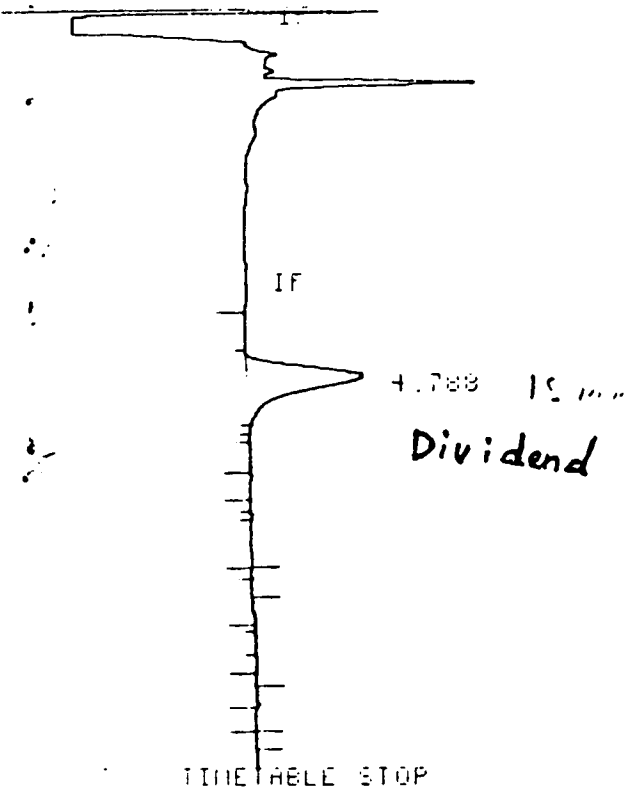
SAMPLE CHROMATOGRAMS

FOR ALL THREE COMMODITIES USING PACKED COLUMN G.C.

STOP DETH A:010 @

END START

PUN# 98 SEP 29, 1992 14:47:35  
START



TIMEABLE STOP

Closing signal file A:05304408.BNC

PUN# 98 SEP 29, 1992 14:47:35

SAMPLE NAME: STD SAMPLE# 1  
BAC-19; 5 UL 0.220 UG/ML DIV.

SIGNAL FILE: A:05304408.BNC  
HEIGHT:

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
4.788	246	PK	248	100.00000

Std 0.220ug/ml Dividend

STD

Sample Chromatograms  
For Wheat Grain



S.M.L.  
Wheat Grain Control

Closing signal file R:05304996.BNC

RUN# 80 SEP 25, 1992 15:11:17

SAMPLE NAME: CONTROL SAMPLE# 1  
892-19: S.M.L. US-1

SIGNAL FILE: R:05304996.BNC  
HEIGHT:

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
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TOTAL HEIGHT= 186  
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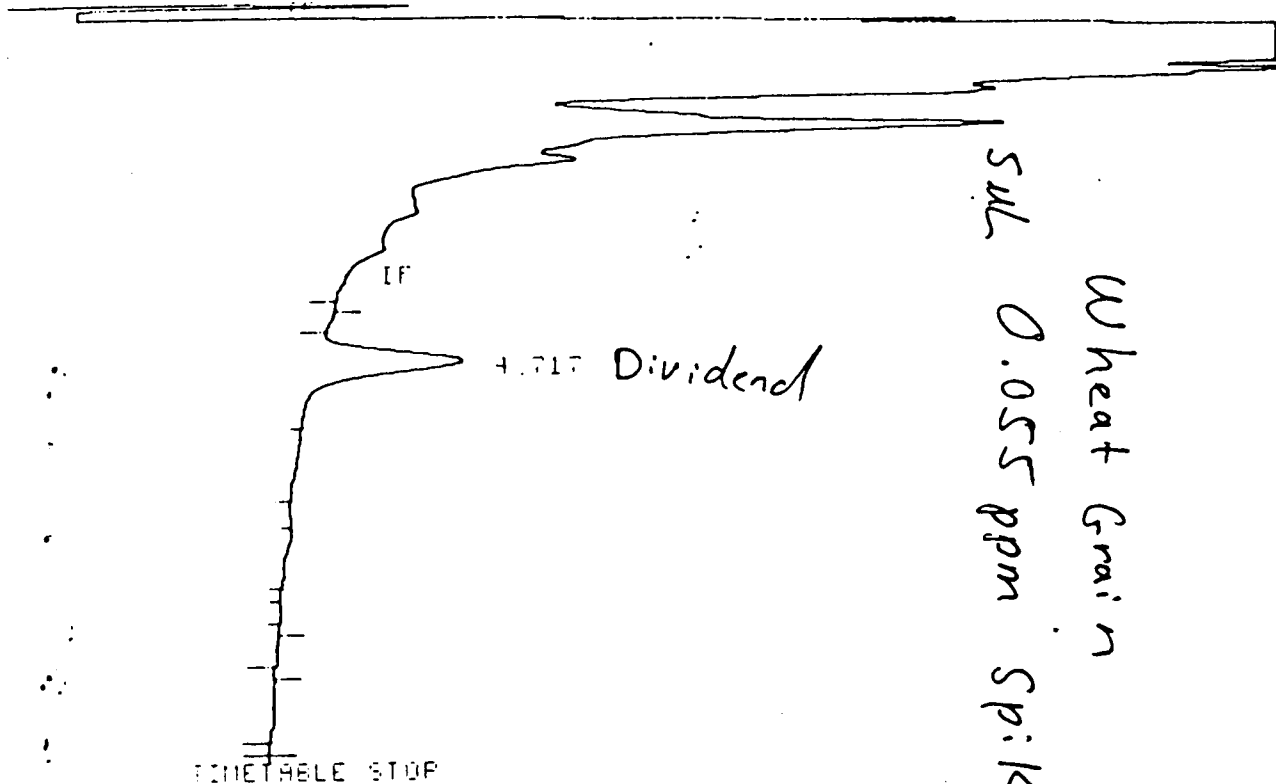


Wheat

PI HEIGHT TYPE WIDTH HEIGHT  
4.017 1053 BF 1.327 100.00000

TOTAL HEIGHT= 1053  
MUL FACTOR=1.0000E+00

PUN # 89 SEP 25, 1992 16:45:52  
START



Closing signal file A:05309FC0.BNC

PUN# 89 SEP 25, 1992 16:45:52

SAMPLE NAME: 89F SAMPLE# 6  
892-19: 5 UL 106-4: 0.055 PPM DIM.

SIGNAL FILE: A:05309FC0.BNC  
HEIGHT:

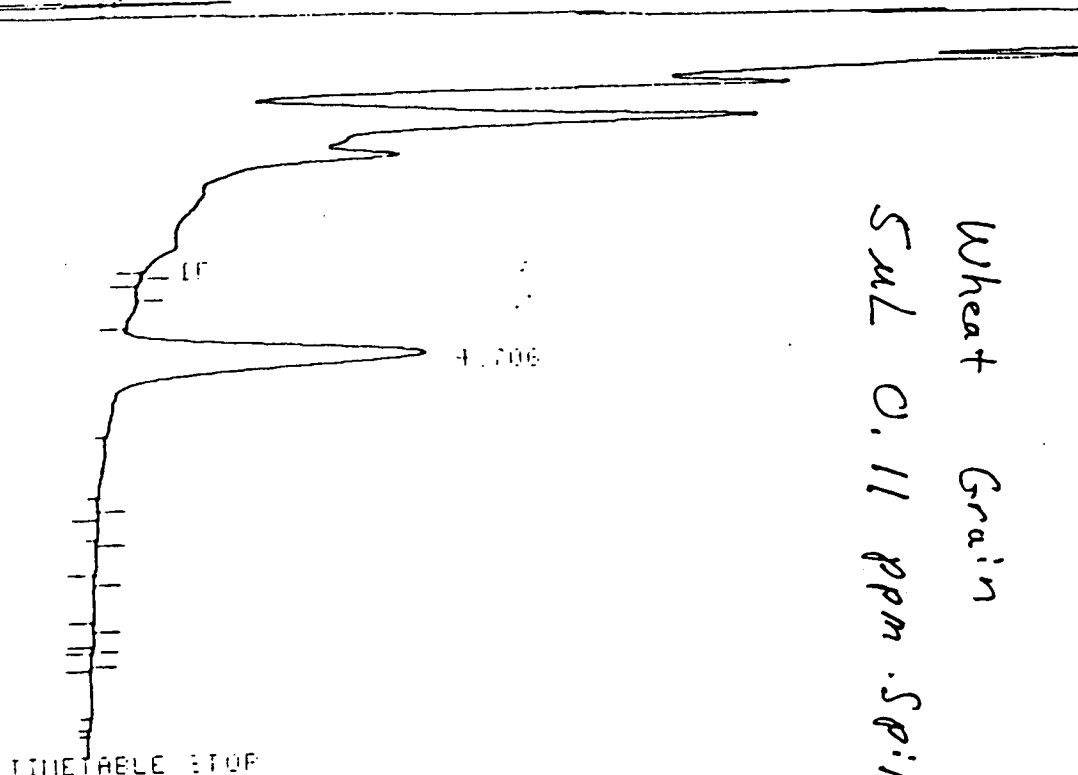
PI	HEIGHT	TYPE	WIDTH	HEIGHT/
4.017	1015	BF	1.327	100.00000

TOTAL HEIGHT= 1015  
MUL FACTOR=1.0000E+00

PUN # 89 SEP 25, 1992 16:57:45  
START

TOTAL HEIGHT= 0149  
DUL FACTOR=1.0000E+00

RUN # 75 SEP 25, 1990 18:09:46  
START



Closing signal file H:\0580730F.BNC

RUN# 75 SEP 25, 1990 18:02:46

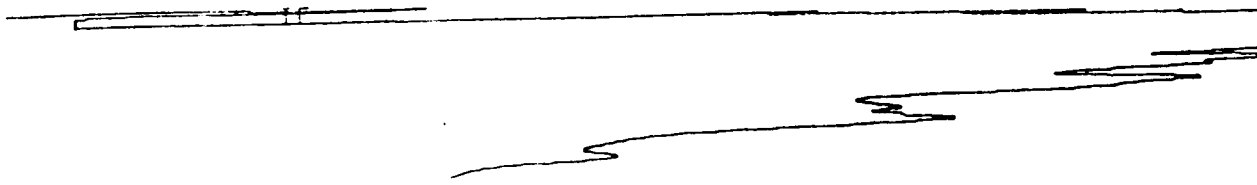
SAMPLE NAME: SP1 SAMPLE# 3  
SAC-13: S UL MS-S: 0.11 PPM DIL.

SIGNAL FILE: H:\0580730F.BNC

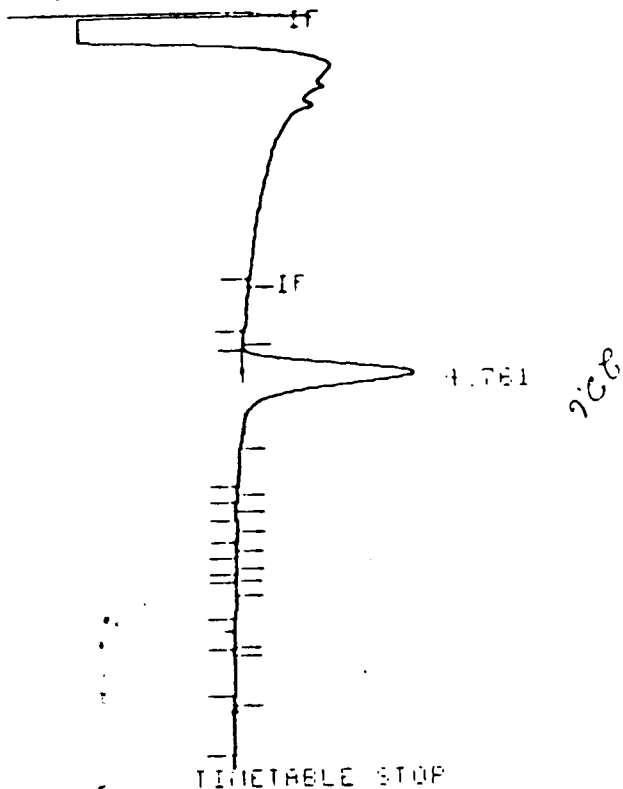
RT	HEIGHT	TYPE	WIDTH	HEIGHT%
4.706	0149	SP	0.335	100.00000

TOTAL HEIGHT= 0149  
DUL FACTOR=1.0000E+00

RUN # 76 SEP 25, 1990 18:20:37  
START



RUN # 201      OCT 14, 1992 10:57:10  
START



5uL  
0.22 ug/mL Dividend STD.

Sample Chromatograms For Wheat Forage

Closing signal file B:05586007.BNC

RUN# 201      OCT 14, 1992 10:57:10

SAMPLE NAME: STD      SAMPLE# 1  
EPC-19: 5 UL 0.22 UG/ML DIV

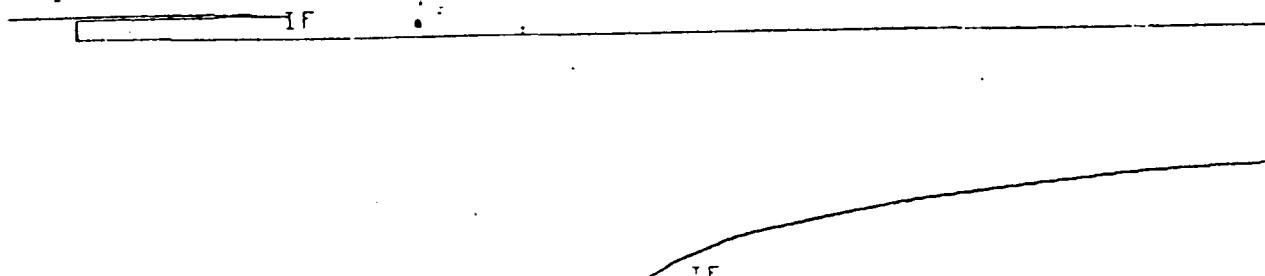
SIGNAL FILE: B:05586007.BNC

004 1890 THY

RT	HEIGHT	TYPE	WIDTH	HEIGHT%
4.781	1016	EE	.341	100.00000

TOTAL HEIGHT= 1016  
INFL FACTOR=1.0000E+00

RUN # 202      OCT 14, 1992 11:09:05  
START



SAMPLE NAME: F-1  
SRC-15: S UL CONTROL

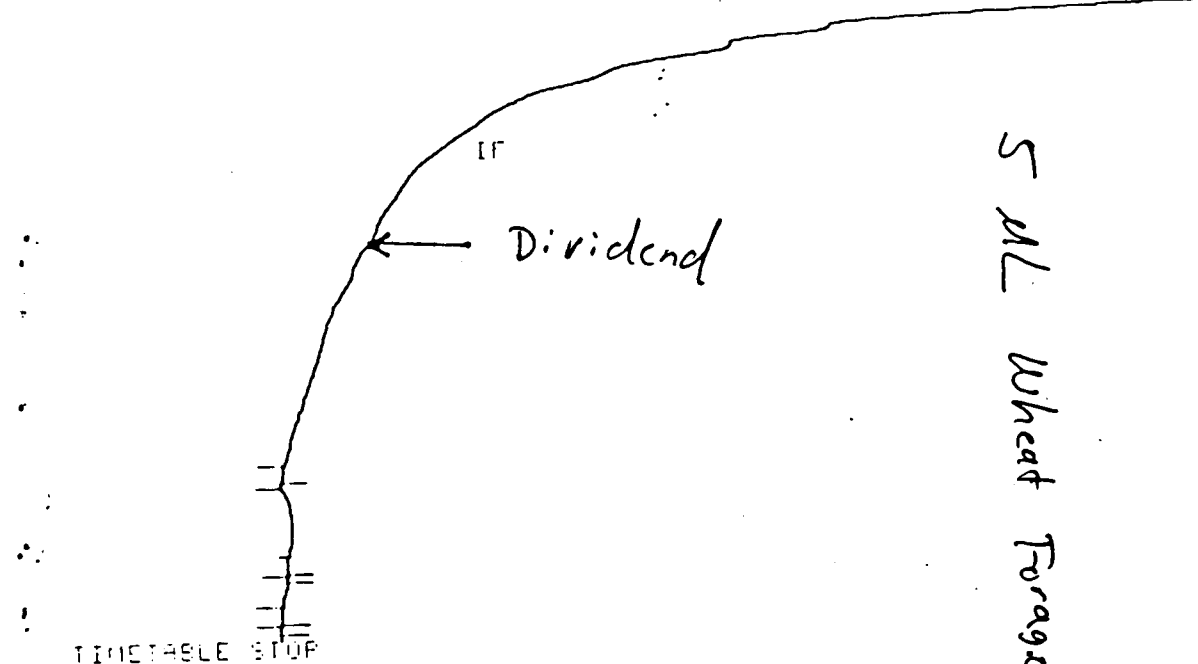
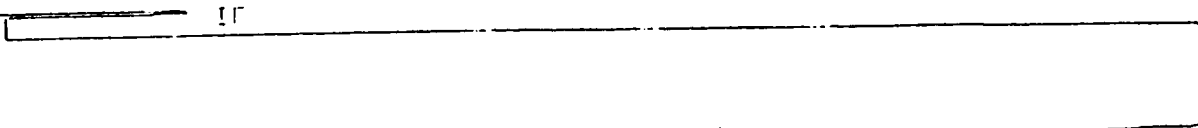
SAMPLER# 3

SIGNAL FILE: B:055018FH.BNC

MON 1300 TUN

NO RUN PER'S STOPED

RUN # 175 OCT 9, 1990 17:00:45  
START



Closing signal file B:055018EE.BNC

RUN # 175 OCT 9, 1990 17:00:45

SAMPLE NAME: F-1  
SRC-15: S UL CONTROL

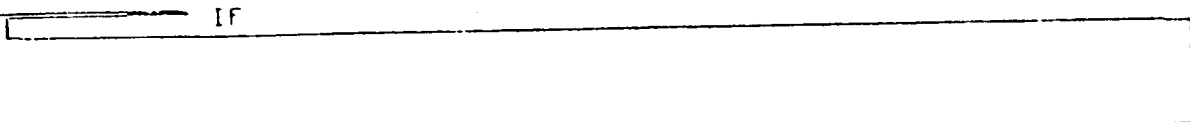
SAMPLER# 3

SIGNAL FILE: B:055018EE.BNC

MON 1300 TUN

NO RUN PER'S STOPED

RUN # 175 OCT 9, 1990 17:12:31  
START



REPORT FILE: E:\555555\1 500

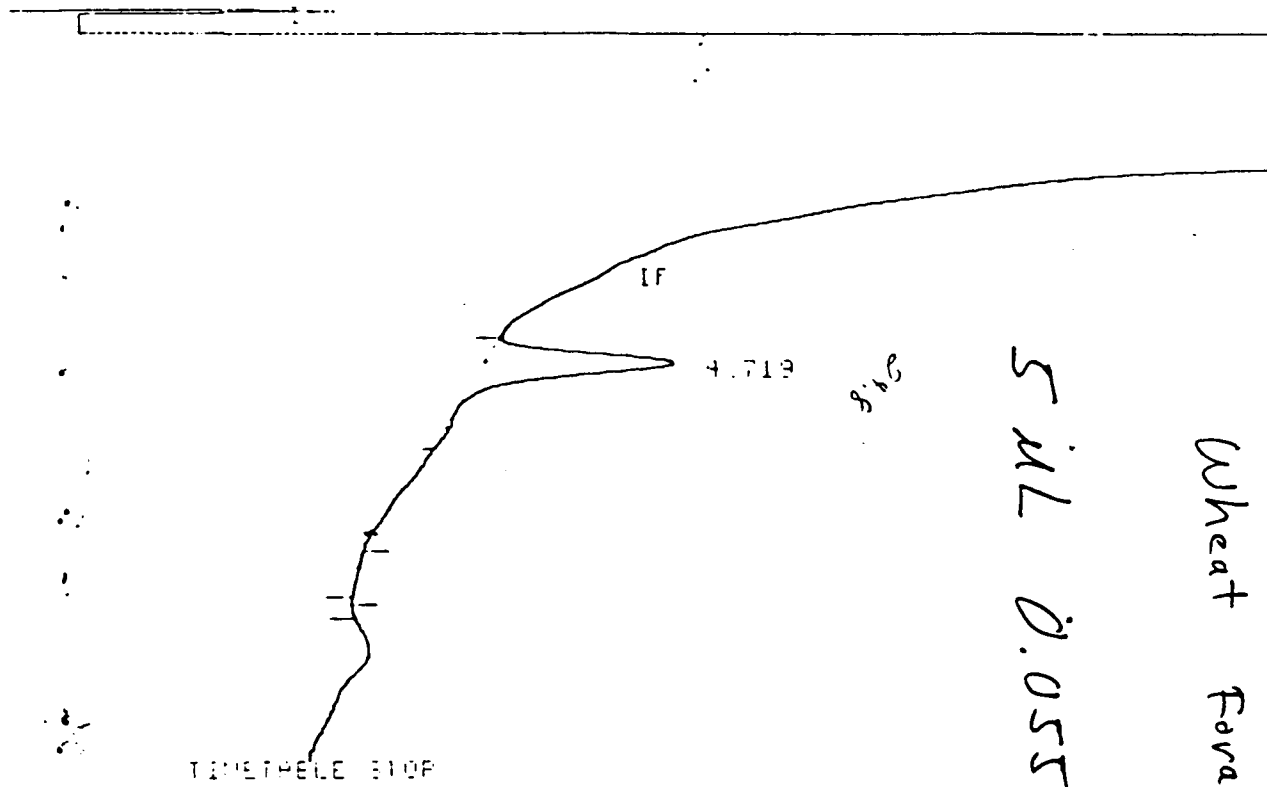
MON 1990 100

HEIGHT:

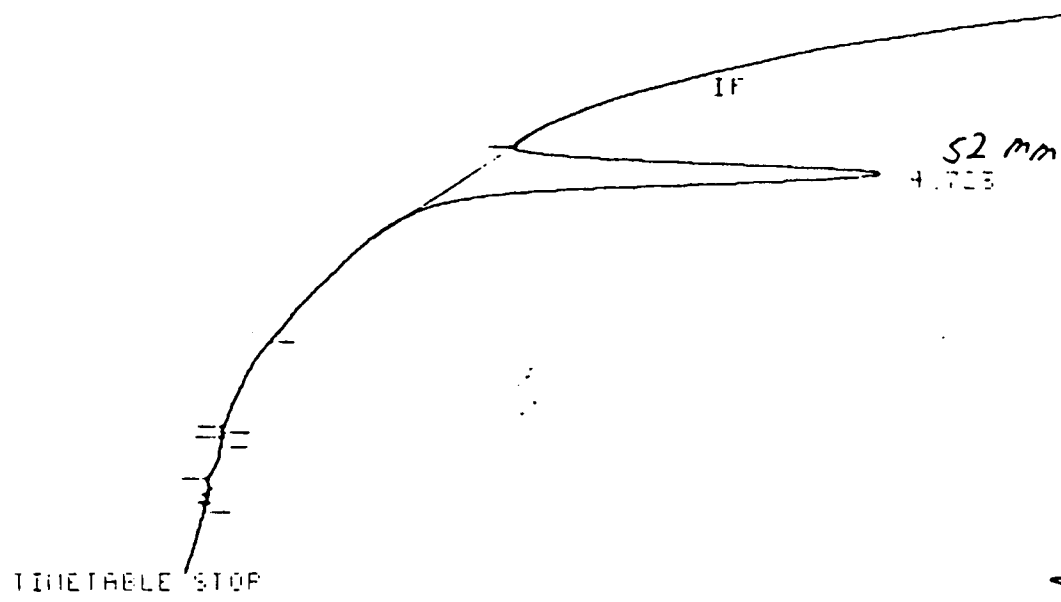
RT	HEIGHT	TYPE	WIDTH	HEIGHT
4.719	1997	EP	309	100.00000

TOTAL HEIGHT= 1997  
GWL FACTOR=1.0000E+00

RUN # 103      OCT 11, 1991 11:20:57  
ETH-1



Wheat Forage  
5 mL 0.055 ppm spike



Wheat Forage  
Sul 0.11 ppm  
Sp:Kc

Closing signal file: E:\055E949E.BNC

RUN# 125 OCT 20, 1990 15:28:13

SAMPLE NAME: F-4 SAMPLE# 3  
E90-19: S UL 0.11 PPM EPI - PEDD

SIGNAL FILE: E:\055E949E.BNC

CON 13300 PPM

RT	HEIGHT	TYPE	WIDTH	HEIGHT
4.723	2917	BB	0.44	100.00000

TOTAL HEIGHT= 2917  
GUL FACTOR=1.0000E+00

RUN# 126 OCT 20, 1990 15:40:11  
START

