

CLOMAZONE

FMC CORPORATION
AGRICULTURAL CHEMICAL GROUP
Princeton, New Jersey

P-2640
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STUDY TITLE: Residue Analytical Method for the Determination of Clomazone in/on Crop and Processed Part Matrices of Corn, Cottonseed, Soybean, and Tobacco

TEST SUBSTANCE: Clomazone

DATA REQUIREMENT: Pesticide Assessment Guidelines Subdivision O, 171-4: Residue Analytical Method

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STUDY NUMBERS: 164MVL91R3


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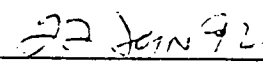
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Company: FMC Corporation



Ronald F. Cook
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Date

GOOD LABORATORY PRACTICES STATEMENT

To the best of my knowledge, the data and procedures reported herein (Study Number: 164MVL91R3, "Residue Analytical Method for the Determination of Clomazone in/on Crop and Processed Part Matrices of Corn, Cottonseed, Soybean, and Tobacco", FMC Corporation, Agricultural Chemical Group, P-2640) were gathered from studies which were conducted in compliance with the Good Laboratory Practice Standards set forth in Title 40, Part 160 of the Code of Federal Regulations of the United States of America with the following exceptions. Analysis of crude and refined oils from soybean and corn grain were validated during method development and were not part of a GLP compliant study. However, it is the intention of FMC Corporation that all studies conducted by our facility shall be of the highest quality. Consequently, all data and results contained in this report were obtained using credible experimental procedures and modern technology and are considered scientifically valid. In addition, the data and report have been audited and archived by the FMC ACG/R&D Quality Assurance Unit.

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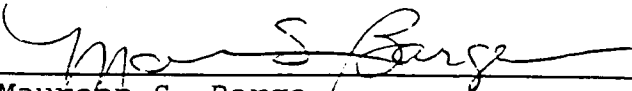
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QUALITY ASSURANCE STATEMENT

It is the intent of FMC Corporation that all studies conducted by our facility shall be of the highest quality and meet or exceed the criteria promulgated by the EPA to assure the quality and integrity of the data generated. The data reported herein, P-2640, Residue Analytical Method for the Determination of Clomazone in/on Crop and Processed Part Matrices of Corn, Cottonseed, Soybean, and Tobacco was compiled from six separate studies and the non-GLP method development for crude and refined corn oil. The six GLP studies were inspected by the ACG/R&D Quality Assurance Units and the findings submitted to the Study Director and Management on the following dates.

<u>FMC Report Number</u>	<u>Inspection Date</u>	<u>Date Submitted to Study Director</u>	<u>Date Submitted to Management</u>	<u>Date Submitted to Director</u>
P-2352	09/25/89	09/27/89	10/02/89	10/03/89
P-2478	04/11/90	04/12/90	04/16/90	04/19/90
P-2482	05/29/90	06/01/90	06/04/90	06/05/90
P-2551	09/27/90	09/27/90	11/06/90	11/15/90
P-2558	12/18/90	12/19/90	01/20/91	02/01/91
P-2630	05/20-21/91	07/30/91	07/30/91	08/12/91

This report and all records have been audited by the FMC ACG/R&D Assurance Unit. The report was found to be an accurate reflection of the methods described and the data generated. All raw data will be maintained by FMC Corporation, PO Box 8, Princeton, N.J. 08543 in the Quality Assurance Archives.


Maureen S. Barge
Quality Assurance Group Leader

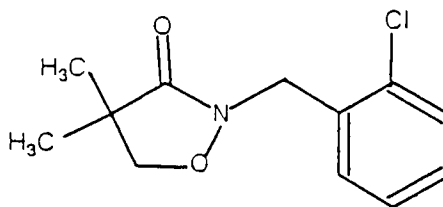
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I. INTRODUCTION

Clomazone, the common name of the active ingredient in Command® 4EC herbicide, is currently being developed by FMC Corporation for the control of grasses and broadleaf weeds in a variety of crops. The chemical name of clomazone is 2-[(2'-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone, and is code numbered FMC 57020. The structure is as follows:



CLOMAZONE

The objective of this report is to describe the two methods, which have been proven successful for the determination of clomazone in/on a variety of crops and processed commodities. The analytical method recoveries and procedures reported here are a compilation of data generated from six completed studies and a supplementary data package, which was created for additional method applications. This report encompasses 19 matrices which can be categorized as either non-oil or oil type samples. The analytical procedures described in this report are exactly the same as in FMC report P-2352M (Section XI, Reference 1) for corn non-oil matrices, and in report P-2551M (Section XI, Reference 2) for cottonseed and its processed parts. However, this report presents the methods in a more detailed fashion.

Analytical methods using a C₁₈ (octadecyl) solid phase extraction cartridge, and a Florisil® or a silica gel cartridge for cleanup have been developed to assay corn raw agricultural commodities (grain, silage, and stover), corn processed parts (grits, meal, flour,

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starch, crude and refined oils), delinted cottonseed, cottonseed processed parts (meal, hulls, soapstock, crude and refined oils), green and cured tobacco, and soybean crude and refined oils. The methods are rapid, easy and use only small volumes of solvents.

II. SUMMARY

The analytical method for clomazone in/on non-oil matrices consists of an acid hydrolysis, a C₁₈ solid phase extraction (SPE) cartridge, and a Florisil® cartridge for cleanup. The non-oil matrices to which the method is applied include corn grain, silage, stover, corn processed grits, meal, flour, starch, delinted cottonseed, cottonseed processed meal, hulls, and green and cured tobacco.

The assay method for clomazone in/on oil matrices is initiated with a dissolution with hexane, followed by a C₁₈ SPE cartridge and a Florisil or a silica gel cartridge for cleanup. The oil matrices to which the method is applied include crude and refined oils of corn grain, cottonseed, and soybean.

The method for cottonseed soapstock involves an acid hydrolysis step and hexane partition of the acid solution, followed by the oil method described in the preceding paragraph with a Florisil cartridge for cleanup.

Final sample solutions from all of the above methods are quantitated using a gas chromatograph equipped with a Megabore® capillary column and a nitrogen/phosphorus detector. The determination of method recovery is based on an external standard calibration.

The two methods were validated at a limit of quantitation (LOQ) of 0.05 ppm. The limit of detection (LOD) was set at 0.01 ppm. An exception was the case of green and cured tobacco samples, where the LOQs were set at 0.1 and 0.2 ppm and the LODs at 0.02 and 0.04 ppm, respectively. The average method recovery ranges from 72 to 104% with standard deviation ranging from ± 3 to $\pm 16\%$, depending on the

method used and the matrices analyzed. The overall average recovery and the standard deviation for the non-oil and oil methods are $84\% \pm 13\%$ (n=115) and $90\% \pm 13\%$ (n=28), respectively.

The above two analytical methods to determine the clomazone in/on 19 matrices have been successfully validated by an independent laboratory. The method validations were performed on the following eight matrices: corn silage, corn stover, cottonseed meal, green tobacco, corn deodorized oil, soybean crude oil, cottonseed crude oil, and cottonseed soapstock. The range of the average recovery and the standard deviation (n=4) found by the independent laboratory were similar to the results obtained in the FMC residue laboratory .

III. SUMMARY TABLES AND GRAPHICS

A. Summary of Method Recoveries

TABLE 1
CLOMAZONE METHOD RECOVERY VALUES
FROM NON-OIL CONTROL SAMPLES

MATRIX	FORTIFICATION LEVEL (ppm)	NUMBER OF ANALYSES	RECOVERY RANGE (%)	AVERAGE RECOVERY (%)	RECOVERY STD. DEV. (%)
Corn Grain	0.05	23	80 - 97	83	10
Corn Silage	0.05	18	63 - 120	88	16
Corn Stover	0.05	15	66 - 122	96	15
	0.10	3	94 - 110		
Corn Medium Grits	0.05	3	72 - 77	74	3
Corn Meal	0.05	3	72 - 101	83	16
Corn Flour	0.05	3	76 - 85	82	6
Corn Starch	0.05	3	69 - 84	79	9
Delinted Cottonseed	0.05	3	65 - 83	77	12
Cottonseed Meal	0.05	3	65 - 85	72	11
Cottonseed Hulls	0.05	6	69 - 87	78	6
Green Tobacco	0.1	17	64 - 110	84	11
Cured Tobacco	0.2	16	58 - 103	80	12

Overall Average (n=115) 84
Overall Std. Dev. ±13

TABLE 2
CLOMAZONE METHOD RECOVERY VALUES
FROM OIL CONTROL SAMPLES

MATRIX	FORTIFICATION LEVEL (ppm)	NUMBER OF ANALYSES	RECOVERY RANGE (%)	AVERAGE RECOVERY (%)	RECOVERY STD. DEV. (%)
Corn Crude Oil	0.05	3	81 - 108	93	14
Corn Refined Deodorized Oil	0.05	3	88 - 99		
	0.1	2	90 - 98	94	5
Cottonseed Crude Oil	0.05	3	71 - 80	75	4
Cottonseed Refined Deodorized Oil	0.05	3	89 - 105	95	9
Cottonseed Soapstock	0.05	3	70 - 86	77	8
Soybean Crude Oil	0.05	2	95 - 122		
	0.1	3	92 - 111	104	12
Soybean Refined Bleached Oil	0.05	3	71 - 91		
	0.1	3	86 - 106	87	12

Overall Average (n=28) 90
Overall Std. Dev. ±13

B. Method Flow Schemes

FIGURE 1
FLOW SCHEME FOR CLOMAZONE
IN/ON NON-OIL SAMPLES

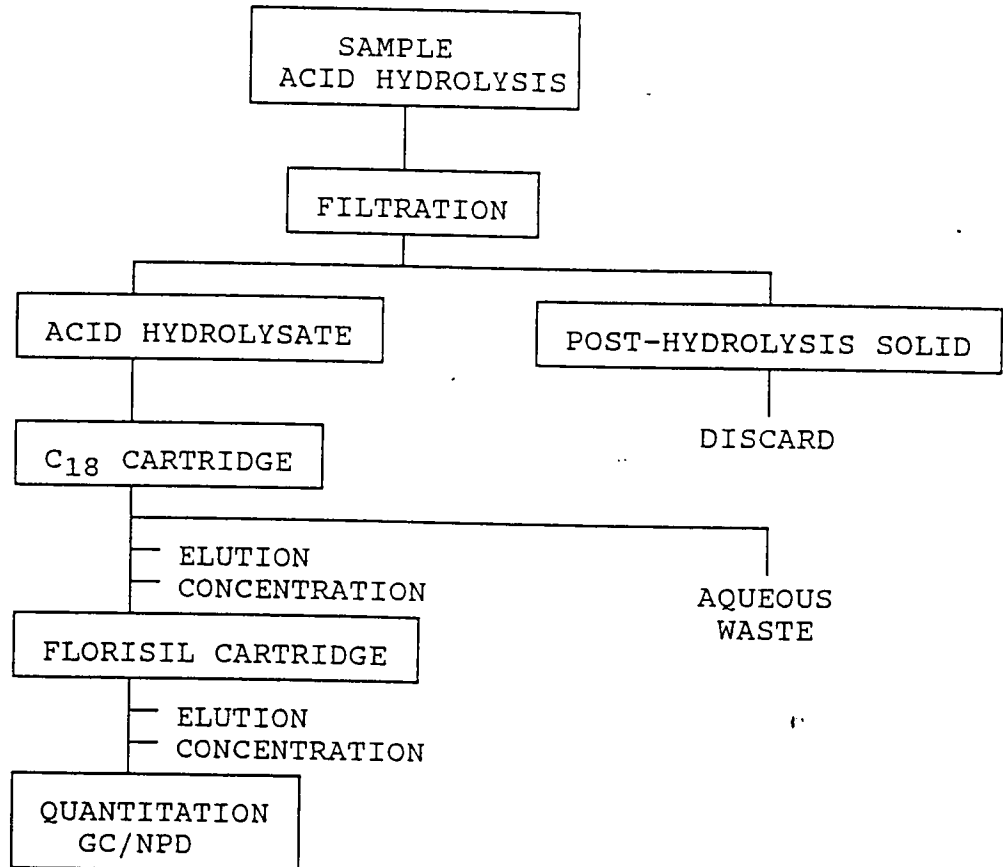


FIGURE 2
METHOD FLOW SCHEME FOR CLOMAZONE
IN CRUDE AND REFINED OILS

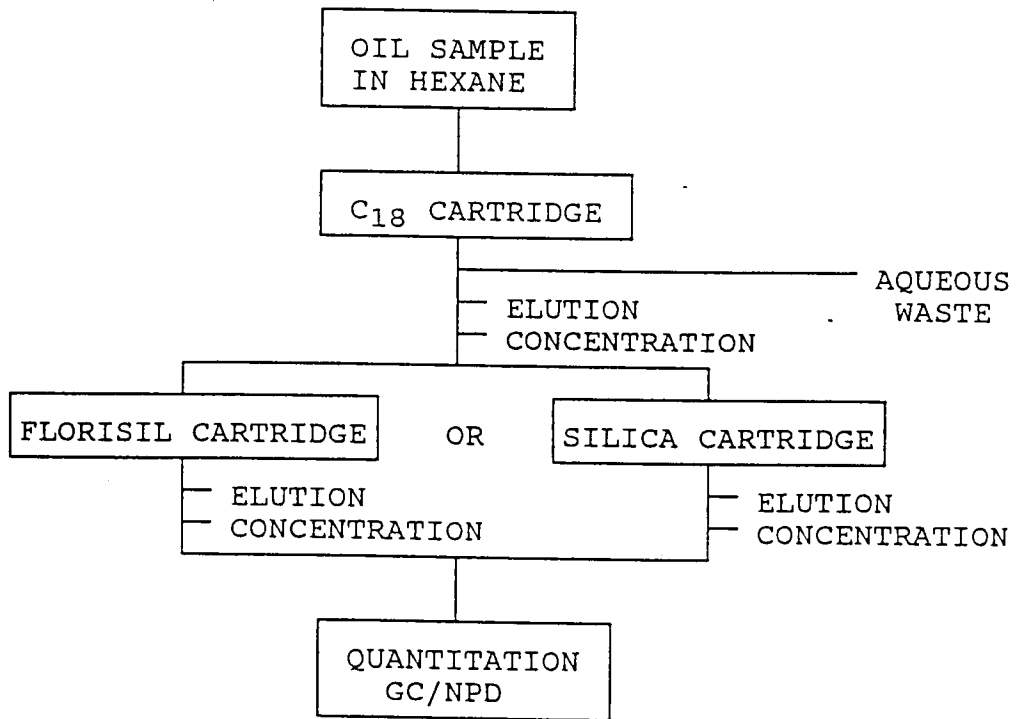
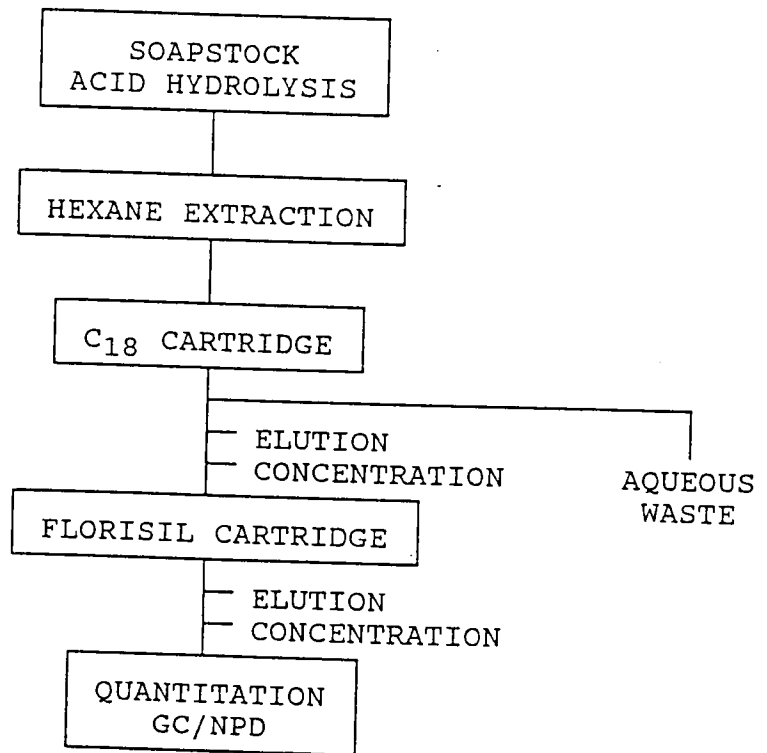


FIGURE 3
METHOD FLOW SCHEME FOR CLOMAZONE
IN/ON COTTONSEED SOAPSTOCK



IV. MATERIALS AND STUDY DESIGN

A. Test Substance

Clomazone is the common name of the active ingredient in Command 4EC herbicide. It has the chemical name 2-[(2'-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone, and a code number FMC 57020. Command 4EC is manufactured by FMC Corporation, and has a CAS number 81777-89-1 and an EPA Registration Number 279-3053.

B. Test Commodities

Test commodities in this project included corn raw agricultural commodities (grain, silage, and stover), corn processed parts (grits, meal, flour, starch, crude and refined oils), delinted cottonseed, cottonseed processed parts (meal, hulls, soapstock, crude and refined oils), green and cured tobacco, and soybean crude and refined oils.

In general, large/leafy samples should be prepared by a large cutter/mixer, and smaller samples of grain and seed are ground by a mill after addition of liquid nitrogen. Processed fractions should be shaken/mixed to a homogeneous condition. All the samples should be maintained frozen (ca. -18°C) during shipping and storage to insure integrity of the residues.

C. Study Design and Procedures

A method recovery set consisted of one control sample and one to five fortified control samples depending on the matrix. Fortification is accomplished by adding a known amount of clomazone standard in hexane solution directly onto the control sample matrix by syringe or pipette. After fortification, sample containers should leave open at room temperature to allow the hexane to evaporate. The fortified samples should be carried through as part of an assay set with the control sample to determine the method recovery.

D. Analytical Standards

The purity of the clomazone analytical standard should be determined before preparing the standard solution. A stock solution of 1000 ng/ μ L should be prepared by dissolving the appropriate amount of the above analytical standard in hexane. Working solutions in concentrations from 0.05 to 1.0 ng/ μ L are prepared by appropriate dilutions of the stock solution in hexane. Working solutions are used for fortification, injection standard, and instrument linearity calibrations. Stock and working solutions should be stored in volumetric containers in a refrigerator/freezer unit to insure maintenance of proper concentrations.

E. Equipment

Balance, top-loading (Mettler PM600)
Boiling chips, granules, plain (Hengar Co.)
Capillary column, DB-1 (J&W Scientific)
Capillary column, DB-5 (J&W Scientific)
Capillary column, Rt_x-1 (Restek Corp.)
Cartridge, C₁₈, 1 g (Varian Sample Preparation Products, previously Analytichem International)
Cartridge, Florisil, 1 g (J.T. Baker Inc.)
Cartridge, Florisil, 1 g (Varian Sample Preparation Products)
Cartridge, silica gel, 1 g (Varian Sample Preparation Products)
Centrifuge tube, Pyrex[®], 13 mL, 0.1 mL graduation
Condenser, Pyrex, graham coil, 41 mm X 500 mm with $\text{\textcircled{24/40}}$ joint
Cylinder, graduated, 100 mL, 250 mL
Filtering flask, 500 mL, Pyrex
Flask, Erlenmeyer, 250 mL, 500 mL, 1000 mL
Flask, boiling, 500 mL with $\text{\textcircled{24/40}}$ joint
Flask, volumetric, 100 mL
Fluted filter papers (515, 18.5 cm, Filtration Sciences Corp.)
Gas chromatograph (Hewlett-Packard 5890A with NPD or MSD)
Glass microfibre filters (934-AH, 11.0 cm, Whatman)
Heating mantles (Glas-Col[®])
Hobart[®] large cutter/mixer, HCM-300
Mini-stirrer (Model 200, VWR Scientific)

N-Evap[®] evaporator (Organomation Associates 111)
PE Nelson chromatography workstation (The Perkin-Elmer Corporation)
Pipette (E2-1000, Rainin Instrument Co.)
Porcelain Buchner filter funnel, 10.5 cm i.d. (Coors)
Reservoir (75 mL, Analytichem International)
Rotavapor[®] evaporator (Buchi/Brinkman R-110)
Separatory funnel, 250 mL
Solvent dispenser (501, VWR Scientific)
Syringe, 0.5 mL (Hamilton[®])
Teflon[®] stirring bars (VWR Scientific)
Test tube mixer (Bernstead/Thermolyne M16715)
Thomas-Wiley Mill, ED-5 (Thomas Co.)
Visidry[®] vacuum manifold drying attachment (Supelco)
Visiprep[®] manifold (Supelco)

F. Reagents

Acetone, ethyl acetate, hexane, cyclohexane, all Resi-analyzed[®] grade solvent (J.T. Baker Inc.)
Hydrochloric acid, reagent grade (J.T. Baker Inc.)
0.25N HCl solution, prepared from reagent grade HCl
Distilled deionized water (house still)
Sodium sulfate, anhydrous, granular, reagent grade (J.T. Baker Inc.)

V. ANALYTICAL PROCEDURE

A. Residue Method

1. Method for Non-oil Matrices

a. Acid Hydrolysis

Weigh an appropriate amount of subsample into a 500 mL boiling flask. See Section X, Table 3 for the specific sample size and the acid volume required for a particular matrix. Apply the fortification procedure at this time. The boiling flask should be left open for ~30 min to allow the solvent to evaporate. Add the solution of 0.25N HCl and

a teflon stirring bar or boiling chips into the flask and then attach the boiling flask to a condenser. Set the heating mantle variac power supply at about 60 and reflux the sample solution under gentle boiling for one hour.

Cool the hydrolysate to room temperature and filter the solution through a Whatman glass microfibre filter (No. 934-AH) with a Buchner funnel under vacuum. Rinse and wash the flask and the sample matrix with ~100 mL of deionized water or 0.25N HCl, because no recovery difference is observed with either of the solution. The entire sample solution is used for the following procedures.

b. C₁₈ Cartridge

Install the C₁₈ cartridge (1 g, 6 cc) on a vacuum manifold and condition it first with 12 mL of ethyl acetate/hexane (5/95, v/v), completely dry the cartridge with full vacuum for ~2 min, and then condition it with 12 mL of deionized water (or 0.25N HCl). Turn off the vacuum and attach a 75 mL reservoir to the cartridge with an adaptor. Keep the cartridge wet and pass the acid filtrate (200-400 mL) through the cartridge by regulating the vacuum. Maintain the solution flow rate at ~5 mL/min. After sample loading, completely blow dry the cartridge by nitrogen with a manifold drying attachment (~30 min). Elute and collect the clomazone residue with 12 mL of ethyl acetate/hexane (5/95, v/v) in a 13 mL graduated test tube with a collection rate at ~2 mL/min. Concentrate the solution to ~1 mL with a N-Evap. The temperature of the N-Evap is kept between 30 to 40°C.

c. Florisil Cartridge

The sample solution should be further cleaned-up with a Florisil cartridge (1 g, 6 cc). Condition the cartridge first with 12 mL of ethyl acetate/hexane (20/80, v/v) and then with 12 mL of ethyl acetate/hexane

(5/95, v/v). It is not necessary to dry the cartridge between the two condition steps. Keep the cartridge wet and control the sample solution flow rate through the cartridge by gravity or a vacuum at ~2 mL/min. Load the sample solution directly in the cartridge barrel by a pipette. Add ~1 mL of hexane to rinse the test tube and then transfer it to the cartridge. Elute and collect the clomazone residue with 12 mL of ethyl acetate/hexane (20/80, v/v) in a clean graduated test tube. Concentrate the sample solution via a N-Evap to exactly 0.5 or 1.0 mL depending on the matrix analyzed (see Section X, Table 5 for the specific final sample volume needed for analysis). The final solution is quantitated by a gas chromatograph equipped with a nitrogen/phosphorus detector. Figure 1 in Section III presents the method flow scheme for non-oil matrices.

2. Method for Crude and Refined Oils

a. C₁₈ Cartridge

Weigh 2.5 g oil subsample into a 13 mL graduated test tube. Fortify the oil sample at this point. Add hexane to dissolve the oil, and make the total solution volume to 6 mL. Attach the C₁₈ cartridge (1 g, 6 cc) to a vacuum manifold and condition it first with 12 mL of ethyl acetate/hexane (5/95, v/v), and then with 12 mL of hexane. Keep the cartridge wet, and load the sample solution into the cartridge barrel. Maintain the solution flow rate through the cartridge at ~2 mL/min via a vacuum. After the sample solution is passed through, add hexane (~2.5 mL) to rinse the test tube and wash the cartridge. Repeat the washing step two more times to give a total wash volume no more than 8 mL. Elute and collect the clomazone residue with 12 mL of ethyl acetate/hexane (5/95, v/v) in a clean graduated test tube (collection rate ~2 mL/min). Concentrate the solution with a N-Evap to ~1 mL. The temperature of the N-Evap is kept between 30 to 40°C.

b. Florisil or Silica Gel Cartridge

- i. The oil samples except corn crude oil (see step ii) should be further cleaned-up by a Florisil cartridge (1 g, 6 cc). Condition the cartridge first with 12 mL of ethyl acetate/hexane (10/90, v/v) and then with 12 mL of ethyl acetate/hexane (5/95, v/v). Load the sample solution in the cartridge barrel by a pipette. Rinse the test tube with ~2 mL of hexane and transfer it to the cartridge. Elute the clomazone residues with 12 mL of ethyl acetate/hexane (10/90, v/v) and collect the solution in a clean graduated test tube. Sample flow rate through the cartridge can be controlled by the gravity.
- ii. When analyzing the corn crude oil, a silica gel cartridge is used instead of the Florisil for cleanup. Condition procedures are first with 12 mL of ethyl acetate/hexane (10/90, v/v) and then with 12 mL of ethyl acetate/hexane (5/95, v/v). After sample loading, rinse the cartridge with 10 mL of ethyl acetate/hexane (5/95, v/v), and collect with 12 mL of ethyl acetate/hexane (10/90, v/v). The solution flow rate through the cartridge should be maintained at ~2 mL/min by a vacuum pump.

The collected solution is then concentrated via the N-Evap to exactly 0.5 mL. The final solution is quantitated by a gas chromatograph equipped with a nitrogen/phosphorus detector. Figure 2 in Section III presents the method flow scheme for oil matrices.

3. Method for Cottonseed Soapstock

a. Acid Hydrolysis

Weigh 2.5 g of soapstock into a 500 mL boiling flask. Apply the fortification at

this time. Add 100 ml of 0.25N HCl and a Teflon stirring bar or boiling chips into the flask. Attach the boiling flask to a condenser. Set the heating mantle variac power supply at about 60 and reflux the sample solution under gentle boiling for one hour.

b. Hexane Partition

Cool the hydrolysate to room temperature after the reflux and transfer the solution into a 500 mL separatory funnel. Extract the acid solution twice, each with 200 mL of hexane. Collect the combined hexane solution in a 1000 mL boiling flask and concentrate it to ~50 mL by a rotary evaporator. Filter the hexane through a fluted filter paper, which is half-filled with anhydrous sodium sulfate, to remove the precipitate and any trace of water. Rinse and wash the glassware and sodium sulfate with 100 mL of hexane. Collect the sample solution in a 500 mL boiling flask and further concentrate it to ~2 mL via the rotary evaporator. Transfer the sample solution from the boiling flask to a 13 mL graduated test tube and rinse the flask with ~3 mL of hexane. The rinse and transfer steps are repeated two to three times to give a total solution volume of ~11 mL. Concentrate the sample solution in the test tube to ~4 mL by the N-Evap. The concentrated sample solution is then ready to be loaded onto a C₁₈ SPE cartridge.

c. C₁₈ and Florisil Cartridges

Method procedures for C₁₈ SPE cartridge and Florisil cleanup cartridge are similar to the method for the oil samples. The only difference is that during the wash step for the Florisil cartridge, 12 ml of hexane is used instead of 2 ml.

B. Instrumentation

Clomazone residues are quantitated by a Hewlett-Packard 5890A gas chromatograph equipped with a nitrogen/phosphorus detector, a HP 7673A autosampler, and a HP 3392A integrator. Equivalent gas chromatograph, integrator, data acquisition system, and autosampler can be used. Several megabore capillary columns, including DB-1, DB-5, DB-17, and RT_x-1 have been used to detect clomazone. Section XII, Appendix A1 shows one example of the operating conditions. The chromatographic conditions can be modified or optimized for best detection sensitivity. The chromatographic system should be calibrated after every two sample injections by external standard method. A linearity curve should be generated with appropriate standard solutions to insure the linear response of the instrument during analysis.

C. Method Validation and Quality Control

A method recovery set should consist of one control sample and at least three fortified samples. The analytical method recovery is determined by the results from the fortified control samples. The control sample should be pre-determined to be clomazone residue free.

D. Method of Calculation

The magnitude of clomazone in each sample is quantitated by an external standard calibration method based on the average of all run standards in an assay set. The run standard is injected at the beginning of every set and subsequently after every two sample solutions. The amount of clomazone is quantitated from the detector response transmitted to the data acquisition station. Normally the responses as peak areas are calculated as nanogram (ng) of clomazone based on the injection of run standards. Corn crude oil from the wet milling is the only exception. Peak height may have to be used for the calculation because the noisy background seems to interfere with the integration accuracy.

The nanogram value reported is calculated by comparing the area units of unknown sample to the average run standard using the following formula:

$$\text{ng of clomazone in sample} = \frac{\text{area unit (sample)}}{\text{average area (standard)}} \times \text{ng injected (standard)}$$

Results of each analysis are reported on a ppm ($\mu\text{g/g}$) basis by using the following formula:

$$\text{clomazone content ppm } (\mu\text{g/g}) = \frac{\text{ng of clomazone in sample}}{\text{mg of sample injected}}$$

Method recovery is then obtained by comparing the clomazone content recovered from the sample to the initial fortification level.

$$\text{method recovery (\%)} = \frac{\text{clomazone content (ppm)}}{\text{fortification level (ppm)}} \times 100$$

E. Interferences

1. **Sample Matrices** - No interference was noted in the control non-oil and oil matrices near the limit of detection level.
2. **Other Pesticides** - No interference due to other pesticides was expected.
3. **Solvents and Labware** - No interference was observed from solvents and labware.

F. Confirmatory Techniques

Clomazone residues can be confirmed by a Hewlett-Packard 5890A gas chromatograph equipped with a mass selective detector 5970, and a HP 7673A autosampler. The operating conditions are listed in Section XII, Appendix A2.

G. Time Required for Analysis

The analytical procedures require approximately eight hours for non-oil matrices, four hours for oil samples, and 12 hours for cottonseed soapstock. During this time, one person can complete a set of eight samples from initial weighing to gas chromatographic measurement.

H. Modification or Potential Problems

1. The effect of the initial sample weight and the acid volume on the method recovery for corn stover and cottonseed samples have been investigated with ¹⁴C-labeled clomazone. Method recoveries increase as the sample size is reduced and the acid volume increased. Similar results have been observed with cottonseed meal and hulls, and cured tobacco samples. The specific fiber content in each matrix seems to be the responsible factor. When a particular matrix is analyzed, the higher the fiber content it has, the more acid will be needed to obtain an acceptable method recovery.
2. The variac power supply of the heating mantle should be set to maintain a gentle boiling. Overheating will cause some of the non-oil matrices to float and stay inside the condenser or around the boiling flask neck. Lower recovery (~10% less) has been observed when this happens. The cooling water must be circulated during reflux to prevent the loss of clomazone from volatility.
3. The filtration step is often slow for fine powder samples, such as grain or meal. A thin layer of glasswool on top of the microfiber paper will accelerate the filtration procedure.
4. The volume of deionized water (or 0.25N HCl) used to rinse and wash the sample matrix during the filtration step is important, because ~10% loss of recovery has been observed when the amount of wash water is decreased from 100 mL to 50 mL.

5. After the acid solution is passed through the C₁₈ cartridge, the cartridge must be blown completely dry before proceeding with the elution step.
6. When analyzing oil and soapstock samples, the total sample volume in hexane passed through the C₁₈ cartridge is very critical. A sample volume of more than 6 mL will result in loss of clomazone during sample loading. In addition, the C₁₈ cartridge wash step with hexane is also crucial. The total hexane wash volume can not exceed 8 mL, otherwise clomazone residues will be eluted from the cartridge. The above observations have been proven by analyzing matrices fortified with ¹⁴C-labeled clomazone.
7. Florisil cartridges from the J.T. Baker Inc. were used to analyze corn silage, stover, cottonseed, soybean, and tobacco matrices. When cartridges from other manufacturer were used for corn silage and stover samples, a peak with retention time of -0.2 min (depends on the GC conditions) after the clomazone peak was observed in the chromatogram. Such interference was not observed when using Florisil cartridge from J.T. Baker Inc. In addition, different elution patterns have been observed with cartridges of other brands. Therefore, elution pattern must be evaluated if cartridges other than recommended will be used.
8. When cured tobacco is analyzed, wash the Florisil cartridge with 6 mL of hexane and then collect the residue with 12 mL of ethyl acetate/hexane (10/90, v/v) will reduce the chromatogram background noise.
9. The oven temperature of the gas chromatograph should be programmed to a higher final temperature after the initial isothermal conditions to bake out any possible matrix interferences.

VI. STORAGE STABILITY

Clomazone analytical standard should be assayed on a regular basis for percent purity. The standard has a proven pattern of stability. Stock solution (1000 $\mu\text{g/mL}$) should be prepared annually in hexane solution. Fresh dilute solutions are prepared at suitable concentrations on a monthly basis. All solutions should be stored in volumetric containers in a refrigerator/freezer unit and have a proven stability for their respective storage periods.

VII. RESULTS AND DISCUSSION

A. Accuracy and Precision

The accuracy and the precision of the analytical method are determined by the average recovery and standard deviation of the results from the fortified control samples. Table 1 and 2 in Section III present the average method recovery and standard deviation for each matrix. The average method recovery for clomazone in 19 matrices tested ranges from 72 to 104%, with standard deviation ranging from ± 3 to $\pm 16\%$ depending on the method used and the matrix analyzed. Individual method recovery data can be found in Section X, Tables 4 to 12. The overall average recovery and the standard deviation for the non-oil and oil methods are $84\% \pm 13\%$ ($n=115$) and $90\% \pm 13\%$ ($n=28$), respectively.

B. Limits of Detection and Quantitation

For all the matrices except tobacco, the limit of quantitation (LOQ) has been validated at 0.05 ppm based on acceptable fortified recovery values. The limit of detection (LOD) or recognition of detector response has been set at 0.01 ppm (signal/noise ratio = 3). In tobacco assays, the LOQs are established at 0.1 and 0.2 ppm based on tolerance values, with LODs at 0.02 and 0.04 ppm for green and cured tobacco, respectively. Any response below the limit of detection is considered non-detectable (ND).

C. Ruggedness Testing

The non-oil method has been applied on corn matrices (grain, grits, meal, flour, starch, silage, stover), cottonseed matrices (cottonseed, meal, hulls), and tobacco samples. The overall average method recovery for the non-oil matrices is 84% (115 assays) with a standard deviation of $\pm 13\%$.

The oil method has been applied to crude and refined oils from corn grain, cottonseed, and soybean, and cottonseed soapstock. The overall average method recovery is 90% (28 assays) with a standard deviation of $\pm 13\%$.

The above results indicated that these methods are reliable and accurate.

D. Limitations

No potential limitations have been experienced during the assay analyses.

E. Summary of Independent Validation

The non-oil and oil methods have been successfully validated by an independent laboratory. The validation was first conducted on cottonseed meal and corn deodorized oil (Section XI, Reference 3). The two matrices were selected to be the representative matrices of non-oil and oil matrices. Results of the average recovery and standard deviation (n=4) were $81 \pm 6\%$ for cottonseed meal, and $98 \pm 8\%$ for corn deodorized oil. The validation was further tested on the following matrices with the resulting average recovery and standard deviation included: corn silage ($96\% \pm 10\%$), corn stover ($82\% \pm 8\%$), green tobacco ($95\% \pm 10\%$), soybean crude oil ($104\% \pm 3\%$), cottonseed crude oil ($105\% \pm 5\%$), and cottonseed soapstock ($80\% \pm 7\%$) (Section XI, Reference 4).

VIII. CONCLUSION

The two Analytical methods utilizing a C₁₈ SPE cartridge, and a Florisil or a silica cartridge for

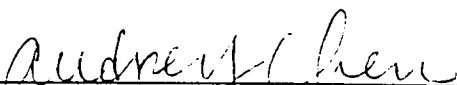
cleanup have been developed to determine the clomazone residue in/on corn raw agricultural commodities (grain, silage, and stover), corn processed parts (grits, meal, flour, starch, crude and refined oils), delinted cottonseed, cottonseed processed parts (meal, hulls, soapstock, crude and refined oils), green and cured tobacco, and soybean crude and refined oils. These methods are fast, easy to operate, and consume only small volumes of solvents.

The above two analytical methods have been successfully validated by an independent laboratory on four non-oil matrices (corn silage, corn stover, cottonseed meal, and green tobacco) and four oil matrices (corn deodorized oil, soybean crude oil, cottonseed crude oil, and cottonseed soapstock). The two methods were proven satisfactorily with no communication needed regarding technical issues during validation performance.

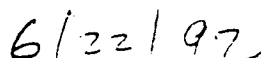
All the equipment needed to perform the analysis, e.g., gas chromatograph with nitrogen/phosphorus detector, is readily available in most residue analytical laboratories. An experienced residue analyst following the procedure exactly as written, and being aware of the possible potential problems, should not experience interference problems and should obtain adequate recoveries.

IX. CERTIFICATION


We, the undersigned, hereby declare that this study was performed under our supervision according to the procedures herein described, and that this report provides a true and accurate record of the results obtained.



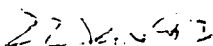
Audrey W. Chen
Research Chemist
AUTHOR/STUDY DIRECTOR



Date



Ronald F. Cook
Manager, Residue Chemistry
SUPERVISOR



Date

ADDITIONAL STUDY PERSONNEL:

George M. Singer, Research Chemist
George P. Barrett, Senior Chemist
Anthony Barros, Chemist
John R. Arabinick, Senior Research Technician
Harvey R. Wendt, Research Technician
Dave Baffuto, Research Technician

X. TABLES AND FIGURES

TABLE 3

THE SPECIFIC
SAMPLE SIZE, ACID VOLUME, AND FINAL SOLUTION VOLUME
FOR CLOMAZONE ANALYSIS

MATRIX	SAMPLE SIZE (g)	ACID VOLUME (mL)	FINAL VOLUME (mL)
corn grain	5	100	1.0
corn medium grits	5	100	1.0
corn meal	5	100	1.0
corn flour	5	100	1.0
corn silage	5	100	1.0
corn stover	2.5	200	0.5
cottonseed meal	2.5	200	0.5
cottonseed hulls	2.5	300	0.5
green tobacco	5	200	1.0
cured tobacco	2.5	250	1.0

TABLE 4

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL CORN PROCESSED PARTS

MATRIX	SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (ppm)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)	AVERAGE RECOVERY (%)
Corn Grain	88-CRS-16C	11-2	0.05	ND	85	87
		11-3	0.05	ND	80	
		11-4	0.05	ND	97	
Medium Grits	88-CRS-16C	13-2	0.05	ND	73	74
		13-3	0.05	ND	77	
		13-4	0.05	ND	72	
Meal	88-CRS-16C	14-2	0.05	ND	101	83
		14-3	0.05	ND	72	
		14-4	0.05	ND	75	
Flour	88-CRS-16C	15-2	0.05	ND	85	82
		15-3	0.05	ND	85	
		15-4	0.05	ND	76	
Starch	88-CRS-16C	16-2	0.05	ND	69	79
		16-3	0.05	ND	84	
		16-4	0.05	ND	84	
Crude Oil* (wet milling)	88-CRS-16C	CC3-2	0.05	ND	81	93
		CC3-3	0.05	ND	90	
		CC3-4	0.05	ND	108	
Refined Deodorized Oil* (wet milling)	88-CRS-16C	CR1-2	0.1	ND	98	94
		CR1-4	0.1	ND	90	
		CR2-2	0.05	ND	88	
		CR2-3	0.05	ND	99	
		CR2-4	0.05	ND	95	

Recovery data of non-oil matrices compiled from Table 2 in FMC report P-2352M (Section XI, Reference 1).

* Crude and refined deodorized oils were analyzed by SPE cartridge method instead of liquid-liquid extraction method. Recovery data compiled from the supplementary package.

ND = Non-Detectable (< 0.01 ppm)

TABLE 5

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL CORN GRAIN SAMPLES

SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (ppm)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)
88-CRS-8C	A-2	0.05	ND	81
	A-3	0.05	ND	95
	A-4	0.05	ND	106
88-RSH-02C	B	0.05	ND	88
88-SFT-3C	C	0.05	ND	76
88-AFC-2C	D	0.05	ND	97
88-JPG28-30C	E	0.05	ND	79
88-SFT-5C	F	0.05	ND	72
88-RSP-42C	G	0.05	ND	94
88-CRS-12C	H-2	0.05	ND	68
	H-3	0.05	ND	83
	H-4	0.05	ND	89
88-CFC-2C	I	0.05	ND	72
88-RSP-46C	J	0.05	ND	86
89-JJK-04-6C	1	0.05	ND	77
89-CGR-18C	2	0.05	ND	71
89-CDA-02C	3	0.05	ND	72
89-TKP-29CD	4	0.05	ND	77
89-JMT-28C	5	0.05	ND	78
89-TWM-003C	6	0.05	ND	77
OVERALL AVG/20				82
OVERALL STD. DEV.				±10

Recovery data compiled from Table 5 in FMC report P-2478 (Section XI, Reference 5) and Table 4 in report P-2482 (Section XI, Reference 6).

ND = Non-Detectable (< 0.01 ppm)

TABLE 6

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL CORN SILAGE SAMPLES

SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (ppm)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)
88-CRS-1C	A-2	0.05	ND	80
	A-3	0.05	ND	89
	A-4	0.05	ND	96
88-RSH-01C	B	0.05	ND	103
88-SFT-1C	C	0.05	ND	111
88-AFC-1C	D	0.05	ND	73
88-JPG28-15C	E	0.05	ND	78
88-SFT-4C	F	0.05	ND	120
88-RSP-20C	G	0.05	ND	94
88-CRS-3C	H	0.05	ND	81
88-CFC-1C	I	0.05	ND	70
88-RSP-22C	J	0.05	ND	73
89-JJK-04-3C	1	0.05	ND	87
89-CGR-17C	2	0.05	ND	84
89-CDA-01C	3	0.05	ND	63
89-TKP-25C	4	0.05	ND	70
89-JMT-27C	5	0.05	ND	110
89-TWM-001C	6	0.05	ND	106
OVERALL AVG/18				88
OVERALL STD. DEV.				±16

Recovery data compiled from Table 5 in FMC report P-2478 and Table 4 in report P-2482.
ND = Non-Detectable (< 0.01 PPM)

TABLE 7

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL CORN STOVER SAMPLES

SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (ppm)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)
88-CRS-9C	A-2	0.1	ND	110
	A-3	0.1	ND	94
	A-4	0.1	ND	97
88-RSH-03C	B	0.05	ND	109
88-SFT-2C	C	0.05	ND	112
88-AFC-3C	D	0.05	ND	89
88-JPG28-33C	E	0.05	ND	99
88-SFT-6C	F	0.05	ND	66
88-RSP-41C	G	0.05	ND	97
88-CRS-13C	H	0.05	ND	75
88-CFC-3C	I	0.05	ND	101
88-RSP-45C	J	0.05	ND	86
89-JJK-04-9C	1	0.05	ND	85
89-CGR-19C	2	0.05	ND	81
89-CDA-03C	3	0.05	ND	122
89-TKP-33C	4	0.05	ND	90
89-JMT-29C	5	0.05	ND	91
89-TWM-002C	6	0.05	ND	117
OVERALL AVG/18				96
OVERALL STD. DEV.				±11

Recovery data compiled from Table 5 in FMC report P-2478 and Table 4 in report P-2482.
ND = Non-Detectable (< 0.01 PPM)

TABLE 8

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL COTTONSEED PROCESSED PARTS

MATRIX	SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (ppm)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)	AVERAGE RECOVERY (%)
Delinted Cottonseed	88-HRM-01C	1-2	0.05	ND	83	73
		1-3	0.05	ND	69	
		1-4	0.05	ND	65	
Meal	88-HRM-01C	2-2	0.05	ND	65	72
		2-3	0.05	ND	85	
		2-4	0.05	ND	67	
Hulls	88-HRM-01C	3-2	0.05	ND	87	78
		3-3	0.05	ND	80	
		3-4	0.05	ND	69	
		3B-2	0.05	ND	80	
		3B-3	0.05	ND	73	
		3B-4	0.05	ND	79	
Crude Oil	88-HRM-01C	4-2	0.05	ND	74	75
		4-3	0.05	ND	80	
		4-4	0.05	ND	71	
Refined Deodorized Oil	88-HRM-01C	5-2	0.05	ND	90	95
		5-3	0.05	ND	89	
		5-4	0.05	ND	105	
Soapstock	88-HRM-01C	6-2	0.05	ND	76	77
		6-3	0.05	ND	70	
		6-4	0.05	ND	86	

Recovery data compiled from Table 3 in FMC report P-2551M (Section XI, Reference 2).
ND = Non-Detectable (< 0.01 ppm)

TABLE 9

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL COTTONSEED SAMPLES

SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (PPM)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)
R90-EVG-15C	01	0.05	ND	69
R90-EVG-05C	02	0.05	ND	65
90-HRM-100C	03	0.05	ND	81
90-HRM-101C	04	0.05	ND	72
90-LDH-101C	05	0.05	ND	73
90-LDH-102C	06	0.05	ND	106
90-LDH-100C	06	0.05	ND	86
90-RDK-64C	08	0.05	ND	84
90-HGH-07C	08	0.05	ND	74
			OVERALL AVG/9	79
			OVERALL STD. DEV.	±12

Recovery data compiled from Table 6 in FMC report P-2558 (Section XI, Reference 7).
ND = Non-Detectable (< 0.01 ppm)

TABLE 10

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL GREEN TOBACCO SAMPLES

SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (PPM)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)
89-TKP-01C	01	0.1	ND	72
89-TKP-09C	01	0.1	ND	89
89-TKP-17C	02	0.1	ND	70
89-RSH-03C	02	0.1	ND	80
89-RSH-04C	03	0.1	ND	80
89-RSH-05C	03	0.1	ND	80
89-RAE-07C	04	0.1	ND	87
89-RAE-08C	04	0.1	ND	110
89-RAE-09C	05	0.1	ND	96
89-AEP-10C	05	0.1	ND	84
89-AEP-12C	06	0.1	ND	64
89-AEP-14C	06	0.1	ND	73
89-RAE-01C	07	0.1	ND	95
89-RAE-03C	08	0.1	ND	87
89-RAE-05C	08	0.1	ND	89
<u>REPEAT ANALYSIS</u>				
89-TKP-17C	09	0.1	ND	85
89-RAE-03C	09	0.1	ND	95
OVERALL AVG/17				84
OVERALL STD. DEV.				±11

Recovery data compiled from Table 7 in FMC report P-2630 (Section XI, Reference 8).
ND = Non-Detectable (< 0.02 ppm)

TABLE 11
METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL CURED TOBACCO SAMPLES

SAMPLE IDENTIFICATION	SET NUMBER	FORTIFICATION LEVEL (PPM)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)
89-TKP-03C	11	0.2	ND	71
89-TKP-11C	11	0.2	ND	74
89-TKP-19C	12	0.2	ND	58
89-RSH-12C	12	0.2	ND	86
89-RSH-13C	13	0.2	ND	81
89-RSH-14C	13	0.2	ND	95
89-RAE-10C	14	0.2	ND	77
89-RAE-11C	14	0.2	ND	73
89-RAE-12C	15	0.2	ND	79
89-AEP-11C	15	0.2	ND	68
89-AEP-13C	16	0.2	ND	82
89-AEP-15C	16	0.2	ND	103
89-RAE-02C	17	0.2	ND	71
89-RAE-04C	18	0.2	ND	84
89-RAE-06C	18	0.2	ND	94
OVERALL AVG/15				80
OVERALL STD. DEV.				±12

Recovery data compiled from Table 8 in FMC report P-2630.
ND = Non-Detectable (< 0.04 ppm)

TABLE 12

METHOD RECOVERY OF CLOMAZONE FROM
LABORATORY FORTIFIED CONTROL SOYBEAN OILS

MATRIX	SET NUMBER	FORTIFICATION LEVEL (ppm)	CONTROL BACKGROUND	CLOMAZONE RECOVERY (%)	AVERAGE RECOVERY (%)
Crude Oil	SC1-2	0.1	ND	111	104
	SC1-3	0.1	ND	101	
	SC1-4	0.1	ND	92	
	SC2-2	0.05	ND	121	
	SC2-4	0.05	ND	95	
Refined Bleached Oil	SR1-2	0.1	ND	86	87
	SR1-3	0.1	ND	90	
	SR1-4	0.1	ND	106	
	SR2-2	0.05	ND	76	
	SR2-3	0.05	ND	91	
	SR2-4	0.05	ND	71	
			OVERALL AVG/11	95	
			OVERALL STD. DEV.	±15	

ND = Non-Detective (< 0.01 ppm)

Data compiled from the supplementary package.

XI. REFERENCES

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2. Chen, A. W., "Residue Analytical Method for the Determination of Clomazone in/on Cottonseed and the Processed Parts," FMC Corporation, ACG, Princeton, NJ, P-2551M, February 1991, MRID No. 42165703.
3. Brunk, J. Y., "Independent Laboratory Confirmation of the Residue Analytical Method for the Determination of Clomazone in/on Cottonseed Meal and Corn Deodorized Oil," FMC Corporation, ACG, Princeton, NJ, PC-0169, April 1992, MRID No. 42325302.
4. Brunk, J. Y., "Independent Laboratory Confirmation of the Residue Analytical Method for the Determination of Clomazone in/on Corn Stover, Corn Silage, Green Tobacco, Cottonseed Crude Oil, Soybean Crude Oil, and Cottonseed Soapstock," FMC Corporation, ACG, Princeton, NJ, PC-0177, June 1992.
5. Chen, A. W., "Magnitude of the Residue of Clomazone in/on Field Corn Grain, Silage, and Stover," FMC Corporation, ACG, Princeton, NJ, P-2478, Revised, November 1990, MRID No. 41663307.
6. Barros, A., "Magnitude of the Residue of Clomazone in/on Field Corn," FMC Corporation, ACG, Princeton, NJ, P-2482, Revised, November 1990, MRID No. 41663308.
7. Barrett, G. P., "Magnitude of the Residue of Clomazone in/on Cottonseed from Fields Treated Pre-Emergent or Pre-Plant Incorporated with Command® 4EC," FMC Corporation, ACG, Princeton, NJ, P-2558, September 1991, MRID No. 42165701.
8. Barrett, G. P., "Magnitude of the Residue of Clomazone in/on Tobacco Treated Post-Transplant with Command® 4EC," FMC Corporation, ACG, Princeton, NJ, P-2630, November 1991, MRID No. 42162402.

XII. APPENDICES

A. Instrument Parameters

1. GC/NPD*

COLUMN: Rt_x-1, dimethyl silicone
30 m x 0.53 mm x 1.0 μm

INLET: Direct injection (250°C)

OVEN TEMPERATURE:

Initial Temp: 190°C
Initial Time: 10 min
Rate: 20°C/min
Final Temp: 225°C
Final Time: 10 min

DETECTOR TEMPERATURE: 300°C

GAS FLOW RATE: He, carrier, ~5 mL/min
He, make-up, ~25 mL/min
H₂, ~3.5 mL/min
Air, ~85 mL/min

RETENTION TIME: ~6 min

- * Equivalent GC and GC columns can be used to determine the clomazone residue. Chromatographic conditions can be modified or optimized for best detection sensitivity.

2. GC/MSD*

COLUMN: DB-17, 50% phenyl methyl
silicone 15 m x 0.25 mm x
0.25 μ m

INLET: Splitless mode (250°C)

OVEN TEMPERATURE:

Initial Temp:	45°C
Initial Time:	2 min
Rate 1:	70°C/min
Temp 2:	145°C
Time 2:	0.25 min
Rate 2:	10°C/min
Temp 3:	250°C
Final Time:	2 min

DETECTOR TEMPERATURE: 275°C

GAS FLOW RATE: He, carrier, ~1 mL/min

RETENTION TIME: ~10 min

ION MONITORED: 125, 204

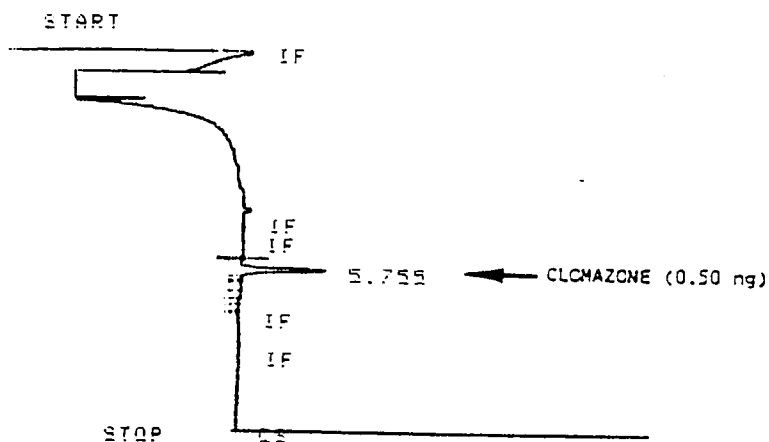
* Equivalent GC/MSD and GC columns can be used to determine the clomazone residue. Chromatographic conditions can be modified or optimized for best detection sensitivity.

Appendix B. Chromatograms

FIGURE NUMBER	DESCRIPTION	AMOUNT INJECTED
4	Standard, Clomazone	0.50 ng
5	Corn silage, Control	10 mg
6	Corn silage, Fortified	10 mg
7	Standard, Clomazone	0.50 ng
8	Cottonseed meal, Control	10 mg
9	Cottonseed meal, Fortified	10 mg
10	Standard, Clomazone	1.00 ng
11	Tobacco, Cured, Control	10 mg
12	Tobacco, Cured, Fortified	10 mg
13	Standard, Clomazone	0.50 ng
14	Corn Deodorized Oil, Control	10 mg
15	Corn Deodorized Oil, Fortified	10 mg
16	Standard, Clomazone	0.50 ng
17	Cottonseed Crude Oil, Control	10 mg
18	Cottonseed Crude Oil, Fortified	10 mg
19	Standard, Clomazone	0.25 ng
20	Soybean Crude Oil, Control	10 mg
21	Soybean Crude Oil, Fortified	10 mg
22	Standard, Clomazone	0.50 ng
23	Cottonseed Soapstock, Control	10 mg
24	Cottonseed Soapstock, Fortified	10 mg

FIGURE 4

Clomazone Standard
0.25 ng/ μ L, 2 μ L injection, (#307-51)



RUN# 562 MAR 17 1992 15:09:05

CLOMAZONE

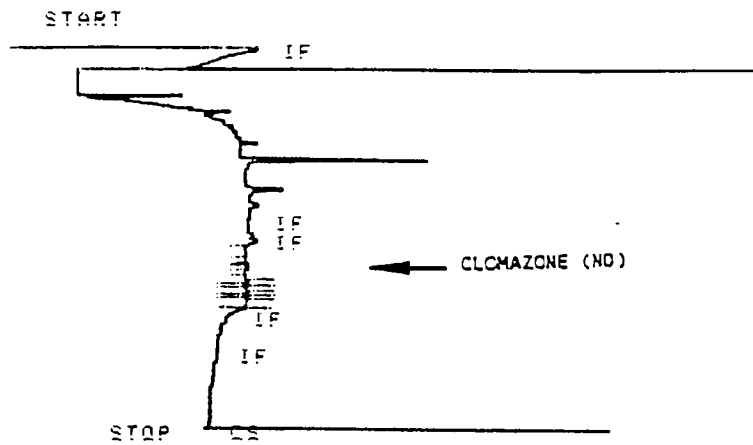
ESTD%-AREA

RT	AREA	TYPE	CAL#	MG
5.755	7242	BV	10	91.336

TOTAL AREA= 7242
MUL FACTOR=1.0000E+00
SAMPLE AMT=5.0000E-01

FIGURE 5

Corn Silage, Control, 10 mg injected
(PRE-320, 88-CRS-1C, #A2-1)



RUN# 568

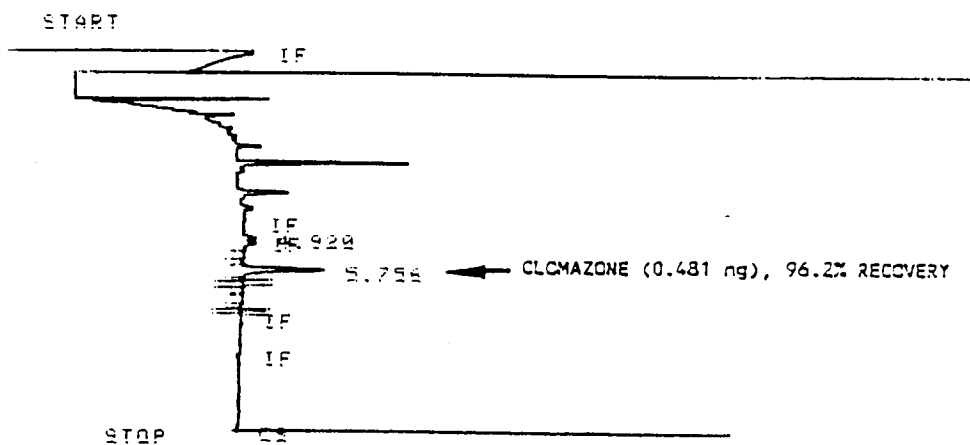
MAR 17 1998 14:09:22

CLOMAZONE

NO RUN PEAKS STORED

FIGURE 6

Corn Silage, Fortified @ 0.05 ppm, 10 mg injected
(PRE-320, 88-CRS-1C, #A2-4)



RUN# 564 MAR 17, 1990 16:00:40

CLOMAZONE

ESTO%-AREA

RT	AREA	TYPE	CAL#	MG
5.756	6940	VP	10	07.527

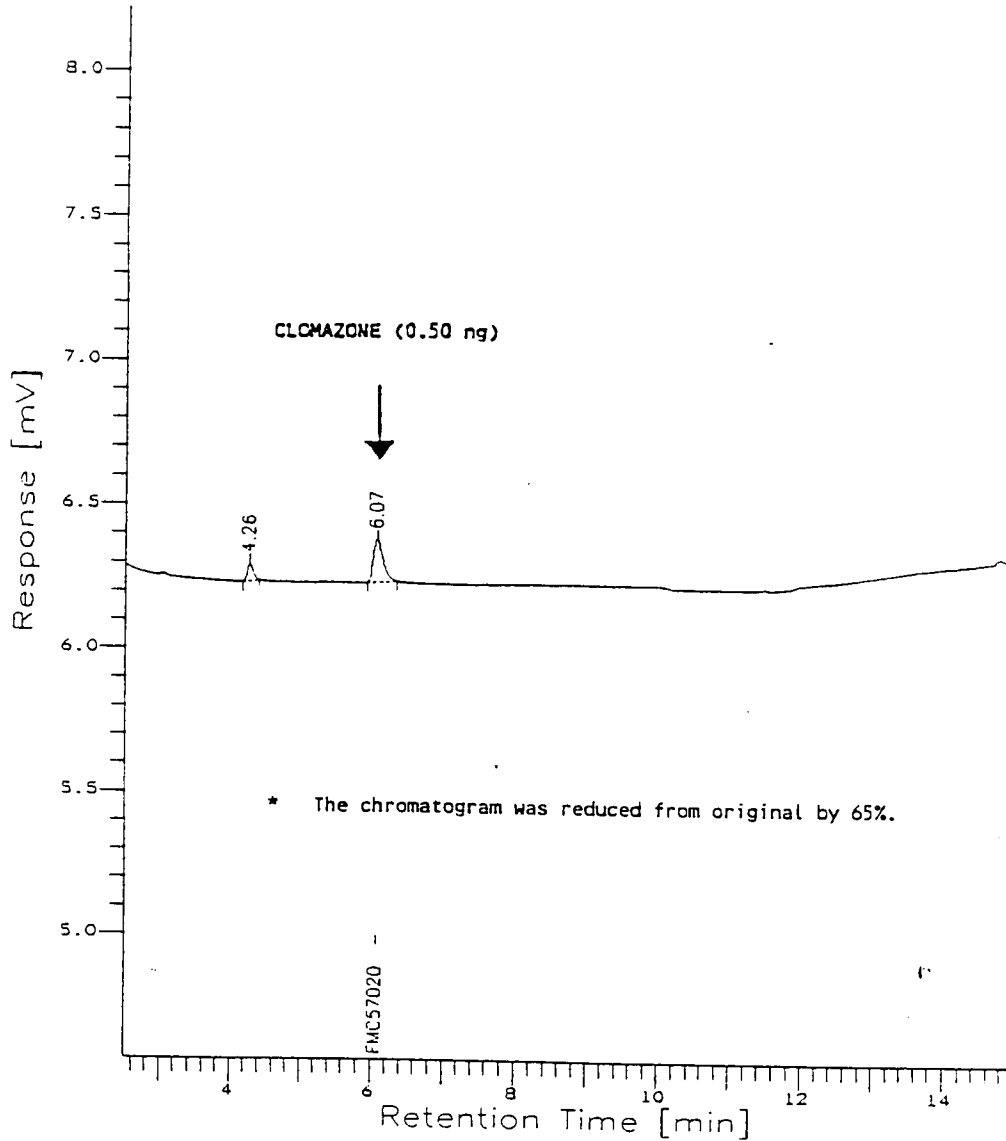
TOTAL AREA= 7954

MUL FACTOR=1.0000E+00

SAMPLE AMT=5.0000E-01

FIGURE 7

Clomazone Standard
0.25 ng/ μ L, 2 μ L injection, (#352-26)



Peak #	Ret Time [min]	Component Name	Area [uV-sec]	Height [uV]	Area %	BL	Amount [ng]
2	6.085	FMC57020	1330.50	143.13	100.00	MM	0.4926
			1330.50	143.13	100.00		0.4926

FIGURE 8

Cottonseed Meal, Control, 10 mg injected
(PRF-07, 88-HRM-01C, #2-1)

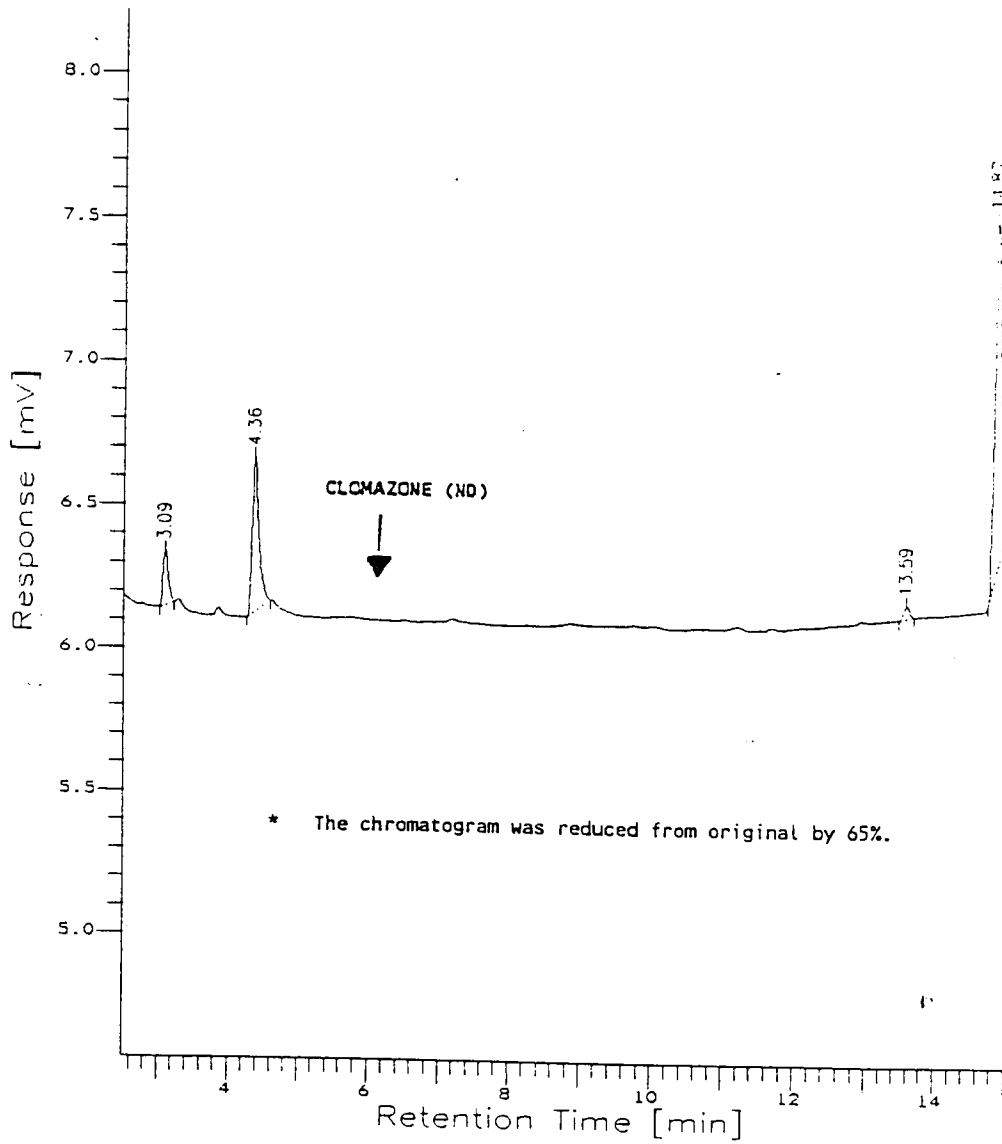
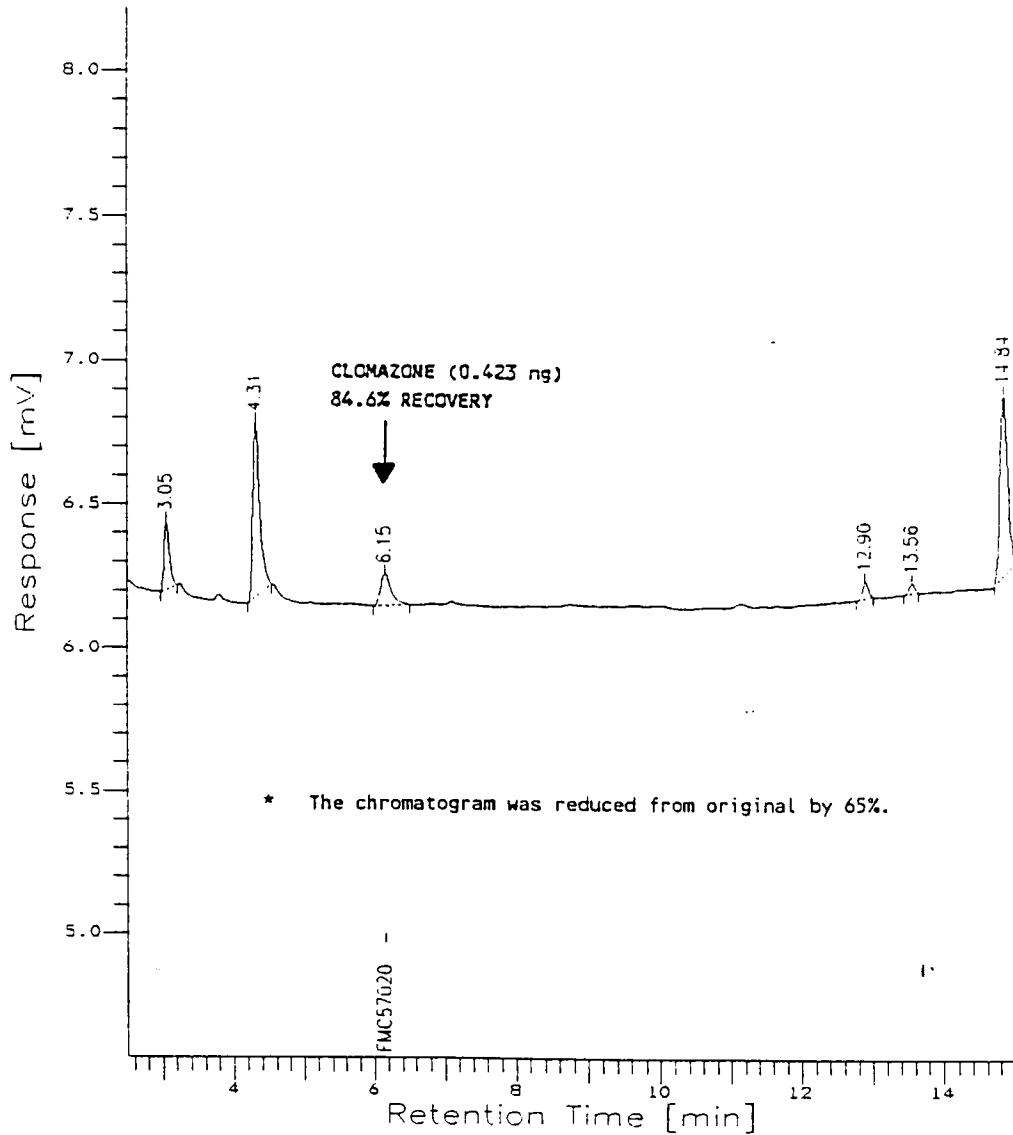


FIGURE 9

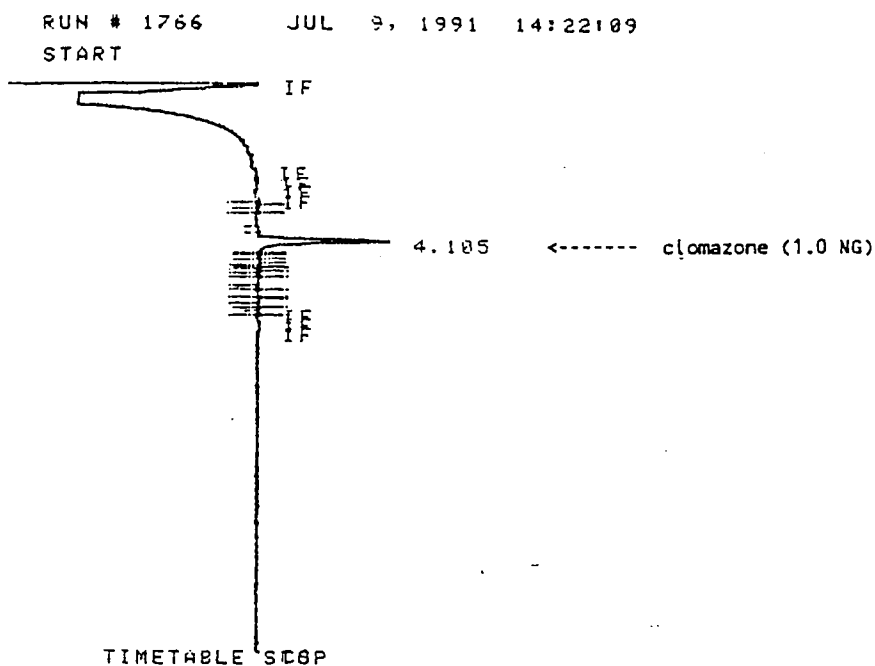
Cottonseed Meal, Fortified @ 0.05 ppm, 10 mg injected
(PRF-07, 88-HRM-01C, #2-3)



Peak #	Ret Time [min]	Component Name	Area [uV-sec]	Height [uV]	Area %	BL	Amount [ng]
3	6.154	FMC57020	1111.00	110.21	100.00	MM	0.4148
			1111.00	110.21	100.00		0.4148

FIGURE 10

Clomazone Standard
0.5 ng/ μ L, 2 μ L injection, (#427-12)



RUN# 1766 JUL 9, 1991 14:22:09

SAMPLE NAME: #427-12 SAMPLE# 8
CLOMAZONE STD - 0.5 NG/UL

CLOMAZONE - TOBACCO STUDY

ESTD-AREA

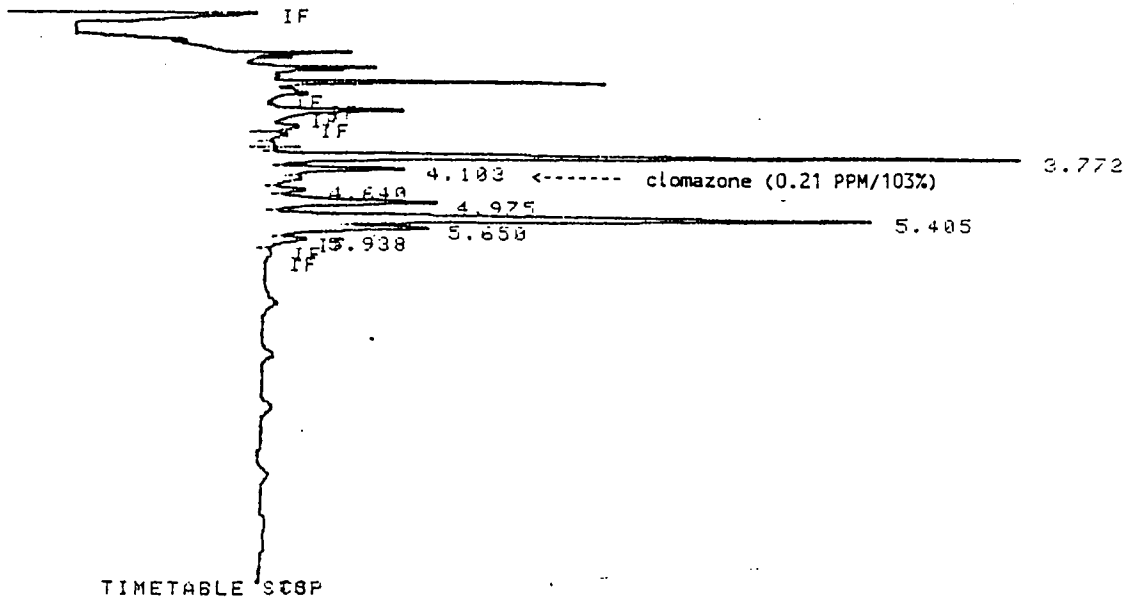
RT	AREA	TYPE	CAL#	AMOUNT
4.105	13384	PB	1R	1.162

TOTAL AREA= 13384
MUL FACTOR=1.0000E+00

FIGURE 12

Tobacco, Cured
Fortified @ 0.2 ppm, 10 mg injected
(PRF-95, 89-AEP-15C, #16-134)

RUN # 1768 JUL 9, 1991 15:07:07
START



RUN# 1768 JUL 9, 1991 15:07:07

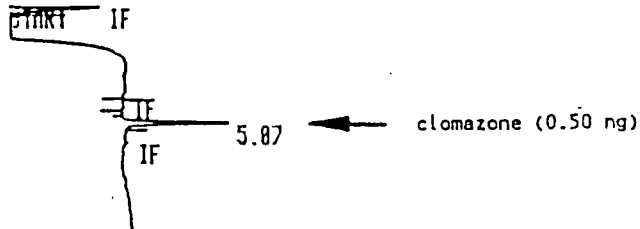
SAMPLE NAME: SA #134 SAMPLE# 10
TOBACCO, CURED - CK + 0.2 PPM (NC, 3RD PRIMING)

CLOMAZONE - TOBACCO STUDY

ESTD-AREA	RT	AREA	TYPE	CAL#	AMOUNT
	3.772	68966	VV		.000
	4.103	13359	VV	1R	.999
	4.640	3700	VV		.000
	4.975	23554	VV		.000
	5.405	79485	VV		.000
	5.650	20220	VV		.000
	5.938	4874	VP		.000

FIGURE 13

Clomazone Standard
0.25 ng/ μ L, 2 μ L injection, (#307-15)

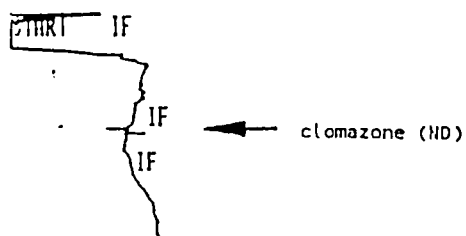


RUN # 930 OCT/25/89 14:22:58
WORKFILE ID: C8
WORKFILE NAME:
ID: 57020
SAMPLE # 1

ESTD	RT	AREA	TYPE	CAL #	AMOUNT
	5.07	1542	PB	1R	1.283

FIGURE 14

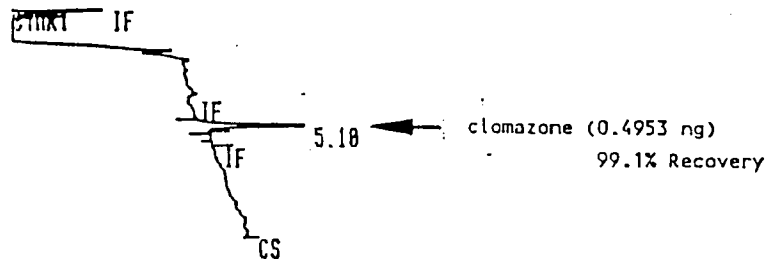
Corn Wet Milling Refined Deodorized Oil
Control, 10 mg injected
(PRF-16, 88-CRS-16C, #17-1)



RUN # 931 OCT/25/89 14:34:17
WORKFILE ID: C8
WORKFILE NAME:
ID: 57020
SAMPLE # 2
NO RUN PEAKS STORED

FIGURE 15

Corn Wet Milling Refined Deodorized Oil
Fortified @ 0.05 ppm, 10 mg injected
(PRF-15, 88-CRS-16C, #17-3)

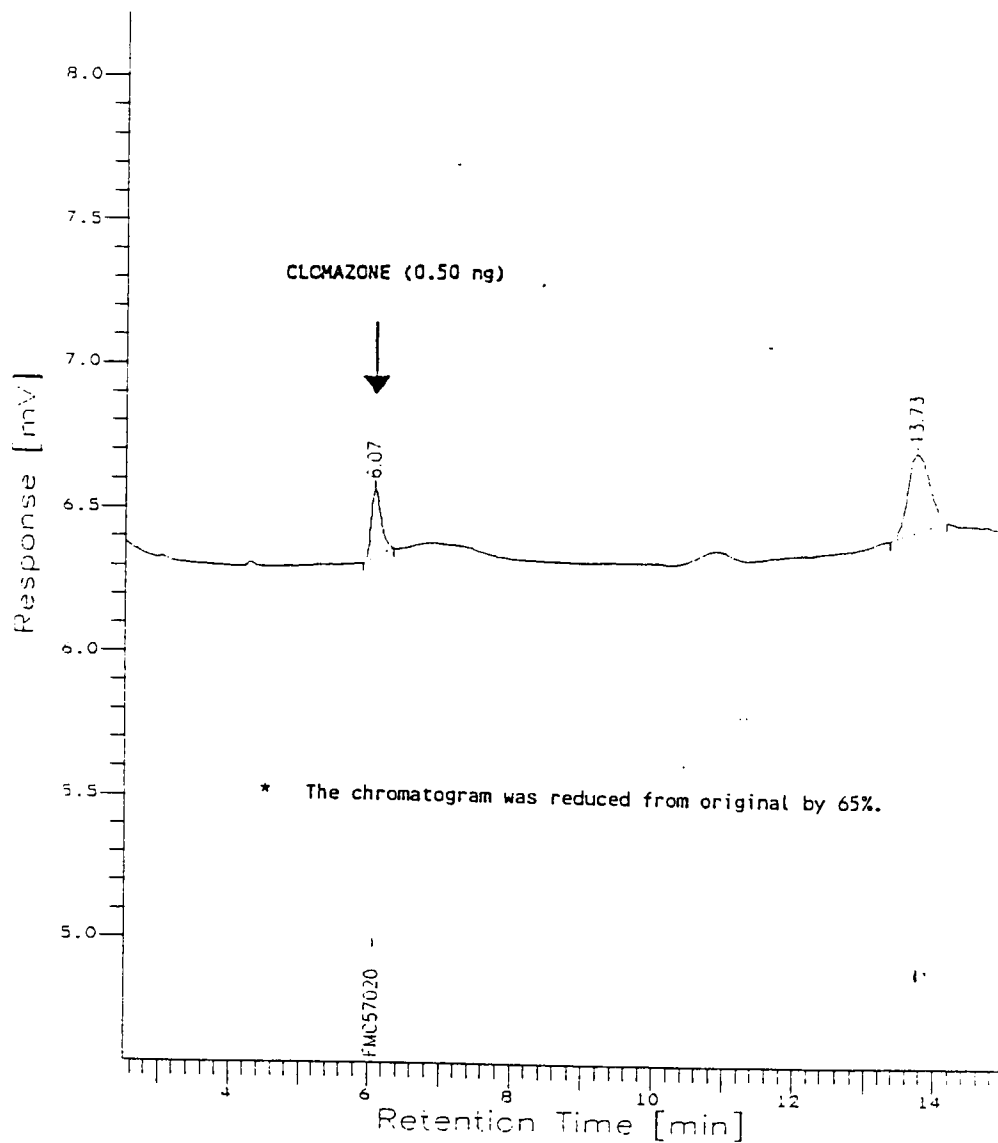


RUN # 934 OCT/25/89 15:17:02
WORKFILE ID: C8
WORKFILE NAME:
ID: 57020
SAMPLE # 5

ESTD	RT	AREA	TYPE	CAL #	AMOUNT
	5.10	1540	PB	1R	1.201

FIGURE 16

Clomazone Standard
0.25 ng/ μ L, 2 μ L injection, (#352-26)



Peak #	Ret Time [min]	Component Name	Area [uV-sec]	Height [uV]	Area %	BL	Amount [ng]
1	6.065	FMC57020	2245.50	234.50	100.00	88	0.7433
			2245.50	234.50	100.00		0.7433

FIGURE 17

Cottonseed Crude Oil, Control, 10 mg injected
(PRF-07, 88-HRM-01C, #4-1)

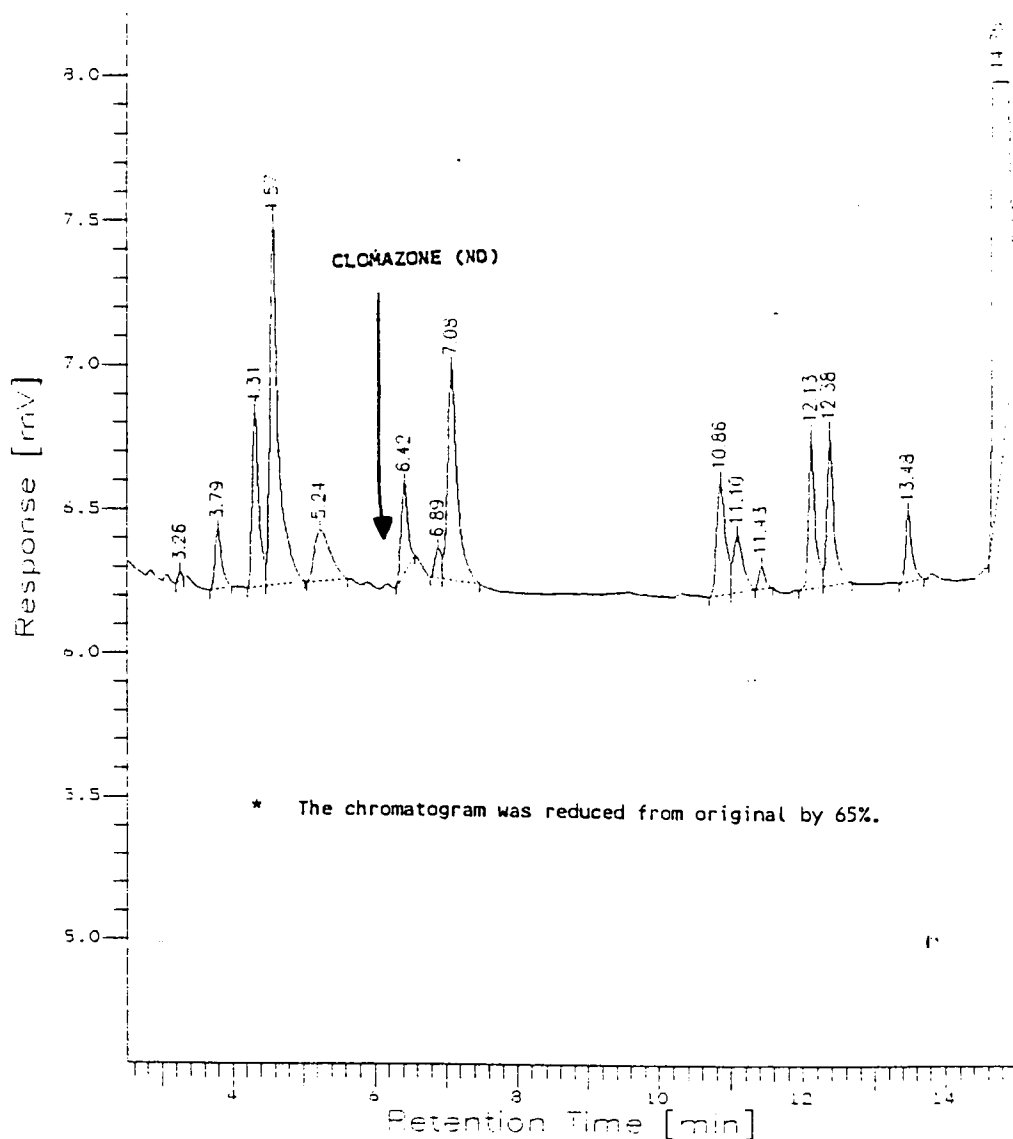
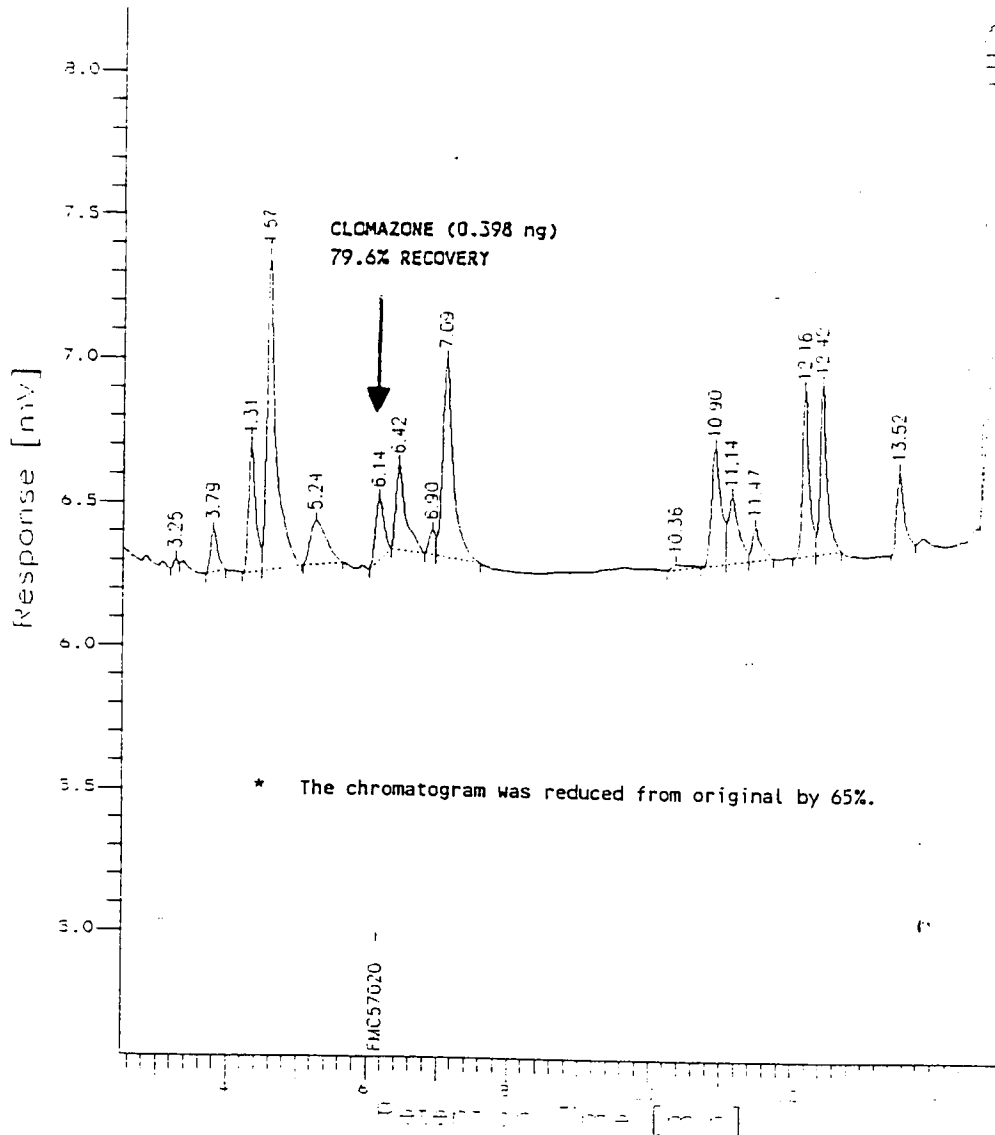


FIGURE 18

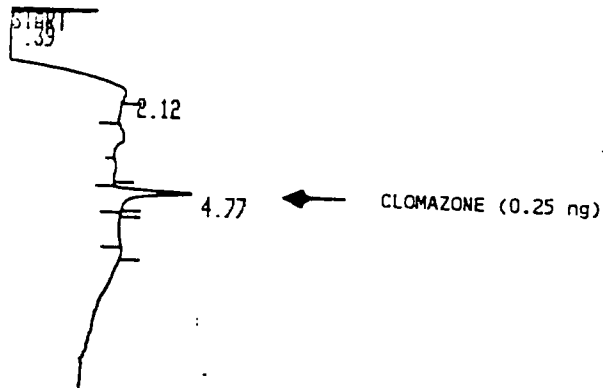
Cottonseed Crude Oil
Fortified @ 0.05 ppm, 10 mg injected
(PRF-07, 88-HRM-01C, #4-3)



Peak #	Ret Time [min]	Component Name	Area [uV-sec]	Height [uV]	Area %	EL	Amount [ng]
6	6.140	FMC57020	1761.50	214.33	100.00	MM	0.6116
			1761.50	214.33	100.00		0.6116

FIGURE 19

Clomazone Standard
0.125 ng/ μ L, 2 μ L injection, (#427-8)



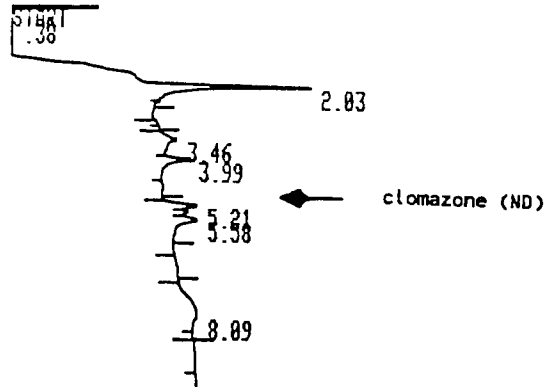
RUN # 2954
WORKFILE ID: C
WORKFILE NAME:
SAMPLE # 24

JUL/03/91 10:03:09

ESTD	RT	AREA	TYPE	CAL #	AMOUNT
	4.77	10826	BB	1R	0.049

FIGURE 20

Soybean Crude Oil, Control, 10 mg injected
(PRH-134, #SC2-1)

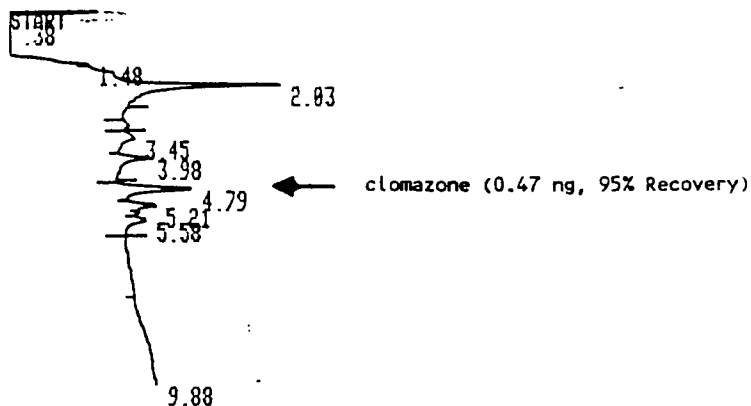


RUN # 2949
WORKFILE ID: C
WORKFILE NAME:
SAMPLE # 19
NO CALIB PEAKS FOUND

JUL/03/91 09:05:49

FIGURE 21

Soybean Crude Oil
Fortified @ 0.05 ppm, 10 mg injected
(PRH-134, #SC2-4)



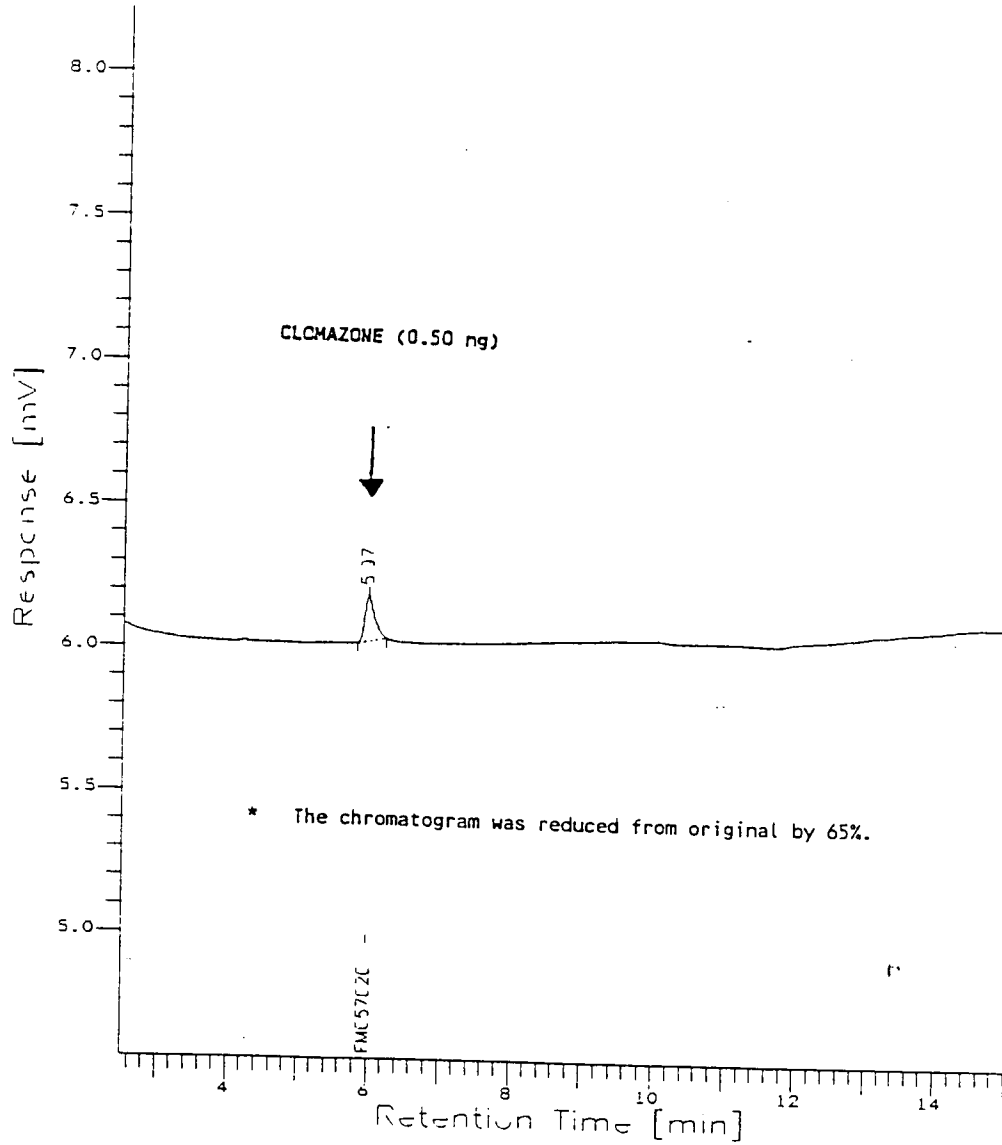
RUN # 2953
WORKFILE ID: C
WORKFILE NAME:
SAMPLE # 23

JUL/03/91 09:51:42

ESTD	RT	AREA	TYPE	CAL #	AMOUNT
	4.79	10203	BY	1R	0.047

FIGURE 22

Clomazone Standard
0.25 ng/ μ L, 2 μ L injection, (#352-26)



Peak #	Ret Time [min]	Component Name	Area [μ V-sec]	Height [μ V]	Area %	BL	Amount [ng]
1	6.054	FMC57020	1460.50	159.38	100.00	MM	0.5297
			1460.50	159.38	100.00		0.5297

FIGURE 23

Cottonseed Soapstock, Control, 10 mg injected
(PRF-07, 88-HRM-01C, #6-1)

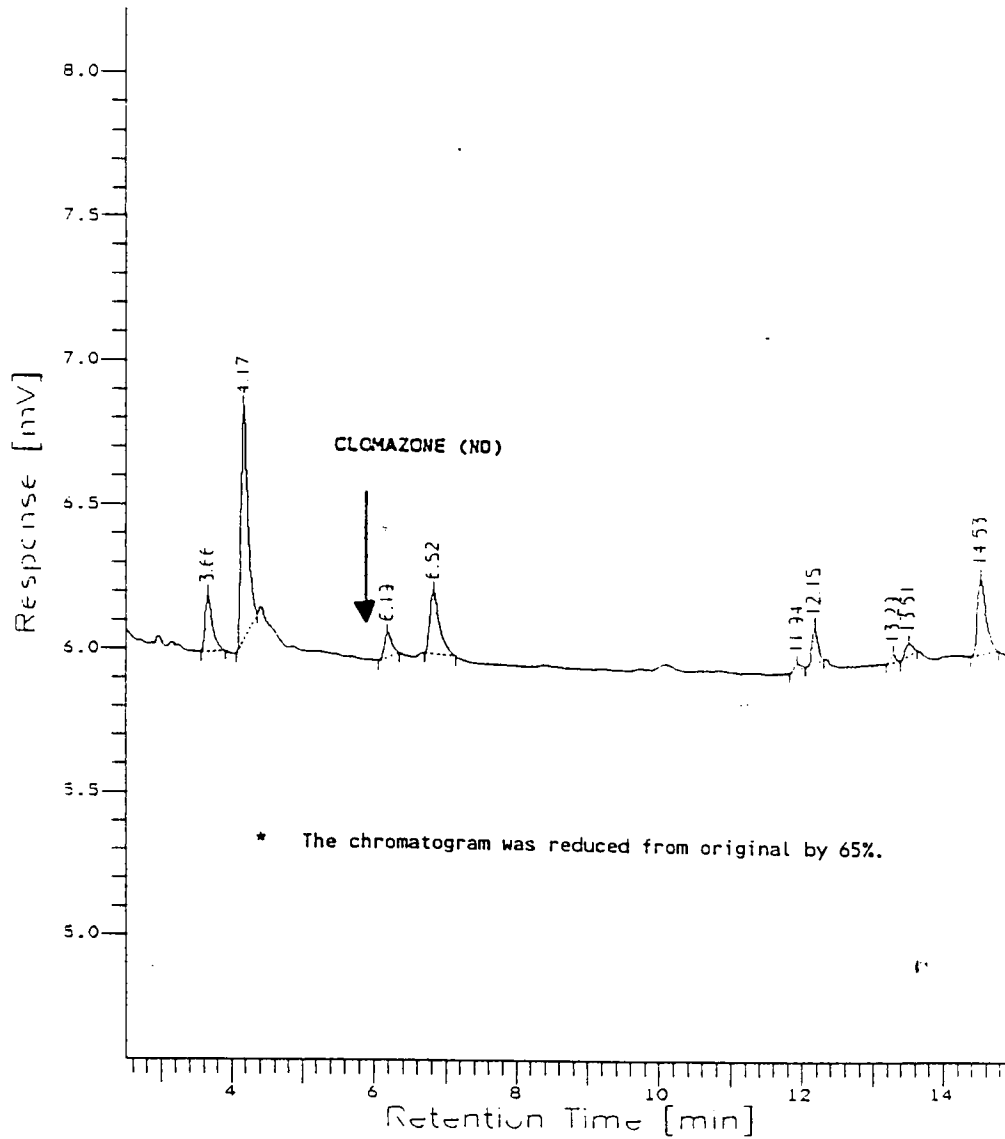
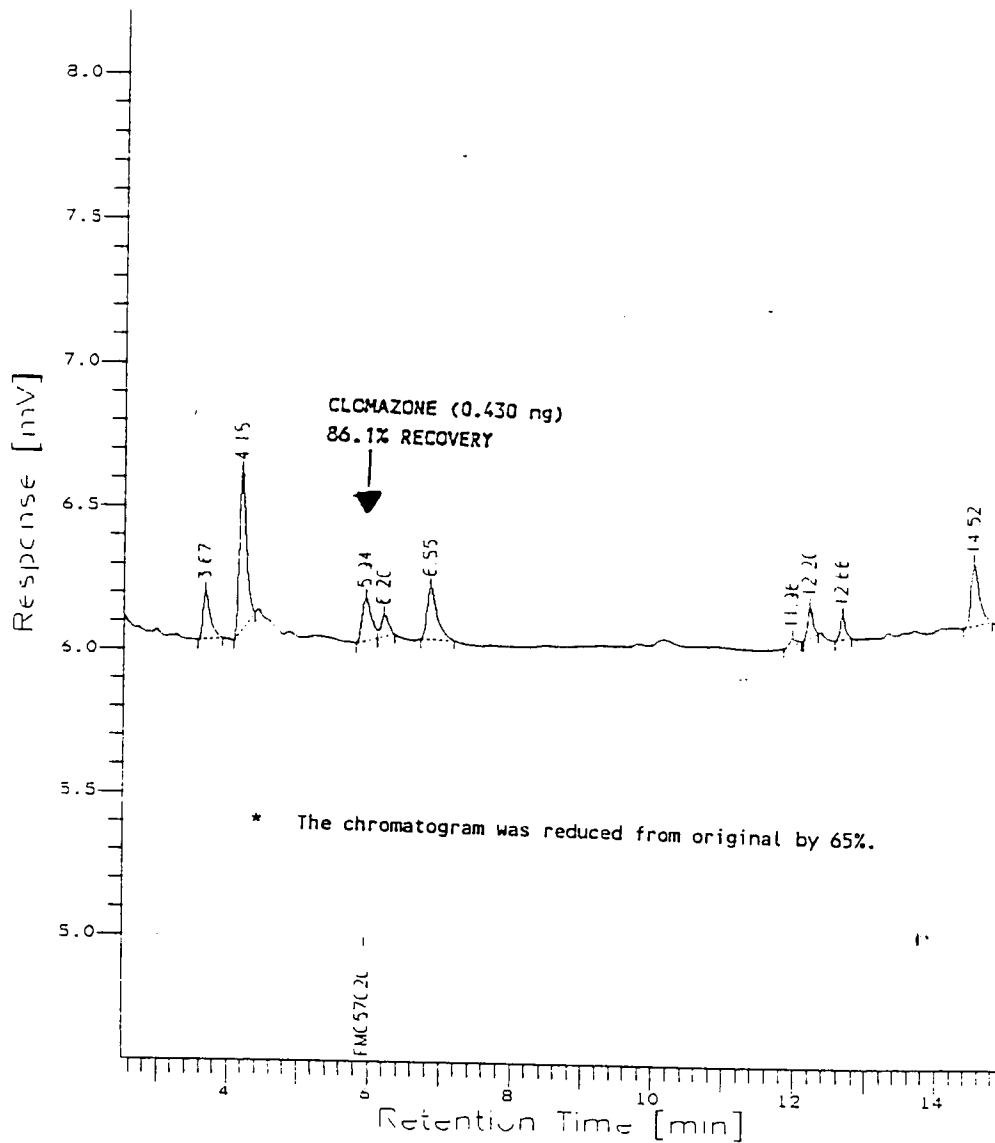


FIGURE 24

Cottonseed Soapstock
Fortified @ 0.05 ppm, 10 mg injected
(PRF-07, 88-HRM-01C, #6-4)



Peak #	Ret Time [min]	Component Name	Area [uV-sec]	Height [uV]	Area %	SL	Amount [ng]
3	5.942	FMC57020	1339.88	148.50	100.00	BV	0.4959
			1339.88	148.50	100.00		0.4959