

Study Title

Napropamide: Analytical Method Validation
in Citrus

Data Requirement

EPA Guideline 40 CFR 171-4(c)

Author

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Study Completion Date

August 26, 1991

Performing Laboratory

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Laboratory Study No.

NAPR-91-MV-01

Report Number

RR 91-041B

STATEMENT OF DATA NON-CONFIDENTIALITY CLAIMS

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA §10(d)(1)(A), (B), or (C).

Company: ICI AMERICAS INC.

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Study Number: NAPR-91-MV-01

Report Number: RR 91-041B

GOOD LABORATORY PRACTICE COMPLIANCE STATEMENT

This study meets the requirements for 40 CFR Part 160.

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Study No.: NAPR-91-MV-01

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QUALITY ASSURANCE STATEMENT

In accordance with ICIA policy and procedures for complying with the provisions of the EPA's FIFRA Good Laboratory Practice Standards (Final Rule, 40 CFR Part 160, August 17, 1989), the conduct of this study has been inspected/audited by the Quality Assurance Unit at the Western Research Center, Richmond, California, United States of America.

<u>Date</u>	<u>Inspection/Audit</u>	<u>Report Date</u>
April 26, 1991	Study Conduct	June 28, 1991
July 31, 1991	Draft Final Report and Raw Data	July 31, 1991
August 13, 1991	Final Report	August 13, 1991

In addition, the following facility inspection associated with this type of study was made.

April 11, 1991	Laboratory Facility	May 21, 1991
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So far as can be reasonably established, the methods described and results incorporated in this report accurately reflect the raw data produced during the study.

Renee J. Pejovich

Renee J. Pejovich
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CERTIFICATION OF AUTHENTICITY

Study No.: NAPR-91-MV-01

Report No.: RR 91-041B

This is to certify that this is a complete and unaltered report prepared by the Environmental Chemistry Department of ICI Americas, Agricultural Products Division, Western Research Center, Richmond, California, USA.

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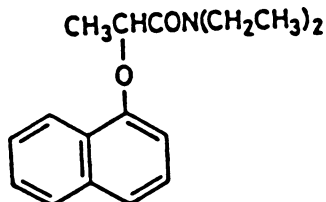
1 SUMMARY/INTRODUCTION

1.1 Scope

A method for the determination of napropamide residues in the raw agricultural commodities of citrus oranges, lemons, and grapefruits, has been validated. This method has been updated from a variety of sources summarized and reformatted by ICI Americas Inc.: Napropamide in oranges Phase 3 Summary report RR 90-031B (MRIDs #'s 23235, 33035, 35663, 49485, 70779, 70780, 113821, 115121, and 115128 and related MRID's #'s 25882, 32356, 49482 and 49483), and Phase 3 Reformat report RR 90-1032B (MRIDs #'s same as above); napropamide in grapefruits Phase 3 Summary report RR 90-033B (MRIDs #'s 23235, 32300, 35665, 49485, 113821, and related MRID's #'s 25882, 49482 and 49483), and Phase 3 Reformat report RR 90-1034B; napropamide in lemons Phase 3 Summary report RR 90-041B (MRIDs #'s 32300, 33035, 35665, 113821, and related MRID's # 25882), and Phase 3 Reformat report RR 90-1042B (MRID's same as above).

1.2 Principles

Napropamide is the active herbicidal ingredient in formulated products marketed by ICI Americas, Inc, under the trademark "DEVIRINOL[®]". The chemical name for napropamide is (IUPAC) (RS)-N,N-diethyl-2-(1-naphthyloxy)propionamide (I); (C.A.) N,N-diethyl-2-(1-naphthalenyloxy)propanamide (9CI); I (8CI); CAS Reg. No. [15299-99-7] (Ref. 1). The chemical structure is given below.



This method is intended for determining residues of napropamide at levels of 0.05 to 0.25 microgram(s) per gram in the raw agricultural products of citrus oranges, lemons, and grapefruits. The method is applicable for other citrus raw agricultural commodities, providing accuracy and freedom from interferences are demonstrated by analyses of control and fortified samples. The lower limit of quantitation is 0.05 $\mu\text{g/g}$ which is half of the established tolerance limit, 0.1 $\mu\text{g/g}$ (Ref. 2). The definition of the lower limit of quantitation (LOQ) is a "substance-specific level that a method must be able to routinely and reliably detect specific sample matrices. It is not the lowest detectable level achievable, but rather the level that a method should reasonably quantify." (ICIA ECS010.SOP).

Napropamide residues are extracted from a measured weight of macerated whole oranges, lemons or grapefruits by blending the samples with toluene. The organic phase is filtered and dried. The toluene extract is analyzed for napropamide by capillary gas chromatography with splitless injection and nitrogen/phosphorous (GC/NP) detection. Confirmation of unexpected peaks in the control or treated samples is done by capillary gas chromatography with mass selective detection (GC/MSD). This method validation was conducted according to Good Laboratory Practice guidelines and ICIA standard operating procedures, and fulfills the Environmental Protection Agency requirements under 40 CFR 171-4(c).

2 **MATERIALS/METHODS**

The equipment and reagents described below were used to generate the data and chromatograms presented in this report. Equipment capable of providing equivalent sensitivity and selectivity and reagents of comparable purity can be used.

2.1 Equipment

- 2.1.1 Gas chromatograph. Hewlett-Packard Model 5880 designed for use with capillary columns and temperature programming of the column oven. The gas chromatograph is equipped with an HP 7672A automatic injector, a Series II plotter, and an HP LAS on-line data acquisition system.
- 2.1.2 Gas-purification traps. Supelco In-line Gas Purifier and a Supelco trap for removing oxygen from the helium carrier gas.
- 2.1.3 Gas-chromatographic column. 15 m length by 0.53 mm i.d. fused silica capillary column with a 1.0 μm film thickness of 6 % cyanopropylphenyl (J & W, DB-1301).
- 2.1.4 Syringes. 10 μL capacity (Hamilton 701N) syringe for the autosampler and 100 μL and 250 μL capacity syringes (Hamilton 1700 series) for fortification.
- 2.1.5 Blender. Waring Blender, and an Eberbach container (#8470, small size), 500 mL.
- 2.1.6 Filter paper. Whatman #2, Qualitative, 24 cm.
- 2.1.7 Glass bottles. 8 ounce narrow mouth bottles with Polyseal-lined screw-capped lids.

- 2.1.8 Gas chromatograph with mass selective detector. Hewlett Packard HP 5890 II gas chromatograph, HP 5970 mass selective detector, and HP UNIX workstation computer and integration. Column: HP-1 12 m x 0.2 mm i.d. x 0.33 μ m film thickness of cross-linked methyl silicone.
- 2.2 Reagents and Standards
- 2.2.1 Solvents. Toluene and acetone. Reagent grade toluene and acetone are acceptable. All solvents must be of high purity and suitable for use in trace organic analyses by gas chromatography.
- 2.2.3 Gases. High-purity helium carrier gas supplied to the gas chromatograph via lines equipped with gas purification traps and appropriate pressure regulators. Other detector gases used are hydrogen and air.
- 2.2.4 Napropamide analytical reference standard. ICIA Analytical Standard ASW 1079-R 99.8% purity or equivalent, available from ICI Americas Inc., 1200 South 47th Street, Box No. 4023, Richmond, CA 94804-0023; Attention: Environmental Sciences Department Manager.
- 2.2.5 Calibration and fortification solutions. Two napropamide stock solutions are prepared, a stock calibration solution, and a stock fortification solution. Calibration solutions are used to calibrate the instrument. Fortification solutions are used to fortify samples and demonstrate procedural recoveries. The stock calibration solution is prepared in toluene, and the stock fortification solution is prepared in acetone. To prepare these stock solutions, at nominal concentrations of 1000 μ g/mL, place a known quantity (0.0500 g \pm .0025 g) of primary standard napropamide of known purity into a clean 4 ounce narrow-mouthed bottle. Add a sufficient, quantitative volume of

the appropriate solvent to the bottle. Calculate the weight of solvent to add, based on the weight of primary standard taken, the purity of the primary standard, and the density of the solvent, as follows:

$$S = W \times P \times D \times \ell$$

where S = the weight of solvent to add (g)

W = the weight of primary standard taken (mg std)

P = the purity of the primary standard (mg a.i./mg std)

D = the density of the solvent (g/mL)

ℓ = 1 = the required volume of solvent per mg of active ingredient (mL solvent/mg a.i.)

Add the calculated weight of the appropriate solvent to the bottle. Cap the bottle with a Polyseal-lined cap, mix the contents thoroughly and store in a freezer at approximately -20°C when not in use. Use toluene ($D = 0.867$ g/mL) for calibration solutions, and acetone ($D = 0.792$ g/mL) for fortification solutions.

To prepare working standard solutions for fortification purposes, dilute the stock fortification solution with acetone, by volume or weight, to give 10 and 100 $\mu\text{g/mL}$ solutions. To prepare a working standard solution for calibration purposes, dilute the stock calibration solution with toluene to give 0.1, 0.025, 0.05, and 0.01 $\mu\text{g/mL}$ solutions. Keep the stock calibration and fortification solutions in a freezer (at $-20^{\circ} \pm 10^{\circ}\text{C}$) when not in use.

2.3 Analytical Procedure

2.3.1 Preparation of citrus oranges, lemons, and grapefruit.

Untreated control samples of fresh oranges, lemons, and grapefruit were purchased from a local produce store. The oranges, lemons, and grapefruits were collected in residue bags and stored frozen within two hours. The ICIA Sample

Preparation Unit macerated these samples in a Hobart VCM 40 food chopper with dry ice.

The bulk samples are contained in 32-ounce glass jars closed with caps lined with Teflon, and are stored at $-20 \pm 10^{\circ}\text{C}$ with temperatures monitored.

2.3.2 Extraction of Citrus. A 30.0 g (± 0.1 g) subsample of the macerated crop part is weighed directly into the blender jar and allowed to thaw.

A graduated cylinder or laboratory-calibrated pipetter is used to add 120 mL of toluene into the blender jars. Alternatively, 104 g of toluene is directly weighed into the blender jar.

The top of the blender jar is covered with aluminum foil, the cap is screwed on tightly, and the contents are blended in the Waring Blender at moderate speed for three minutes.

If emulsions are formed, they are broken by any appropriate means, such as centrifugation, addition of sodium chloride, freezing, etc. Any steps taken to break the emulsions are recorded. No emulsions were formed in any of the extracts.

The unemulsified extracts are filtered through 25 to 30 g of anhydrous sodium sulfate in the filter paper (Whatman #2). The filtrate is collected in a 8 ounce glass bottle containing a layer of sodium sulfate about 0.5 cm deep. The bottle is capped with a Polyseal cap and the extract retained for analysis.

2.3.3 Napropamide fortification. Unfortified and fortified untreated control samples are analyzed to demonstrate method recovery and freedom from interferences. It is recommended that one unfortified and one fortified sample

be analyzed for each crop matrix for every set of ten or fewer field samples extracted. Appropriate concentrations and volumes are used to fortify at the method's lower limit of quantitation (LOQ, 0.05 $\mu\text{g/g}$). For example, 30.0 g of crop sample fortified at the LOQ would require application of 0.15 mL of a 10 $\mu\text{g/mL}$ fortification solution. The fortification solution must have ambient temperature before use. Higher fortification levels may be needed depending on expected residue levels. In this study, macerated and thawed citrus were fortified at 0.05 and 0.25 $\mu\text{g/g}$ by syringe injection and then extracted with toluene.

- 2.3.4 Clean-up. No clean-up is required in this method; however, if it is necessary to remove unwanted interferences, clean-up steps or capillary gas chromatography with mass selective detection analysis can be performed on all the interfering extracts including the untreated control and fortified samples.
- 2.3.5 Derivatization. No derivatization is necessary for the analysis of napropamide.
- 2.3.6 Safety considerations. Personnel untrained in the routine safe handling of chemicals and good laboratory practices must not attempt to use this procedure. Information on any first aid procedures can be found in the Material Safety Data Sheets accompanying the chemical or available from the chemical supplier. In general, always wear safety glasses with side shields, work in well ventilated areas, avoid inhaling vapors, and avoid contact of the chemicals with skin and clothing. Flammable solvents should be kept away from potential sources of ignition.

Flammable solvents used are toluene, acetone and other washing or cleaning organic solvents. Avoid breathing vapor and work in a well ventilated area. Avoid contact with the skin and clothing.

In case of personal napropamide contamination, remove all contaminated clothing and wash the affected skin area with soap and water. Wash eyes with plenty of water after any accidental contact.

2.4 Instrumentation

2.4.1 Description of the instrumentation. The manufacturer's instructions are followed for operation of the GC/NP and/or the GC/MSD. The extracts are analyzed with splitless injection, capillary gas chromatography and nitrogen/-phosphorous detection. Confirmation, if necessary, is done using a capillary gas chromatograph with mass selective detection. All details of the analysis are recorded. The specific conditions listed below were used to generate the GC/NP and GC/MSD data presented in this report.

	<u>GC/NP</u>	GC/MSD
Carrier Gas:	Helium	Helium
Column:	J&W DB-1301 fused silica capillary: 0.53 mm x 15 m x 1 μ m film thickness	HP-1 fused silica capillary: 12 m x 0.2 mm x 1 μ m film thickness
Column Head Pressure:	18 psig	5 psig
Inlet Type:	splitless	splitless
Carrier Flow:	7.2 mL/min	
Data Acquisition:	HP laboratory automated system	HP UNIX workstation

2.4.2 Instrument operating conditions.

	<u>GC/NP</u>	<u>GC/MSD</u>
Initial Oven Temperature:	100°C	100°C
Initial Time:	0.01 minute	0.01 minute
Oven Temperature Program Rate:	30°C/min	30°C/min
Oven Final Temperature:	235°C	260°C
Final Time:	5.5 minutes	9 minutes
Other Conditions:		
Volume Injected:	3 µL	2 µL
Splitless Valve: Off:	0.8 minutes	0.5 minutes
Total Run Time:	10.0 minutes	14.3 minutes

Using the above conditions for the gas chromatography, the GC/NP elution time of napropamide is 5.8 minutes and 5.3 minutes for the GC/MSD. Operation of the GC/MSD was in the selective ion monitoring mode (SIM) at 271 m/z. See Figures 1, 2, 3, 4, 5, 6 and 7 for typical chromatograms.

2.4.3 Calibration. Quantitation is performed using an external standard method. The GC/NP and GC/MSD are calibrated by using the calibration standards described in section 2.2.5. The 0.1, 0.05, 0.025 and 0.01 µg/mL solutions are injected at the beginning and at the end of each run to assure linearity. After every four or five samples, one or more of the calibration solutions is analyzed to assure that the analyte response is stable. If no residues are detected and only the lower LOQ method fortifications are used, only the 0.01 µg/mL calibration solution and another standard solution are needed (for example, the 0.025 µg/mL solution).

The sample extracts are injected using the same conditions as those for the calibration solutions. The identity of the analyte peak in the sample chromatogram is assigned based upon the coincidence of the retention time (± 0.05 min) with that of the analyte peak in the calibration solution chromatograms.

2.5 Interferences

Extracts of control samples from untreated oranges, lemons and grapefruits showed slight ($<0.05 \mu\text{g/g}$) co-extractive impurities that eluted at the retention time of the analyte peak. This interference was confirmed to be an ion similar to the parent of napropamide as detected by GC/MSD. There were no interferences found in the reagent blank sample. Figures 1,2 and 3 show gas chromatograph plots of calibration solutions of napropamide and sample chromatograms for the analysis of napropamide in untreated oranges, lemons and grapefruit. Analyses of extracts of samples from untreated oranges, lemons and grapefruits demonstrate the absence of significant interferences from sample matrices, solvents, and labware.

2.6 Confirmatory Techniques

All apparent residues above the LOQ, as in untreated controls or treated samples, should be confirmed by other means. Confirmation and quantitation can be achieved by using capillary GC/MSD and monitoring the ion m/z 271. Use of an alternative mass selective ion(s), a GC column of different polarity, or a different detection scheme are other possible methods of confirmation. Quantitation is performed using the external standard method. The analyses reported herein were performed to show the applicability of GC/MSD to residue confirmation. Figures 4,5,6 and 7 show

example GC/MSD chromatograms of calibration solutions of napropamide, sample chromatograms of oranges, lemons, and grapefruits, and a napropamide full scan.

2.7 Time Required for Analysis

The analysis of each matrix can be completed by one person in an 8 hour period, provided that the samples or set of oranges, lemons or grapefruits is available and prepared.

2.8 Modifications or Potential Problems

No potential problems were observed during method validation. Any modifications, such as, clean-up, use of different solvents, equipment, or instrumentation, must be validated by demonstrating adequate recovery, selectivity, and freedom from interferences, according to ICIA ECS00201.SOP.

2.9 Calculations

2.9.1 Calibration factor determination. The concentration of the analyte in the matrix is calculated by an appropriate external standard method; i.e., the response obtained for the analyte in the sample extract is compared to the response obtained from a separate injection of a known amount of analyte (calibration solution). In order to use the linear response calculation method shown below, the injection volumes for all calibration solutions and sample extracts are fixed at the same volume.

Calculation of the response factor from a calibration solution: The response factor, F , is calculated from an injection of a calibration solution as follows:

$$F = \frac{C_{\text{std}}}{R_{\text{std}}}$$

where C_{std} = concentration of calibration solution,
 $\mu\text{g/mL}$

R_{std} = response units (e.g., peak height, peak area) from detector for the calibration solutions

2.9.2 Analyte, napropamide in sample. The concentration of napropamide is determined in the crop sample in $\mu\text{g/g}$ (ppm), C , using the average response factor, F , over the range of calibration as follows:

$$C (\mu\text{g/g}) = R_{\text{sample}} \times [F \div D]$$

where R_{sample} = response units (e.g., peak heights, peak area) from detector for sample extract

F = response factor, $(\mu\text{g/mL})/\text{response unit}$

D = concentration of the injected solution
 g/mL (crop g/solvent mL)

$[F \div D]$ = sample calculation factor

2.10 Other: Matrix Effects Test and Extractability Study

2.10.1 Matrix effects test. A matrix effects test was made to determine if any enhancement or reduction of the instrument detector response to the napropamide in the extract occurs. The procedure is to fortify an aliquot of untreated liquid sample extract with a known amount of a calibration standard and determine the analyte recovery from this fortified matrix. The recovery should be within 70% to 120% of the nominal concentration. Recoveries of the matrix

fortifications and the corresponding calibration solutions are compared. In this study 10 mL aliquots of each control extract were fortified with napropamide at 0.025 $\mu\text{g/mL}$ by syringe injections of 0.025 ml of a 10 $\mu\text{g/mL}$ napropamide/acetone solution. These fortified aliquots were analyzed with gas chromatography and gas chromatography with mass selective detection using the same operating conditions as the method.

2.10.2 Extractability study. Metabolism radioactive extractability studies are used to compare and validate the different residue extraction methods. A napropamide extractability study could not be done on any of the citrus crops, because there were no radioactive residues found in the ICI metabolism studies on tree crops.

3 RESULTS/DISCUSSION

3.1 Accuracy of the Residue Method

A set of six fortified samples was prepared for each citrus crop matrix as described under section 2.3.3 and analyzed according to this method to establish accuracy. The project initiation date was April 24, 1991. Tables 1, 2, and 3 list the recoveries for each set. Using the gas chromatography method, recoveries of napropamide from oranges fortified at 0.05 and 0.25 $\mu\text{g/g}$ ranged from 92.2 % to 107.5 % with a mean recovery of 98.9 %. Recoveries of napropamide from lemons fortified at 0.05 and 0.25 $\mu\text{g/g}$ ranged from 92.2 % to 114.2 % with a mean recovery of 104.5 %. Recoveries of napropamide from grapefruits fortified at 0.05 and 0.25 $\mu\text{g/g}$ ranged from 87.6 % to 112.9 % with a mean recovery of 102.0 %.

Table 4 lists the results of the analyses using gas chromatography with mass selective detection.

Recoveries of napropamide in oranges, lemons and grapefruits were 106.2 %, 110.1 and 110.1 %, respectively.

3.2 Precision

The precision of a method depends on variations in extraction and instrumental analysis. The variations in extraction and instrumental analyses can be evaluated from the data obtained during analyses of fortified samples. The coefficients of variation given in Tables 1, 2, and 3 are a measure of precision. For the recoveries of oranges, lemons, and grapefruits, the coefficients of variation (CV) were between 6% and 9%. In all the analyses, the instrumental precision of the GC/NP at 0.025 $\mu\text{g/mL}$ was less than 5.7 % coefficient of variation.

3.3 Limits of Quantitation

The limit of quantitation for the method is 0.05 $\mu\text{g/g}$ for napropamide as determined by fortifications at the 0.05 $\mu\text{g/g}$ level. Adequate GC/NP sensitivity was achieved using the HP LAS data acquisition system. With the sample weight and extractant volume specified, this value is equivalent to 0.0125 $\mu\text{g/mL}$ of injected solution.

3.4 Ruggedness Testing

The system was not tested for ruggedness.

3.5 Limitations

The level of quantitation was between 0.05 and 0.25 $\mu\text{g/g}$ (ppm). The upper limit could be increased by the analyst if the residues occurring warrant it, although the method must be validated by analyses of untreated control samples fortified at a higher amount.

3.6 Matrix Effects

Matrix effects were tested in the method; results are given in Tables 5 and 6. There was no significant increase or decrease in detector responses to napropamide in this test on these crops. This effect is sometimes seen in some crops and analytes; however, matrix effect testing is not required as part of routine pesticide analyses using this method.

3.7 Extractability Results

There are no extractability results because no radioactive residues were found in the metabolism study with which to compare with this residue method.

4 CONCLUSION

A method for the analysis of napropamide in raw agricultural products of citrus at levels of 0.05 $\mu\text{g/g}$ to 0.25 $\mu\text{g/g}$, has been validated. A confirmatory technique was performed using gas chromatography with mass selective detection.

The method is specific for the analysis of napropamide in whole oranges, lemons and grapefruits. Only commercially available laboratory equipment and reagents are required. The analysis can be completed for each matrix by one person in an 8 hour period if the citrus samples are prepared. Untreated and fortified untreated samples should be extracted and analyzed with each set of treated samples to demonstrate absence of interferences and adequate recovery. If determination of napropamide at a concentration other than 0.05 $\mu\text{g/g}$ to 0.25 $\mu\text{g/g}$ is required, suitably fortified samples must be analyzed to validate the method at that concentration.

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Table 1. GC/NP Recoveries of Napropamide from Oranges

Sample Number	Weight Crop (g)	Amount Added ($\mu\text{g/g}$)	Response (Height)	Amount Found ($\mu\text{g/g}$)	Recovery ^a (%)
G3019-01	0	0	0	<0.05	
G3019-02	30.0	0	63	<0.05	
G3019-03	30.0	0	177	<0.05	
G3019-04	30.0	0.05	585	0.058	92.4
G3019-05	30.0	0.05	584	0.058	92.2
G3019-06	30.0	0.05	584	0.058	92.2
G3019-07	30.0	0.25	2702	0.268	102.6
G3019-08	30.0	0.25	2806	0.279	106.7
G3019-09	30.0	0.25	2824	0.281	107.5

Total Number of Fortified Samples Analyzed:
Mean Recovery:

6
98.9%

^aRecoveries are corrected for background by subtracting the means of the untreated sample responses from the response of the fortified sample.

Table 2. GC/NP Recoveries of Napropamide from Lemons

Sample Number	Weight Crop (g)	Amount Added ($\mu\text{g/g}$)	Response (Height)	Amount Found ($\mu\text{g/g}$)	Recovery ^a (%)
G3020-01	0	0	0	<0.05	
G3020-02	30.0	0	66	<0.05	
G3020-03	30.0	0	38	<0.05	
G3020-04	30.0	0.05	551	0.061	109.5
G3020-05	30.0	0.05	517	0.057	102.0
G3020-06	30.0	0.05	472	0.052	92.2
G3020-07	30.0	0.25	2655	0.292	114.2
G3020-08	30.0	0.25	2529	0.278	108.7
G3020-09	30.0	0.25	2338	0.257	100.3

Total Number of Fortified Samples Analyzed:
Mean Recovery:

6
104.5%

^aRecoveries are corrected for background by subtracting the means of the untreated sample responses from the response of the fortified sample.

Table 3. GC/NP Recoveries of Napropamide from Grapefruits

Sample Number	Weight Crop (g)	Amount Added ($\mu\text{g/g}$)	Response (Height)	Amount Found ($\mu\text{g/g}$)	Recovery ^a (%)
G3021-01	0	0	0	<0.05	
G3021-02	30.0	0	1.0	<0.05	
G3021-03	30.0	0	1.0	<0.05	
G3021-04	30.0	0.05	7.0	0.059	101.1
G3021-05	30.0	0.05	6.8	0.057	97.8
G3021-06	30.0	0.05	6.2	0.052	87.6
G3021-07	30.0	0.25	34.0	0.287	111.2
G3021-08	30.0	0.25	34.5	0.291	112.9
G3021-09	30.0	0.25	31.5	0.265	102.8

Total Number of Samples Analyzed: 6
Mean Recovery: 102.0%

^aRecoveries are corrected for background by subtracting the means of the untreated sample responses from the response of the fortified sample.

Table 4. GC/MSD Recoveries of Napropamide from Oranges, Lemons and Grapefruits

Sample Number	Weight Crop (g)	Amount Added (ug/g)	Response (Area)	Amount Found (ug/g)	Recovery ^a %
Oranges: G3019-02	30.0	0	3014	<0.050	106.2
G3019-04	30.0	0.05	24883	0.060	
Lemons: G3020-02	30.0	0	4785	<0.050	110.1
G3020-04	30.0	0.05	27453	0.067	
Grapefruit: G3021-02	30.0	0	3195	<0.050	110.1
G3021-04	30.0	0.05	25877	0.063	

^aRecoveries are corrected for background by subtracting each of the untreated sample responses from the respective fortified samples.

Table 5. GC/NP Recoveries of Napropamide from Orange, Lemon and Grapefruit Matrices

Sample Number	Spiked Solution Concentration ($\mu\text{g/mL}$)	Response (Height)	Amount Found ($\mu\text{g/mL}$)	Recovery ^a (%)
Oranges: G3019-2	0	63	<0.01	99.8
G3019-10	0.025	1067	0.027	
Lemons: G3020-2	0	66	<0.01	102.2
G3020-10	0.025	997	0.027	
Grapefruits: G3021-2	0	1.0	<0.01	99.4
G3021-10	0.025	12.8	0.027	

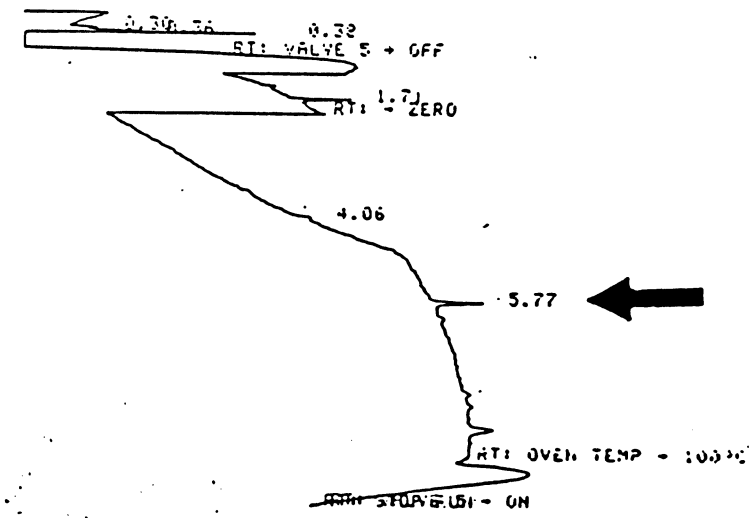
^aRecoveries are corrected for background by subtracting each of the untreated sample responses from the respective fortified samples.

Table 6. GC/MSD Recoveries of Napropamide from Orange, Lemon and Grapefruit Matrices

Sample Number	Spiked Solution Concentration (µg/mL)	Response (Area)	Amount Found (µg/mL)	Recovery ^a (%)
Oranges: G3019-02 G3019-10	0 0.025	3014 49782	<0.01 0.030	113.5
Lemons: G3020-2 G3020-10	0 0.025	4785 51242	<0.01 0.031	112.8
Grapefruits: G3021-2 G3021-10	0 0.025	3195 50295	<0.01 0.031	114.4

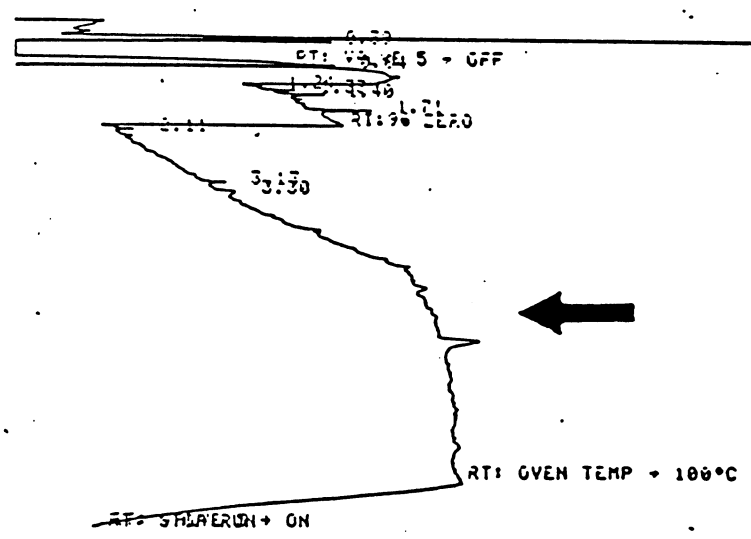
^aRecoveries are corrected for background by subtracting each of the untreated sample responses from the respective fortified samples.

FIGURE 1. EXAMPLE OF ORANGES GC/NP CHROMATOGRAMS



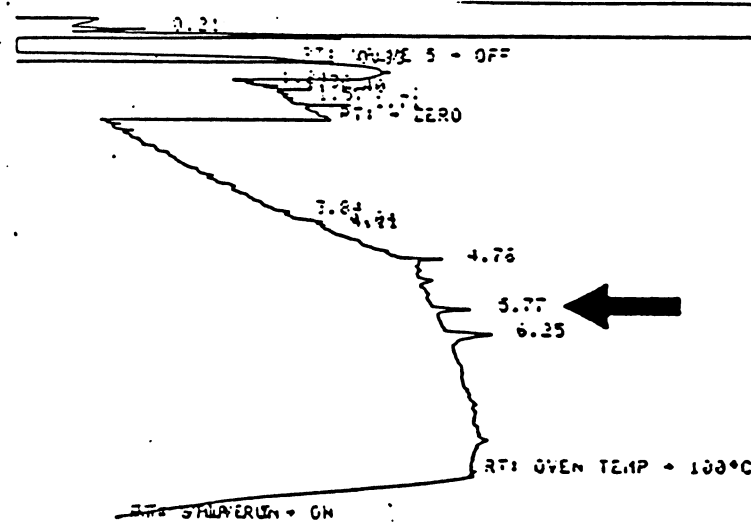
Calibration Standard
0.025 µg/mL Napropamide

EXP 5880A SAMPLER INJECTION @ 15:16 APR 24, 1991.
SAMPLE # : ID CODE :
1 : 0.025



Oranges
Untreated Control
G3019-02

EXP 5880A SAMPLER INJECTION @ 16:31 APR 24, 1991
SAMPLE # : ID CODE :
6 : 3019-2



Oranges Fortified
at 0.05 ppm
Napropamide

EXP 5880A SAMPLER INJECTION @ 17:33 APR 24, 1991
SAMPLE # : ID CODE :
10 : 3019-3

FIGURE 2. EXAMPLE OF LEMONS GC/np CHROMATOGRAPHY

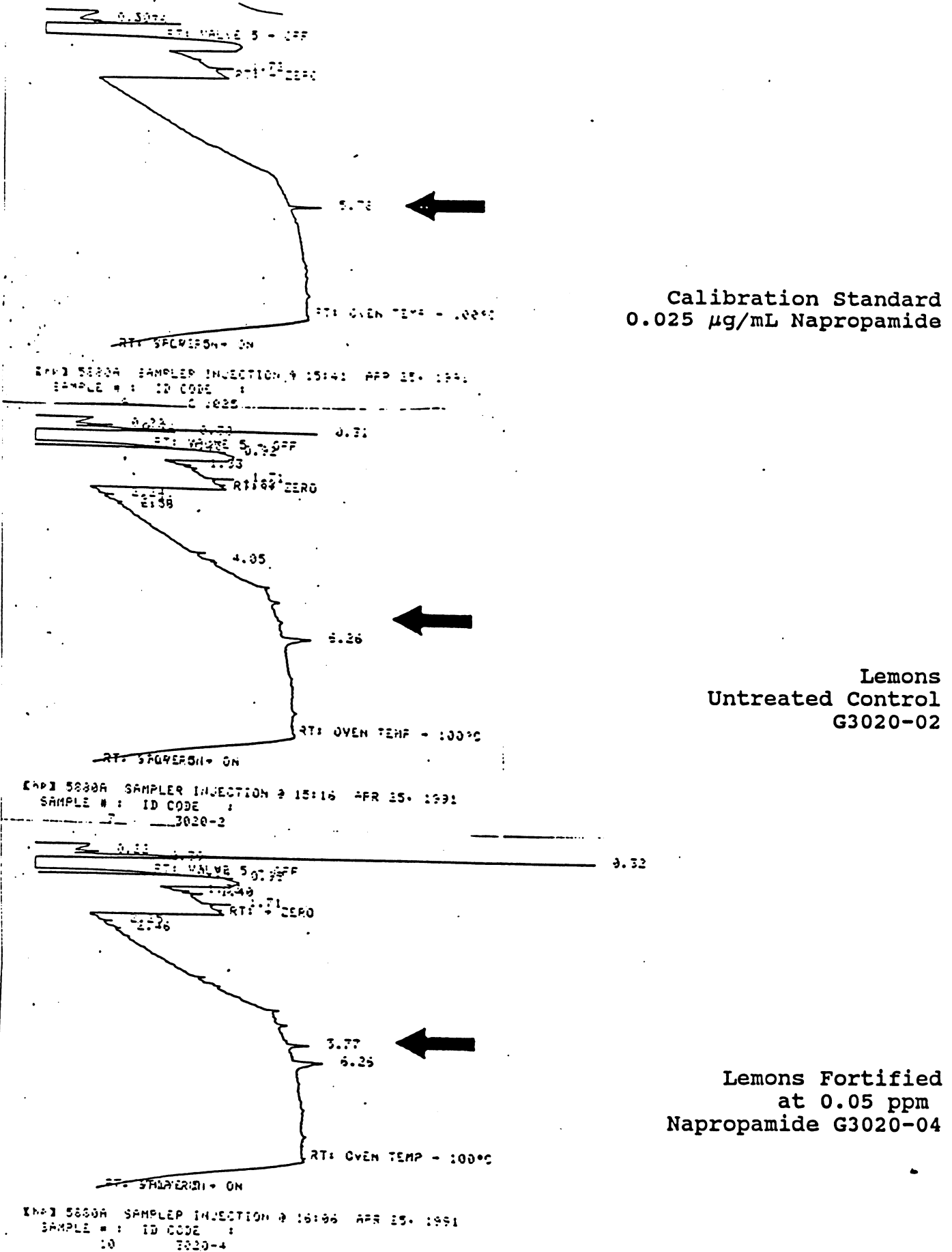
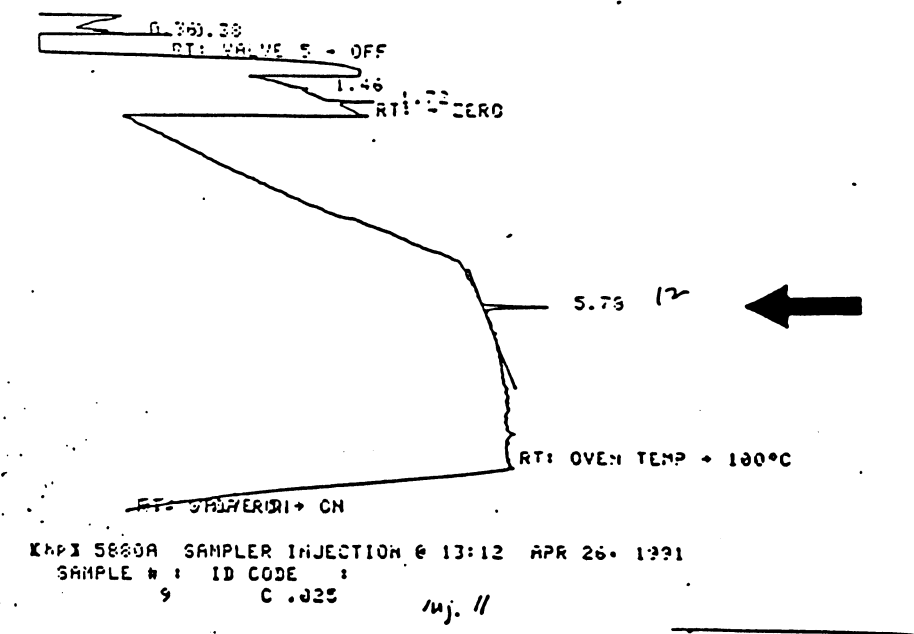
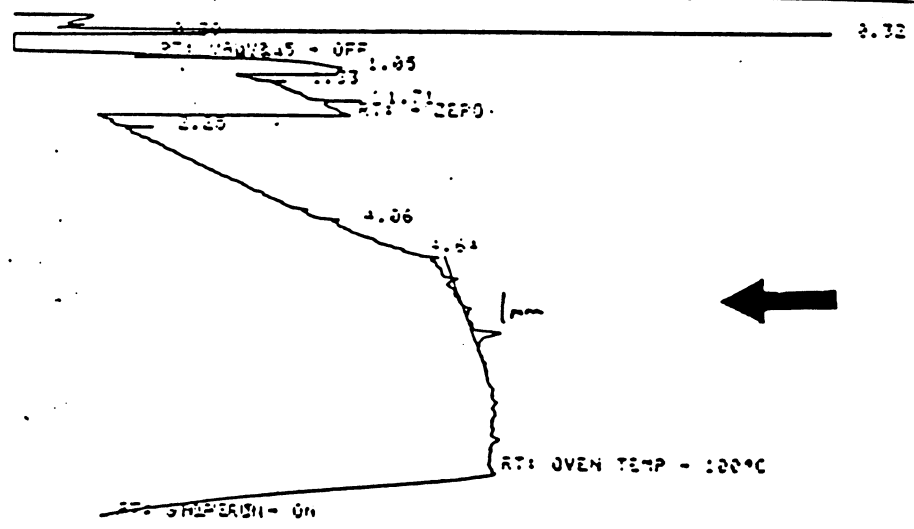


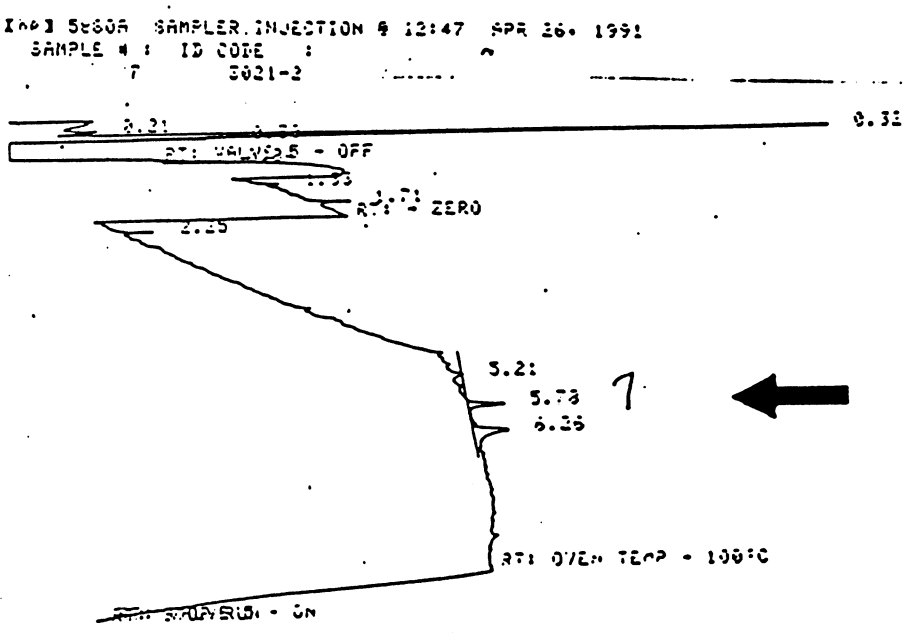
FIGURE 3. EXAMPLE OF GRAPEFRUITS GC/NP CHROMATOGRAPHY



Calibration Standard
1.025 µg/mL Napropamide



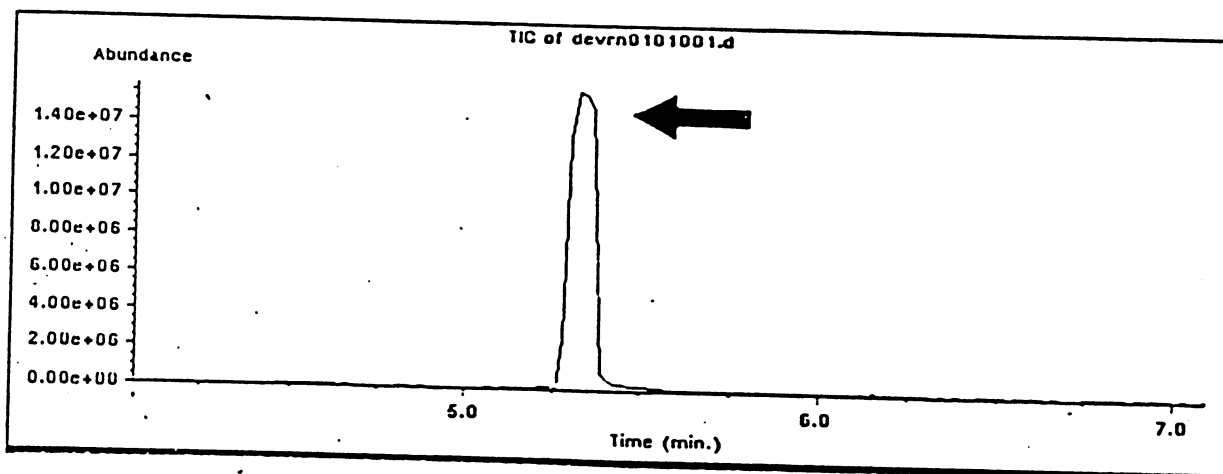
Grapefruits
Untreated Control
G3021-2



Grapefruits Fortified
: 0.05 ppm Napropamide
G3021-5

FIGURE 4. GC/MSD OF NAPROPAMIDE (ion 271 m/z)

a) Selective Ion Monitoring (SIM) of Napropamide, 50 $\mu\text{g/mL}$



b) Full GC/MSD Scan of Napropamide, 50 $\mu\text{g/mL}$

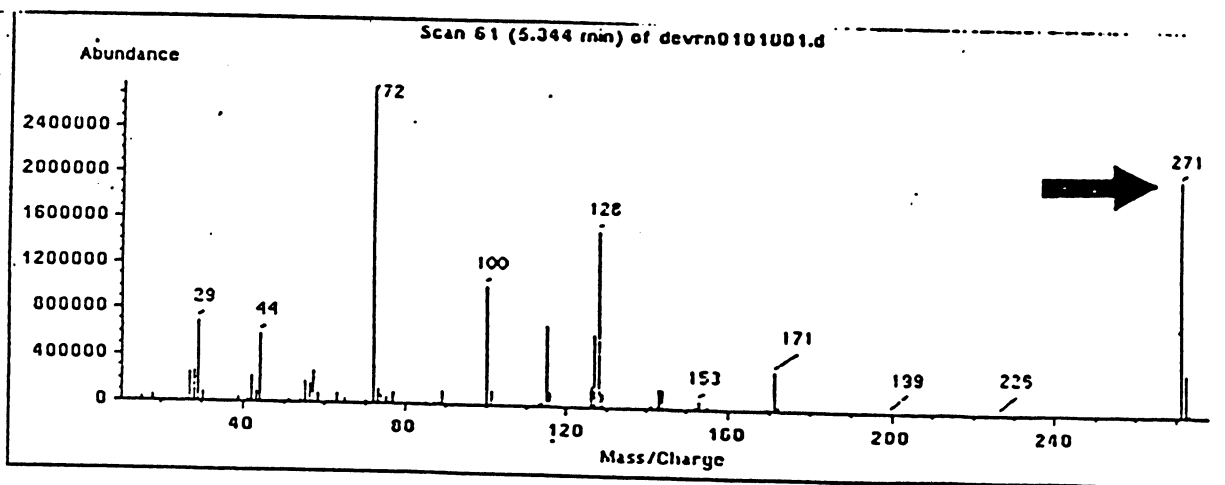
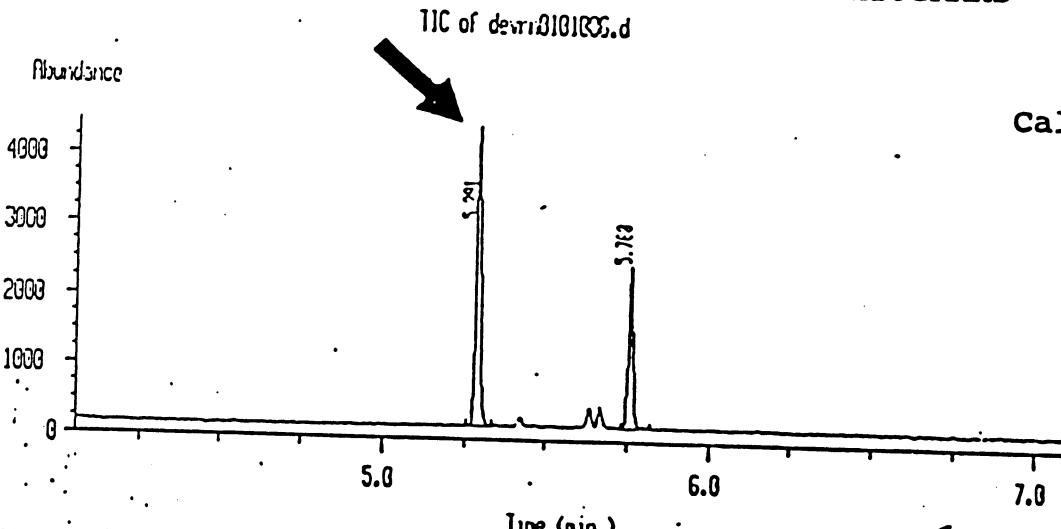
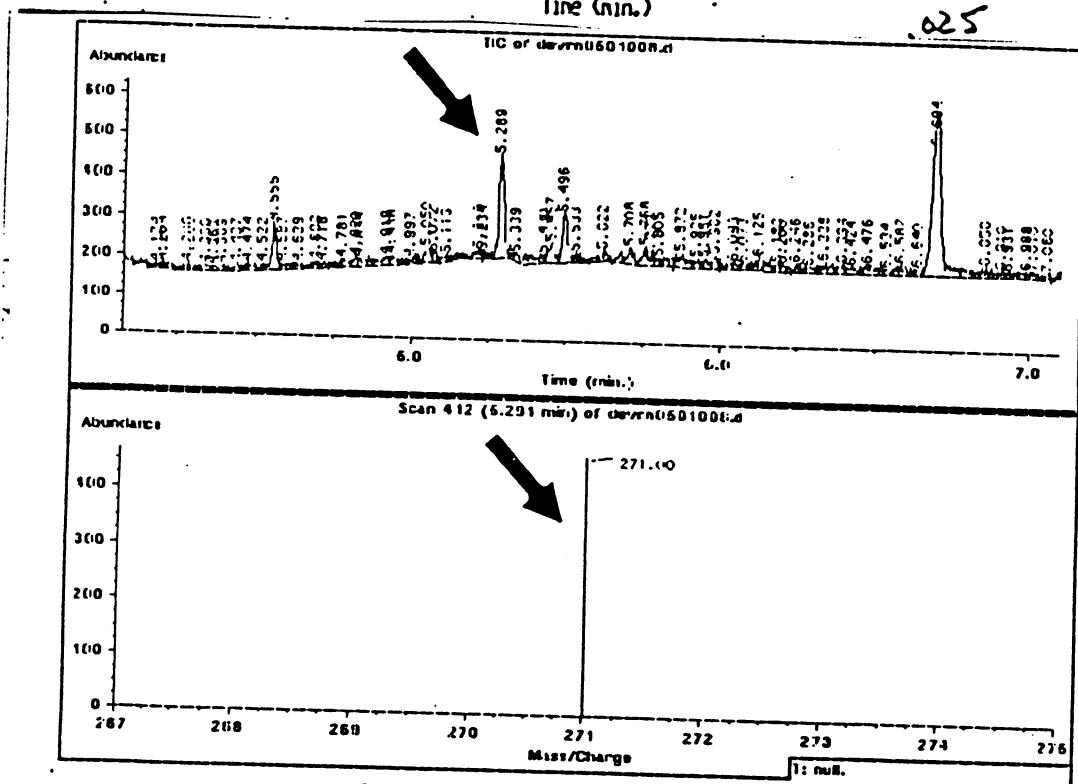


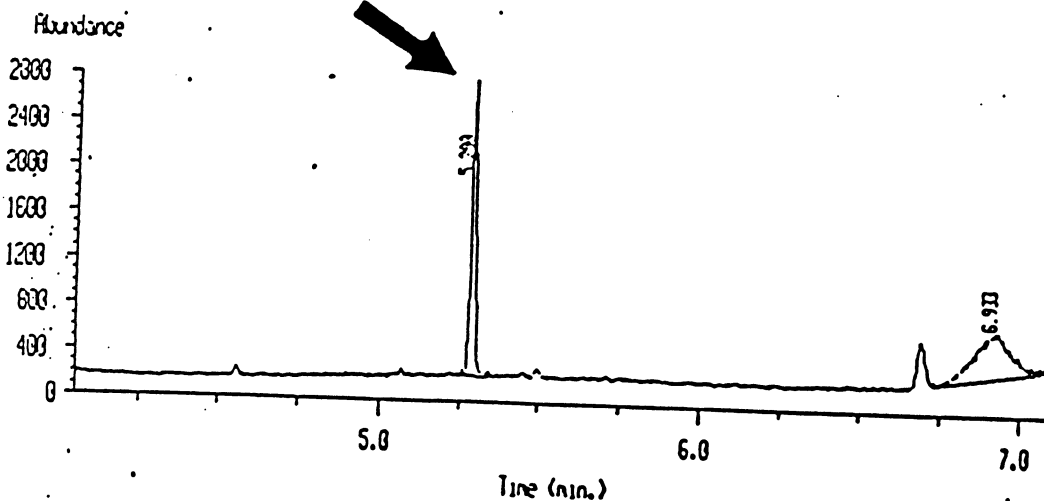
FIGURE 5. EXAMPLE GC/MSD ORANGE TIC CHROMATOGRAMS



Calibration Standard
0.025 $\mu\text{g/mL}$
Napropamide



Oranges
Untreated Control



Oranges Fortified
0.05 ppm Napropamide

FIGURE 6. EXAMPLE GC/MSD LEMONS TIC CHROMATOGRAMS

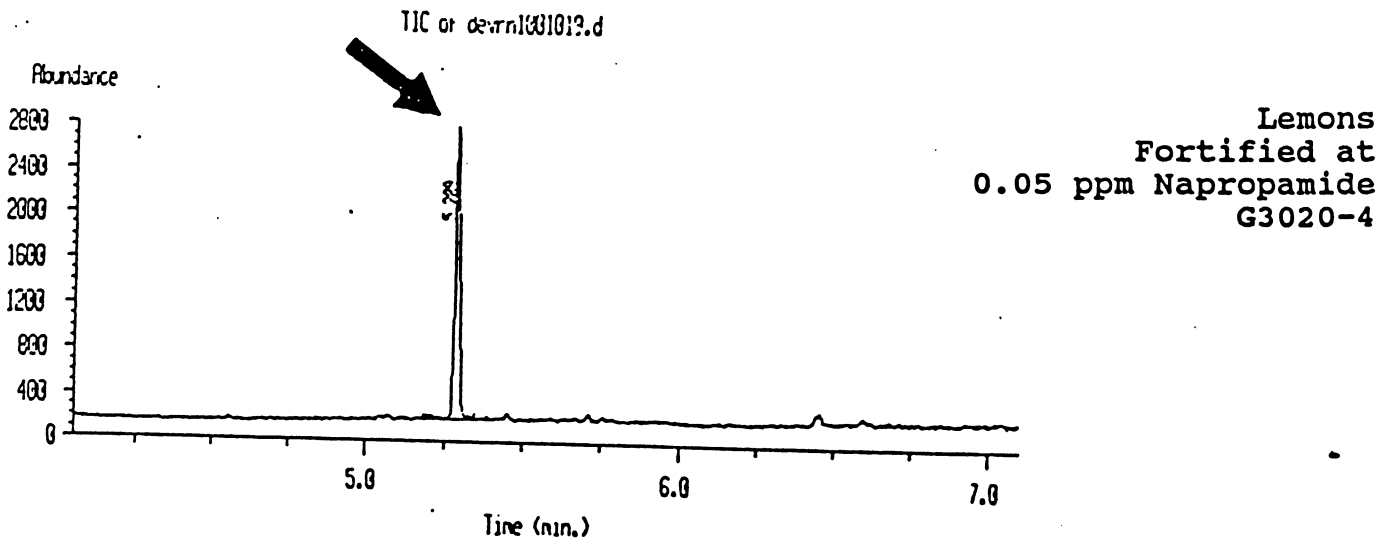
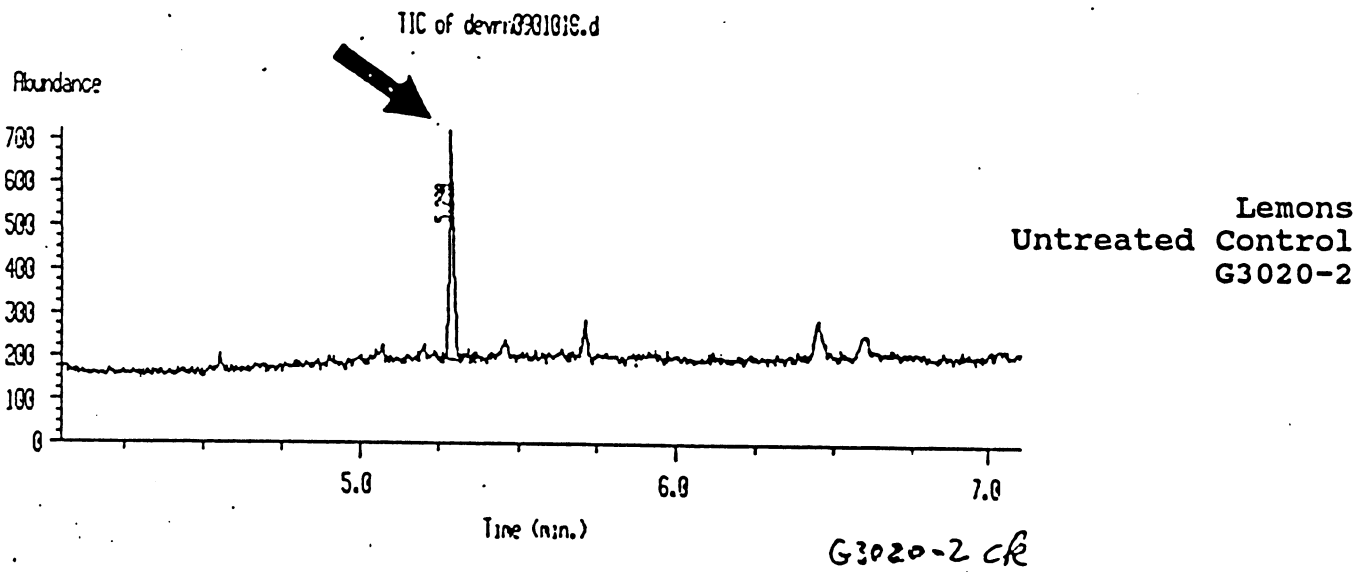
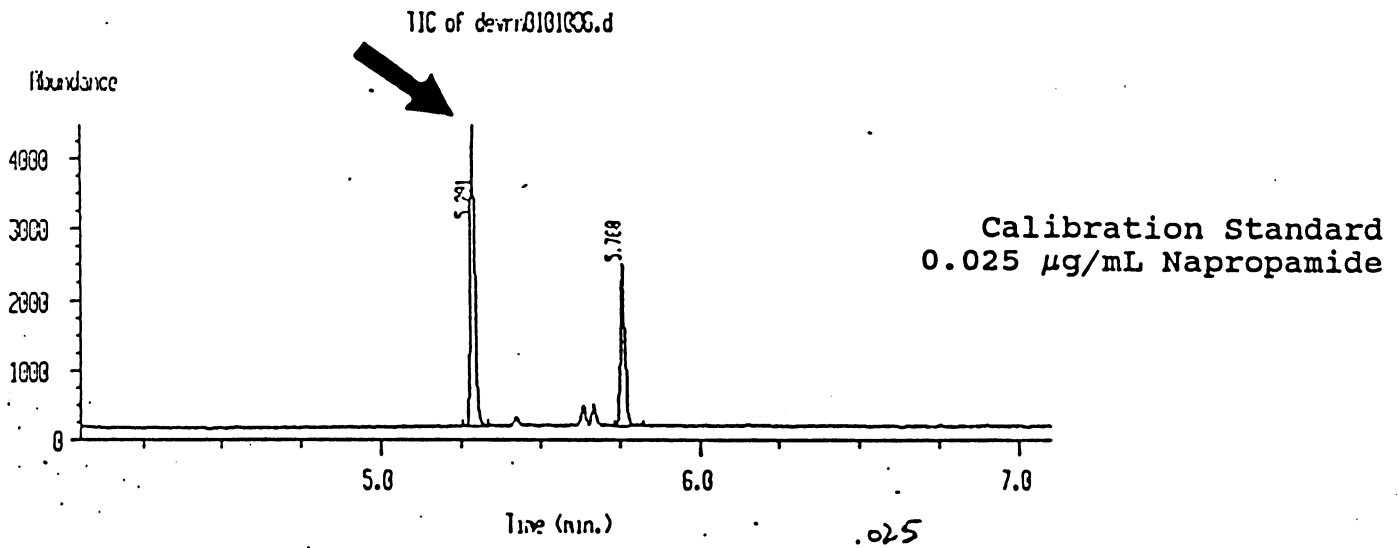
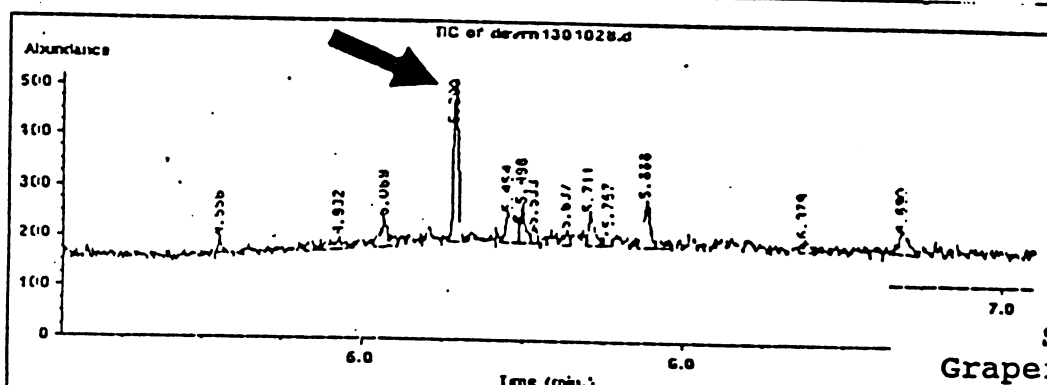
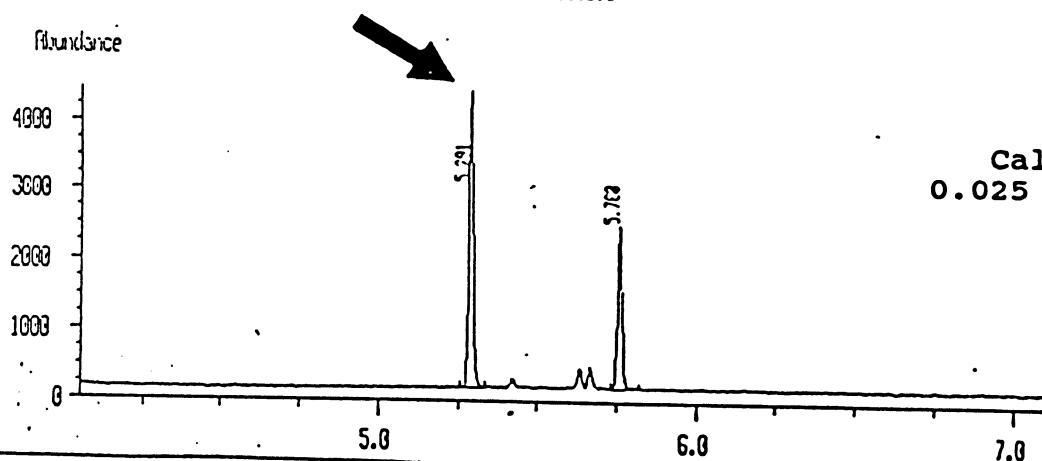
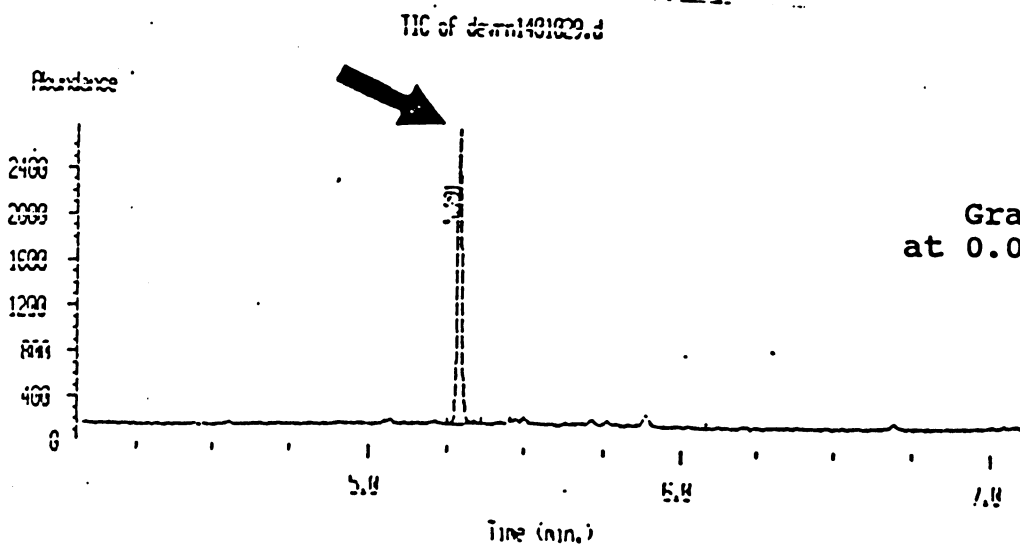
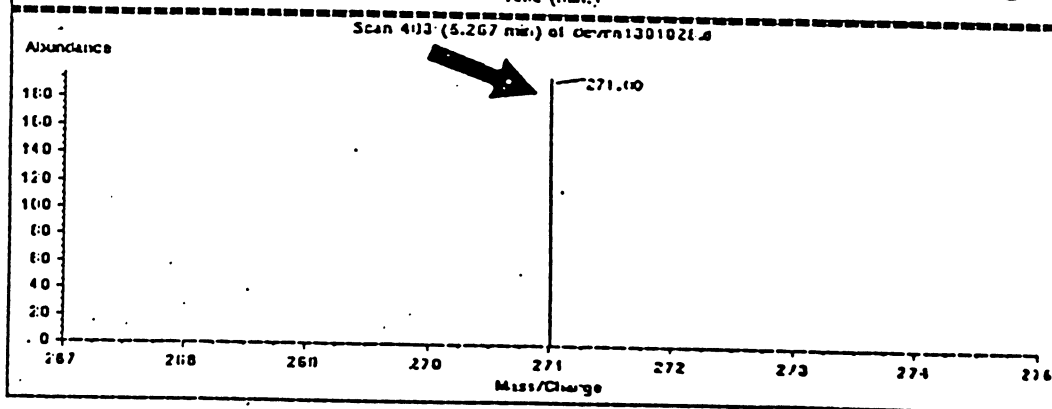


FIGURE 7. EXAMPLE GC/MSD GRAPEFRUIT TIC CHROMATOGRAMS
TIC of dearr0101000.d



Scan and TIC of
Grapefruits Untreated
G3021-2



6 RETENTION OF RECORDS

All of the raw data, protocol, and the final report are located in the GLP Archive of ICI Americas Inc., Western Research Center, 1200 S. 47th St., Richmond, CA 94804-0023.

7 REFERENCES

1. The Pesticide Manual, ed. by Worthing, Charles R., Hance, Raymond J., Published by the British Crop Protection Council, Unwin Books, 1991, pages 611-612.

2. Code of Federal Regulations. 40 CFR 180.328, page 343, July 1, 1990, United States Government Printing Office.

3. WRC Notebook No. 12439-14.