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VOLUME 1 OF 1 OF SUBMISSION

PROPICONAZOLE

STUDY TITLE

Determination of Total Residues of Propiconazole  
in Meat, Milk and Eggs as 2,4-Dichlorobenzoic Acid  
by Capillary Gas Chromatography

EPA Guideline 171-4

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STUDY COMPLETED ON January 9, 1987

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LABORATORY/STUDY NO. AG-517

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

Company: CIBA-GEIGY Corporation

Company Representative: Richard L. Conn

Date: 14 January 1987

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Statement Concerning Good Laboratory Practices

To the best of my knowledge, the study contained in this volume has been conducted in accordance with good and acceptable scientific practices. Because GLP's are not in effect for the study contained in this volume, certification of compliance with Good Laboratory Practices is not applicable.

L. Ballantine 1/14/87  
Signature of Agent of Submitter/Sponsor

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CERTIFICATION OF GOOD LABORATORY PRACTICE

To the best of my knowledge, the Good Laboratory Practice Statements found on Page 37 of this volume and signed by the Study Director, are truthful and accurate.

L. Ballantine  
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EDITION	1/9/87	
SUBMITTED BY: P. J. Manuli		

P. J. Manuli 1/9/87	APPROVED BY: M. W. Chung
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I. SUMMARY/INTRODUCTION

Ia. SCOPE

This method is used for the determination of total residues of propiconazole, 1-[ [2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole in meat, milk and eggs as 2,4-dichlorobenzoic acid (DCBA) (see Figure 1 for structures).

Ib. PRINCIPLE

Animal tissues are extracted with 20% water/ acetonitrile using a Polytron homogenizer. Milk and eggs are extracted by shaking with acetonitrile on a mechanical shaker. The mixture is filtered and an aliquot of the extract is evaporated to dryness, and the residue dissolved in NaOH. The sample is then heated for one hour and fifteen minutes with potassium permanganate, where propiconazole and its metabolites are converted to 2,4-dichlorobenzoic acid. After addition of water, the sample is partitioned with 10% diethyl ether/hexane. The organic phase containing 2,4-dichlorobenzoic acid is evaporated to dryness and derivatized with diazomethane in the presence of dodecane which acts as a keeper to reduce volatile losses of the derivative in subsequent steps. The derivative is cleaned up using an acidic alumina Sep-Pak®. The cleaned extract is analyzed by capillary gas chromatography.

The limit of detection for the method is 0.05 ppm for meat and eggs and 0.02 ppm for milk expressed as propiconazole equivalents.

The flow diagram for the method is shown in Figure 2.

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## II. MATERIALS/METHODS

### IIa. Equipment

- IIa.1 Concentration tubes, 50 ml (Fisher Catalog No. 05-538-40B, Kimax Brand or equivalent).
- IIa.2 Cotton, absorbent (Fisher Catalog No. 07-900 or equivalent).
- IIa.3 Distillation column, Snyder, 3 ball (Kontes Catalog No. K-503000-012 or equivalent).
- IIa.4 Funnel, 12.5 cm. size.
- IIa.5 Glass jars, wide mouth, square, 16 oz.
- IIa.6 Multi-Blok Heater, (Cole-Parmer, Catalog No. J-3128-00 or Thomas, Catalog No. 5891-C10 or equivalent).
- IIa.7 N-evap or equivalent.
- IIa.8 Rotary evaporator, Buchi or equivalent.
- IIa.9 Sample vials, GC autosampler.
- IIa.10 Sample concentrator (Thomas, Catalog No. 4367-B20 or equivalent)
- IIa.11 Separatory funnel, 125 ml with Teflon stopcock.
- IIa.12 Sep-Pak, acidic alumina (Waters Associates, Catalog No. 51800).
- IIa.13 Shaker, mechanical.

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- IIa.14 Syringe, 25 ml, LuerLok®.
- IIa.15 Test tubes, 24/40 joint, 18.5 cm x 22 mm.  
(Ace Glass Co., Catalog No. 8645-38) or  
equivalent.
- IIa.16 Thermometer, -10 to 360°C.
- IIa.17 Thermometer, -20 to 110°C.
- IIa.18 Vortex mixer or equivalent.
- IIa.19 Stirring rods, 10 x 300 mm.

**IIb. Reagents and Standards**

- IIb.1 Acetone, Pesticide Grade (Fisher Catalog No.  
A-40-4 or equivalent).
- IIb.2 Acetonitrile, HPLC Grade (Fisher Catalog No.  
A998-4).
- IIb.3 20% (v/v) distilled water in acetonitrile.
- IIb.4 Propiconazole analytical standard.
- IIb.5 Diazomethane, diethyl ether solution,  
prepared according to AG-345<sup>1</sup>.
- IIb.6 2,4-Dichlorobenzoic acid (DCBA), Aldrich  
Chemical Co., Catalog No. 13957-2.
- IIb.7 Diethyl ether, distilled in glass (American  
Scientific, Catalog No. 106-40 or  
equivalent).
- IIb.8 10% (v/v) Diethyl ether in hexane.
- IIb.9 Distilled water.

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I Ib.10 Dodecane, 99%, Aldrich Chemical Co., Catalog No. D22, 110-4.

I Ib.11 1% (w/v) Dodecane in acetone.

I Ib.12 Ethyl acetate, Certified Grade (Fisher Scientific, Catalog No. E145-4 or equivalent).

I Ib.13 1.0% (v/v) distilled water in ethyl acetate.

I Ib.14 Hexane, HPLC Grade (Fisher, Catalog No. H302-4 or equivalent).

I Ib.15 Methanol, Certified Grade (Fisher, Catalog No. A412-4 or equivalent).

I Ib.16 Potassium permanganate, Reagent Grade (Fisher, Catalog No. P287 or equivalent).

I Ib.17 Sodium meta-bisulfite, reagent grade, Baker.

I Ib.18 Sodium hydroxide, reagent grade, Baker.

I Ib.19 Sodium hydroxide, 1N solution.

I Ib.20 Hydrochloric acid, reagent grade.

I Ib.21 Hydrochloric acid, 6N solution.

I Ic. Analytical Procedure

I Ic.1 Preparation of Sample

I Ic.1.1 Milk and eggs require no preparation. Tissue samples are cut into small pieces prior to weighing. Only the amount needed is prepared.

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**IIC.2 Extraction and Fortification**

IIC.2.1 Weigh a 15-g representative sample (Section IIC.1.1) into a 16 oz. square wide mouth jar.

IIC.2.2 Fortification of one or more control samples will be performed at this step.

IIC.2.2.1 Prepare the fortification standard by dissolving 100 + 0.1 mg propi-conazole (using an analytical balance) in 100 ml of hexane in a volumetric flask. Make serial dilution of the standard such that the fortification volume will not exceed 1.0 ml.

IIC.2.2.2 Add parent propiconazole standard in 1.0 ml or less of hexane to the control samples before extraction.

IIC.2.2.3 Let the spiked samples stand for at least 30 minutes before adding extraction solvent.

IIC.2.3 Tissue Sample: Add 200 ml of 20% water/acetonitrile solution. Homogenize and extract the sample for 2-3 minutes using a Polytron homogenizer.

Milk and Eggs: Add 200 ml of acetonitrile. Shake using a mechanical shaker for 15 minutes.

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<p>IIC.2.4 Filter the extract through a Reeve Angel Grade 802 filter paper inside a Whatman 2V filter paper into an <u>8</u> oz. bottle.</p> <p>IIC.2.5 Transfer a 0.225-g equivalent aliquot (3.0 ml) for tissue, 0.213-g equivalent aliquot (3.0 ml) for eggs, and 5.62-g equivalent aliquot (75.0 ml) for milk to a 24/40 test tube (18.5 cm x 22 mm) and add 0.1 ml of conc. acetic acid (See Section IIE.1). Concentrate the solution to dryness using either an N-EVAP or a sample concentrator at a temperature <u>&lt;40°C</u>.</p> <p>The acetic acid prevents possible losses of parent propiconazole during the concentration step.</p> <p>IIC.3 <u>Potassium Permanganate Reflux</u></p> <p>IIC.3.1 Add 0.4 g (0.6 g for milk) of potassium permanganate to the test tube.</p> <p>IIC.3.2 Add 6 ml of 1N sodium hydroxide. Stopper and mix well on a vortex mixer.</p> <p>NOTE: After addition of NaOH and <math>KMnO_4</math> and mixing well, the sample color must be dark purple. If sample appears to be brownish to dark green, additional <math>KMnO_4</math> must be added in increments of 0.1 g. Mix sample well each time.</p> <p>IIC.3.3 Rinse sides of test tube with 2 ml of <u>1N</u> sodium hydroxide. Add boiling chips.</p>		

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Iic.3.4 Place test tubes fitted with Snyder columns on a heating block which has been pre-heated to 125°C, and heat for one hour and fifteen minutes.

Iic.3.5 Remove the test tubes from the heating block and add 5 ml of water through the top of the Snyder column. Allow to cool for 15 minutes.

Iic.3.6 Add 6 g of sodium meta-bisulfite, stopper and mix well on a vortex mixer. Sample will gradually turn white.

Iic.3.7 Add 14 ml of 6N hydrochloric acid slowly. Sample will effervesce. Mix sample carefully using glass stirring rod until completely clear.

NOTE: Stained glassware which has been used in the  $KMnO_4$  reaction may be rinsed with a dilute solution of sodium meta-bisulfite to remove stains. Continue with usual wash and rinse.

Iic.4 Diethyl Ether/Hexane Partition

Iic.4.1 Transfer the sample solution in the test tube to a 125-ml separatory funnel. Add 15 ml of 10% (v/v) diethyl ether/hexane and stopper. Partition for one minute and allow the layers to separate. Drain the lower aqueous layer back into the test tube. Transfer the organic phase through a filter tube or powder funnel containing absorbent cotton into a 100-ml round bottom flask.

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<p>IIC.4.2 Repeat the partition twice using 15 ml of 10% diethyl ether/hexane each time as described in Section IIC.4.1. Combine the organic phases.</p> <p>IIC.4.3 Rinse the separatory funnel with 10 ml of 10% diethyl ether/hexane. Use this and an additional 20 ml of 10% diethyl ether/hexane to rinse the absorbent cotton.</p> <p>IIC.4.4 Add 2 ml of 1% (w/v) dodecane solution in acetone to the flask and evaporate to dryness using a rotary evaporator (bath temperature <u>&lt;40°C</u>).</p> <p>NOTE: The added dodecane coats the surface of the round bottom flask uniformly after the evaporation step and acts as a keeper to minimize volatile losses of the methyl derivative of 2,4-dichlorobenzoic acid during the subsequent evaporation steps.</p> <p>IIC.5 <u>Derivatization with Diazomethane</u></p> <p>IIC.5.1 Add 2 ml of diazomethane/diethyl ether reagent solution (AG-345<sup>1</sup>) to the residues in the test tube in Step IIC.4.4. Swirl gently to dissolve the residues.</p> <p>IIC.5.2 Allow the solution to stand for at least 30 minutes with occasional gentle swirling. Add more diazomethane as required to maintain a yellow color.</p>		

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CAUTION: Add diazomethane inside a well ventilated hood. Extreme care should be exercised in handling diazomethane because of the potential toxic effects and explosion hazards that exist upon contact with sharp or rough surfaces.

IIC.5.3 Evaporate the diethyl ether off after the derivatization using a rotary evaporator at room temperature (do not use a bath). Continue the evaporation at room temperature for an additional one and no longer than two minutes to ensure the complete removal of diethyl ether.

NOTE: Evaporation at higher temperature to total dryness may cause losses of the derivative.

IIC.6 Alumina Sep-Pak Cleanup

IIC.6.1 Fit an acidic alumina Sep-Pak cartridge to the LuerLok end of a 25 ml syringe with the plunger removed (see Figure 3).

IIC.6.2 Add 10 ml of 1.0% (v/v) water/ethyl acetate to the barrel of the syringe and allow it to flow by gravity through the Sep-Pak. (A rate of 2-3 ml per minute is normal).

NOTE: The 1.0% (v/v) water/ethyl acetate wash is used to deactivate the acidic alumina.

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Iic.6.3 Prewash the Sep-Pak cartridge with 10 ml of hexane by gravity flow.

Iic.6.4 Dissolve the residue from IIC.5.3 in 5 ml of hexane and transfer into the barrel of the syringe. Elute the hexane through the Sep-Pak by gravity flow. - *Discard*

Iic.6.5 Rinse the round bottom flask with 8 ml of 10% (v/v) diethyl ether/hexane and transfer to the barrel of the syringe. Elute the acidic alumina Sep-Pak by gravity flow, collecting the eluant in a 50-ml concentration tube. *22 8144*

NOTE: Distilled in glass diethyl ether is used for the elution steps.

Iic.6.6 Add hexane to bring to a volume of 10.0 ml for tissues and eggs and to 50.0 ml for milk. Dilute with hexane if necessary.

IId. Instrumentation

IId.1 Description

The sample in Step Iic.6.6 is analyzed by capillary gas chromatography using an electron capture detector. The gas chromatographic conditions are given in Table I.

IId.2 Operating Conditions

See Table No. 1

IId.3 Calibration

IId.3.1 The GC system should be calibrated with each analytical run, by checking the retention time of DCBA

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methyl ester. The retention time should not vary by more than + 2% on a daily basis, otherwise the system should be inspected and proper maintenance should be performed in order to achieve the narrow range of variation.

#### II d. 3.2 Method of Calculation

The gas chromatograph is standardized by injecting 2- $\mu$ l aliquots of the diluted DCBA-methyl ester solutions during residue analysis. This represents a working range of 0.5 to 10.0 picograms of the derivative (expressed as dichlorobenzoic acid).

#### II e. Interference(s)

II e. 1 Sample matrices. Analytical Method AG-517 has been used to analyze round meat, perirenal fat, milk and eggs (Table II). With the exception of liver, no interferences were found in meat, fat, eggs (<0.05 ppm) or in milk (<0.02 ppm). In one liver control sample, 0.16 ppm was detected. This residue could have been real propiconazole residue resulting from contamination, since the treated liver had residues up to 5.0 ppm. In the case of milk, interferences of up to 0.009 ppm were found. These interferences are believed to be the cause of the wide variations found at the 0.01 ppm recovery level (Table II). Our studies showed that these interferences originated mainly from reagents and apparatus used in the analysis. To minimize interferences, a much larger milk aliquot (5.62 g, Section II e. 2.5) is used such that the interferences can be diluted (50.0 ml, Section II c. 6.6) prior to injection.

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<p>Ile.2 No interferences from chemicals having permanent or Section 18 tolerances in or on pecans, peanuts, grapes or apples were detected when determined as 2,4-dichlorobenzoic acid. Two studies were conducted (ABR-83075<sup>2</sup> and ABR-85040<sup>3</sup>). In one of the studies, ABR-85040, maximum tolerance level amounts of the pesticide chemicals having permanent tolerances or Section 18 tolerances in or on grapes and apples were subjected to the procedures of Analytical Method AG-445<sup>4</sup>, "Determination of CGA-71818 Residues in Grapes and Apples by Conversion to 2,4-Dichlorobenzoic Acid and Analysis by Capillary Gas Chromatography." Analytical Methods AG-517 and AG-445 are nearly identical in every step with slight differences in the extraction solvents, in the length of basic permanganate hydrolysis time (1.25 vs. 2.0 hours), in the partition solvents (diethyl ether/hexane vs. methyl tert-butyl ether) and in the Sep-Pak columns (acidic alumina vs. silica gel). Propiconazole and CGA-71818 are also very similar in chemical structures and properties. In the second study (ABR-83075), pesticidal chemicals having permanent or Section 18 tolerances in or on pecans or peanuts were subjected to the analytical procedures of AG-356<sup>5</sup> which was an earlier version of the method for determination of propiconazole residues as DCBA in crops. No interferences were detected.</p> <p>Ile.3 No interference from the solvents used in this method has been detected.</p> <p>Ile.4. The roto evaporator should be rinsed with fresh acetone solvent between each sample evaporation to eliminate possible cross contamination.</p>		

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**IIf. Confirmatory Techniques**

IIf.1 GC/MS according to Analytical Method AG-3565.

**IIg. Time Required**

IIg.1 A total of eleven hours is needed. This includes the actual injection time. When several sets of samples are being worked up, many steps can be overlapped and performed concurrently.

**IIh. Modifications**

IIh.1 None

**III. Preparation of Standard 2,4-Dichlorobenzoic Acid Methyl Derivative**

**III.1 Calibration Factors**

III.1.1 Weigh 20.0 mg of 2,4-dichlorobenzoic acid into a 200-ml volumetric flask.

III.1.2 Add 3 ml of diazomethane as in Steps IIc.5.1 to IIc.5.2.

III.1.3 Bring to volume with hexane. The standard solution of the derivative is 100 ng/ $\mu$ l expressed as 2,4-dichlorobenzoic acid equivalents. Serial dilutions of the standard solution are made with hexane until working solutions containing 0.25, 0.50, 1.0, 2.5, and 5.0 picograms per microliter are achieved.

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- Iii.1.4 Inject 2- $\mu$ l aliquots of the diluted solutions during residue analysis. This represents a working range of 0.5 to 10.0 picograms of the derivative (expressed as dichlorobenzoic acid).
- Iii.1.5 Determine the peak height for the injected standards. Typical chromatograms of standards are shown in Figure 4.
- Iii.1.6 Construct a standard curve by plotting detector response versus picograms injected or enter the standardization data into an appropriate electronic calculator (e.g., Hewlett-Packard Model HP-11C) or a computer system (e.g., HP-1000 Lab Automation System [LAS]) which utilizes integration software to calculate a least square standard curve. A typical standard curve is shown in Figure 5.

Iii.2 Detection of Sample Residues

- Iii.2.1 Inject a 2- $\mu$ l aliquot of the sample in Step Iic.6.6 into a gas chromatograph equipped with an electron capture detector. Make appropriate dilutions of the sample to have the sample peak height within the range of the standard curve. Compare peak heights of unknown samples with the standard curve, manually or by either using an electronic calculator or a computer system as mentioned in Iii.1.6, to determine the amounts of

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the derivative in the aliquot injected. Typical chromatograms of checks and recovery samples are shown in Figures 6 through 10.

Iii.2.2 Calculate residue results as ppm equivalents of propiconazole using the following equation:

$$\text{PPM Found} = \frac{\text{Amount 2,4-Dichlorobenzoic Acid Found (pg)}}{(\text{mg injected}) (1000 \text{ pg/ng})} \times 1.79$$

Correct the ppm found in recoveries by subtracting the ppm found, real or apparent, in the controls. Calculate the recovery factor by the following equation:

$$R = \frac{\text{Corrected PPM Found in Fortified Sample}}{\text{PPM Added}}$$

where R is the recovery factor determined using a fortified control sample carried through the procedure and is expressed as a decimal (100% = 1.00, etc.). If the recovery is >100%, use the factor 1.00.

Correct the propiconazole ppm found in samples by the following equation:

$$\text{Corrected ppm} = \frac{(\text{PPM Found in Sample})}{R}$$

The factor 1.79 is used to convert residues of 2,4-dichlorobenzoic acid found into propiconazole equivalents.

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IIj. DISCUSSION

- IIj.1 Preparation of diazomethane can be carried out as specified in AG-345.
- IIj.2 The average recovery of propiconazole from tissue and egg samples fortified at 0.05 to 5.0 ppm was  $93 \pm 23\%$ ,  $N = 14$ . The average recovery of propiconazole from milk samples fortified at 0.02-0.10 ppm was  $75 \pm 8\%$ ,  $N = 7$  (excluding the 0.01 ppm recoveries). The overall average recovery was  $84 \pm 27\%$ ,  $N = 21$ .
- IIj.3 Accountability of the total method was tested, using five propiconazole related metabolites present in crops and animal tissues (Table III). Average recovery of all metabolites was  $93 \pm 11\%$  (refer to Analytical Method AG-454A<sup>6</sup>).
- IIj.4 Analytical Method AG-517 is a modified version of the corresponding crop method, AG-454A<sup>6</sup>. The two methods differ only in the extraction step. AG-454A has been validated.

III. RESULTS AND DISCUSSION

IIIa. Accuracy

- IIIa.1 The average recovery was  $84 \pm 27\%$ ,  $N = 21$ , at a fortification range of 0.02 ppm to 5.0 ppm. No dependency of percent recovery on fortification level was found.

IIIb. Precision

- IIIb.1 Not performed.

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IIIc. Limits of Detection and Quantitation

IIIc.1 The limit of detection is 0.05 ppm in tissue and eggs and 0.02 ppm in milk detected as 2,4-DCBA and reported as propiconazole equivalents.

IIIId. Ruggedness

Testing not performed.

IIIe. Limitation

None

IV. REFERENCES

1. Ross, J. A., AG-345, "Preparation of Diazomethane."
2. R. K. Williams, P. J. Manuli, J. A. Ross, ABR-83075, "Specificity of Analytical Method AG-356 for the Determination of Total Residues of CGA-64250 as 2,4-Dichlorobenzoic Acid (Methyl Ester)."
3. W. T. Beidler, J. A. Ross, ABR-85040, "Specificity of Analytical Method AG-445 for the Determination of the Total Residues of CGA-71818 in Grapes and Apples."
4. P. Manuli, J. W. Smith, S. G. Burge, Ag-445, "Determination of CGA-71818 Residues in Grapes and Apples by Conversion to 2,4-Dichlorobenzoic Acid and Analysis by Capillary Gas Chromatography."
5. K. Balasubramanian, B. Gold, M. W. Cheung, AG-356, "Determination of Total CGA-64250 Residues in Crops by Conversion to 2,4-Dichlorobenzoic Acid and Analysis by Gas Chromatography - Mass Spectrometry."
6. J. Toth, P. J. Manuli, AG-454A, "Determination of Total Residue of Propiconazole in Crops as 2,4-Dichlorobenzoic Acid by Capillary Gas Chromatography."

PAGE 18 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLORO BENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

TABLE I: CAPILLARY GAS CHROMATOGRAPHIC CONDITIONS

Instrument: Hewlett-Packard Model 5880 Capillary Gas Chromatograph with Model 7672A Automatic Sampler.

Carrier Gas: Helium, flow adjusted to give 17 psi (1-2 ml per minute).

Makeup Gas: 5% argon/methane, 30 ml per minute.

Column: J & W capillary, DB-5, 30 meter, 0.25  $\mu$ m film thickness, 0.32 mm i.d.

Injection: Splitless.

Detector: Electron capture.

Temperatures:

Injector: 250°C  
Detector: 300°C

Oven Program and Run Table

OVEN TEMP=60°C SETPT=60°C LIMIT=405°C  
EQUIB TIME = 3.00 MIN

OVEN TEMP PROFILE: (ANNOTATION OFF)

INITIAL VALUE = 60°C  
INITIAL TIME = 1.00 MIN  
LEVEL 1  
PRGM RATE = 30.00°C/MIN  
FINAL VALUE = 130°C  
FINAL TIME = 5.50 MIN  
POST VALUE = 250°C  
POST TIME = 5.00 MIN

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PG0023 CF0043

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EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

TABLE I: CAPILLARY GAS CHROMATOGRAPHIC CONDITIONS  
(continued)

DET 1 TEMP=270°C SETPT=270°C LIMIT=405°C  
DET 2 TEMP=300°C SETPT=300°C LIMIT=405°C  
INJ 1 TEMP=230°C SETPT=230°C LIMIT=405°C  
INJ 2 TEMP=230°C SETPT=230°C LIMIT=405°C  
AUX 1 TEMP=0°C SETPT=50°C(OFF) LIMIT=405°C  
AUX 2 TEMP=0°C SETPT=50°C(OFF) LIMIT=405°C

DEVICE 2: GC TERMINAL 1  
SIGNAL = C  
PLOT = ???  
CHART SPEED = 0.01 CM/MIN  
ATTN = 2↑15  
XOFFSET = 10  
ZERO = 130.56

DEVICE 5: EMP LOOP 1  
SIGNAL = C  
PLOT = ???  
ATTN = 2↑0 ←  
XOFFSET = 0  
ZERO = 126.17

DETECTOR B (OFF): NITROGEN-PHOSPHORUS IONIZATION  
ELEMENT=0; CALIBRATION: H=1482600 L1=1414510 L2=1413860

DETECTOR C: NICKEL 63 ECD  
CALIBRATION: H=1708220 L1=1638400 L2=1638400

LIST RUN TBL

RUN TABLE: (ANNOTATION OFF)  
0.00 VALVE 6 ON  
0.75 VALVE 6 OFF  
7.00 ATTN 2↑4  
7.01 CHART SPEED 2  
7.02 ZERO  
7.03 RUN TIME ANNOTATION ON  
7.88 ZERO

AVAILABLE MEMORY (BYTES): 26336

Minimum Detection Limit: 0.5 picogram

Volume Injected: 2 µl

Retention Time: 8.06 ± 0.1 minutes

PAGE 20 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLOROBENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

TABLE II: TYPICAL PROPICONAZOLE RECOVERIES

<u>Substrate</u>	<u>Fortification Level (ppm)</u>	<u>Recovery (%)</u>
Liver	0.05	116.
	0.05	78.
	0.50	86.
	0.50	89.
	1.7	135.
	5.0	70.
Round Tissue	0.05	127.
	0.50	82.
Perirenal Fat	0.05	128.
	0.05	64.
	0.50	87.
	0.50	77.
Poultry Eggs	0.05	77.
	0.50	90.
Milk	0.01	45.*
	0.01	156.*
	0.01	92.*
	0.01	119.*
	0.01	65.*
	0.01	38.*
	0.02	70.
	0.02	76.
	0.02	87.
	0.02	76.
	0.02	76.
	0.10	80.
	0.10	63.

Overall recovery =  $84. \pm 27. \%$ , N = 21

\*Excluding the 0.01 ppm recoveries in the statistical calculation.

Reference: AG-A 10034

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PG0025 DF0043

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EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

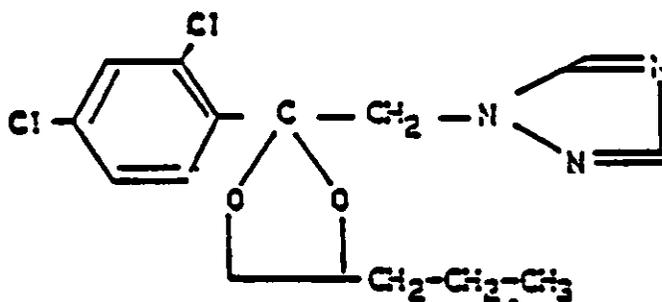
TABLE III: RECOVERIES OF RELATED METABOLITES

<u>Metabolite</u>	<u>Recovery</u>
CGA-91305, alkanol	101%
CGA-91304, ketone	76%
CGA-104284, olefin	105%
CGA-118244, $\beta$ -hydroxy	89%
CGA-121676, $\gamma$ -acid	93%
Average recovery	93 $\pm$ 11%

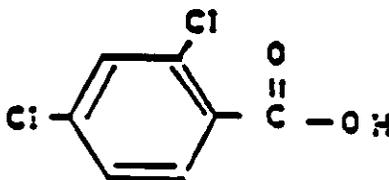
PAGE 22 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLORO BENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

FIGURE 1: STRUCTURES

CGA-64250



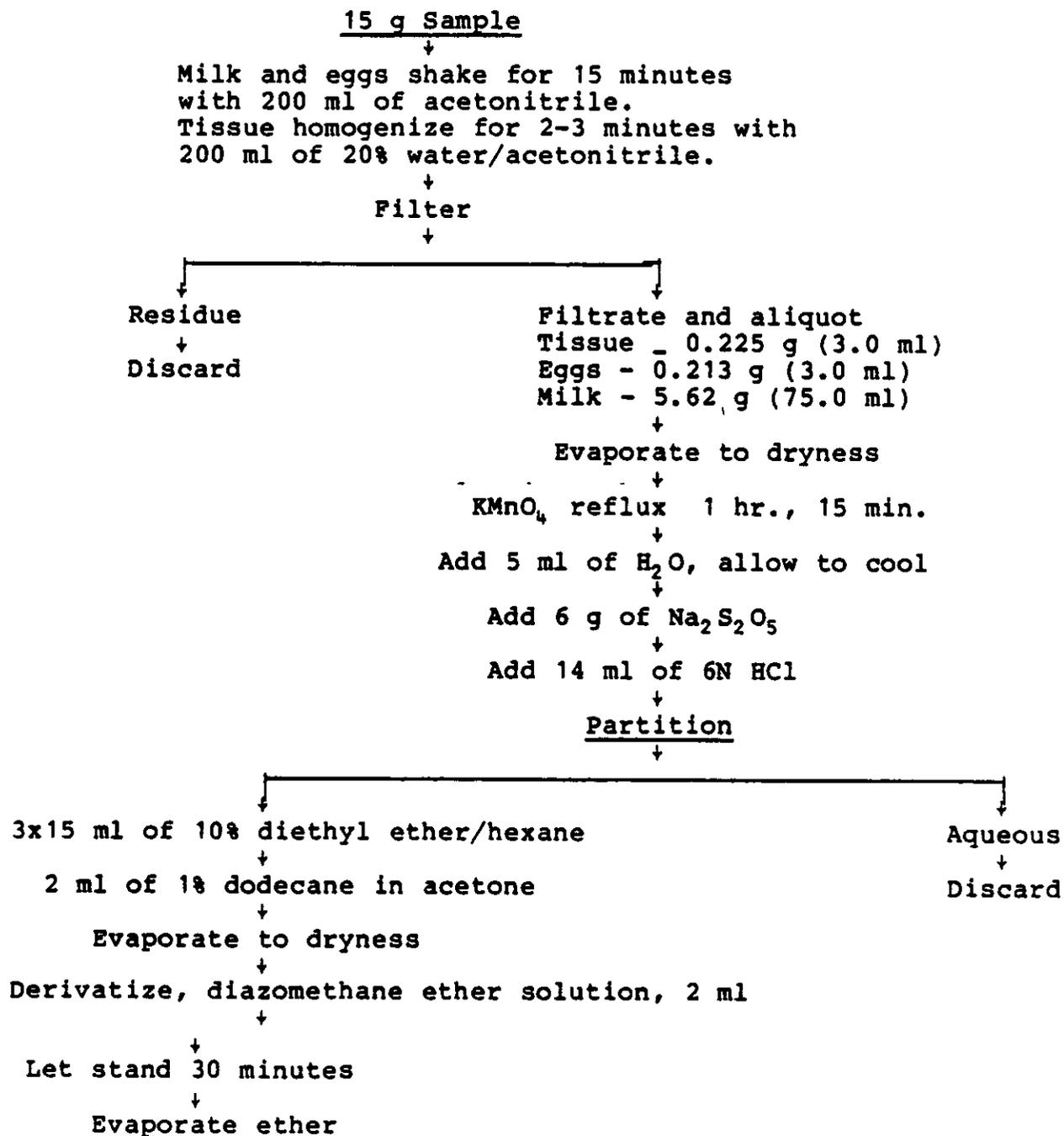
1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole



2,4-Dichlorobenzoic Acid

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EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY: --

FIGURE 2: FLOW DIAGRAM OF METHOD



(Continued on following page)

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EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

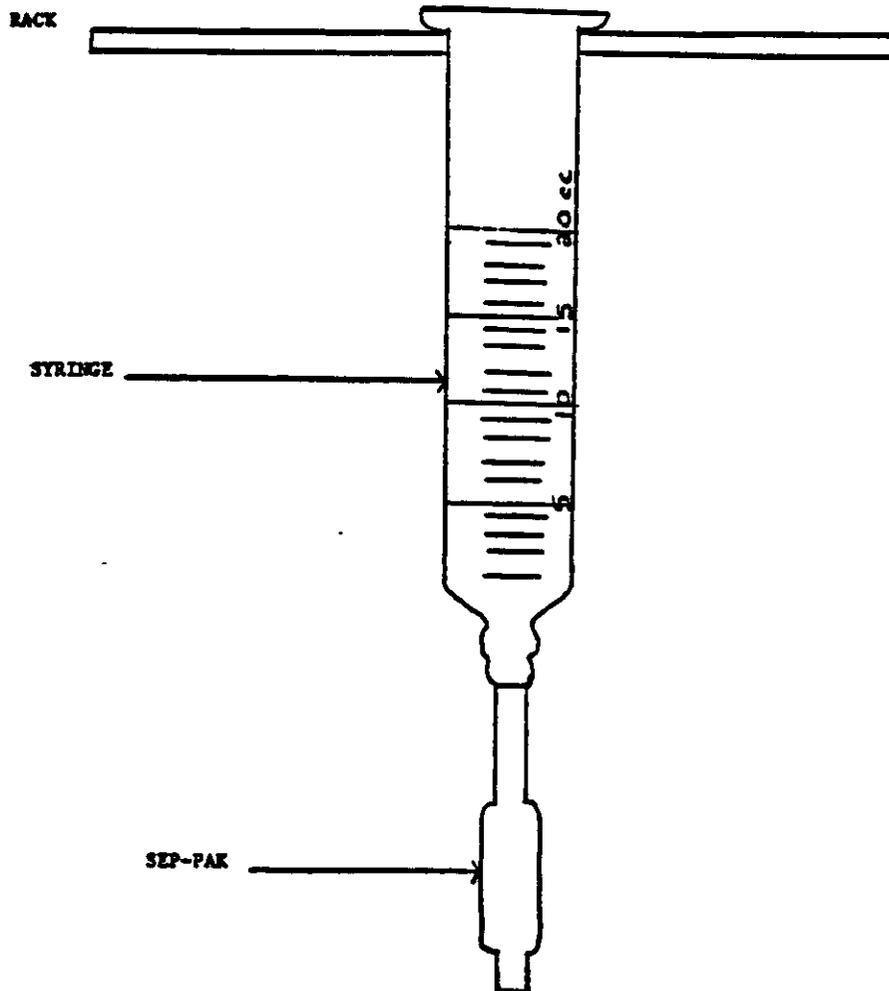
FIGURE 2: FLOW DIAGRAM FOR THE DETERMINATION OF TOTAL CGA-64250  
(Continued)

Sep-Pak Cleanup

+  
Prewash acidic alumina with  
10 ml of 1.0% (v/v) water/ethyl  
acetate, and 10 ml of hexane.  
+  
Load sample in 5 ml of hexane,  
and elute.  
+  
Rinse sample flask with 8 ml of  
10% diethyl ether/hexane,  
transfer to column and elute.  
+  
Dilute to 10.0 ml or 50.0 ml  
+  
Analyze by Capillary GC.

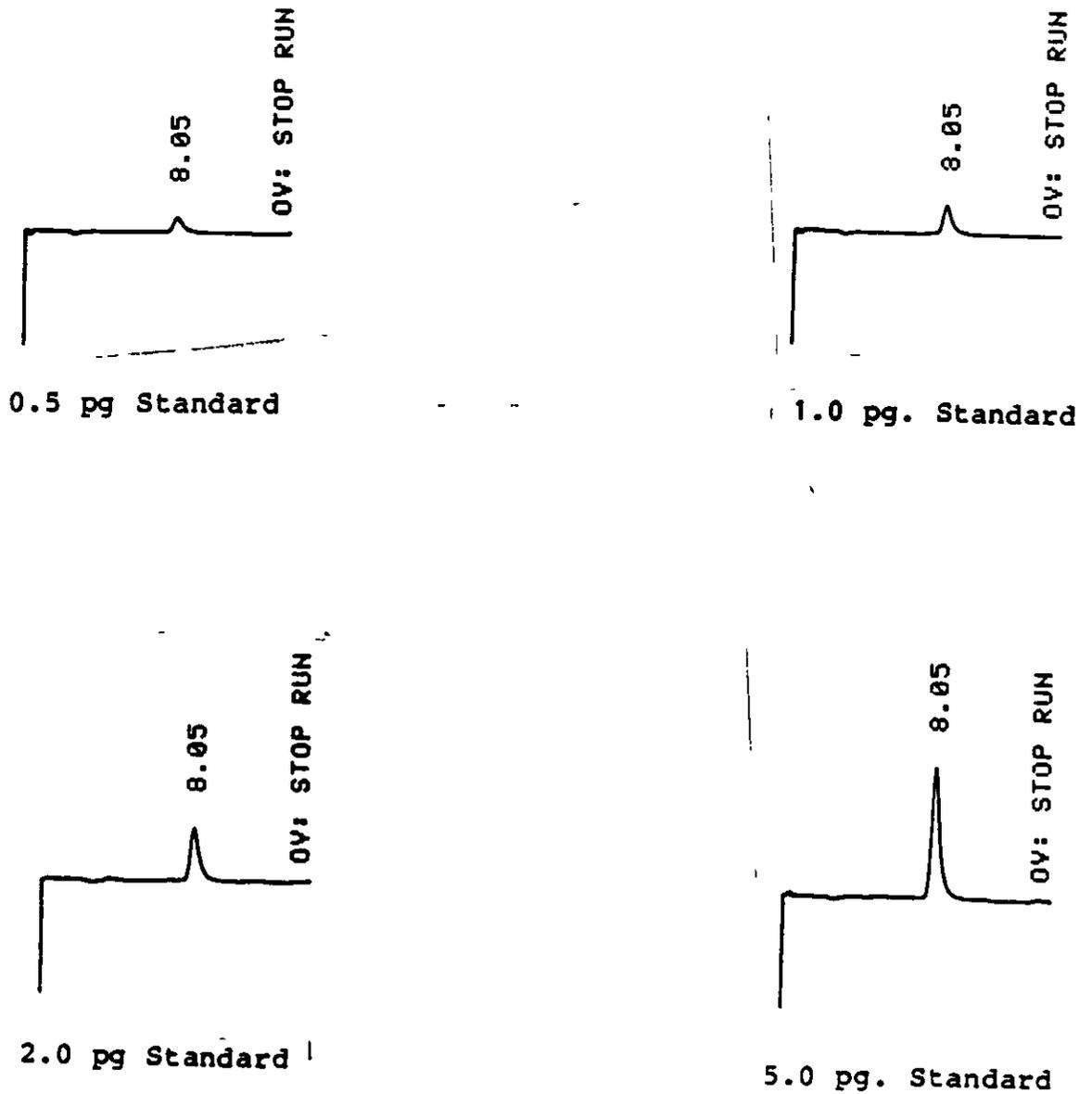
PAGE 25 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLOROBENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

FIGURE 3: DIAGRAM OF SEP-PAK CLEANUP



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EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY: _____

FIGURE 4: TYPICAL STANDARD CHROMATOGRAMS OF 2,4-DICHLOROBENZOIC ACID METHYL DERIVATIVE

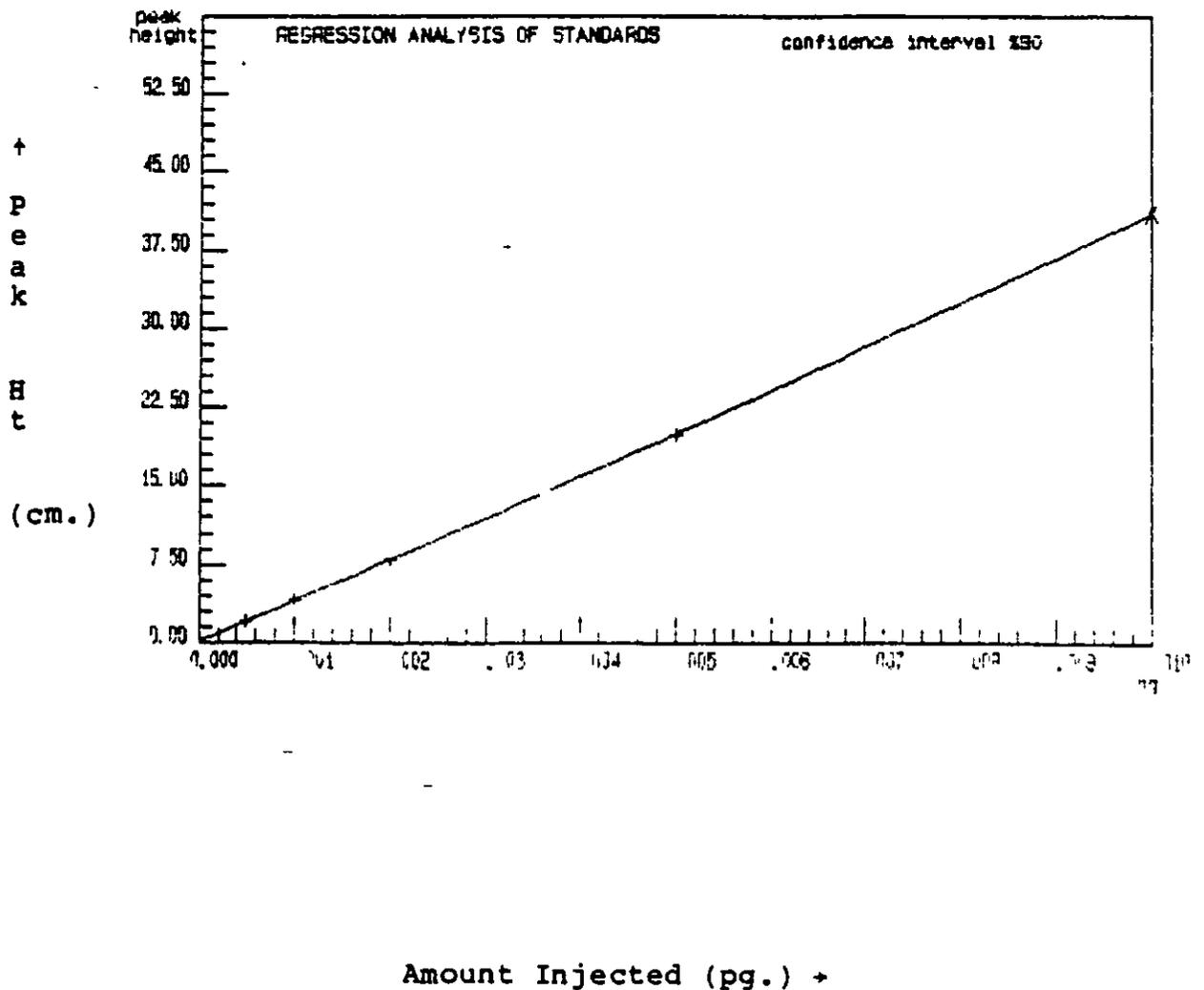


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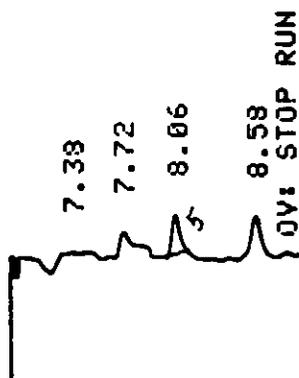
PAGE 27 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLORO BENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

FIGURE 5: TYPICAL STANDARD CURVE

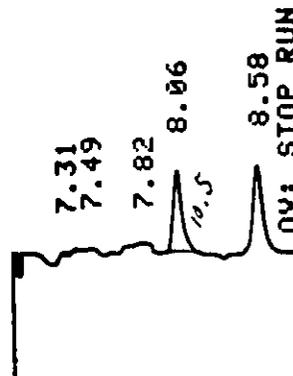


PAGE 28 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLORO BENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

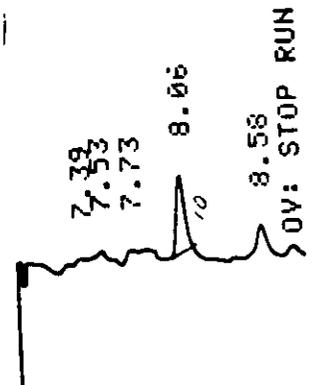
FIGURE 6: TYPICAL CHROMATOGRAMS FOR THE DETERMINATION OF RESIDUES OF PROPICONAZOLE IN ROUND MEAT



Check sample  
0.045 mg injected  
Found: <0.05 ppm  
of propiconazole  
Ref.: AGA-10034



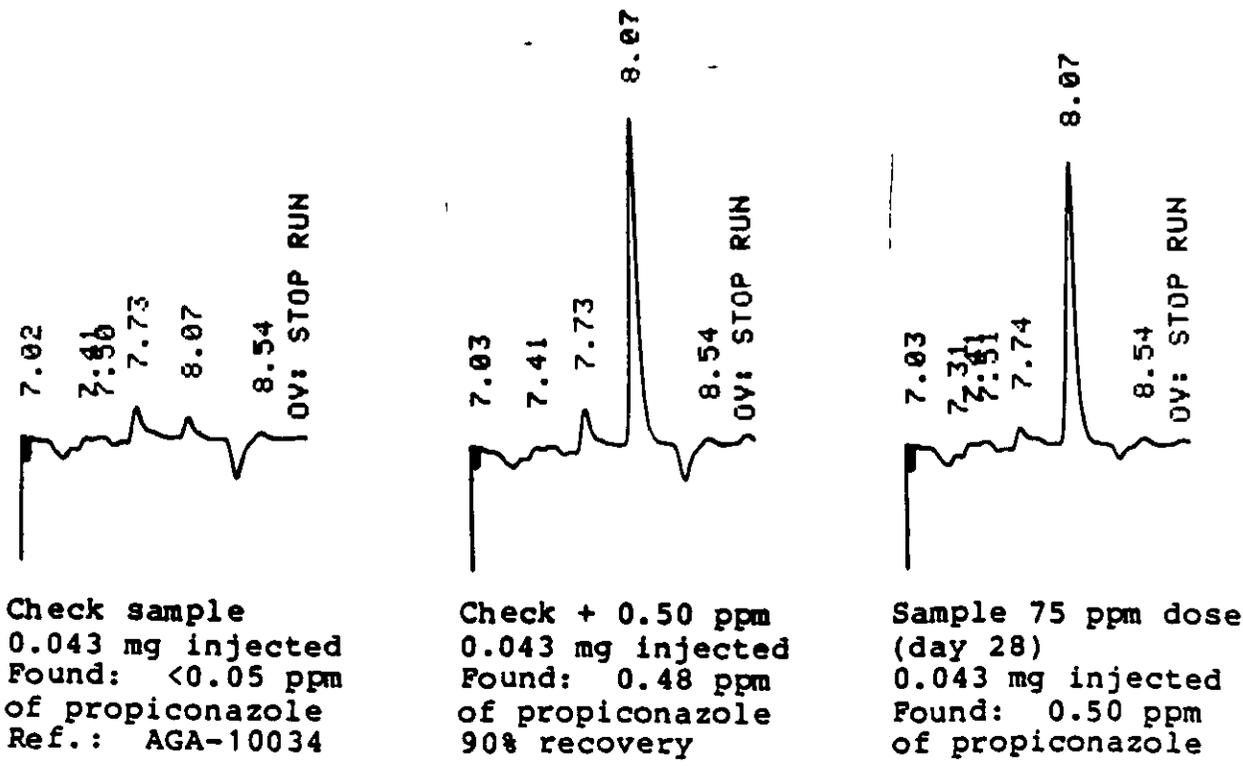
Check + 0.05 ppm  
0.045 mg injected  
Found: 0.06 ppm  
(corrected for  
check) of  
propiconazole  
127% recovery



Sample 150 ppm  
(28 day)  
0.045 mg injected  
Found: 0.10 ppm  
of propiconazole

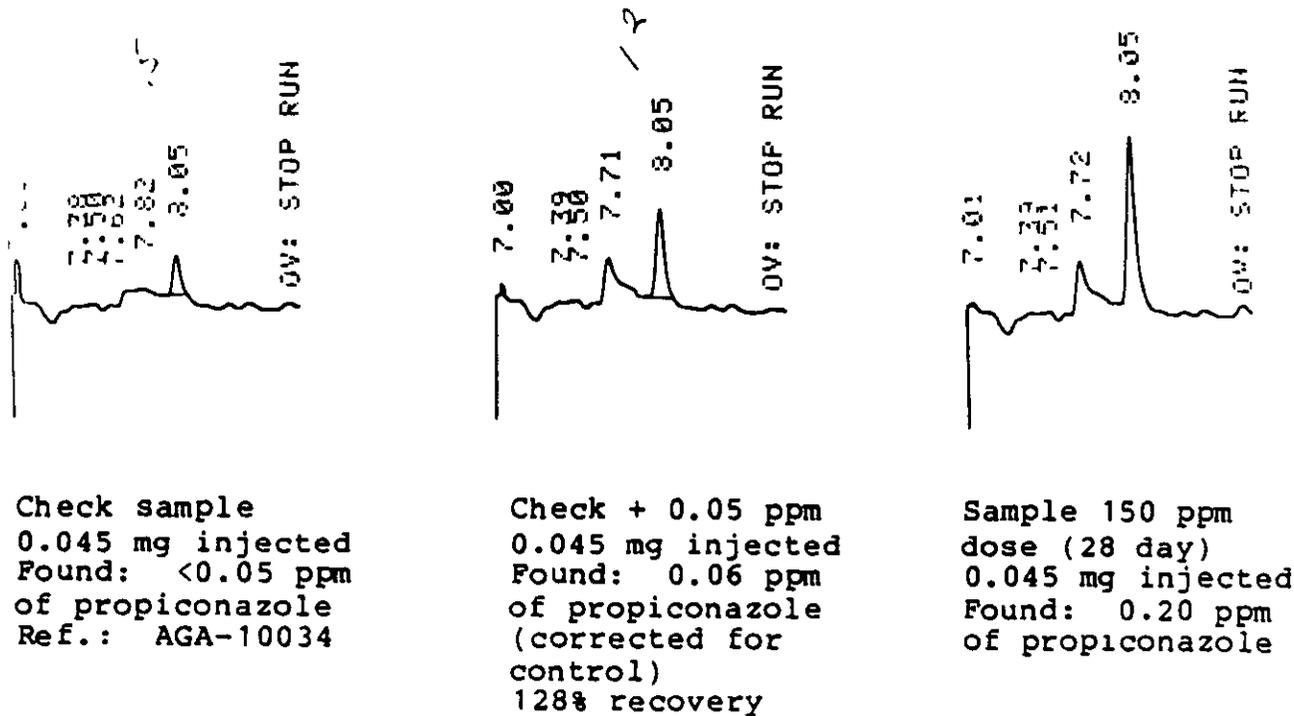
PAGE 29 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLOROBENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

FIGURE 7: TYPICAL CHROMATOGRAMS FOR THE DETERMINATION  
OF RESIDUES OF PROPICONAZOLE IN EGGS



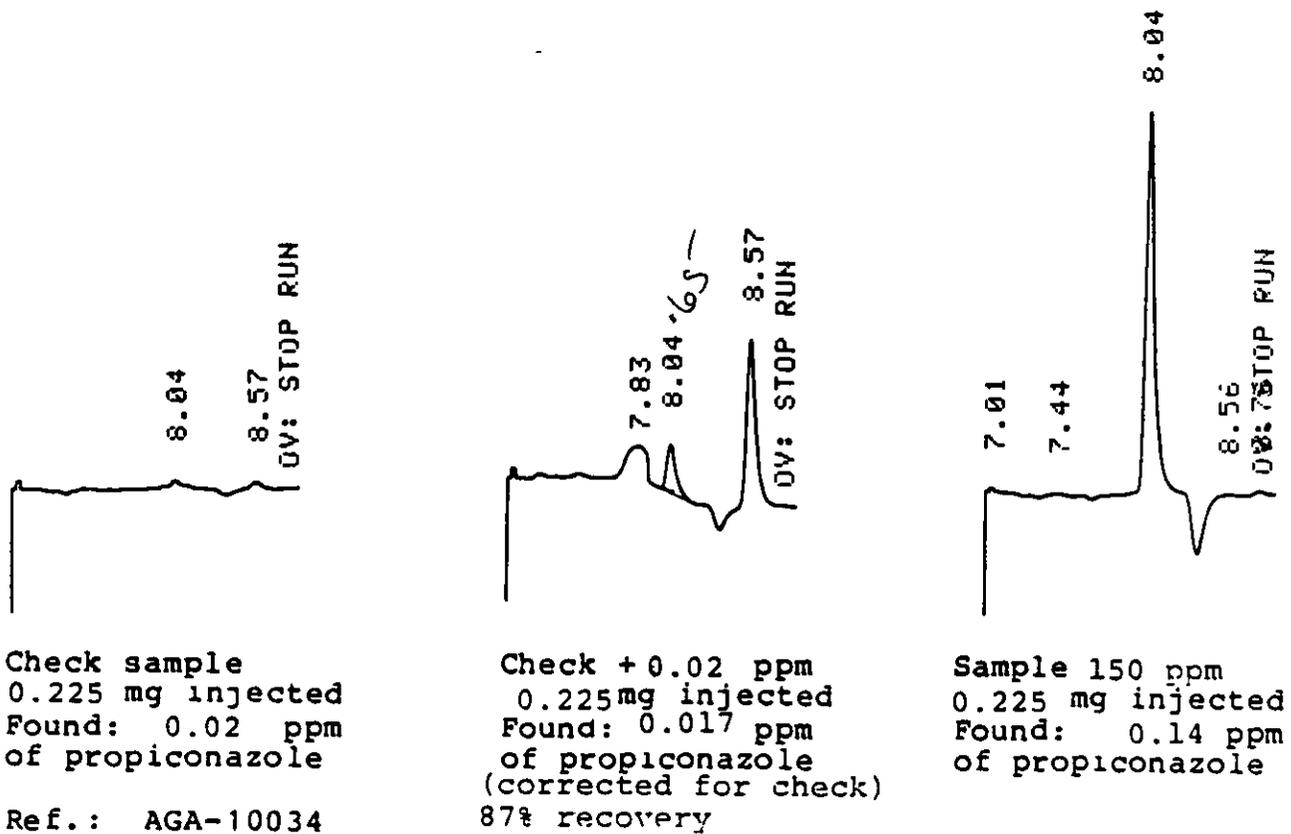
PAGE 30 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLORO BENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

FIGURE 8: TYPICAL CHROMATOGRAMS FOR THE DETERMINATION OF RESIDUES OF PROPICONAZOLE IN PERIRENAL FAT



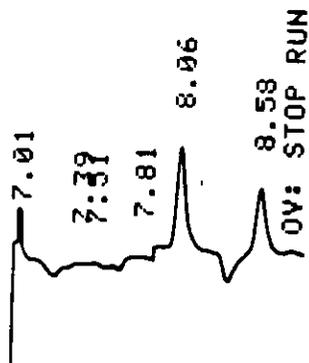
PAGE 31 of 33	METHOD NO. AG-517	SUBJECT
EDITION		DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLOROBENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

FIGURE 9: TYPICAL CHROMATOGRAMS FOR THE DETERMINATION OF RESIDUES OF PROPICONAZOLE IN MILK



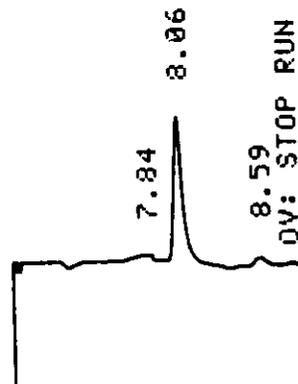
PAGE 32 of 33	METHOD NO. AG-517	SUBJECT DETERMINATION OF TOTAL RESIDUES OF PROPICONAZOLE IN MEAT, MILK AND EGGS AS 2,4-DICHLOROBENZOIC ACID BY CAPILLARY GAS CHROMATOGRAPHY
EDITION		
SUBMITTED BY: P. J. Manuli		
		APPROVED BY:

FIGURE 10: TYPICAL CHROMATOGRAMS FOR THE DETERMINATION  
OF RESIDUES OF PROPICONAZOLE IN LIVER

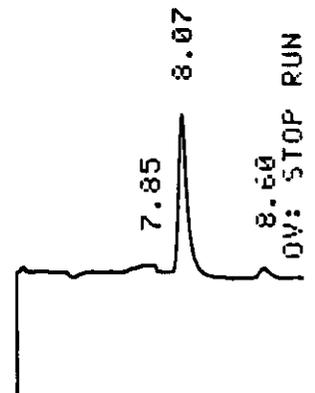


Check sample  
0.045 mg injected  
Found:           ppm  
of propiconazole

Ref.: AGA-10034



Check +           ppm  
0.045 mg injected  
Found:           ppm  
of propiconazole  
recovery



Sample 150 ppm  
(28 day)  
mg injected  
Found:           ppm  
of propiconazole



Compound(s) and Formulations(s): Propiconazole (technical)		Commodity: Dairy Cows & Poultry		Substrate: Dairy: Milk, Round, Liver, Perirenal Fat Poultry: Eggs	
C-G Rep.: Seim	Plot Location: FL	Growth Stages Sampled: Dairy: Lactating		Cooperator Name and Address: CIBA-GEIGY Research Farm Vero Beach, Florida	
Soil Type: --	Date Planted: --				
Treatment Rates: Poultry: 75 ppm in daily feed Dairy: 150 ppm in daily feed		Method of Application: Mixed in feed		Equipment: --	Vol. per Acre: --
Dates of Application: Poultry: Initiated on 2/17/81 Dairy: Initiated on 4/2/81		Sampling Date(s): Poultry: 2/20/81, 3/3/81, 3/17/81 Dairy: 4/16, 23, 30/81			
Other Materials Applied: --		Sample Care Before Storage: --			
Storage Information: Frozen	No. of Analyses: 61	Plot Maintenance, i.e., Cultivation, Irrigation, etc.: --			
Summary of Results: Milk, liver, perirenal fat and round meat tissues were taken from AGA-6305; and eggs were taken from AGA-6300 to develop Analytical Method AG-517. Control samples were used to determine backgrounds and to generate recovery data. Selected treated samples were analyzed to determine total (as DCBA) residues of propiconazole. Results are summarized on page 2.					
Propiconazole 1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1-H-1,2,4-triazole					
*Distribution: L. G. Ballantine M. W. Cheung Main File					
Date Received: 11/26/86	Date Extracted: 12/86, 1/87	Date Analyzed: 12/86, 1/87	Analyst: <i>Fym 1/14/87</i> PM, BM, CG		
Method of Analysis: AG-517					
Analysis Approved By: <i>M.W. Cheung</i>			Date Approved: <i>1/14/87</i>		

P60038 CT0043

Summary of Results

Sample Code	ppm In Daily Feed	Interval (Days)	Total Propiconazole (ppm)*				
			Round	P. Fat	Liver	Milk	
Cow #11	0.	-	<0.05	<0.05, <0.05	0.16, 0.08	<0.02, <0.02, <0.02, <0.02	-
Cow #2	150.	14	0.17	0.42, 0.59	8.9, 8.4	0.14, 0.09,	-
Cow #1	150.	21	0.10	0.19, 0.21	7.4, 6.4	0.11, 0.07	-
Cow #9	150.	28	0.10	0.20, 0.29	5.0, 5.0	0.14, 0.10	-
A	0.	-	-	-	-	-	<0.05
D	75.	14	-	-	-	-	0.57
D	75.	28	-	-	-	-	0.50

\*Detected as 2,4-dichlorobenzoic acid methyl ester and converted to propiconazole equivalents.

Propiconazole: 1-[[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1-H-1,2,4-triazole

Note 1: The average procedural recovery in tissues, milk and eggs at 0.02 to 5.0 ppm fortification levels (not including the 0.01 ppm fortification samples in milk) was 84 ± 27%, N=21 (See pages 4-6).

Note 2: The 0.01 ppm recoveries in milk are included in this report to show the large variation at the 0.01 ppm fortification level. The milk screening level is 0.02 ppm.

00039 00043

Compound(s)		Propiconazole				Substrate				
Sample Code	ppm In Feed	Formulation Spray Additives Other Treatment Data	Application Date(s)	Sample Date(s)	Interval (Days)	Round	P. Fat	Liver	Milk	Eggs
Cow #11	0.	Control	-	4/30/81	-	<0.05	<0.05, <0.05	0.16, 0.08	<0.02, <0.02, <0.02, <0.02	-
Cow #2	150.	Technical	**	4/16/81	14	0.17	0.42, 0.59	8.9, 8.4	0.14, 0.09,	-
Cow #1	150.	Technical	**	4/23/81	21	0.10	0.19, 0.21	7.4, 6.4	0.11, 0.07	-
Cow #9	150.	Technical	**	4/30/81	28	0.10	0.20, 0.29	5.0, 5.0	0.14, 0.10	-
A	0.	Control	-	2/20/81	-	-	-	-	-	<0.05
D	75.	Technical	**	3/3/81	14	-	-	-	-	0.57
D	75.	Technical	**	3/17/81	28	-	-	-	-	0.50

\*Detected as 2,4-dichlorobenzoic acid methyl ester and converted to propiconazole equivalents.

\*\*Dairy: Initiated on 4/2/81 and fed daily until sacrificed  
Poultry: Initiated on 2/17/81 and fed daily until sacrificed.

Comments: Residue results have not been corrected for control values.  
Residue results have been corrected for procedural recoveries.

sbh/Jan

PG 0040 CR 0043

## RESIDUE RECOVERY REPORT

PG0041 CF0043  
Page 4 of 6

AG-A No. 10034,01

Compound(s)		Substrate(s)					
Propiconazole		Liver, Round, Fat					
		Pesticide Added					
		Propiconazole					
SUBSTRATE	SAMPLE WEIGHT µg	AMOUNT ADDED		FOUND			
		pg	ppm	TOTAL		NET	
				pg	ppm*	ppm	%
Control Liver	45.0	0.00	0.00	3.2	0.13	0.13	
Propiconazole	45.0	2.25	0.05	4.2	0.17	0.04	78
Propiconazole	45.0	22.5	0.50	14.4	0.57	0.44	89
Propiconazole	2.2	11.0	5.0	4.6	3.6	3.5	70
Control Liver	45.0	0.00	0.00	2.0	0.08	0.08	
Propiconazole	45.0	2.25	0.05	3.5	0.14	0.06	116
Propiconazole	45.0	22.5	0.50	12.8	0.51	0.43	86
Propiconazole	2.2	3.7	1.7	3.0	2.4	2.3	135
Control Round	45.0	0.00	0.00	1.1	0.04	<0.05	
Propiconazole	45.0	2.25	0.05	2.7	0.11	0.07	127
Propiconazole	45.0	22.5	0.50	11.4	0.45	0.41	82
Control Fat	45.0	0.00	0.00	1.2	0.04	<0.05	
Propiconazole	45.0	2.25	0.05	2.8	0.11	0.07	128
Propiconazole	45.0	22.5	0.50	12.2	0.49	0.45	87

Comments: Recoveries were added prior to extraction.

\*Detected as 2,4-dichlorobenzoic acid methyl ester and converted to Propiconazole equivalents by the factor 1.79.

AG-A No. 10034,01

Compound(s)		Substrate(s)					
Propiconazole		Fat, Milk					
		Pesticide Added Propiconazole					
SUBSTRATE	SAMPLE WEIGHT µg	AMOUNT ADDED		FOUND			
		pg	ppm	TOTAL		NET	
				pg	ppm	ppm	%
Control Fat	45.0	0.00	0.00	0.50	0.02	<0.05	
Propiconazole	45.0	2.25	0.05	1.3	0.05	0.03	64
Propiconazole	45.0	22.5	0.50	10.1	0.40	0.38	77
Control Milk	225.	0.00	0.00	0.00	<0.01	<0.02	
Propiconazole	225.	2.25	0.01	0.60	0.004	0.004	45
Propiconazole	225.	22.5	0.10	10.0	0.08	0.08	80
Control Milk	225.	0.00	0.00	0.30	0.002	<0.02	
Propiconazole	225.	2.25	0.01	2.2	0.018	0.016	156
Propiconazole	225.	22.5	0.10	8.2	0.065	0.063	63
Control Milk	84.8	0.00	0.00	0.20	0.004	<0.02	
Propiconazole	84.8	0.84	0.01	0.60	0.013	0.009	92
Propiconazole	84.8	0.84	0.01	0.70	0.016	0.012	119
Propiconazole	84.8	0.84	0.01	0.50	0.010	0.006	65
Propiconazole	84.8	0.84	0.01	0.40	0.008	0.004	38

Comments: Recoveries were added prior to extraction.

\*Detected as 2,4-dichlorobenzoic acid methyl ester and converted to Propiconazole equivalents by the factor 1.79.

## RESIDUE RECOVERY REPORT

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AG-A No. 10034,01

Compound(s)		Substrate(s)					
Propiconazole		Milk, Eggs					
		Pesticide Added					
		Propiconazole					
SUBSTRATE	SAMPLE WEIGHT ug	AMOUNT ADDED		FOUND			
		PB	ppm	TOTAL		NET	
				pg	ppm*	ppm	%
Control Milk	225.	0.00	0.00	0.00	<0.01	<0.02	
Propiconazole	225.	4.5	0.02	1.8	0.014	0.014	70
Propiconazole	225.	4.5	0.02	1.9	0.015	0.015	76
Propiconazole	225.	4.5	0.02	2.2	0.017	0.017	87
Propiconazole	225.	4.5	0.02	1.9	0.015	0.015	76
Propiconazole	225.	4.5	0.02	1.9	0.015	0.015	76
Control Eggs	42.6	0.00	0.00	0.70	0.03	<0.05	
Propiconazole	42.6	2.1	0.05	1.6	0.07	0.04	77
Propiconazole	42.6	21.3	0.50	11.4	0.48	0.45	90

Comments: Recoveries were added prior to extraction.

\*Detected as 2,4-dichlorobenzoic acid methyl ester and converted to Propiconazole equivalents by the factor 1.79.